Supporting Information

Unveiling the Synthetic Potential of Substituted Phenols as Fully Recyclable Organophotoredox Catalysts for the Iodosulfonylation of Olefins

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A. GENERAL INFORMATION

NMR spectra were recorded on Bruker 400 Avance III HD equipped with a BBI-z grad probe head 5mm and Bruker 500 Avance III equipped with a BBI-ATM-z grad probe head 5mm (^{1}H: 400 MHz, ^{13}C: 100.5 MHz, ^{19}F: 376 MHz). The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm for ^{1}H NMR, and @ 77.16 ppm for ^{13}C NMR; $CFCl_3$ @ 0.0 ppm for ^{19}F NMR spectra). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. NMR yields were calculated by using trichloroethylene as internal standard.

High-Resolution Mass Spectra (HRMS) were obtained using Bruker micrOTOF-Q (ESI-TOF).

Absorption spectroscopy studies have been performed on a Varian Cary 50 UV-Vis double beam spectrophotometer (more info at: www.varianinc.com). All the spectra were recorded at room temperature using a 10 mm path length Hellma Analytics quartz cuvettes.

All the cyclic voltammograms were recorded with a scan rate of 0.1 V/s. A typical three-electrode cell was employed, which was composed of a glassy carbon (GC) working electrode (3 mm diameter), a platinum wire as counter electrode and a saturated aqueous calomel electrode (SCE) as reference electrode. The glass electrochemical cell was kept closed with a stopper annexed to the potentiostat. Oxygen was removed by purging the solvent with high-purity Nitrogen (N_2), introduced from a line into the cell by means of a glass pipe. The potential of ferrocenium/ferrocene (Fc^+/Fc) couple was used as internal reference system to calibrate the potentiostat. All the results are subsequently converted in V vs SCE, in agreement with the value reported in literature [$E_{1/2}(Fc^+/Fc)$ = +0.38 V vs SCE].[1,2]

Light source at 450 nm: The LED strips at 450 nm were purchased from eBay webpage: https://www.ebay.it/SMD2835 LUCE A LED STRISCIA 440nm-450nm.

Light source at 456 nm: The Kessil lamp PR160L-456 (50W) was purchased from Kessil webpage: https://www.kessil.com/science/PR160L.php.

The quantum yield measurement was performed with a ferrioxalate actinometer, following a procedure previously described in literature.[3]

General Procedures. The batch ATRA reactions were set-up under an argon atmosphere in Schlenk tubes, unless otherwise stated. The continuous flow reactions were carried out using capillary reactors made with FEP tubing (0.8 mm I.D., 1.58 mm O.D.) and fitting connections purchased from BGB® (www.bgb-info.com). Chromatographic purification of products was accomplished using flash chromatography on silica gel (SiO_2, 0.04-0.063 mm, 60 Å) purchased from Machery-Nagel, with the indicated solvent system according to the standard techniques or using a Biotage Isolera automated flash chromatography system with cartridges packed with silica (SiO_2, 0.04-0.063 mm, 60 Å). Thin-layer chromatography (TLC) analysis was performed on pre-coated Merck TLC plates (silica gel 60 GF254, 0.25 mm). Visualization of the developed chromatography was performed by checking UV absorbance (254 nm) as well as with potassium

permanganate or ninhydrin stain solution. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

Materials. Commercial grade reagents and solvents were purchased at the highest commercial quality from Sigma Aldrich or FluoroChem and used as received, unless otherwise stated. Phenols **6a-d** were commercially available. The preparation of phenol **6e** is detailed in Section B.3 of the SI. Olefins **3a-d**, **3g** and **3m-o** were commercially available. The preparation of olefins **3e-f**, **3h-l** and α-iodo sulfones **4a-k** is detailed in Section B of the SI.

Computational details. All geometry optimizations were performed using M06-2X functional,[4] including the integral equation formalism of the polarizable continuum model (IEFPCM) to model solvation effects.[5] The def2TZVP basis set was employed.[6] Frequencies were calculated in order to ensure that the structures are actual relative minima of energy. TD-DFT calculations were performed at the same level of theory on the optimized structures to compute the corresponding UV-vis absorption spectra. All the calculations were carried out using Gaussian 09 software package.[7]

A.1. BATCH PHOTOCHEMICAL SET-UP

Figure S1 shows a schematic representation of the batch photoreactor system employed in the present study.

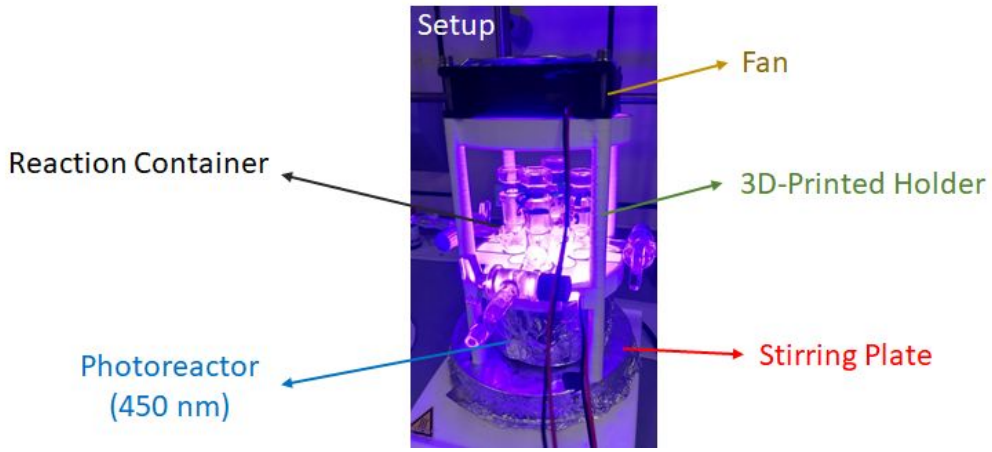


Figure S1. Batch photochemical set-up.

A.2. MICROFLUIDIC PHOTOREACTOR SETUP

Figure S2 shows a schematic representation of the microfluidic circuit employed in the present study. Reaction mixtures are introduced in continuous flow into the micro-photoreactor via a double syringe pump (Syrris Atlas, see general information). The microfluidic reactor consists of a transparent TFE capillary (BGB®; internal diameter: 800 µm; inner volume: 210 µL; microreactor tubing length: 42 cm). The microreactor is then irradiated by the selected light source. The crude is collected in a vial, connected to the exit of the microreactor.

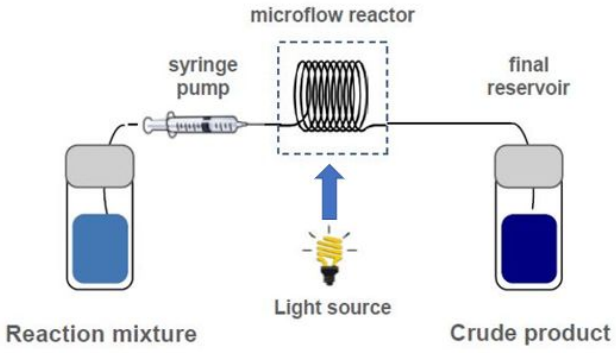


Figure S2. Schematic representation of the micro-photoreactor setup.

Figure S3 shows the assembled microfluidic reactor (left side) and the general setup of a reaction using a Kessil lamp (right side). The lamp is placed at a fixed distance of 1 cm. Aluminum foil is used to avoid undesired irradiation of the tubing. To maintain a stable reaction temperature, a fan is placed at 3 cm from the reactor.

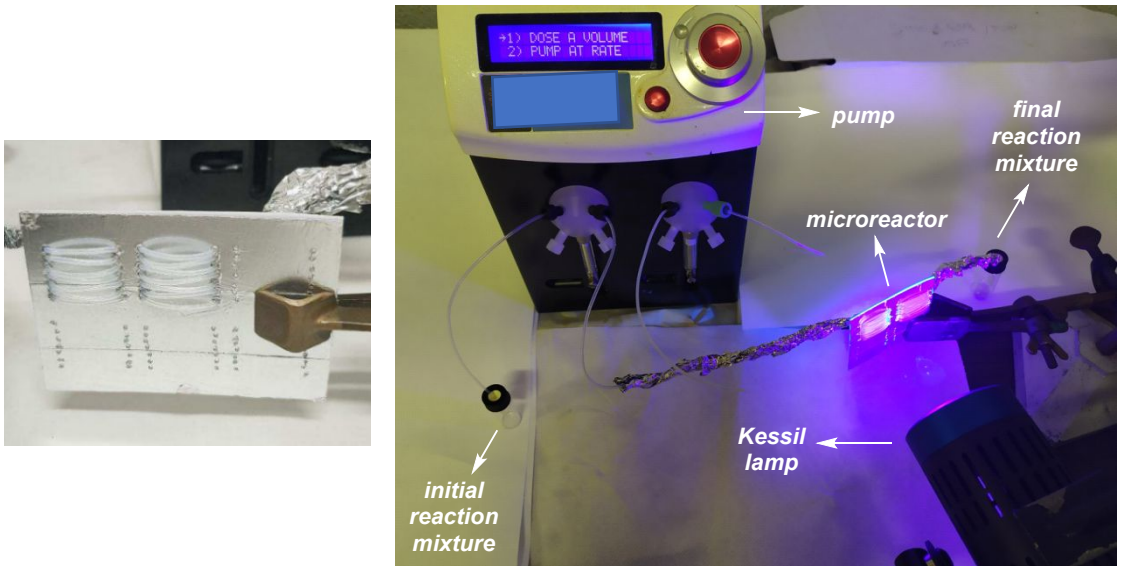
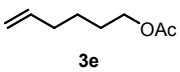


Figure S3. *left:* Assembled microfluidic photoreactor. *right:* Microfluidic photoreactor setup.

B. GENERAL PROCEDURES FOR THE SYNTHESIS OF STARTING MATERIALS

B.1. PREPARATION OF TERMINAL OLEFINS (3e-f, 3h-l)

Hex-5-en-1-yl acetate (3e)

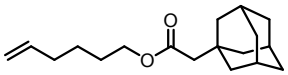


3e

In a two-neck round-bottomed flask, purged under argon, a solution of 5-hexen-1-ol **3g** (420 µL, 3.5 mmol, 1 equiv.) and 2,6-lutidine (408 µL, 3.5 mmol, 1 equiv.) in dry THF (10 mL) was stirred at 0°C for 10 minutes. Acetyl bromide

(260 µL, 3.5 mmol, 1 equiv.) was added dropwise and the solution was stirred at room temperature over 3 hours. The reaction was quenched by the addition of water (10 mL) and then extracted with diethyl ether (3 x 10 mL). The organic phases were combined and washed with brine (10 mL) and then dried over sodium sulfate. The solvent was removed under reduced pressure to give the corresponding alkene **3e** as a pale-yellow oil (363 mg, 73% yield). The characterization data matched with the reported one.[8]

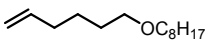
Hex-5-en-1-yl 2-(adamantan-1-yl)acetate (3f)


3f

In a two-neck round-bottomed flask, purged under argon, a solution of 1-adamantaneacetic acid (583 mg, 3 mmol, 1 equiv.), 5-hexen-1-ol **3g** (540 µL, 4.5 mmol, 1.5 equiv.), 4-(dimethylamino)pyridine (73 mg, 0.6 mmol, 0.2 equiv.) and *N,N′*-dicyclohexylcarbodiimide (928 µL, 4.5 mmol, 1.5 equiv.) in dry DCM (6 mL, 0.5 M) was stirred at room temperature overnight. The reaction mixture was then filtered to remove the urea derivative and washed with DCM (20 mL). The filtrate was washed with HCl 1M (20 mL), water and $NaHCO_3$ (5% w/v), respectively. The organic phase was dried over sodium sulfate and the solvent was removed under reduced pressure. The residue was then purified by flash column chromatography (cyclohexane/ethyl acetate) to give the corresponding alkene **3f** as a pale-yellow oil (620 mg, 75% yield).

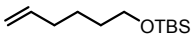
^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05-4.9 (m, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.11-2.06 (m, 2H), 2.05 (s, 2H), 1.94 (d, *J* = 15.7 Hz, 3H), 1.70 (d, *J* = 6.4 Hz, 1H), 1.68 (d, *J* = 2.8 Hz, 2H), 1.64 (t, *J* = 6.4 Hz, 4H), 1.61 (t, *J* = 3.0 Hz, 8H), 1.51-1.41 (m, 2H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 172.04 (s), 138.50 (s), 114.90 (s), 63.96 (s), 49.18 (s), 42.55 (s), 36.88 (s), 33.40 (s), 32.86 (s), 28.76 (s), 28.27 (s), 25.44 (s); **HRMS (ESI, positive mode)** calculated for $C_{18}H_{28}O_2$ $[M+Na]^+$: 299.1982, found: 299.1981.

1-(hex-5-en-1-yloxy)octane (3h)


3h

In a two-neck round-bottomed flask, purged under argon, a solution of 5-hexen-1-ol **3g** (420 µL, 3.5 mmol, 1 equiv.) and 1-bromooctane (610 µL, 3.5 mmol, 1 equiv.) in dry THF (14 mL) was stirred at 0°C for 10 minutes. Sodium hydride (170 mg, 4.2 mmol, 1.2 equiv.) was added portion-wise and the solution was heated up to reflux and stirred overnight. The reaction was quenched by the addition of ammonium chloride (10 mL) and then extracted with ethyl acetate (3 x 10 mL). The organic phases were combined and washed with brine (10 mL) and then dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (cyclohexane/ethyl acetate) to give the corresponding alkene **3h** as a pale-yellow oil (494 mg, 67% yield). The characterization data matched with the reported one.[9]

***Tert*-butyl(hex-5-en-1-yloxy)dimethylsilane (3i)**

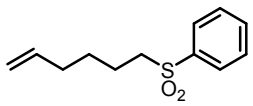

3i

In a two-neck round-bottomed flask, purged under argon, a solution of 5-hexen-1-ol **3g** (360 µL, 3 mmol, 1 equiv.), triethylamine (836 µL, 6 mmol, 2 equiv.) in dry THF (6 mL, 0.5 M) was stirred at 0°C for 10 minutes. *tert*-

butyldimethylchlorosilane (543 mg, 3.6 mmol, 1.2 equiv.) was added and the solution was stirred at room temperature overnight. The reaction was quenched by the addition of water (20 mL) and then extracted with ethyl acetate (3 x 20 mL). The organic phases were combined and washed with brine (20 mL) and then dried over sodium sulfate. The solvent was removed under reduced pressure and residue was purified by flash column chromatography (cyclohexane/ethyl acetate) to give the corresponding alkene **3i** as a colorless oil (643 mg, 80% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.81(ddt, *J* = 16.9, 10.2, 6.7, 1H), 5.04-4.90 (m, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.12-2.01 (m, 2H), 1.59-1.48 (m, 2H), 1.48-1.37 (m, 2H), 0.95-0.85 (m, 9H), 0.08-0.01 (m, 6H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.06 (s), 114.50 (s), 63.12 (s), 33.70 (s), 32.46 (s), 26.13 (s), 25.32 (s), 18.52 (s), -5.13 (s); it was not possible to measure the **HRMS (ESI, positive mode)** of compound **3i** due to its poor tendency to ionize. The characterization data matched with the reported one.[10]

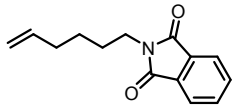
(Hex-5-en-1-ylsulfonyl)benzene (3j)



3j

In a two-neck round-bottomed flask, purged under argon, a mixture of 6-bromo-1-hexene **3m** (260 µL, 2 mmol, 1 equiv.), sodium benzenesulfinate (391 mg, 2.4 mmol, 1.2 equiv.) tetrabutylammonium iodide (74 mg, 0.2 mmol, 0.1 equiv.) in dry DMF (2 mL) was heated up to 60°C and stirred over 5 hours. The reaction was quenched by the addition of brine (5 mL) and then extracted with ethyl acetate (3 x 5 mL). The organic phases were combined and washed with brine (5 mL) and then dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (cyclohexane/ethyl acetate) to give the corresponding alkene **3j** as a colorless oil (369 mg, 81% yield). The characterization data matched with the reported one.[11]

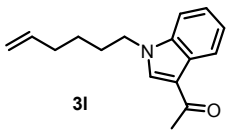
2-(hex-5-en-1-yl)isoindoline-1,3-dione (3k)



3k

In a two-neck round-bottomed flask, purged under argon, a mixture of 6-chloro-1-hexene **3n** (400 µL, 3 mmol, 1 equiv.), potassium phthalimide (610 mg, 3.3 mmol, 1.1 equiv.) and potassium iodide (50 mg, 0.3 mmol, 0.1 equiv.) in dry DMF (5 mL) was heated up to 90°C and stirred overnight. The reaction was quenched by the addition of water (10 mL) and then extracted with dichloromethane (3 x 10 mL). The organic phases were combined and washed with KOH 0.2 M (10 mL), brine (10 mL) and then dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (cyclohexane/ethyl acetate) to give the corresponding alkene **3k** as a pale-yellow oil (480 mg, 69% yield). The characterization data matched with the reported one.[12]

1-(1-(hex-5-en-1-yl)-1H-indol-3-yl)ethan-1-one (3l)



3l

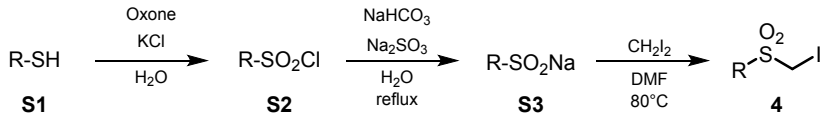
In a two-neck round-bottomed flask, purged under argon, a mixture of 3-acetylindole (478 mg, 3 mmol, 1 equiv.), 6-bromo-1-hexene **3m** (481 µL, 3.6 mmol, 1.2 equiv.), and potassium hydroxide (202 mg, 3.6 mmol, 1.2 equiv.) in dry DMF (6 mL, 0.5 M) was heated up to 70°C and stirred over

3 hours. The reaction was quenched by the addition of water (10 mL) and then extracted with ethyl acetate (3 x 20 mL). The organic phases were combined and washed with brine (20 mL) and then dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (cyclohexane/ethyl acetate) to give the corresponding alkene **3l** as a pale-yellow oil (675 mg, 93% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.41-8.35 (m, 1H), 7.72 (s, 1H), 7.37-7.31 (m, 1H), 7.31-7.25 (m, 2H), 5.82-5.69 (m, 1H), 5.05-4.95 (m, 2H), 4.13 (t, *J* = 7.2 Hz, 2H), 2.52 (s, 3H), 2.14-2.04 (m, 2H), 1.95-1.82 (m, 2H), 1.50-1.38 (m, 2H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 193.04 (s), 137.89 (s), 136.84 (s), 134.84 (s), 126.43 8s), 123.27 (s), 122.69 (s), 122.54 (s), 117.02 (s), 115.36 (s), 109.90 (s), 47.03 (s), 33.23 (s), 29.33 (s), 27.69 (s), 26.15 (s); **HRMS (ESI, positive mode)** calculated for $C_{16}H_{19}NO$ $[M+Na]^+$: 264.1359, found: 264.1358.

B.2. PREPARATION OF α-IODO SULFONES

B.2.1. Synthesis of 4a-d and 4f-i



STEP 1, according to a modified literature procedure.[13] A mixture of thiol **S1** (10 mmol, 1 equiv.), Oxone (25 mmol, 2.5 equiv.), KCl (10 mmol, 1 equiv.) and water (30 mL) was vigorously stirred at room temperature for 2 hours. The aqueous phase was extracted with ethyl acetate (4 × 50 mL). The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by flash column chromatography (cyclohexane) affording the desired product **S2** (R = Cl: 90% yield, R = cyclohexyl: 83% yield). The characterization data matched with the reported one.

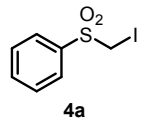
STEP 2, according to a literature procedure.[14] The corresponding sulfonyl chloride **S2** (7 mmol, 1 equiv.) was dissolved in water (25 mL). Sodium sulfite (11.2 mmol, 1.6 equiv.) and sodium bicarbonate (11.2 mmol, 1.6 equiv.) were added and the reaction mixture was refluxed for 3 hours. Water was 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 under reduced pressure. Sodium sulfinate **S3** was used without any further purification (R = F: 93%, R = Cl: 92% yield, R = Br: 88% yield, R = cyclohexyl: 75% yield, R = naphthalenyl: 72% yield). The characterization data matched with the reported one.

STEP 3, according to a literature procedure.[14] A solution of sodium sulfinate **S3** (5 mmol, 1 equiv.) in DMF (20 mL, 0.25 M) was stirred at room temperature for 15 minutes. Diiodomethane (6 mmol, 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 sodium sulfate before concentration in vacuo. The residue

was purified by flash column chromatography (cyclohexane/ethyl acetate) to afford the desired α-iodo sulfone **4a-j**.

Characterization Data

(Iodomethyl)sulfonyl)benzene (4a)

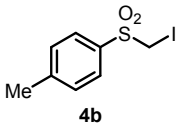


4a

4a was synthesized according to the general procedure **B.2.1** from sodium benzenesulfinate (821 mg, 5 mmol). The final α-iodo sulfone **4a** was obtained as a white solid (1.24 g, 88% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, *J*= 8.5, 1.6 Hz, 2H), 7.74-7.68 (m, 1H), 7.60 (dt, *J*= 8.0, 1.2 Hz, 2H), 4.46 (s, 2H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 136.09 (s), 134.66 (s), 129.47 (s), 129.11 (s), 16.84 (s). The characterization data matched with the reported one.[14]

1-((Iodomethyl)sulfonyl)-4-methylbenzene (4b)

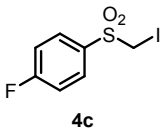


4b

4b was synthesized according to the general procedure **B.2.1** from sodium 4-methylbenzenesulfinate (891 mg, 5 mmol). The final α-iodo sulfone **4b** was obtained as a white solid (1.20 g, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 4.44 (s, 2H), 2.46 (s, 3H). The characterization data matched with the reported one.[14]

1-fluoro-4-((iodomethyl)sulfonyl)benzene (4c)

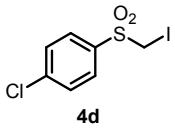


4c

4c was synthesized according to the general procedure **B.2.1** from 4-fluorobenzenesulfonyl chloride (1.36 g, 7 mmol). The final α-iodo sulfone **4c** was obtained as a white solid (1.12 g, 75% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04-7.95 (m, 2H), 7.32-7.22 (m, 2H), 4.46 (s, 2H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.59 (s), 165.02 (s), 132.07 (d), 116.85 (d), 16.58 (s); **^{19}F-NMR (376 MHz, $CDCl_3$)** δ -101.70 (m, 1F); **HRMS (ESI, positive mode)** calculated for $C_7H_6FIO_2S$ $[M+Na]^+$: 322.9009, found: 332.9010.

1-chloro-4-((iodomethyl)sulfonyl)benzene (4d)

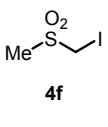


4d

4d was synthesized according to the general procedure **B.2.1** from 4-chlorobenzenesulfonyl chloride (1.48 g, 7 mmol). The final α-iodo sulfone **4d** was obtained as a white solid (807 mg, 51% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 4.46 (s, 2H**); ^{13}C-NMR (101 MHz, $CDCl_3$)** δ 141.56 (s), 134.47 (s), 130.64 (s), 129.82 (s), 16.51 (s); **HRMS (ESI, positive mode)** calculated for $C_7H_6ClIO_2S$ $[M+Na]^+$: 338.8714, found: 338.8713.

Iodo(methylsulfonyl)methane (4f)

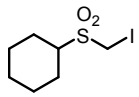


4f

4f was synthesized according to the general procedure **B.2.1** from sodium methanesulfinate (510 mg, 5 mmol). The final α-iodo sulfone **4f** was obtained as a white solid (746 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39 (s, 2H), 3.17 (s, 3H). The characterization data matched with the reported one.[14]

((Iodomethyl)sulfonyl)cyclohexane (4g)

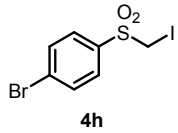


4g

4g was synthesized according to the general procedure **B.2.1** from cyclohexanethiol (1.22 mL, 10 mmol). The final α-iodo sulfone **4g** was obtained as a white solid (504 mg, 35% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.30 (s, 2H), 3.35 (tt, *J* = 12.1, 3.5 Hz, 1H), 2.13 (dd, *J* = 19.3, 14.6 Hz, 2H), 1.91 (d, *J* = 13.4 Hz, 2H), 1.71 (d, *J* = 12.4 Hz, 1H), 1.55 (qd, *J* = 12.4, 3.2 Hz, 2H), 1.40-1.14 (m, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 58.64 (s), 25.25 (s), 24.95 (s), 10.60 (s); **HRMS (ESI, positive mode)** calculated for $C_7H_{13}IO_2S$ $[M+Na]^+$: 310.9573, found: 310.9574. The characterization data matched with the reported one.[15]

1-bromo-4-((iodomethyl)sulfonyl)benzene (4h)

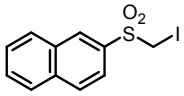


4h

4h was synthesized according to the general procedure **B.2.1** from 4-bromobenzenesulfonyl chloride (1.79 g, 7 mmol). The final α-iodo sulfone **4h** was obtained as a white solid (902 mg, 50% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86–7.81 (m, 2H), 7.77-7.52 (m, 2H), 4.45 (s, 2H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 135.05 (s), 132.84 (s), 130.69 (s), 130.25 (s), 15.41 (s); **HRMS (ESI, positive mode)** calculated for $C_7H_6BrIO_2S$ $[M+Na]^+$: 382.8209, found: 382.8215. The characterization data matched with the reported one.[16]

1-((iodomethyl)sulfonyl)naphthalene (4i)

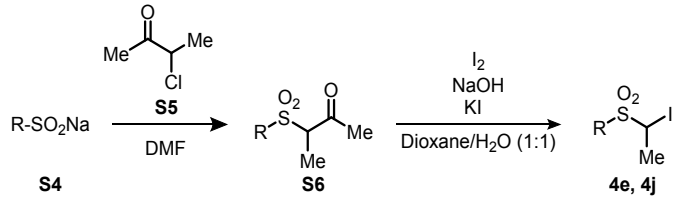


4i

4i was synthesized according to the general procedure **B.2.1** from naphthalene-1-sulfonyl chloride (1.59 g, 7 mmol). The final α-iodo sulfone **4i** was obtained as a white solid (631 mg, 38% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.5 Hz, 1H), 8.35 (d, *J* = 7.3 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.62 (dd, *J* = 15.6, 7.9 Hz, 2H), 4.65 (s, 2H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 136.11 (s), 134.23 (s), 132.24 (s), 130.77 (s), 129.57 (s), 129.22 (s), 128.99 (s), 127.31 (s), 124.41 (s), 123.63 (s), 17.27 (s); **HRMS (ESI, positive mode)** calculated for $C_{11}H_9IO_2S$ $[M+Na]^+$: 354.9260, found: 354.9263.

B.2.2. Synthesis of the secondary α-iodo sulfones 4e and 4j

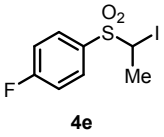


STEP 1, according to a modified literature procedure.[14] To a solution of commercially available 3-chloro butanone **S5** (5 mmol, 1 equiv.) in DMF (10 mL, 0.5 M) was added the sodium sulfinate **S4** (5 mmol, 1 equiv.) in one portion. The reaction mixture was stirred at room temperature for 24 hours. The reaction was quenched by the addition of water (50 mL), the mixture was extracted with ethyl acetate (3 x 35 mL), dried over sodium sulfate and the solvent was removed under

reduced pressure. The corresponding adduct **S6** was used without any further purification (R = phenyl: 85% yield, R = 4-fluorophenyl: 82% yield).

STEP 2, according to a modified literature procedure.[14] To a dioxane-water (1:1, 0.5 M) solution of the starting material **S6** (2.5 mmol, 1 equiv.) and iodine (10 mmol, 4 equiv.) in the presence of potassium iodide (20 mmol, 8 equiv.), 1 M solution of NaOH is added under stirring at room temperature until discoloration 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 sulfones **4e** and **4j** were used without any further purification.

Characterization Data



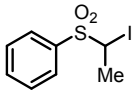
4e

1-fluoro-4-((1-iodoethyl)sulfonyl)benzene (4e)

4e was synthesized according to the general procedure **B.2.2** from sodium 4-fluorobenzenesulfinate (911 mg, 5 mmol). The final α-iodo sulfone **4e** was obtained as a white solid (385 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.31 – 7.23 (m, 2H), 5.00 (q, *J* = 7.1 Hz, 1H), 2.10 (d, *J* = 7.1 Hz, 3H). **^{19}F-NMR (376 MHz, $CDCl_3$)** δ -101.96 (m, 1F). The characterization data matched with the reported one.[14]

((1-iodoethyl)sulfonyl)benzene (4j)

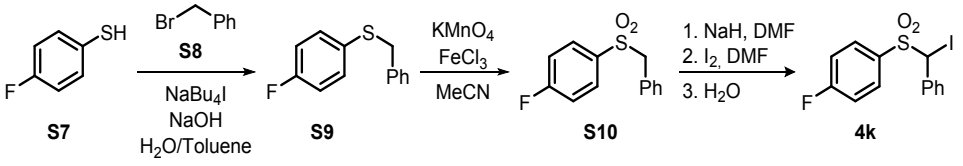


4j

4j was synthesized according to the general procedure **B.2.2** from sodium benzenesulfinate (821 mg, 5 mmol). The final α-iodo sulfone **4j** was obtained as a white solid (376 mg, 51% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97–7.88 (m, 2H), 7.74-7.67 (m, 1H), 7.62-7.52 (m, 2H), 5.05-4-97 (m, 1H), 2.08 (d, *J* = 7.1, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 134.55 (s), 134.27 (s), 130.05 (s), 129.08 (s), 35.04 (s), 22.46 (s); **HRMS (ESI, positive mode)** calculated for $C_8H_9IO_2S$ $[M+Na]^+$: 318.9260, found: 318.9259.

B.2.3. Synthesis of the phenyl α-iodo sulfone 4k



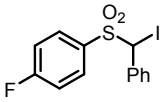
STEP 1, according to a modified literature procedure.[14] A solution of 4-fluorobenzenethiol **S7** (10 mmol, 1 equiv., 1.07 mL) and benzyl bromide **S8** (10.5 mmol, 1.05 equiv., 1.25 mL) in toluene (10 mL) was added to a solution containing NaOH (17 mmol, 1.7 equiv., 680 mg) and Bu_4NI (0.3 mmol, 0.03 equiv., 111 mg) in H_2O (10 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 sodium sulfate before concentration in vacuo. The residual **S9** was used without any further purification (2.1 g, 96% yield).

STEP 2, according to a modified literature procedure.[14] A solution of the starting material **S9** (5 mmol, 1 equiv., 1.09 g), $FeCl_3$ (0.18 mmol, 0.04 equiv., 29.2 mg), and $KMnO_4$ (19 mmol, 3.8 equiv., 3 g) in acetonitrile (20 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 (cyclohexane/ethyl acetate) affording the desired product **S10** as a white solid (725 mg, 58% yield).

STEP 3, according to a modified literature procedure.[14] The starting material **S10** (2.5 mmol, 1 equiv., 625 mg) was placed in a two necked round-bottom flask and dissolved with 14 mL of dry DMF at room temperature under argon. To this solution was added sodium hydride (10 mmol, 4 equiv., 400 mg of a 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 iodine (2.5 mmol, 1 equiv., 635 mg) in 4 mL of dry DMF under argon. The resulting mixture was poured into 80 mL of water and the precipitate was collected and recrystallized from acetone to give the final compound **4k** (267 mg, 28% yield).

Characterization Data

1-fluoro-4-((iodo(phenyl)methyl)sulfonyl)benzene (4k)

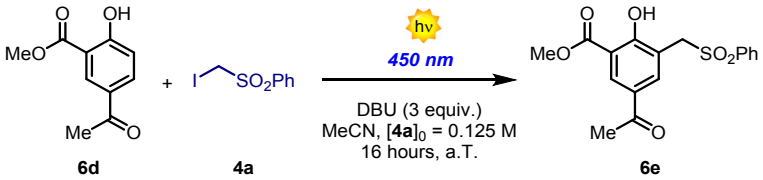


4k

4k was synthesized according to the general procedure **B.2.3** from 4-fluorobenzenethiol (1.07 mL, 10 mmol). The final α-iodo sulfone **4k** was obtained as a pale-yellow solid (267 mg, 28% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 7.35 – 7.26 (m, 3H), 7.24 – 7.19 (m, 2H), 7.10 – 7.00 (m, 2H), 5.91 (s, 1H). The characterization data matched with the reported one.[14]

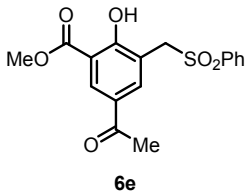
B.3. PREPARATION OF THE PRE-PHOTOCATALYST 6e



Pre-photocatalyst **6e** was prepared though the following procedure: a 20 mL Schlenk tube was charged with the α-iodo sulfone **4a** (282 mg, 1 mmol, 1 equiv.), phenol **6d** (583 mg, 3 mmol, 3 equiv.), DBU (449 µL, 3 mmol, 3 equiv.). To this mixture was then added acetonitrile (8 mL; $[\mathbf{4a}]_0$ = 0.125 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 photoreactor (λ = 450 nm). The temperature was kept at around 30°C by using a fan. Stirring was maintained for 16 hours, and then the irradiation was stopped. The reaction mixture was then quenched with an aqueous solution of HCl (5 mL, 0.5 M). The reaction was extracted with ethyl acetate (3 x 10 mL). The volatiles were removed in vacuo and the residue was purified by column chromatography (hexane/EtOAc 7:3) to give the product **6e** as a white solid (142 mg, 41% yield).

Characterization Data

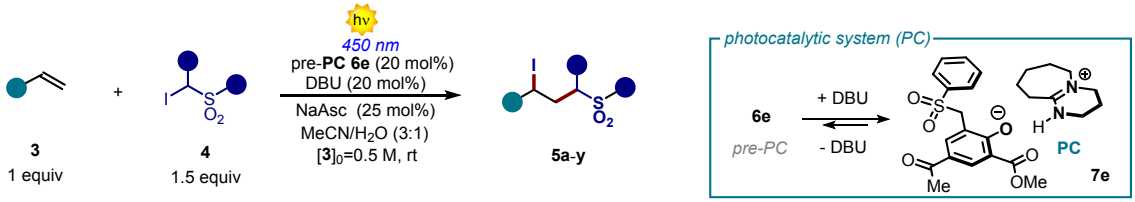
methyl 5-acetyl-2-hydroxy-3-((phenylsulfonyl)methyl)benzoate (6e)



6e

^{1}H-NMR (400 MHz, $CDCl_3$): δ 11.39 (s, 1H), 8.47 (d, *J* = 2.3 Hz, 1H), 8.01 (d, *J* = 2.3 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.65 – 7.59 (m, 1H), 7.51 – 7.44 (m, 2H), 4.51 (s, 2H), 3.96 (s, 3H), 2.55 (s, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 195.5, 170.1, 163.6, 138.4, 138.3, 134.1, 131.9, 129.1 (x2), 128.7 (x2), 128.6, 117.5, 112.4, 55.6, 53.1, 26.4. **HRMS (ESI, positive mode)** calculated for $C_{17}H_{16}O_6S$ $[M+H]^+$: 349.0740, found 349.0721.

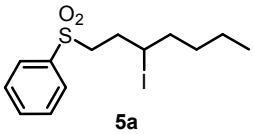
C. GENERAL PROCEDURE FOR THE PHOTO-ORGANOCATALYTIC ATRA REACTIONS BETWEEN OLEFINS AND α-IODO SULFONES



A 10 mL Schlenk tube was charged with the α-iodo sulfone **4** (0.3 mmol, 1.5 equiv.), phenol **6e** (0.04 mmol, 20 mol%), sodium ascorbate (NaAsc, 0.05 mmol, 25 mol%), DBU (0.04 mmol, 20 mol%), and the appropriate olefin **3** (0.2 mmol, 1 equiv.). To this mixture was then added acetonitrile and water in a 3:1 ratio (300 µL, 100 µL respectively; $[\mathbf{3}]_0$ = 0.50 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 photoreactor (λ = 450 nm). The temperature was kept at around 30°C by using a fan. Stirring was maintained for the indicated time (generally 8-24 hours), and then the irradiation was stopped. The reaction mixture was then quenched with an aqueous solution of HCl (5 mL, 0.5 M). The reaction was extracted with ethyl acetate (3 x 10 mL). The volatiles were removed in vacuo and the residue was purified by column chromatography (hexane/EtOAc) to give the ATRA products **5** in the stated yield.

Characterization Data

((3-iodoheptyl)sulfonyl)benzene (5a)



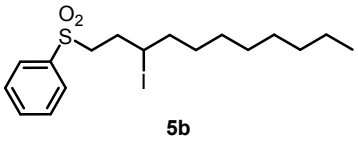
5a

5a was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-hexene **3a** (25.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 8 hours. The final product **5a** was obtained as a colorless oil (60.0 mg, 82% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97–7.88 (m, 2H), 7.73-7.64 (m, 1H), 7.62-7.57 (m, 2H), 4.12–4.01 (m, 1H), 3.37 (ddd, *J* = 14.0, 9.9, 5.6, 1H), 3.21 (ddd, *J* = 13.9, 10.0, 5.7, 1H), 2.28-2.09 (m, 2H), 1.91-1.78 (m, 1H), 1.72-1.62 (m, 1H), 1.50-1.40 (m, 1H), 1.40-1.16 (m, 4H), 0.93-0.86 (m, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.19 (s), 134.06 (s), 129.57 (s), 128.14 (s), 56.72 (s),

40.39 (s), 35.08 (s), 33.25 (s), 31.62 (s), 21.95 (s), 14.03 (s); **HRMS (ESI, positive mode)** calculated for $C_{13}H_{19}IO_2S$ $[M+Na]^+$: 389.0046, found: 389.0043.

((3-iodoundecyl)sulfonyl)benzene (5b)

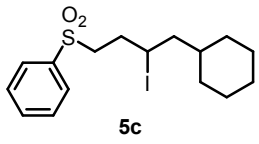


5b

5b was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-decene **3b** (38.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 8 hours. The final product **5b** was obtained as a colorless oil (65.8 mg, 78% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97–7.89 (m, 2H), 7.71-7.64 (m, 1H), 7.62-7.55 (m, 2H), 4.11–4.01 (m, 1H), 3.42-3.32 (m, 1H), 3.21 (ddd, *J* = 13.9, 10.0, 5.7 Hz, 1H), 2.27-2.09 (m, 2H), 1.90-1.78 (m, 1H), 1.65 (ddt, *J* = 12.3, 8.1, 4.1 Hz, 1H), 1.53-1.40 (m, 1H), 1.33-1.18 (m, 11H), 0.87 (t, *J* = 6.9 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.17 (s), 134.04 (s), 129.55 (s), 128.12 (s), 56.70 (s), 40.66 (s), 35.17 (s), 33.24 (s), 31.93 (s), 29.48 (s), 29.46 (s), 29.30 (s), 29.79 (s), 22.77 (s), 14.24 (s); **HRMS (ESI, positive mode)** calculated for $C_{17}H_{27}IO_2S$ $[M+H]^+$: 423.0849, found: 423.0859.

((4-cyclohexyl-3-iodobutyl)sulfonyl)benzene (5c)

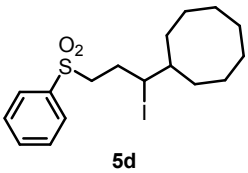


5c

5c was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and allylcyclohexane **3c** (31.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 8 hours. The final product **5c** was obtained as a colorless oil (59.3 mg, 73% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96–7.87 (m, 2H), 7.68 (ddd, *J* = 8.7, 2.5, 1.3 Hz, 1H),7.62-7.56 (m, 2H), 4.13 (ddd, *J* = 13.6, 8.9, 4.5 Hz, 1H), 3.38 (ddd, *J* = 14.0, 10.1, 5.3 Hz, 1H), 3.23 (ddd, *J* = 14.0, 10.2, 5.4 Hz, 1H), 2.27-2.07 (m, 2H), 1.83 (ddd, *J* = 14.3, 9.9, 4.3 Hz, 1H), 1.72-1.55 (m, 4H), 1.53-1.35 (m, 2H), 1.31-1.05 (m, 4H), 1.04-0.90 (m, 1H), 0.84-0.69 (m, 1H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.16 (s), 134.04 (s), 129.55 (s), 128.13 (s), 56.67 (s), 48.15 (s), 37.55 (s), 33.54 (s), 33.28 (s), 32.91 (s), 31.97 (s), 26.50 (s), 26.18 (s), 26.00 (s); **HRMS (ESI, positive mode)** calculated for $C_{16}H_{23}IO_2S$ $[M+Na]^+$: 429.0356 , found: 429.0368.

(1-iodo-3-(phenylsulfonyl)propyl)cyclooctane (5d)



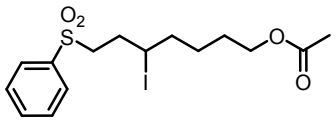
5d

5d was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and allylcyclohexane **3d** (30.6 µl, 0.2 mmol, 1 equiv.). Reaction time: 8 hours. The final product **5d** was obtained as a colorless oil (37.8 mg, 45% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96–7.87 (m, 2H), 7.72-7.64 (m, 1H),7.64-7.54 (m, 2H), 4.08 (dt, *J* = 10.5, 3.3 Hz, 1H), 3.40 (ddd, *J* = 13.9, 9.9, 5.3 Hz, 1H), 3.20-3-07 (m, 1H), 2.30-2.07 (m, 2H), 1.78-1.29 (m, 15H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.28 (s), 134.04 (s), 129.56 (s),

128.07 (s), 57.03 (s), 48.58 (s), 44.33 (s), 34.35 (s), 32.01 (s), 30.68 (s), 26.69 (s), 26.55 (s), 26.50 (s), 26.02 (s), 25.92 (s); **HRMS (ESI, positive mode)** calculated for $C_{17}H_{25}IO_2S$ $[M+Na]^+$: 443.0512, found: 443.0495.

5-iodo-7-(phenylsulfonyl)heptyl acetate (5e)

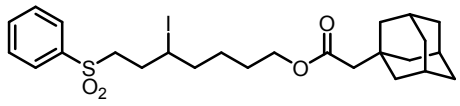


5e

5e was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 5-hexenyl acetate **3e** (32.2 µl, 0.2 mmol, 1 equiv.). Reaction time: 16 hours. The final product **5e** was obtained as a colorless oil (72.1 mg, 85% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.68 (ddd, *J* = 6.7, 3.8, 1.2 Hz, 1H), 7.62-7.56 (m, 2H), 4.11–4.01 (m, 3H), 3.43-3.30 (m, 1H), 3.20 (ddd, *J* = 13.9, 9.6, 6.0 Hz, 1H), 2.29-2.09 (m, 2H), 2.04 (s, 3H), 1.92-1.80 (m, 1H), 1.76-1.51 (m, 4H), 1.50-1.34 (m, 1H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 171.25 (s), 139.15 (s), 134.09 (s), 129.58 (s), 128.10 (s), 64.06 (s), 56.43 (s), 40.14 (s), 34.36 (s), 33.27 (s), 27.78 (s), 26.04 (s), 21.13 (s); **HRMS (ESI, positive mode)** calculated for $C_{15}H_{21}IO_4S$ $[M+Na]^+$: 447.0097, found: 447.0097.

5-iodo-7-(phenylsulfonyl)heptyl 2-(adamantan-1-yl)acetate (5f)

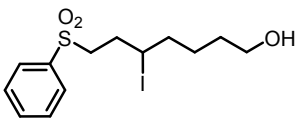


5f

5f was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and hex-5-en-1-yl 2-(adamantan-1-yl)acetate **3f** (55.5 mg, 0.2 mmol, 1 equiv.). Reaction time: 16 hours. The final product **5f** was obtained as a colorless oil (44.6 mg, 43% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.96–7.88 (m, 2H), 7.73-7.64 (m, 1H),7.64-7.55 (m, 2H), 4.12-3.96 (m, 3H), 3.37 (ddd, *J* = 14.1, 9.5, 5.8 Hz, 1H), 3.21 (ddd, *J* = 14.0, 9.6, 5.9 Hz, 1H), 2.27-2.11 (m, 2H), 2.05 (d, *J* = 6.9 Hz, 2H), 1.96 (s, 3H), 1.91-1.80 (m, 1H), 1.75-1.52 (m, 16H), 1.48-1.40 (m, 1H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 172.00 (s), 139.17 (s), 134.09 (s), 129.59 (s), 128.12 (s), 63.56 (s), 56.67 (s), 49.15 (s), 42.58 (s), 40.18 (s), 36.88 (s), 34.46 (s), 33.33 (s), 32.91 (s), 28.75 (s), 27.94 (s), 26.25 (s); **HRMS (ESI, positive mode)** calculated for $C_{25}H_{35}IO_4S$ $[M+Na]^+$: 581.1193, found: 581.1193.

5-iodo-7-(phenylsulfonyl)heptan-1-ol (5g)



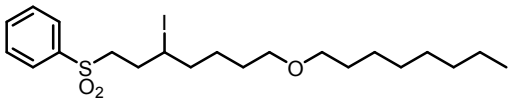
5g

5g was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 5-hexen-1-ol **3g** (24.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 8 hours. The final product **5g** was obtained as a colorless oil (52.0 mg, 68% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94–7.88 (m, 2H), 7.71-7.65 (m, 1H), 7.63-7.55 (m, 2H), 4.12–4.04 (m, 1H), 3.66-3.61 (m, 2H), 3.37 (ddd, *J* = 14.0, 9.5, 5.8 Hz, 1H), 3.21 (ddd, *J* = 13.9, 9.7,

5.9 Hz, 1H) 2.28-2.10 (m, 2H), 1.93-1.82 (m, 1H), 1.71 (qd, *J* = 9.9, 5.2 Hz, 1H), 1.62-1.52 (m, 4H), 1.50-1.39 (m, 1H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.10 (s), 134.08 (s), 129.57 (s), 128.10 (s), 62.56 (s), 56.62 (s), 40.32 (s), 34.70 (s), 33.24 (s), 31.72 (s), 25.88 (s); **HRMS (ESI, positive mode)** calculated for $C_{13}H_{19}IO_3S$ [M+Na]$^+$: 404.9992, found: 404.9991.

((3-iodo-7-(octyloxy)heptyl)sulfonyl)benzene (5h)

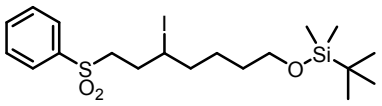


3h

5h was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-(hex-5-en-1-yloxy)octane **3h** (43.0 mg, 0.2 mmol, 1 equiv.). Reaction time: 8 hours. The final product **5h** was obtained as a colorless oil (67.2 mg, 68% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94–7.90 (m, 2H), 7.71-7.65 (m, 1H), 7.62-7.56 (m, 2H), 4.07 (tt, *J* = 9.0, 4.6, 1H), 3.43-3.32 (m, 5H), 3.21 (ddd, *J* = 13.9, 9.9, 5.8 Hz, 1H), 2.27-2.09 (m, 2H), 1.92-1.81 (m, 1H), 1.69 (dd, *J* = 12.2, 7.0 Hz, 1H), 1.48-1.37 (m, 2H), 1.28 (dd, *J* = 18.1, 13.5 Hz, 14H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.18 (s), 134.06 (s), 129.58 (s), 128.15 (s), 71.26 (s), 70.48 (s), 56.72 (s), 40.50 (s), 33.27 (s), 31.99 (s), 29.90 (s), 29.62 (s), 29.43 (s), 28.95 (s), 26.39 (s), 26.35 (s), 22.82 (s), 14.27 (s); **HRMS (ESI, positive mode)** calculated for $C_{21}H_{35}IO_3S$ [M+Na]$^+$: 517.1244, found: 517.1245.

***tert*-butyl((5-iodo-7-(phenylsulfonyl)heptyl)oxy)dimethylsilane (5i)**

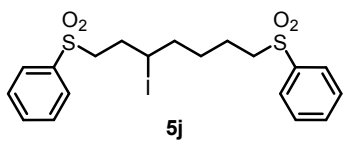


5i

5i was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and *tert*-butyl(hex-5-en-1-yloxy)dimethylsilane **3i** (42.9 mg, 0.2 mmol, 1 equiv.). Reaction time: 16 hours. The final product **5i** was obtained as a colorless oil (73.5 mg, 74% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.92 (dt, *J* = 8.6, 1.8 Hz, 2H), 7.71-7.65 (m, 1H), 7.62-7.56 (m, 2H), 4.06 (qd, *J* = 13.3, 4.6 Hz, 1H), 3.59 (t, *J* = 6.0 Hz, 2H), 3.38 (ddd, *J* = 14.0, 9.7, 5.7 Hz, 1H), 3.21 (ddd, *J* = 13.9, 9.9, 5.8 Hz, 1H) 2.27-2.09 (m, 2H), 1.86 (ddd, *J* = 13.1, 11.5, 7.0 Hz, 1H), 1.68 (ddd, *J* = 14.2, 9.8, 5.1 Hz, 1H), 1.55-1.35 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.18 (s), 134.06 (s), 129.57 (s), 128.14 (s), 62.86 (s), 56.73 (s), 40.46 (s), 34.98 (s), 33.31 (s), 31.92 (s), 26.12 (s), 26.05 (s), 18.48 (s), -5.12 (s); **HRMS (ESI, positive mode)** calculated for $C_{19}H_{33}IO_3SSi$ [M+Na]$^+$: 519.0857, found: 519.0854.

(3-iodoheptane-1,7-diyldisulfonyl)dibenzene (5j)

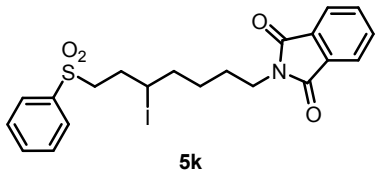


5j

5j was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and (hex-5-en-1-ylsulfonyl)benzene **3j** (36.9 mg, 0.2 mmol, 1 equiv.). Reaction time: 8 hours. The final product **5j** was obtained as a colorless oil (101.9 mg, 68% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.95–7.87 (m, 4H), 7.72-7.64 (m, 2H), 7.63-7.54 (m, 4H), 4.00 (qd, *J* = 13.2, 4.4 Hz, 1H), 3.38-3.28 (m, 1H), 3.18 (ddd, *J* = 14.0, 9.2, 6.4, 1H), 3.08 (t, *J* = 7.9 Hz, 2H) 2.24-2.00 (m, 2H), 1.87-1.59 (m, 5H), 1.45 (ddd, *J* = 16.0, 10.9, 6.0 Hz, 1H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.19 (s), 139.12 (s), 134.14 (s), 133.94 (s), 129.62 (s), 129.51 (s), 128.17 (s), 128.10 (s), 56.55 (s), 56.04 (s), 39.95 (s), 33.57 (s), 33.29 (s), 28.30 (s), 21.94 (s); **HRMS (ESI, positive mode)** calculated for $C_{19}H_{23}IO_4S_2$ $[M+Na]^+$: 528.9975, found: 528.9975.

2-(5-iodo-7-(phenylsulfonyl)heptyl)isoindoline-1,3-dione (5k)

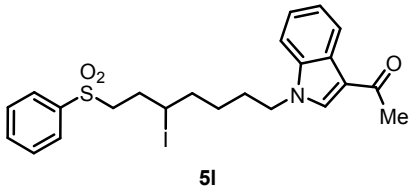


5k

5k was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 2-(hex-5-en-1-yl)isoindoline-1,3-dione **3k** (45.8 mg, 0.2 mmol, 1 equiv.). Reaction time: 16 hours. The final product **5k** was obtained as a colorless oil (74.6 mg, 73% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94–7.88 (m, 2H), 7.86-7.80 (m, 2H), 7.74-7.68 (m, 2H), 7.66 (dt, *J* = 2.6, 1.7 Hz, 1H), 7.62-7.55 (m, 2H), 4.03 (ddd, *J* = 13.4, 8.9, 4.7 Hz, 1H), 3.66 (t , *J* = 7.2 Hz, 2H), 3.41-3.31 (m, 1H), 3.20 (ddd, *J* = 14.0, 9.5, 6.1 Hz, 1H) 2.24-2.09 (m, 2H), 1.92-1.81 (m, 1H), 1.78-1.62 (m, 3H), 1.62-1.48 (m, 1H), 1.47-1.32 (m, 1H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 168.35 (s), 138.95 (s), 133.95 (s), 133.90 (s), 132.04 (s), 129.42 (s), 127.98 (s), 123.22 (s), 56.42 (s), 39.73 (s), 37.43 (s), 34.08 (s), 33.18 (s), 27.55 (s), 26.57 (s); **HRMS (ESI, positive mode)** calculated for $C_{21}H_{22}INO_4S$ $[M+Na]^+$: 534.0206, found: 534.0207.

1-(1-(5-iodo-7-(phenylsulfonyl)heptyl)-1H-indol-3-yl)ethan-1-one (5l)

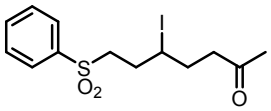


5l

5l was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-(1-(hex-5-en-1-yl)-1H-indol-3-yl)ethan-1-one **3l** (48.3 mg, 0.2 mmol, 1 equiv.). Reaction time: 24 hours. The final product **5l** was obtained as a colorless oil (67.0 mg, 64% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.40-8.34 (m, 1H), 7.89 (ddd, *J* = 7.3, 3.9, 1.9 Hz, 2H), 7.74 (s, 1H), 7.69-7.63 (m, 2H), 7.60-7.54 (m, 2H), 7.36-7.25 (m, 3H), 4.15 (t, *J* = 7.1 Hz, 2H), 4.02 (ddd, *J* = 13.3, 9.0, 4.5 Hz, 1H), 3.37-3.26 (m, 1H), 3.17 (ddd, *J* = 14.0, 9.0, 6.4 Hz, 1H), 2.53 (s, 3H), 2.24-2.11 (m, 2H),1.98-1.78 (m, 3H), 1.77-1.52 (m, 3H), 1.43 (tdd, *J* = 13.1, 10.1, 5.1 Hz, 1H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 193.10 (s), 139.09 (s), 136.77 (s), 134.78 (s), 134.12 (s), 129.59 (s), 126.51 8s), 123.44 (s), 122.86 (s), 122.70 (s), 117.24 (s), 109.83 (s), 56.50 (s), 46.89 (s), 39.94 (s), 34.02 (s), 33.33 (s), 28.99 (s), 27.83 (s), 26.97 (s); **HRMS (ESI, positive mode)** calculated for $C_{23}H_{26}INO_3S$ $[M+Na]^+$: 546.0570, found: 524.0751.

5-iodo-7-(phenylsulfonyl)heptan-2-one (5m)

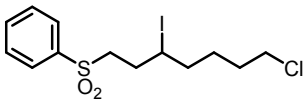


5m

5m was synthesized according to the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (84.6 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 5-hexen-2-one **3o** (23.2 µl, 0.2 mmol, 1 equiv.). Reaction time: 24 hours. The final product **5m** was obtained as a colorless oil (45.6 mg, 60% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 2H), 7.71 – 7.66 (m, 1H), 7.62 – 7.58 (m, 2H), 4.14 – 4.05 (m, 1H), 3.37 (ddd, J = 15.3, 10.6, 6.8 Hz, 1H), 3.21 (ddd, J = 17.1, 14.3, 8.0 Hz, 1H), 2.73 – 2.55 (m, 2H), 2.26 – 2.17 (m, 2H), 2.15 (s, 3H), 2.05 – 1.91 (m, 2H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 206.96 (s), 139.08 (s), 134.10 (s), 129.59 (s), 128.15 (s), 56.51 (s), 43.33 (s), 34.05 (s), 33.97 (s), 33.66 (s), 30.28 (s); **HRMS (ESI, positive mode)** calculated for $C_{13}H_{17}IO_3S$ $[M+Na]^+$: 402.9835, found: 402.9836.

((7-chloro-3-iodoheptyl)sulfonyl)benzene (5n)

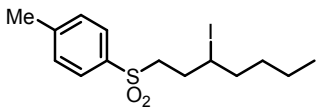


5n

5n was synthesized according to a modified version of the general procedure **C** from (iodomethyl)sulfonyl)benzene **4a** (56.4 mg, 0.2 mmol, 1 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 6-chloro-1-hexene **3n** (53.0 µl, 0.4 mmol, 2 equiv.). Reaction time: 24 hours. The final product **5n** was obtained as a colorless oil (46.1 mg, 58% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.72 – 7.66 (m, 1H), 7.63 – 7.57 (m, 2H), 4.07 (tt, J = 8.9, 4.4 Hz, 1H), 3.53 (t, J = 6.5 Hz, 2H), 3.37 (ddd, J = 14.0, 9.4, 5.8 Hz, 1H), 3.21 (ddd, J = 13.9, 9.6, 5.9 Hz, 1H), 2.29 – 2.12 (m, 2H), 1.93 – 1.61 (m, 6H). **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.17 (s), 134.11 (s), 129.61 (s), 128.14 (s), 56.65 (s), 44.64 (s), 39.86 (s), 34.08 (s), 33.29 (s), 31.66 (s), 26.92 (s).; **HRMS (ESI, positive mode)** calculated for $C_{13}H_{18}ClIO_2S$ $[M+Na]^+$: 422.9653, found: 422.9654.

1-((3-iodoheptyl)sulfonyl)-4-methylbenzene (5p)

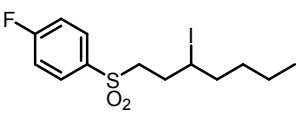


5p

5p was synthesized according to the general procedure **C** from 1-((iodomethyl)sulfonyl)-4-methylbenzene **4b** (88.8 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-hexene **3a** (25.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 24 hours. The final product **5p** was obtained as a colorless oil (31.9 mg, 42% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82–7.75 (m, 2H), 7.37 (dd, *J* = 8.5, 0.5, 2H), 4.10-4.01 (m, 1H), 3.34 (ddd, *J* = 14.0, 9.7, 5.8 Hz, 1H), 3.18 (ddd, *J* = 13.9, 9.9, 5.8 Hz, 1H), 2.46 (s, 3H), 2.26-2.07 (m, 2H), 1.90-1.78 (m, 1H), 1.66 (qd, *J* = 9.9, 5.0 Hz, 1H), 1.51-1.39 (m, 1H), 1.39-1.21 (m, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 145.06 (s), 136.21 (s), 130.16 (s), 128.14 (s), 56.78 (s), 40.37 (s), 35.19 (s), 33.35 (s), 31.60 (s), 21.93 (s), 21.80 (s), 14.02 (s); **HRMS (ESI, positive mode)** calculated for $C_{14}H_{21}IO_2S$ $[M+Na]^+$: 403.0199, found: 403.0204.

1-fluoro-4-((3-iodoheptyl)sulfonyl)benzene (5q)

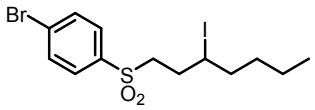


5q

5q was synthesized according to the general procedure **C** from 1-fluoro-4-((iodomethyl)sulfonyl)benzene **4c** (90.0 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-hexene **3a** (25.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 24 hours. The final product **5q** was obtained as a colorless oil (49.9 mg, 65% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97-7.90 (m, 2H), 7.30-7.23 (m, 2H), 3.37 (tt, *J* = 8.9, 4.7 Hz, 1H), 3.37 (ddd, *J* = 14.0, 9.9, 5.5 Hz, 1H), 3.21 (ddd, *J* = 13.9, 10.1, 5.6 Hz, 1H), 2.27-2.08 (m, 2H) 1.92-1.79 (m, 1H), 1.67 (ddd, *J* = 19.6, 10.0, 5.1 Hz, 2H), 1.53-1.41 (m, 1H), 1.40-1.21 (m, 2H), 0.93-0.86 (m, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 167.20 (s), 164.64 (s), 135.09 (d), 130.93 (d), 116.87 (s), 116.65 (s), 56.74 (s), 40.23 (s), 34.75 (s), 33.10 (s), 31.46 (s), -21.77 (s), -13.85 (s);); ^{19}F-NMR (376 MHz, $CDCl_3$) δ -103.06 (m, 1F); **HRMS (ESI, positive mode)** calculated for $C_{13}H_{18}FIO_2S$ $[M+Na]^+$: 406.9948, found: 406.9954.

1-bromo-4-((3-iodoheptyl)sulfonyl)benzene (5r)

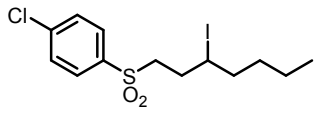


5r

5r was synthesized according to the general procedure **C** from 1-bromo-4-((iodomethyl)sulfonyl)benzene **4h** (108.0 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-hexene **3a** (25.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 24 hours. The final product **5o** was obtained as a colorless oil (38.3, 43% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82–7.69 (m, 4H), 4.06 (tt, *J* = 8.9, 4.6 Hz, 1H), 3.36 (ddd, *J* = 14.0, 10.0, 5.6 Hz, 1H), 3.20 (ddd, *J* = 14.0, 10.0, 5.6 Hz, 1H), 2.26-2.08 (m, 2H),1.91-1.79 (m, 1H), 1.67 (qd, *J* = 10.0, 5.0 Hz, 1H), 1.52-1.40 (m, 1H), 1.40-1.22 (m, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 138.16 (s), 132.92 (s), 129.70 (s), 129.47 (s), 56.79 (s), 40.39 (s), 34.84 (s), 33.20 (s), 31.63 (s), 21.94 (s), 14.03 (s); **HRMS (ESI, positive mode)** calculated for $C_{13}H_{18}BrIO_2S$ $[M+Na]^+$: 466.9147, found: 466.9142.

1-chloro-4-((3-iodoheptyl)sulfonyl)benzene (5s)

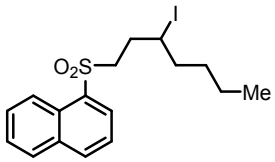


5s

5s was synthesized according to the general procedure **C** from 1-chloro-4-((iodomethyl)sulfonyl)benzene **4d** (94.5 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-hexene **3a** (25.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 24 hours. The final product **5s** was obtained as a colorless oil (36.9, 46% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89–7.81 (m, 2H), 7.61-7.52 (m, 2H), 4.18-3.91 (m, 1H), 3.37 (ddd, *J* = 14.0, 10.0, 5.5 Hz, 1H), 3.20 (ddd, *J* = 14.0, 10.1, 5.6 Hz, 1H), 2.28-2.04 (m, 2H), 1.85 (dtd, *J* = 14.4, 9.5, 4.6 Hz, 1H), 1.67 (qd, *J* = 10.0, 5.0 Hz, 1H), 1.54-1.39 (m, 1H), 1.40-1.20 (m, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 140.88 (s), 137.83 (s), 129.92 (s), 129.64 (s), 56.81 (s), 40.38 (s), 34.86 (s), 33.21 (s), 31.62 (s), 21.94 (s), 14.02 (s); **HRMS (ESI, positive mode)** calculated for $C_{13}H_{18}ClIO_2S$ $[M+Na]^+$: 422.9653, found: 422.9659.

1-((3-iodooctyl)sulfonyl)naphthalene (5t)

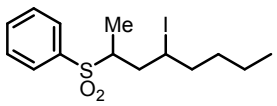


5t

5t was synthesized according to the general procedure **C** from 1-((iodomethyl)sulfonyl)naphthalene **4i** (99.3 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-hexene **3a** (25.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 24 hours. The final product **5t** was obtained as a colorless oil (32.7, 38% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, *J* = 8.6, 0.7 Hz, 1H), 8.31 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.74 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.68-7.57 (m, 2H), 4.11-4.01 (m, 1H), 3.62-3.51 (m, 1H), 3.43 (ddd, *J* = 14.0, 9.6, 6.0 Hz, 1H), 2.30-2.11 (m, 2H), 1.89-1.73 (m, 1H), 1.69-1.52 (m, 1H), 1.48-1.35 (m, 1H), 1.36.16 (m, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 135.56 (s), 134.41 (s), 134.16 (s), 130.76 (s), 129.49 (s), 129.04 (s), 128.99 (s), 127.29 (s), 124.55 (s), 124.15 (s), 56.23 (s), 40.36 (s), 35.20 (s), 33.27 (s), 31.57 (s), 21.92 (s), 14.01 (s); **HRMS (ESI, positive mode)** calculated for $C_{17}H_{21}IO_2S$ $[M+Na]^+$: 439.0199, found: 439.0195.

((4-iodooctan-2-yl)sulfonyl)benzene (5u)

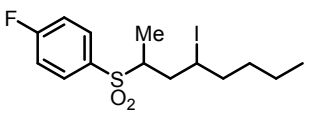


5u

5u was synthesized according to the general procedure **C** from ((1-iodoethyl)sulfonyl)benzene **4j** (88.8 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-hexene **3a** (25.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 24 hours. The final product **5u** was obtained as a colorless oil (70.0 mg, 92% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ [7.92–7.86 (m, 2H), 7.70-7.64 (m, 1H),7.61-7.55 (m, 2H)] *minor*+*major*, 4.31 (ddd, *J* = 13.2, 9.1, 4.6, 1H) *minor*, 3.99-3.89 (m, 1H) *major*, 3.46-3-31 (m, 2H) *minor*+*major*, 2.46 (ddd, *J* = 15.8, 7.3, 4.6, 1H) *minor*, 2.35 (ddd, *J* = 14.8, 11.8, 3.2 Hz, 1H) *major*, [1.90-1.78 (m, 1H), 1.66 (qd, *J* = 9.9, 5.0, 2H), 1.51-1.39 (m, 1H), 1.39-1.21 (m, 7H), 0.88 (q, *J* = 7.1 Hz, 3H)] *minor*+*major*; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ [137.28 (s), 133.99 (s), 133.95 (s), 129.38 (s), 129.35 (s), 129.02 (s), 129.00 (s)] *minor*+*major*, 60.86 (s) *major*, 60.34 (s) *minor*, 41.55 (s) *minor*, 41.05 (s) *major*, 40.28 (s) *major*, 39.05 (s) *major*, 34.49 (s) *minor*, 31.68 (s) *major*, 31.45 (s) *minor*, [21.99 (s), 15.70 (s), 14.05 (s), 14.02 (s)] *minor*+*major*; **HRMS (ESI, positive mode)** calculated for $C_{14}H_{21}IO_2S$ $[M+Na]^+$: 403.0199, found: 403.0198.

1-fluoro-4-((4-iodooctan-2-yl)sulfonyl)benzene (5v)



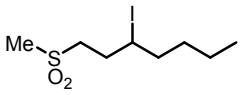
5v

5v was synthesized according to the general procedure **C** from 1-fluoro-4-((1-iodoethyl)sulfonyl)benzene **4e** (94.2 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and 1-hexene **3a** (25.0 µl, 0.2 mmol, 1 equiv). Reaction time: 24 hours. The final product **5v** was obtained as a colorless oil (52.6 mg, 66% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ [7.95–7.86 (m, 2H), 7.31-7.22 (m, 2H)] *minor*+*major*, 4.34 (ddd, *J* = 13.2, 9.1, 4.6, 1H) *minor*, 3.99-3.88 (m, 1H) *major*, 3.46-3.30 (m, 1H) *minor*+*major*, 2.45 (ddd, *J* = 15.8, 7.4, 4.6 Hz, 1H) *minor*, 2.33 (ddd, *J* = 14.7, 11.8, 3.1 Hz, 1H) *major*, [2.00-1.96

(m, 1H), 1.85-1.62 (m, 2H), 1.56-1.27 (m, 4H), 1.25 (dd, *J* = 6.9, 1.4 Hz, 3H), 0.88 (dt, *J* = 7.2, 2.2 Hz, 3H)] *minor*+*major*; **^{13}C-NMR (101 MHz, $CDCl_3$)** δ [165.34 (s), 164.79 (s), 133.58 (d), 133.36 (d), 131.93 (d), 131.83 (d), 116.86 (s), 116.85 (s), 116.63 (s)] *minor*+*major*, 61.08 (s) *major*, 60.56 (s) *minor*, 41.52 (s) *minor*, 41.08 (s) minor, 40.30 (s) *major*, 39.13 (s) *major*, 36.41 (s) *minor*, 34.34 (s) *major*, [31.69 (s), 31.49 (s), 22.00 (s), 15.80 (s), 14.05 (s), 14.03 (s), 12.09 (s)] *minor*+*major*; **^{19}F-NMR (376 MHz, $CDCl_3$)** δ -103.26 (m, 1F) *minor*, -103.13 (m, 1F) *major*; **HRMS (ESI, positive mode)** calculated for $C_{14}H_{20}FIO_2S$ $[M+Na]^+$: 421.0105, found: 421.0109.

3-iodo-1-(methylsulfonyl)heptane (5w)

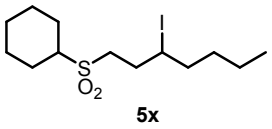


5w

5w was synthesized according to the general procedure **C** from iodo(methylsulfonyl)methane **4f** (66.0 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and the 1-hexene **3a** (25.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 24 hours. The final product **5w** was obtained as a colorless oil (37.1mg, 75% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.19-4.09 (m, 1H), 3.32 (ddd, *J* = 13.9, 9.9, 5.7, 1H), 3.19-3.07 (m, 1H), 2.94 (s, 3H), 2.38-2.20 (m, 2H), 1.99-1.85 (m, 1H), 1.74 (ddd, *J* = 14.8, 10.1, 5.2 Hz, 1H), 1.58-1.26 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 55.28 (s), 41.21 (s), 40.47 (s), 35.19 (s), 32.87 (s), 31.63 (s), 21.97(s), 14.03 (s); **HRMS (ESI, positive mode)** calculated for $C_8H_{17}IO_2S$ $[M+Na]^+$: 326.9886, found: 326.9889.

3-iodo-1-(methylsulfonyl)heptane (5x)

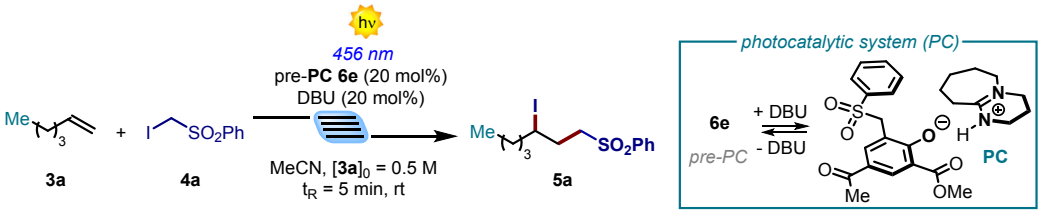


5x

5x was synthesized according to the general procedure **C** from ((iodomethyl)sulfonyl)cyclohexane **4g** (86.4 mg, 0.3 mmol, 1.5 equiv.), phenol **6e** (13.9 mg, 0.04 mmol, 20 mol%), sodium ascorbate (9.9 mg, 0.05 mmol, 25 mol%), DBU (6 µl, 0.04 mmol, 20 mol%) and the 1-hexene **3a** (25.0 µl, 0.2 mmol, 1 equiv.). Reaction time: 24 hours. The final product **5x** was obtained as a colorless oil (70.5, 95% yield).

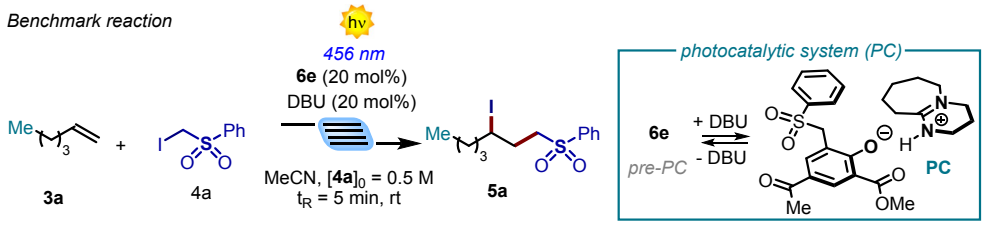
^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.20-4.09 (m, 1H), 3.20 (ddd, *J* = 13.5, 9.9, 5.6 Hz, 1H), 3.00 (ddd, *J* = 13.5, 10.1, 5.6 Hz, 1H), 2.84 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.27 (dddd, *J* = 28.1, 22.7, 9.4, 6.0 Hz, 4H), 2.00-1.85 (m, 3H), 1.80-1.68 (m, 2H), 1.65-1.45 (m, 3H), 1.44-1.18 (m, 6H), 0.91 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 61.52 (s), 49.86 (s), 40.52 (s), 32.01 (s), 31.62 (s), 25.32 (s), 25.19 (s), 25.17 (s), 25.03 (s), 21.95 (s), 14.02 (s); **HRMS (ESI, positive mode)** calculated for $C_{13}H_{25}IO_2S$ $[M+Na]^+$: 395.0512, found: 395.0511.

D. GENERAL PROCEDURE FOR THE ATRA REACTION IN MICROFLUIDIC CONDITIONS



The alkene (**3a**) (500 µL, 4 mmol, 1 equiv.), the α-iodosulfone (**4a**) (1.7 gr, 6 mmol, 1.5 equiv.) and the pre-catalyst **6e** (278.7 mg, 0.8 mmol, 0.2 equiv, 20 mol%) were introduced into a vial and dissolved in 8 mL of acetonitrile (MeCN, $[\mathbf{3a}]_0$ = 0.5 M). The mixture was degassed with Argon (Ar) for 5 minutes. Then, DBU (120 µL, 0.8 mmol, 0.2 equiv, 20 mol%) was added to the vial under Ar atmosphere. The reaction mixture was connected to the flow setup (Figure S in Section A.2) and introduced in continuous-flow with a flow rate of 42 µL/min (residence time, t_R = 5 min). The crude was collected in a vial connected to the exit of the microreactor (collected volume = 8 mL *ca.*). To 7 mL of the crude were added 10 mL of a saturated solution of ammonium chloride (NH_4Cl), and the organic layer was extracted with dichloromethane (DCM) three times. The organic layer was then separated, dried over magnesium sulfate ($MgSO_4$) and filtered. The final residue was purified by flash column chromatography on silica gel (hexane/EtOAc 8:2) to afford the ATRA product **5a** as a colorless oil (53% yield, 490 mg, 1.8 mmol).

E. GENERAL PROCEDURE FOR THE RECOVERY AND REUSE OF THE PRE-CATALYST 6e



All the reactions are independent runs where the pre-PC **6e** has been reused after purification by extraction and filtration. The process has been developed as follow:

In the first run, 5 mL of reaction mixture composed by olefin **3a** (1 mmol, 1 equiv.), α-iodosulfone **4a** (1.5 mmol, 1.5 equiv., 0.5 M in MeCN), the pre-PC **6e** (0.2 mmol, 0.2 equiv, 20 mol%) and DBU (0.2 mmol, 0.2 equiv., 20 mol%) was pumped into a MFP with a t_R of 5 min. To the crude reaction, the internal standard (trimethoxybenzene) was added, and the mixture was analyzed by ^{1}H-NMR inferring the NMR yield of the ATRA product **5a**. Subsequently, the crude was basified with an aqueous solution of Na_2CO_3 and washed (x3) with Et_2O. The aqueous phase was then acidified with AcOH and extracted with EtOAc (x3). The organic phase was dried over $MgSO_4$, filtered and concentrate under vacuum. The crude **6e** was then filtered on a pad of silica using a solution 6:4 hexane:EtOAc affording the pre-PC **6e** in the stated yield (Figure S4).

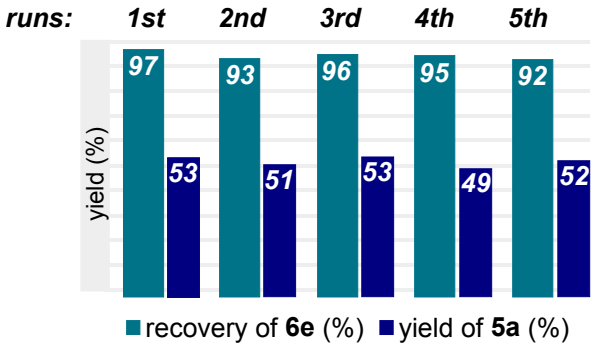
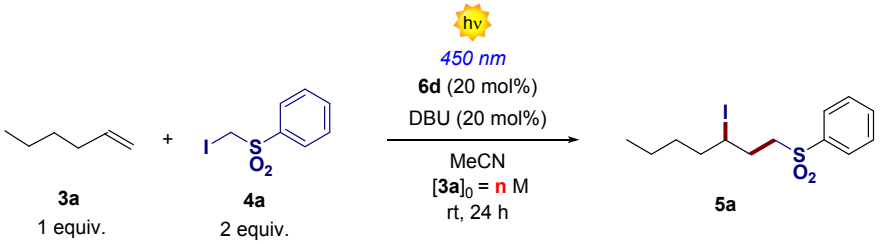


Figure S4. Recovery and reuse of the pre-PC **6e** in 5 independent runs.

F. SCREENING OF THE REACTION CONDITIONS

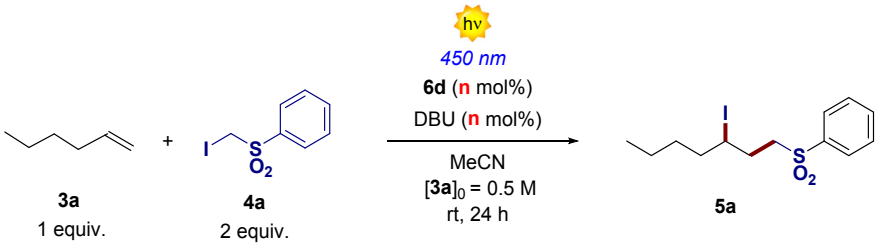
The following screening of the reaction conditions have been carried out by employing the commercially available disubstituted phenol **6d** as pre-photocatalyst under blue light irradiation (450 nm).

Table S1. Screening of the concentration with respect to alkene **3a**. Reactions were performed on 0.2 mmol scale. [a]Yield determined by ^{1}H-NMR analysis, using trichloroethylene as internal standard.



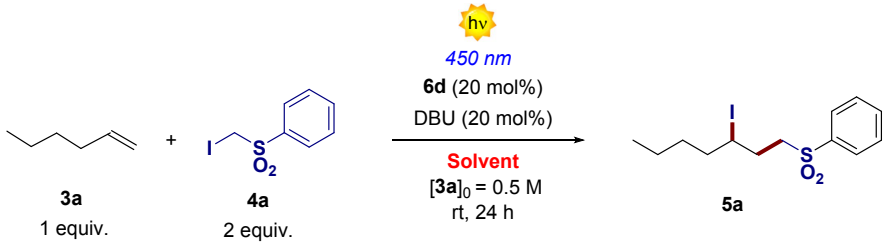
Entry	conc [M]	Yield 5a[a]
1	0.25	58%
2	0.125	30%
3	0.5	94%

Table S2. Screening of the role of the catalyst loading. Reactions were performed on 0.2 mmol scale. [a]Yield determined by ^{1}H-NMR analysis, using trichloroethylene as internal standard.



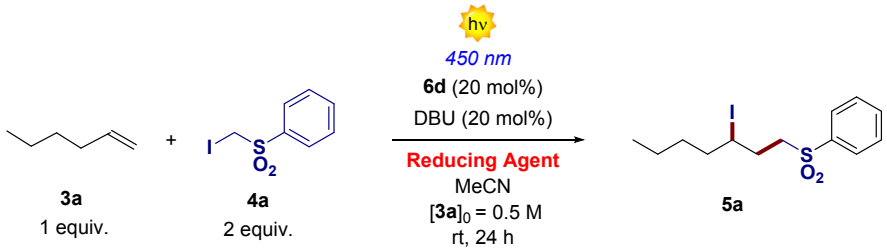
Entry	6d (mol%)	DBU (mol%)	Yield 5a[a]
1	20	20	94%
2	15	15	74%
3	10	10	66%

Table S3. Screening of the role of the solvent. Reactions were performed on 0.2 mmol scale. [a]Yield determined by [1]H-NMR analysis, using trichloroethylene as internal standard.



Entry	Solvent	Yield 5a[a]
1	MeCN	94%
2	EtOAc	70%
3	DMSO	47%
4	DMF	25%
5	THF	12%

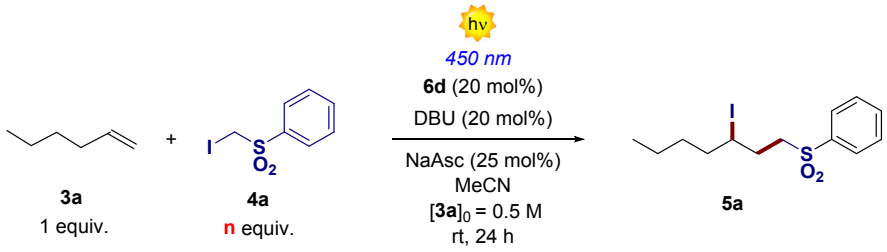
Table S4. Screening of the role of the reducing agents. Reactions were performed on 0.2 mmol scale. [a]Yield determined by [1]H-NMR analysis, using trichloroethylene as internal standard. NaAsc = sodium ascorbate.



Entry	Reducing Agent	Loading (mol%)	Yield 5a[a]
1	None	-	94%
2	$Na_2S_2O_3$	25	94%
3	NaAsc	25	>99%

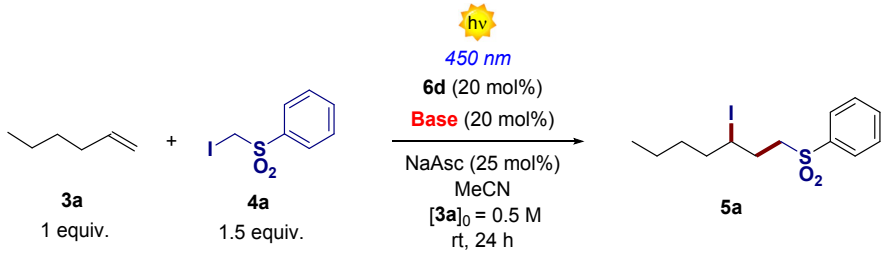
The following screening experiments have been carried out by using a lower amount of **4a** for being able to appreciate the different outcome in terms of reactivity.

Table S5. Screening of the role of the α-iodo sulfone amount. Reactions were performed on 0.2 mmol scale. [a]Yield determined by ^{1}H-NMR analysis, using trichloroethylene as internal standard. NaAsc = sodium ascorbate.



Entry	4a (equiv.)	NaAsc (mol%)	Yield 5a[a]
1	2	25	>99%
2	1.5	25	80%

Table S6. Screening of the role of the bases. Reactions were performed on 0.2 mmol scale. [a]Yield determined by ^{1}H-NMR analysis, using trichloroethylene as internal standard. NaAsc = sodium ascorbate. DBU = 1,5-diazabiciclo(5.4.0)undec-7-ene. TMG = 1,1,3,3-tetramethylguanidine. DABCO = 1,4-diazabicyclo[2.2.2]octane. DBN = 1,5-diazabicyclo(4.3.0)non-5-ene.



Entry	Base	NaAsc (mol%)	Yield 5a[a]
1	DBU	25	80%
2	TMG	25	80%
3	DABCO	25	64%
4	DBN	25	79%
5	K_2CO_3	25	17%
6	Cs_2CO_3	25	67%
7	NaAsc	25	20%
8	NaH	25	18%

G. UNSUCCESFULL SUBSTRATES

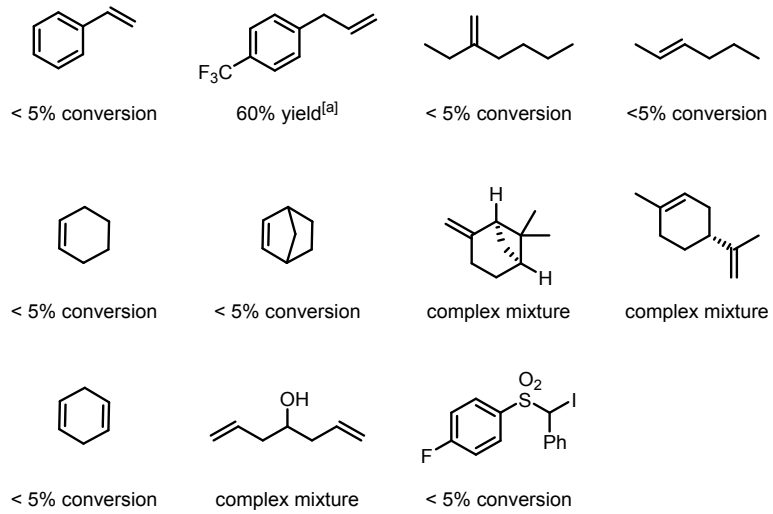
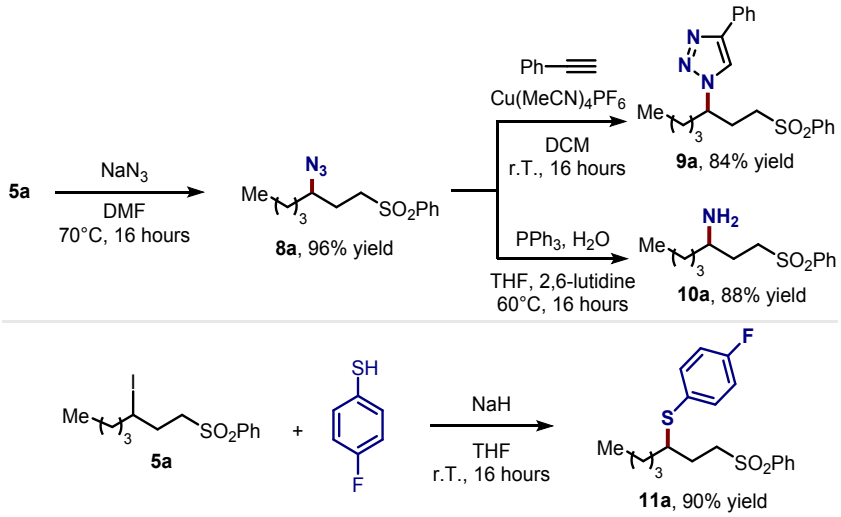


Figure S5. Unsuccessful substrates in the photochemical ATRA process. Conversions and yields determined by ^{1}H-NMR analysis, using trichloroethylene as internal standard. [a] The corresponding product was not separable from the iodosulfone reagent **4a**.

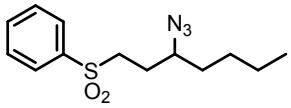
H. PRODUCT MANIPULATIONS



Azidation of 5a. STEP 1. To a round-bottom flask containing **5a** (1 equiv) under N_2, it was added dry DMF (0.1 M) followed by sodium azide (2 equiv). The mixture was stirred vigorously at 70 ºC for 16 hours. The reaction was quenched by adding an aqueous solution of LiCl (5% w/v) and extracted with ethyl acetate (x3 times). The organic phases were combined and dried over Na_2SO_4 before concentration *in vacuo*. The mixture was purified by flash column chromatography (hexane/ethyl acetate 9:1) to give the product **8a** in the stated yield.

Characterization Data

((3-azidoheptyl)sulfonyl)benzene (8a)



8a

8a was synthesized according to the abovementioned procedure from ((3-iodoheptyl)sulfonyl)benzene **5a** (100 mg, 0.27 mmol, 1 equiv.). The final product **8a** was obtained as a colorless oil (74 mg, 96% yield).

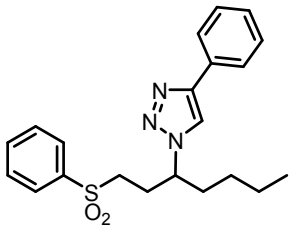
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.70 – 7.64 (m, 1H), 7.62 – 7.55 (m, 2H), 3.44 – 3.35 (m, 1H), 3.28 – 3.10 (m, 2H), 2.07 – 1.96 (m, 1H), 1.83 – 1.71 (m, 1H), 1.64 – 1.45 (m, 2H), 1.43 – 1.26 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.13 (s), 134.01 (s), 129.54 (s), 128.10 (s), 61.22 (s), 53.20 (s), 34.17 (s), 28.09 (s), 27.55 (s), 22.52 (s), 14.01 (s); **HRMS (ESI, positive mode)** calculated for $C_{13}H_{19}N_3O_2S$ $[M+Na]^+$: 304.1090, found: 304.1092.

STEP 2a. To a round-bottom flask containing **8a** (1 equiv.) under N_2, it was added dry DCM (0.1 M) followed by phenylacetylene (1.1 equiv.), $Cu(MeCN)_4PF_6$ (0.2 equiv.) and 2,6-lutidine (0.2 equiv). The mixture was stirred vigorously at room temperature for 16 hours. The reaction was quenched by adding water and extracted with DCM (x3 times). The organic phases were combined and dried over Na_2SO_4 before concentration *in vacuo*. The mixture was purified by flash column chromatography (hexane/ethyl acetate 8:2) to give the product **9a** in the stated yield.

STEP 2b. To a round-bottom flask containing **8a** (1 equiv.) under N_2, it was added dry THF (0.1 M) followed by triphenylphosphine (2 equiv.), and water (6 equiv.). The mixture was stirred vigorously at 50°C for 16 hours. The reaction mixture was concentrated *in vacuo*, then a saturated solution of potassium carbonate was added, and it was extracted with DCM (x3 times). The organic phases were combined and dried over Na_2SO_4 before concentration *in vacuo*. The mixture was purified by flash column chromatography (hexane/ethyl acetate 9:1) to give the product **10a** in the stated yield.

Characterization Data

4-phenyl-1-(1-(phenylsulfonyl)heptan-3-yl)-1H-1,2,3-triazole (9a)

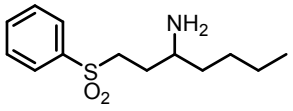


9a

9a was synthesized according to the abovementioned procedure (STEP 2a) from ((3-azidoheptyl)sulfonyl)benzene **8a** (74 mg, 0.26 mmol, 1 equiv.). The final product **9a** was obtained as a white solid (84 mg, 84% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.82 (ddd, *J* = 7.2, 2.9, 1.3 Hz, 4H), 7.78 (s, 1H), 7.66 – 7.59 (m, 1H), 7.55 – 7.48 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.30 (m, 1H), 4.69 (tt, *J* = 9.7, 5.0 Hz, 1H), 2.99 (ddd, *J* = 14.2, 8.7, 7.1 Hz, 1H), 2.86 (ddd, *J* = 14.1, 8.3, 5.8 Hz, 1H), 2.51 – 2.33 (m, 2H), 2.05 – 1.93 (m, 1H), 1.88 (ddd, *J* = 15.1, 10.4, 5.2 Hz, 1H), 1.37 – 1.16 (m, 3H), 1.14 – 1.00 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 138.88 (s), 134.10 (s), 130.40 (s), 129.55 (s), 128.97 (s), 128.41 (s), 127.93 (s), 125.76 (s), 118.98 (s), 60.53 (s), 52.59 (s), 35.38 (s), 28.56 (s), 28.03 (s), 22.19 (s), 13.86 (s); **HRMS (ESI, positive mode)** calculated for $C_{21}H_{25}N_3O_2S$ $[M+H]^+$: 384.1740, found: 384.1744.

4-phenyl-1-(1-(phenylsulfonyl)heptan-3-yl)-1H-1,2,3-triazole (10a)



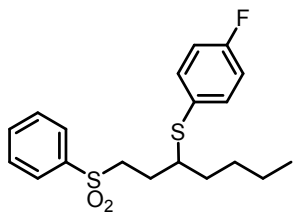
10a

10a was synthesized according to the abovementioned procedure (STEP 2b) from ((3-azidoheptyl)sulfonyl)benzene **8a** (74 mg, 0.26 mmol, 1 equiv.). The final product **10a** was obtained as a colorless oil (60 mg, 88% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.67 – 7.62 (m, 1H), 7.59 – 7.53 (m, 2H), 3.29 (ddd, *J* = 13.9, 11.1, 4.9 Hz, 1H), 3.17 (ddd, *J* = 13.9, 11.1, 5.2 Hz, 1H), 2.78 – 2.72 (m, 1H), 1.93 – 1.84 (m, 1H), 1.66 – 1.56 (m, 1H), 1.39 – 1.34 (m, 3H), 1.33 – 1.20 (m, 5H), 0.87 (t, *J* = 7.0 Hz, 3H); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 139.42 (s), 133.73 (s), 129.38 (s), 128.11 (s), 53.64 (s), 50.25 (s), 38.14 (s), 30.21 (s), 28.25 (s), 22.75 (s), 14.12 (s); **HRMS (ESI, positive mode)** calculated for $C_{13}H_{21}NO_2S$ $[M+Na]^+$: 256.1366, found: 256.1362.

Thionation of 5a. In a two-neck round-bottomed flask, dried under argon, a solution of 4-fluorobenzenethiol (1 equiv.) in dry THF (0.25 M) was stirred at 0°C for 10 minutes. Sodium hydride (1 equiv.) was added portion-wise, and the mixture was stirred at 0°C for 1 hour. Then, **5a** (1 equiv.) was added and the resulting solution was stirred at room temperature for 16 hours. The reaction was quenched by the addition of ammonium chloride and then extracted with ethyl acetate (x3 times). The organic phases were combined and washed with brine and then dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (cyclohexane/ethyl acetate) to give the corresponding thiol **11a** in the stated yield.

3-((4-fluorophenyl)thio)heptyl benzenesulfinate (11a)



11a

11a was synthesized according to the abovementioned procedure from ((3-iodoheptyl)sulfonyl)benzene **5a** (183 mg, 0.5 mmol, 1 equiv.). The final product **11a** was obtained as a colorless oil (165 mg, 90% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.70 – 7.65 (m, 1H), 7.60 – 7.54 (m, 2H), 7.27 – 7.21 (m, 2H), 6.96 – 6.89 (m, 2H), 3.41 – 3.26 (m, 2H), 2.99 – 2.90 (m, 1H), 2.01 – 1.90 (m, 1H), 1.86 – 1.73 (m, 1H), 1.51 – 1.21 (m, 6H), 0.87 (t, J = 7.2 Hz, 3H); **^{19}F-NMR (376 MHz, $CDCl_3$)** δ -113.36 (m, 1F); **^{13}C-NMR (101 MHz, $CDCl_3$)** δ 163.99 (s), 161.52 (s), 139.17 (s), 136.07 (d, J = 8.2 Hz), 133.86 (s), 129.48 (s), 128.21 (s), 116.26 (d, J = 21.7 Hz), 53.51 (s), 48.85 (s), 34.06 (s), 29.17 (s), 27.11 (s), 22.53 (s), 14.07 (s); **HRMS (ESI, positive mode)** calculated for $C_{19}H_{23}FO_2S_2$ $[M+Na]^+$: 389.1016, found: 389.1018.

I. MECHANISTIC INSIGHTS

I.1. CYCLIC VOLTAMMETRY MEASUREMENTS

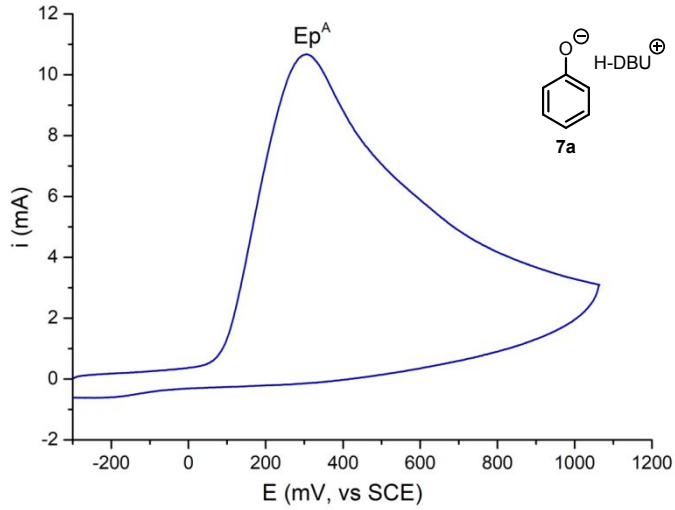


Figure S6. Cyclic voltammogram for the phenolate **7a** (5 mM), formed upon deprotonation of the phenol **6a** (5 mM) with DBU (5 mM); in $TBAPF_6$ in CH_3CN (0.1 M). Scan rate: 0.1 V/s. Glassy carbon working electrode; Ag/AgCl (3M, NaCl) reference electrode; Glassy carbon auxiliary electrode. Irreversible oxidation, $Ep^A \approx E_{ox}$ (**7a**$^{\bullet+}$/**7a**) = +0.30 V vs SCE. E_p^A refers to the anodic peak potential, while the E^{ox} value describes the electrochemical properties of **7a**.

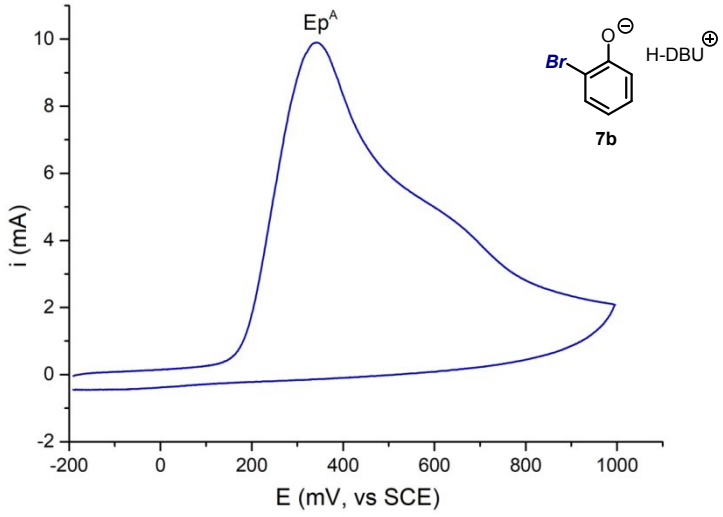


Figure S7. Cyclic voltammogram for the phenolate **7b** (5 mM), formed upon deprotonation of the phenol **6b** (5 mM) with DBU (5 mM); in $TBAPF_6$ in CH_3CN (0.1 M). Scan rate: 0.1 V/s. Glassy carbon working electrode; Ag/AgCl (3M, NaCl) reference electrode; Glassy carbon auxiliary electrode. Irreversible oxidation, $Ep^A \approx E_{ox}$ (**7b**$^{\bullet+}$/**7b**) = +0.34 V vs SCE. E_p^A refers to the anodic peak potential, while the E^{ox} value describes the electrochemical properties of **7b**.

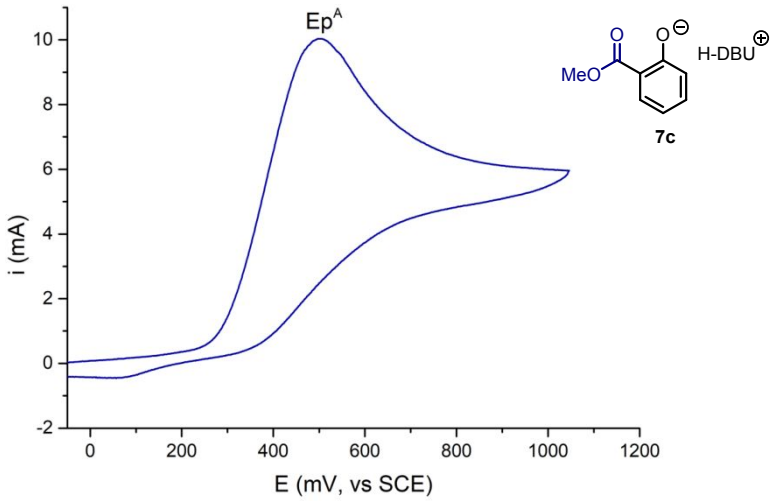


Figure S8. Cyclic voltammogram for the phenolate **7c** (5 mM), formed upon deprotonation of the phenol **6c** (5 mM) with DBU (5 mM); in $TBAPF_6$ in CH_3CN (0.1 M). Scan rate: 0.1 V/s. Glassy carbon working electrode; Ag/AgCl (3M, NaCl) reference electrode; Glassy carbon auxiliary electrode. Irreversible oxidation, $Ep^A \approx E_{ox}$ (**7c**$^{\bullet+}$/**7c**) = +0.50 V vs SCE. $E_p{}^A$ refers to the anodic peak potential, while the E^{ox} value describes the electrochemical properties of **7c**.

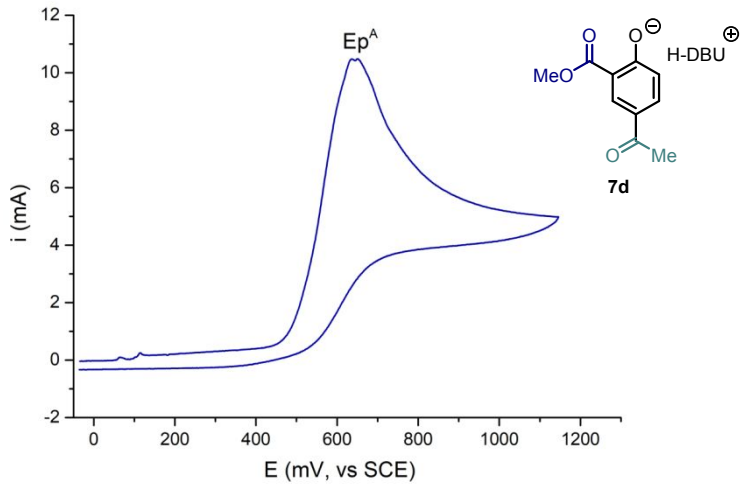


Figure S9. Cyclic voltammogram for the phenolate **7d** (5 mM), formed upon deprotonation of the phenol **6d** (5 mM) with DBU (5 mM); in $TBAPF_6$ in CH_3CN (0.1 M). Scan rate: 0.1 V/s. Glassy carbon working electrode; Ag/AgCl (3M, NaCl) reference electrode; Glassy carbon auxiliary electrode. Irreversible oxidation, $Ep^A \approx E_{ox}$ (**7d**$^{\bullet+}$/**7d**) = +0.65 V vs SCE. $E_p{}^A$ refers to the anodic peak potential, while the E^{ox} value describes the electrochemical properties of **7d**.

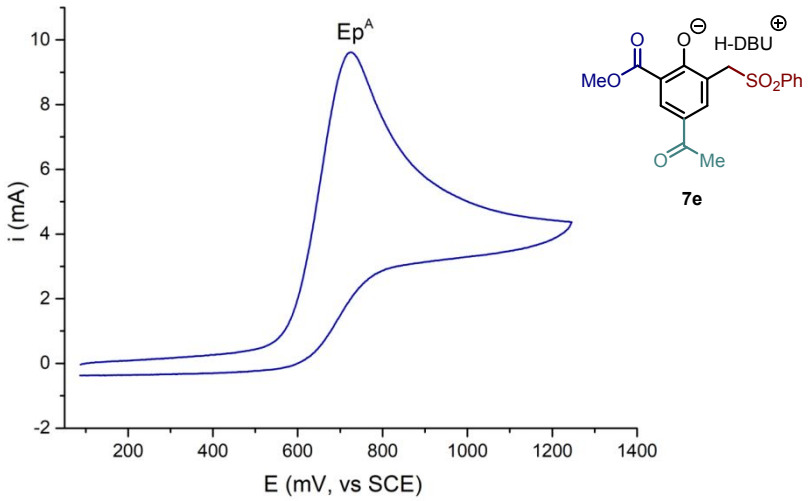


Figure S10. Cyclic voltammogram for the phenolate **7e** (5 mM), formed upon deprotonation of the phenol **6e** (5 mM) with DBU (5 mM); in $TBAPF_6$ in CH_3CN (0.1 M). Scan rate: 0.1 V/s. Glassy carbon working electrode; Ag/AgCl (3M, NaCl) reference electrode; Glassy carbon auxiliary electrode. Irreversible oxidation, $Ep^A \approx E_{ox}$ (**7e**$^{\bullet+}$/**7e**) = +0.74 V vs SCE. E_p^A refers to the anodic peak potential, while the E^{ox} value describes the electrochemical properties of **7e**.

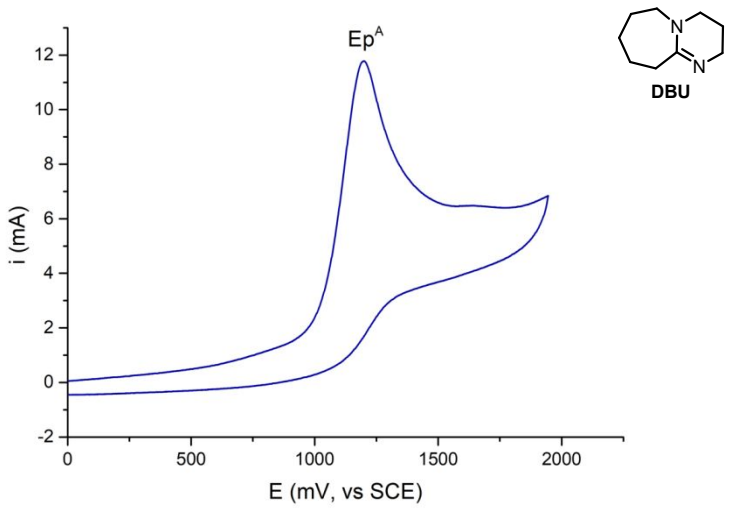


Figure S11. Cyclic voltammogram for 1,5-diazabiciclo(5.4.0)undec-7-ene (**DBU**, 5 mM) in $TBAPF_6$ in CH_3CN (0.1 M). Scan rate: 0.1 V/s. Glassy carbon working electrode; Ag/AgCl (3M, NaCl) reference electrode; Glassy carbon auxiliary electrode. Irreversible oxidation, $Ep^A \approx E_{ox}$ (**DBU**$^{\bullet+}$/**DBU**) = +1.19 V vs SCE. E_p^A refers to the anodic peak potential, while the E^{ox} value describes the electrochemical properties of **DBU**.

I.2. DFT STUDIES

The DFT geometry optimizations were performed using M06-2x density functional[17] in combination with the integral equation formalism of the polarizable continuum model (IEF-PCM) to take into account the effect of solvent (CH_3CN). The def2-TZVP basis set[6] was used in the calculations. Frequencies were calculated in order to ensure that the species are actual relative minima of energy.
All DFT computations were carried out with the Gaussian 16 software package.[18]

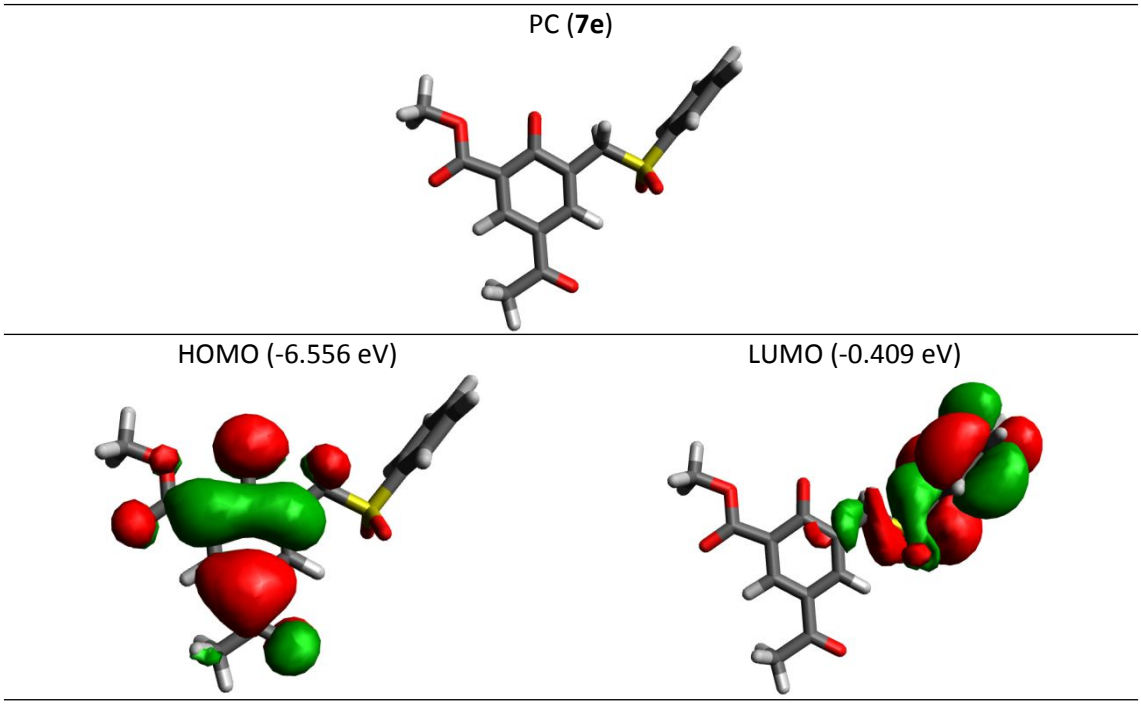


Figure S12. Structure of photocatalyst **7e** computed at the M06-2x/Def2TZVP/IEFPCM(CH3CN) level of theory and the corresponding highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. The HOMO is located on the aromatic core while and the LUMO lies on the sulphone moiety.

I.3. QUANTUM YIELD MEASUREMENT

A ferrioxalate actinometry solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in Handbook of Photochemistry.[19] Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline (complete complexation takes about an hour), and monitored by UV/Vis absorbance at 510 nm.[20] The moles of iron-phenanthroline complex formed are related to moles of photons absorbed.

The following solutions were prepared and stored in the dark:

1. *Potassium ferrioxalate solution*: 589.5 mg of potassium ferrioxalate (commercially available from Alfa Aesar) and 278 µL of sulfuric acid (96%) were added to a 100 mL volumetric flask and filled to the mark with water (MilliQ grade).

2. *Phenantroline solution:* 0.2% by weight of 1,10-phenanthroline in water (200 mg in 100 mL volumetric flask).

3. *Buffer solution*: 4.94 g of NaOAc and 1 mL of sulfuric acid (96%) were added to a 100 mL volumetric flask, and filled to the mark with water (MilliQ grade).

4. *Model reaction solution*: 1-hexene **3a** (0.4 mmol), α-iodo sulfone **4a** (0.6 mmol), the phenol catalyst **6e** (0.08 mmol) and sodium ascorbate (0.1 mmol) were dissolved in acetonitrile (HPLC grade) and water (milliQ grade) in a 3:1 ratio (600 µL and 200 µL, respectively). Then, DBU (0.08 mmol) was added.

The actinometry measurements were done as follows:

A. 456 nm LED: 1 mL of the actinometer solution was added to a quartz cuvette (l = 10 mm). The actinometry solution (placed 1 cm away from the lamp) were irradiated with 3 W 456 nm LED for specified time intervals (0, 15, 30, 45, 60) seconds.[21]

B. After irradiation all the actinometer solution was removed and placed in a 10 mL volumetric flask. 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution was added to this flask and filled to the mark with water (MilliQ grade).

C. The UV-Vis spectra of actinometry samples were recorded for each time interval (Figure S13). The absorbance of the actinometry solution was monitored at 510 nm.

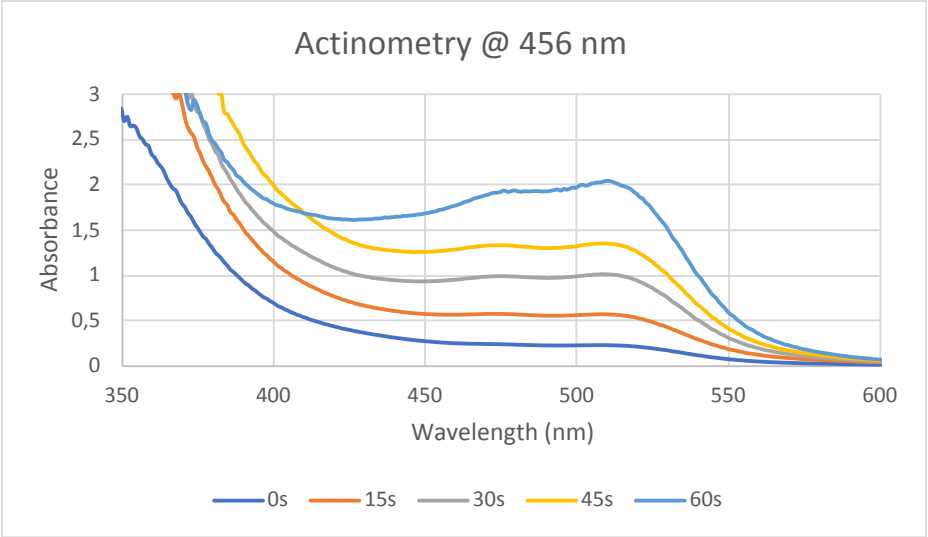


Figure S13. UV-Vis spectra of actinometry samples irradiated with 456 nm light for the indicated time intervals.

D. The moles of Fe^{2+} formed for each sample is determined using Beer's Law:

$$mmoles\ Fe^{2+} = \frac{V_1 V_3 \Delta A_{(510\ nm)}}{10^3 V_2 l \varepsilon_{(510\ nm)}}$$

Equation S1. Lambert-Beer's law.

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), $\Delta A_{(510\ nm)}$ the optical difference in absorbance between the irradiated solution and that taken in the dark, $\varepsilon_{(510\ nm)}$ is the molar extinction coefficient of the complex $Fe(phen)_3^{2+}$ (11100 L mol^{-1} cm^{-1}).

E. The moles of Fe^{2+} formed (N) are plotted as a function of time (t) (Figure S14).

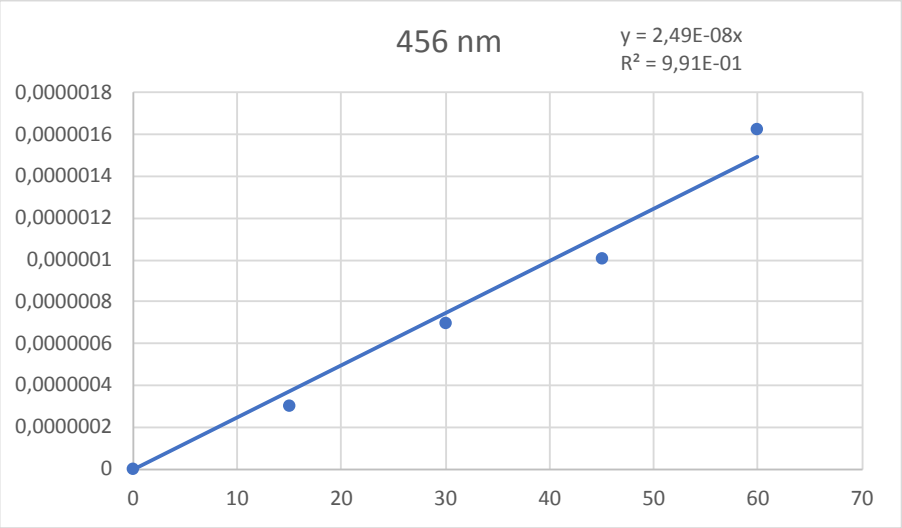


Figure S14. Moles of Fe^{2+} formed after irradiation with 456 nm light as a function of time.

The slope is a product of the photon flux (F) and the quantum yield for Fe^{2+} (φFe^{2+} = 1.13), since $F = N/\Phi Fe^{2+} t$. The F was determined to be **$2.20 \cdot 10^{-8}$ einstein s^{-1}**.

Since the ferrioxalate actinometer absorbance at 456 nm is 0.12, and inferior to 2 in both cases (if it is major than 2 at the wavelength used, it can be assumed that the entire incident light is absorbed), a correction factor (C) based on the fraction of light absorbed by the actinometer has to be considered to calculate the photon flux and the final quantum yield of the reaction (note that is also needed if the absorbance of the reaction under study at the optimized concentration is inferior to 2 at the wavelength used). Thus, according to the definition of quantum yield:[20]

$$\Phi_{Fe^{2+}} = \frac{(\frac{\delta_{molesFe^{2+}}}{\delta_{time}})}{F C_{Fe^{2+}}} \rightarrow F = \frac{(\frac{\delta_{molesFe^{2+}}}{\delta_{time}})}{\Phi_{Fe^{2+}}\, C_{Fe^{2+}}} \qquad C_{Fe^{2+}} = [1 - 10^{-A(\lambda)}]$$

Equation S2. Correlation between quantum yield equation and the correction factor.

The photon flux (F) previously found has to be divided by the appropriate correction factor C.

456 nm: C= 0.242, calculated with A_{456nm} = 0.12; corrected F = **$5.33 \cdot 10^{-9}$ einstein s^{-1}**.

F. The *model reaction solution* described at point 4 was transferred to a Schlenk tube and degassed via the freeze-pump-thaw technique (3 cycles). The degassed suspension was then transferred to a screw-cap quartz cuvette (l = 10 mm) as a suspension, and irradiated using the same system as described in point **A** (*i.e.* cuvette placed 1 cm away from the 3 W 456 nm LED). The moles of product formed were determined by ^{1}H-NMR analysis using trichloroethylene as internal standard. The moles of product formed per unit of time were related to the number of photons absorbed (Figure S15).

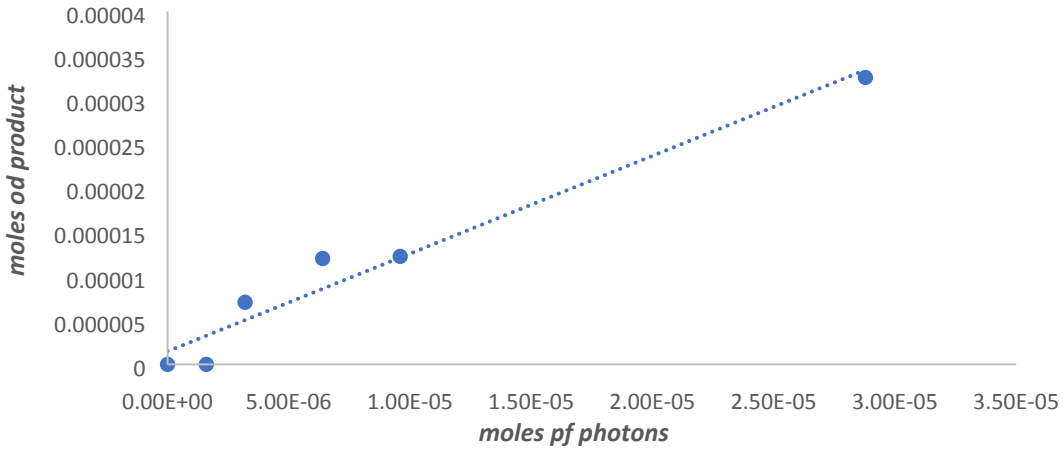


Figure S15. Moles of product formed after irradiation with 456 nm light as a function of the moles of emitted photons.

The absorbance of the reaction at the irradiation wavelength (456 nm) is A_{456nm}= 0.47. The correction factor is C= 0.66 (see Equation S2). Therefore, by applying the correction factor (slope/C), the **quantum yield (φ)** is **1.7**.

Note: All the components of the *model reaction solution* are not completely soluble in the optimized solvent system, and the formation of a biphasic system is observed during the irradiation period. This fact can result in the underestimation of the quantum yield value.

I.4. REDOX POTENTIAL OF THE PHOTOCATALYST 7e AND POSSIBLE EDA COMPLEX FORMATION

The redox potential of the excited phenolate (E_{7e*}^0) was estimated by means of the Rehm-Weller equation:[22]

$$E_{\boldsymbol{7e}^*}^0 = E_{\boldsymbol{6e}}^0 - E_{00}$$

where the redox potential of the ground state phenolate (E_{7e}^0) was determined by cyclic voltammetry measurements (+0.74 V *vs* SCE, Section **I.1**.). The excitation energy (E_{00}) of phenolate **7e** was determined from the cross point between the absorption and the emission profile (378 nm, that corresponds to 3.28 eV, Figure S16).[23] As a result, E_{7e*}^0 turned out to be **-2.54 V *vs* SCE**. Thus, a single electron transfer (SET) between the excited phenolate **7e** and iodo sulfone **4a** could take place, according to the redox potential of this radical source (-1.4 V *vs* SCE).[14]

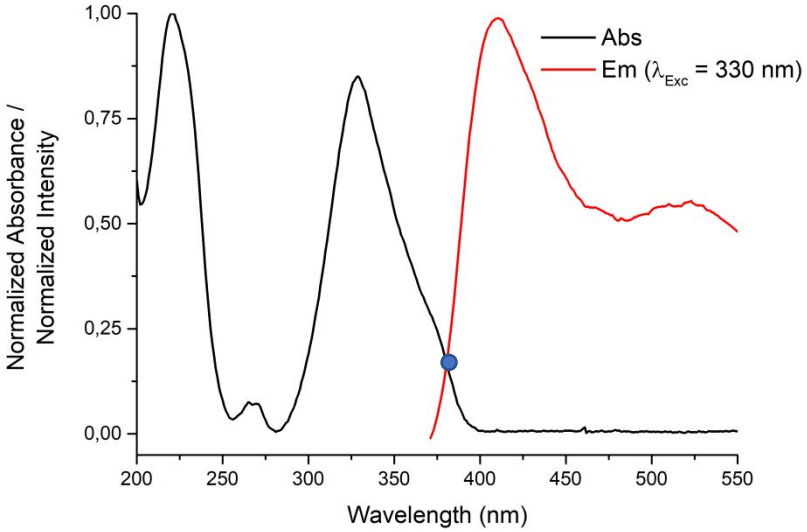


Figure S16. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7e** obtained by mixing phenol **6e** and DBU. Recorded in CH_3CN in quartz cuvettes (1 cm path). [**6e**] = [DBU] = 5 x 10^{-6} M.

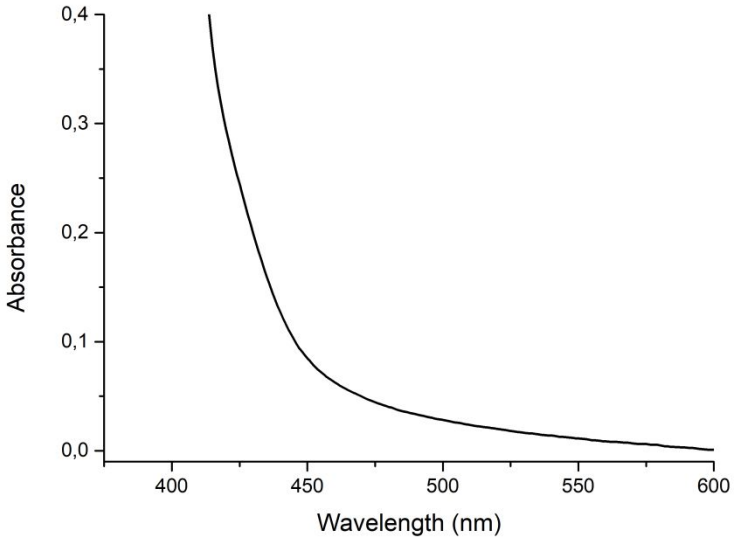


Figure S17. Optical absorption spectrum of phenolate **7e** in the reaction conditions, obtained by mixing phenol **6e** and DBU. Recorded in CH_3CN in quartz cuvettes (1 cm path). [**6e**] = [DBU] = 0.1 M.

Alternatively, the possible formation of an EDA complex between **7e** and **4a** in acetonitrile was evaluated by UV/Vis and NMR spectroscopy. In the first case, the optical absorption of the sole **7e** resulted to be very close to that obtained from a mixture of **7e** and **4a**, even in large excess of α-iodo sulfone **4a** (Figure S18).

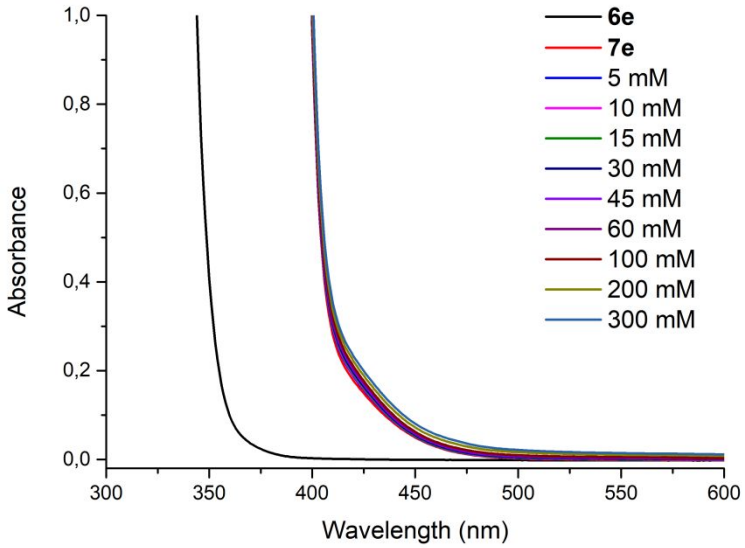


Figure S18. Optical absorption spectrum of phenol **6e** (blue line), phenolate **7e** (obtained by mixing phenol **6e** and DBU), and various mixtures of **7e** and **4a** at increasing concentration of **4a** (values in brackets within the legend). Recorded in CH_3CN in quartz cuvettes (1 cm path). [**6e**] = [DBU] = 1.5 x 10^{-2} M. [**4a**] = 5 x 10^{-3} to 3 x 10^{-1} M.

Similarly, the diagnostic NMR signals of phenolate **7e** resonate close to that obtained from a mixture of **7e** and **4a**, even in large excess of iodo sulfone **4a** (Figure S19-S35).

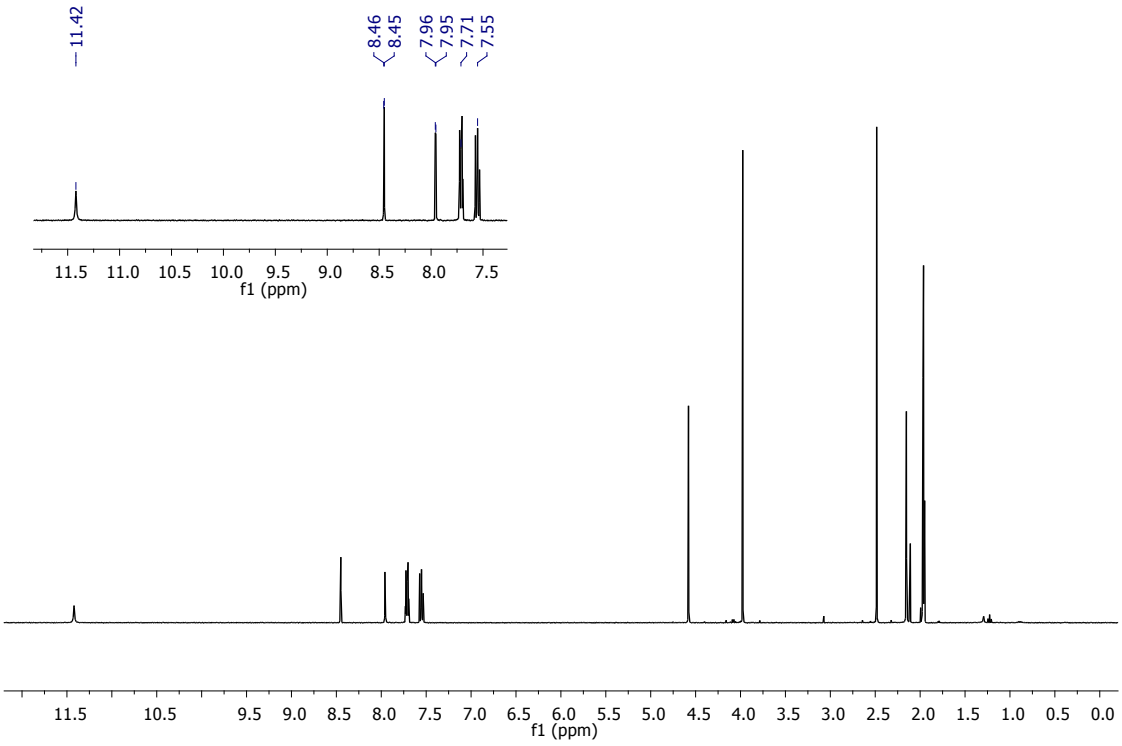


Figure S19. ^{1}H-NMR spectrum of phenol **6e** in CD_3CN (0.1 M).

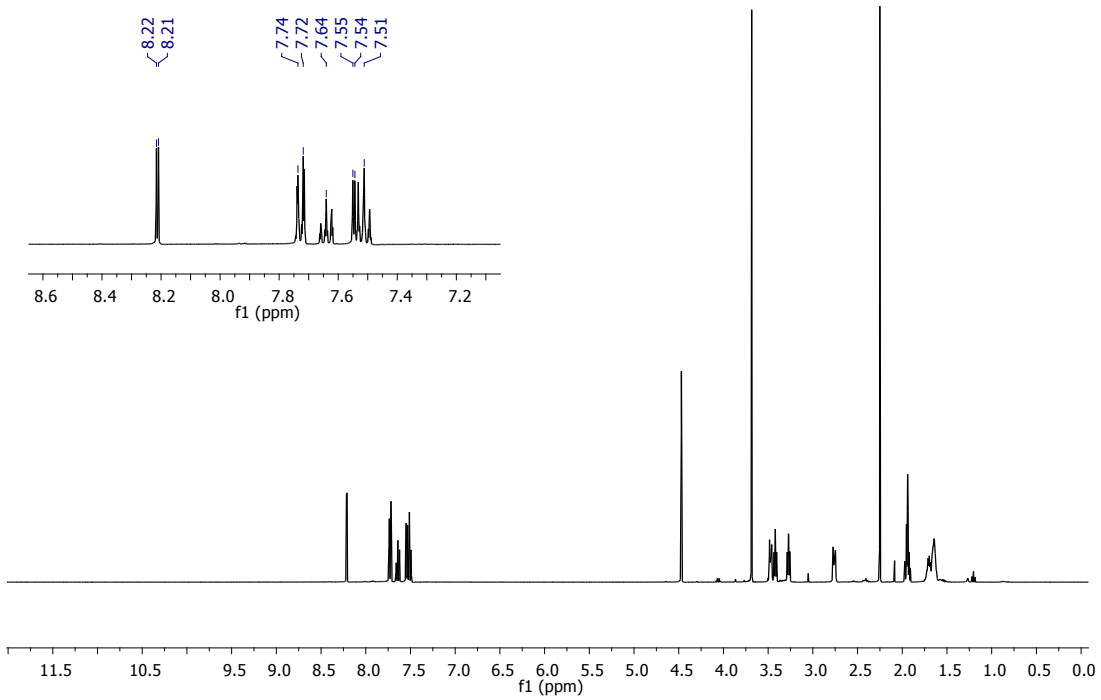


Figure S20. ^{1}H-NMR spectrum of phenolate **7e** (obtained by mixing phenol **6e** and DBU in 1:1 ratio) in CD_3CN (0.1 M).

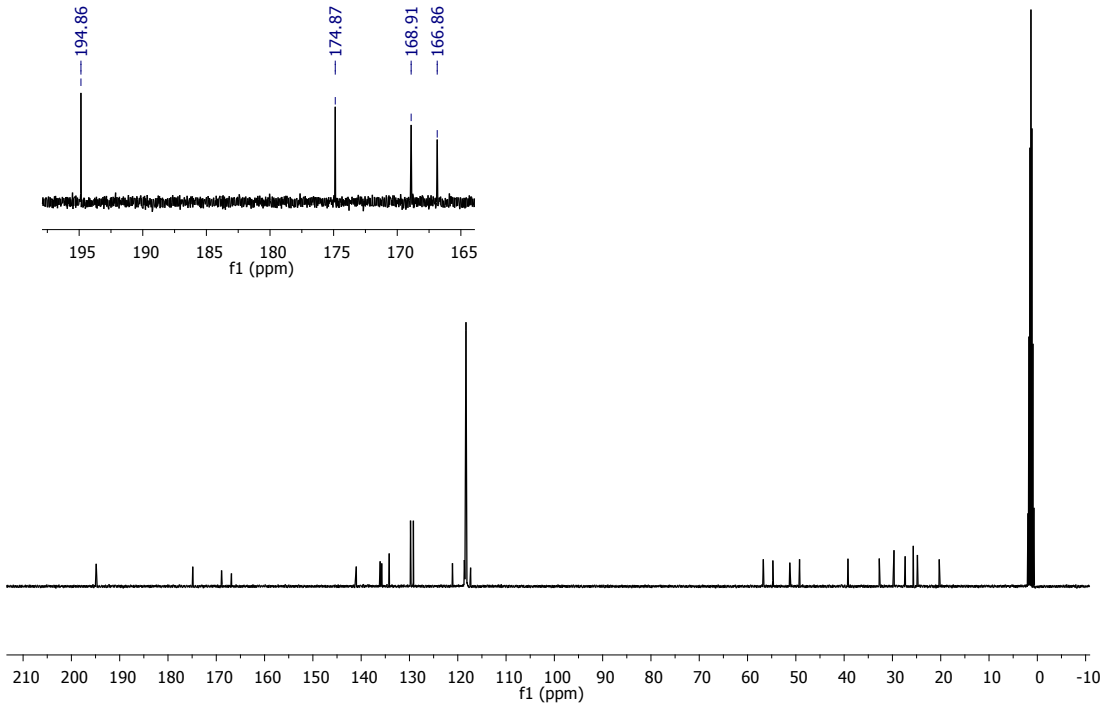


Figure S21. ^{13}C-NMR spectrum of phenolate **7e** (obtained by mixing phenol **6e** and DBU in 1:1 ratio) in CD_3CN (0.1 M).

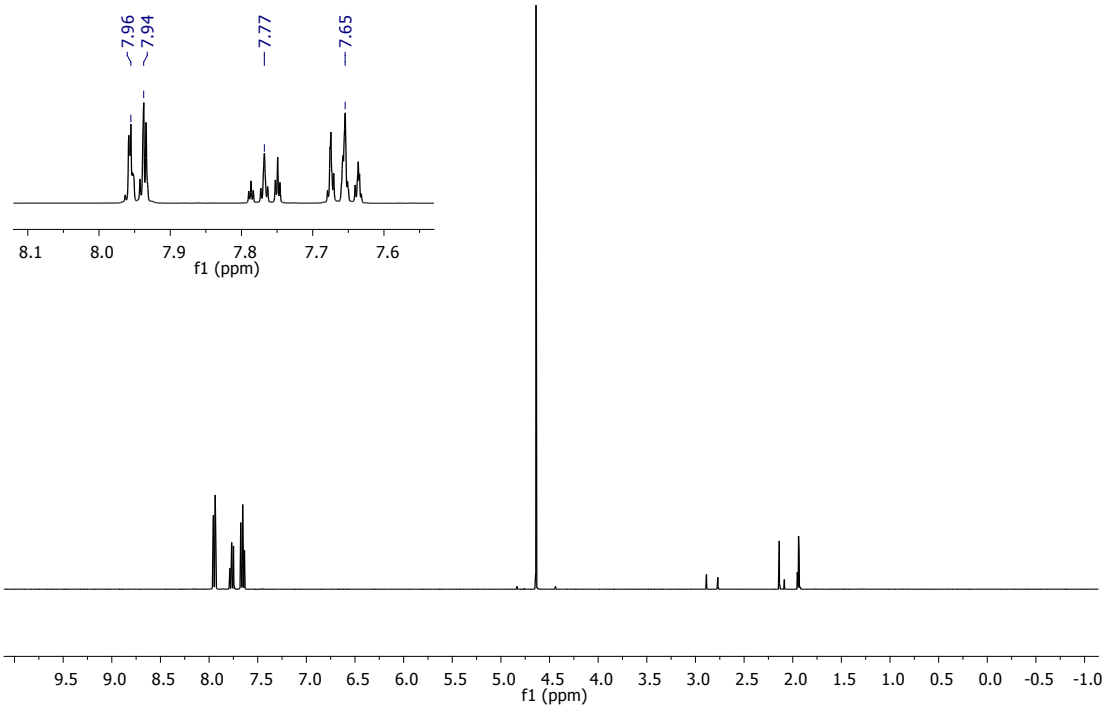


Figure S22. ^{1}H-NMR spectrum of iodo sulfone **4a** in CD_3CN (0.1 M).

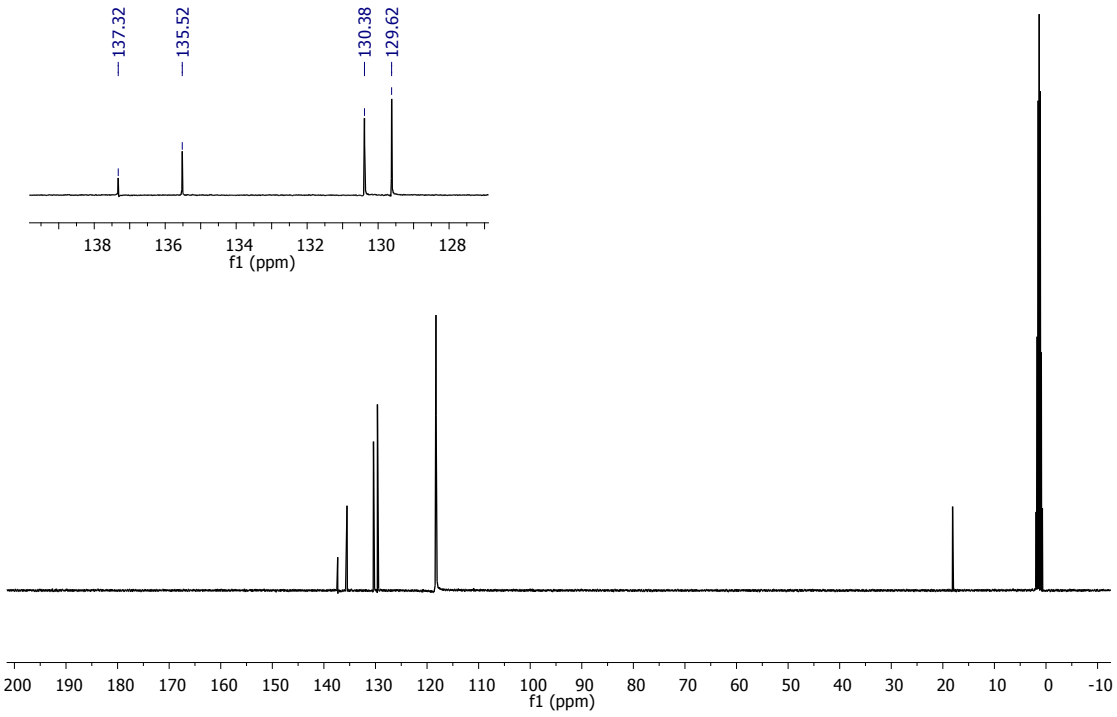


Figure S23. ^{13}C-NMR spectrum of iodo sulfone **4a** in CD_3CN (0.1 M).

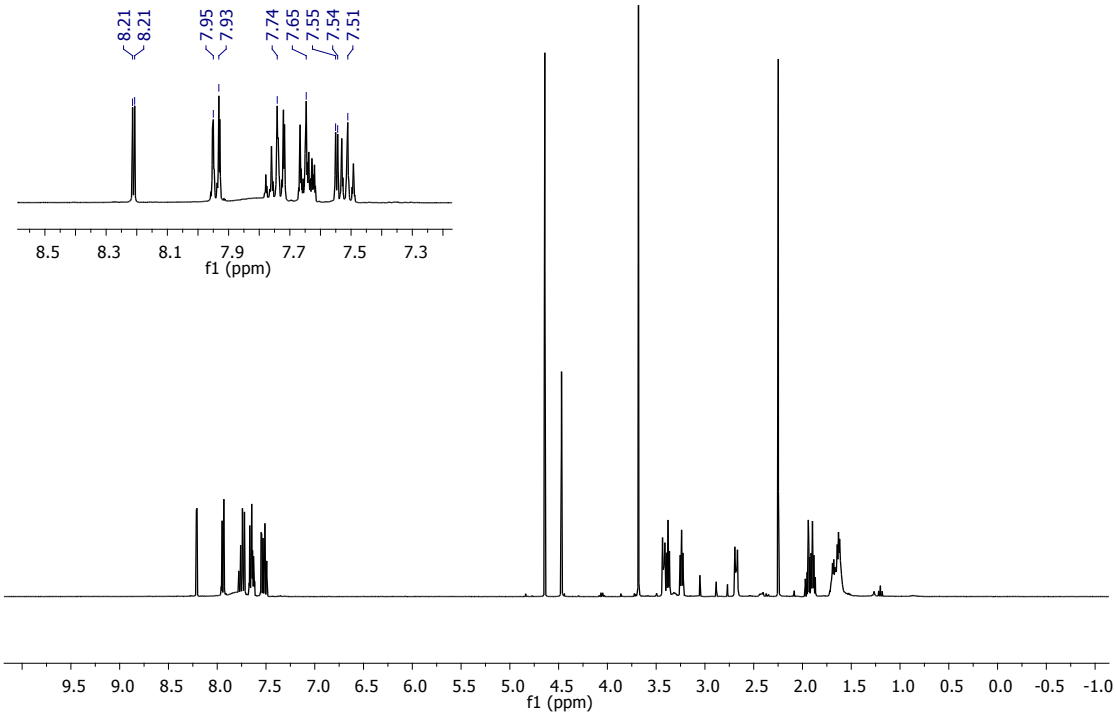


Figure S24. ^{1}H-NMR spectrum of a 1:1 mixture of phenolate **7e** (obtained by mixing phenol **6e** and DBU in 1:1 ratio) and iodo sulfone **4a** in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

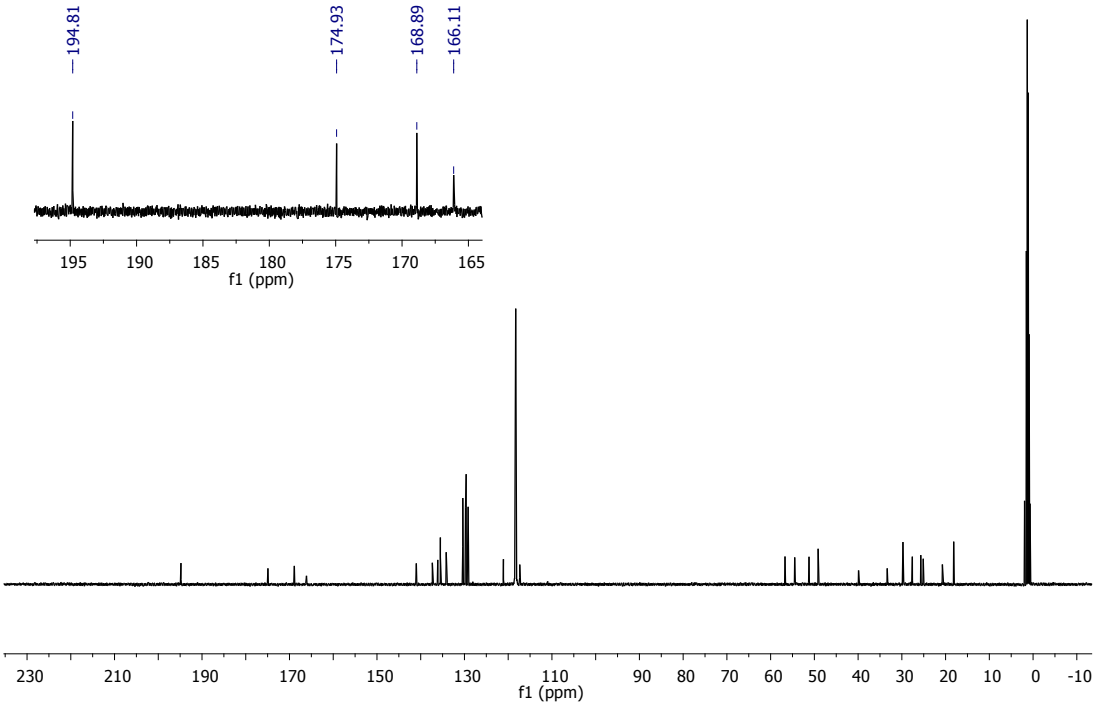


Figure S25. ^{13}C-NMR spectrum of a 1:1 mixture of phenolate **7e** (obtained by mixing phenol **6e** and DBU in 1:1 ratio) and iodo sulfone **4a** in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

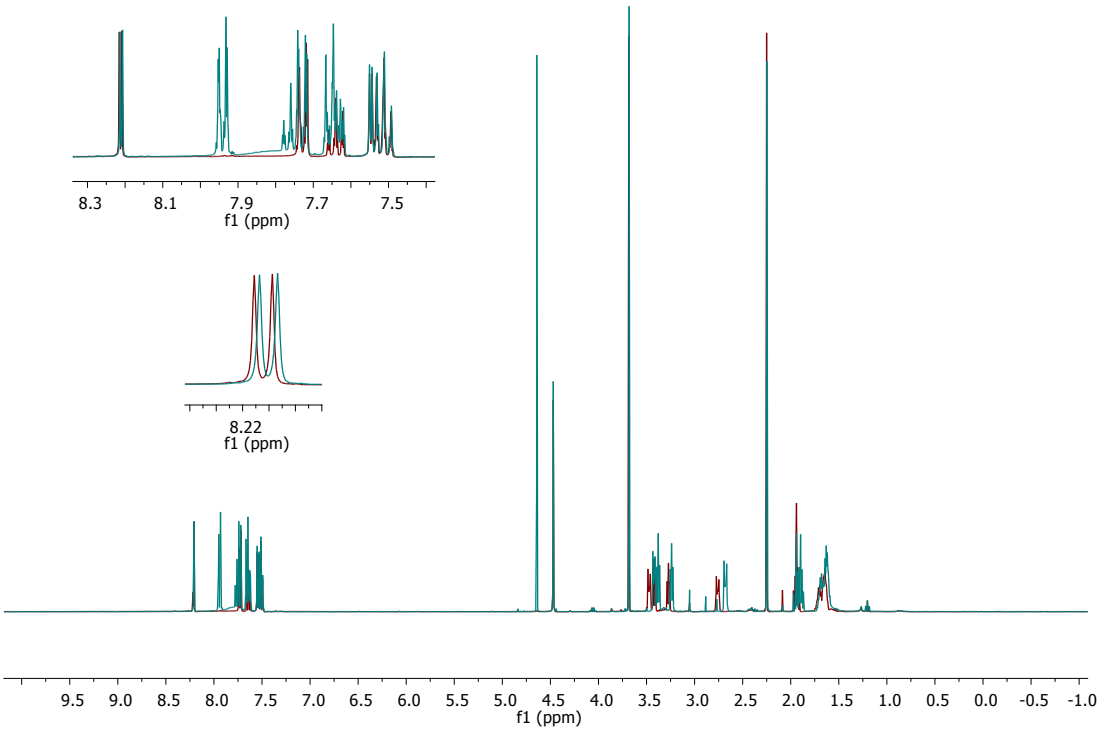


Figure S26. Superimposed ^{1}H-NMR spectra of phenolate **7e** (red trace) and a 1:1 mixture of phenolate **7e** and iodo sulfone **4a** (blue trace) in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

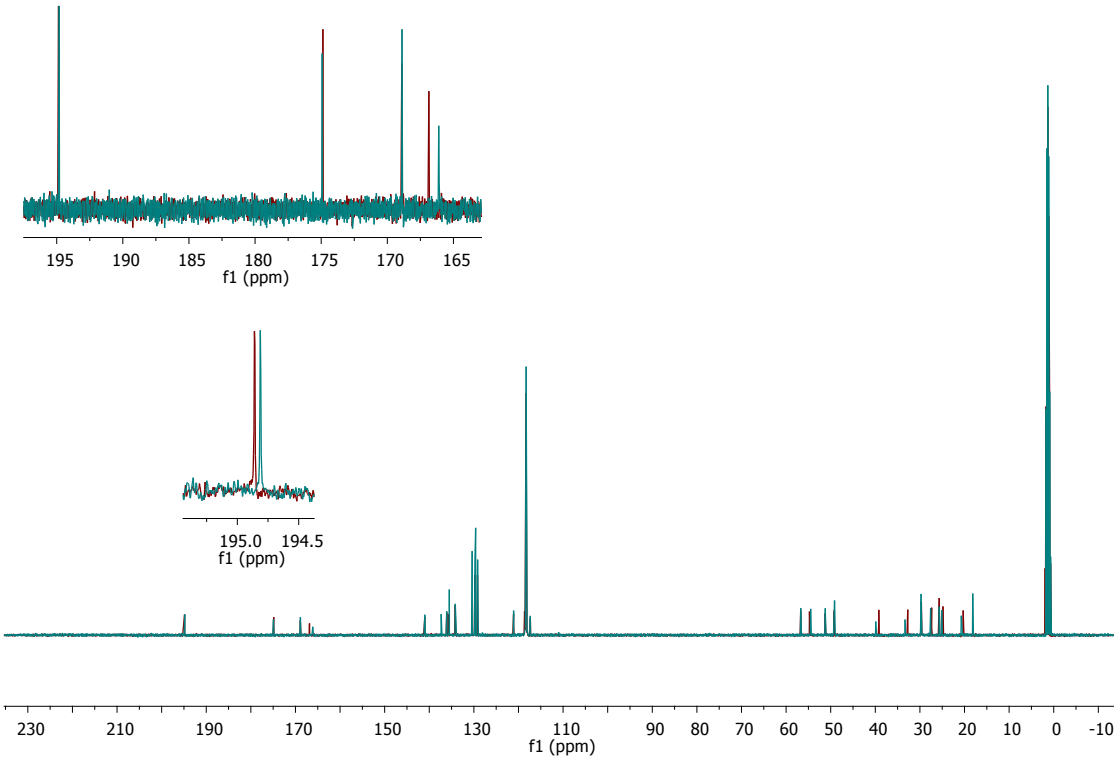


Figure S27. Superimposed ^{13}C-NMR spectra of phenolate **7e** (red trace) and a 1:1 mixture of phenolate **7e** and iodo sulfone **4a** (blue trace) in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

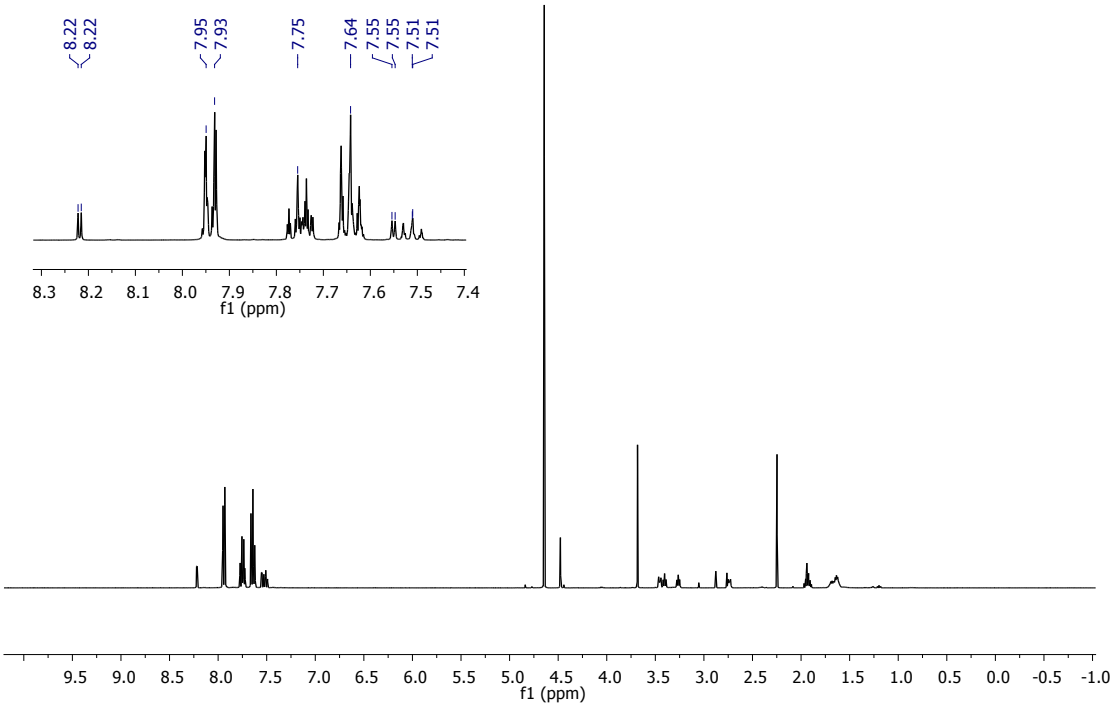


Figure S28. ^{1}H-NMR spectrum of a 1:5 mixture of phenolate **7e** (obtained by mixing phenol **6e** and DBU in 1:1 ratio) and iodo sulfone **4a** in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

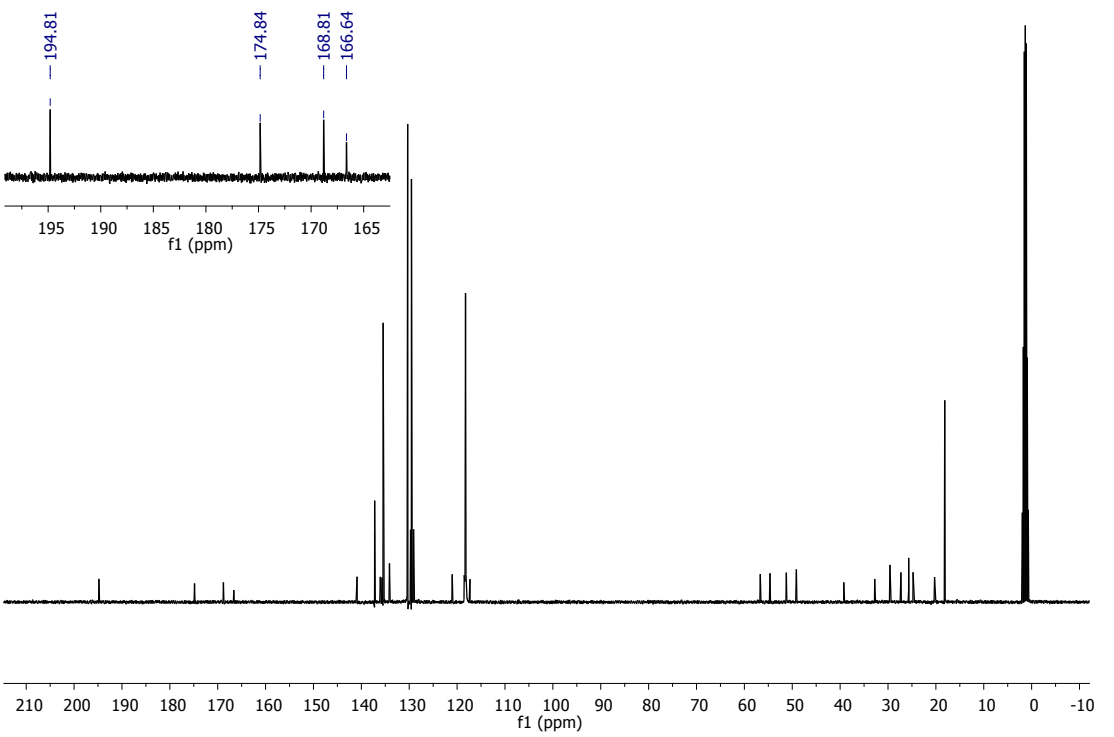


Figure S29. ^{13}C-NMR spectrum of a 1:5 mixture of phenolate **7e** (obtained by mixing phenol **6e** and DBU in 1:1 ratio) and iodo sulfone **4a** in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

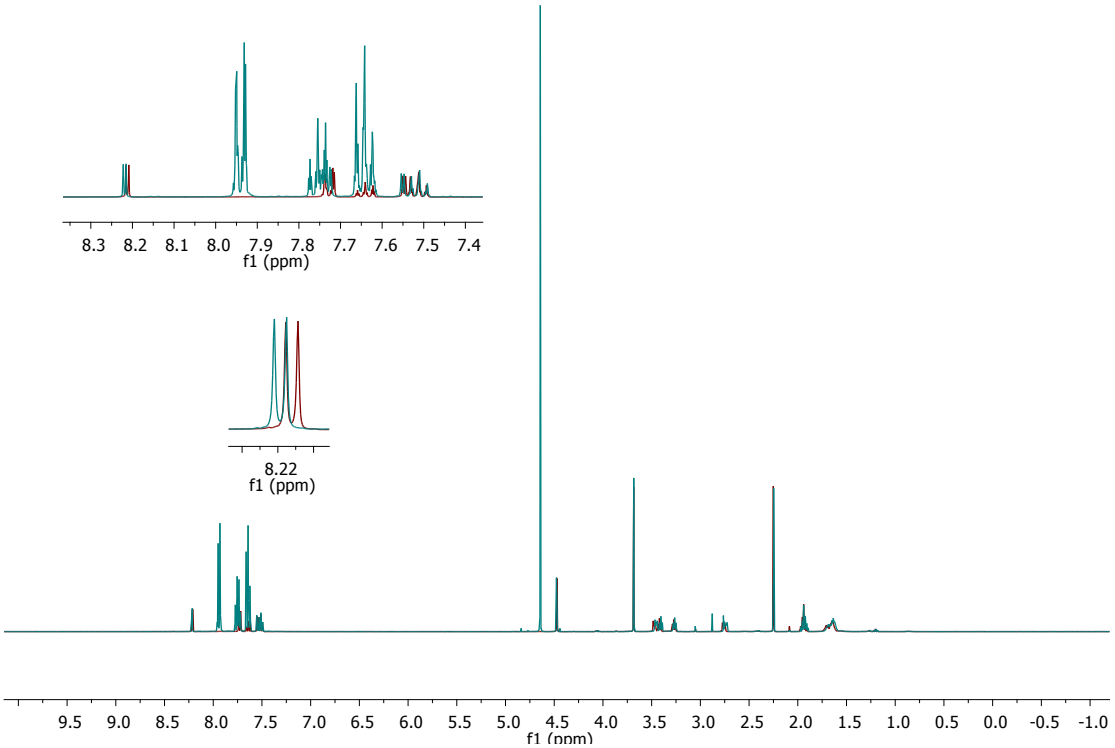


Figure S30. Superimposed ^{1}H-NMR spectra of phenolate **7e** (red trace) and a 1:5 mixture of phenolate **7e** and iodo sulfone **4a** (blue trace) in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

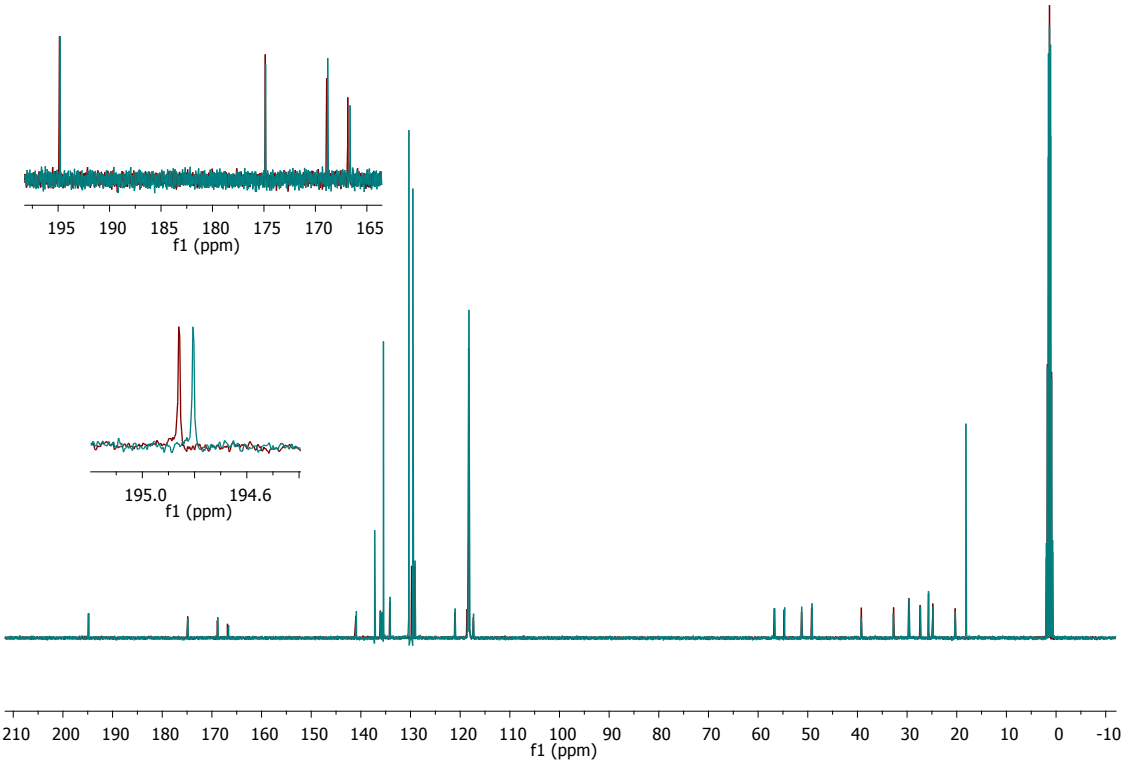


Figure S31. Superimposed ^{13}C-NMR spectra of phenolate **7e** (red trace) and a 1:5 mixture of phenolate **7e** and iodo sulfone **4a** (blue trace) in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

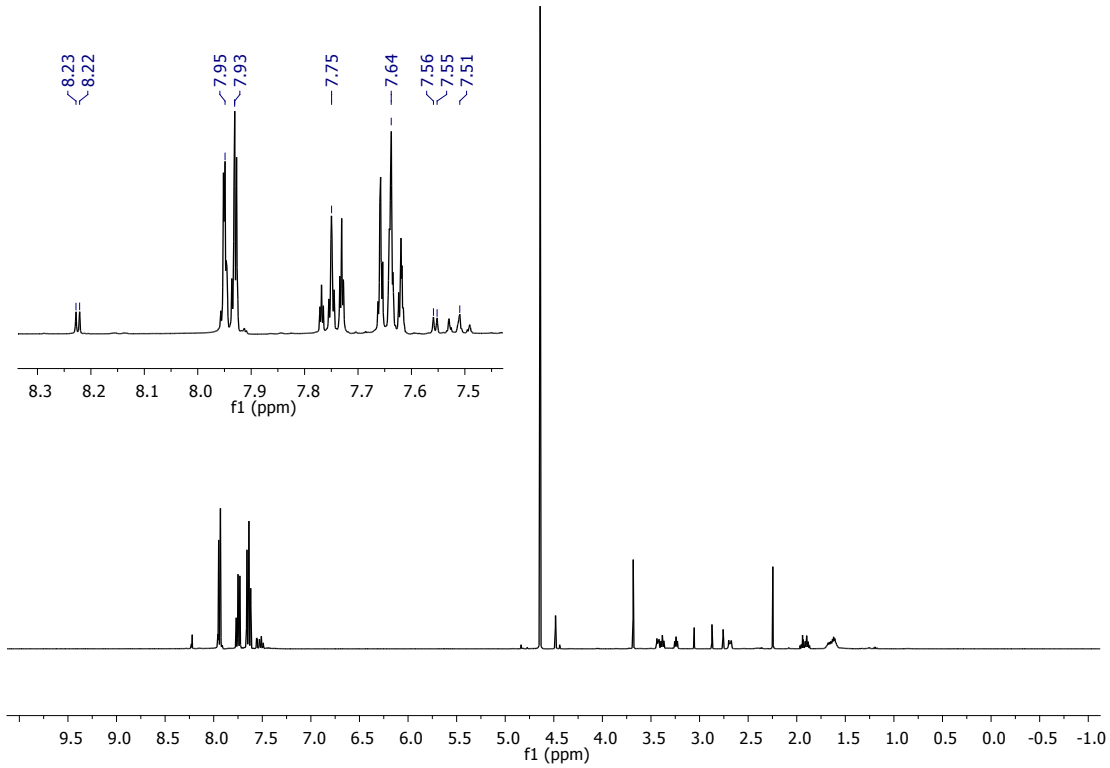


Figure S32. ^{1}H-NMR spectrum of a 1:10 mixture of phenolate **7e** (obtained by mixing phenol **6e** and DBU in 1:1 ratio) and iodo sulfone **4a** in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

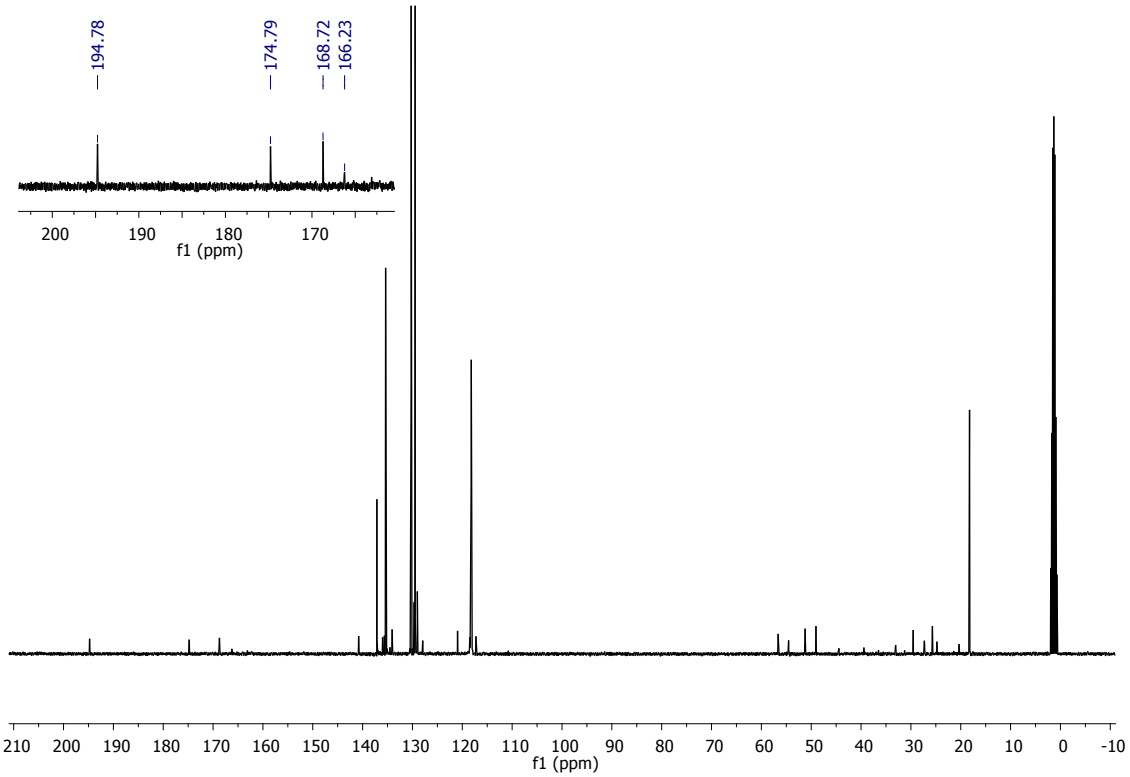


Figure S33. ^{13}C-NMR spectrum of a 1:10 mixture of phenolate **7e** (obtained by mixing phenol **6e** and DBU in 1:1 ratio) and iodo sulfone **4a** in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

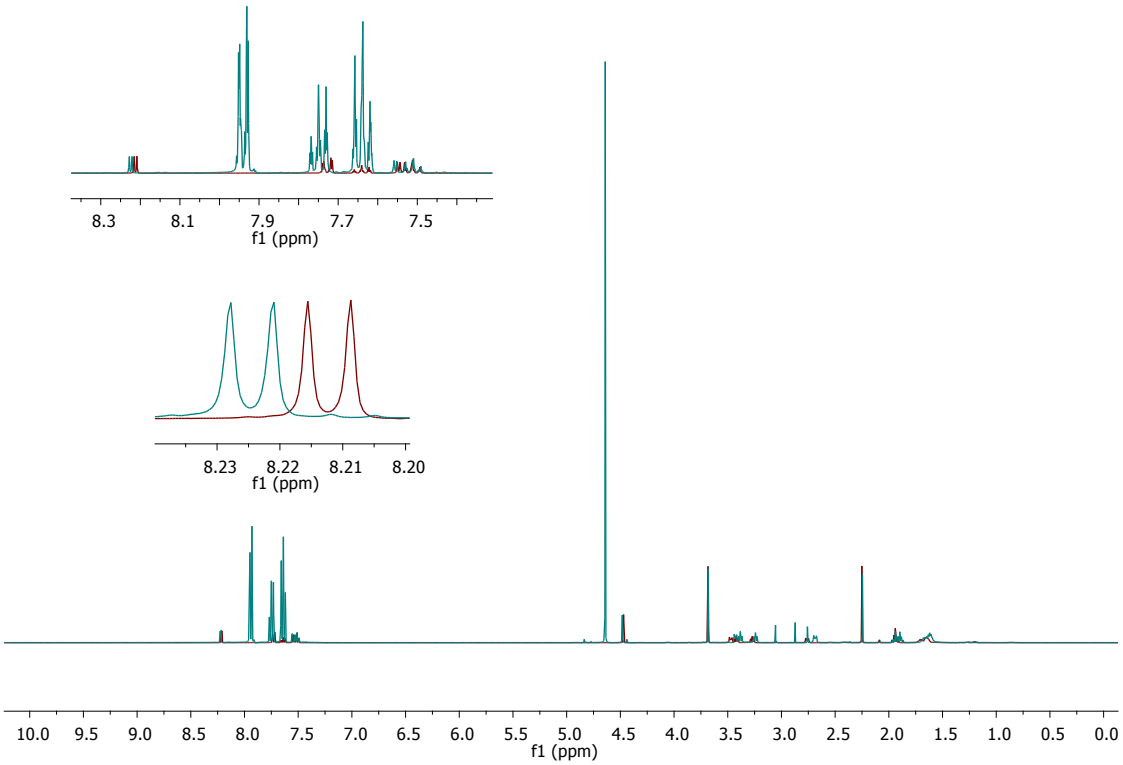


Figure S34. Superimposed ^{1}H-NMR spectra of phenolate **7e** (red trace) and a 1:10 mixture of phenolate **7e** and iodo sulfone **4a** (blue trace) in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

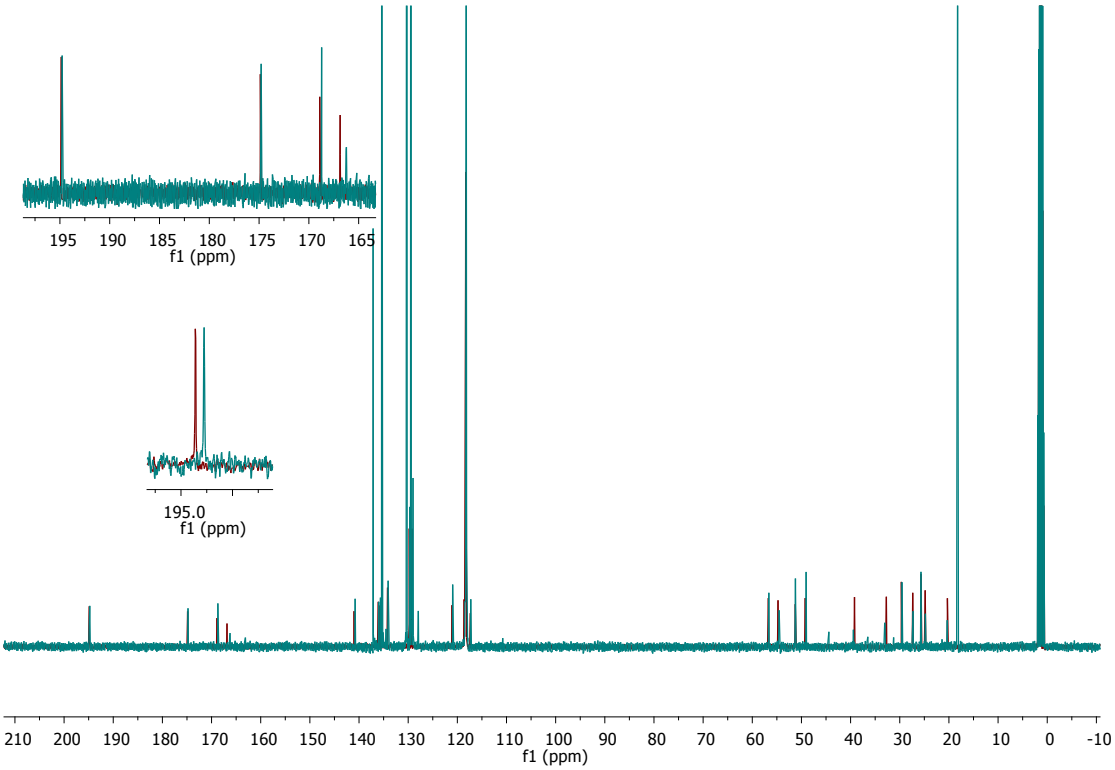


Figure S35. Superimposed ^{13}C-NMR spectra of phenolate **7e** (red trace) and a 1:10 mixture of phenolate **7e** and iodo sulfone **4a** (blue trace) in CD_3CN ($[\mathbf{6e}]_0$ = 0.1 M).

On the contrary, in the previously reported cases, the formation of an EDA complex between the reaction components is typically accompanied by a significant shift of the signals involved.[24,25] Altogether, the possible formation of an EDA complex between **7e** and **4a** can be reasonably excluded.

I.5. STERN-VOLMER STUDIES

To further demonstrate the feasibility of a SET between phenolate **7e** and α-iodo sulfone **4a**, a series of Stern-Volmer quenching studies were performed in acetonitrile. The emission spectrum, obtained upon excitation at 410 nm, showed a decreased intensity when **4a** was added and this fluorescence quenching turned out to be linear in the range 5 ÷ 45 x 10^{-3} M, with a Stern-Volmer constant of 1.57 x 10^{-2} M^{-1} (Figure S36 and Figure S37).

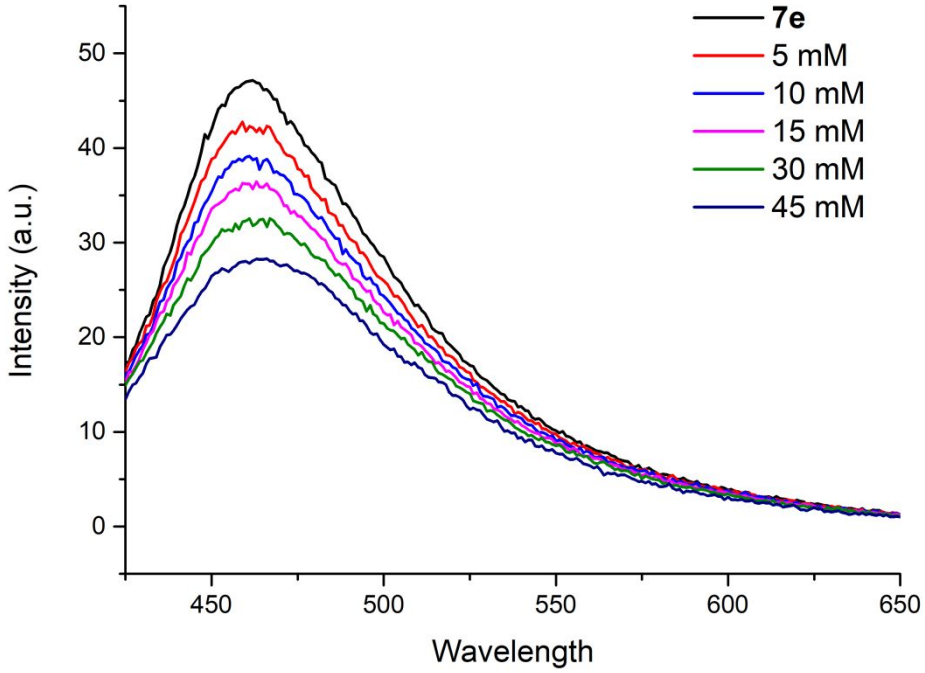


Figure S36. Emission spectra of phenolate **7e** (blue line), obtained by mixing phenol **6e** and DBU, and various mixtures of **7e** and **4a** at increasing concentration of **4a** (values in brackets within the legend). Recorded in CH_3CN in quartz cuvettes (1 cm path). [**6e**] = [DBU] = 1.5 x 10^{-2} M. [**4a**] = 5 x 10^{-3} to 4.5 x 10^{-3} M.

[**4a**] (mM)	Intensity (I)	Initial intensity (I_0)	I_0/I
0	47.00996399	47.00996399	1
5	41.77465057	47.00996399	1.12532
10	39.04601288	47.00996399	1.20396
15	36.19675827	47.00996399	1.29873
30	32.30458069	47.00996399	1.45521
45	28.03398514	47.00996399	1.67689

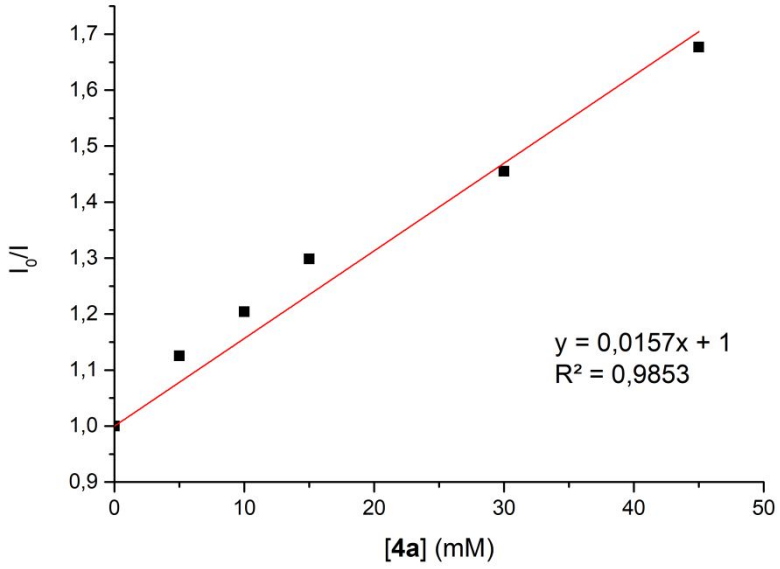


Figure S37. Stern-Volmer quenching study.

I.6. REDOX POTENTIAL OF THE EXCITED STATE PHENOLATES 7a-d

Phenolate **7a** obtained by mixing phenol **6a** and DBU in equimolar ratio in acetonitrile. The corresponding excitation energy (E_{00}) turned out to be 277 nm that corresponds to 4.48 V *vs* SCE (Figure S38). The ground state potential was determined by cyclic voltammetry and resulted in +0.30 V *vs* SCE (see Section I.1). Thus, the calculated redox potential of the excited phenolate **7a** was proved to be **-4.18 V *vs* SCE**.

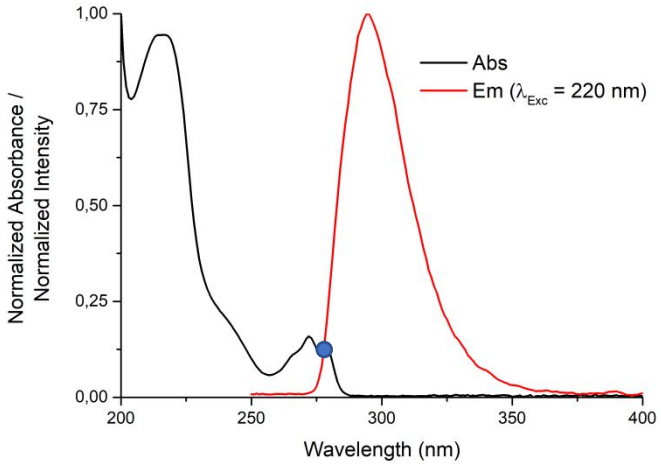


Figure S38. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7a** obtained by mixing phenol **6a** and DBU. Recorded in CH_3CN in quartz cuvettes (1 cm path). [**6e**] = [DBU] = 2 x 10^{-5} M.

Phenolate **7b** obtained by mixing 2-bromophenol **6b** and DBU in equimolar ratio in acetonitrile. The corresponding excitation energy (E_{00}) turned out to be 258 nm that corresponds to 4.81 V *vs*

SCE (Figure S39). The ground state potential was determined by cyclic voltammetry and resulted in +0.34 V *vs* SCE (see Section I.1). Thus, the calculated redox potential of phenolate **7b** proved to be **-4.47 V *vs* SCE**.

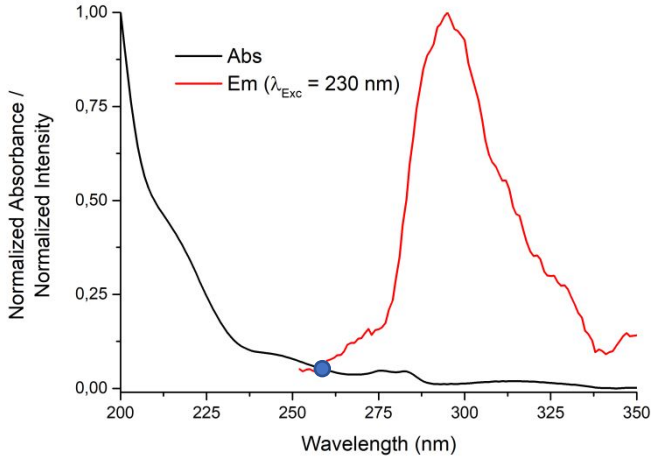


Figure S39. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7b** obtained by mixing 2-bromophenol **6b** and DBU. Recorded in CH_3CN in quartz cuvettes (1 cm path). [**6b**] = [DBU] = 2 x 10^{-5} M.

Phenolate **7c** obtained by mixing methyl salicylate **6c** and DBU in equimolar ratio in acetonitrile. The corresponding excitation energy (E_{00}) turned out to be 312 nm that corresponds to 3.97 V *vs* SCE (Figure S40). The ground state potential was determined by cyclic voltammetry and resulted in +0.50 V *vs* SCE (see Section I.1). Thus, the calculated redox potential of phenolate **7c** proved to be **-3.47 V *vs* SCE**.

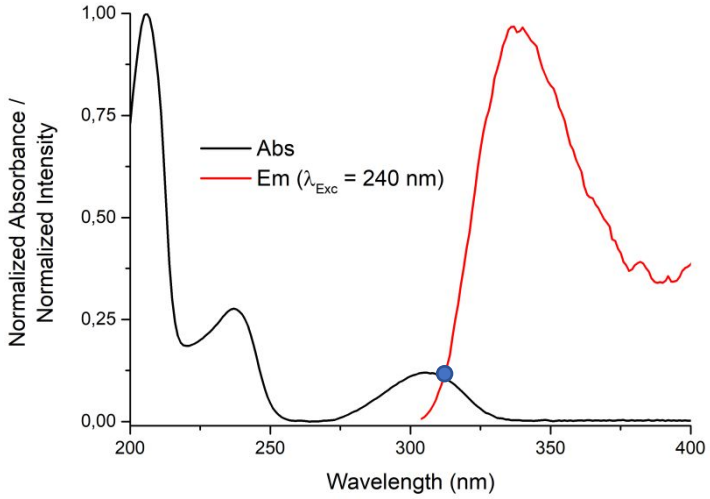


Figure S40. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7c** obtained by mixing methyl salicylate **6c** and DBU. Recorded in CH_3CN in quartz cuvettes (1 cm path). [**6c**] = [DBU] = 1 x 10^{-5} M.

Phenolate **7d** obtained by mixing methyl 5-acetylsalicylate **6d** and DBU in equimolar ratio in acetonitrile. The corresponding excitation energy (E_{00}) turned out to be 372 nm that corresponds to 3.33 V *vs* SCE (Figure S41). The ground state potential was determined by cyclic voltammetry and resulted in +0.65 V *vs* SCE (see Section I.1). Thus, the calculated redox potential of phenolate **7d** proved to be **-2.68 V *vs* SCE**.

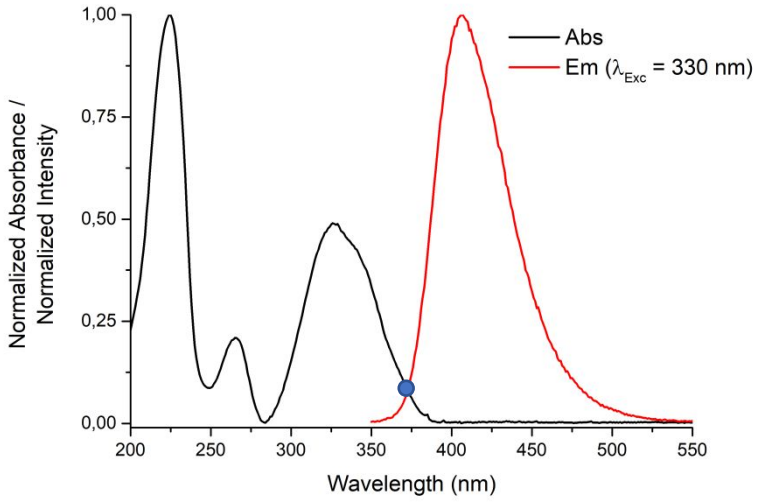


Figure S41. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7d** obtained by mixing methyl 5-acetylsalicylate **6d** and DBU. Recorded in CH_3CN in quartz cuvettes (1 cm path). [**6d**] = [DBU] = 5 x 10^{-6} M.

I.7. SOLVATOCHROMIC STUDIES OF PHENOLATES 7d-e

The Stokes shifts of phenolates **7d-e**, obtained from a mixture of **6d-e** and DBU (in a 1:1 ratio), were measured in solvents of growing polarity to ascertain the electronic differences between the ground and the excited state in terms of dipole moment. Specifically, four different solvents were selected: toluene, tetrahydrofuran (THF), acetonitrile, and dimethyl sulfoxide (DMSO), and the corresponding UV-Vis absorption and emission spectra were recorded (Figures S42-S45 and Figures S47-S50). An inversely proportional correlation between the Stokes shifts and the polarity of the solvent, which was expressed through their $E_T(30)$ values,[26] was observed for both phenolates **7d-e** (*i.e.* a negative solvatochromism; Tables S7 and S8 and Figures S46 and S51). These results indicate that the excited phenolates **7d-e** have a lower dipole moment with respect their corresponding ground states. This reduction in the dipole moment after the electronic excitation is in agreement with the formation of a charge-transfer state. Indeed, this negative solvatochromism behavior is commonly observed for other phenolate-based dyes that generate charge-transfer states after light-excitation.[26]

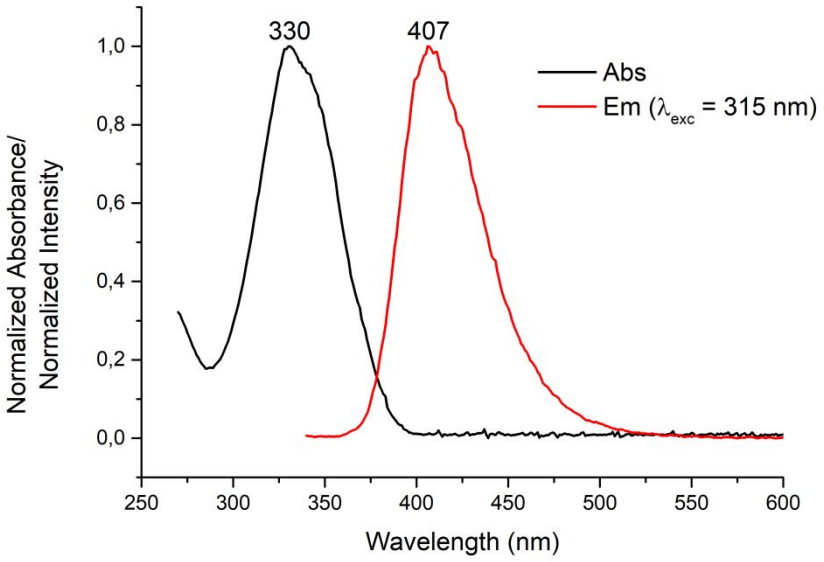


Figure S42. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7d** obtained by mixing methyl 5-acetylsalicylate **6d** and DBU in toluene. Recorded in quartz cuvettes (1 cm path). [**6d**] = [DBU] = 2 x 10^{-5} M.

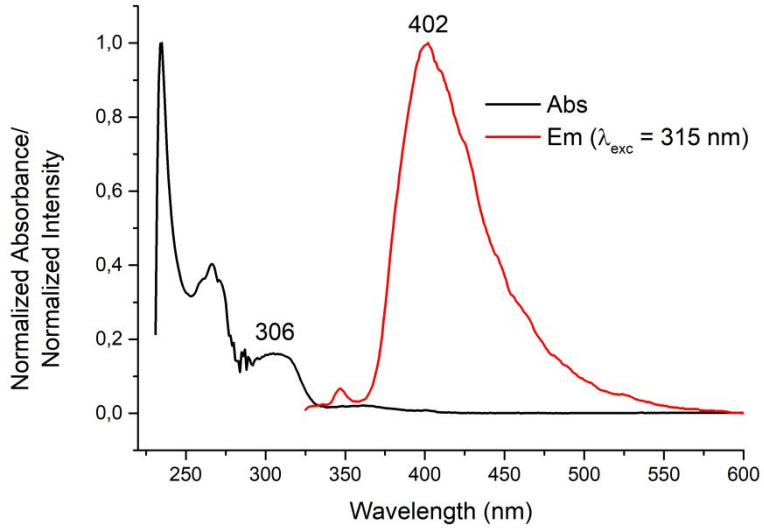


Figure S43. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7d** obtained by mixing methyl 5-acetylsalicylate **6d** and DBU in THF. Recorded in quartz cuvettes (1 cm path). [**6d**] = [DBU] = 1.5 x 10^{-5} M.

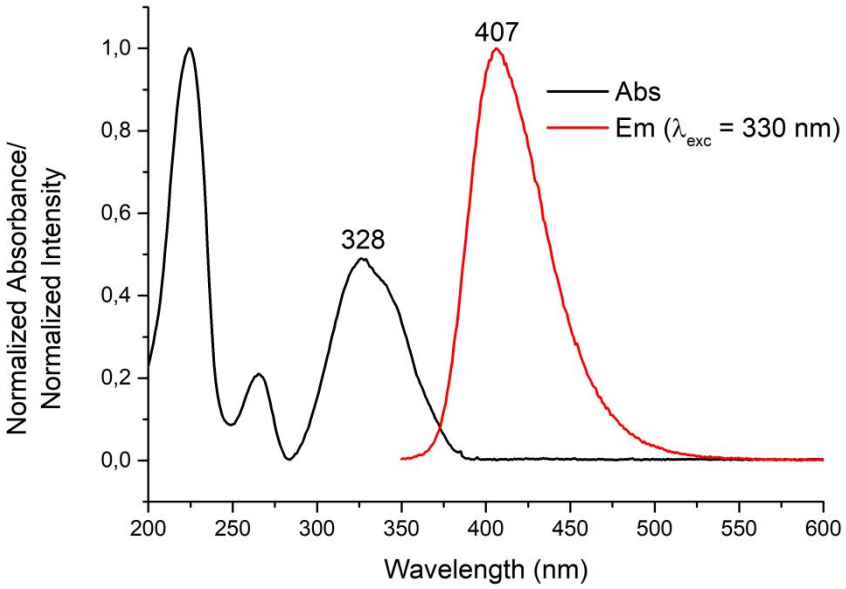


Figure S44. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7d** obtained by mixing methyl 5-acetylsalicylate **6d** and DBU in MeCN. Recorded in quartz cuvettes (1 cm path). [**6d**] = [DBU] = 5 x 10^{-6} M.

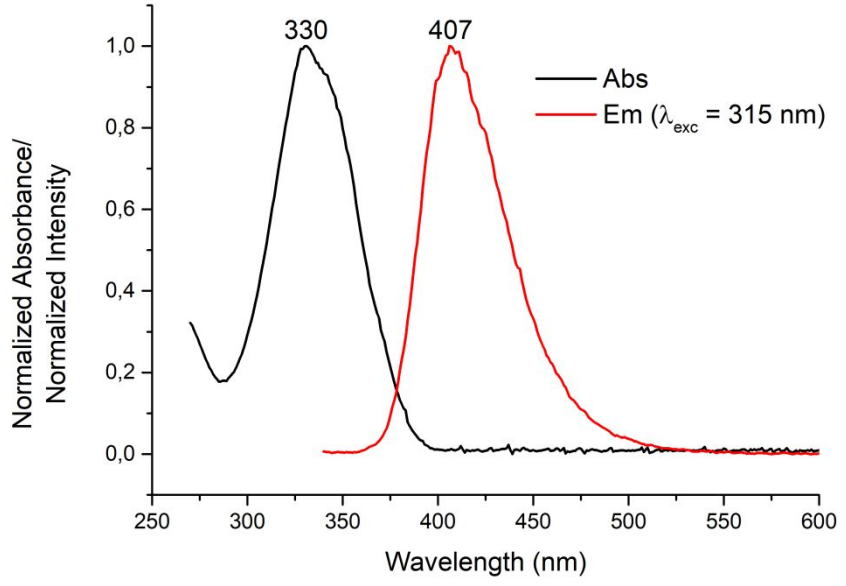


Figure S45. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7d** obtained by mixing methyl 5-acetylsalicylate **6d** and DBU in DMSO. Recorded in quartz cuvettes (1 cm path). [**6d**] = [DBU] = 5 x 10^{-6} M.

Table S7. Solvatochromism studies of phenolate **7d**.

	Toluene	**THF**	**MeCN**	**DMSO**
Max. Abs (nm)	310	306	328	330
Max. Abs (eV)	3,303226	3,346405	3,121951	3,10303
Max. Em (nm)	457	402	407	407
Max Em (eV)	2,2407	2,547264	2,515971	2,515971
$\Delta E=E_{em} - E_{Abs}$ (eV)	1,062526	0,799142	0,605981	0,58706
$E_T(30)$	33,9	37,4	45,6	45,1

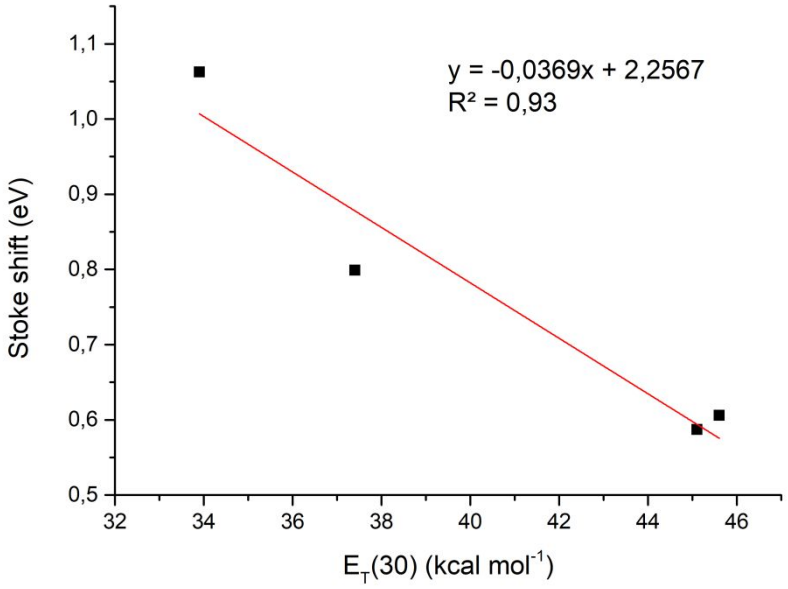


Figure S46. Stokes shifts (ΔE) of phenolate **7d** vs the $E_T(30)$ value of the solvent (see Table S7 for the list of solvents).

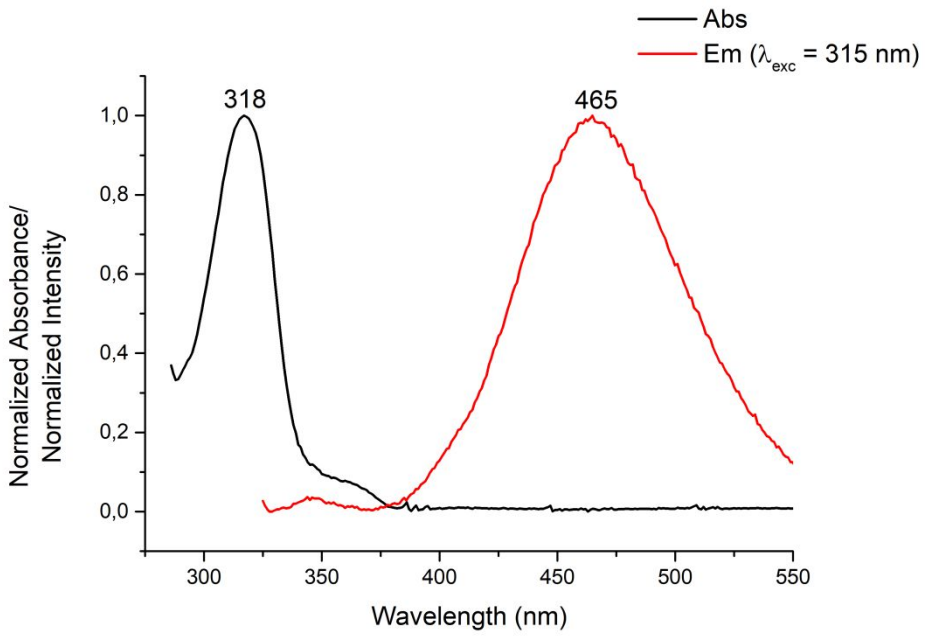


Figure S47. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7e** obtained by mixing phenol **6e** and DBU in toluene. Recorded in quartz cuvettes (1 cm path). [**6e**] = [DBU] = 2 x 10^{-5} M.

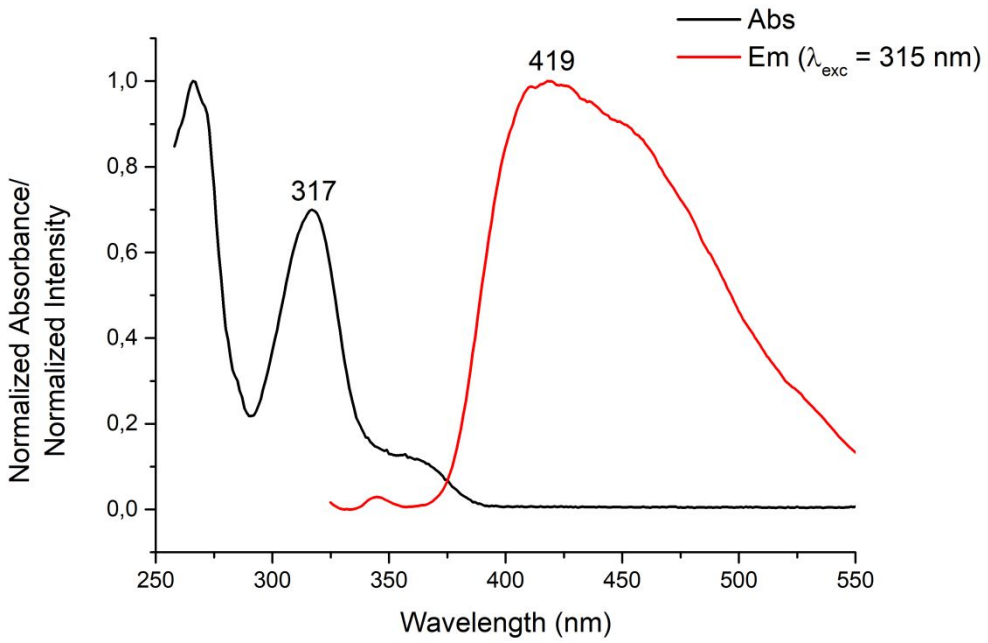


Figure S48. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7e** obtained by mixing phenol **6e** and DBU in THF. Recorded in quartz cuvettes (1 cm path). [**6e**] = [DBU] = 1.5 x 10^{-5} M.

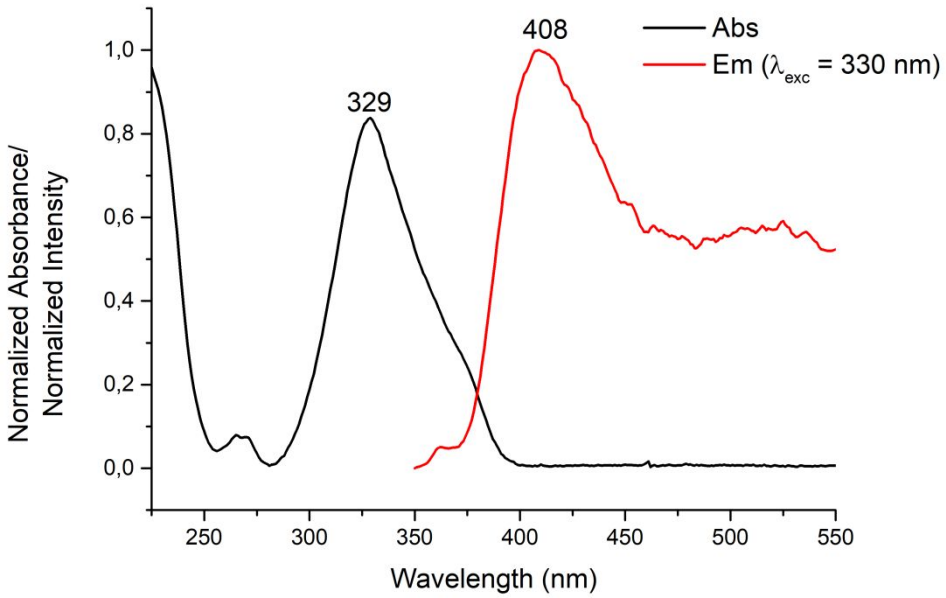


Figure S49. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7e** obtained by mixing phenol **6e** and DBU in MeCN. Recorded in quartz cuvettes (1 cm path). [**6e**] = [DBU] = 5 x 10^{-6} M.

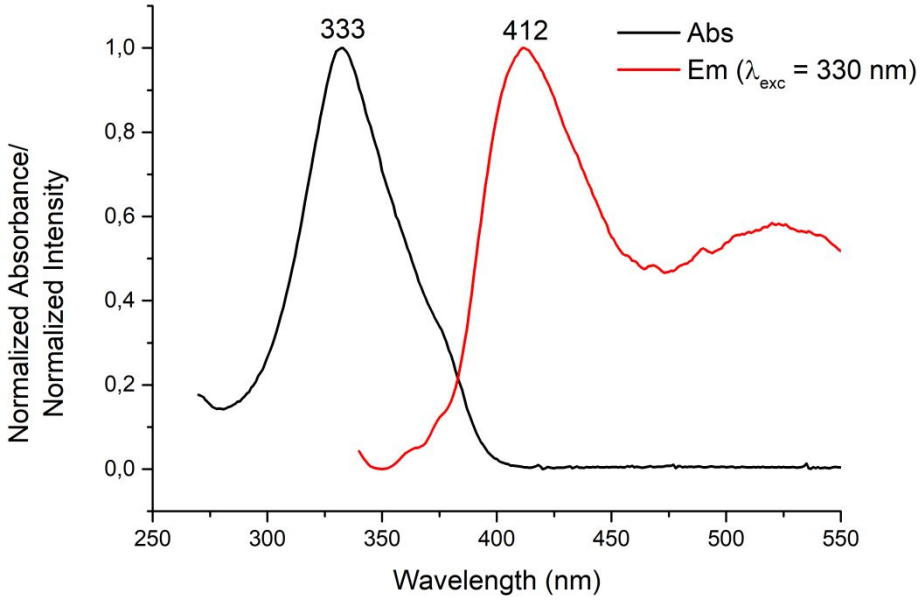


Figure S50. Normalized optical absorption spectrum (black line) and emission spectra (red line) of phenolate **7e** obtained by mixing phenol **6e** and DBU in DMSO. Recorded in quartz cuvettes (1 cm path). [**6e**] = [DBU] = 5 x 10^{-6} M.

Table S8. Solvatochromism studies of phenolate **7e**.

	Toluene	THF	MeCN	DMSO
Max. Abs (nm)	318	317	329	333
Max. Abs (eV)	3,220126	3,230284	3,112462	3,075075
Max Em (nm)	465	419	408	412
Max Em (eV)	2,202151	2,443914	2,509804	2,485437
$\Delta E=E_{em} - E_{Abs}$ (eV)	1,017975	0,78637	0,602658	0,589638
$E_T(30)$	33,9	37,4	45,6	45,1

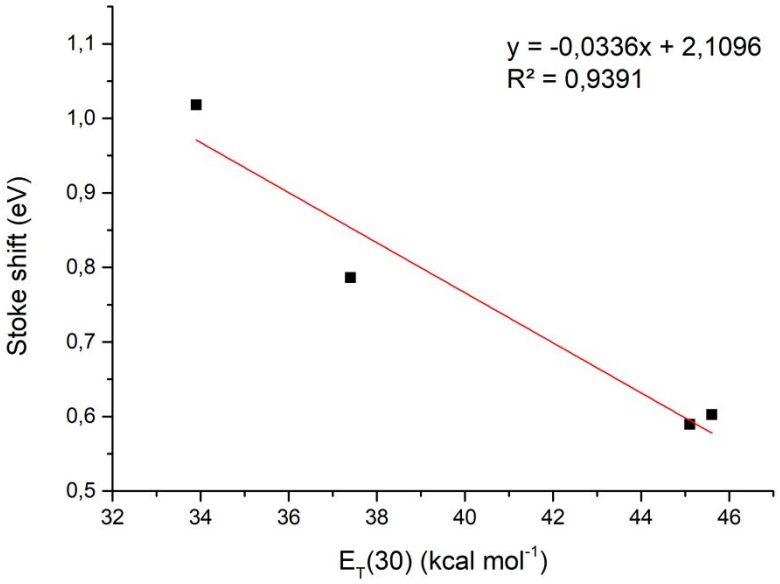


Figure S51. Stokes shifts (ΔE) of phenolate **7e** vs the $E_T(30)$ value of the solvent (see Table S8 for the list of solvents).

J. REFERENCES

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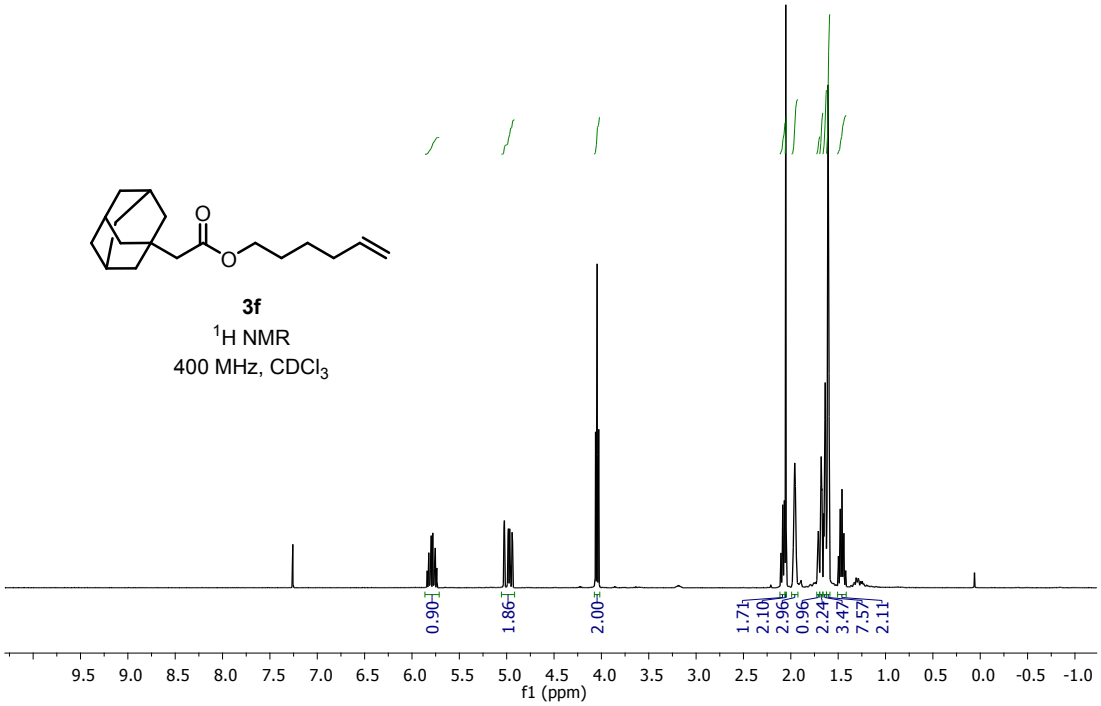
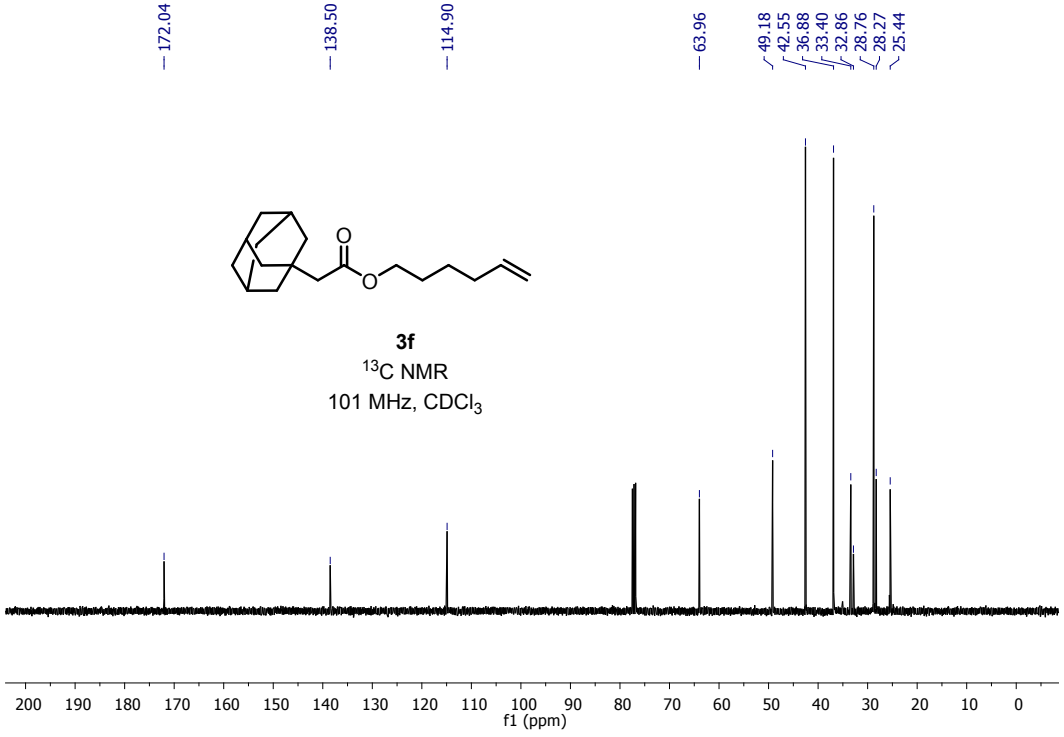
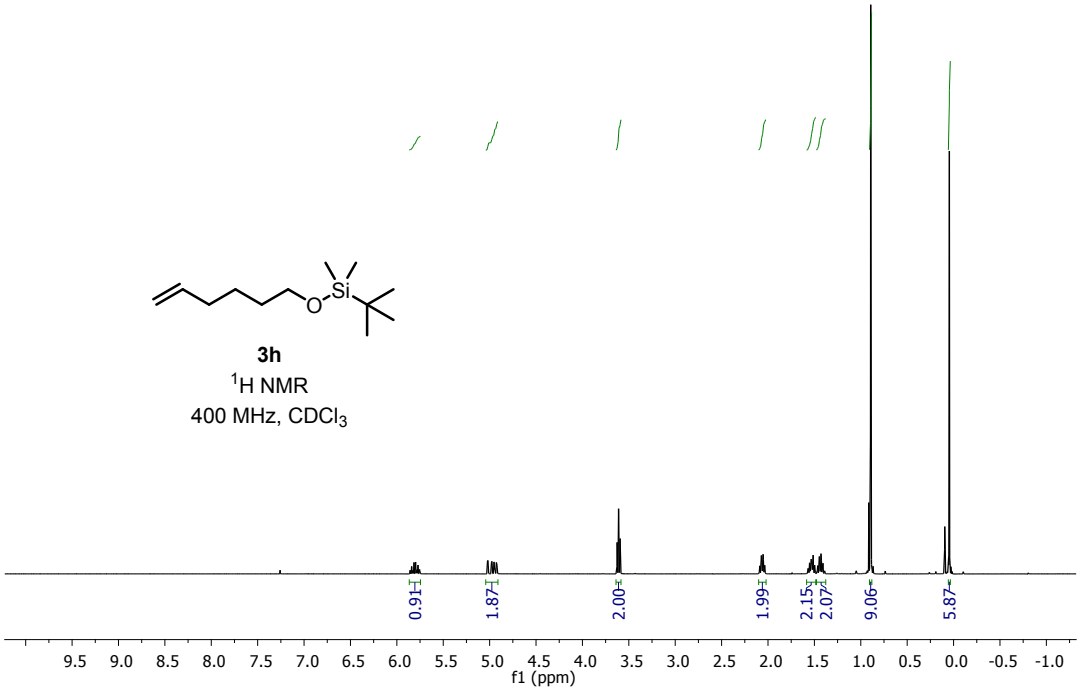
K. NMR SPECTRA







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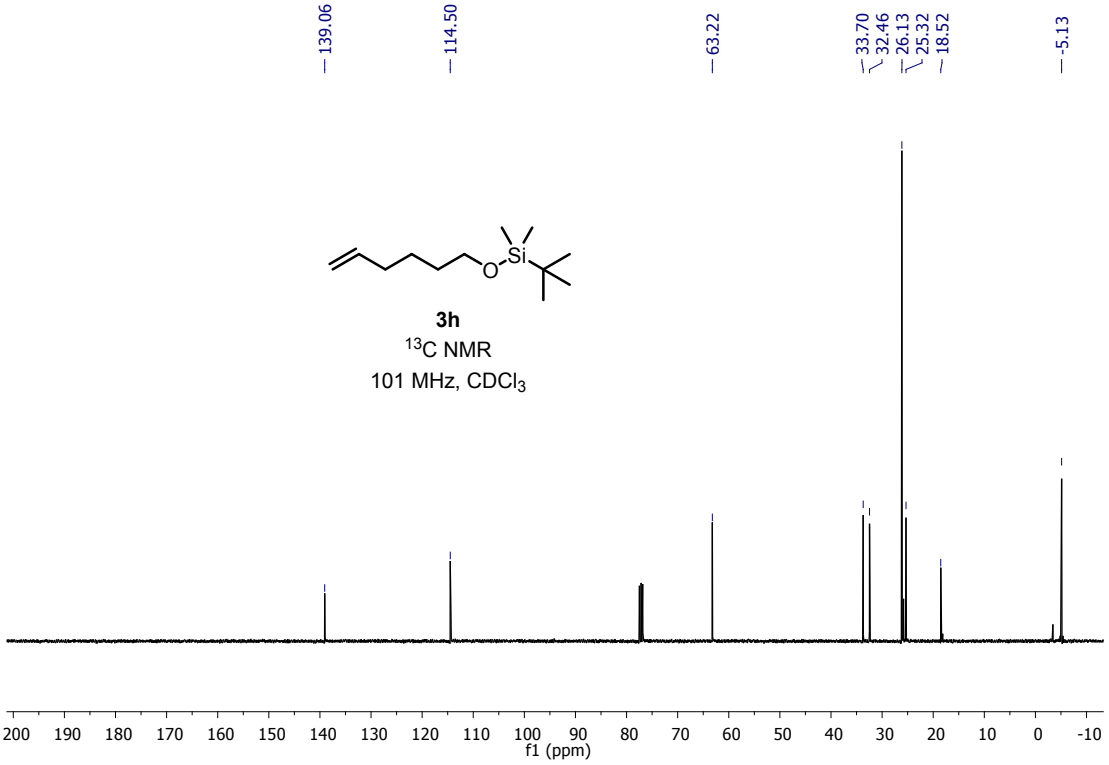

3h

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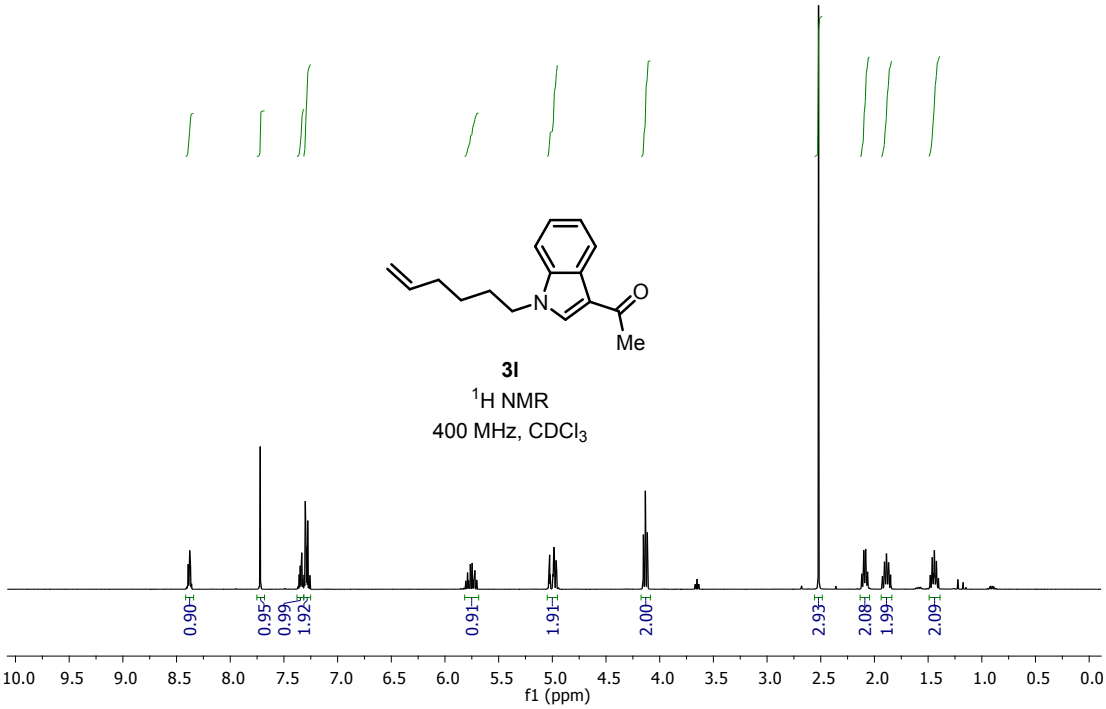
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1.91
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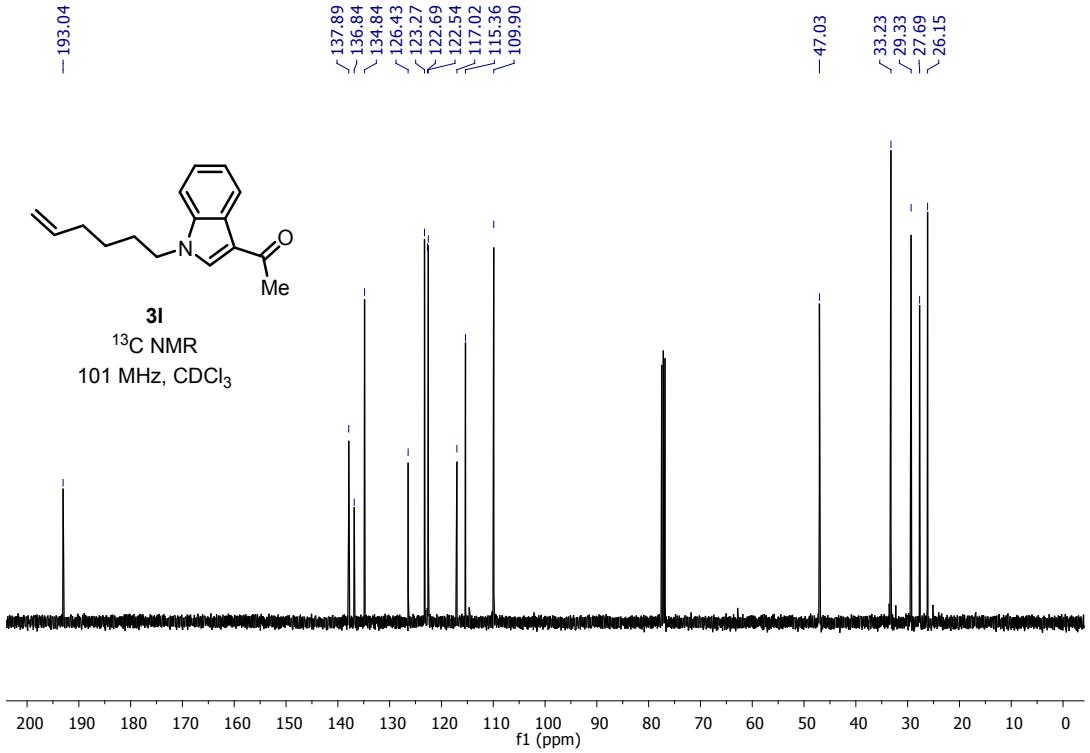
2.93
2.08
1.99
2.09
f1 (ppm)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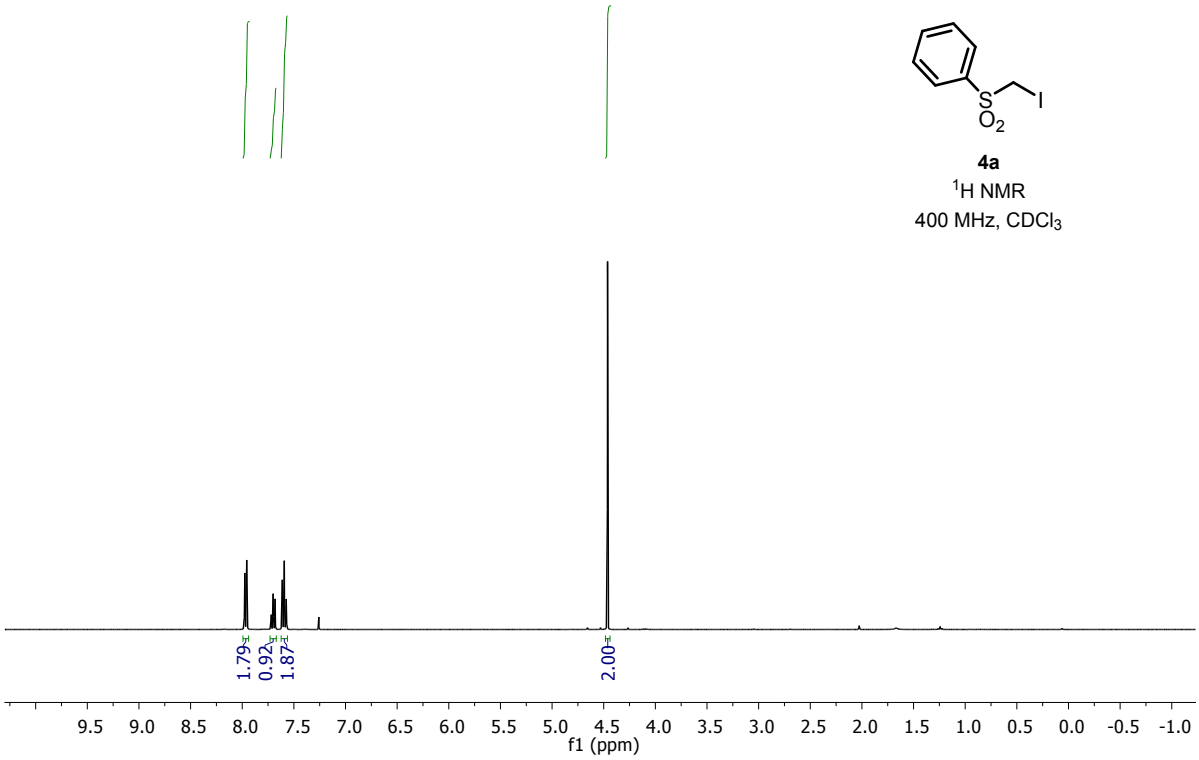
29.33
27.69
26.15
N
O
Me
3l
13C NMR
101 MHz, CDCl3
f1 (ppm)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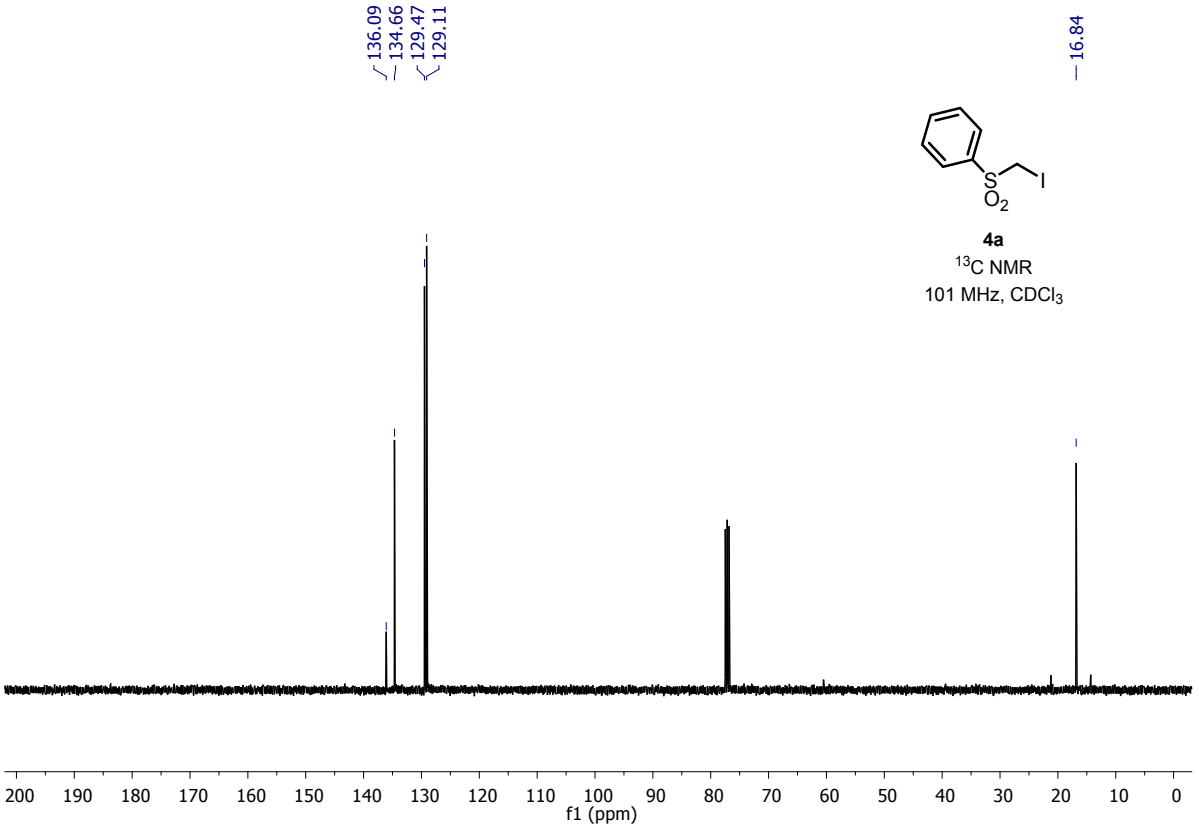
f1 (ppm)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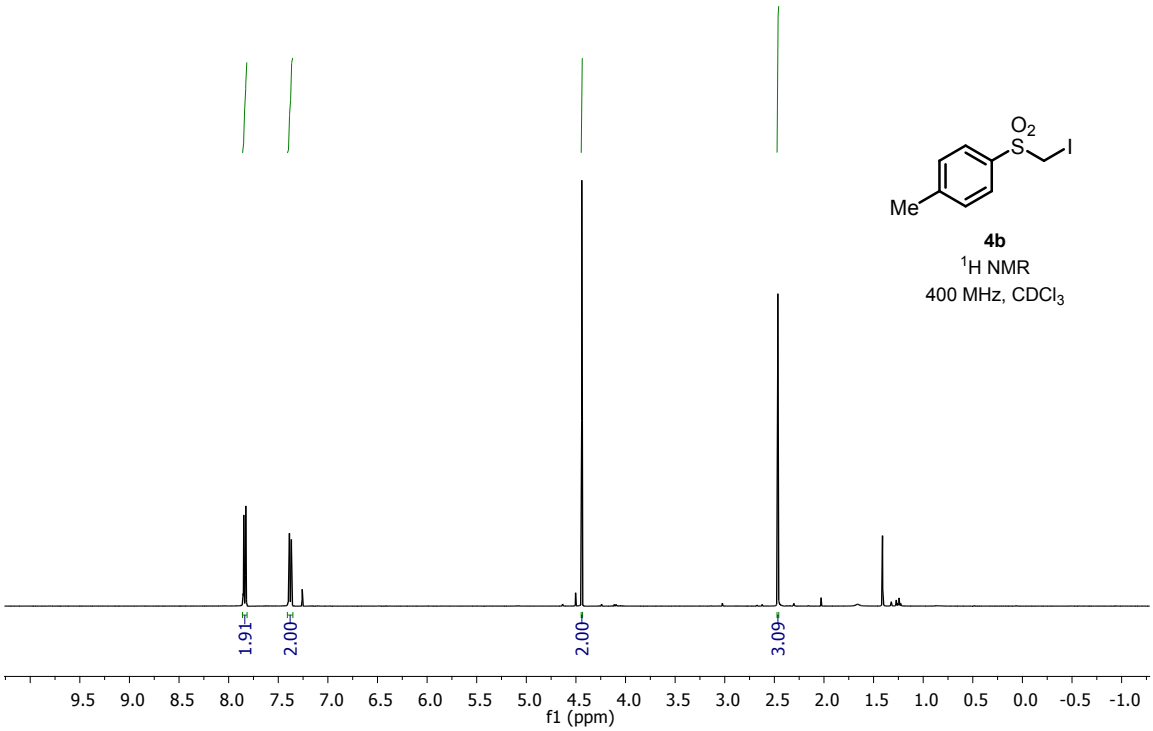
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I
Me
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400 MHz, CDCl3
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2.00
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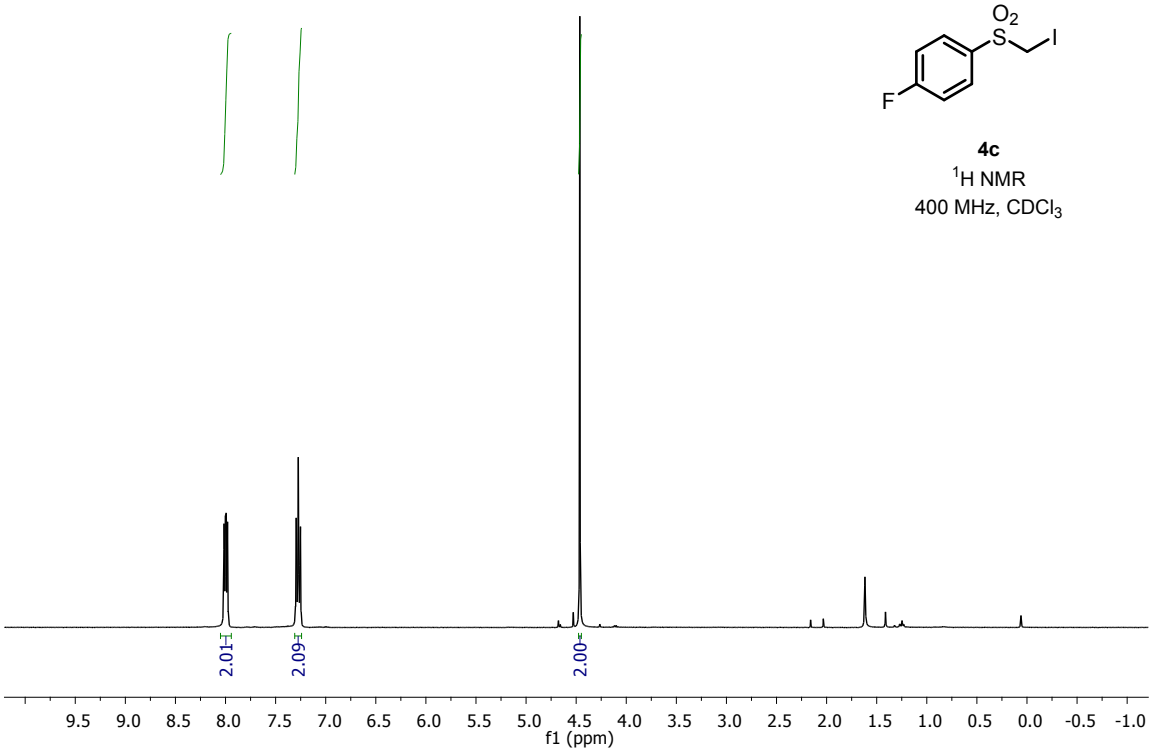
f1 (ppm)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I
F
4c
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2.00
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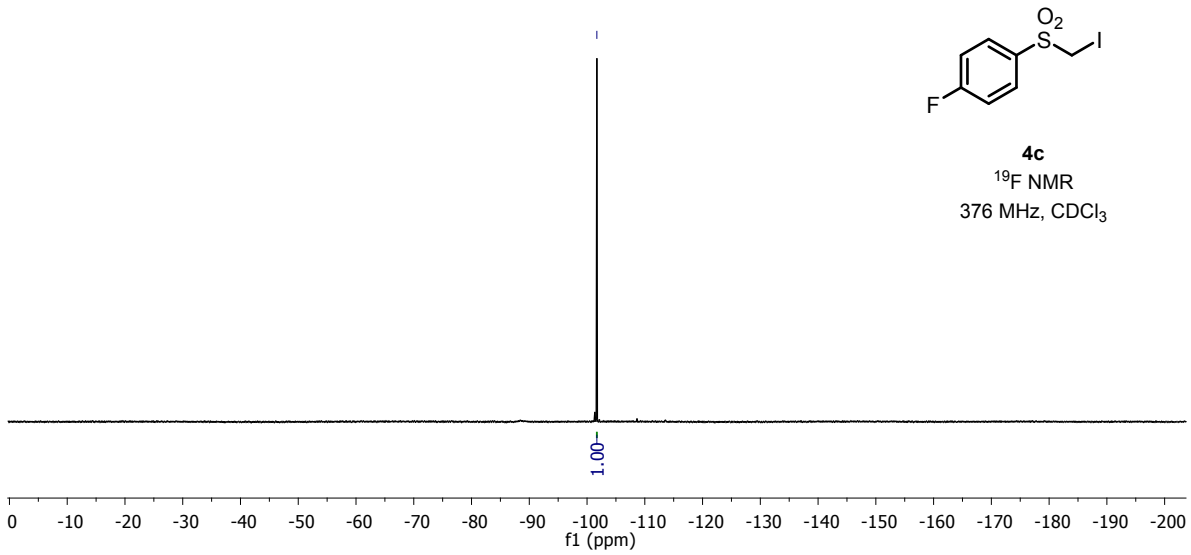
f1 (ppm)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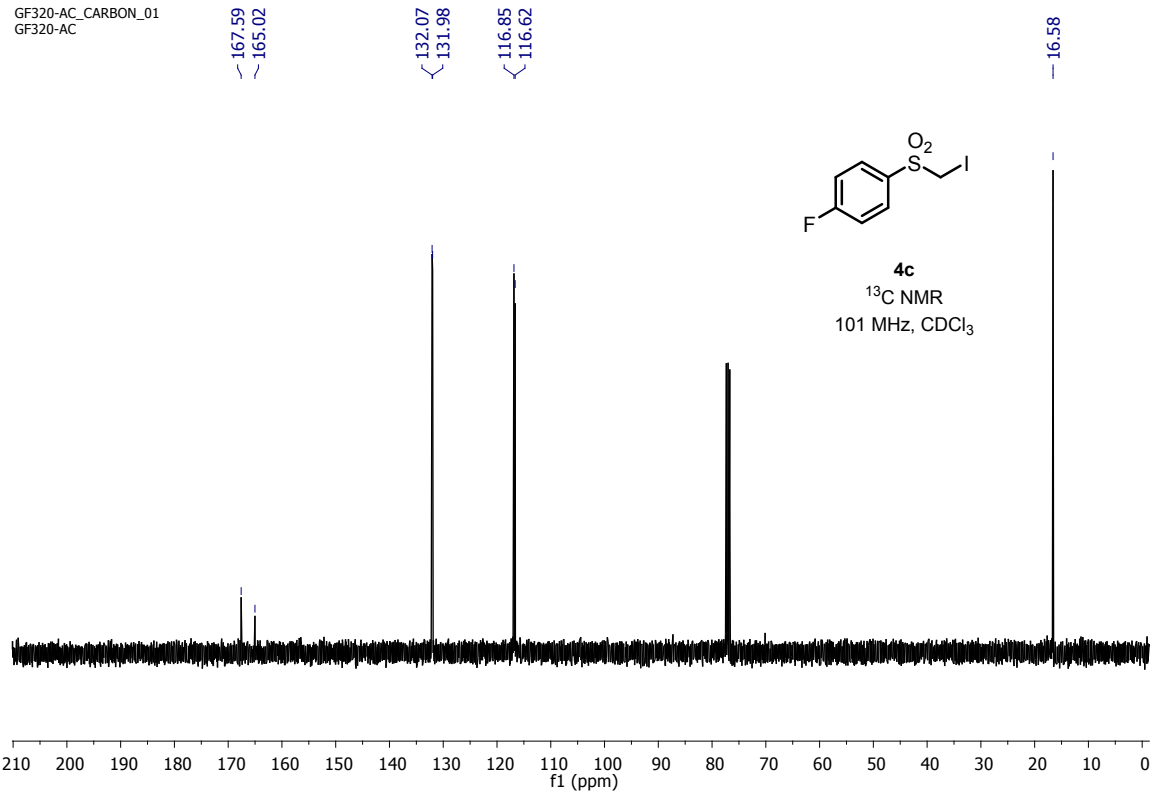
f1 (ppm)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S
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F
4c
13C NMR
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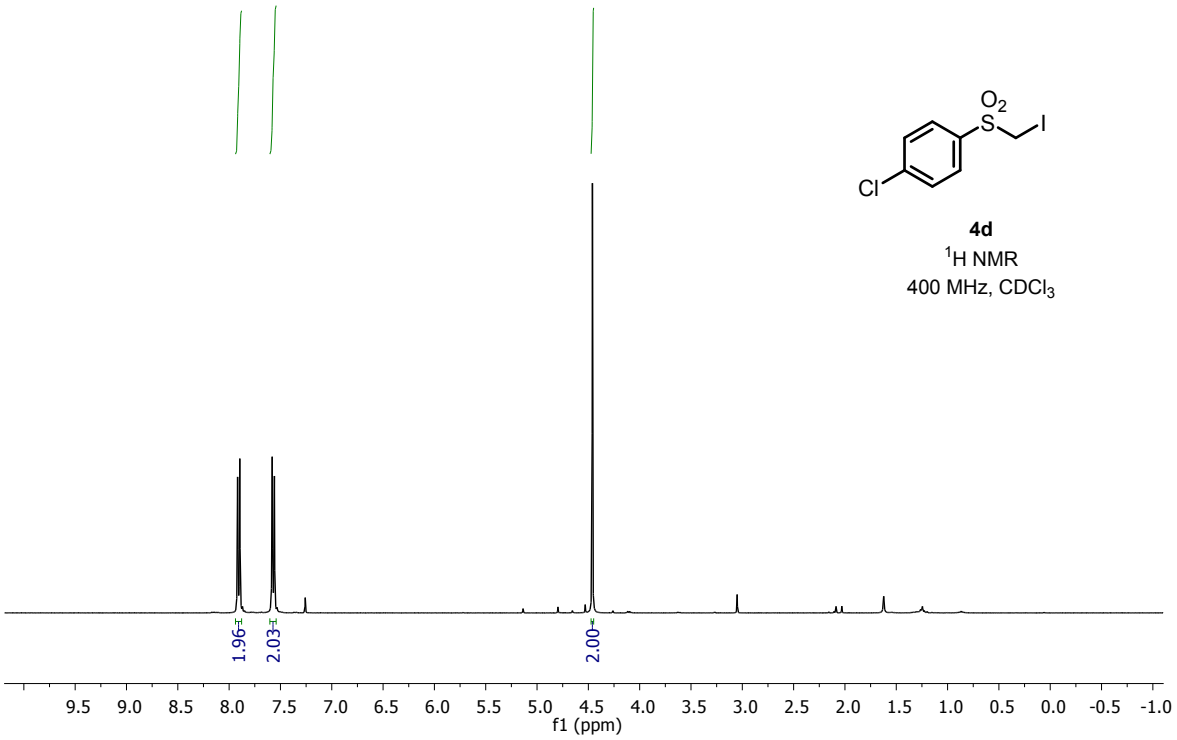
f1 (ppm)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Cl
4d
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2.03
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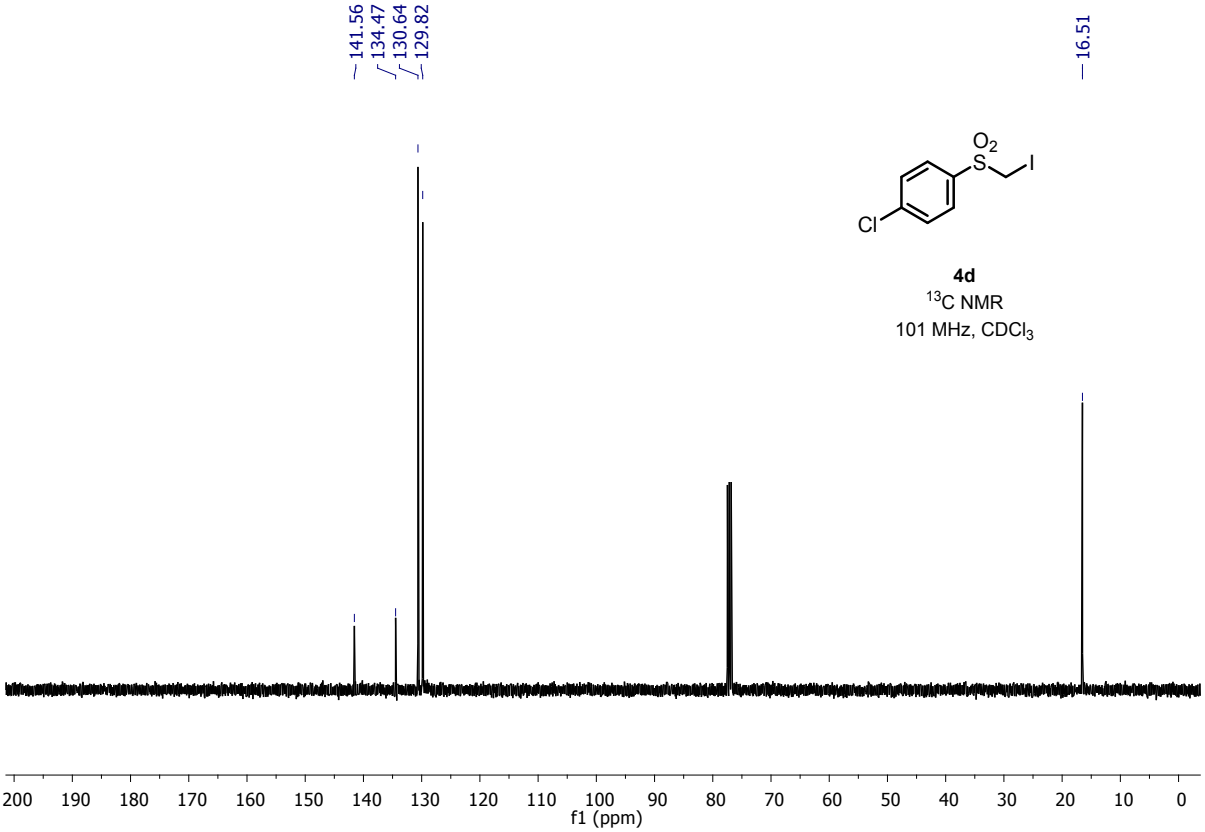
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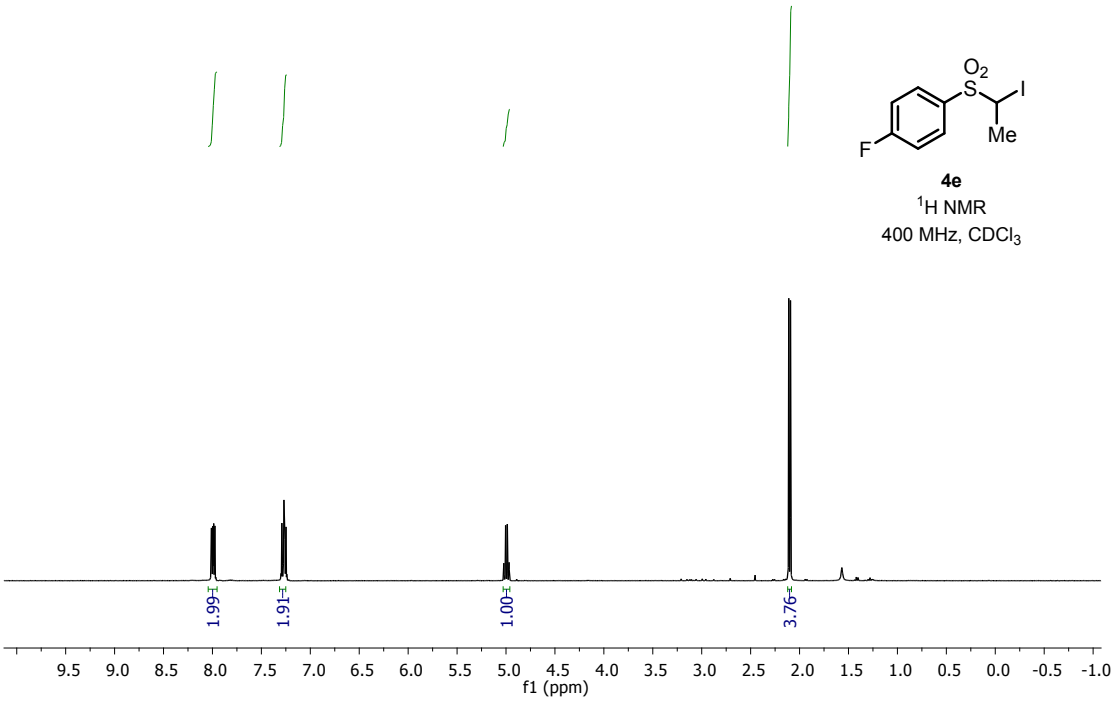

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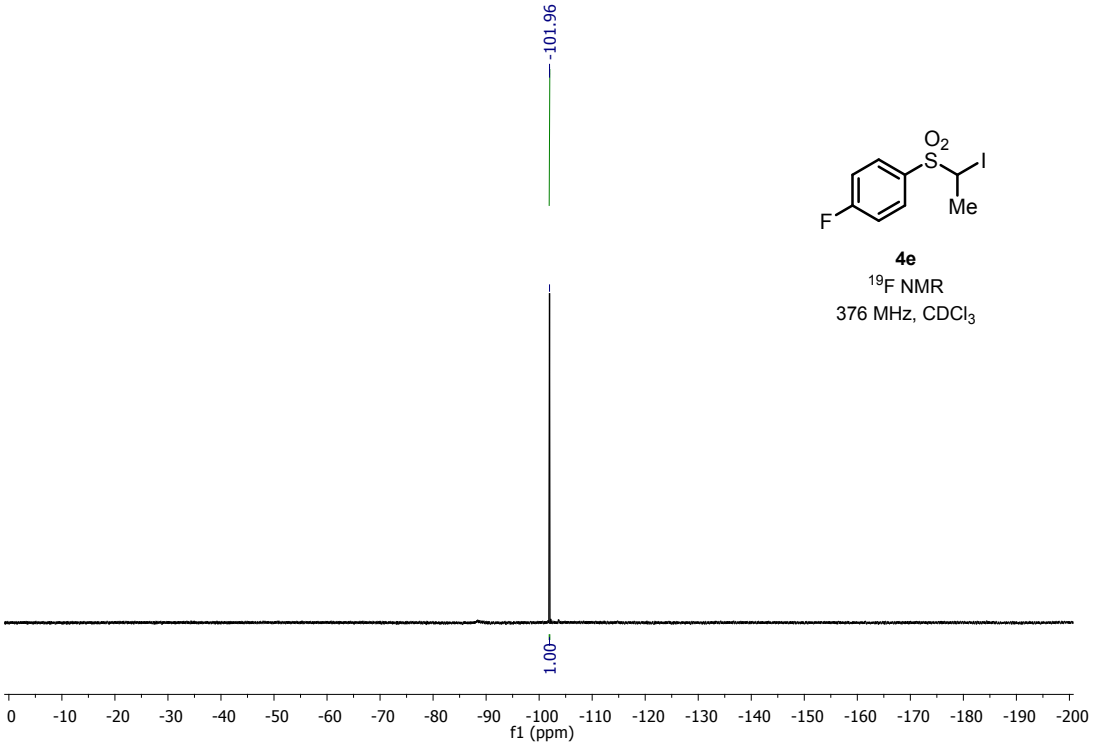

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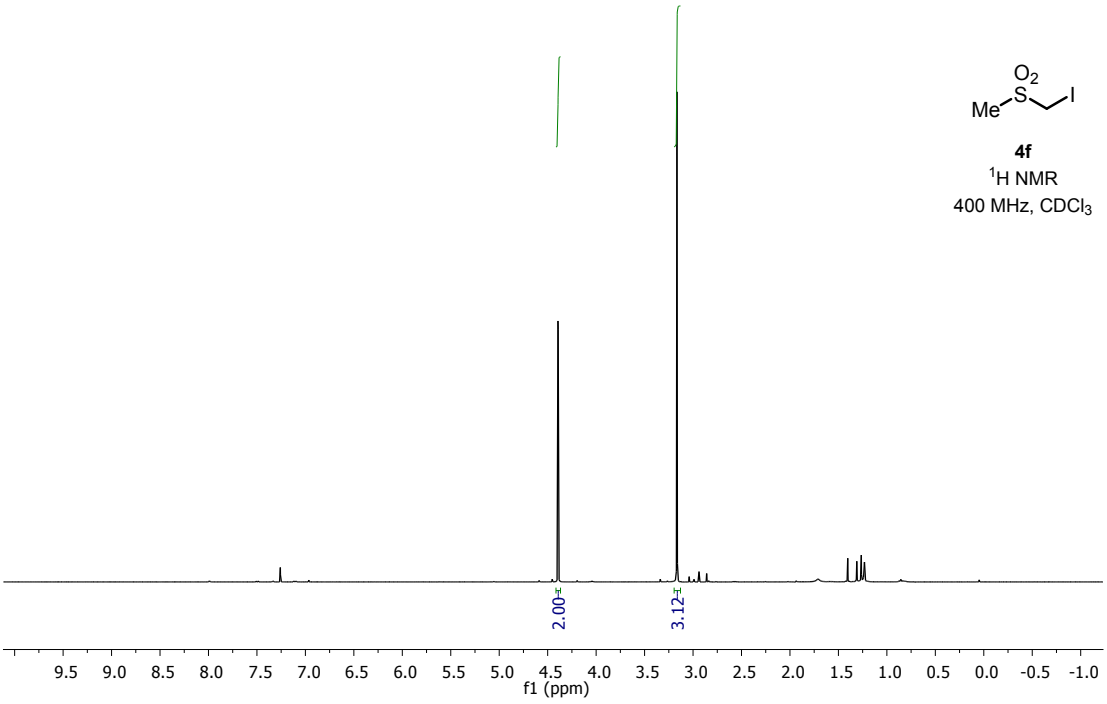
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4f
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3.12
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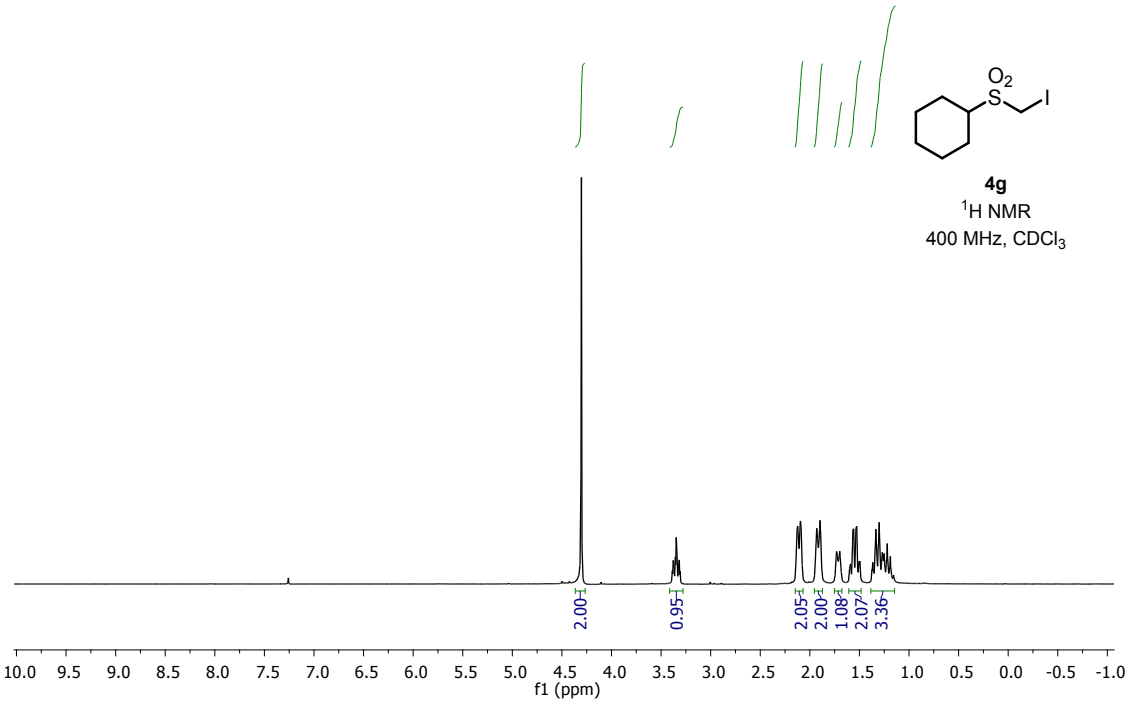
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4g
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1.08
2.07
3.36
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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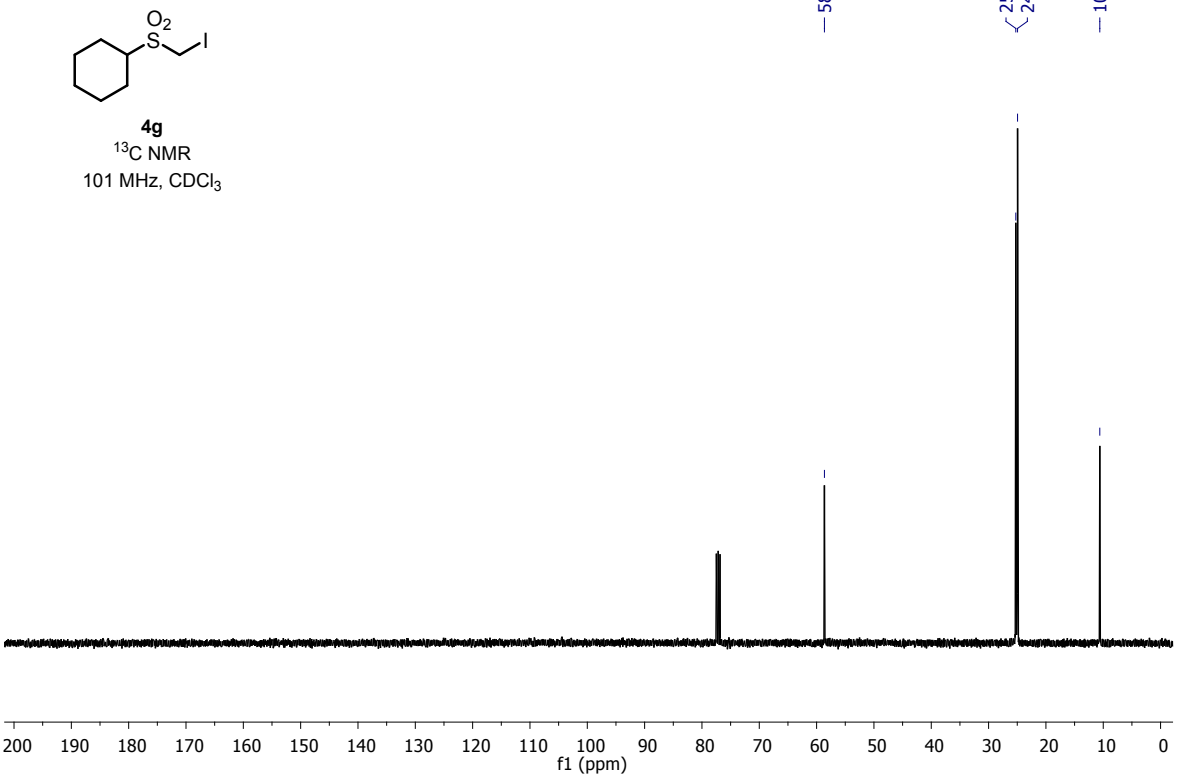
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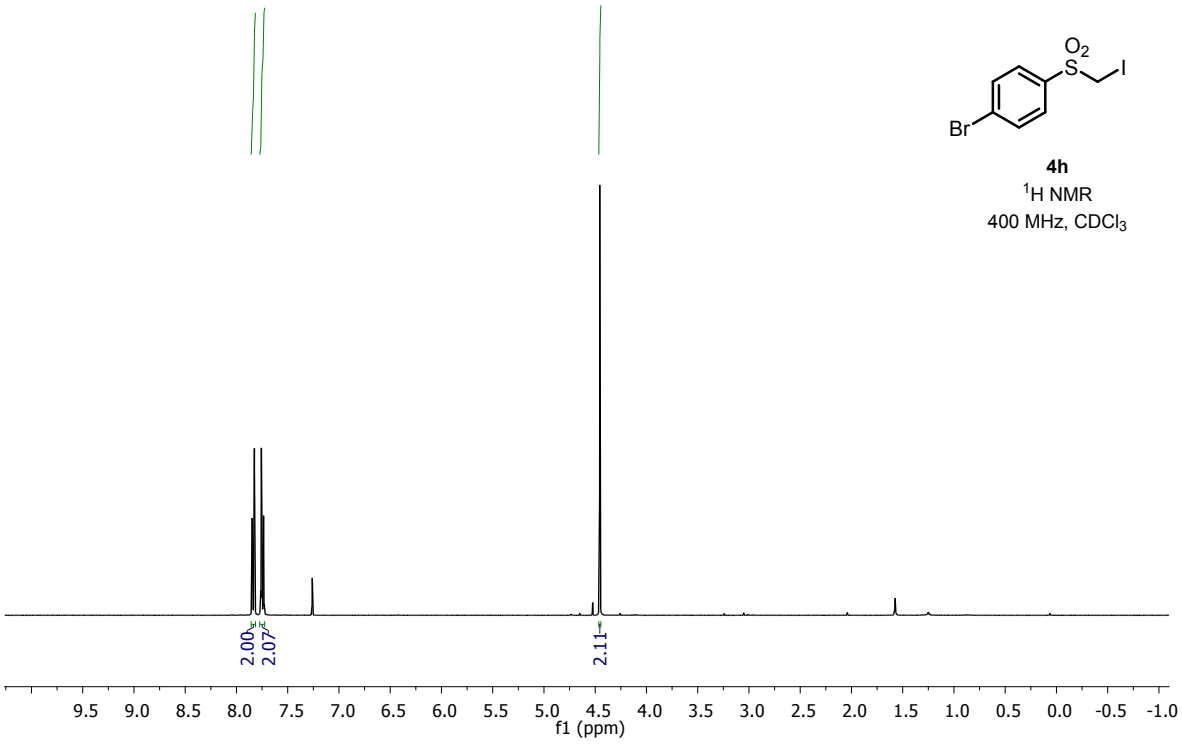
f1 (ppm)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Br
4h
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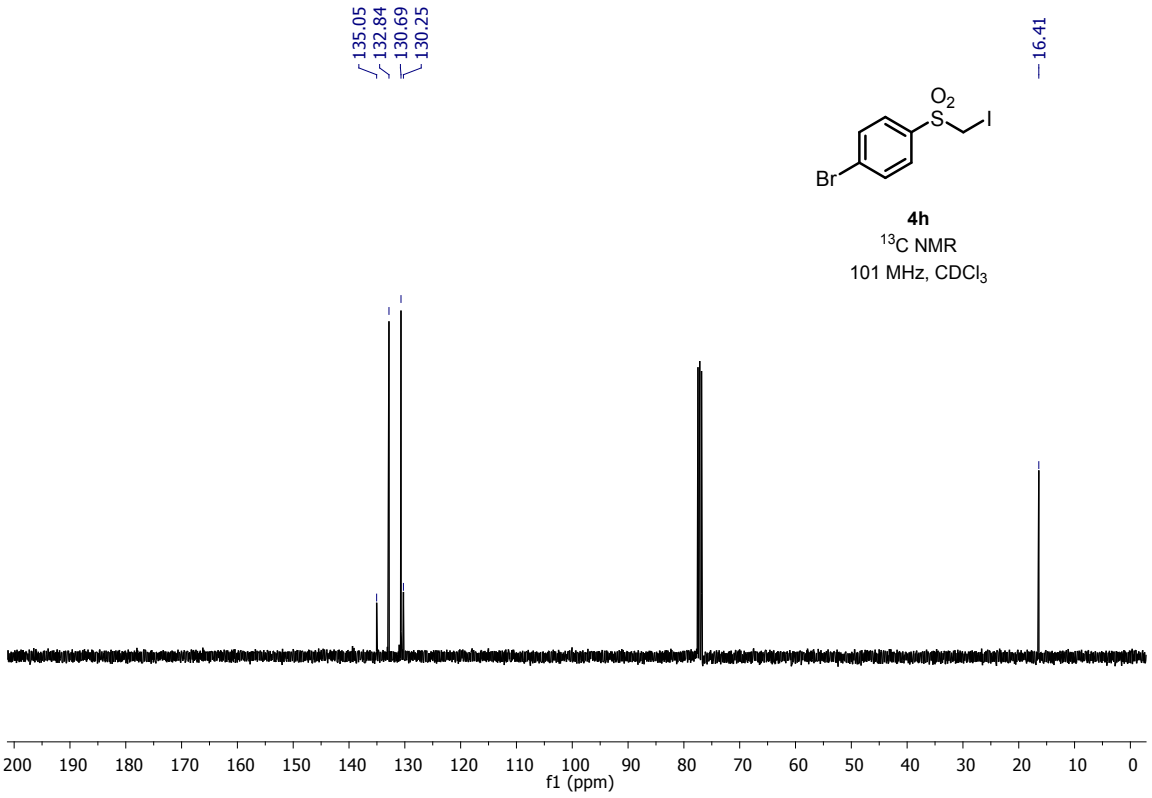
f1 (ppm)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Br
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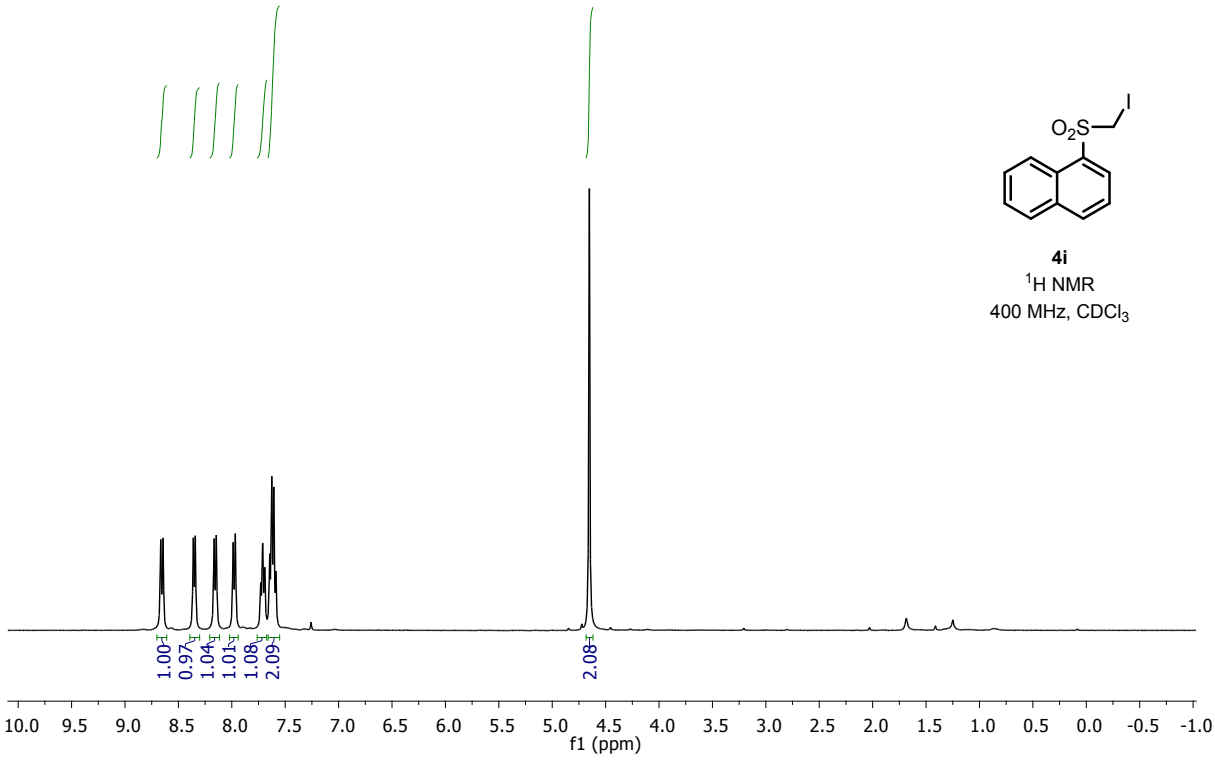
f1 (ppm)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I
4i
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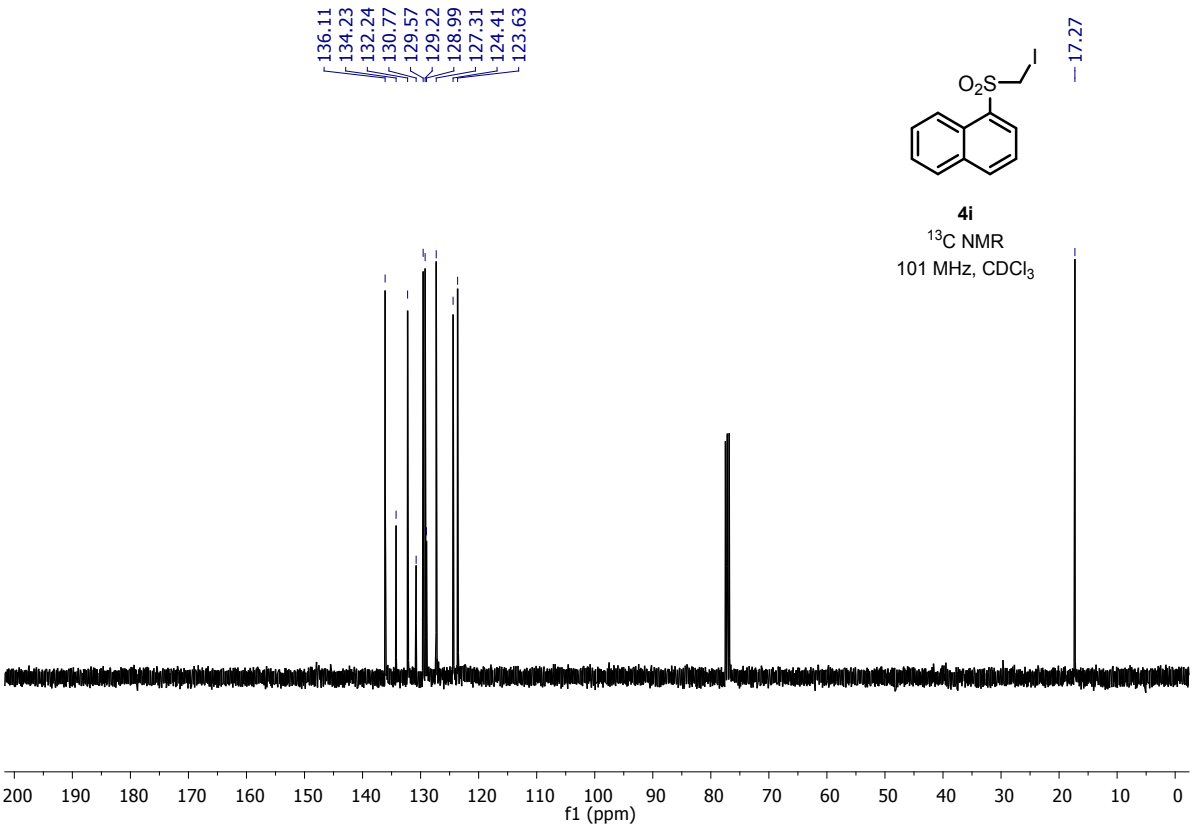
2.09
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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O2S
I
4i
13C NMR
101 MHz, CDCl3
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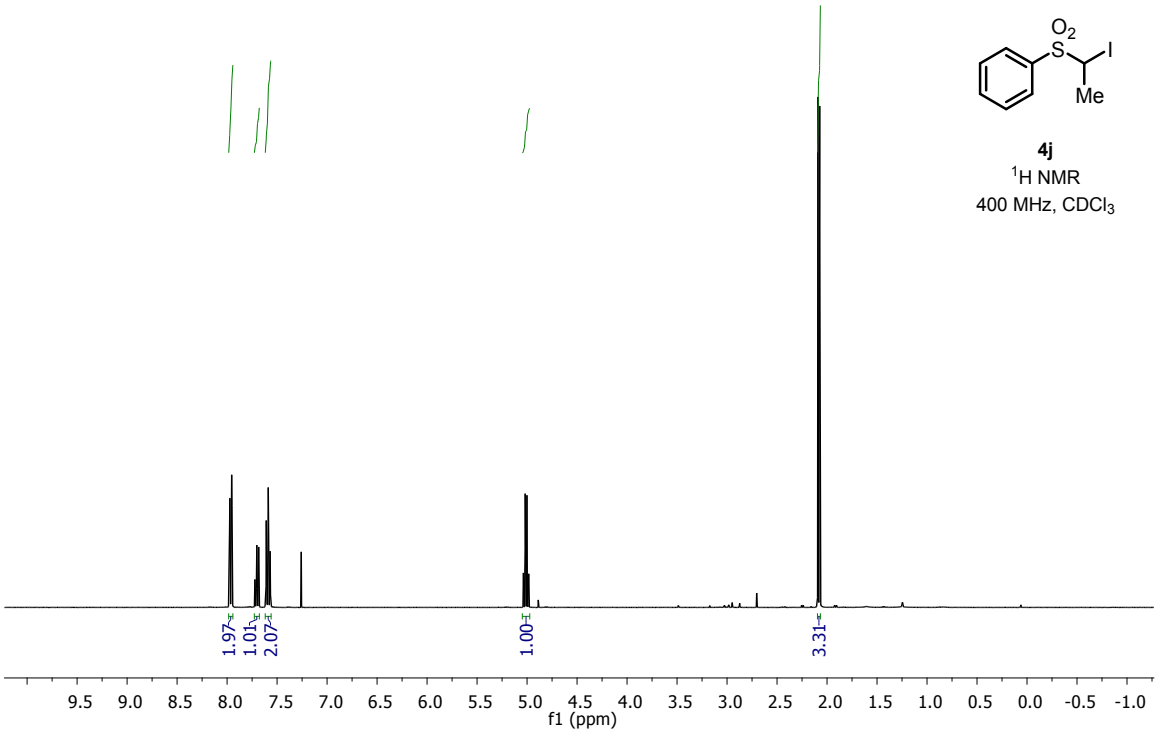
f1 (ppm)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I
Me
4j
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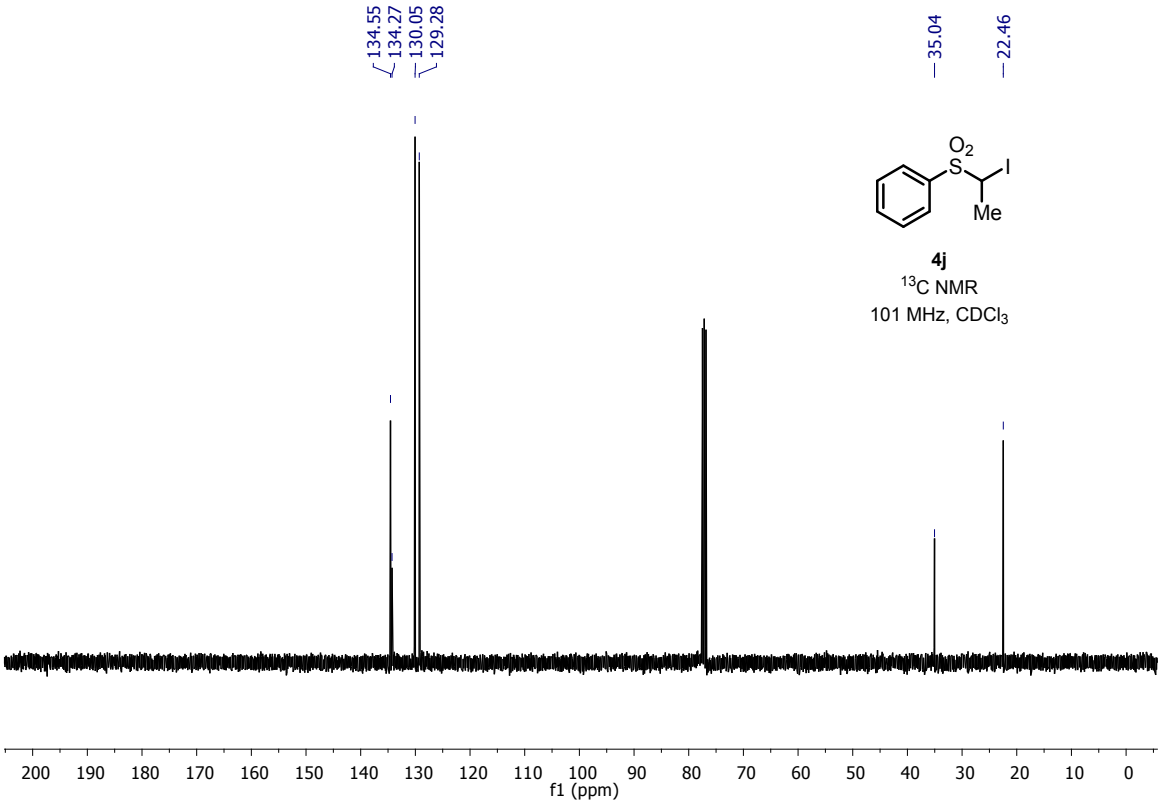
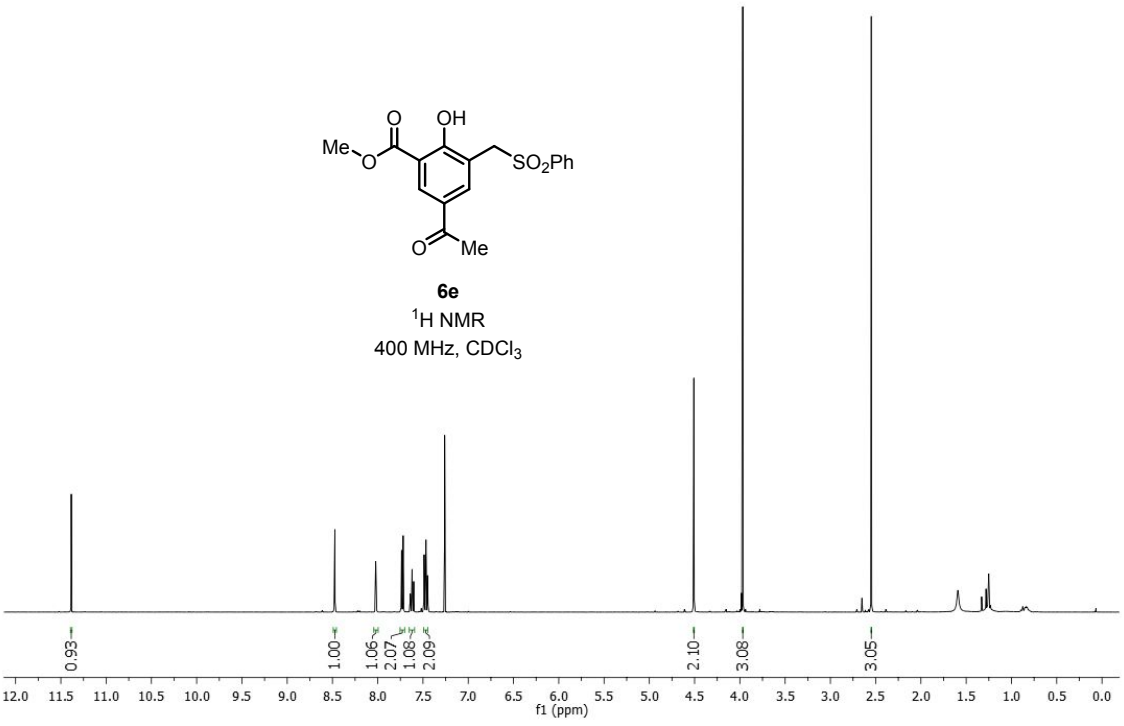
1.00
3.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



4j

^{13}C NMR

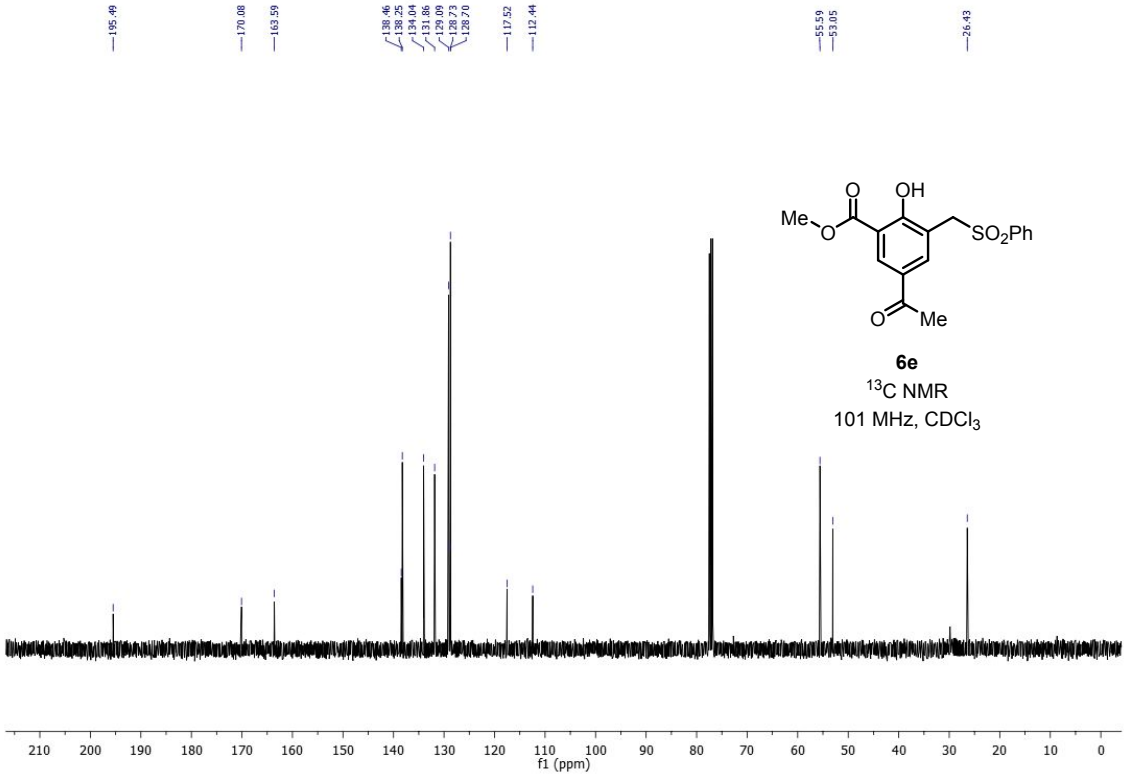
101 MHz, $CDCl_3$



6e

^{1}H NMR

400 MHz, $CDCl_3$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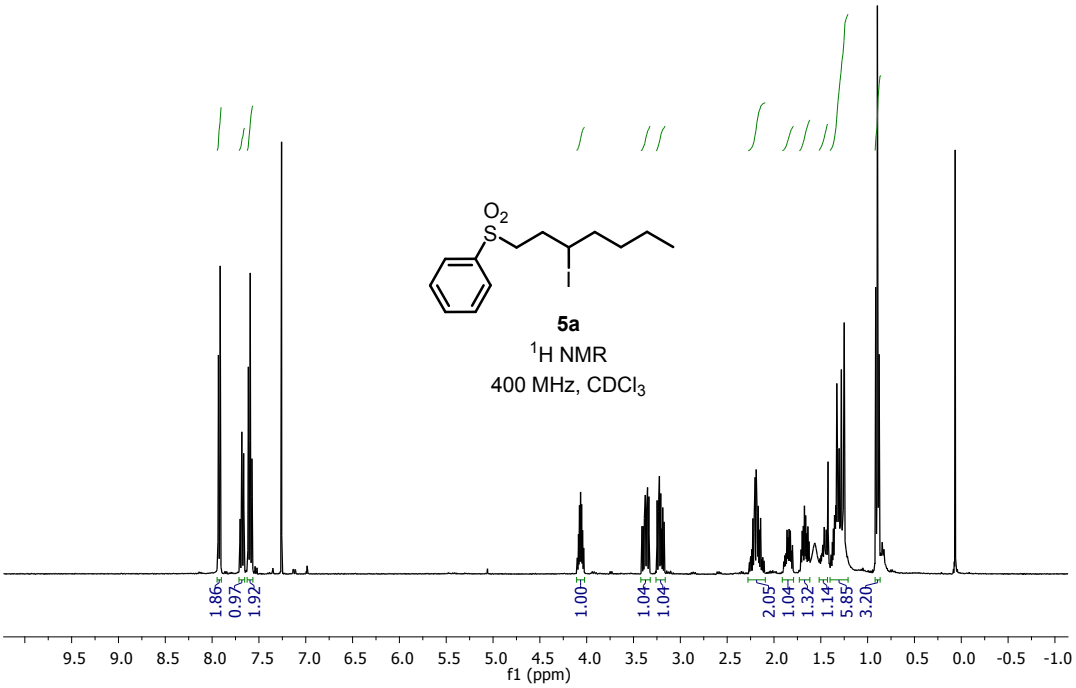
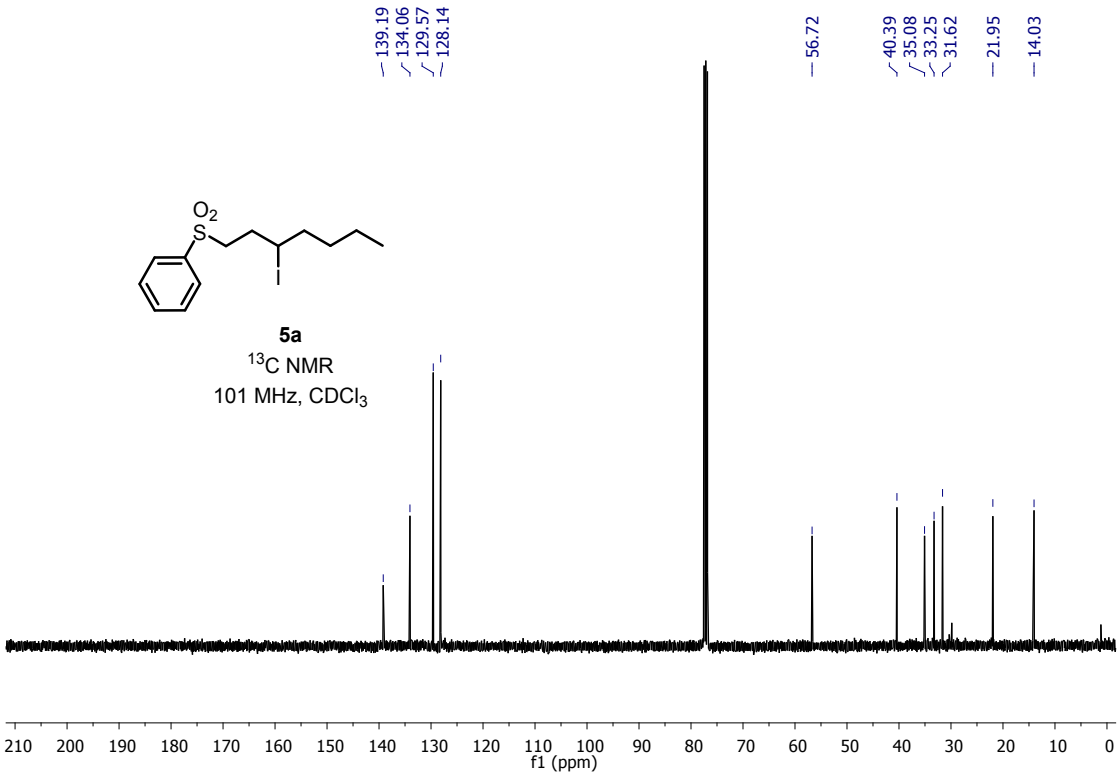
170.08
163.59
138.46
138.25
134.04
131.86
129.09
128.73
128.70
117.52
112.44
55.59
53.05
26.43
O
OH
Me
O
SO2Ph
O
Me
6e
13C NMR
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O2
S
I
5a
1H NMR
400 MHz, CDCl3
1.86
0.97
1.92
1.00
1.04
1.04
2.05
1.04
1.32
1.14
5.85
3.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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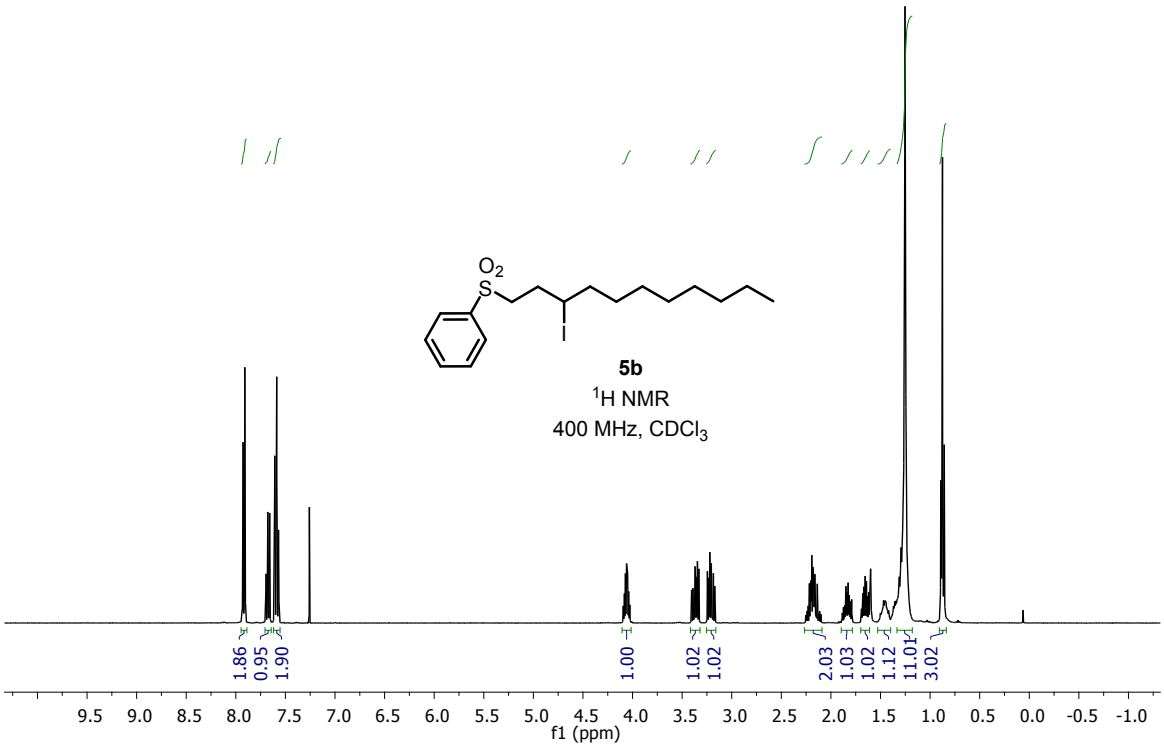
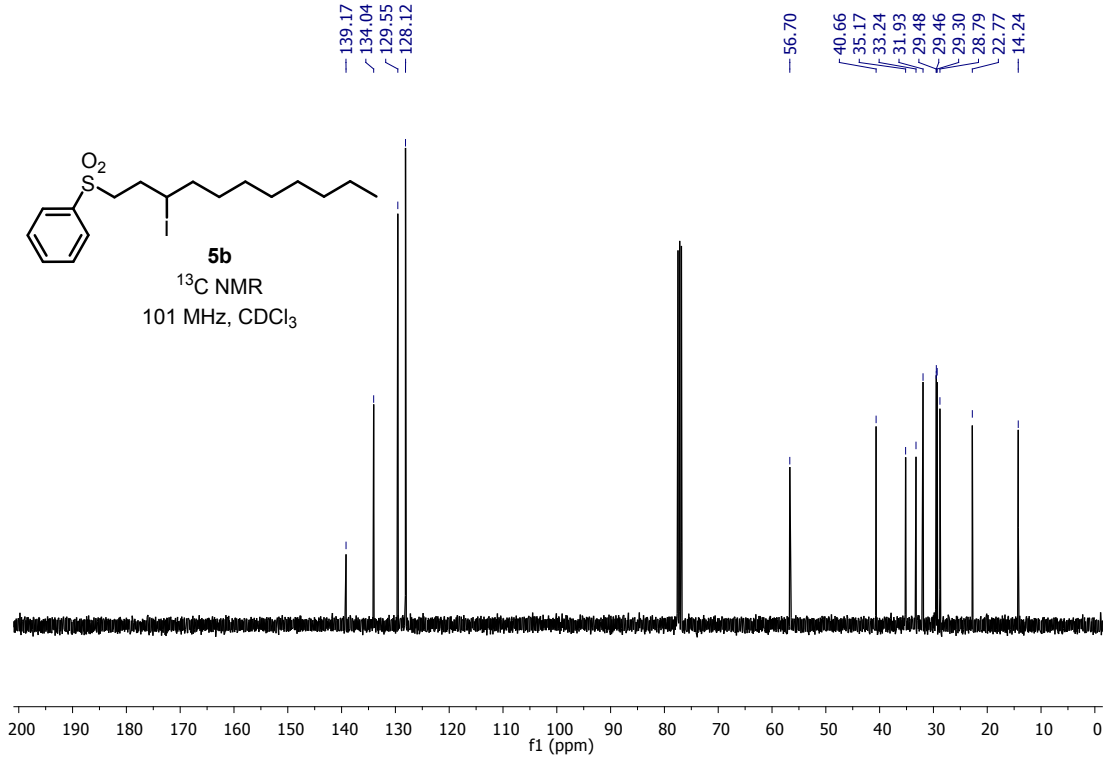
134.06
129.57
128.14
56.72
40.39
35.08
33.25
31.62
21.95
14.03
O2
S
I
5a
13C NMR
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O2
S
I
5b
1H NMR
400 MHz, CDCl3
1.86
0.95
1.90
1.00
1.02
1.02
2.03
1.03
1.02
1.12
11.01
3.02
f1 (ppm)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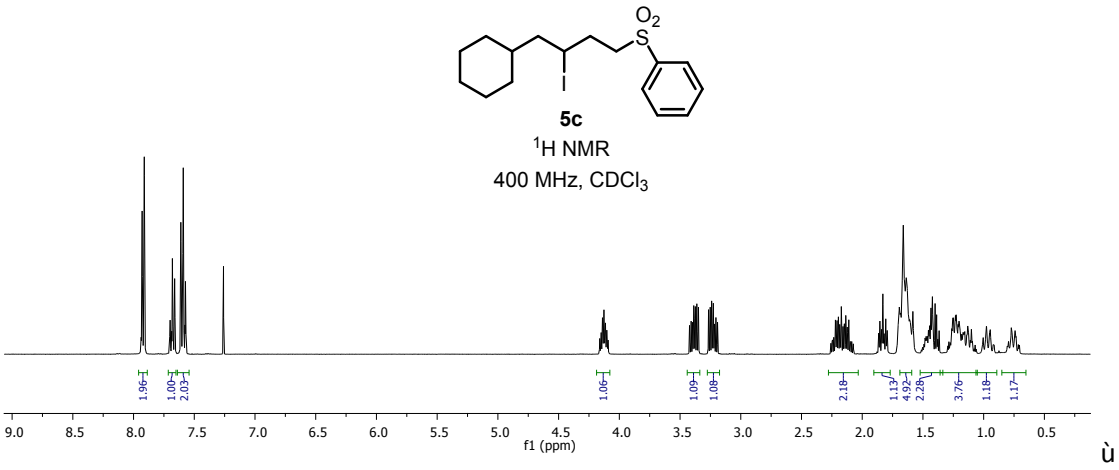
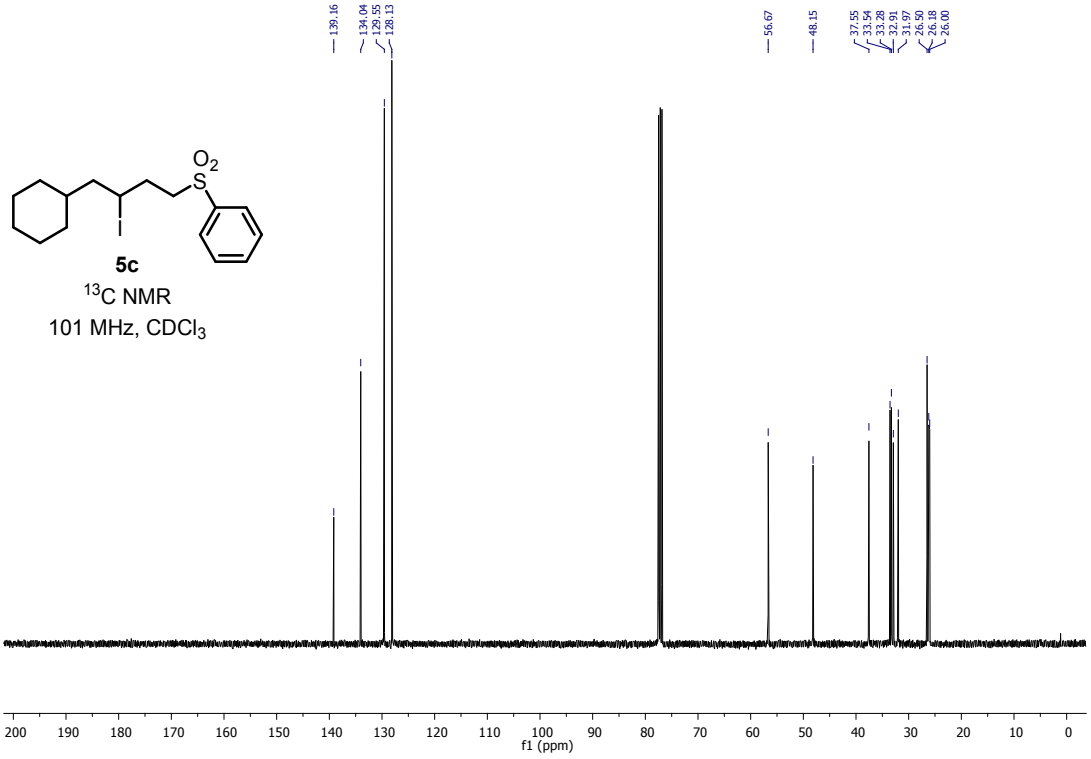
134.04
129.55
128.12
56.70
40.66
35.17
33.24
31.93
29.48
29.46
29.30
28.79
22.77
14.24
O2
S
I
5b
13C NMR
101 MHz, CDCl3
f1 (ppm)


O2
S
I
5c
1H NMR
400 MHz, CDCl3
1.96
1.00
2.03
1.06
1.09
1.08
2.18
1.13
4.92
2.26
3.76
1.18
1.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

ù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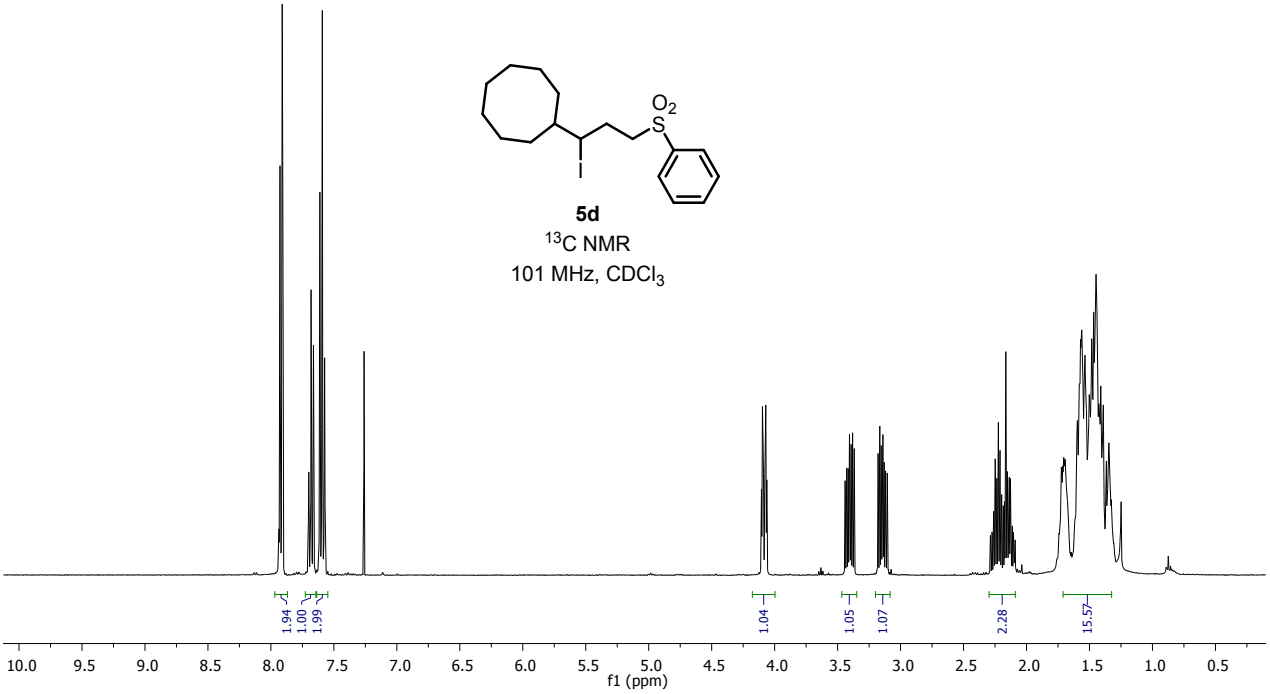
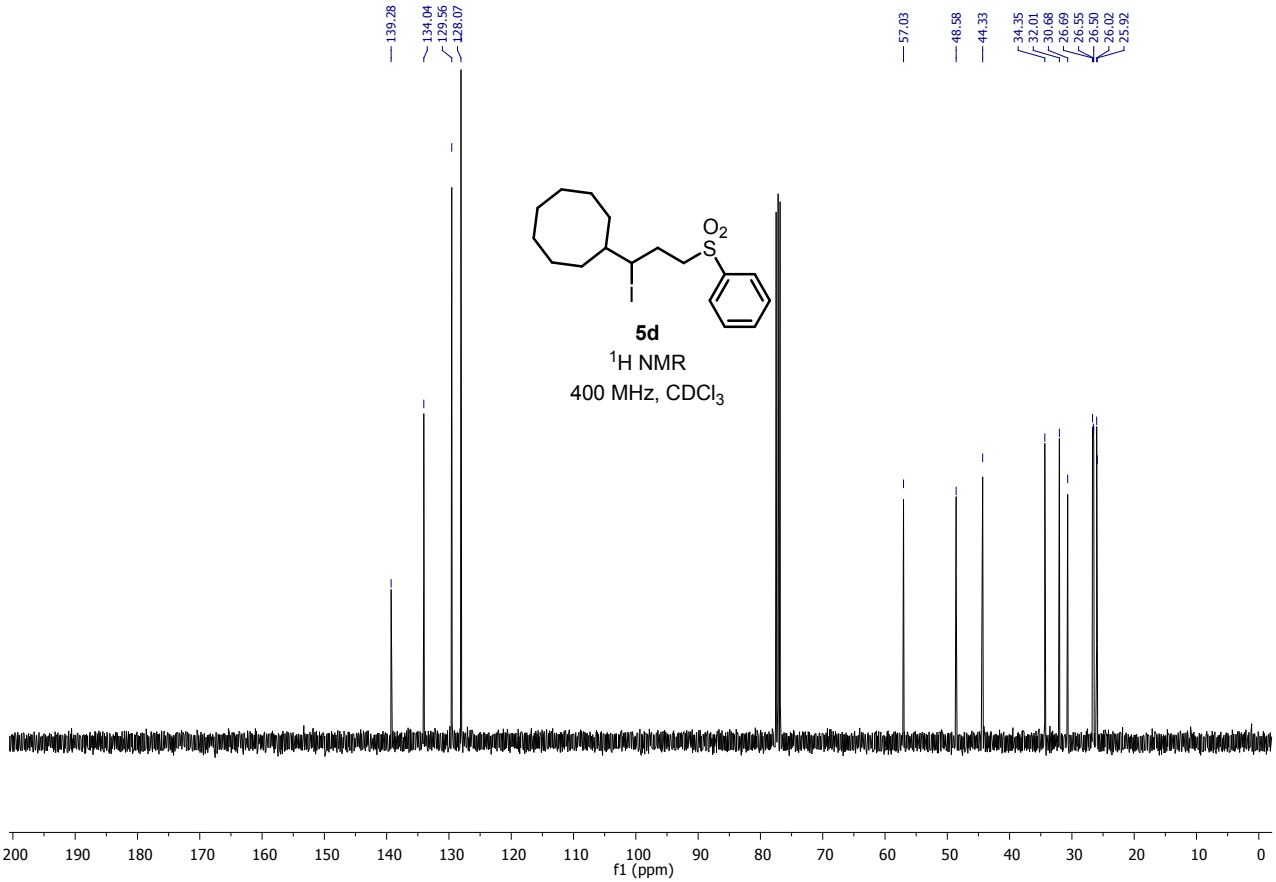
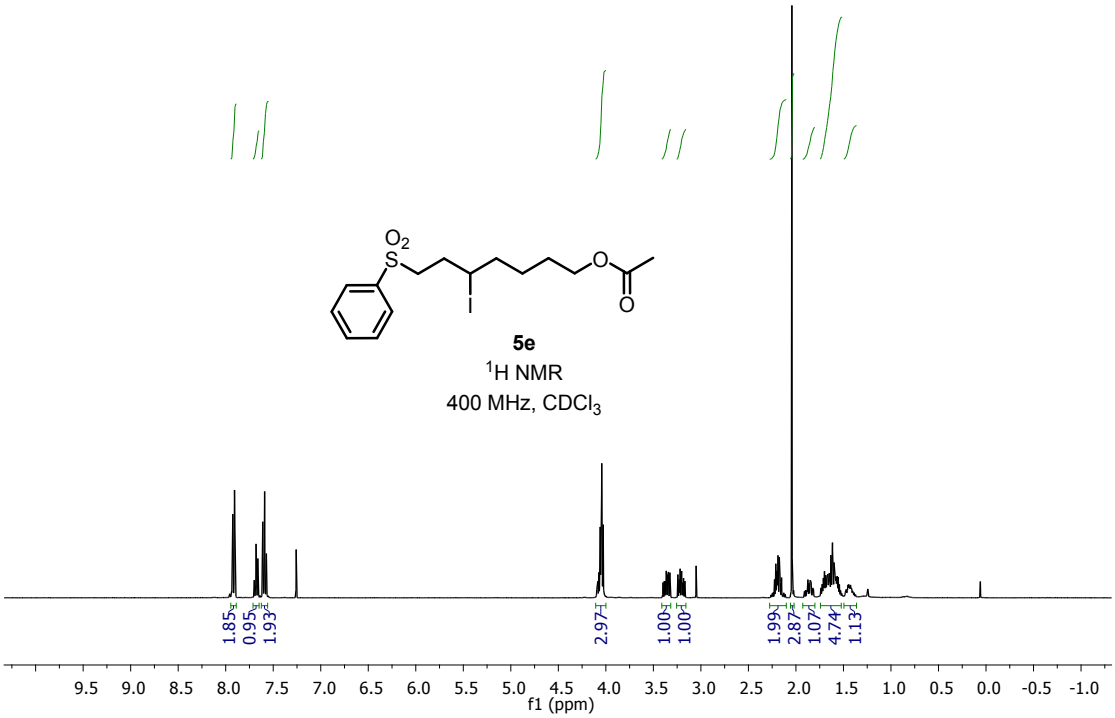
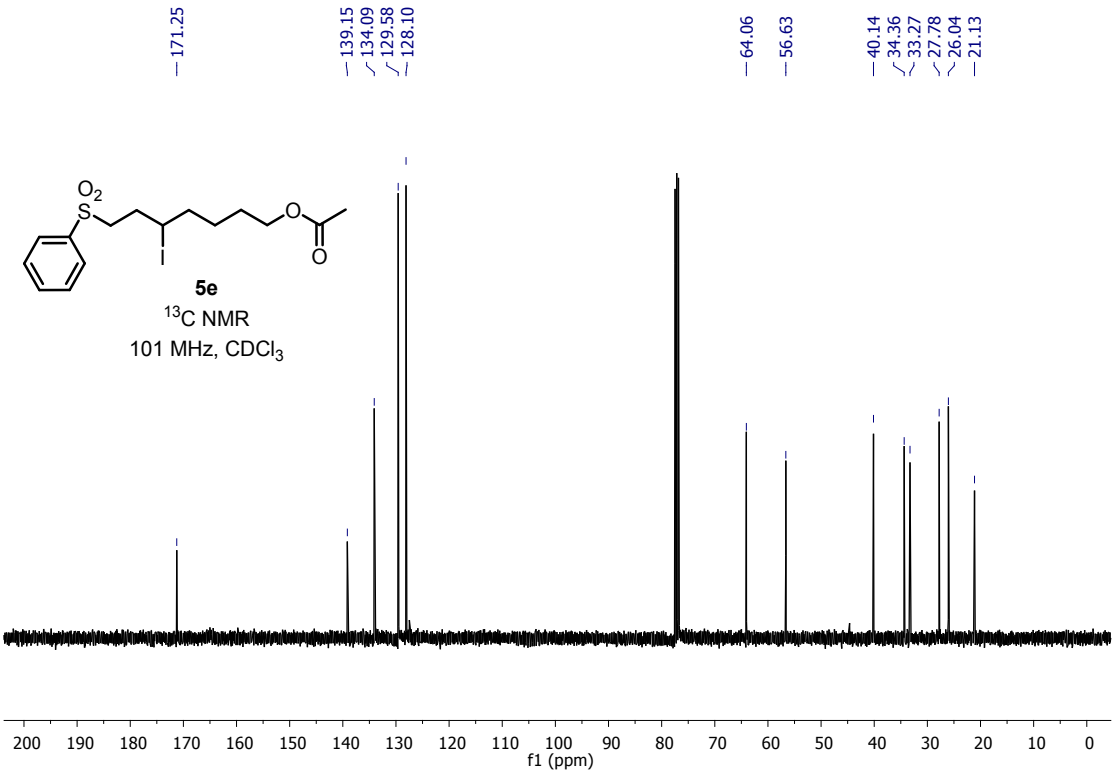
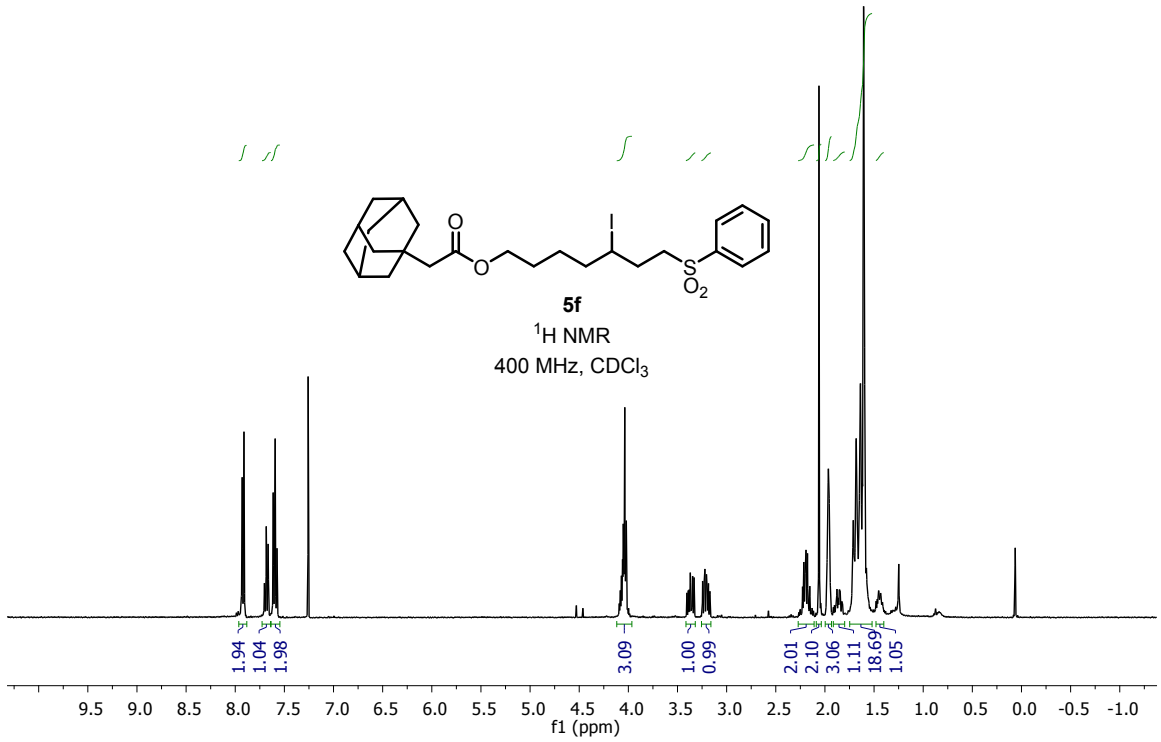
134.04
129.55
128.13
56.67
48.15
37.55
33.54
33.28
32.91
31.97
26.50
26.18
26.00
O2
S
I
5c
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O2
S
I
5d
13C NMR
101 MHz, CDCl3
1.94
1.00
1.99
1.04
1.05
1.07
2.28
15.57
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


139.28
134.04
129.56
128.07
57.03
48.58
44.33
34.35
32.01
30.68
26.69
26.55
26.50
26.02
25.92
O2
S
I
5d
1H NMR
400 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O2
S
O
I
O
5e
1H NMR
400 MHz, CDCl3
1.85
0.95
1.93
2.97
1.00
1.00
1.99
2.87
1.07
4.74
1.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

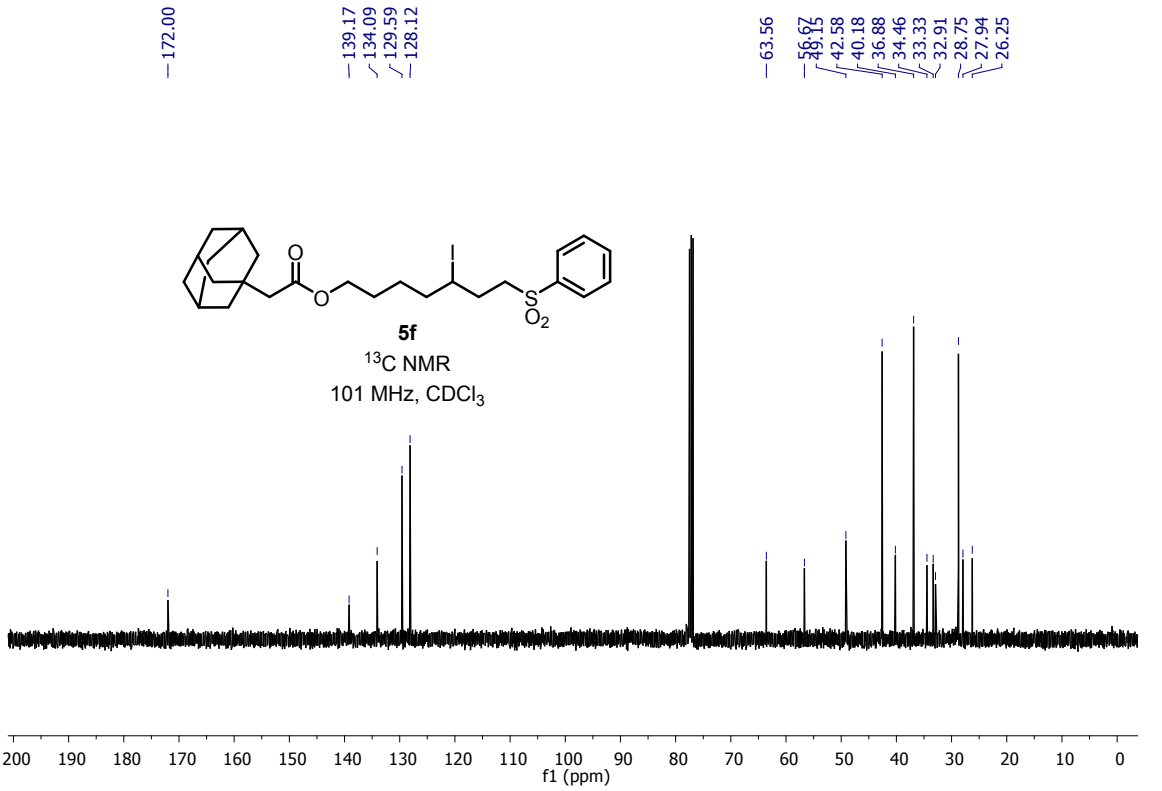

171.25
139.15
134.09
129.58
128.10
64.06
56.63
40.14
34.36
33.27
27.78
26.04
21.13
O2
S
O
I
O
5e
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



5f

^{1}H NMR

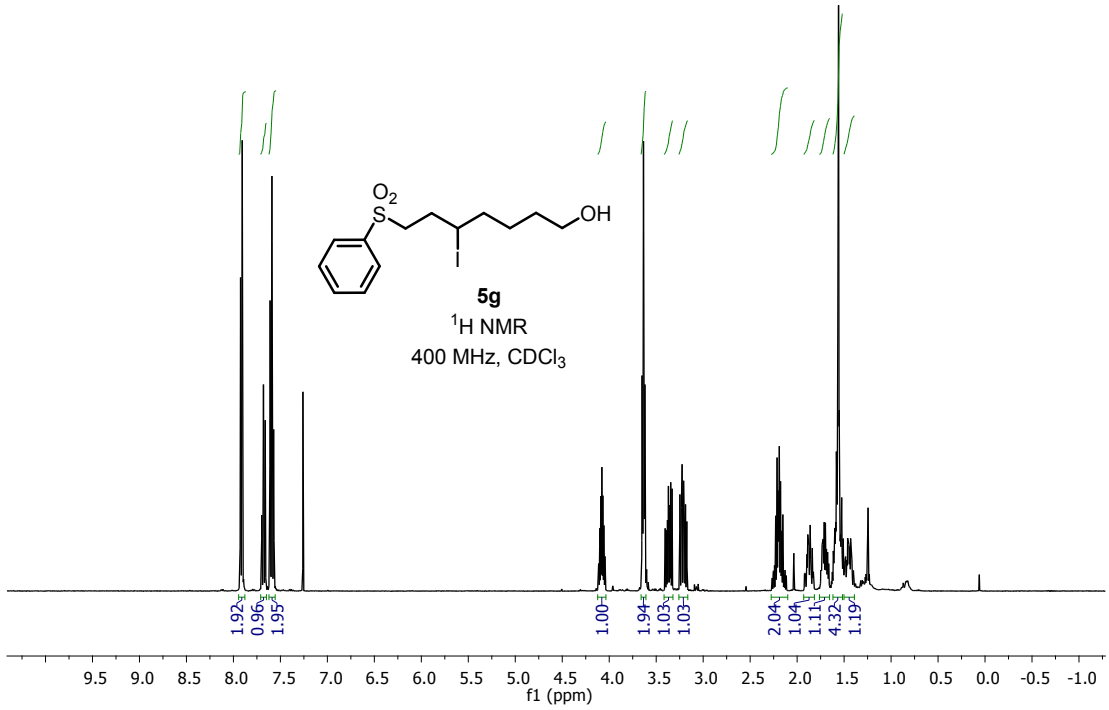
400 MHz, $CDCl_3$

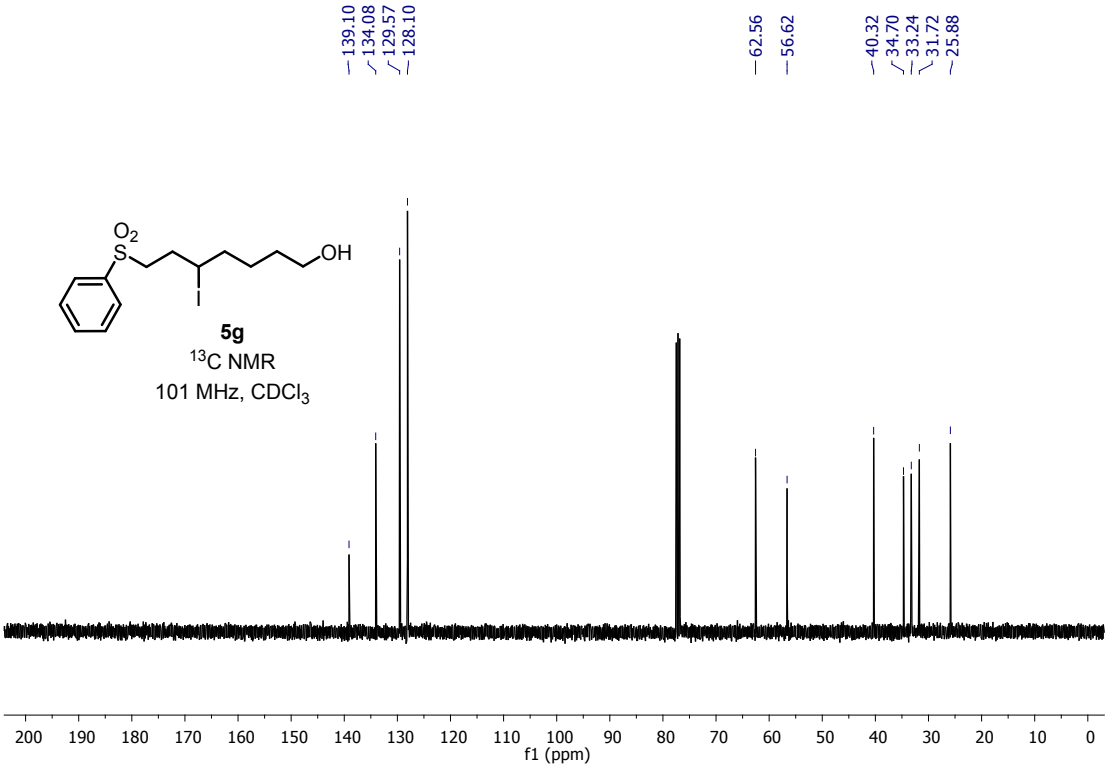


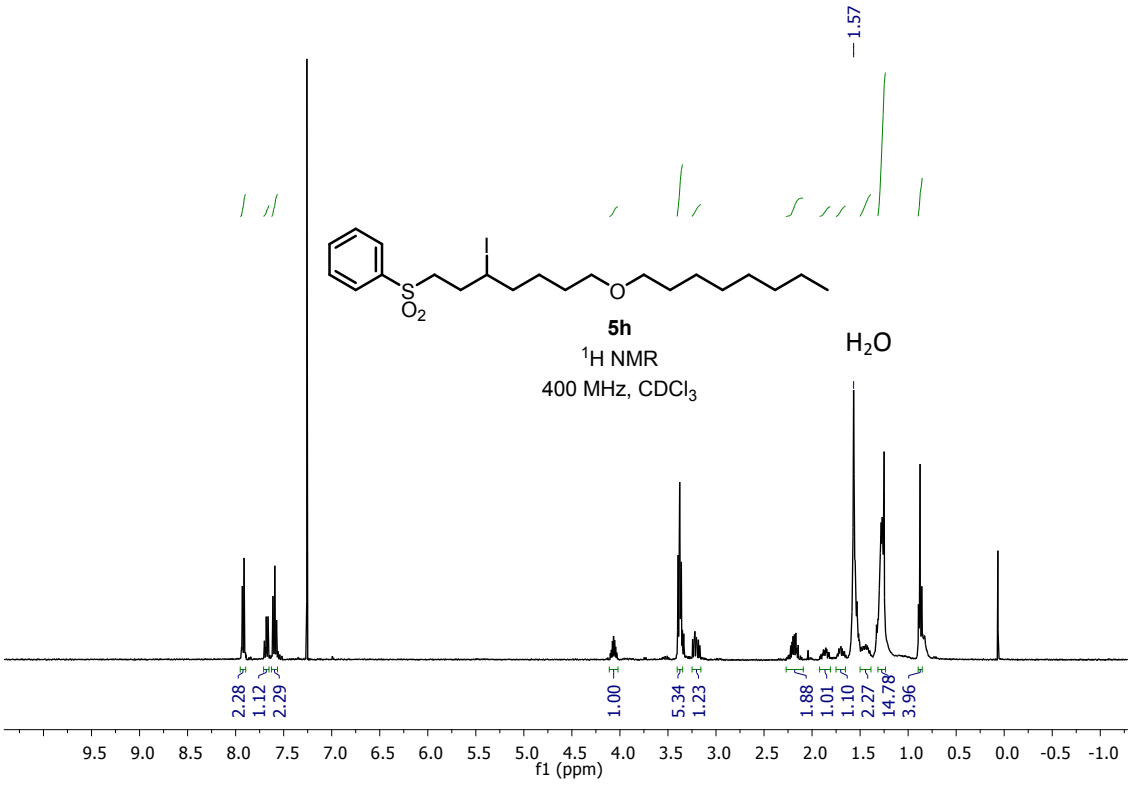
5f

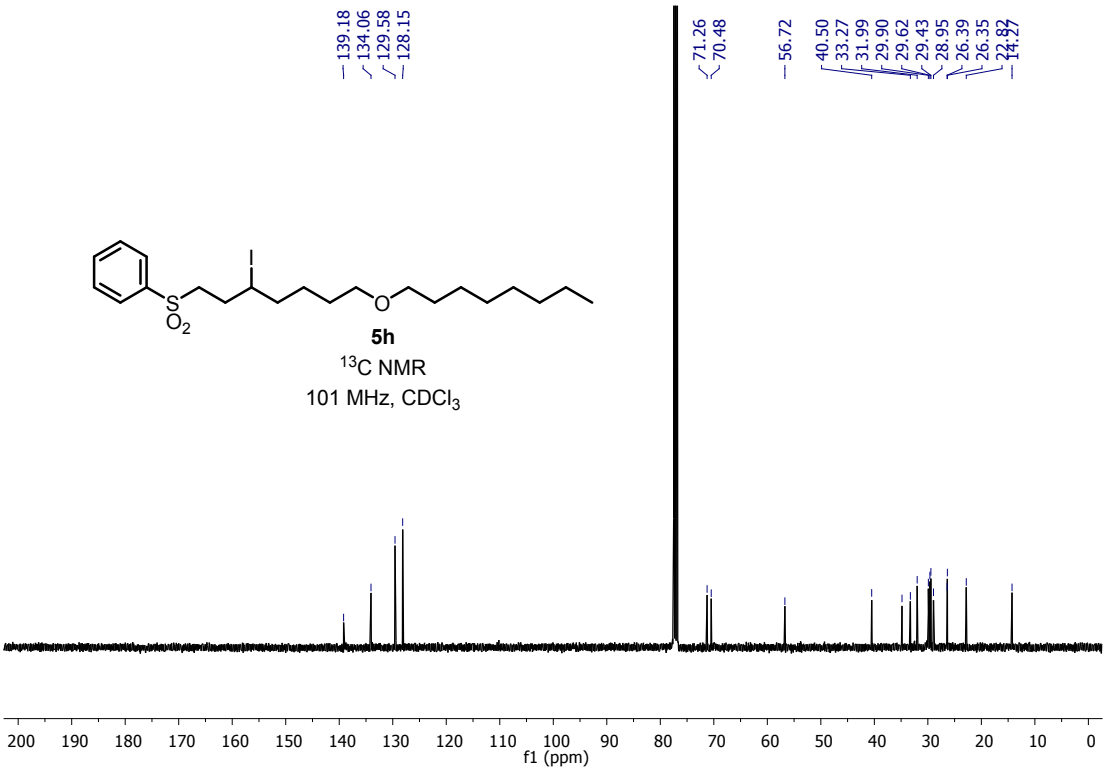
^{13}C NMR

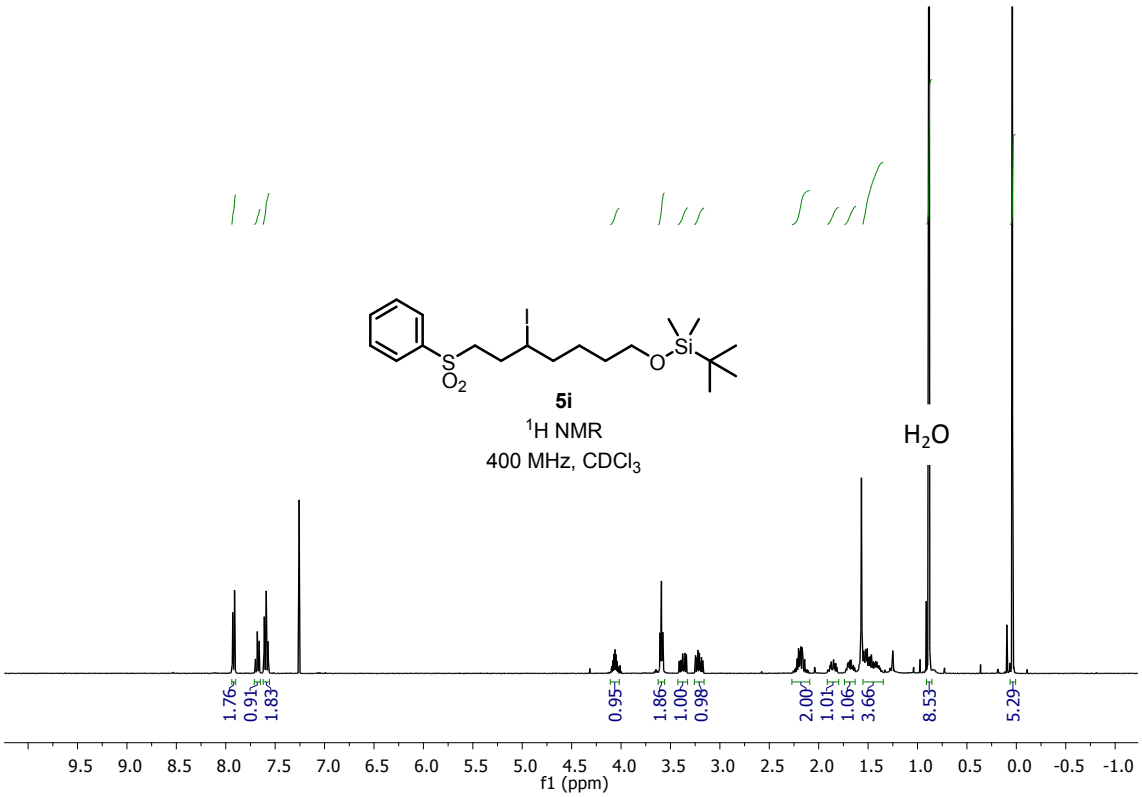
101 MHz, $CDCl_3$

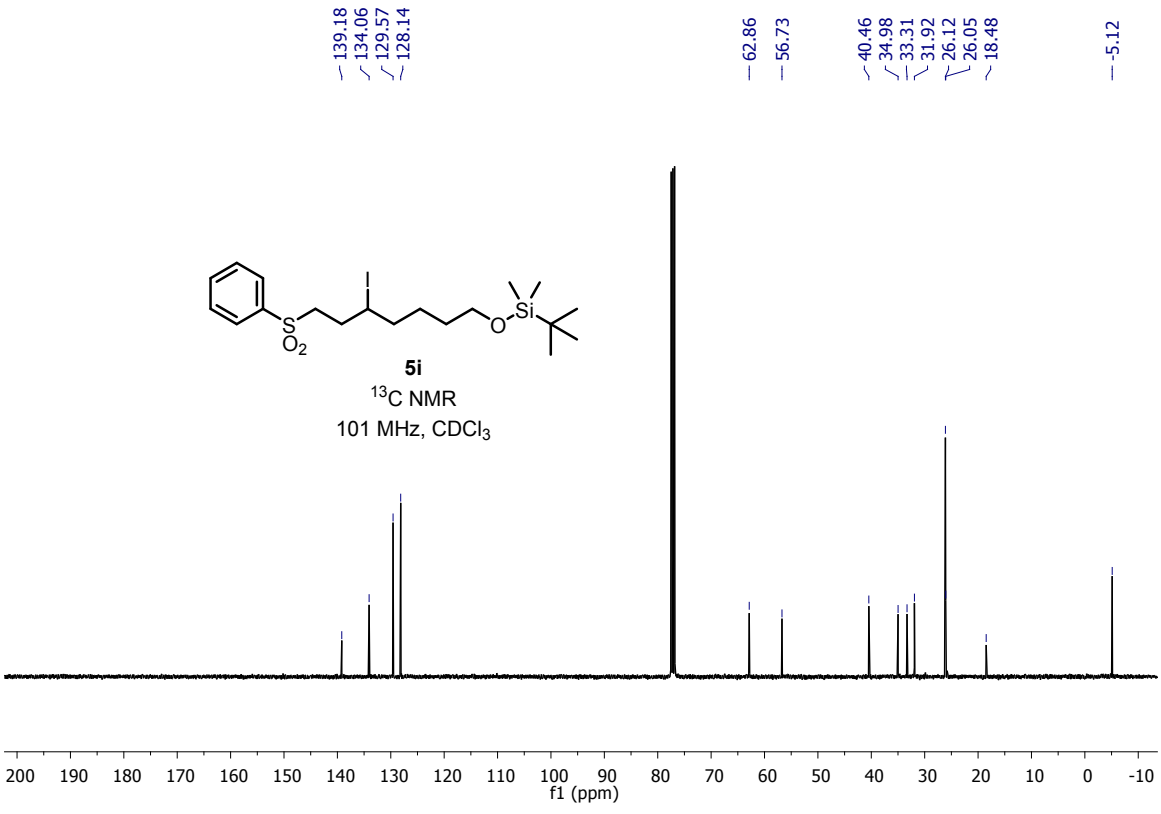

O2
S
OH
I
5g
1H NMR
400 MHz, CDCl3
1.92
0.96
1.95
1.00
1.94
1.03
1.03
2.04
1.04
1.11
4.32
1.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

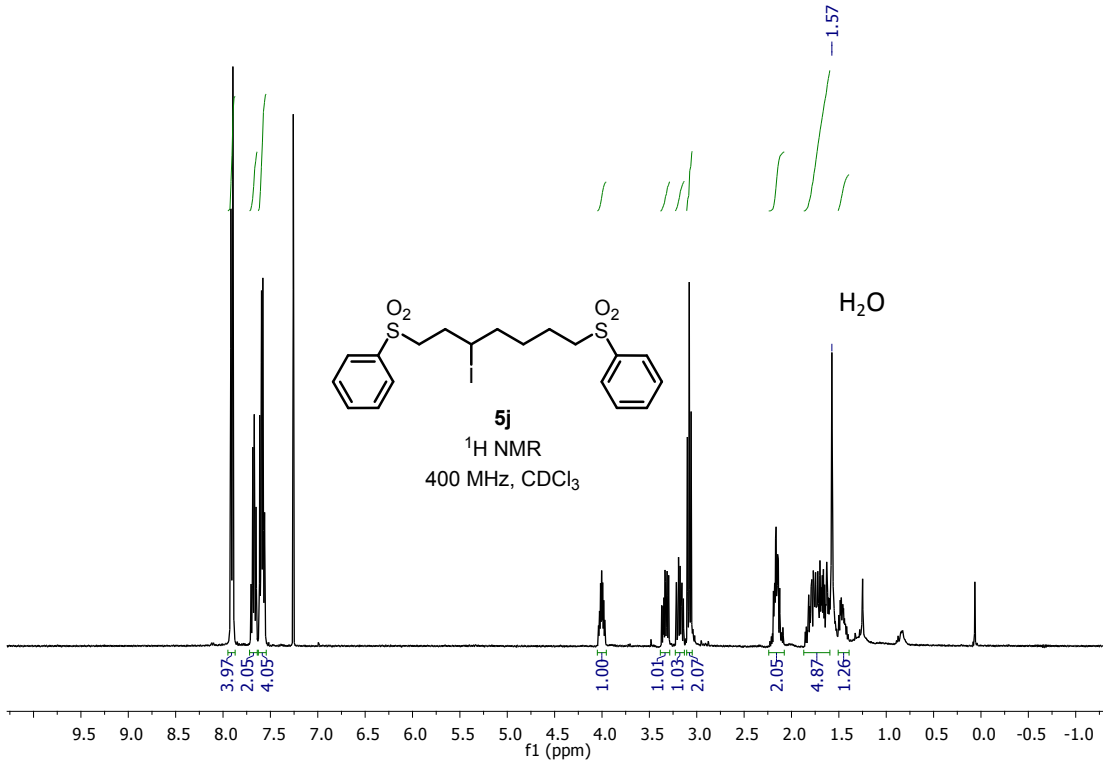

139.10
134.08
129.57
128.10
62.56
56.62
40.32
34.70
33.24
31.72
25.88
O2
S
OH
I
5g
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

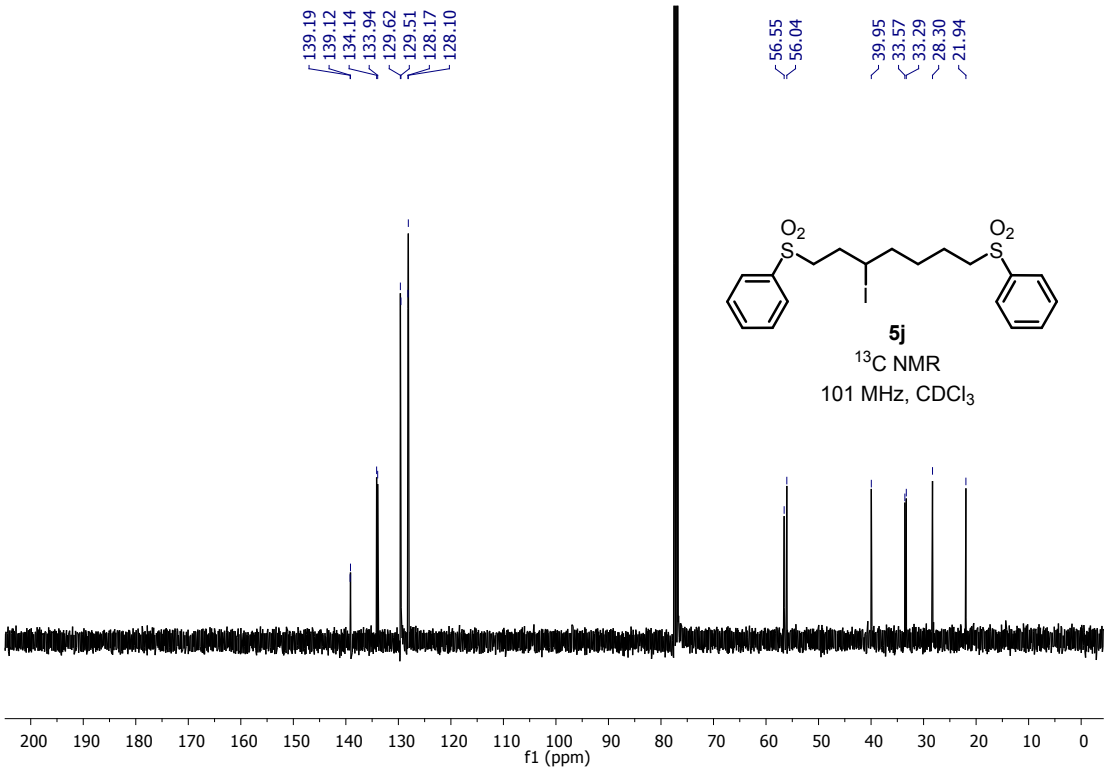

1.57
I
S
O2
O
5h
1H NMR
400 MHz, CDCl3
H2O
2.28
1.12
2.29
1.00
5.34
1.23
1.88
1.01
1.10
2.27
14.78
3.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

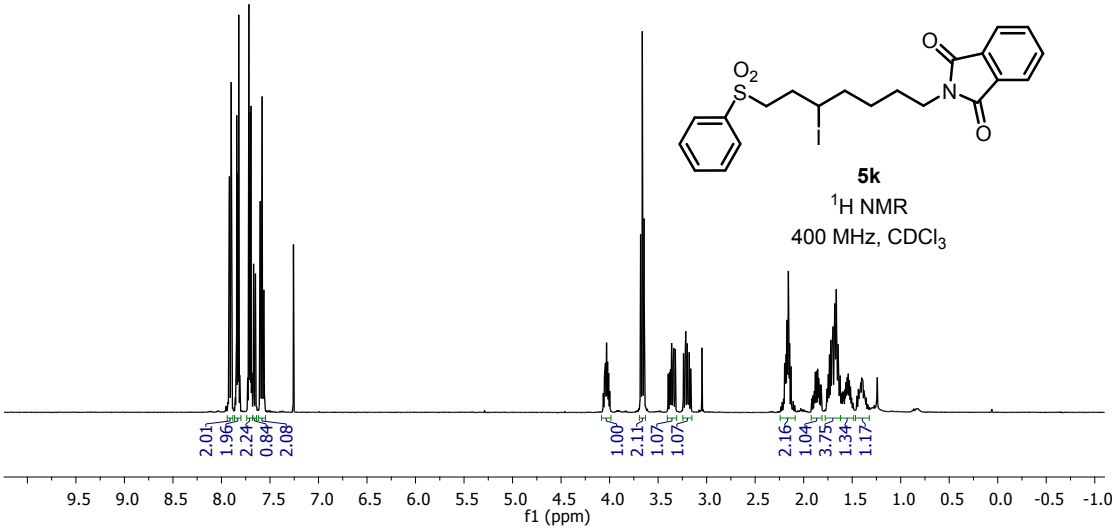

139.18
134.06
129.58
128.15
71.26
70.48
56.72
40.50
33.27
31.99
29.90
29.62
29.43
28.95
26.39
26.35
22.82
14.27
I
S
O2
O
5h
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

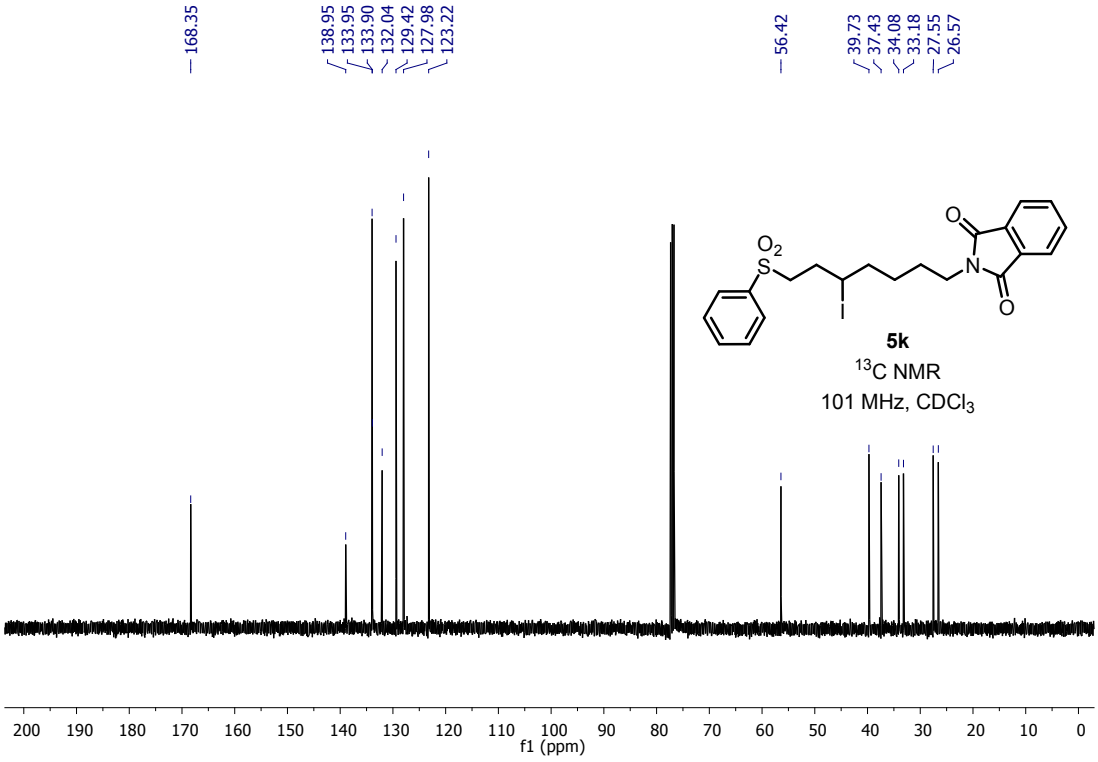

5i
1H NMR
400 MHz, CDCl3
H2O
1.76
0.91
1.83
0.95
1.86
1.00
0.98
2.00
1.01
1.06
3.66
8.53
5.29
f1 (ppm)


139.18
134.06
129.57
128.14
62.86
56.73
40.46
34.98
33.31
31.92
26.12
26.05
18.48
-5.12
5i
13C NMR
101 MHz, CDCl3
f1 (ppm)


1.57
H2O
O2
S
O2
S
I
5j
1H NMR
400 MHz, CDCl3
3.97
2.05
4.05
1.00
1.01
1.03
2.07
2.05
4.87
1.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


139.19
139.12
134.14
133.94
129.62
129.51
128.17
128.10
56.55
56.04
39.95
33.57
33.29
28.30
21.94
O2
S
O2
S
I
5j
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O2
S
O
N
O
I
5k
1H NMR
400 MHz, CDCl3
2.01
1.96
2.24
0.84
2.08
1.00
2.11
1.07
1.07
2.16
1.04
3.75
1.34
1.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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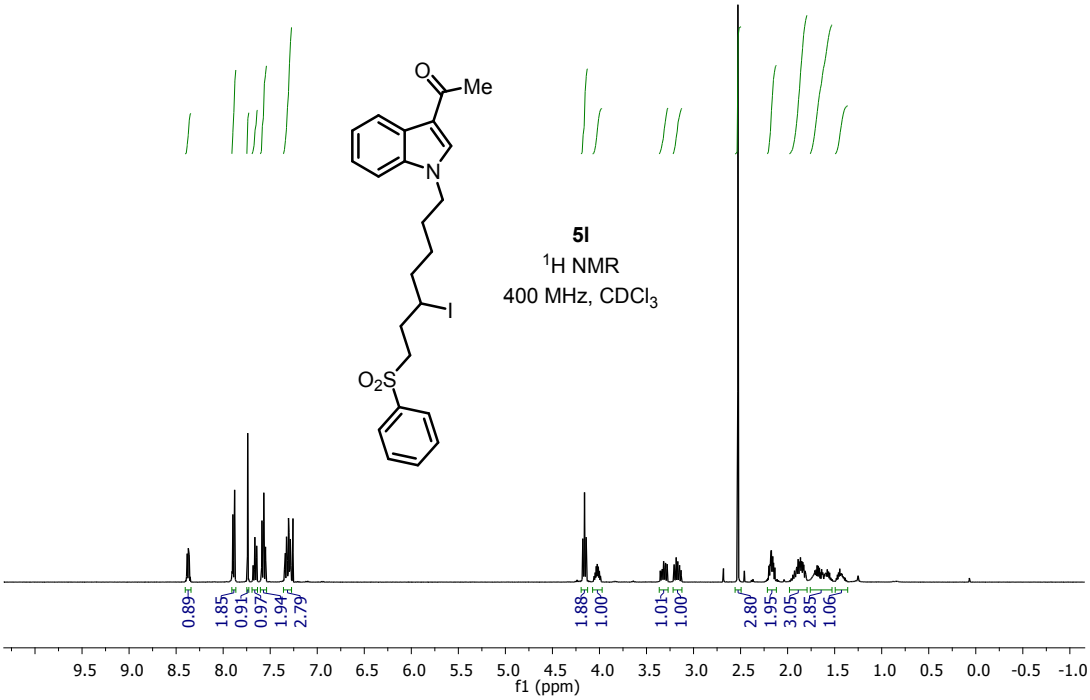
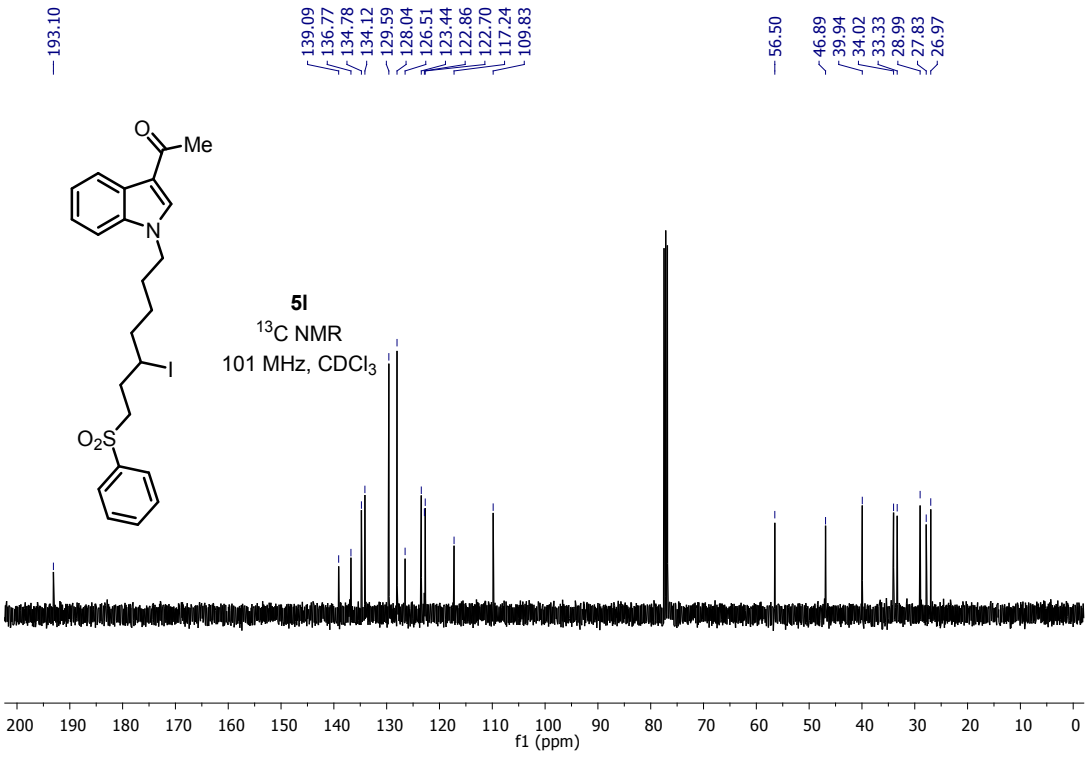
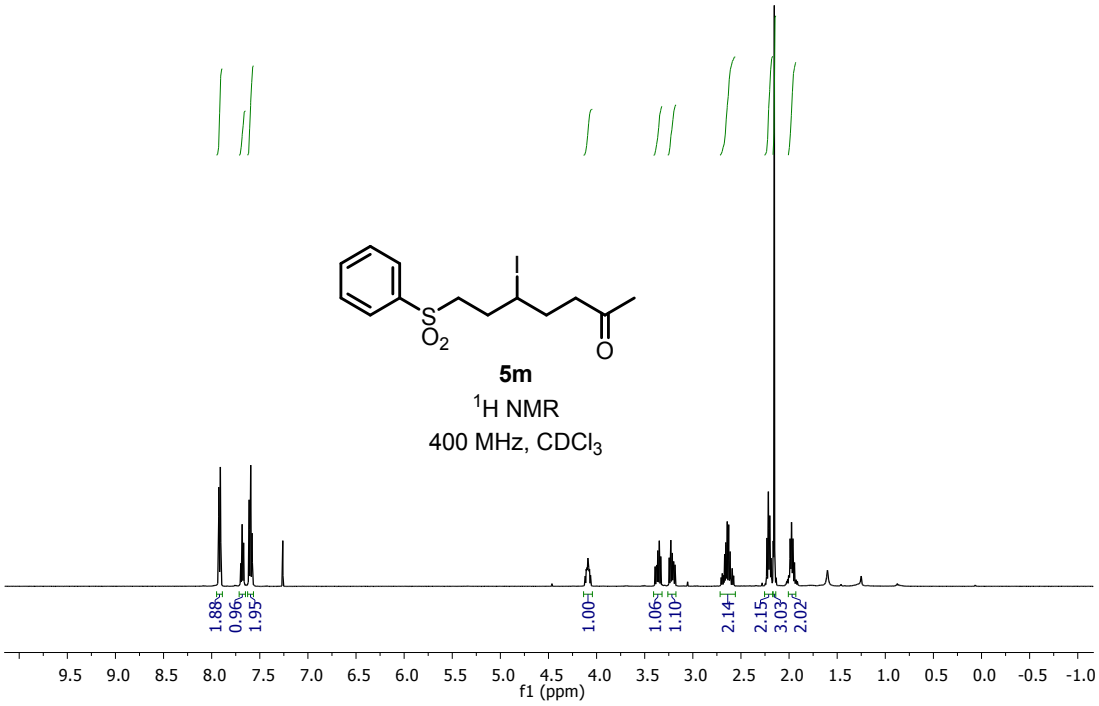
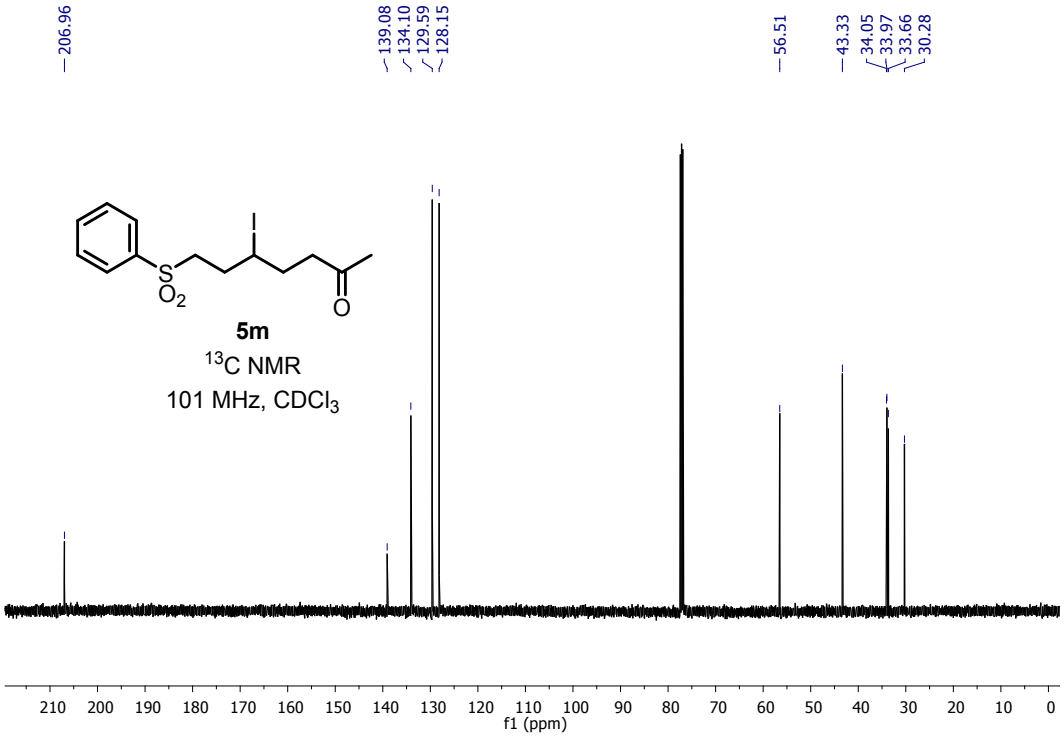
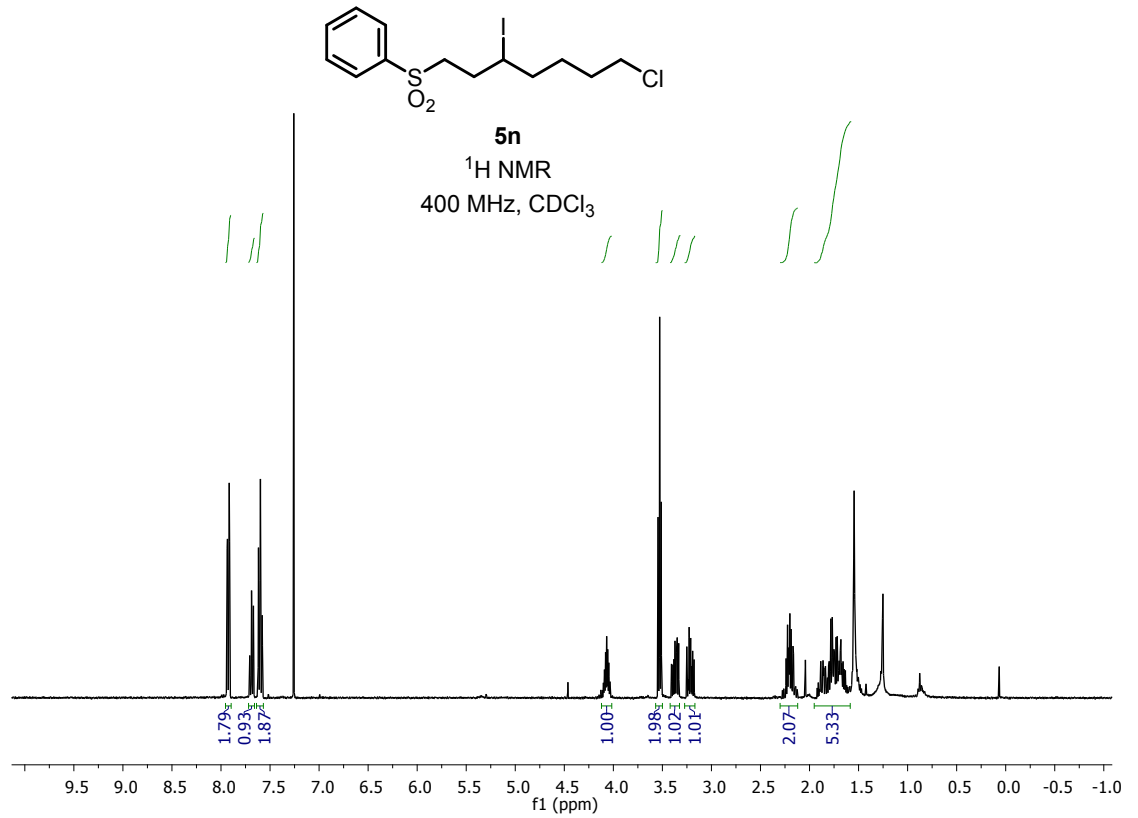
138.95
133.95
133.90
132.04
129.42
127.98
123.22
56.42
39.73
37.43
34.08
33.18
27.55
26.57
O2
S
O
N
O
I
5k
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

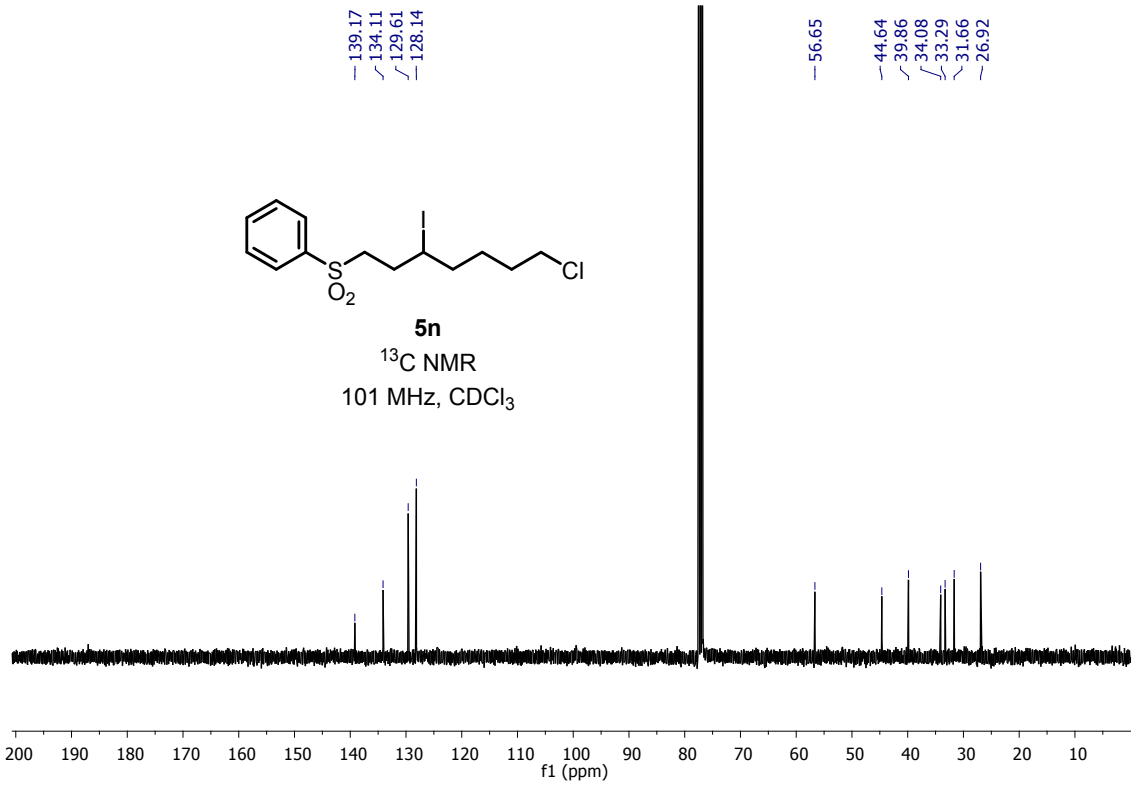

O
Me
N
I
O2S
5l
1H NMR
400 MHz, CDCl3
0.89
1.85
0.91
0.97
1.94
2.79
1.88
1.00
1.01
1.00
2.80
1.95
3.05
2.85
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

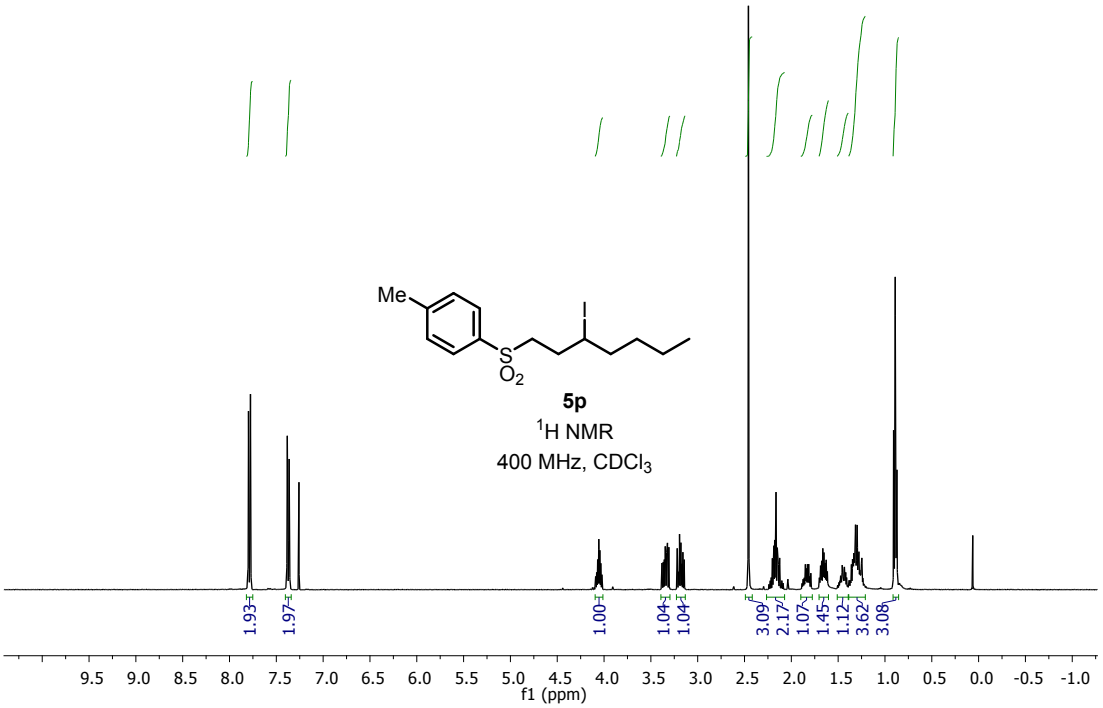

193.10
139.09
136.77
134.78
134.12
129.59
128.04
126.51
123.44
122.86
122.70
117.24
109.83
56.50
46.89
39.94
34.02
33.33
28.99
27.83
26.97
O
Me
N
I
O2S
5l
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

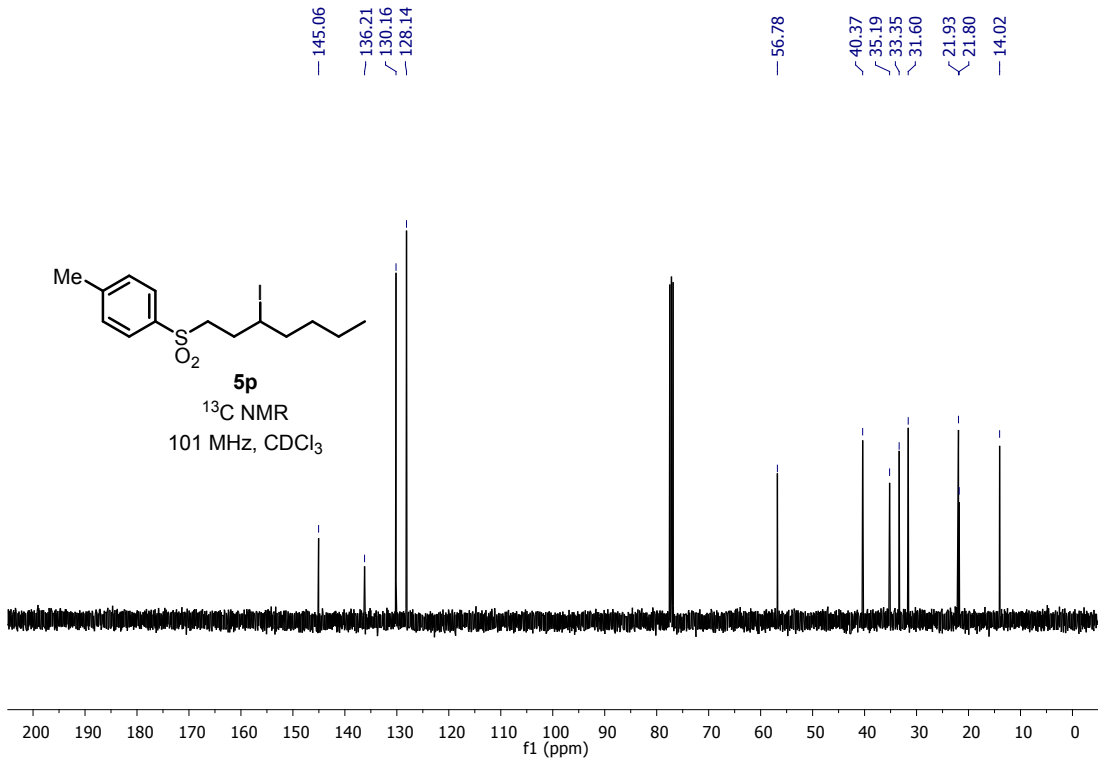

5m
1H NMR
400 MHz, CDCl3
1.88
0.96
1.95
1.00
1.06
1.10
2.14
2.15
3.03
2.02
f1 (ppm)

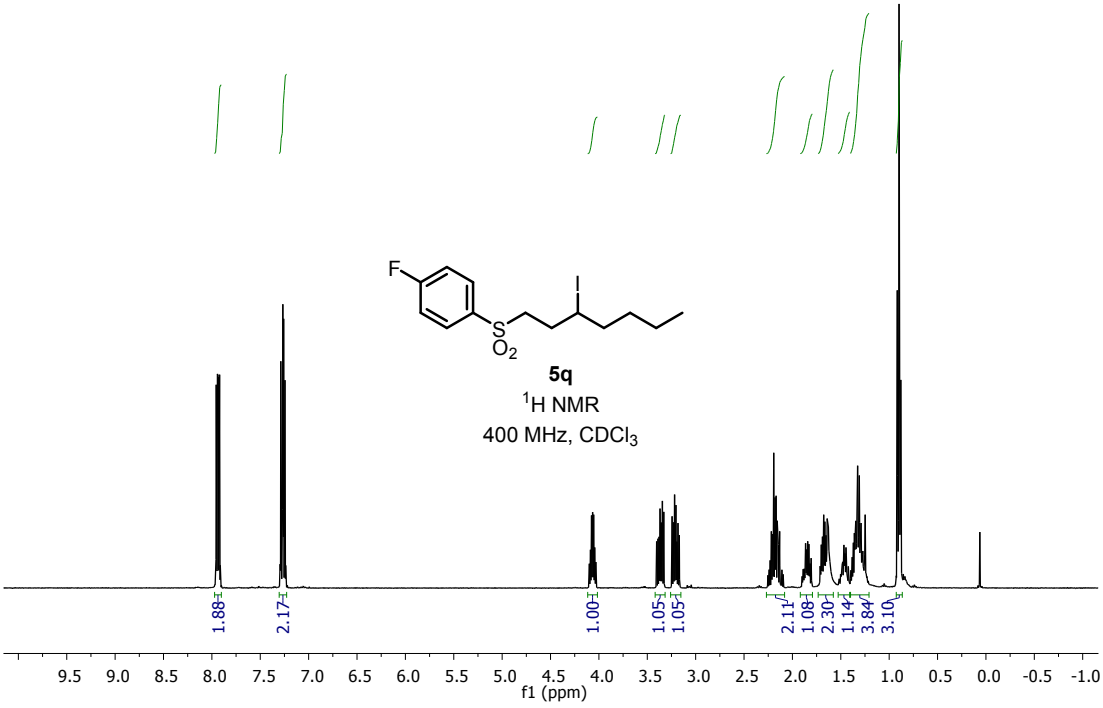

206.96
139.08
134.10
129.59
128.15
56.51
43.33
34.05
33.97
33.66
30.28
5m
13C NMR
101 MHz, CDCl3
f1 (ppm)

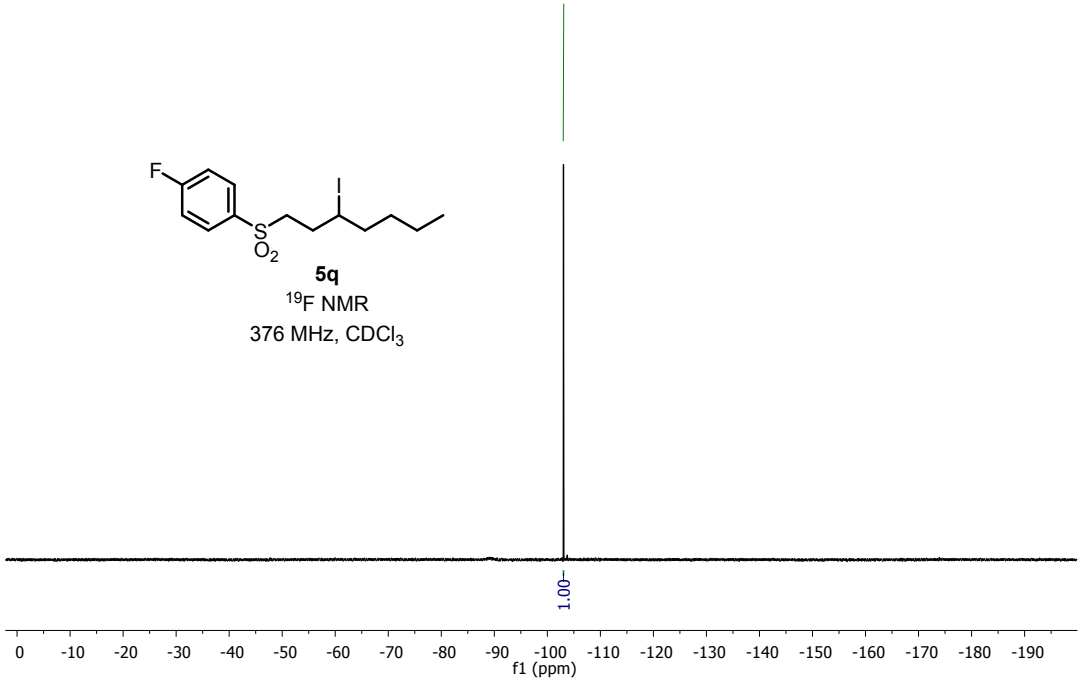

I
S
O2
Cl
5n
1H NMR
400 MHz, CDCl3
1.79
0.93
1.87
1.00
1.98
1.02
1.01
2.07
5.33
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

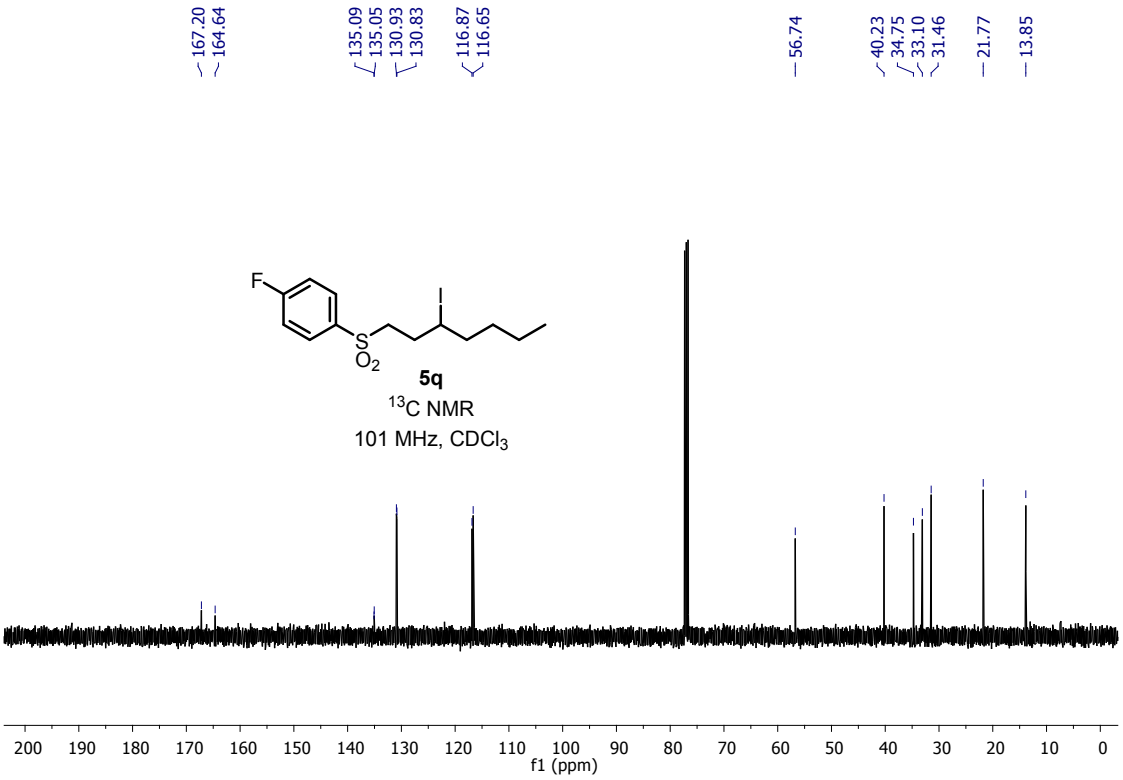

139.17
134.11
129.61
128.14
56.65
44.64
39.86
34.08
33.29
31.66
26.92
I
S
O2
Cl
5n
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

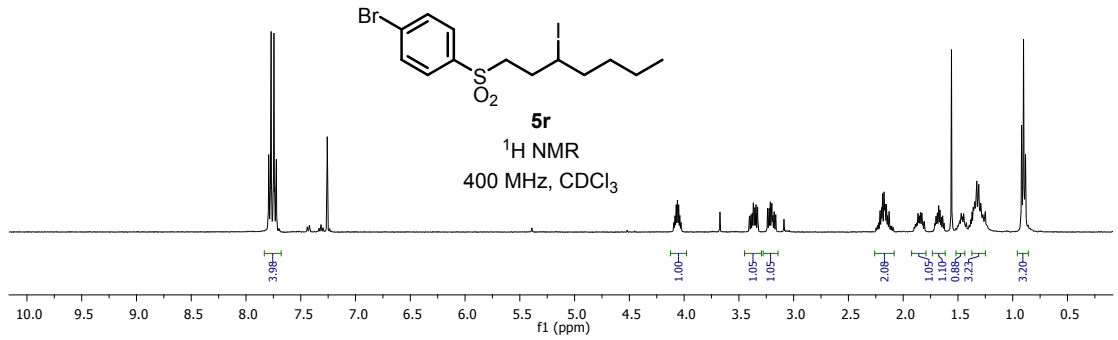

Me
S
O2
I
5p
1H NMR
400 MHz, CDCl3
1.93
1.97
1.00
1.04
1.04
3.09
2.17
1.07
1.45
1.12
3.62
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

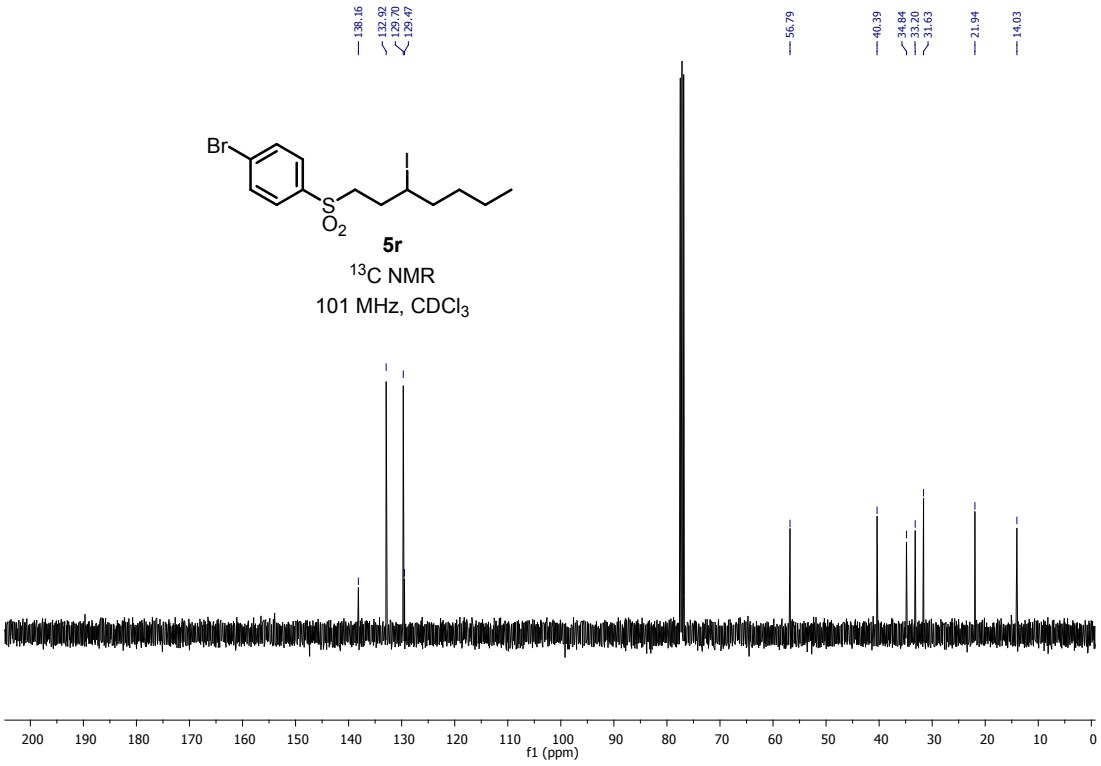

145.06
136.21
130.16
128.14
56.78
40.37
35.19
33.35
31.60
21.93
21.80
14.02
Me
S
O2
I
5p
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

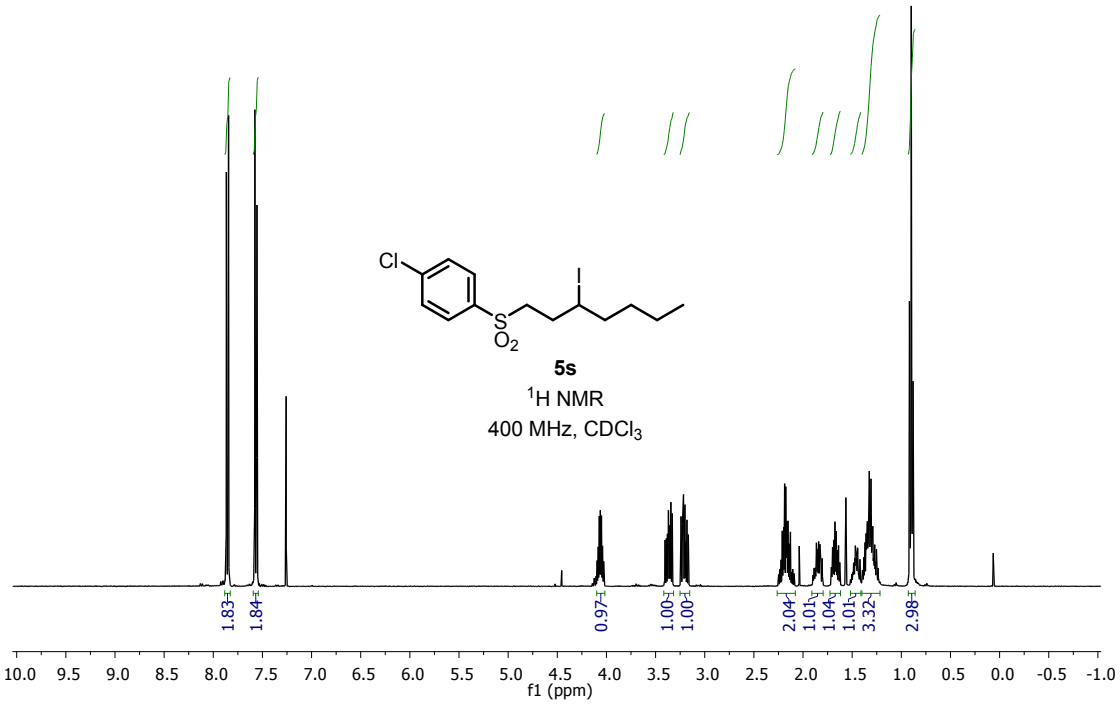

F
I
S
O2
5q
1H NMR
400 MHz, CDCl3
1.88
2.17
1.00
1.05
1.05
2.11
1.08
2.30
1.14
3.84
3.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

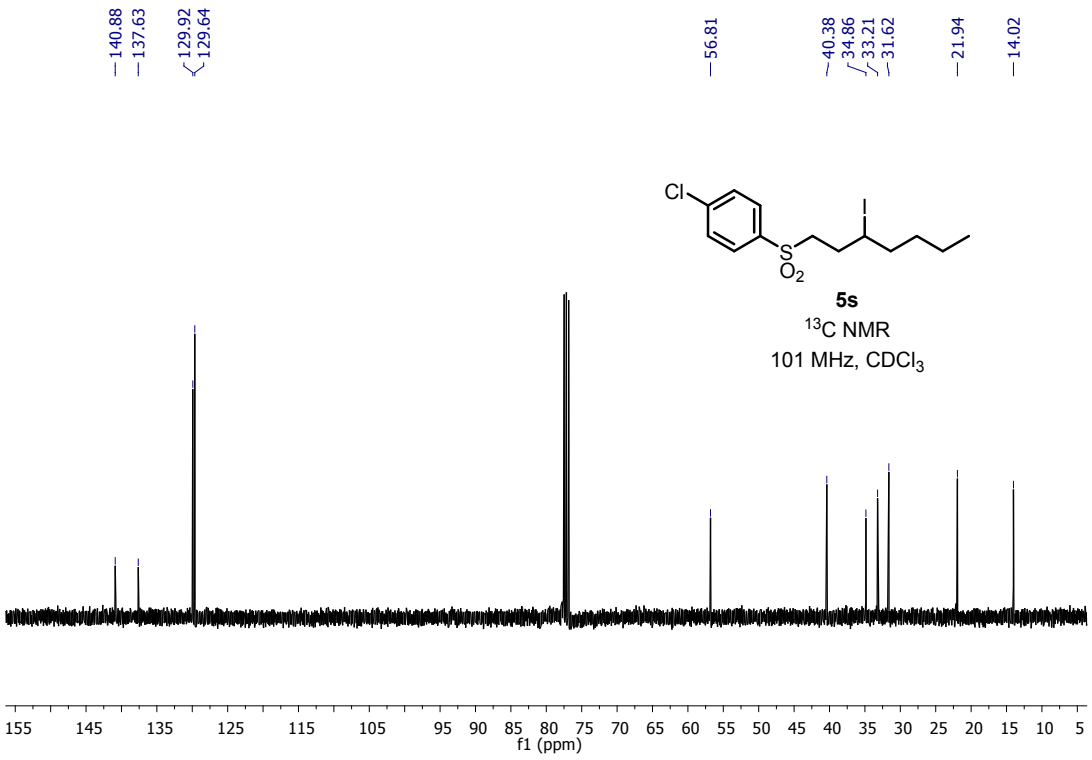

F
I
S
O2
5q
19F NMR
376 MHz, CDCl3
1.00
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

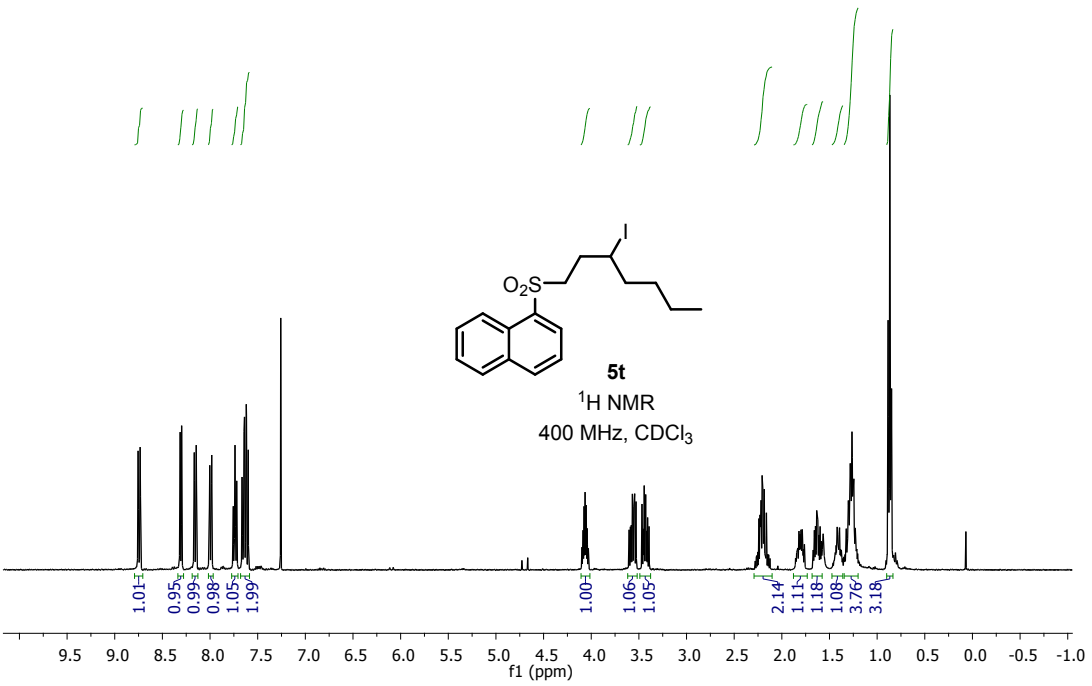

167.20
164.64
135.09
135.05
130.93
130.83
116.87
116.65
56.74
40.23
34.75
33.10
31.46
21.77
13.85
F
I
S
O2
5q
13C NMR
101 MHz, CDCl3
f1 (ppm)

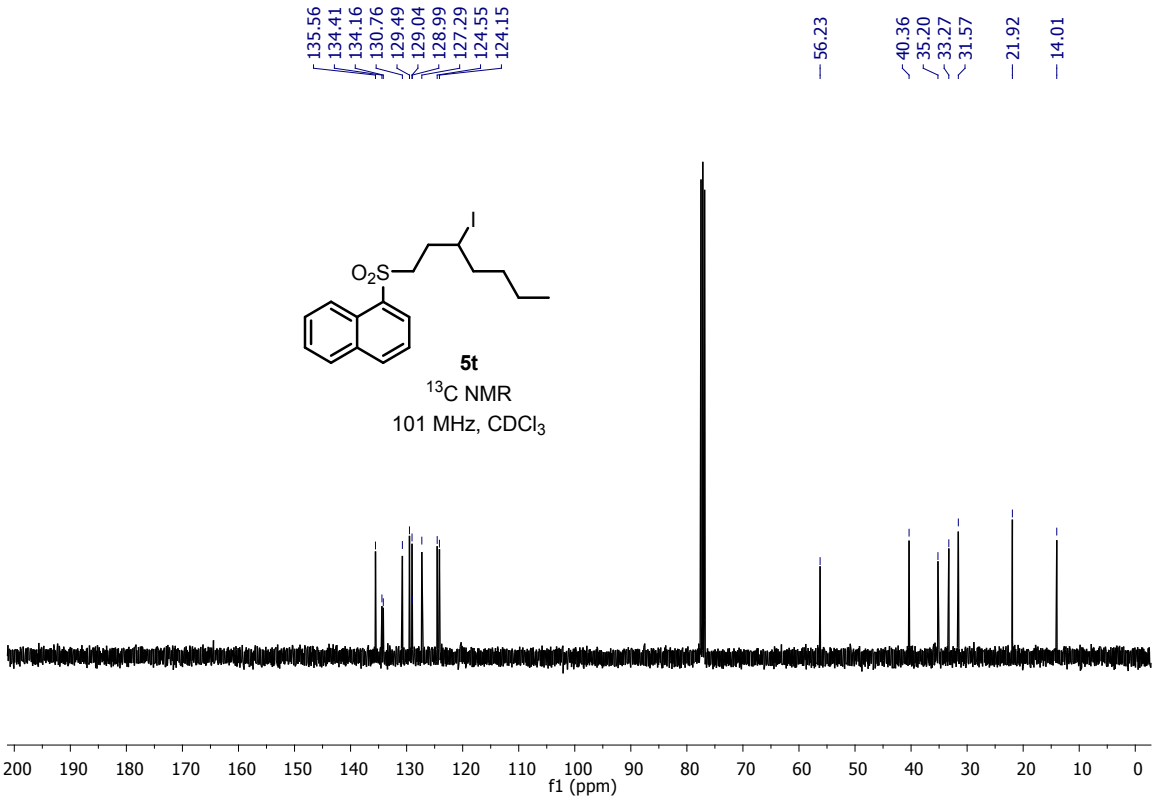

Br
I
S
O2
5r
1H NMR
400 MHz, CDCl3
3.98
1.00
1.05
1.05
2.08
1.05
1.10
0.88
3.23
3.20
f1 (ppm)


138.16
132.92
129.70
129.47
56.79
40.39
34.84
33.20
31.63
21.94
14.03
Br
I
S
O2
5r
13C NMR
101 MHz, CDCl3
f1 (ppm)


Cl
I
S
O2
5s
1H NMR
400 MHz, CDCl3
1.83
1.84
0.97
1.00
1.00
2.04
1.01
1.04
1.01
3.32
2.98
f1 (ppm)


140.88
137.63
129.92
129.64
56.81
40.38
34.86
33.21
31.62
21.94
14.02
Cl
I
S
O2
5s
13C NMR
101 MHz, CDCl3
155 145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


O2S
I
5t
1H NMR
400 MHz, CDCl3
1.01 0.95 0.99 0.98 1.05 1.99 1.00 1.06 1.05 2.14 1.11 1.18 1.08 3.76 3.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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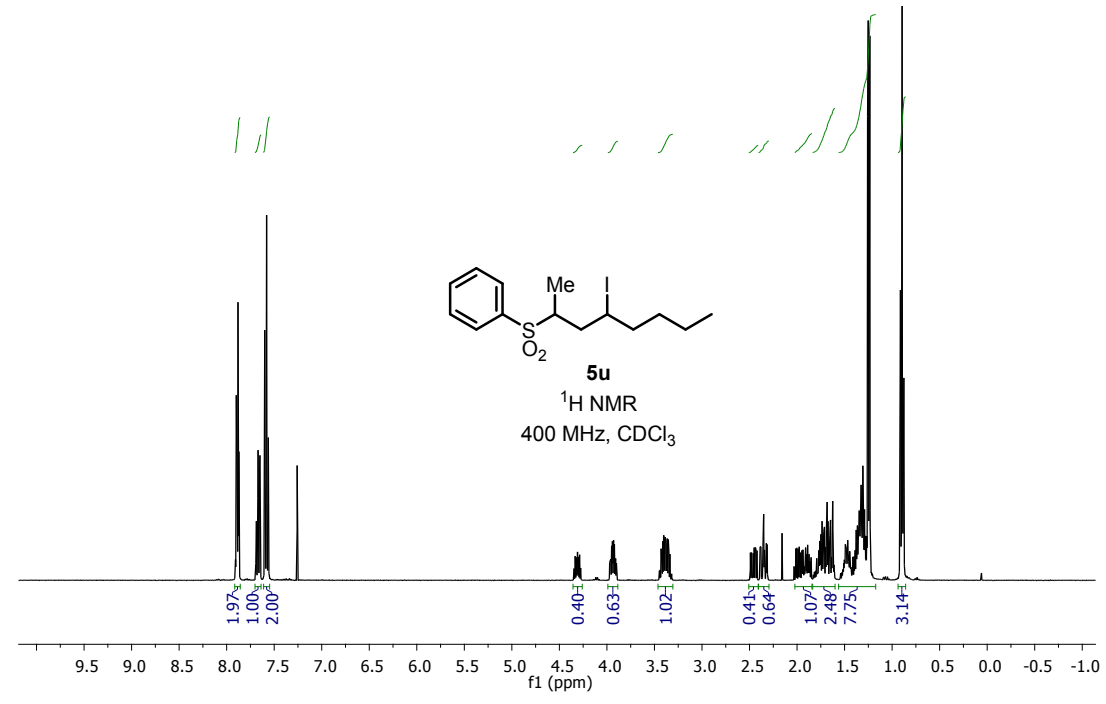
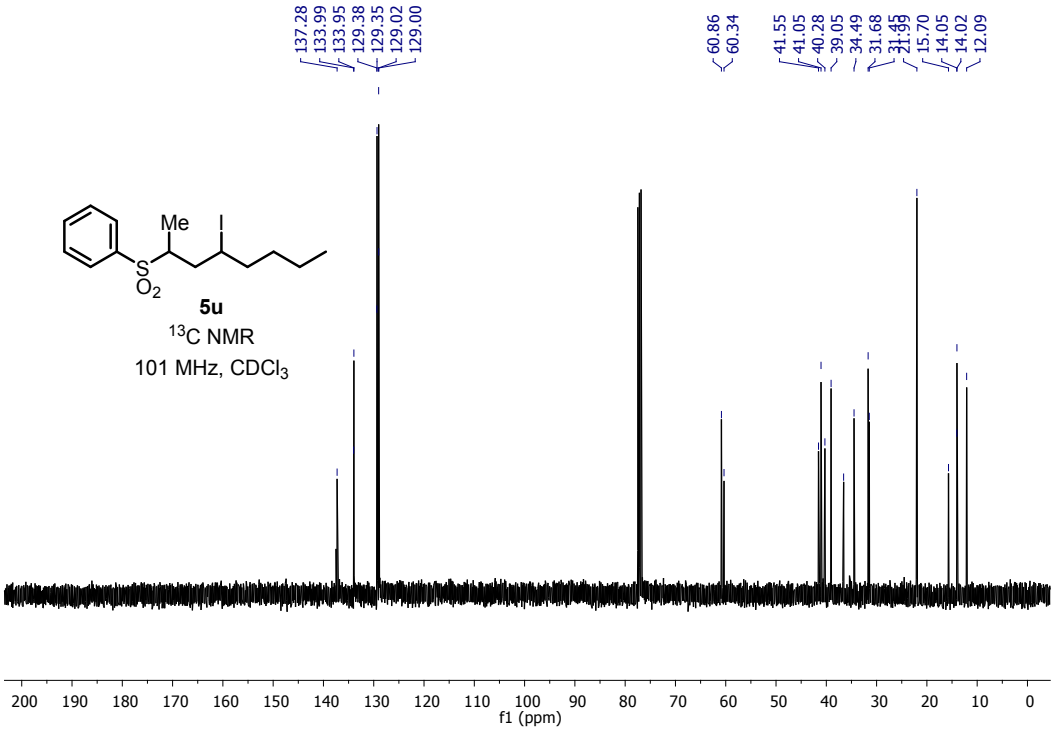
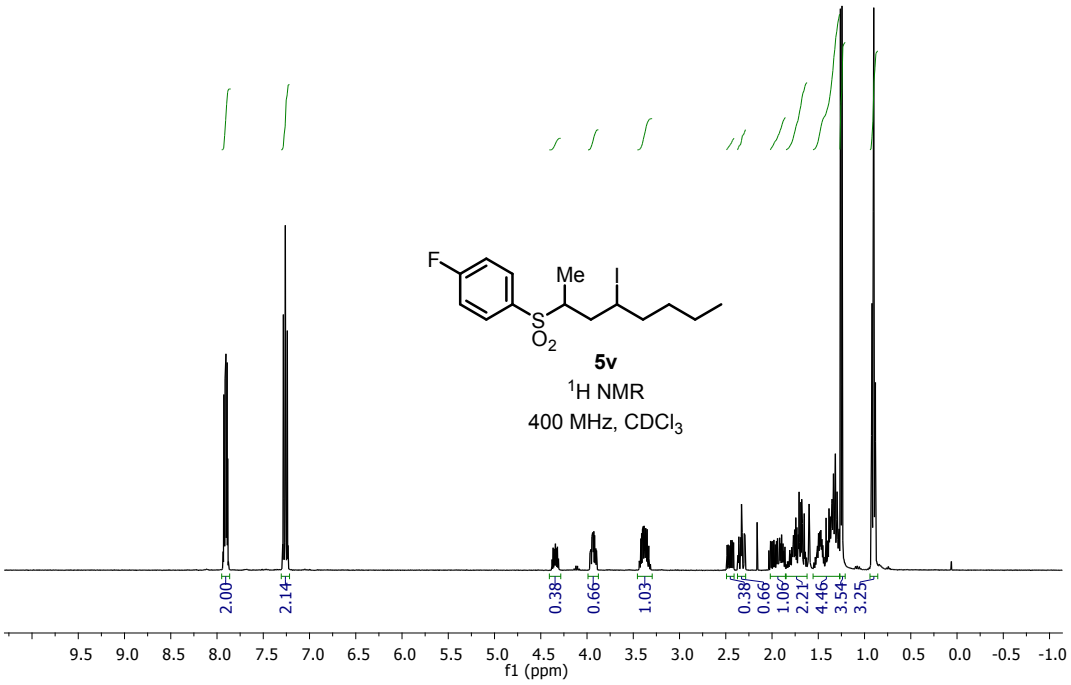
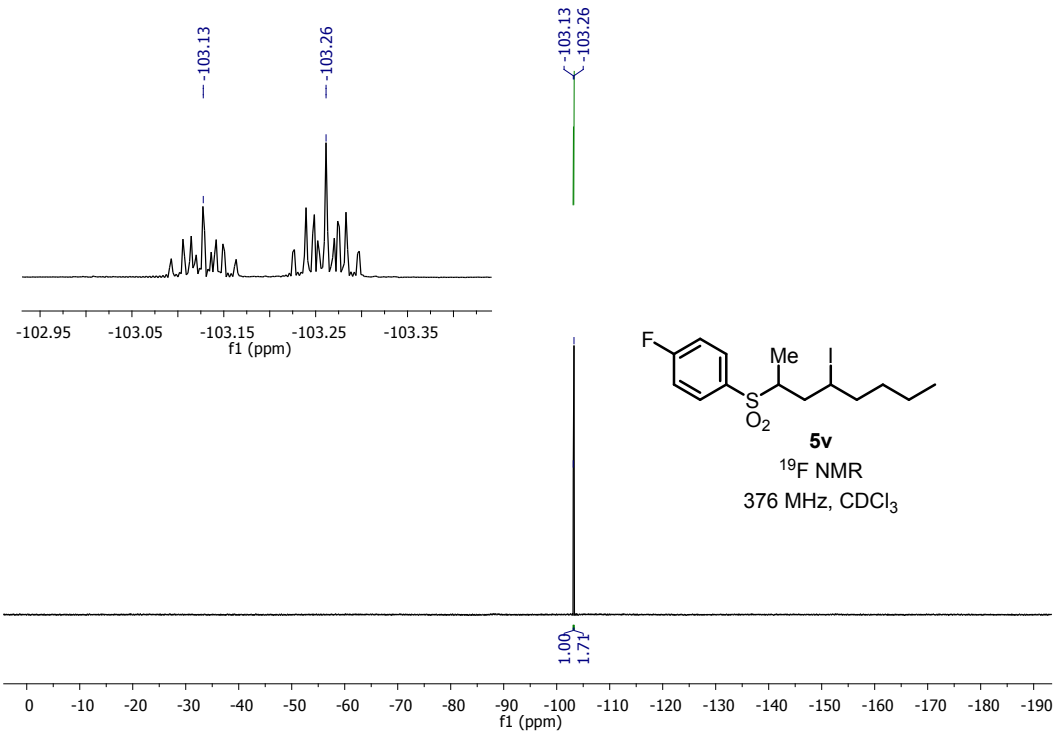
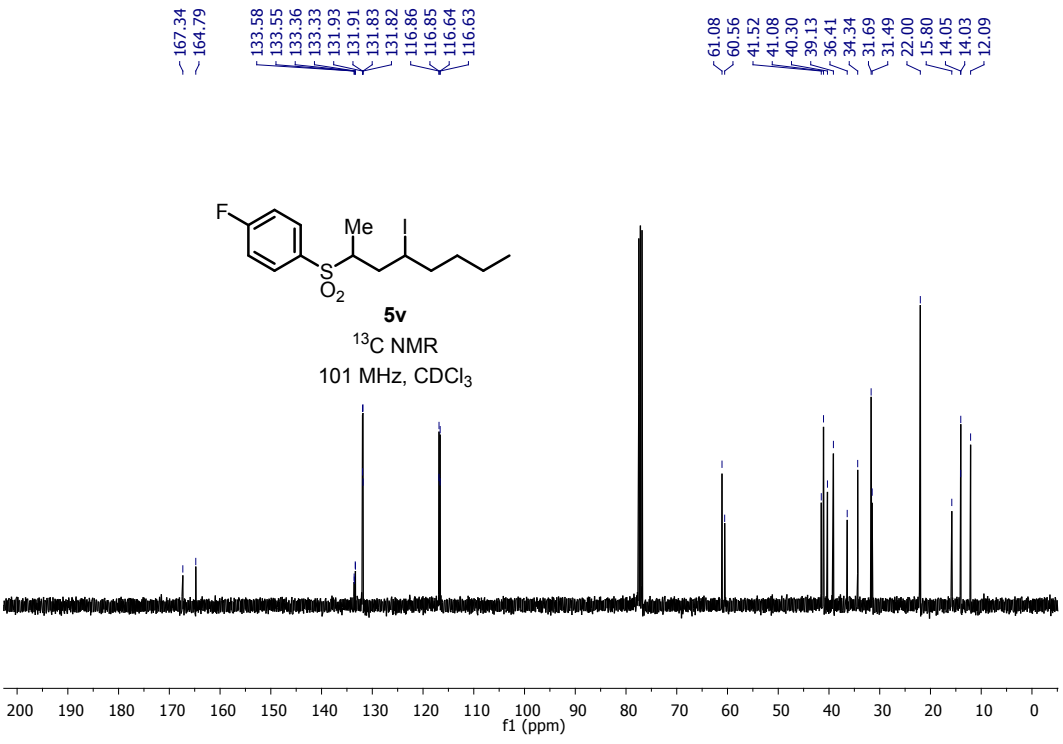
134.41
134.16
130.76
129.49
129.04
128.99
127.29
124.55
124.15
56.23
40.36
35.20
33.27
31.57
21.92
14.01
I
O2S
5t
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

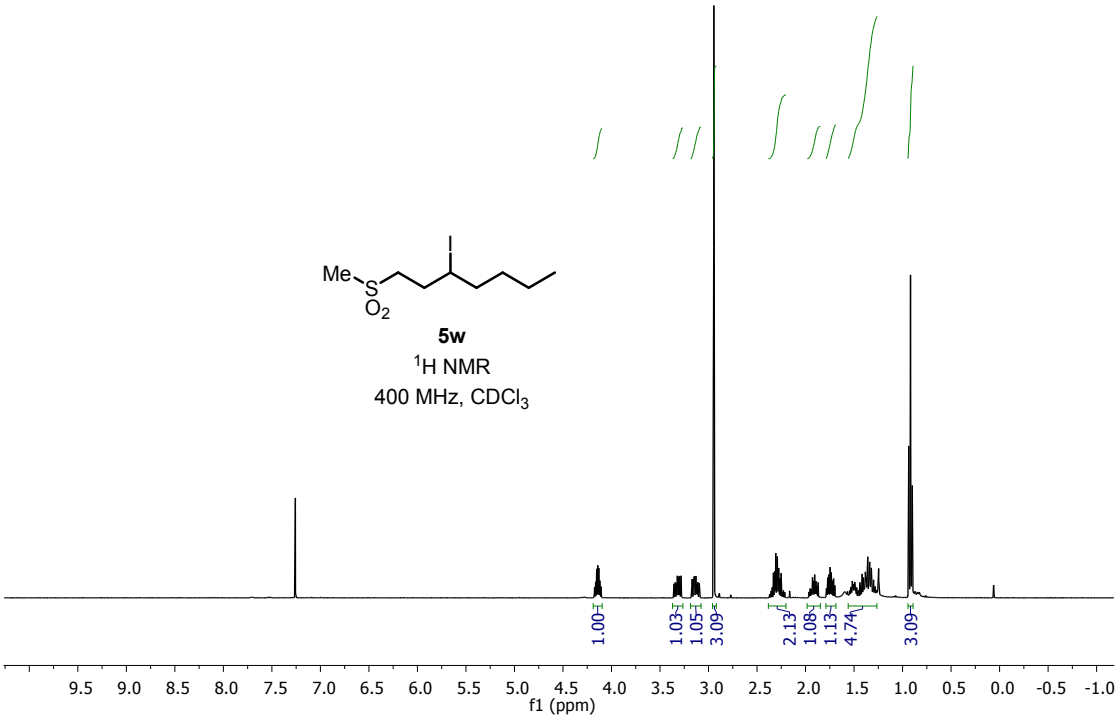

Me
I
S
O2
5u
1H NMR
400 MHz, CDCl3
1.97
1.00
2.00
0.40
0.63
1.02
0.41
0.64
1.07
2.48
7.75
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

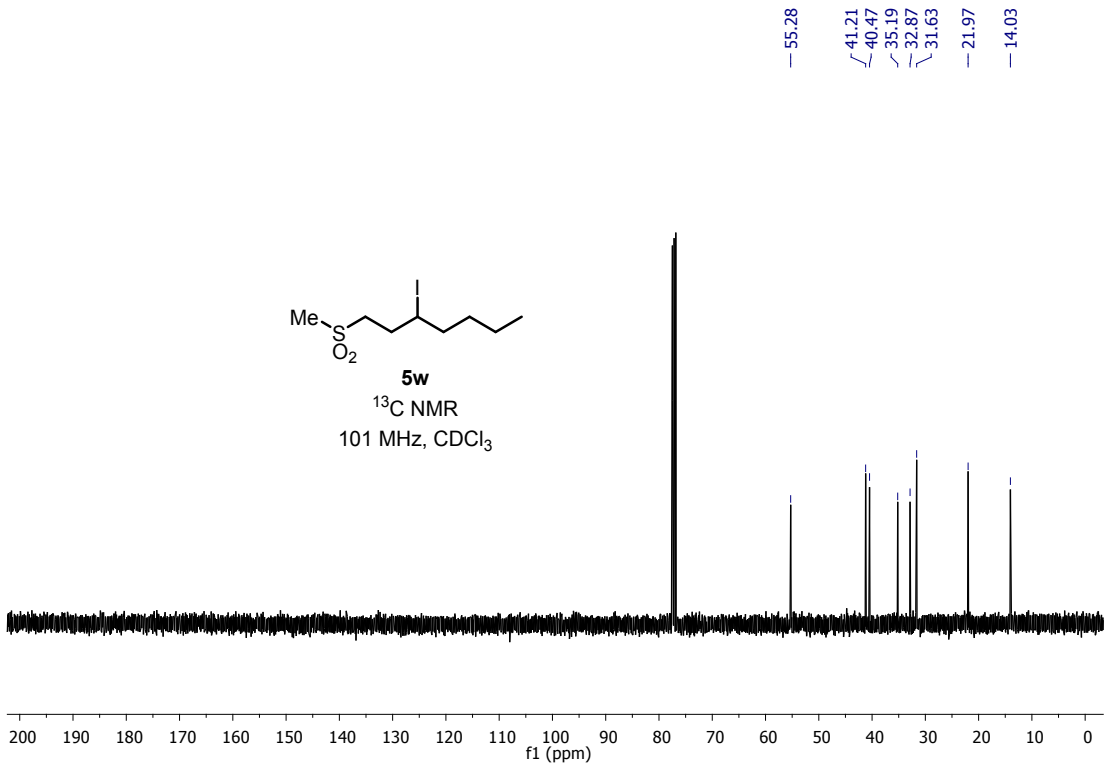

137.28
133.99
133.95
129.38
129.35
129.02
129.00
60.86
60.34
41.55
41.05
40.28
39.05
34.49
31.68
31.45
21.99
15.70
14.05
14.02
12.09
Me
I
S
O2
5u
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

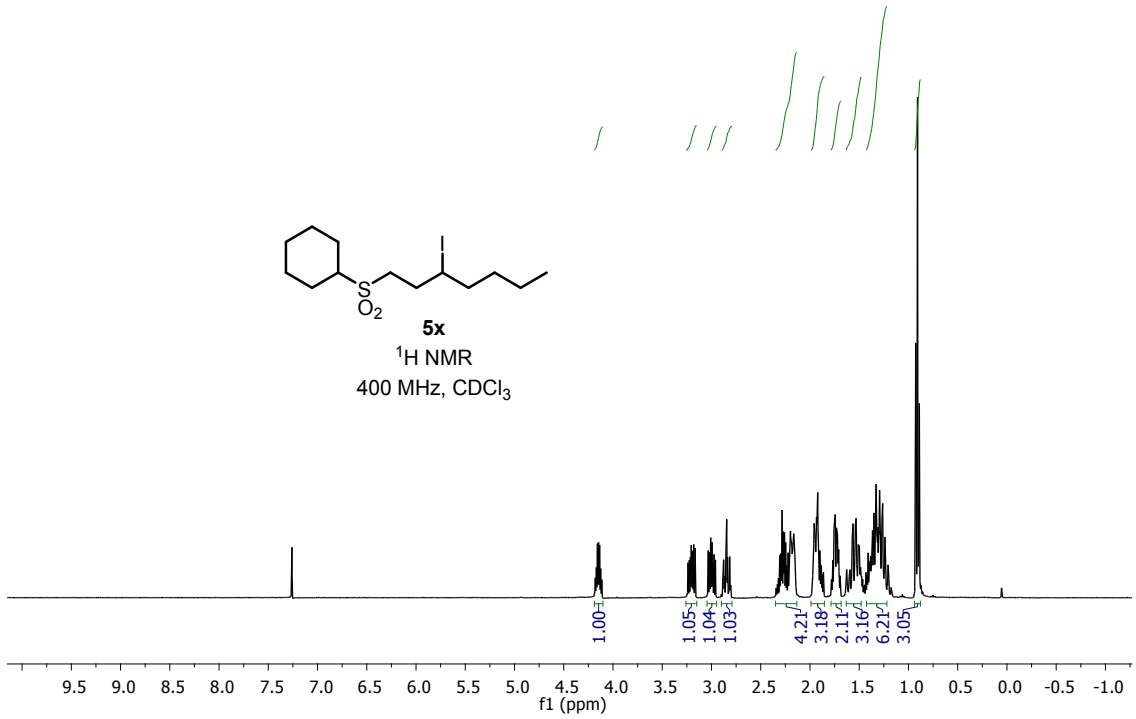

F
Me
I
S
O2
5v
1H NMR
400 MHz, CDCl3
2.00
2.14
0.38
0.66
1.03
0.38
0.66
1.06
2.21
4.46
3.54
3.25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

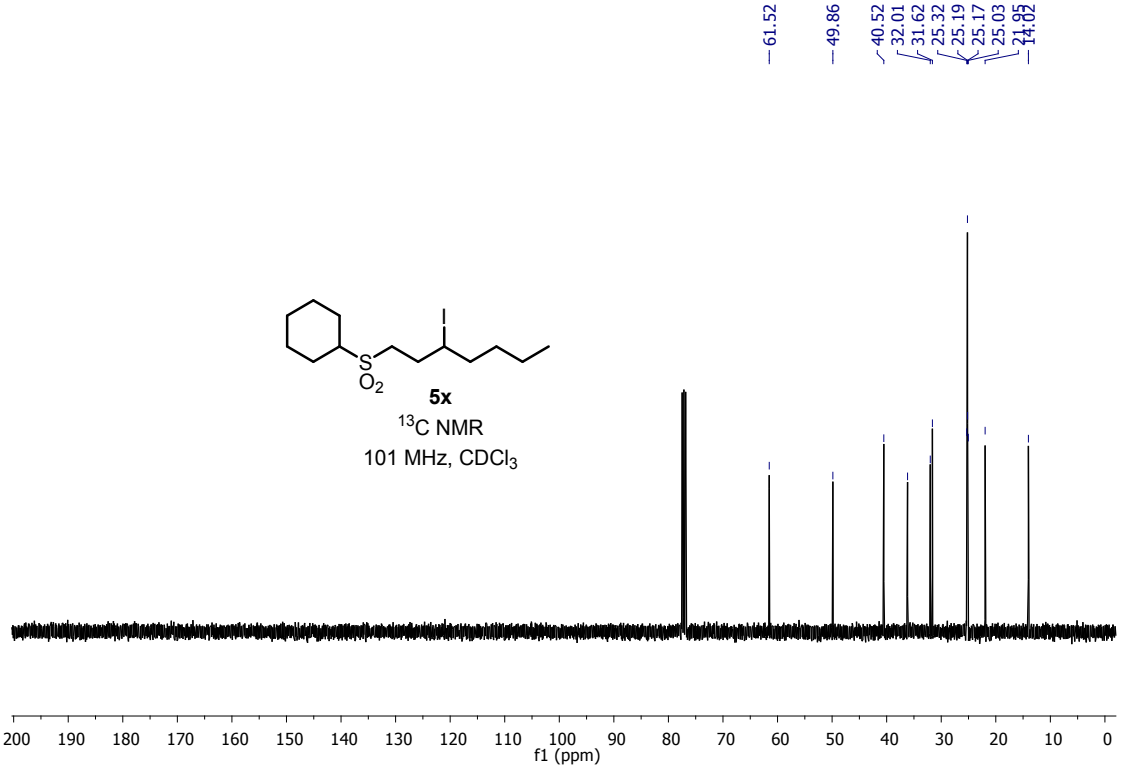

-103.13
-103.26
-103.13
-103.26
-102.95
-103.05
-103.15
-103.25
-103.35
f1 (ppm)
F
Me
I
S
O2
5v
19F NMR
376 MHz, CDCl3
1.00
1.71
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

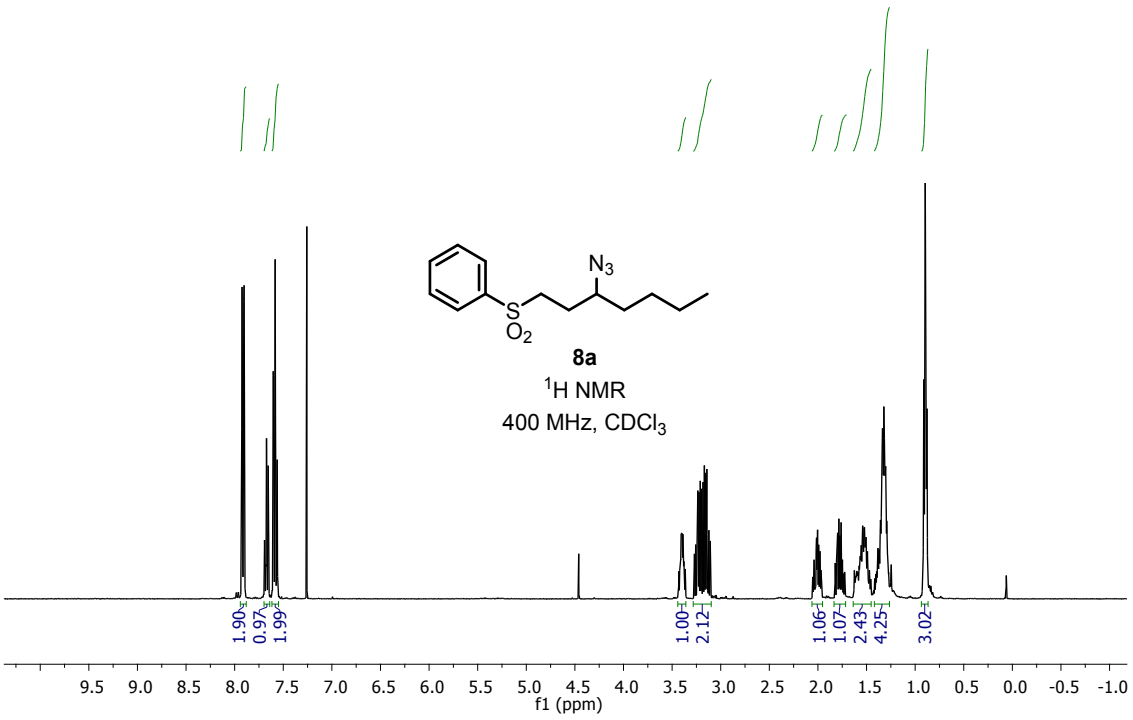

167.34
164.79
133.58
133.55
133.36
133.33
131.93
131.91
131.83
131.82
116.86
116.85
116.64
116.63
61.08
60.56
41.52
41.08
40.30
39.13
36.41
34.34
31.69
31.49
22.00
15.80
14.05
14.03
12.09
F
Me
I
S
O2
5v
13C NMR
101 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

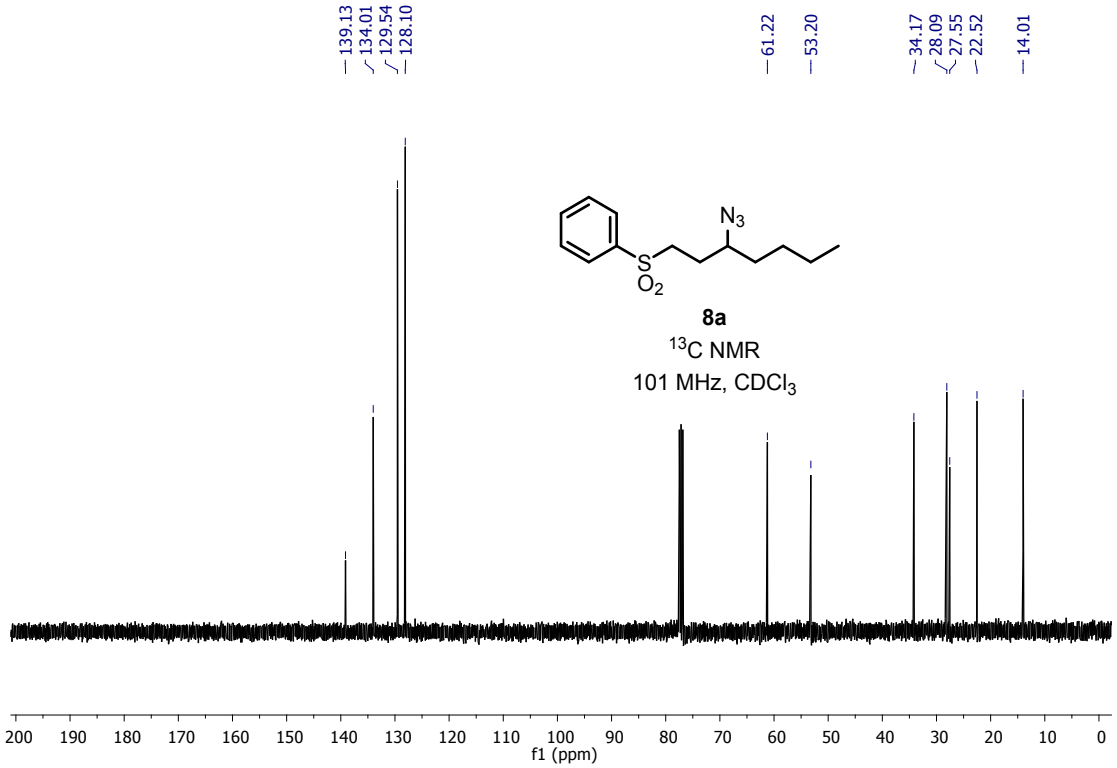

Me
S
O2
I
5w
1H NMR
400 MHz, CDCl3
1.00
1.03
1.05
3.09
2.13
1.08
1.13
4.74
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


55.28
41.21
40.47
35.19
32.87
31.63
21.97
14.03
Me
S
O2
I
5w
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


5x
1H NMR
400 MHz, CDCl3
1.00
1.05
1.04
1.03
4.21
3.18
2.11
3.16
6.21
3.05
f1 (ppm)


61.52
49.86
40.52
32.01
31.62
25.32
25.19
25.17
25.03
5x
13C NMR
101 MHz, CDCl3
f1 (ppm)


N3
S
O2
8a
1H NMR
400 MHz, CDCl3
1.90
0.97
1.99
1.00
2.12
1.06
1.07
2.43
4.25
3.02
f1 (ppm)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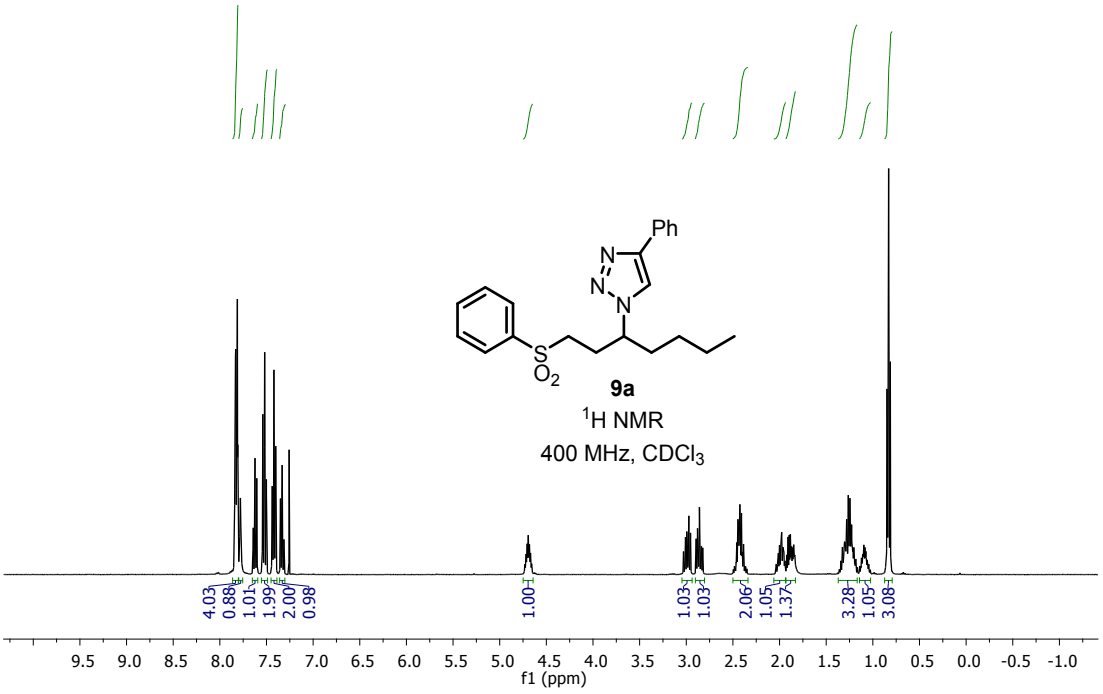
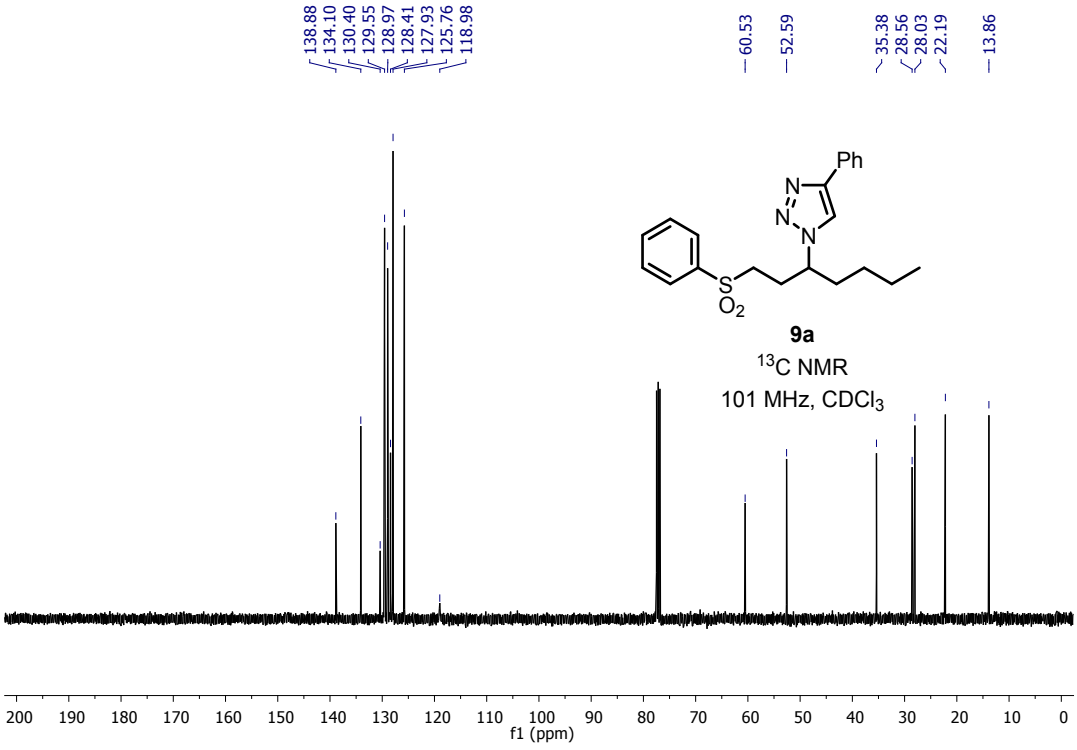
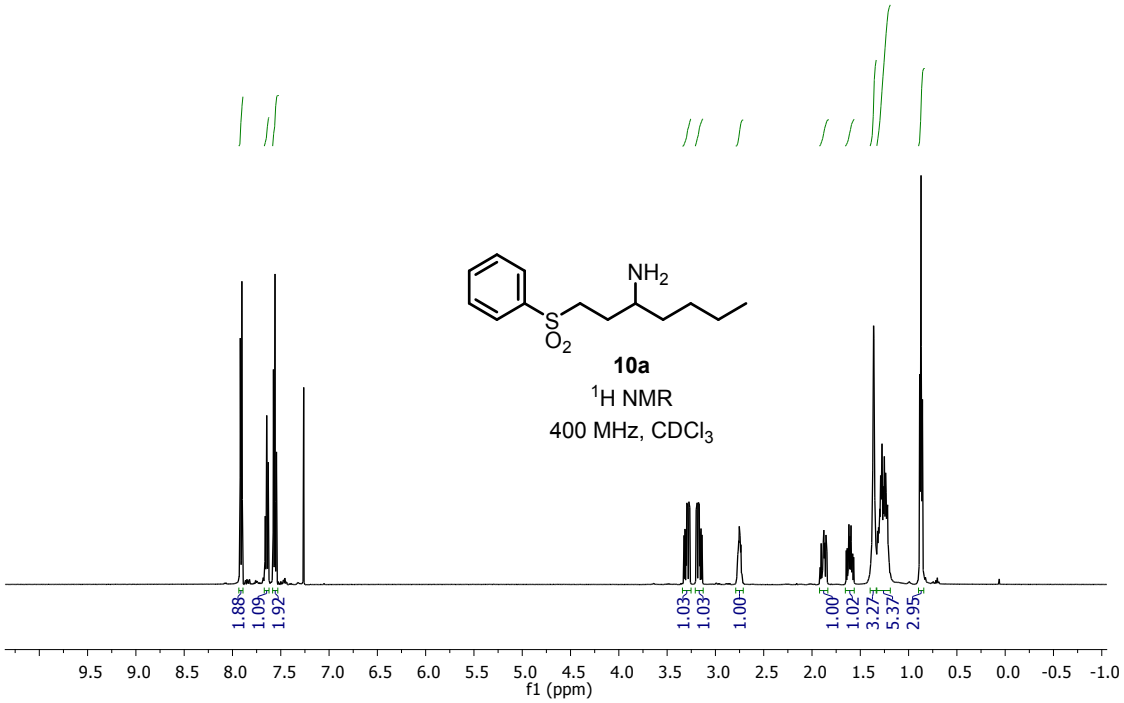
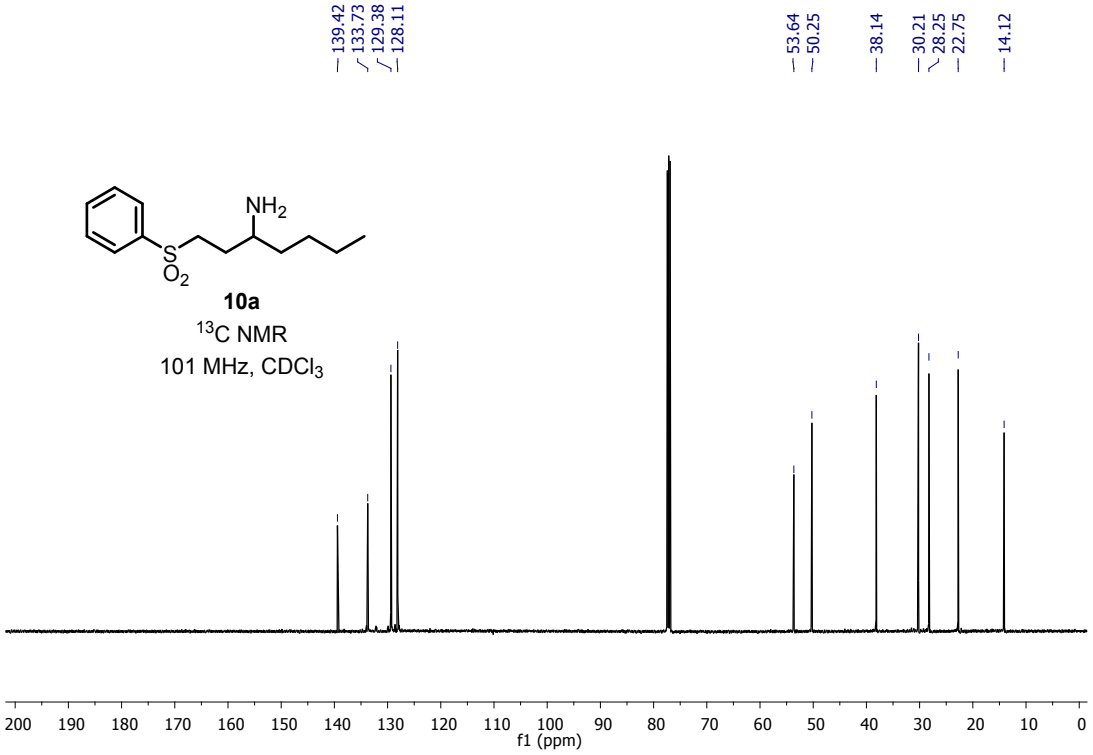
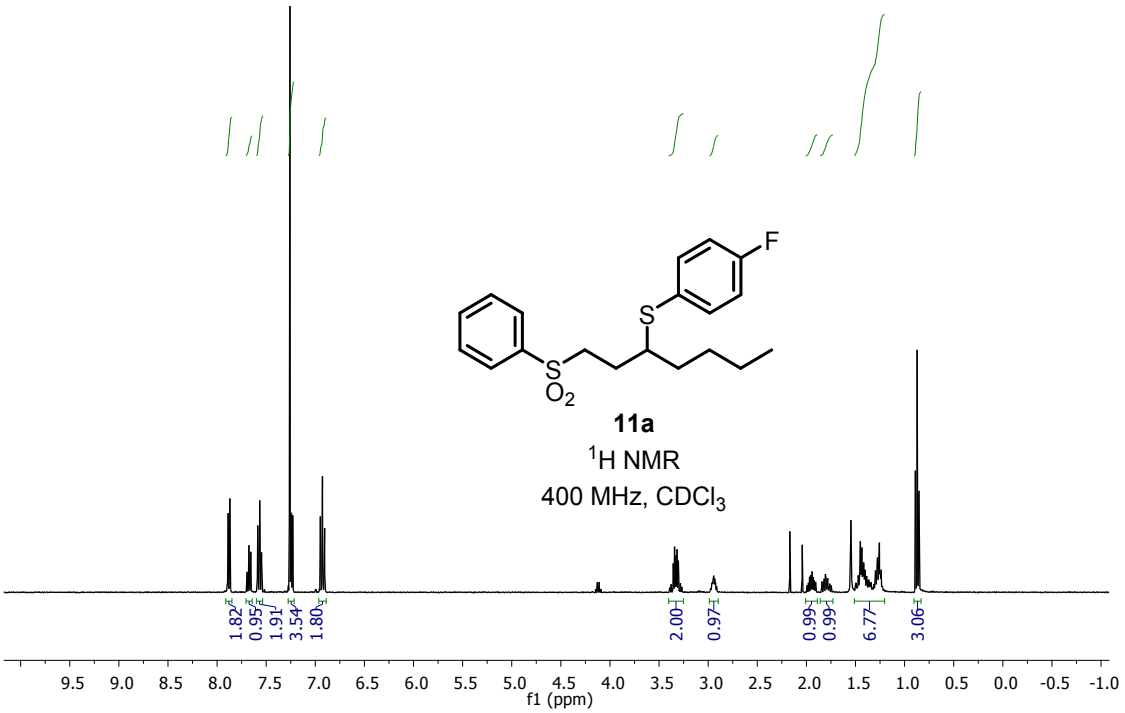
134.01
129.54
128.10
61.22
53.20
34.17
28.09
27.55
22.52
14.01
N3
S
O2
8a
13C NMR
101 MHz, CDCl3
f1 (ppm)

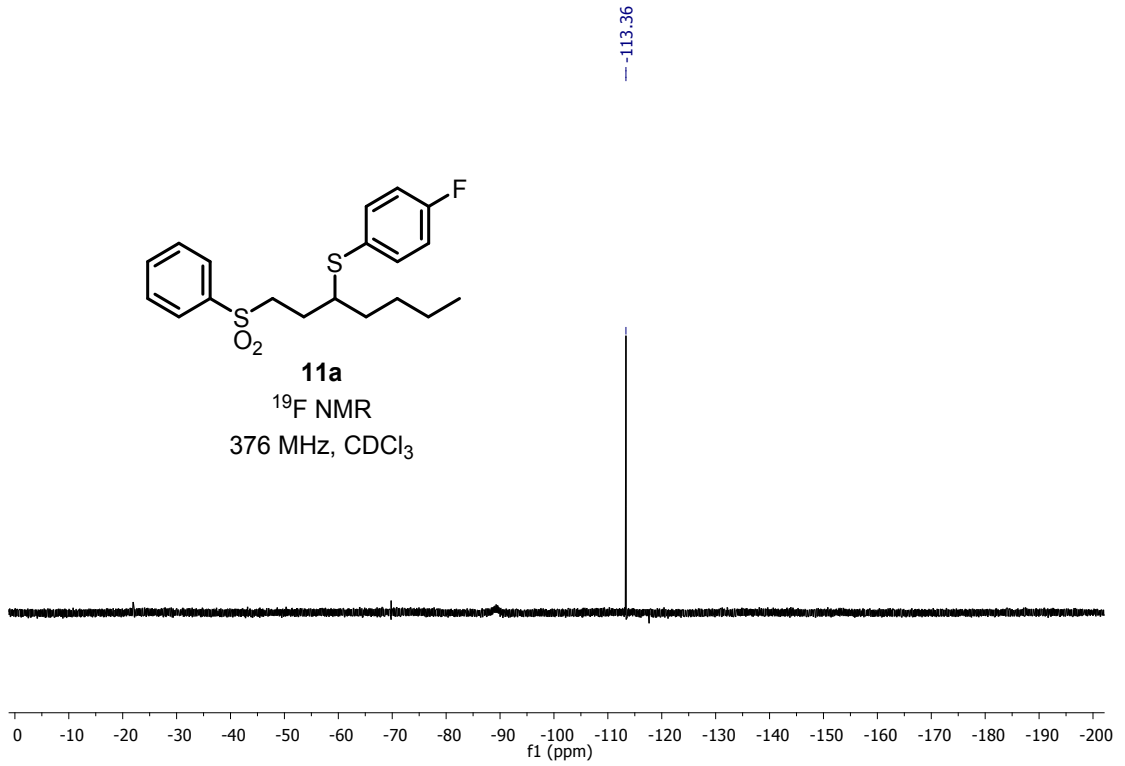

Ph
N
N
N
S
O2
9a
1H NMR
400 MHz, CDCl3
4.03
0.88
1.01
1.99
2.00
0.98
1.00
1.03
1.03
2.06
1.05
1.37
3.28
1.05
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

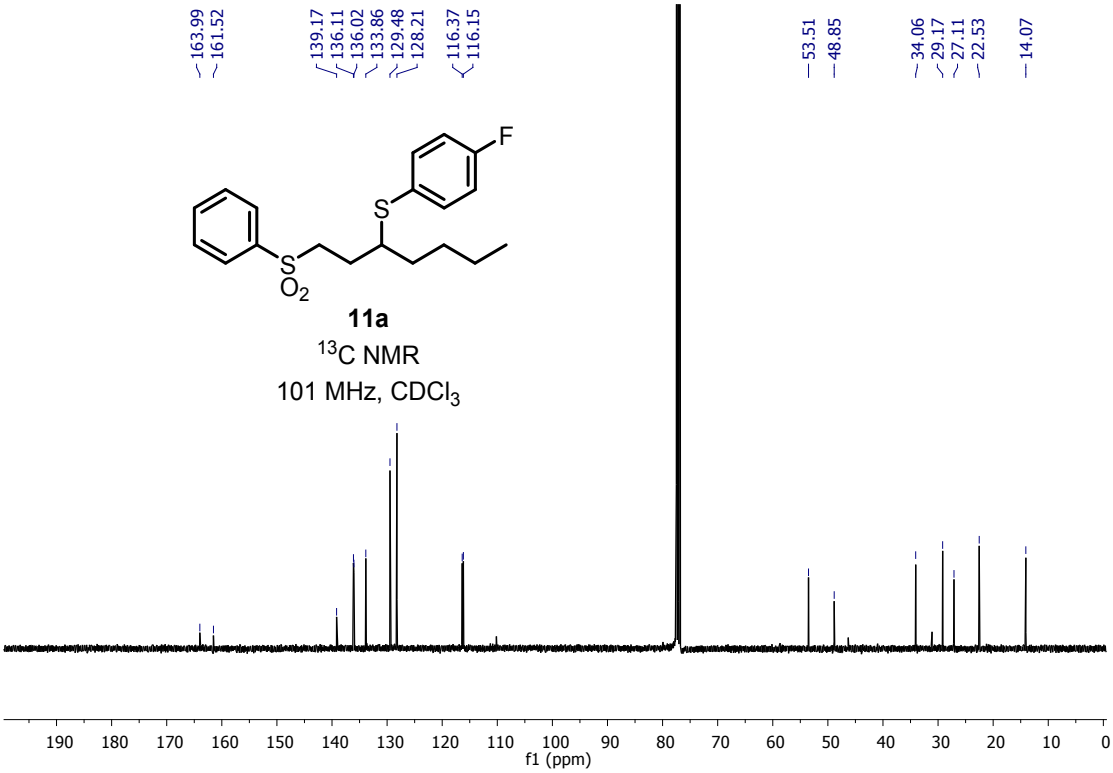

138.88
134.10
130.40
129.55
128.97
128.41
127.93
125.76
118.98
60.53
52.59
35.38
28.56
28.03
22.19
13.86
Ph
N
N
N
S
O2
9a
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NH2
S
O2
10a
1H NMR
400 MHz, CDCl3
1.88
1.09
1.92
1.03
1.03
1.00
1.00
1.02
3.27
5.37
2.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


139.42
133.73
129.38
128.11
53.64
50.25
38.14
30.21
28.25
22.75
14.12
NH2
S
O2
10a
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F
S
S
O2
11a
1H NMR
400 MHz, CDCl3
1.82
0.95
1.91
3.54
1.80
2.00
0.97
0.99
0.99
6.77
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


-113.36
F
S
S
O2
11a
19F NMR
376 MHz, CDCl3
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


163.99
161.52
139.17
136.11
136.02
133.86
129.48
128.21
116.37
116.15
53.51
48.85
34.06
29.17
27.11
22.53
14.07
F
S
S
O2
11a
13C NMR
101 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)