Electronic Supplementary Material (ESI) for ChemComm.

Thiol-Ene/Oxidation Tandem Reaction under Visible Light Photocatalysis: Synthesis of Alkyl Sulfoxides

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Supporting Information

1.- General Methods and Materials.

The analytical grade solvents, commercially available reagents and photocatalysts were used without further purification. The reactions were carried out in vials with a needle in the stopper and stirred with a magnetic bar.

Analytical thin layer chromatography (TLC) was performed using pre-coated aluminium-backed plates, with fluorescence indicator to 254 nm, and visualized by ultraviolet irradiation and/or by treatment with phosphomolybdic acid. Flash column chromatography (FC) was performed on Silica gel (Merck Geduran® Si 60) or porous silica gel (LSI Medience Corporation Iatrobeads 6RS-8060).

NMR spectra were acquired on a *Bruker 300 spectrometer*, running at 300, 75 and 282 MHz for ^{1}H, ^{13}C and ^{19}F, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C NMR). ^{13}C NMR and ^{19}F NMR spectra were acquired on a broadband decoupled mode. The following abbreviations are used to describe peak patterns: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septuplet), m (multiplet). The diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture through integration of diagnostic signals.

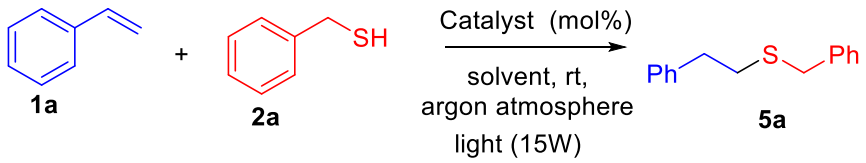
High Resolution Mass Spectra (HRMS) were acquired on a spectrometer *QSTAR (ABSciex)* using electrospray (TOF-ESI+) technique or on an *Agilent Technologies 5977B MSD* using electrospray (ESI) and making use of the *MassWorks software ver. 4.0.0.0. (Cerno Bioscience)* for the formula identification. *MassWorks* is a MS calibration software, which calibrates for isotope profile as well as for mass accuracy allowing highly accurate comparisons between calibrated and theoretical spectra. Obtained data are expressed in mass/charge (m/z) units.

The emission spectrum of the LED source and the intensity of the light were measured with a spectrometer equipment *Stellarnet model UV-VIS-NIR*.

Emission intensities for determination of the Stern-Volmer quenching were recorded on a *JASCO Spectrofluorometer FP-8600* equipped with a *TC-815 Peltier* thermostated single cell holder (water-cooled) controlled by *Spectra Manager Version 2.10.01*. DCM was used for all luminescence quenching experiments. Eosin Y solutions were excited at 516.4 nm, observing the maximum emission peak at 562 nm. In a typical experiment, the appropriate amount of quencher would be added to the DCM solution of Eosin Y in a Teflon-top 10x10 mm precision cell made of Quartz SUPRASIL®. After degassing with Argon for 1 min, the emission spectra of the samples were collected.

UV-Visible spectra for determination of the quantum yield were recorded on an *Agilent 8453 UV-Visible* Spectroscopy System controlled by UV-Visible *ChemStation Software Version B.02.01*.

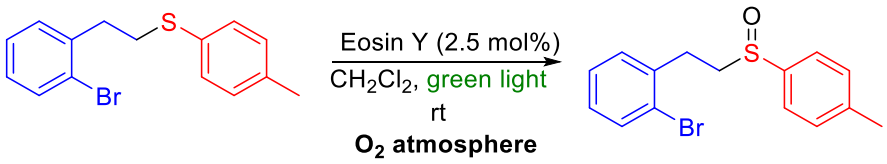
2A.- Table SI-1. Trials in the presence/absence of catalyst.



1a + 2a → 5a

Entry	Solvent	Cat.	Light source	Conv. **5a** (%) 10 min	Conv. **5a** (%) 20 min
1	DCM	-	Green	-	-
2	DCE	-	Green	-	-
3	Toluene	-	Green	-	-
4	DCM	-	Blue	-	-
5	DCM	3h	Green	18	24
6	DCE	3h	Green	15	32
7	Toluene	3h	Green	4	14
8	DCM	3h	Blue	11	24

2B.- Table SI-2. Different reaction conditions for oxidation of **11j** to **4j**.[a]

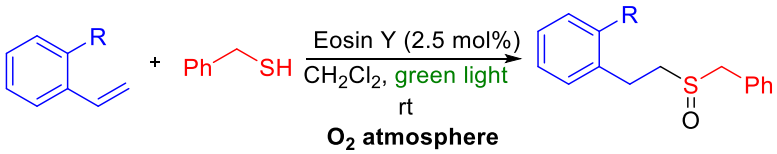


11j → **4j**

Entry	Conditions	Note
1	-	Conversion= 98%[b]
2	DABCO (0.5 equiv)	Conversion= 14%[b]
3	Benzoquinone (0.5 equiv)	Conversion= 87%[b]
4	KI/starch	No peroxide anions
5	Reaction in CD_3OD	Faster Reaction

[a] Reactions were performed in 0.1 mmol scale of **11j** in 0.360 mL of the indicated solvent. [b] Determined by ^{1}H-NMR.

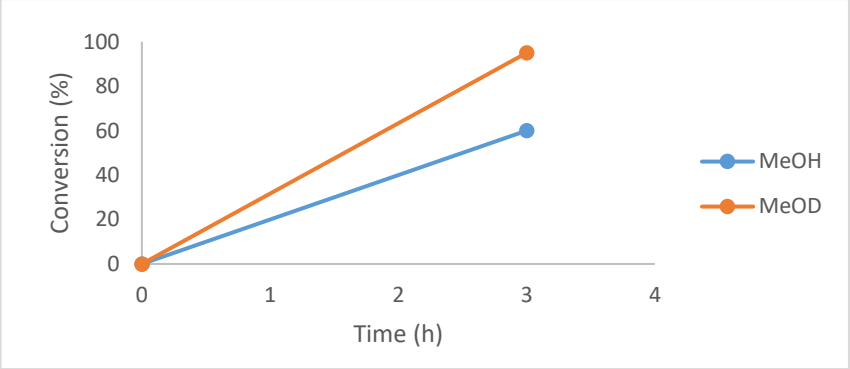
2C.- Table SI-3. Trials with different protecting groups.[a]



Entry	R	Conversion[b]
1	NH_2	<10%
2	NH-Ts	nr
3	NH-Boc	100%

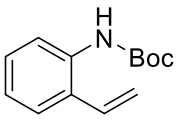
[a] Reactions were performed in 0.1 mmol scale of **alkene**, 0.3 mmol of **thiol**, in 0.360 mL of the indicated solvent. [b] Determined by ^{1}H-NMR

3.- Kinetic profile in the oxidation reaction to give 4j (MeOH versus CD_3OD)



4.- Synthesis of vinyl-amino derivatives 7.[1]

tert-Butyl (2-vinylphenyl)carbamate (**7a**)[1]

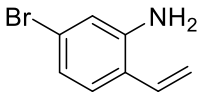


To a solution of 2-vinylaniline (450 µL, 3.78 mmol) in THF (9.45 mL), Boc_2O (1.645 g, 7.54 mmol) and Et_3N (1.05 mL, 7.54 mmol) were added and the mixture was refluxed for 18 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with AcOEt. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. After evaporating the solvent, the residue was purified by column chromatography on silica gel (1/1: chex/CH_2Cl_2) achieving the protecting amine **7a** in 60% yield (497.3 mg, 2.27 mmol) as a white solid. Spectroscopic data are in agreement with published data.[1]

^{1}H NMR δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.38 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.81 (dd, *J* = 17.4, 11.0 Hz, 1H), 6.41 (s, 1H), 5.66 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.41 (dd, *J* = 11.0, 1.4 Hz, 1H), 1.52 (s, 9H).

tert-Butyl (5-bromo-2-vinylphenyl)carbamate (**7b**)

Step 1. Synthesis of 5-bromo-2-vinylaniline



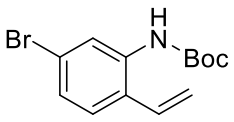
To a solution of $MePPh_3Br$ (0.82 g, 2.3 mmol, 2.3 eq.) in dry THF (3 mL) under argon atmosphere and at -78ºC, ^{t}BuONa 2M in THF (1.15 mL, 2.3 mmol, 2.3 eq.) was added and the mixture was stirred for 30 min. Then, a solution of the 2-amino-4-bromobenzaldehyde (0.20 g, 1 mmol, 1 eq.) in THF (1 mL) was added at -78 ºC and stirred for 24 h at room temperature. The reaction mixture was quenched with sat. aq. NaCl and the aqueous phase was extracted with Et_2O. The combined organic layers were dried over anhydrous $MgSO_4$. After evaporating the solvent, the residue was purified by column chromatography on silica gel (99/1: chex/ethyl acetate) achieving the final product as a yellow oil in 44% yield.

^{1}H NMR δ 7.12 (d, *J* = 8.3 Hz, 1H), 6.90 – 6.79 (m, 2H), 6.66 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.61 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.33 (dd, *J* = 11.2, 1.4 Hz, 1H), 3.90 – 3.69 (s, 2H).

^{13}C NMR δ 144.9, 131.8, 128.7, 122.9, 122.1, 121.7, 118.5, 116.3.

HRMS (TOF-ESI+): calculated for C_8H_9NBr $[M+H]^+$: 197.9912; found: 197.9914

Step 2. Synthesis of *tert*-butyl (5-bromo-2-vinylphenyl)carbamate (**7b**)



To a solution of 5-bromo-2-vinylaniline (0.24 mg, 1.19 mmol) in THF (3 mL), Boc_2O (0.52 mg, 2.38 mmol) and Et_3N (0.33 mL, 2.38 mmol) were added and the mixture was refluxed for 18 h. The reaction was quenched with a sat. aq. NH_4Cl and extracted with AcOEt. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. After evaporating the solvent,

[1] C. Pietraszuk, S. Rogalski, B. Powala, M. Mietkiewski, M. Kubicki, G. Spolnik, W. Danikiewicz, K. Wozniak, A. Pazio, A. Szadkowska, A. Kozlowska, K. Grela, *Chem. Eur. J.* **2012**, *18*, 6465.

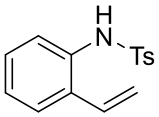
the residue was purified by column chromatography on silica gel (9/1: chex/CH_2Cl_2) achieving the protecting amine **7b** in 14% yield (49.7 mg, 0.17 mmol) as a yellow solid.

^{1}H NMR δ 8.10 (s, 1H), 7.21 – 7.17 (m, 2H), 6.71 (dd, *J* = 17.3, 11.0 Hz, 1H), 6.44 (s, 1H), 5.64 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.44 (dd, *J* = 11.0, 1.1 Hz, 1H), 1.51 (s, 9H).

^{13}C NMR δ 152.5, 136.3, 131.3, 128.2, 127.4, 126.7, 123.7, 122.1, 118.8, 81.1, 28.3.

HRMS (TOF-ESI+): calculated for $C_{13}H_{15}BrNO_2$ [M-H]: 296.0281, found: 296.0282.

4-methyl-*N*-(2-vinylphenyl)benzenesulfonamide (**7c**)



To a solution of 2-vinylaniline (0.25 mL, 2.08 mmol) in anhydrous CH_2Cl_2 (3 mL) under argon atmosphere, tosyl chloride (0.48 g, 2.5 mmol) and piridine (5.10 mL, 6.24 mmol) were added and the mixture was stirred at room temperature for 2 days. The reaction was diluted with water and extracted with AcOEt. The combined organic layers were dried over anhydrous $MgSO_4$. After evaporating the solvent, the residue was purified by recrystallization in CH_2Cl_2/chex achieving the protecting amine **7c** in 65% yield as an orange solid.

^{1}H NMR δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.28 (m, 2H), 7.24 – 7.11 (m, 4H), 6.62 – 6.51 (m, 1H), 6.49 (s, 1H), 5.50 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.26 (dd, *J* = 11.0, 1.2 Hz, 1H), 2.39 (s, 3H).

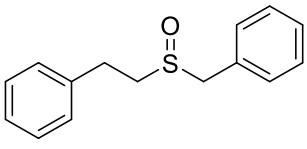
^{13}C NMR δ 143.6, 136.4, 133.2, 132.6, 131.5, 129.6 (2C), 128.6, 127.2 (2C), 127.0, 126.4, 124.7, 118.3, 21.5.

HRMS (TOF-ESI+): calculated for $C_{15}H_{15}NO_2S$ [M-H]: 273.0824, found: 273.0826.

5.- General procedure and characterizations for the thiol-ene/oxidation tandem reaction.

A dry vial was charged with the corresponding photocatalyst (0.025 eq.) and the solvent indicated each case (360 µL). Then, the vinylaniline derivative (1 eq.) and the corresponding thiol (eq. indicated each case) were added. A needle was placed through the stopper to let the oxygen pass into the reaction mixture and the corresponding light was switched on. The reaction was stirred at room temperature for the time indicated each case. The crude product was purified by flash column chromatography (eluent indicated each case).

(2-(Benzylsulfinyl)ethyl)benzene (**4a**)[2]

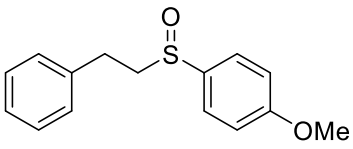


Following the general procedure, from styrene (11.5 µL, 0.1 mmol) and benzyl mercaptan (35 µL, 0.3 mmol) in DCM, after 36 hours at rt, compound **4a** was obtained in 81% yield (19.8 mg, 0.081 mmol) as a light yellow solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

[2] H. -L. Yue, M. Klussmann, *Synlett* **2016**, *27*, 2505.

^{1}H NMR δ 7.49 – 7.42 (m, 4H), 7.40 – 7.34 (m, 4H), 7.32 – 7.27 (m, 2H), 4.13 and 4.03 (AB system, *J* = 12.9 Hz, 2H), 3.29 – 3.03 (m, 2H), 3.00 – 2.87 (m, 2H).

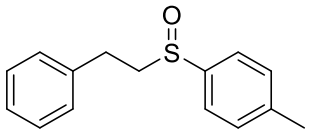
1-Methoxy-4-(phenethylsulfinyl)benzene (**4b**)[3]



Following the general procedure, from styrene (11.5 µL, 0.1 mmol) and 4-methoxybenzenethiol (36.9 µL, 0.3 mmol) in DCM, after 38 hours at rt, compound **4b** was obtained in 30% yield (7.8 mg, 0.03 mmol) as a green solid. The crude product was purified by flash column chromatography on silica gel (1/1: chex/ethyl acetate).

^{1}H NMR δ 7.52 and 6.97 (AA'BB' system, 4H), 7.29 – 7.08 (m, 5H), 3.80 (s, 3H), 3.09 – 2.92 (m, 3H), 2.92 – 2.79 (m, 1H).

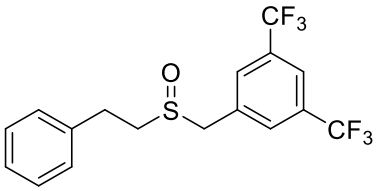
1-Methyl-4-(phenethylsulfinyl)benzene (**4c**)[2]



Following the general procedure, from styrene (11.5 µL, 0.1 mmol) and 4-methylthiophenol (37.3 mg, 0.3 mmol) in DCM, after 38 hours at rt, compound **4c** was obtained in 75% yield (18.3 mg, 0.075 mmol) as a red solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.56 – 7.44 (m, 2H), 7.35 – 7.22 (m, 5H), 7.19 – 7.13 (m, 2H), 3.10 – 2.94 (m, 3H), 2.93 – 2.80 (m, 1H), 2.42 (s, 3H).

1-((Phenethylsulfinyl)methyl)-3,5-bis(trifluoromethyl)benzene (**4d**)



Following the general procedure, from styrene (11.5 µL, 0.1 mmol) and (3,5-bis(trifluoromethyl)phenyl)methanethiol (18.1 mg, 0.3 mmol) in DCM, after 62 hours at rt, compound **4d** was obtained in 93% yield (35.4 mg, 0.093 mmol) as a yellow solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.88 (s, 1H), 7.75 (s, 2H), 7.38 – 7.30 (m, 2H), 7.30 – 7.25 (m, 2H), 7.25 – 7.20 (m, 1H), 4.03 and 3.94 (AB system, *J* = 13.1 Hz, 2H), 3.23 – 3.04 (m, 2H), 3.01 – 2.92 (m, 2H).

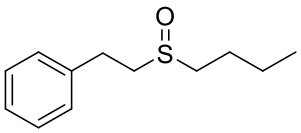
^{13}C NMR δ 138.3, 133.0, 132.2 (q, *J* = 33.7 Hz), 130.2, 128.9 (2C), 128.6 (2C), 127.1, 123.0 (q, *J* = 272.9 Hz), 122.3 (q, *J* = 3.8 Hz), 57.0, 53.4, 28.7.

^{19}F NMR δ -62.88.

HRMS (ESI+): calculated for $C_{17}H_{15}SOF_6$ $[M+H]^+$: 381.0742; found: 381.0733.

[3] B. Wang, Y. Liu, C. Lin, Y. Xu, Z. Liu, Y. Zhang, *Org. Lett.* **2014**, *16*, 4574.

(2-(Butylsulfinyl)ethyl)benzene (**4e**)



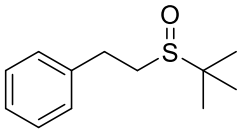
Following the general procedure, from styrene (11.5 µL, 0.1 mmol) and 1-butanethiol (32.1 µL, 0.3 mmol) in DCM, after 72 hours at rt, compound **4e** was obtained in 69% yield (14.5 mg, 0.069 mmol) as an orange oil. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.41 – 7.10 (m, 5H), 3.24 – 2.98 (m, 2H), 2.98 – 2.80 (m, 2H), 2.81 – 2.49 (m, 2H), 1.84 – 1.59 (m, 2H), 1.59 – 1.34 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR δ 138.9, 128.7, 128.4, 126.6, 53.7, 52.2, 28.7, 24.5, 22.0, 13.6.

HRMS (ESI+): calculated for $C_{12}H_{19}OS$ $[M+H]^+$: 211.1151; found: 211.1180.

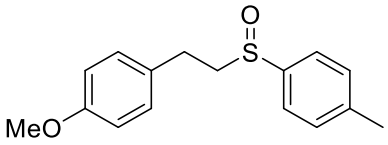
(2-(*tert*-Butylsulfinyl)ethyl)benzene (**4f**)[2]



Following the general procedure, from styrene (11.5 µL, 0.1 mmol) and (34 µL, 0.3 mmol) in DCM, after 41 hours at rt, compound **4f** was obtained in 63% yield (13.2 mg, 0.063 mmol) as an orange oil. The crude product was purified by flash column chromatography on silica gel (2/1: pentane/ethyl acetate).

^{1}H NMR δ 7.38 – 7.34 (m, 1H), 7.35 – 7.32 (m, 1H), 7.31 – 7.28 (m, 2H), 7.27 – 7.26 (m, 1H), 3.23 (ddd, *J* = 15.0, 9.6, 5.8 Hz, 1H), 3.12 – 3.00 (m, 1H), 2.82 – 2.66 (m, 2H), 1.26 (s, 9H).

1-Methoxy-4-(2-(*p*-tolylsulfinyl)ethyl)benzene (**4g**)



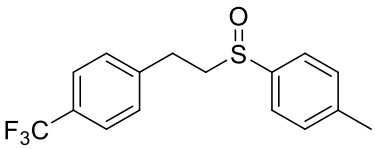
Following the general procedure, from 1-methoxy-4-vinylbenzene (13.3 µL, 0.1 mmol) and 4-methylthiophenol (37.3 mg, 0.3 mmol) in DCM, after 28 hours at rt, compound **4g** was obtained in 72% yield (19.8 mg, 0.072 mmol) as a pink solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.52 and 7.32 (AA'BB' system, 4H), 7.09 and 6.82 (AA'BB' system, 4H), 3.77 (s, 3H), 3.10 – 2.94 (m, 3H), 2.92 – 2.79 (m, 1H), 2.41 (s, 3H).

^{13}C NMR δ 158.3, 141.4, 140.5, 130.8, 129.9 (2C), 129.5 (2C), 124.0 (2C), 114.1 (2C), 58.7, 55.2, 27.4, 21.4.

HRMS (ESI+): calculated for $C_{16}H_{19}SO_2$ $[M+H]^+$: 275.1100; found: 275.1114.

1-Methyl-4-((4-(trifluoromethyl)phenethyl)sulfinyl)benzene (**4h**)



Following the general procedure, from 1-trifluoromethyl-4-vinylbenzene (14.8 µL, 0.1 mmol) and 4-methylthiophenol (37.3 mg, 0.3 mmol) in DCM, after 47 hours at rt, compound **4h** was obtained in 63% yield (19.7 mg, 0.063 mmol) as a white

solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

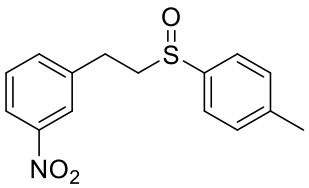
^{1}H NMR δ 7.56 – 7.52 (m, 2H), 7.51 – 7.45 (m, 2H), 7.33 and 7.28 (AA'BB' system, 4H), 3.20 – 2.88 (m, 4H), 2.42 (s, 3H).

^{13}C NMR δ 143.0, 141.7, 140.1, 130.0 (2C), 129.1 (q, *J* = 32.4 Hz), 128.9 (2C), 125.6 (q, *J* = 3.8 Hz, 2C), 124.1 (q, *J* = 271.9 Hz), 124.0, 57.6, 27.8, 21.4.

^{19}F NMR δ -62.51.

HRMS (ESI+): calculated for $C_{16}H_{16}SOF_3$ $[M+H]^+$: 313.0868; found: 313.0866.

1-Nitro-3-(2-(*p*-tolylsulfinyl)ethyl)benzene (**4i**)



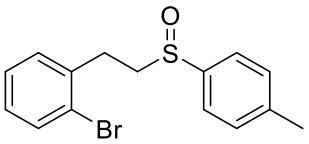
Following the general procedure, from 1-nitro-3-vinylbenzene (11.0 µL, 0.1 mmol) and 4-methylthiophenol (37.3 mg, 0.3 mmol) in DCM, after 37 hours at rt, compound **4i** was obtained in 73% yield (21.1 mg, 0.073 mmol) as a pink solid. The crude product was purified by flash column chromatography on silica sel (2/1: chex/ethyl acetate).

^{1}H NMR δ 8.11 – 8.03 (m, 1H), 8.00 (s, 1H), 7.57 – 7.40 (m, 4H), 7.33 (d, *J* = 7.7 Hz, 2H), 3.29 – 2.88 (m, 4H), 2.42 (s, 3H).

^{13}C NMR δ 148.4, 141.8, 140.9, 139.8, 134.9, 130.1 (2C), 129.6, 124.0 (2C), 123.3, 121.8, 57.1, 27.5, 21.4.

HRMS (ESI+): calculated for $C_{15}H_{16}SO_3N$ $[M+H]^+$: 290.0845; found: 290.0842.

1-Bromo-2-(2-(*p*-tolylsulfinyl)ethyl)benzene (**4j**)



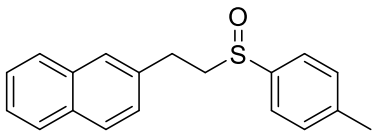
Following the general procedure, from 1-bromo-2-vinylbenzene (12.9 µL, 0.1 mmol) and 4-methylthiophenol (37.3 mg, 0.3 mmol), after 20 hours at rt, compound **4j** was obtained in 76% yield (24.6 mg, 0.076 mmol) as a pink solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.58 – 7.45 (m, 3H), 7.36 – 7.28 (m, 2H), 7.27 – 7.18 (m, 2H), 7.12 – 7.02 (m, 1H), 3.27 – 2.98 (m, 4H), 2.43 (s, 3H).

^{13}C NMR δ 141.4, 140.2, 138.3, 133.0, 130.9, 129.9 (2C), 128.5, 127.8, 124.3, 124.1 (2C), 56.0, 28.8, 21.4.

HRMS (ESI+): calculated for $C_{15}H_{16}SOBr$ $[M+H]^+$:323.0100; found: 323.0108.

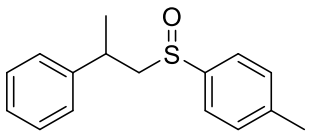
2-(2-(*p*-Tolylsulfinyl)ethyl)naphthalene (**4k**)[4]



Following the general procedure, from 2-vinylnaphthalene (15.4 mg, 0.1 mmol) and 4-methylthiophenol (37.3 mg, 0.3 mmol) in DCM, after 62 hours at rt, compound **4k** was obtained in 45% yield (13.2 mg, 0.045 mmol) as a red solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.83 – 7.72 (m, 3H), 7.63 (s, 1H), 7.54 and 7.33 (AA'BB' system, 4H), 7.48 – 7.42 (m, 2H), 7.29 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.31 – 3.18 (m, 1H), 3.17 – 2.98 (m, 3H), 2.41 (s, 3H).

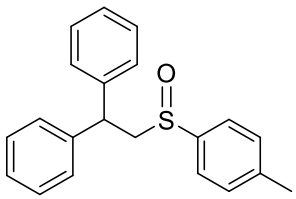
1-Methyl-4-((2-phenylpropyl)sulfinyl)benzene (**4l**)[4]



Following the general procedure, from *α*-methylstyrene (13.0 µL, 0.1 mmol) and 4-methylthiophenol (37.3 mg, 0.3 mmol) in DCM, after 37 hours at rt, compound **4l** was obtained in 64% yield (16.5 mg, 0.064 mmol) as a pink solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.54 – 7.42 (m, 4H, isomers mixture), 7.39 – 7.14 (m, 14H, isomers mixture), 3.47 – 3.21 (m, 2H, isomers mixture), 3.18 – 2.99 (m, 2H, isomers mixture), 2.96 – 2.70 (m, 2H, isomers mixture), 2.39 (s, 6H, isomers mixture), 1.51 (d, *J* = 6.8 Hz, 3H, minor isomer), 1.39 (d, *J* = 7.0 Hz, 3H, mayor isomer).

(2-(*p*-Tolylsulfinyl)ethane-1,1-diyl)dibenzene (**4m**)



Following the general procedure, from 1,1-diphenyletilene (17.7 µL, 0.1 mmol) and 4-methylthiophenol (37.3 mg, 0.3 mmol) in DCM, after 44 hours at rt, compound **4m** was obtained in 42% yield (14.1 mg, 0.044 mmol) as a white solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

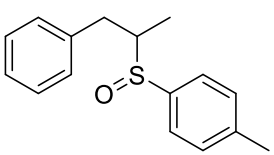
^{1}H NMR δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.14 (m, 12H), 4.55 (dd, *J* = 10.6, 5.4 Hz, 1H), 3.48 (dd, *J* = 12.8, 5.4 Hz, 1H), 3.38 (dd, *J* = 12.8, 10.6 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR δ 142.4, 141.6, 141.5, 141.2, 130.0, 128.9, 128.7, 128.2, 127.7, 127.1, 126.9, 124.1, 64.8, 45.5, 21.4.

HRMS (ESI+): calculated for $C_{21}H_{21}SO$ $[M+H]^+$:321.1308; found: 321.1269.

[4] B. Wang, C. Shen, J. Yao, H. Yin, Y. Zhang, *Org. Lett.* **2014**, *16*, 46.

1-Methyl-4-((1-phenylproan-2-yl)sulfinyl)benzene (**4n**)



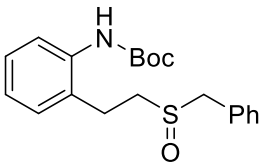
Following the general procedure, from trans *β*-methylstyrene (13.0 µL, 0.1 mmol) and 4-methylthiophenol (37.3 mg, 0.3 mmol) in DCM, after 37 hours at rt, compound **4n** was obtained in 24% yield (6.1 mg, 0.024 mmol) as a pink solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ: 7.48 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.30 – 7.15 (m, 12H), 7.12 (d, *J* = 7.3 Hz, 2H), 7.04 – 7.09 (m, 2H), 3.20 (dd, *J* = 13.1, 5.4 Hz, 1H), 3.07 – 3.01 (m, 1H), 2.88 – 2.76 (m, 2H), 2.52 – 2.46 (m, 2H), 2.36 (s, 6H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR δ: 140.6, 140.2, 137.5, 137.2 (2C), 136.8, 128.7 (2C), 128.2 (2C), 127.6 (2C), 125.6 (2C), 124.2, 123.8, 59.8 (2C), 35.4, 33.6, 20.4 (2C), 11.6, 9.4.

HRMS (ESI+): calculated for $C_{16}H_{19}SO$ $[M+H]^+$: 259,1151; found: 259,1127.

***tert*-Butyl (2-(2-(benzylsulfinyl)ethyl)phenyl)carbamate** (**8a**)



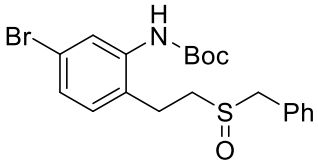
Following the general procedure, from *tert*-butyl (2-vinylphenyl)carbamate (22 mg, 0.1 mmol) and benzyl mercaptan (23 µL, 0.2 mmol) in DCM, after 20 hours at rt, compound **8a** was obtained in 70% yield (25.2 mg, 0.070 mmol) as a yellow oil. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.73 – 7.65 (m, 1H), 7.45 – 7.32 (m, 4H), 7.25 – 7.18 (m, 2H), 7.16 – 7.03 (m, 2H), 4.02 and 3.86 (AB system, *J* = 12.9 Hz, 2H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.88 (t, *J* = 7.0 Hz, 2H), 1.51 (s, 9H).

^{13}C NMR δ 153.9, 136.3, 135.0, 130.0, 129.7, 129.5, 129.1, 128.5, 127.8, 124.6, 124.2, 80.2, 58.0, 50.0, 28.4, 23.3.

HRMS (TOF-ESI+): calculated for $C_{20}H_{26}NO_3S$ $[M+H]^+$: 360.1633; found: 360.1635.

***tert*-Butyl (2-(2-(benzylsulfinyl)ethyl)-5-bromophenyl)carbamate** (**8b**)



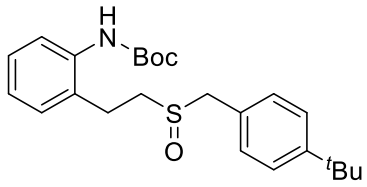
Following the general procedure, from *tert*-butyl (5-bromo-2-vinylphenyl)carbamate (29.8 mg, 0.1 mmol) and benzyl mercaptan (23 µL, 0.2 mmol) in DCM, after 30 hours at rt, compound **8b** was obtained in 62% yield (27.2 mg, 0.062 mmol) as a yellow oil. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.92 (d, *J* = 2.1 Hz, 1H), 7.56 (s, 1H), 7.40 – 7.29 (m, 3H), 7.20 – 7.04 (m, 3H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.99 and 3.80 (AB system, *J* = 12.9 Hz, 2H), 2.99 – 2.86 (m, 2H), 2.81 – 2.70 (m, 2H), 1.44 (s, 9H).

^{13}C NMR δ 153.4, 137.8, 130.9, 129.9, 129.2, 129.1, 128.6, 127.9, 127.1, 126.1, 121.2, 80.6, 57.9, 49.5, 28.3, 22.8.

HRMS (TOF-ESI+): calculated for $C_{20}H_{25}NO_3SBr$ $[M+H]^+$: 438.0733; found: 438.0750

***tert*-Butyl (2-(2-((4-(*tert*-butyl)benzyl)sulfinyl)ethyl)phenyl)carbamate** (**8c**)



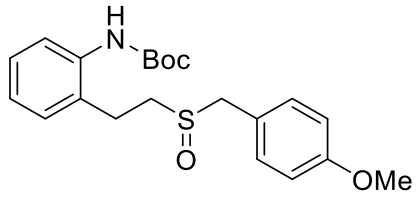
Following the general procedure, from *tert*-butyl (2-vinylphenyl)carbamate (22 mg, 0.1 mmol) and (4-(*tert*-butyl)phenyl)methanethiol (38 µL, 0.2 mmol) in DCM, after 48 hours at rt, compound **8c** was obtained in 53% yield (22.0 mg, 0.053 mmol) as an orange solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.45 (s, 1H), 7.40 – 7.34 (m, 2H), 7.26 – 7.20 (m, 1H), 7.19 – 7.12 (m, 3H), 7.11 – 7.04 (m, 1H), 3.98 and 3.84 (AB system, *J* = 12.9 Hz, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.89 (t, *J* = 6.9 Hz, 2H), 1.52 (s, 9H), 1.30 (s, 9H).

^{13}C NMR δ 153.9, 151.6, 136.3, 130.0, 129.7, 129.6, 127.7, 126.3, 126.0, 124.6, 124.2, 80.2, 57.5, 49.9, 34.6, 31.2, 28.4, 23.2.

HRMS (TOF-ESI+): calculated for $C_{24}H_{34}NO_3S$ $[M+H]^+$: 416.2254; found: 416.2250.

***tert*-Butyl (2-(2-((4-methoxybenzyl)sulfinyl)ethyl)phenyl)carbamate** (**8d**)



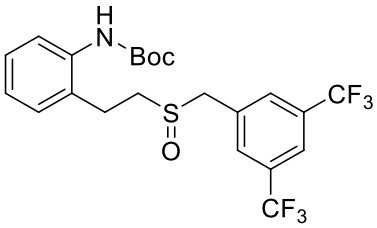
Following the general procedure, from *tert*-butyl (2-vinylphenyl)carbamate (22 mg, 0.1 mmol) and (4-methoxyphenyl)methanethiol (27.74 µL, 0.2 mmol) in DCM, after 48 hours at rt, compound **8d** was obtained in 56% yield (21.8 mg, 0.056 mmol) as a yellow solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.44 (s, 1H), 7.25 – 7.18 (m, 4H), 7.16 – 6.98 (m, 2H), 6.93 – 6.81 (m, 1H), 3.96 and 3.82 (AB system, *J* = 12.8 Hz, 2H), 3.82 (s, 3H), 3.07 (t, *J* = 7.1 Hz, 2H), 2.86 (t, *J* = 7.0 Hz, 2H), 1.51 (s, 9H).

^{13}C NMR δ 159.8, 153.9, 136.3, 131.2, 130.0, 129.6, 127.7, 124.6, 124.2, 121.2, 114.5, 80.2, 57.2, 55.3, 49.8, 28.4, 23.3.

HRMS (TOF-ESI+): calculated for $C_{21}H_{27}NO_4SNa$ $[M+Na]^+$: 412.1553; found: 412.1532.

***tert*-Butyl (2-(2-((3,5-bis(trifluoromethyl)benzyl)sulfinyl)ethyl)phenyl)carbamate** (**8e**)



Following the general procedure, from *tert*-butyl (2-vinylphenyl)carbamate (22 mg, 0.1 mmol) and (3,5-bis(trifluoromethyl)phenyl)methanethiol (52 mg, 0.2 mmol) in DCM, after 48 hours at rt, compound **8e** was obtained in 43% yield (21.3 mg, 0.043 mmol) as an orange solid. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

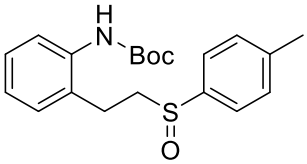
^{1}H NMR δ 7.86 (s, 1H), 7.70 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.32 – 7.08 (m, 4H), 7.12 (td, *J* = 7.4, 1.3 Hz, 1H), 3.92 (s, 2H), 3.23 – 2.92 (m, 4H), 1.50 (s, 9H).

^{13}C NMR δ 154.0, 136.2, 132.9, 132.3 (q, $J_{C\text{-}F}$ = 33.7 Hz, 2xC), 130.3 (2xCH), 130.2, 129.8, 128.1, 125.2, 124.8, 123.0 (q, $J_{C\text{-}F}$ = 273.1 Hz, 2xC), 122.5 (sept, $J_{C\text{-}F}$ = 3.7 Hz), 80.4, 56.8, 51.2, 28.3, 23.5.

^{19}F NMR δ -62.90.

HRMS (TOF-ESI+): calculated for $C_{22}H_{24}F_6NO_3S$ $[M+H]^+$: 496.1376; found: 496.1356.

***tert*-Butyl (2-(2-(*p*-tolylsulfinyl)ethyl)phenyl)carbamate** (**8f**)



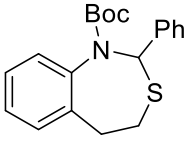
Following the general procedure, from *tert*-butyl (2-vinylphenyl)carbamate (22 mg, 0.1 mmol) and 4-methylthiophenol (37.3 mg, 0.3 mmol) in DCM, after 72 hours at rt, compound **8f** was obtained in 52% yield (18.5 mg, 0.051 mmol) as a yellow oil. The crude product was purified by flash column chromatography on silica gel (2/1: chex/ethyl acetate).

^{1}H NMR δ 7.73 – 7.64 (m, 1H), 7.54 – 7.46 (m, 2H), 7.35 – 7.28 (m, 2H), 7.24 – 7.17 (m, 1H), 7.11 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.04 (td, *J* = 7.4, 1.3 Hz, 1H), 3.18 – 2.94 (m, 3H), 2.91 – 2.78 (m, 1H), 2.41 (s, 3H), 1.53 (s, 9H).

^{13}C NMR δ 153.8, 141.6, 139.7, 136.1, 130.0, 129.8, 129.6, 127.7, 124.6, 124.0, 123.9, 80.3, 56.5, 28.4, 23.5, 21.4.

HRMS (TOF-ESI+): calculated for $C_{20}H_{26}NO_3S[M+H]^+$: 360.1628; found: 360.1642.

6.- Synthesis of *tert*-Butyl 2-phenyl-4,5-dihydrobenzo[*d*][1,3]thiazepine-1(2*H*)-carboxylate (**9**)



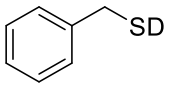
To a solution of sulfoxide **8a** (62.5 mg, 0.2 mmol) in anhydrous toluene (3 mL), under argon atmosphere and at -37 ºC, trifluoroacetic anhydride (55.2 µL, 0.4 mmol) and 2,6-lutidine (69.6 µL, 0.6 mmol) were added. The reaction mixture was stirred for 1 hour at -37 ºC. The crude product was purified by flash column chromatography on Iatrobeads silica gel (5/1: chex/ethyl acetate) and compound **9** was obtained in 71% yield (48.5 mg, 0.14 mmol) as a yellow oil.

^{1}H NMR δ 7.74 – 7.65 (m, 1H), 7.41 – 7.16 (m, 4H), 7.14 – 7.00 (m, 3H), 6.65 (s, 1H), 4.68 (s, 1H), 2.94 – 2.62 (m, 4H), 1.51 (s, 9H).

^{13}C NMR δ 153.8, 140.2, 136.3, 131.4, 130.1, 129.0, 128.5, 128.0, 127.7, 124.8, 123.5, 80.8, 54.3, 32.5, 32.3, 28.7.

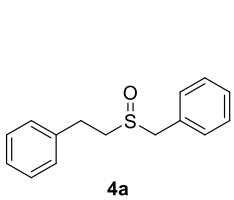
HRMS (TOF-ESI+): calculated for $C_{20}H_{23}NO_2S$ $[M+H]^+$: 342.1522; found: 342.1526.

7.- Synthesis of phenylmethanethiol-*d*

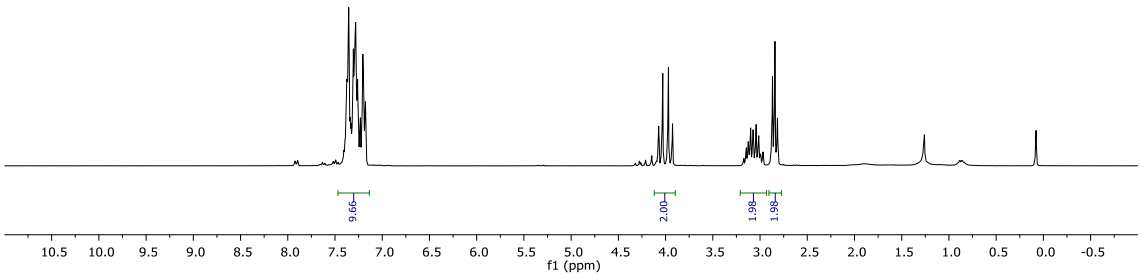


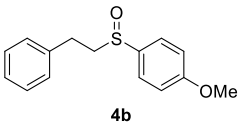
To a 1 eq. of benzylthiol, 10 eq. of CD_3OD were added. The reaction mixture was stirred overnight at room temperature. The solvent was evaporated to obtain the deuterated thiol in a 70%.

8.- NMR spectra

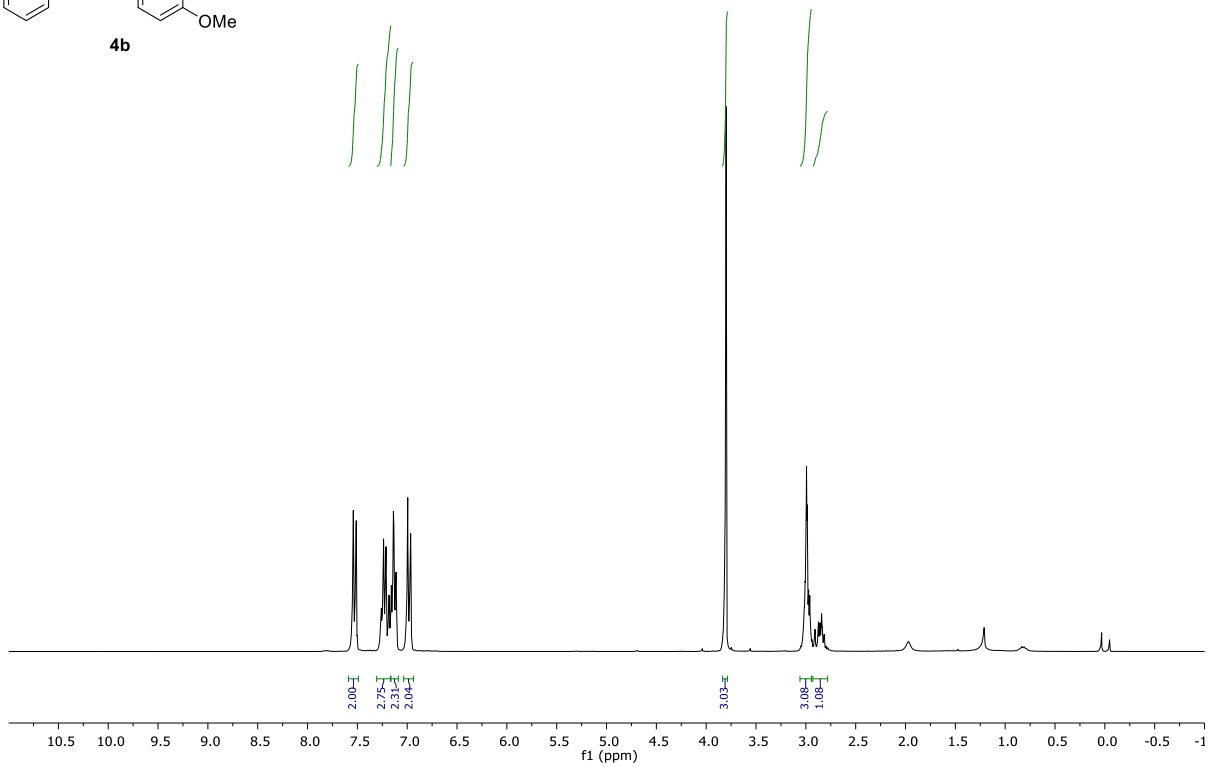


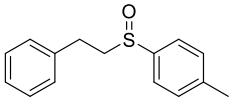
4a



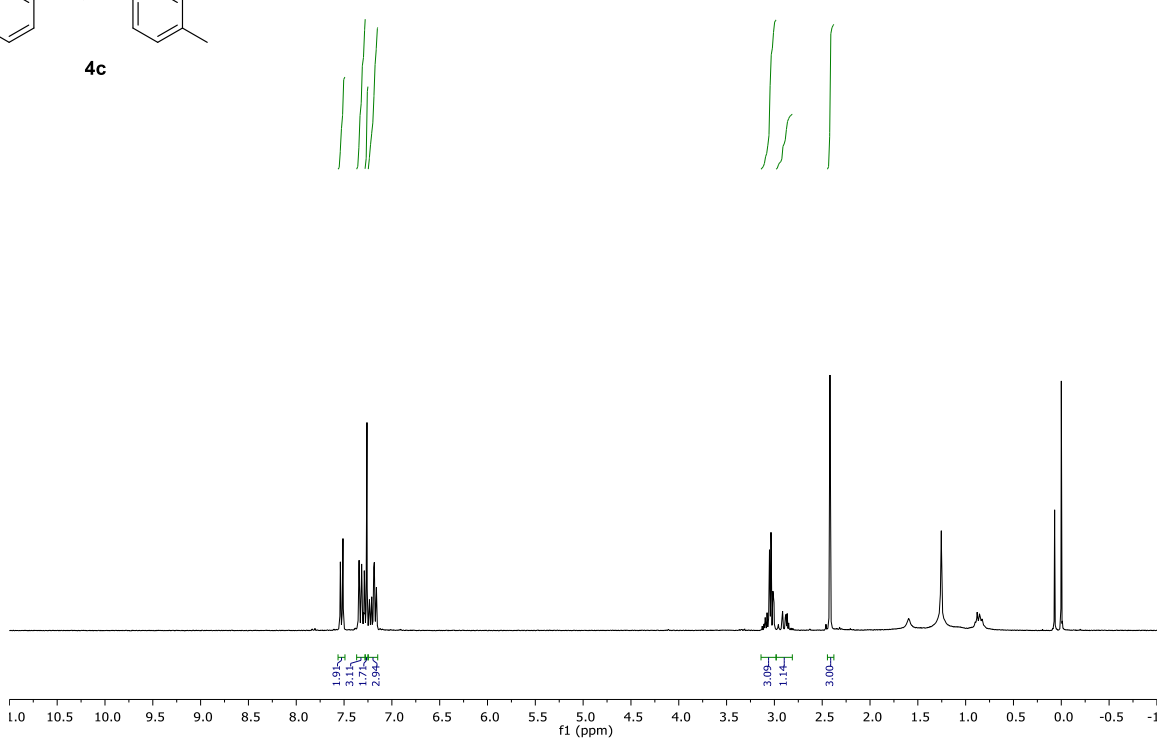


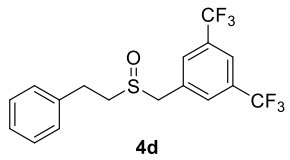
4b





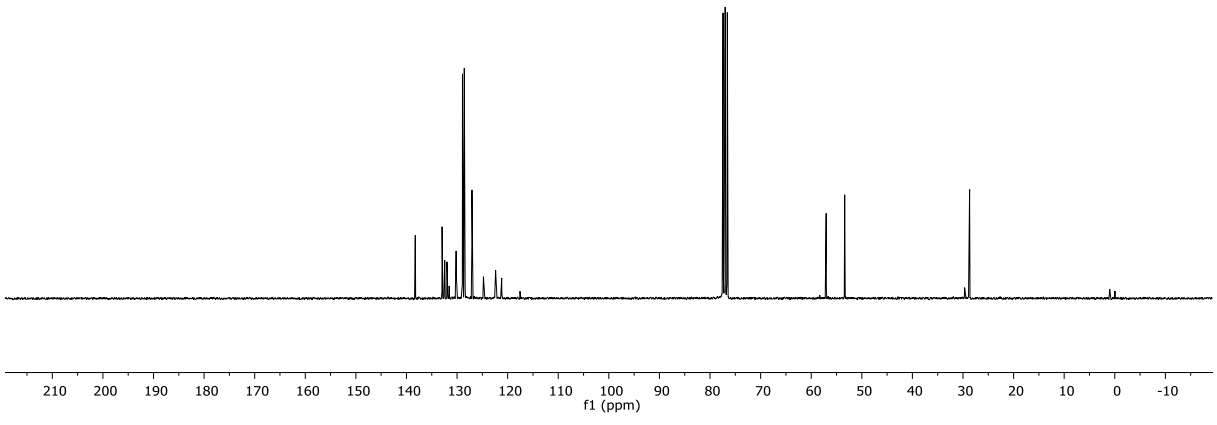
4c




CF3
O
S
CF3

4d

1.00
1.99
2.03
3.19
1.06
1.06
2.19
2.10
1.0 10.5 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
f1 (ppm)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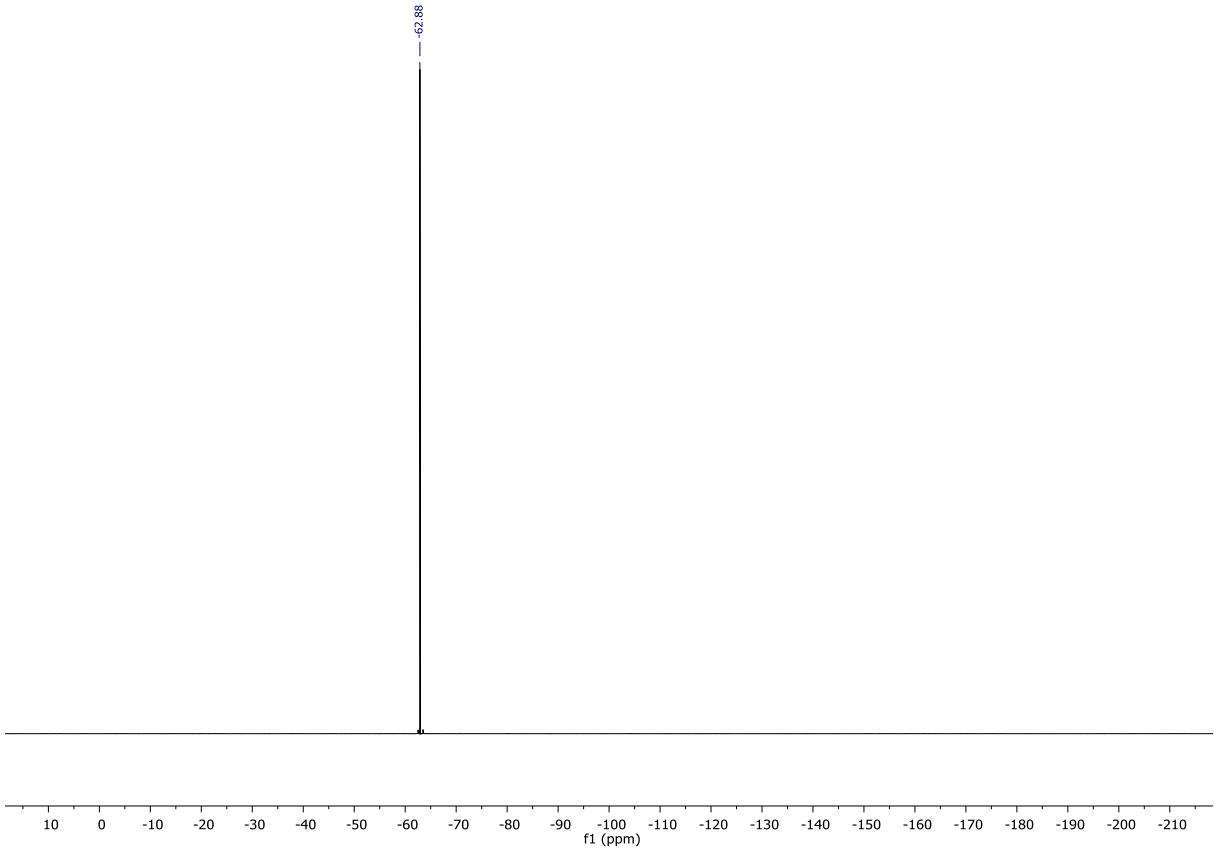
f1 (ppm)


-62.88
10
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-170
-180
-190
-200
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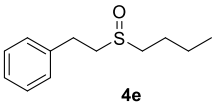
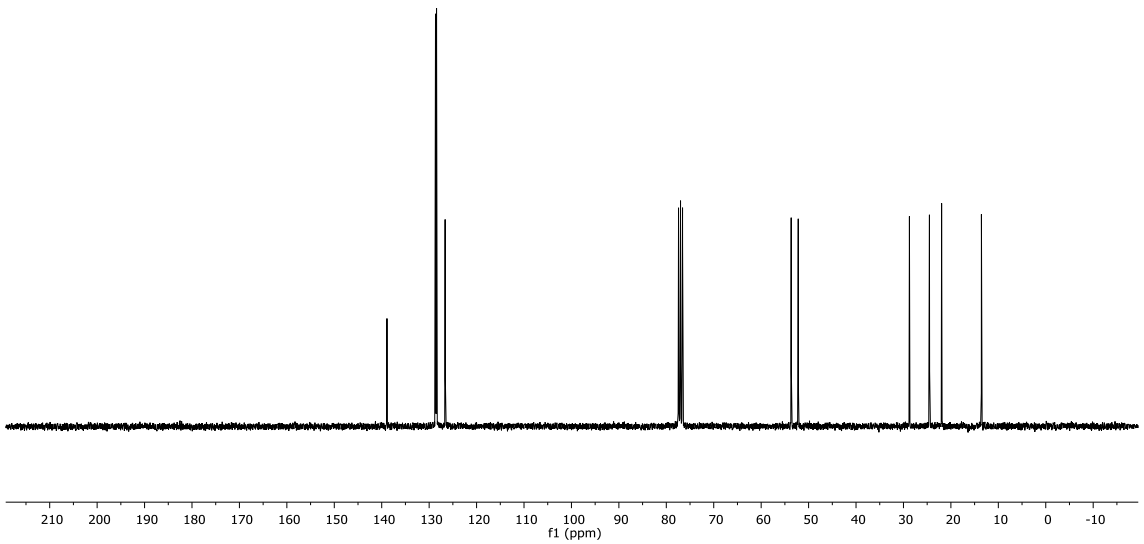
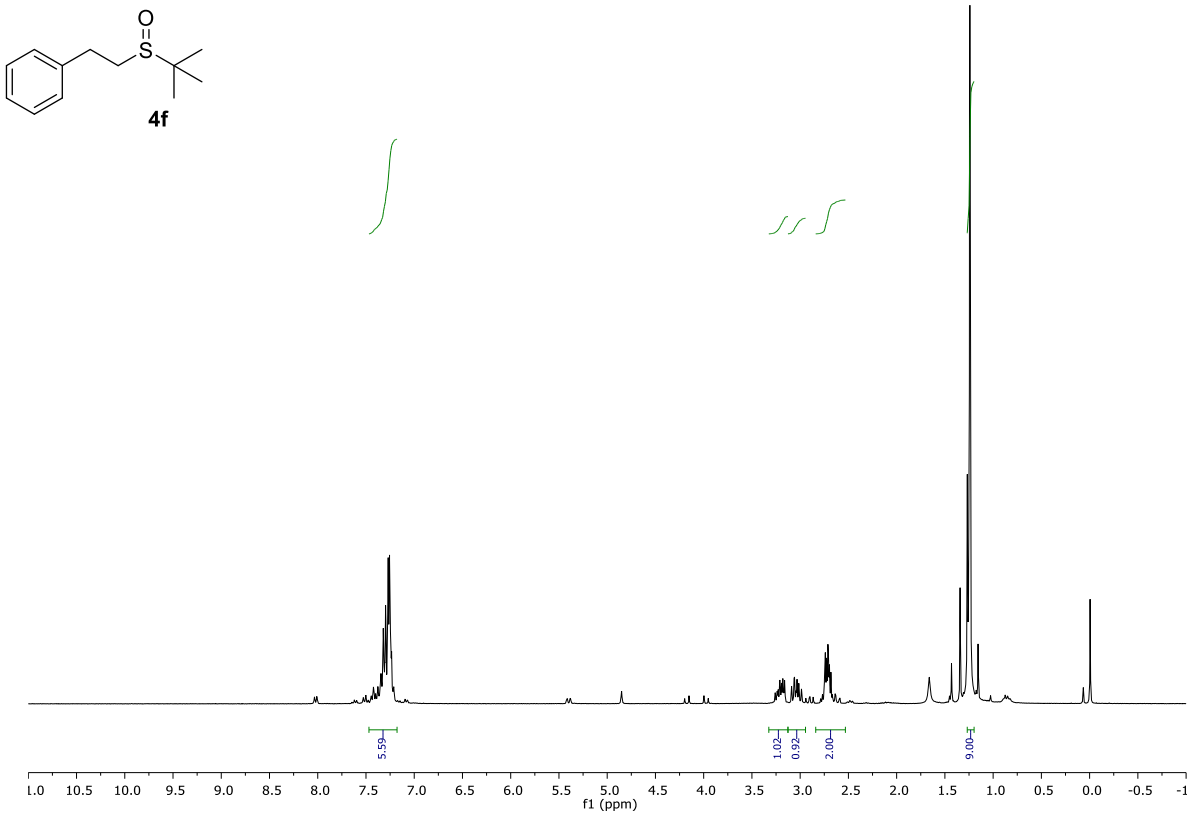
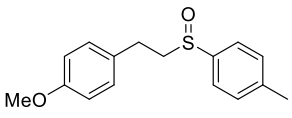
f1 (ppm)



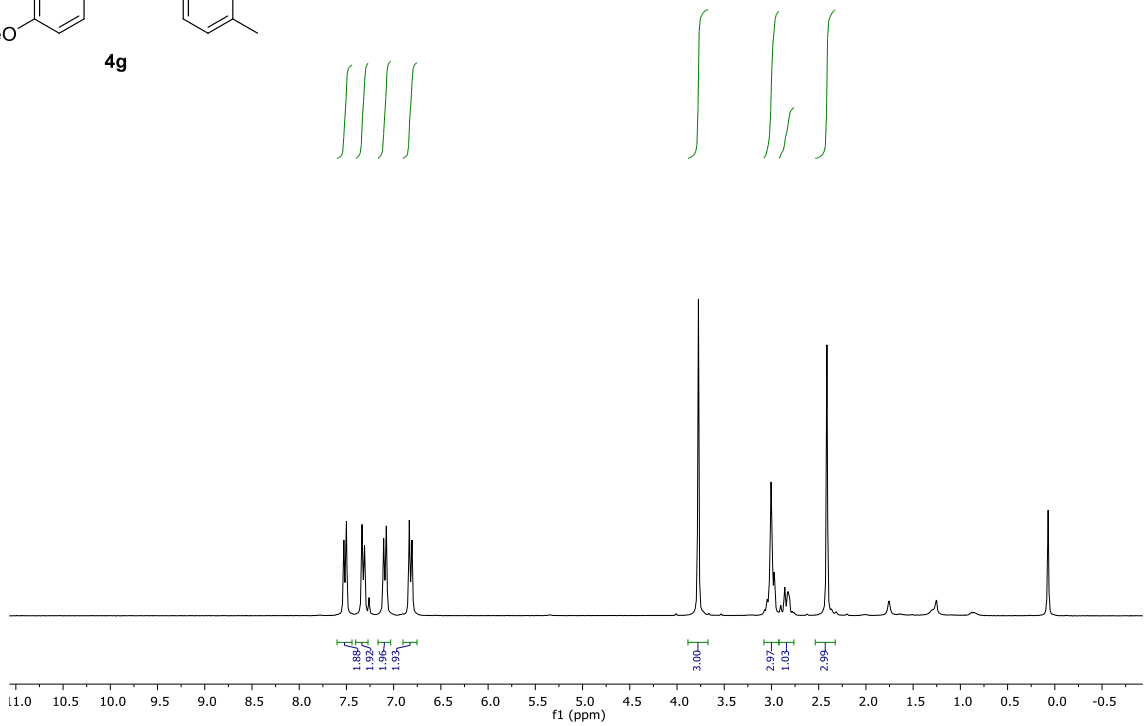
4e

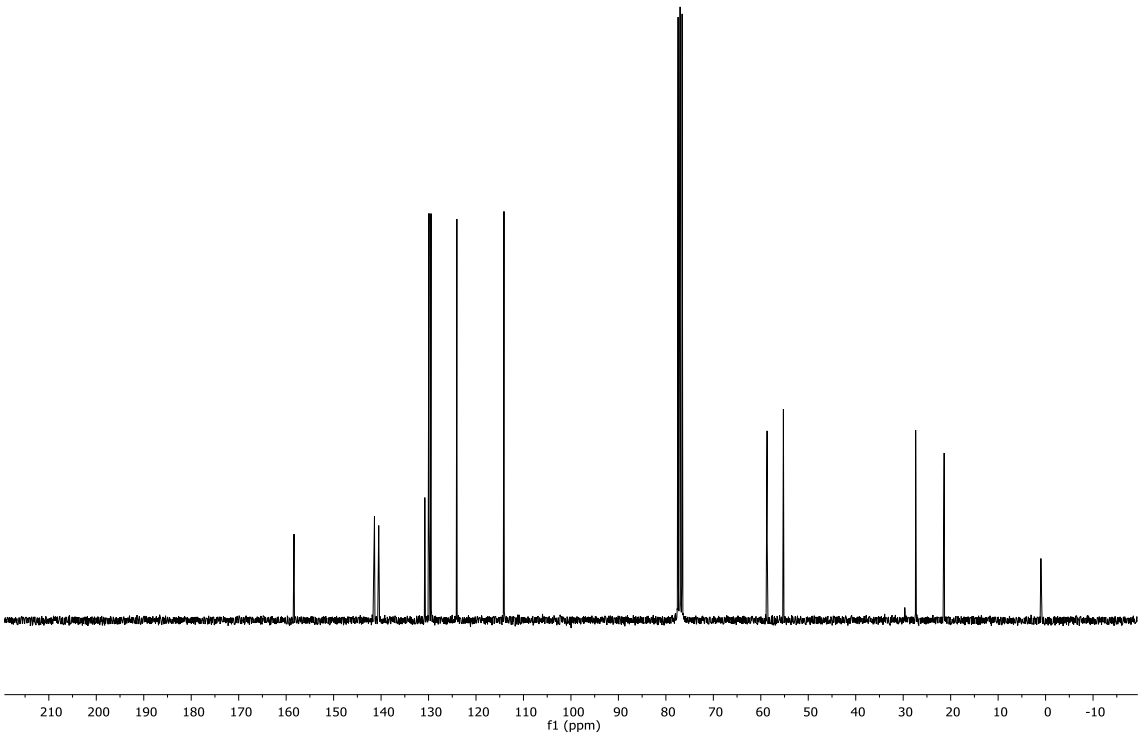


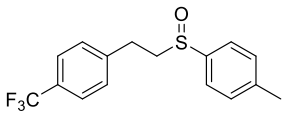

O
S
4f
5.59
1.02
0.92
2.00
9.00
f1 (ppm)


O
S
MeO

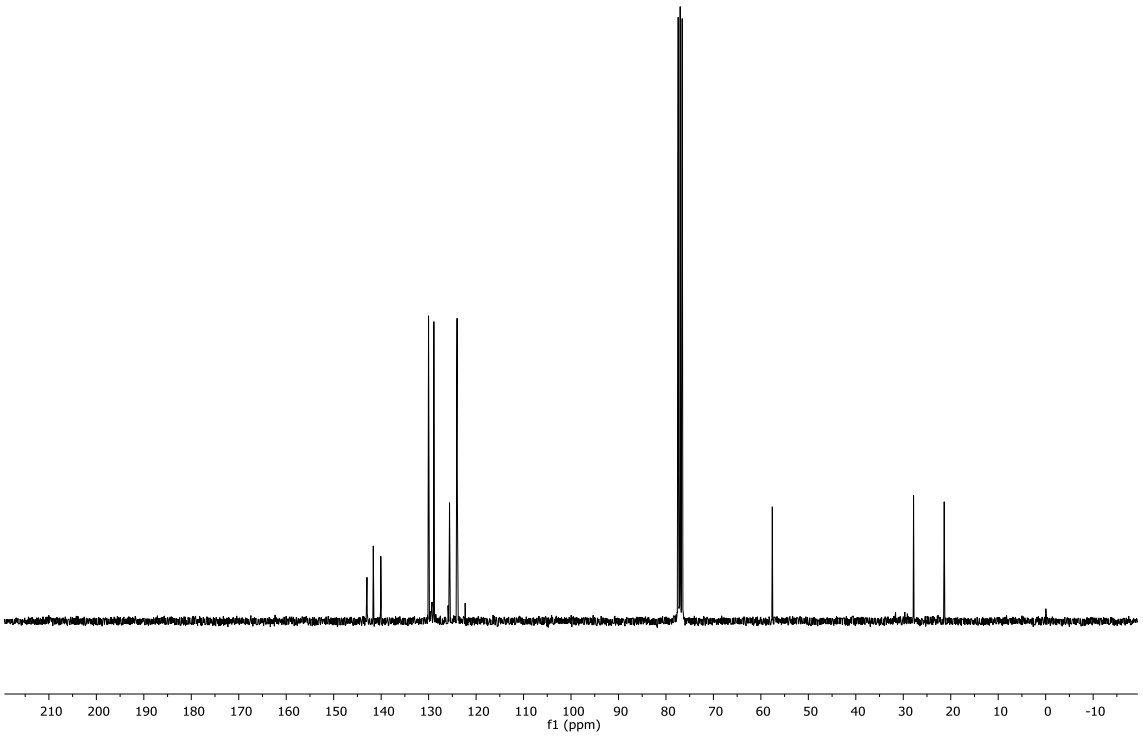
4g

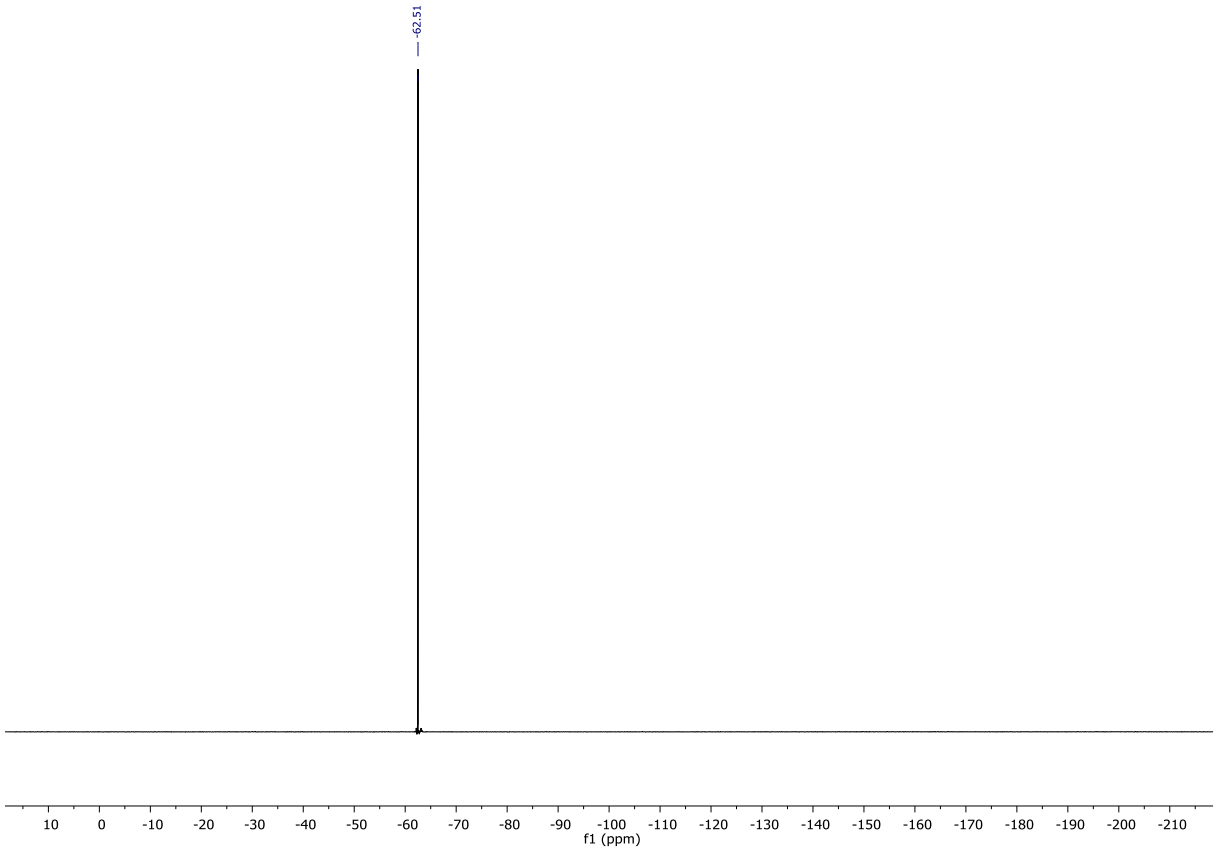

1.89
1.92
1.96
1.93
3.00
2.97
1.03
2.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

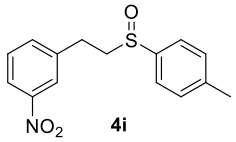

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



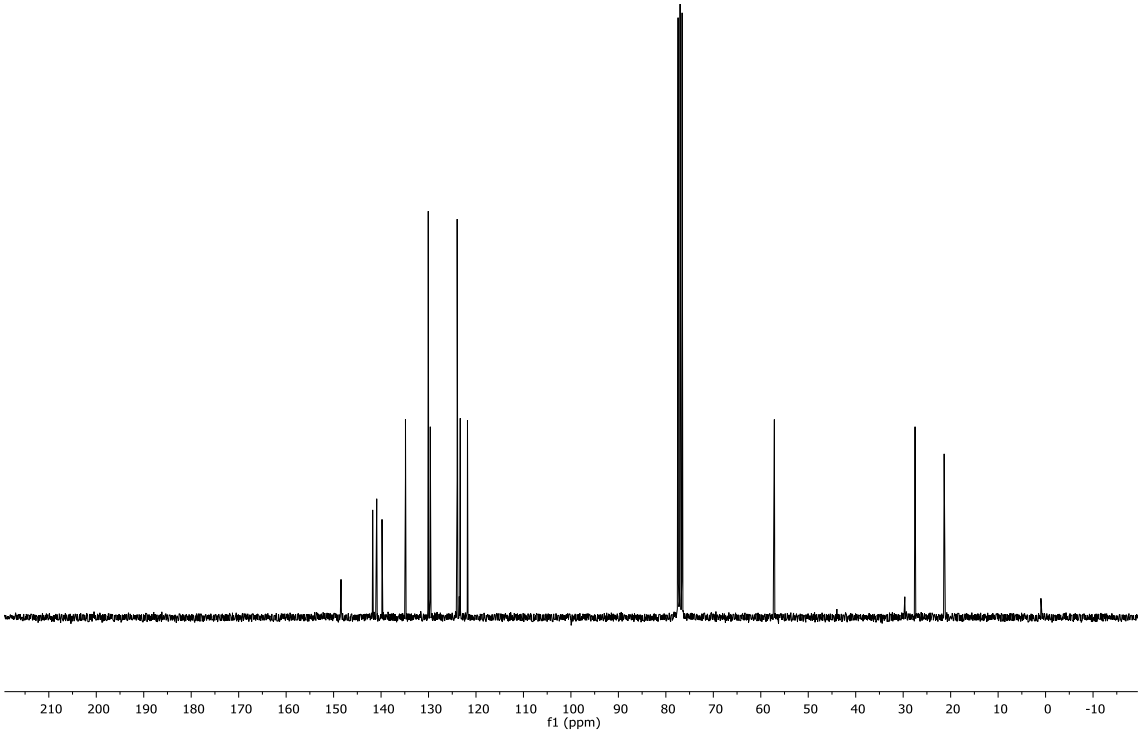
4h

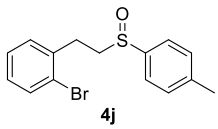



-62.51
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

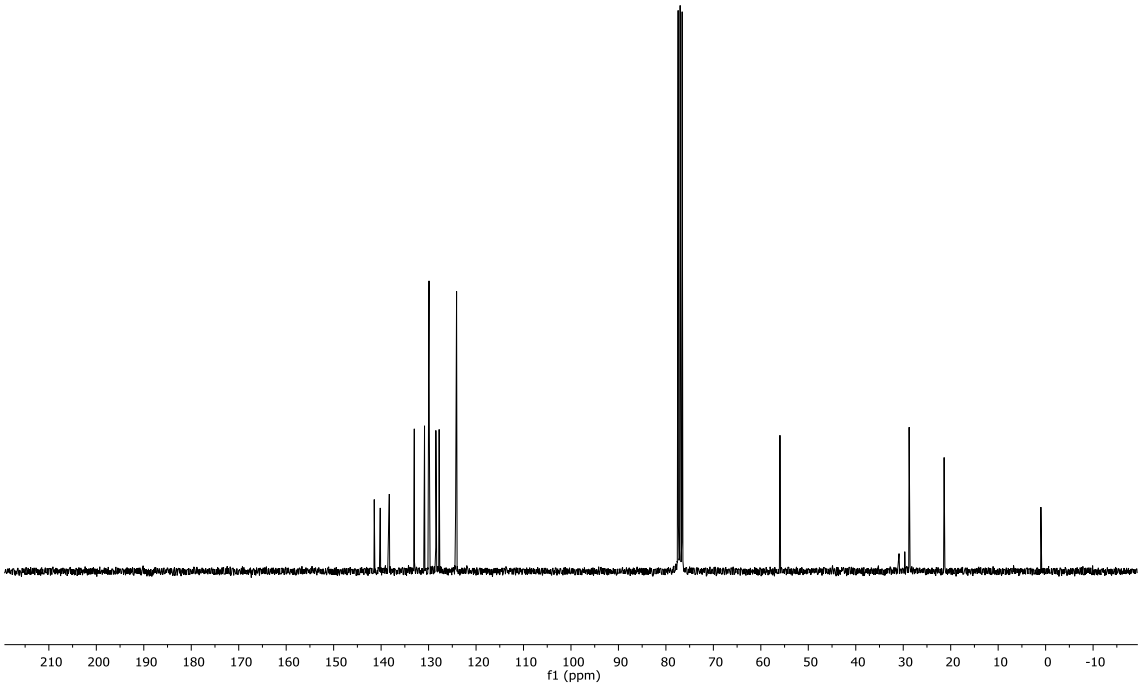


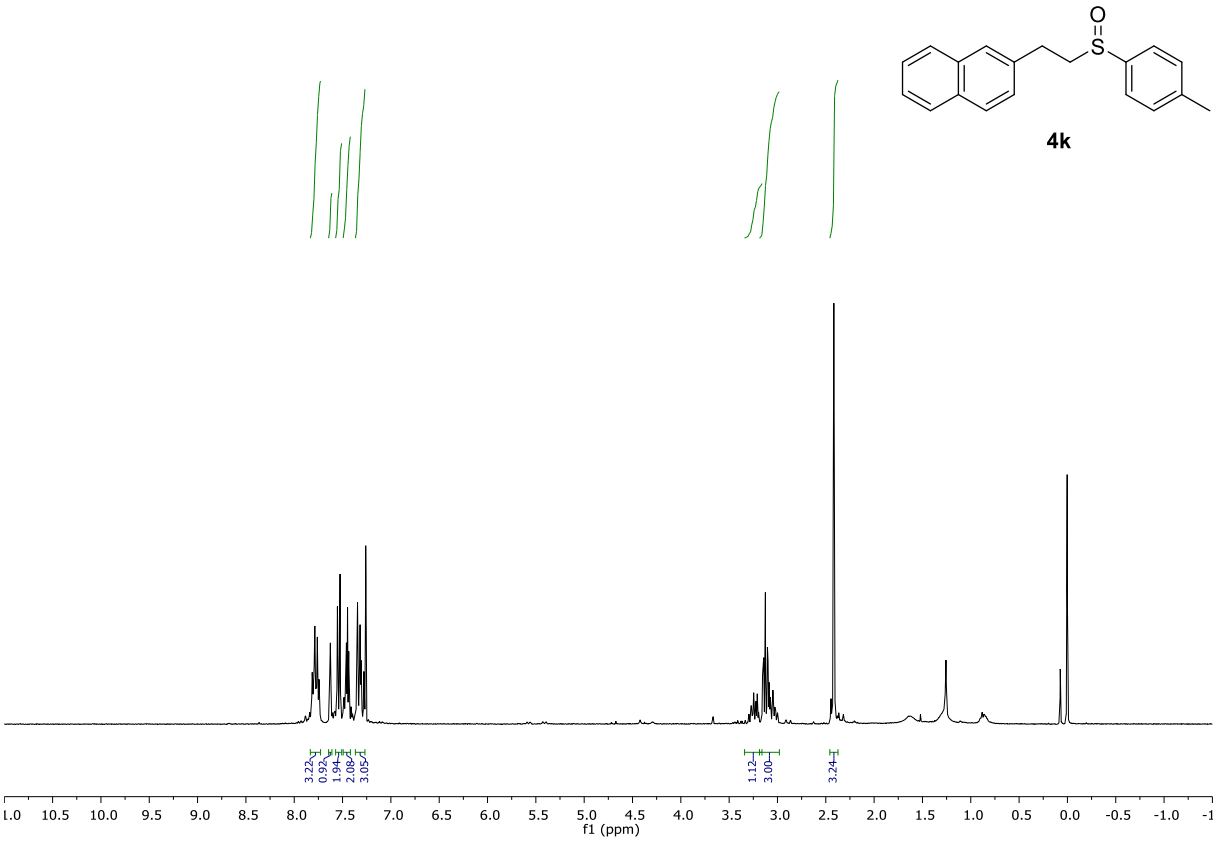
4i

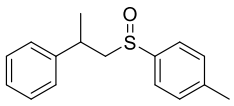




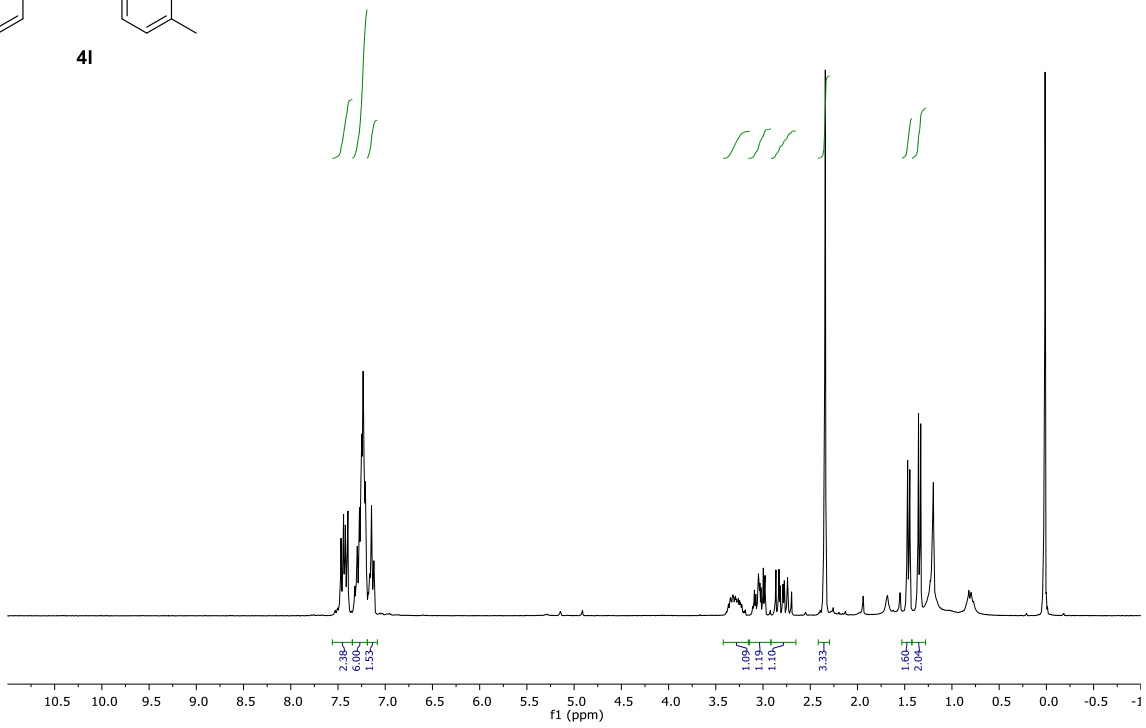
4j

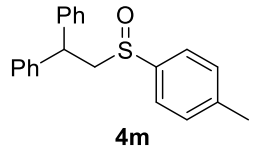



O
S
4k
3.22
0.92
1.94
2.08
3.05
1.12
3.00
3.24
f1 (ppm)

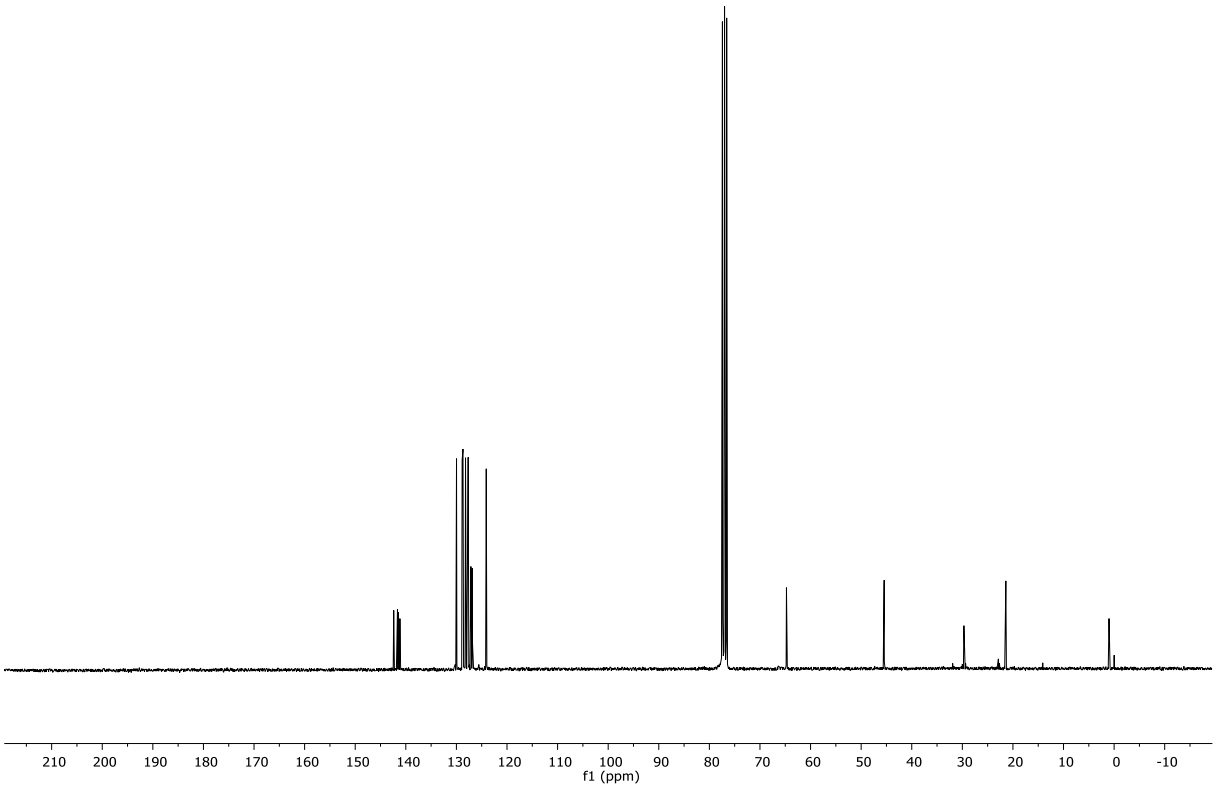


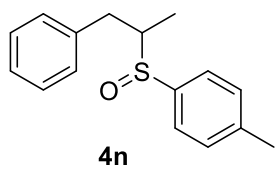
4l


2.38
6.00
1.53
1.09
1.19
1.10
3.33
1.60
2.04
10.5 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
f1 (ppm)

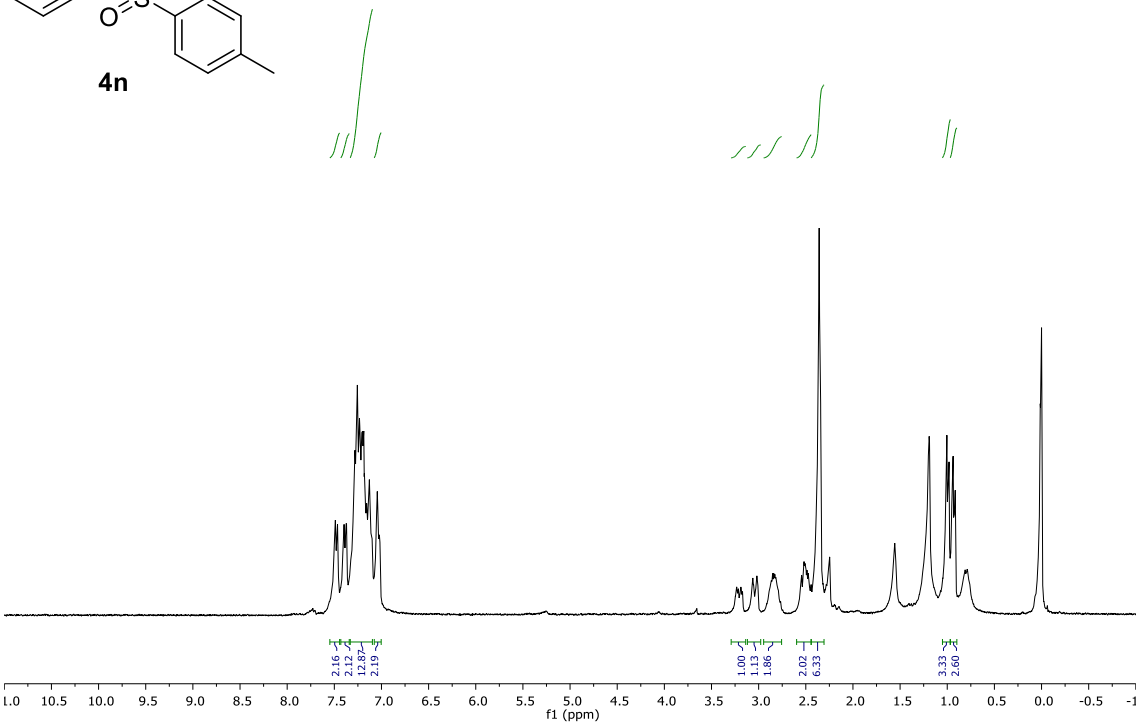


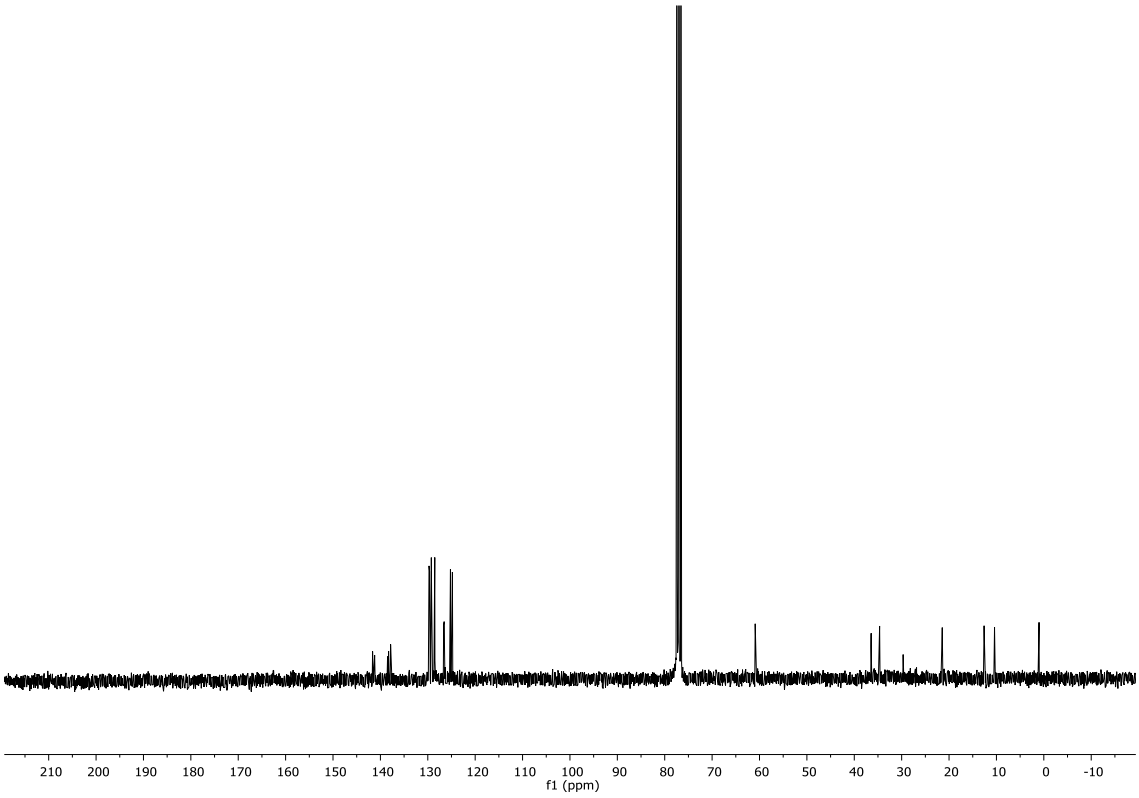
4m

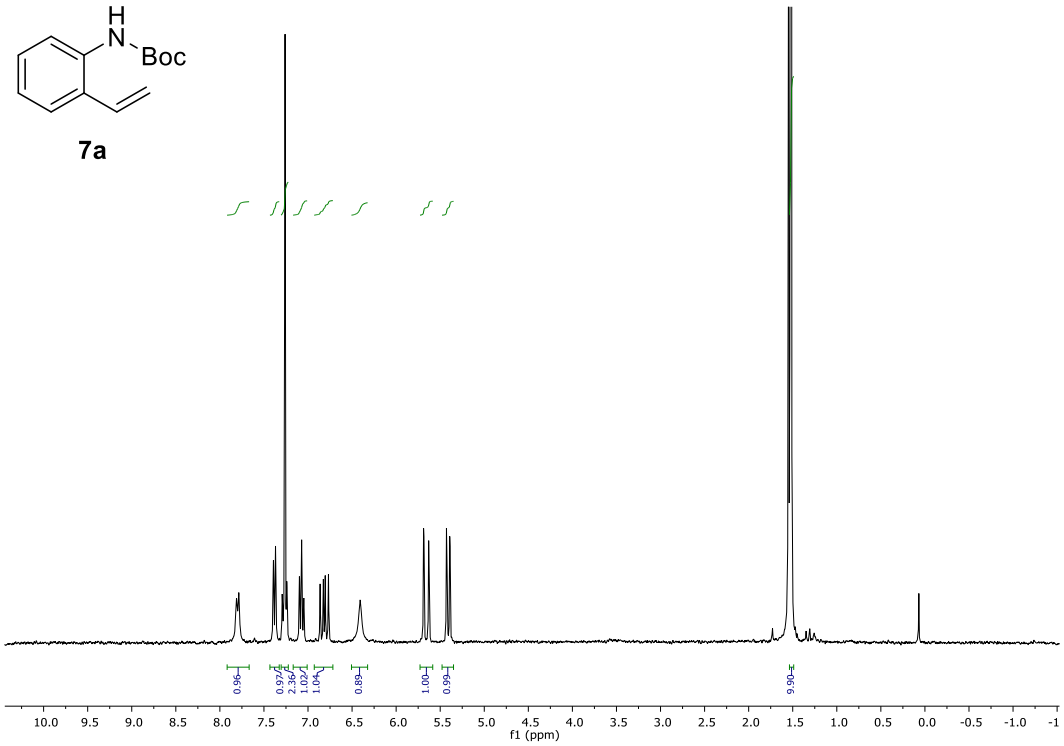




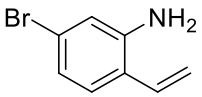
4n

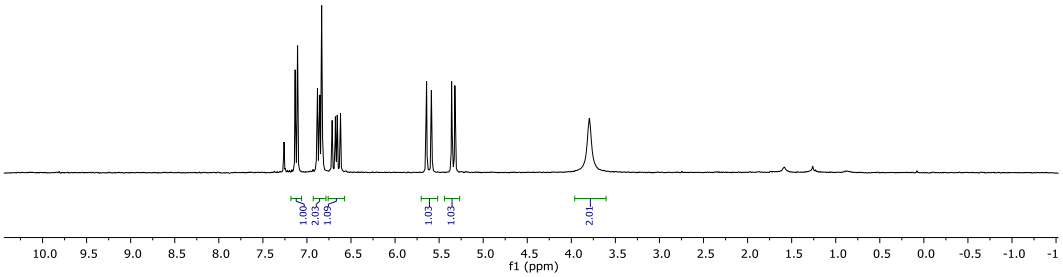


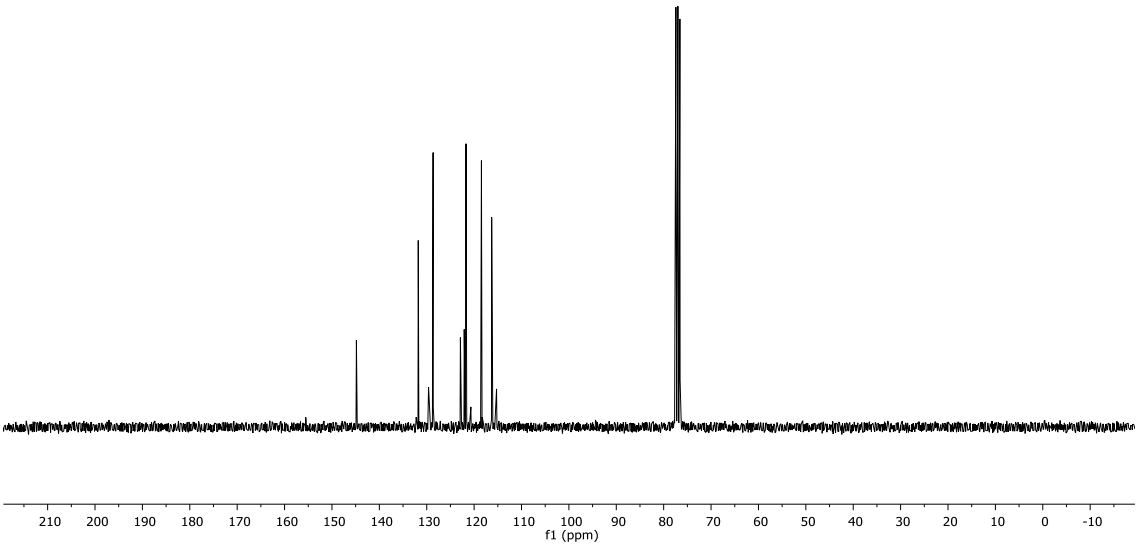


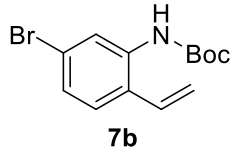

H
N
Boc
0.96
0.97
2.36
1.02
1.04
0.89
1.00
0.99
9.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

7a


Br
NH2

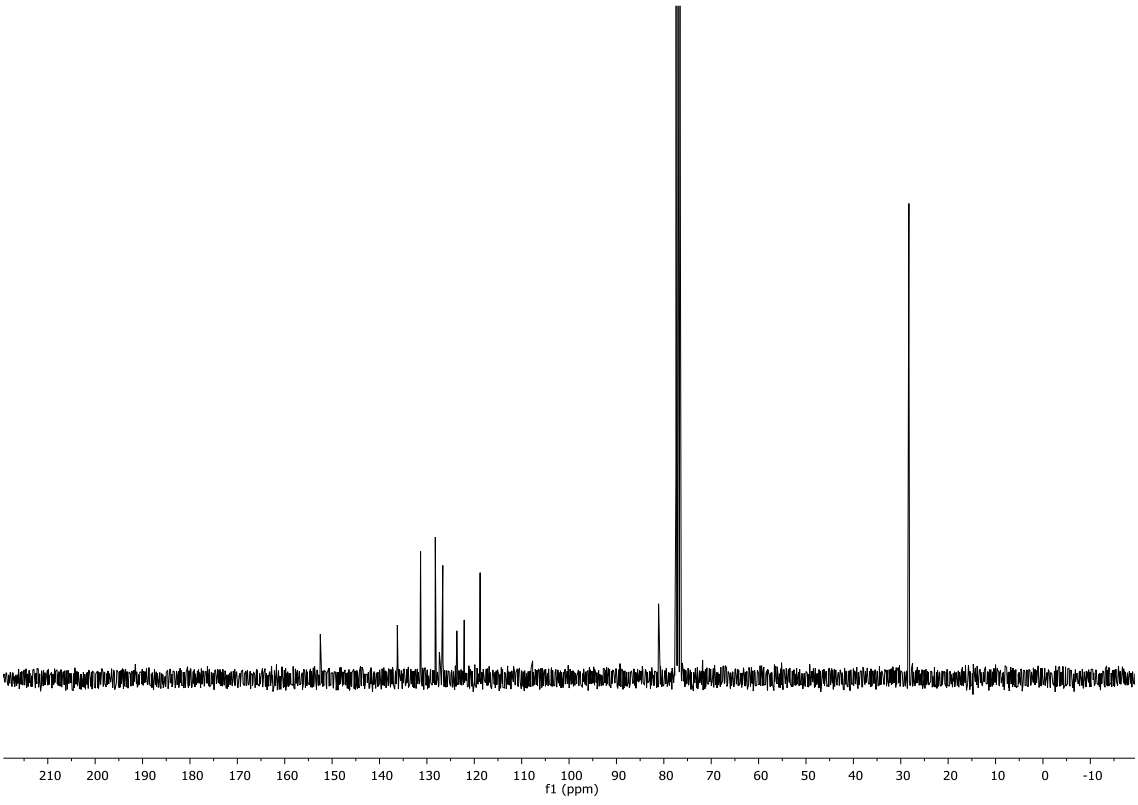

1.00
2.03
1.09
1.03
1.03
2.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

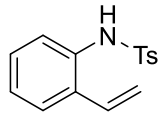

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Br
H
N
Boc

7b

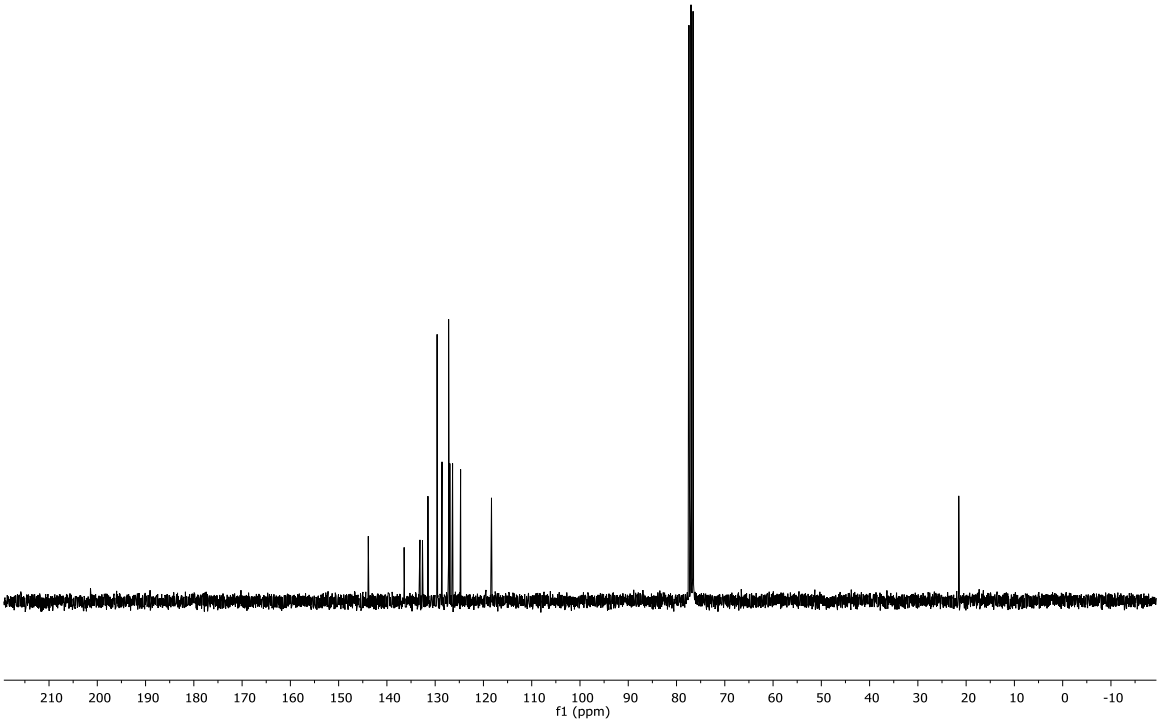
0.90
1.87
1.00
0.94
1.01
0.98
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

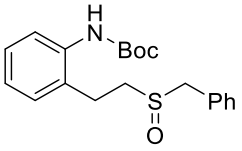

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
N
Ts

7c

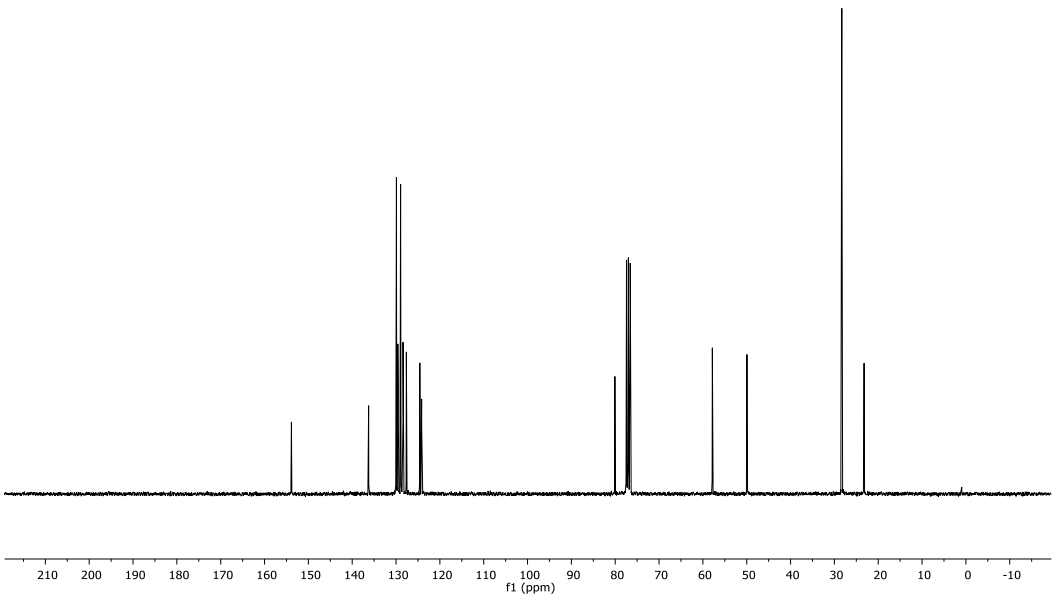
2.00
2.01
4.05
0.80
1.04
1.03
1.02
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

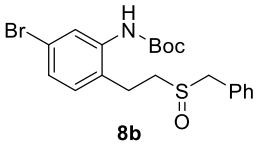

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
N
Boc
S
O
Ph

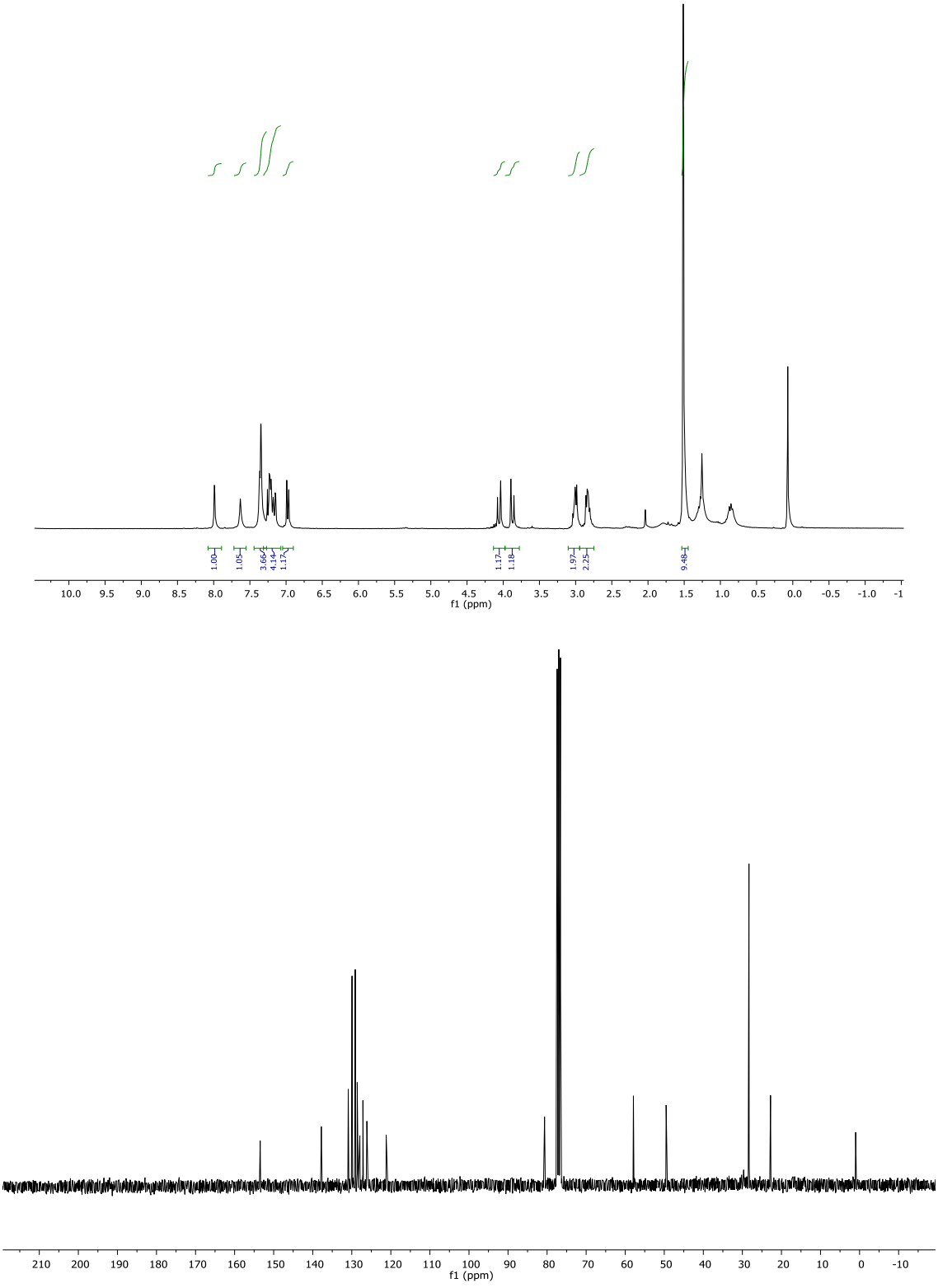
8a

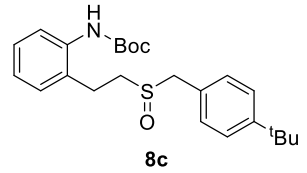
1.00
1.15
3.57
3.52
1.22
0.98
1.05
1.06
2.15
2.10
9.68
f1 (ppm)


f1 (ppm)


Br
H
N
Boc
S
O
Ph

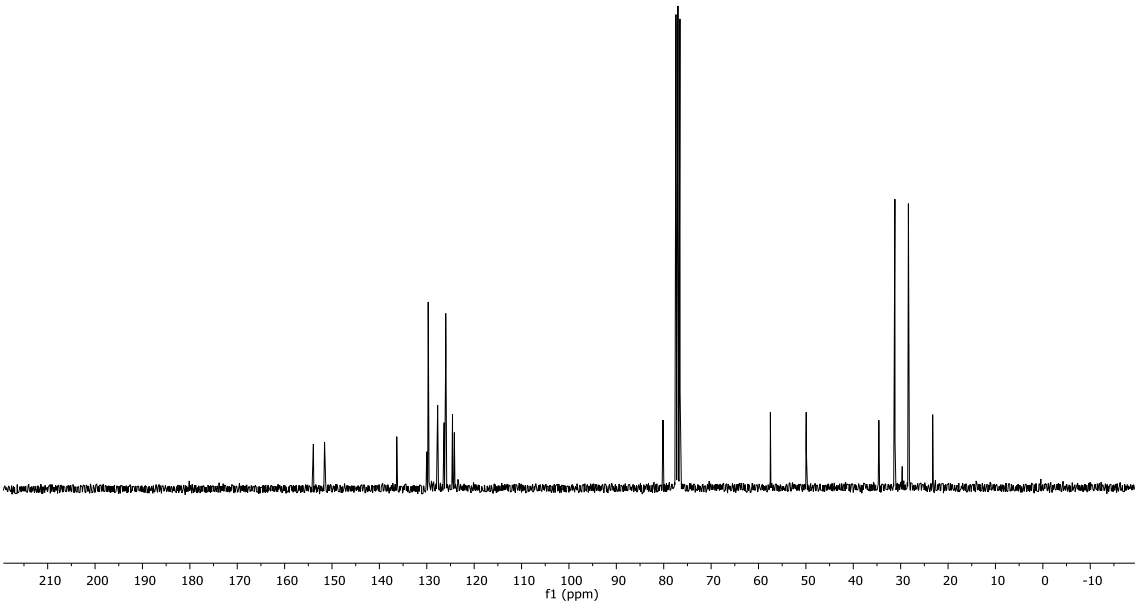
8b

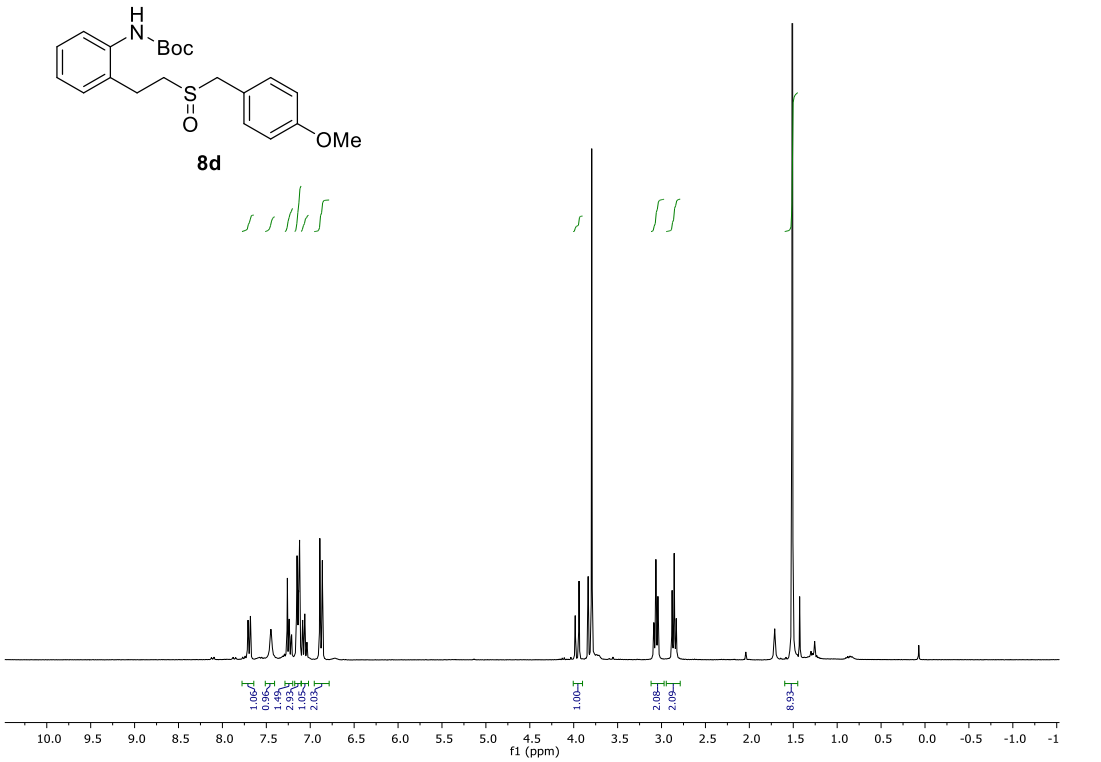

1.00
1.05
3.66
4.14
1.17
1.17
1.18
1.97
2.25
9.48
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
N
Boc
S
O
tBu

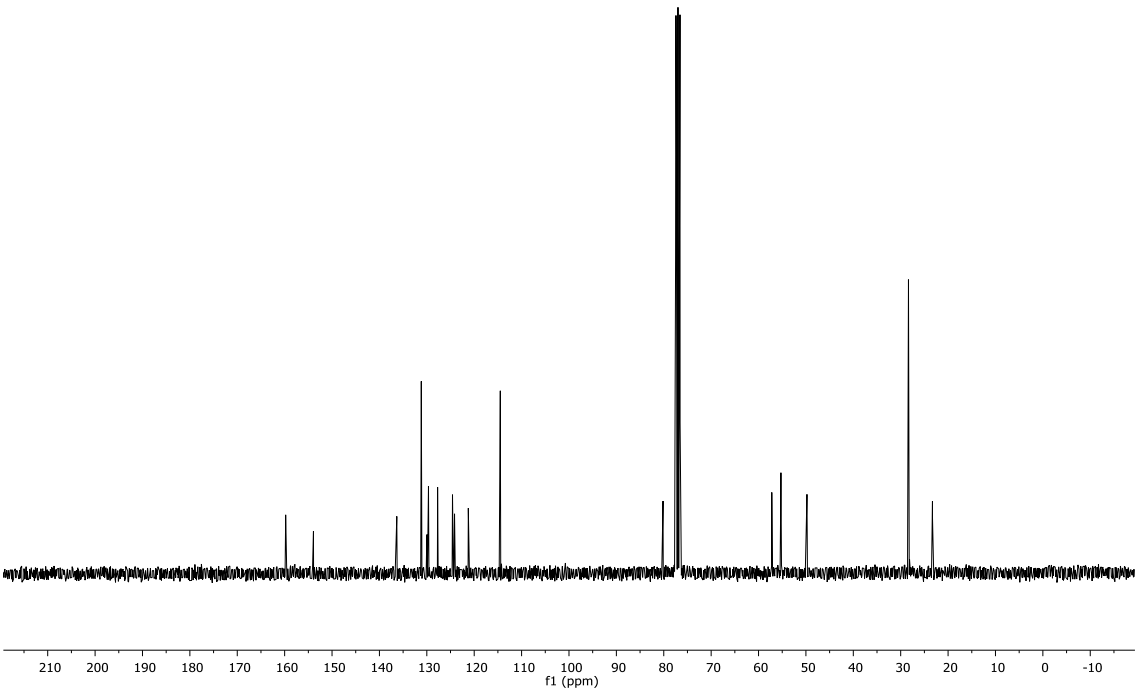
8c

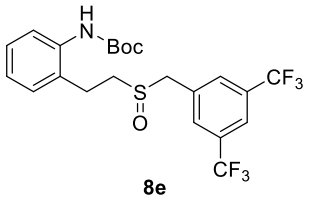
1.00
0.91
2.13
3.20
2.89
1.08
1.03
1.05
1.93
1.99
9.03
9.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
N
Boc
S
O
OMe
1.06
0.96
1.49
2.93
1.05
2.03
1.00
2.08
2.09
8.93
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 -1
f1 (ppm)

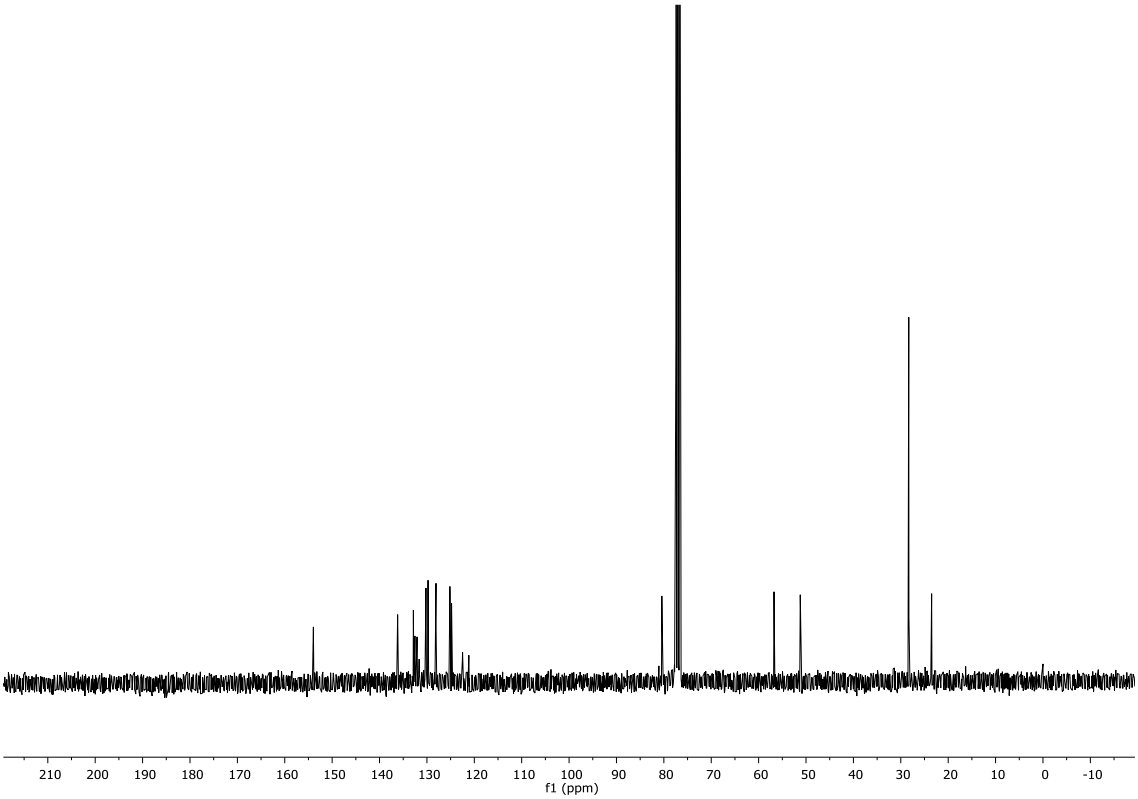
8d

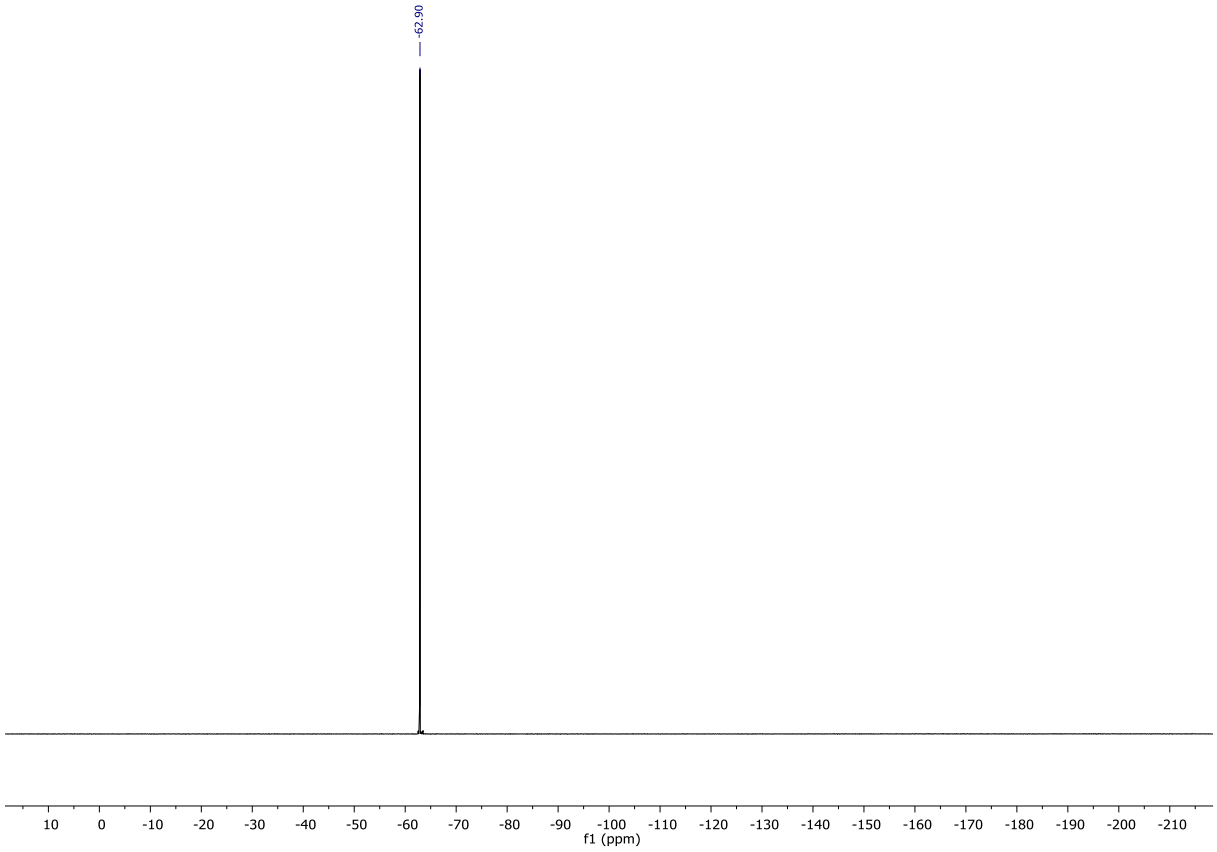

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

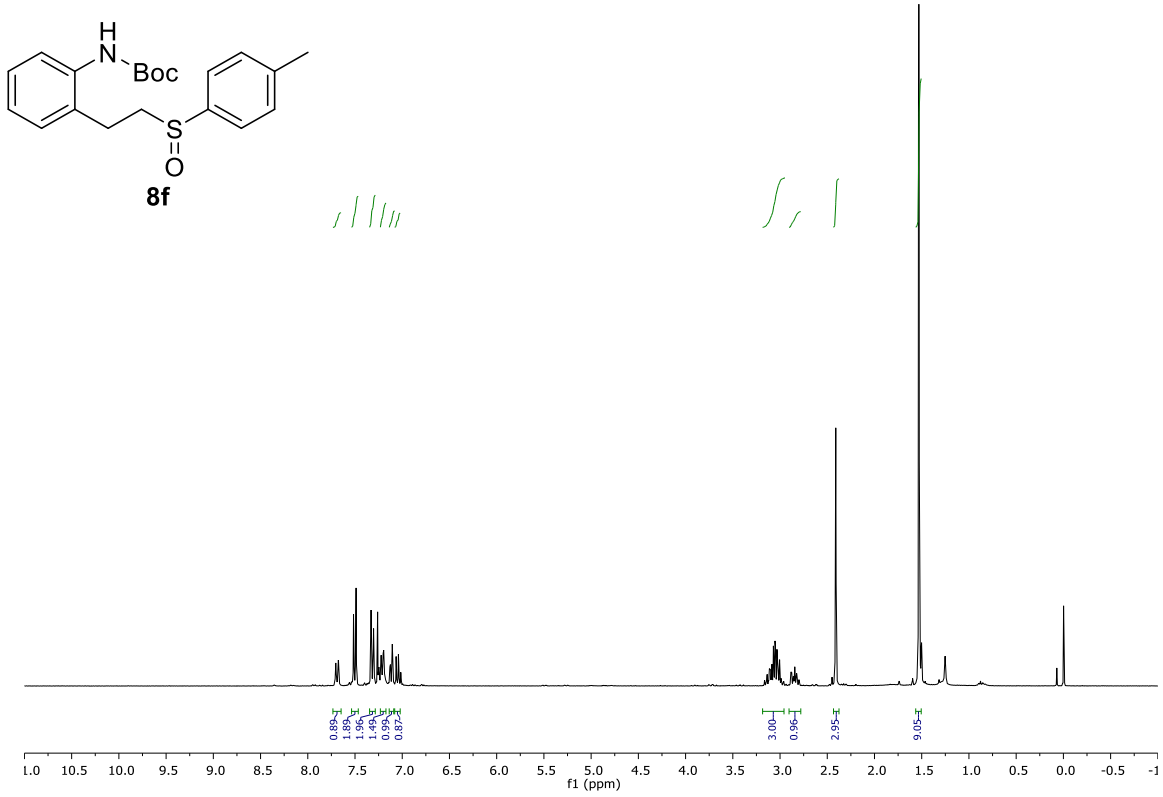

H
N
Boc
S
O
CF3
CF3

8e

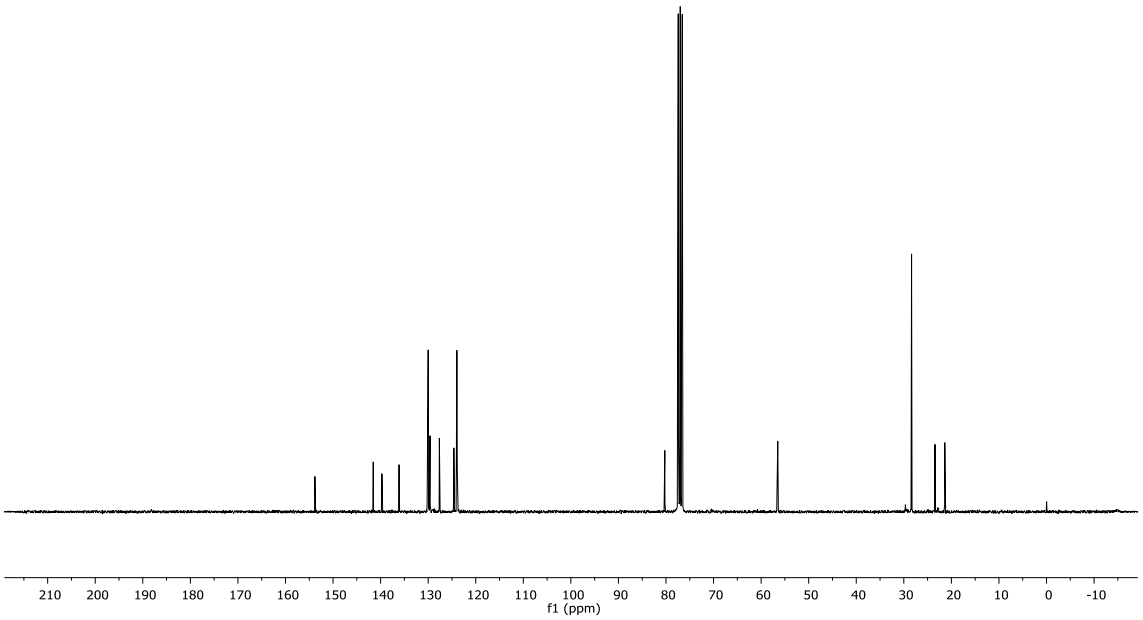
1.11
2.03
1.22
3.84
1.17
2.00
4.22
10.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1
f1 (ppm)

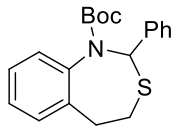

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.90
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

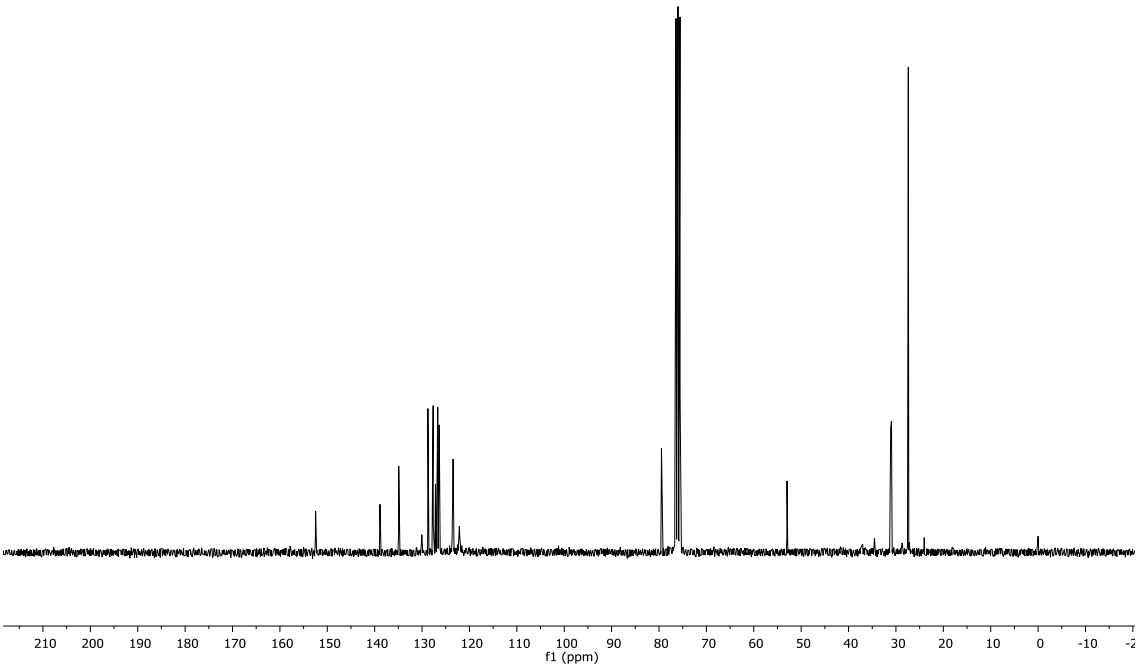


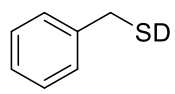
8f

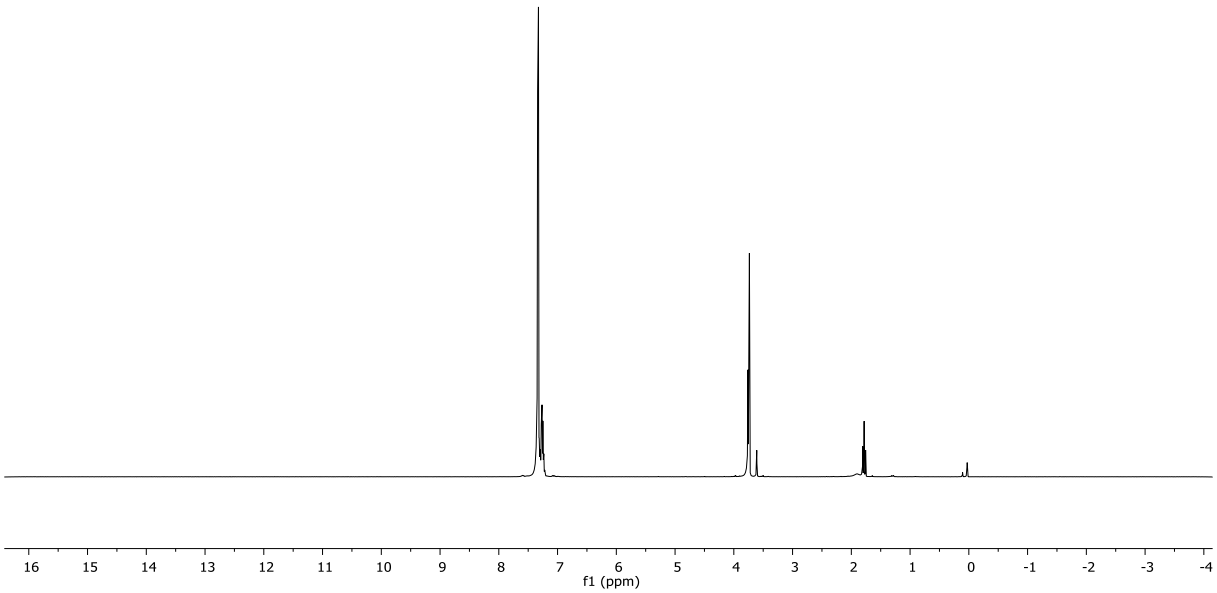




9




SD


16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
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-1
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-3
-4
f1 (ppm)

9.- Quantum Yield Measurement.

We first measured the LED source spectrum detecting a maximum wavelength of emission of 516 nm (**Figure S1**).

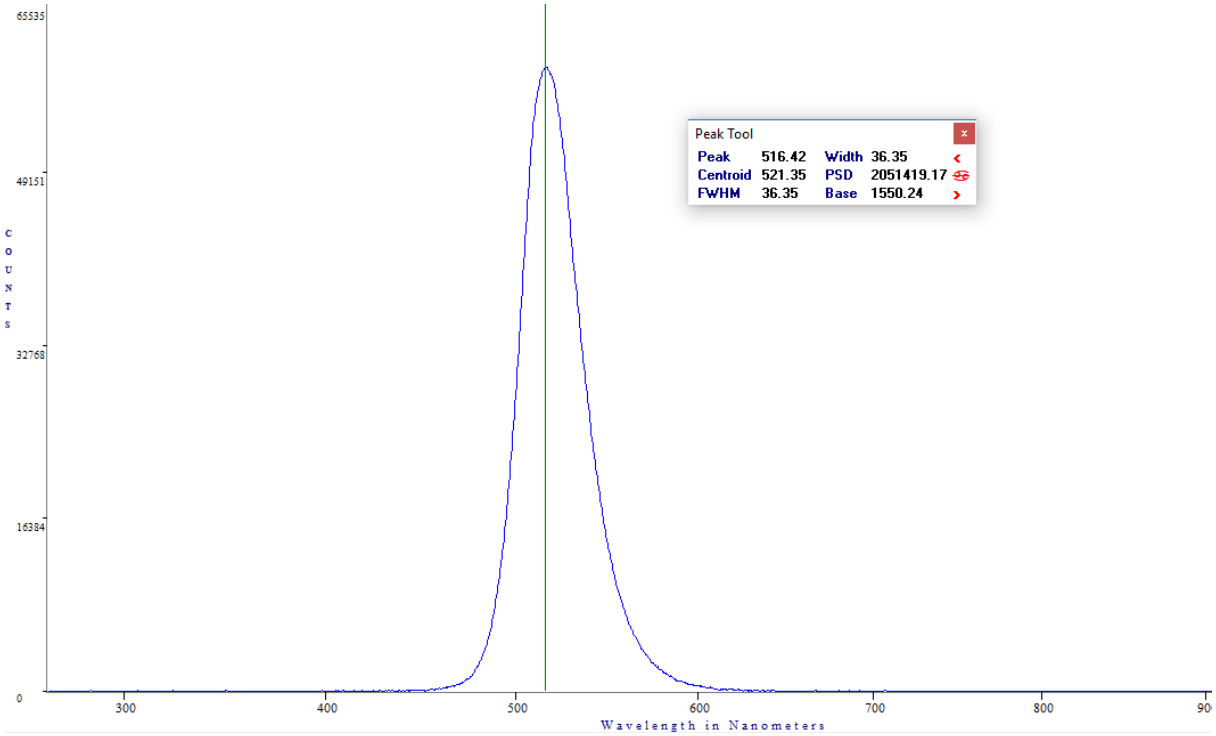


Figure S1. Emission spectrum of the green LED of the photochemical system (λ_{max}=516 nm).

According to the emission of our LED source, a solution of potassium ferrioxalate was possible to be used as actinometer following the procedure described by the IUPAC (subcommittee in photochemistry)[5]. The procedure is based on the decomposition under irradiation of ferric to ferrous ions, which can be complexed by 1,10-phenanthroline. This photochemical transformation has a known quantum yield and the complexation of Fe^{2+} with 1,10-phenanthroline can be monitored by UV-Visible absorption since its extinction coefficient at 510 nm is also known (ε =11100 $M^{-1}\cdot cm^{-1}$). Thus, the transformed moles can be related with the moles of photons absorbed by the equation 1:

$$\phi = \frac{\text{transformed moles}}{\text{absorbed photons}} \qquad eq.1$$

First, green crystals of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$ were prepared according to the following procedure: 55.0 g of potassium oxalate monohydrate were dissolved in 80 mL of water at 90 ºC. Then, 16.2 g of $FeCl_3$ were added to the solution and it was stirred for 10 min while cooling to room temperature. The precipitate was filtered and recrystallized in water obtaining the final product in 50% yield.

The experimental data for the quantum yield of the potassium ferrioxalate solution found close to 516 nm is 0.86[6] at 512 nm for 0.15 M. Therefore, the solutions were prepared as follows and stored in a dark place:

[5] H. J. Kuhn, S. E. Braslavsky, R. Schmidt, *Pure Appl. Chem*. **2004**, *76*, 2105.
[6] Murov, S.L., Carmichael, I., Hug, G.L. *Chemical Actinometry*. *Handbook of Photochemistry*, *2nd Edition*, **1993**.

- Potassium ferrioxalate solution 0.15 M: 0.66 g of $K_3[Fe(C_2O_4)]\cdot 3H_2O$ and 420 µL of H_2SO_4 were added into a 10 mL volumetric flask and filled to the mark with MilliQ water.

- 1,10-phenanthroline 0.01 M: 200 mg of 1,10-phenantroline monohydrate were added to 100 mL volumetric flask and filled to the mark with MilliQ water.

- Buffer solution: 4.94 g of NaOAc and 1 mL of H_2SO_4 were added to 100 mL volumetric flask and filled to the mark with MilliQ water

- Model reaction solution for cycle I: The photocatalyst Eosin Y **3h** (3.2 mg, 0.0050 mmol) was placed in a vial, followed by 2-bromostyrene **1j** (26 µL, 0.2 mmol) and 4-methylbenzenethiol (0.075 g, 0.6 mmol) in 720 µL of CH_2Cl_2. The mixture was degassed by "vacuum-argon" cycles (x3).

- Model reaction solution for cycle II: The photocatalyst Eosin Y **3h** (1.6 mg, 0.0025 mmol) was placed in a vial, followed by (2-bromophenethyl)(*p*-tolyl)sulfane (30.7 mg, 0.1 mmol) in 360 µL of CH_2Cl_2. A needle was set into the vial to let the oxygen pass through the reaction mixture.

To start with the actinometry procedure, a blank sample was prepared with 0.1 mL of potassium ferrioxalate solution (0.15 M) before irradiation, 2 mL of buffer solution and 2 mL of 1,10-phenanthroline (0.01 M) in a 100 mL volumetric flask filled with water until the mark. To start the experiment, 2 mL of potassium ferrioxalate solution were introduced into the photoreactor under dark conditions while being stirred. Then, the green LED was switched on. Every 20 min the light was switched off and a 0.1 mL aliquot was taken. To each aliquot, 2 mL of buffer solution and 2 mL of 1,10-phenanthroline were added and the final volume was raised to 100 mL with MilliQ water. The absorbance spectrum of each sample was monitored at 510 nm, using an *Agilent 8453 spectrometer*. The absorbance to each time was related with the photochemically produced Fe^{2+} ions across the Lambert-Beer Law (Equation 2):

$$\text{moles } Fe^{2+} = \frac{V_1 \cdot V_3 \cdot \Delta A(510\text{ nm})}{10^3 \cdot V_2 \cdot b \cdot \varepsilon(510\text{ nm})} \qquad eq.2$$

where:

- V_1 is the irradiated volume (noting that the initial volume is 2.0 mL but it changes as the aliquots are taken)
- V_2 is the aliquot volume (0.1 mL)
- V_3 is the final volume after addition of 1,10-phenanthroline and buffer solutions (100 mL)
- *b* refers to the optical pathway (1 cm)
- ε (510 nm) is the extinction coefficient of the complex formed by Fe^{2+} and 1,10-phenanthroline (ca. 11100 $M^{-1}\cdot cm^{-1}$).

The obtained moles of Fe^{2+}(x) are plotted as a function of time (t) (**Figure S2**).

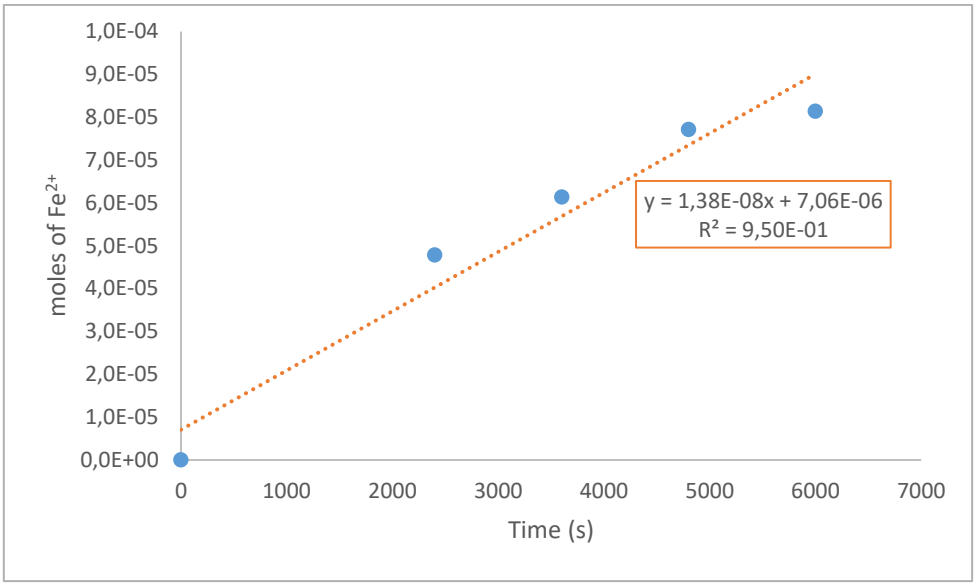


Figure S2. Plotted data of generated moles of Fe^{2+}.

The slope of this line (dx/dt) was correlated to the moles of incident photons by unit of time ($q^0_{n,p}$) using the following equation 3:

$$q^0_{n,p} = \frac{dx/dt}{\phi(\lambda) \cdot [1 - 10^{-A(\lambda)}]} \qquad eq.3$$

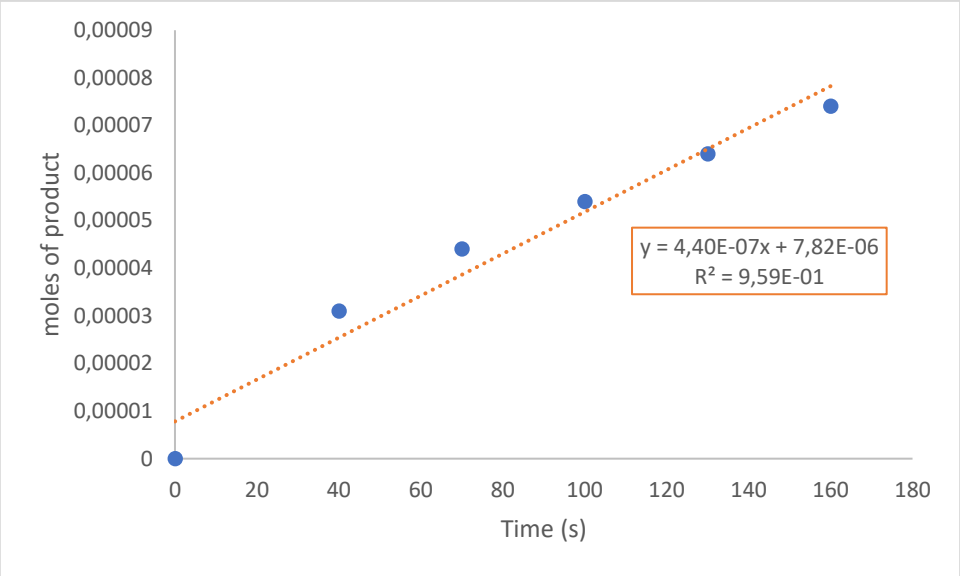
Where:

- (λ) is the quantum yield of the actinometer reaction at the irradiated wavelength, in this case being 0.86[6] at 512 nm for 0.15 M dilution (closest data found to our LED source, 516 nm).
- A(λ) is the absorbance of the actinometer solution (ferrioxalate) at the irradiated wavelength. The absorbance at 516 nm was measured with an *Agilent 8453 spectrometer* using a quartz cuvette with 1 cm of optical pathway, obtaining a value of 0.109.

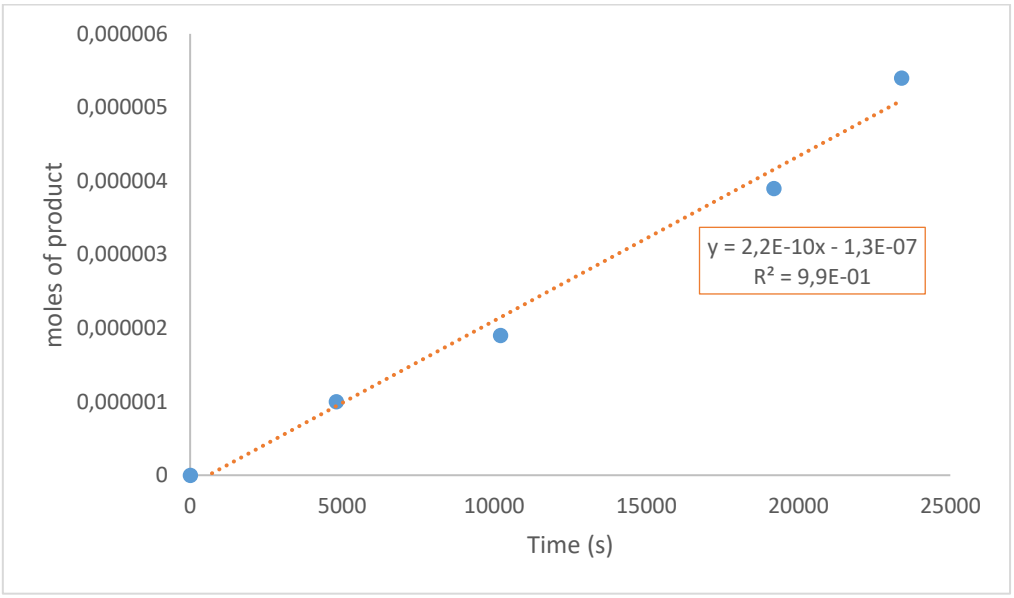
Thus, the moles of incident photons by unit of time ($q^0_{n,p}$) were determined to be $7.22 \cdot 10^{-8}$ einstein$\cdot s^{-1}$ and can be related with the slope of the kinetic of the model reactions across the equation 3 to know the quantum yield of the processes.

To study the kinetics of the two model reactions, the corresponding reaction mixture was placed in the LED system and the light was switched on:

- In the case of the formation of the thioether, every 30 seconds an aliquot of 0.1 mL was taken from the reaction mixture and analyzed by ^{1}H-NMR in $CDCl_3$. With all the data in hand, the conversion of the final product (in mol) was evaluated based in the initial molar concentration. Graphical representation of moles of product versus the irradiation time let us know the slope *dx/dt* of the process with a value of $4.40 \cdot 10^{-7}$ mol$\cdot s^{-1}$.



- In the case of the formation of the sulfoxide, around every 90 minutes an aliquot of 0.1 mL was taken from the reaction mixture and analyzed by ^{1}H-NMR in $CDCl_3$. Again, the conversion of the final product (in mol) was evaluated based in the initial molar concentration. Graphical representation of moles of product versus the irradiation time let us know the slope *dx/dt* of the process with a value of $2.20 \cdot 10^{-10}$ mol·s^{-1}.



Also, the absorbance of the two model reaction solutions (A in the equation 3) was measured adding a model reaction solution to a 1 cm optical pathway cuvette and recording the UV-Visible spectra in an *Agilent 8453 spectrometer*. The absorbance for the thioether at 516 nm was 25.89. The absorbance for the sulfoxide at 516 nm was 82.88.

Lastly, the quantum yield of the two processes was calculated using the slope for each kinetic reaction, the corresponding absorbance and the moles of incident photons by unit of time ($q^0_{n,p}$) calculated before for the actinometry:

$$\phi\ \text{thioether}_{516} = \frac{dx/dt}{q^0_{n,p} \cdot [1 - 10^{A_{516}}]} = \mathbf{5.8}$$

$$\phi\ \text{sulfoxide}_{516} = \frac{dx/dt}{q^0_{n,p} \cdot [1 - 10^{A_{516}}]} = \mathbf{0.003}$$

To conclude, as the value for the quantum yield of the first process is more than one, we can point out to a chain propagation mechanism. On the other hand, as the value of the quantum yield for the second process is less than one we can say that it is a light dependent process but it cannot be discarded a chain propagation mechanism.

Overall quantum yield was calculated taking into account both processes: The photocatalyst Eosin Y **3h** (1,6 mg, 0.0025 mmol) was placed in a vial, followed by 2-bromostyrene **1j** (12,9 µL, 0.1 mmol) and 4-methylbenzenethiol (0.037 g, 0.3 mmol) in 360 µL of CH_2Cl_2. A needle was set into the vial to let the oxygen pass through the reaction mixture. The LED system and the light was switched on and every 2 hours an aliquot of 0.1 mL was taken from the reaction mixture and analyzed by ^{1}H-NMR in $CDCl_3$. With all the data in hand, the conversion of the final product (in mol) was evaluated based in the initial molar concentration. Graphical representation of moles of product versus the irradiation time let us know the slope *dx/dt* of the process with a value of $4.0 \cdot 10^{-10}$ mol·s^{-1} (**Figure S3**).

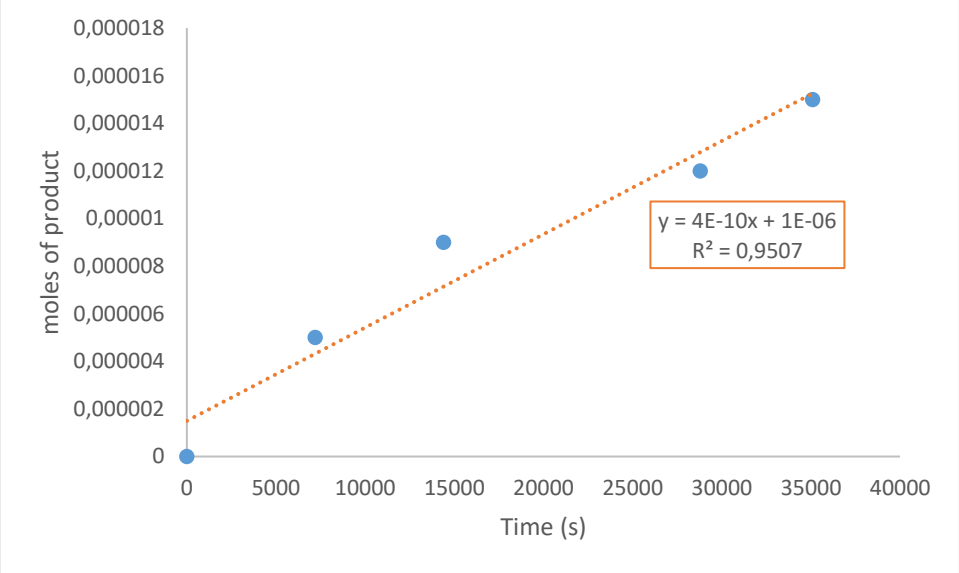


Figure S3. Kinetic profile of the reaction.

The value of the quantum yield for the whole process is 0.006.

$$\phi\ \text{overall quantum yield}_{516} = \frac{dx/dt}{q^0_{n,p} \cdot [1 - 10^{A_{516}}]} = \mathbf{0.006}$$

10.- Stern-Volmer quenching

The Stern-Volmer quenching measurement was carried out in a Spectrofluorometer. The following solutions were prepared:

- Eosin Y solution 0.0069 M: 223.5 mg of EY were added into a 50 mL volumetric flask and filled to the mark with DCM.

- *o*-Bromostyrene solution 0.0035 M: 9 µL of alkene were added into a 20 mL volumetric flask and filled to the mark with DCM.

- 4-Methylbenzenethiol solution 0.0035 M: 8.7 mg of thiol were added into a 20 mL volumetric flask and filled to the mark with DCM.

First, a blank solution with the photocatalyst was measured obtaining a maximum wavelength of emission of 562 nm (**Figure S4**).

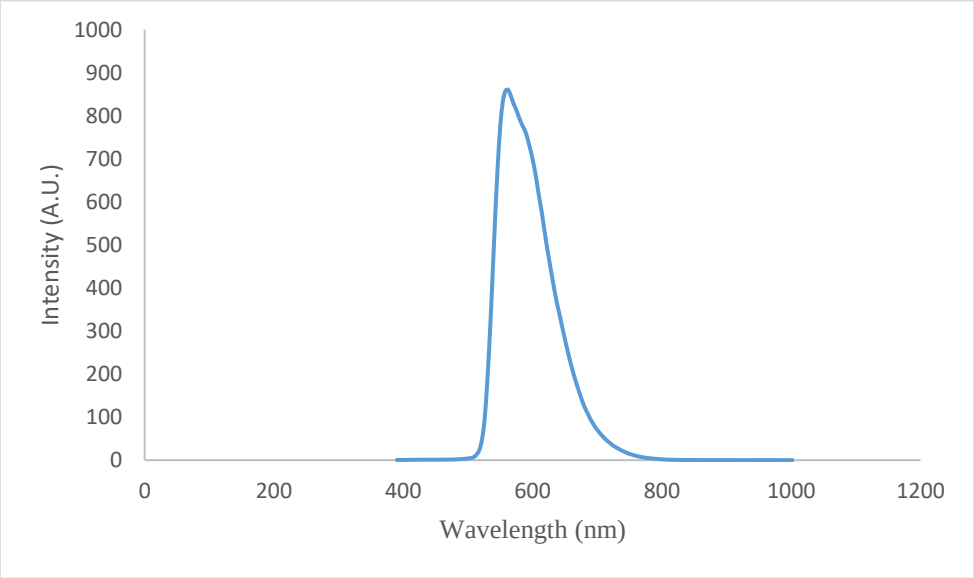
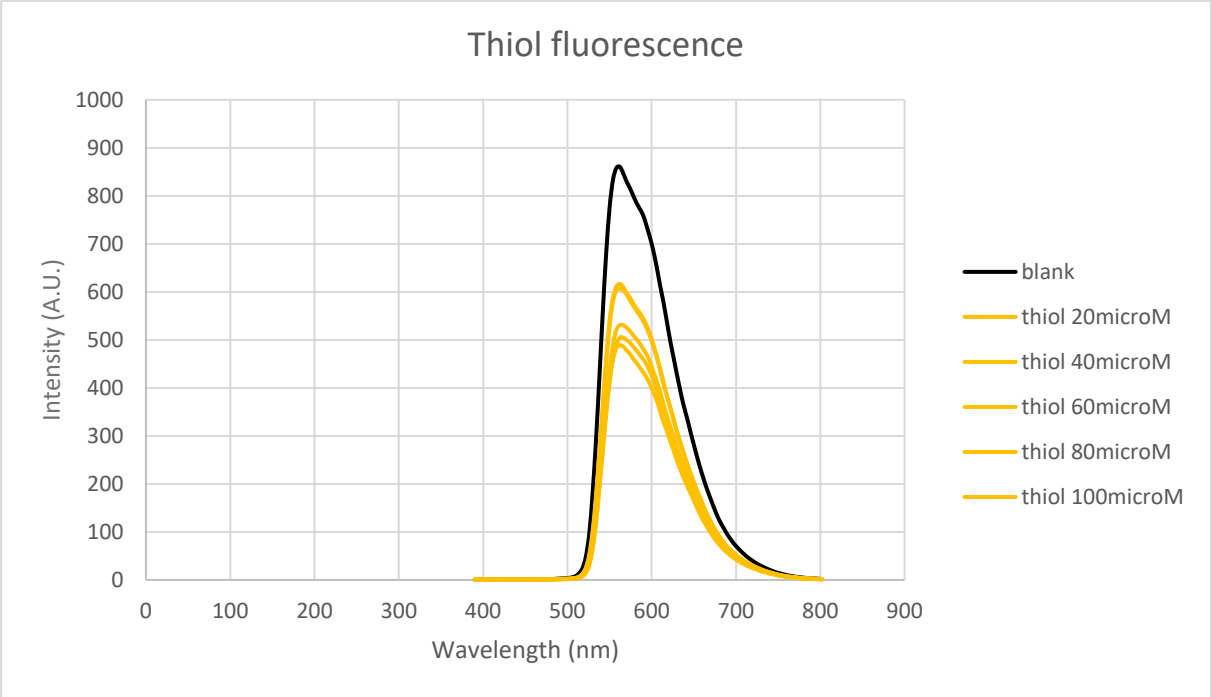
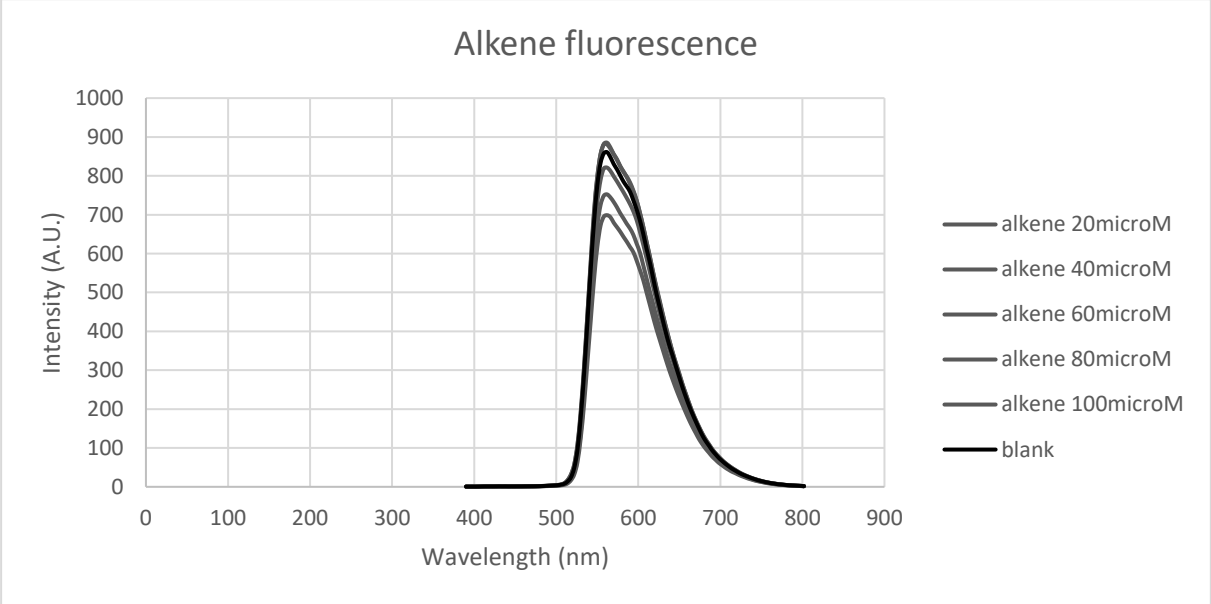


Figure S4. Fluorescence spectrum of EY.

Then, 0.8 mL of photocatalyst solution was added to the cuvette and was filled until 2.4 mL with the corresponding amount of alkene or thiol and DCM. Thus, the concentration in the cuvette was constant during the experiment. The cuvette was degassed for 5 minutes before measurement of the samples.

Plotting the intensity of fluorescence of each, the thiol and alkene, versus the wavelength we could see that the thiol is quenching the EY more than the alkene. For that we can say that the excited photocatalyst specie reacts first with the thiol.





The Stern-Volmer quenching plots were calculated plotting I^0/I versus the concentration of alkene and thiol in each case (**Figure S5**).

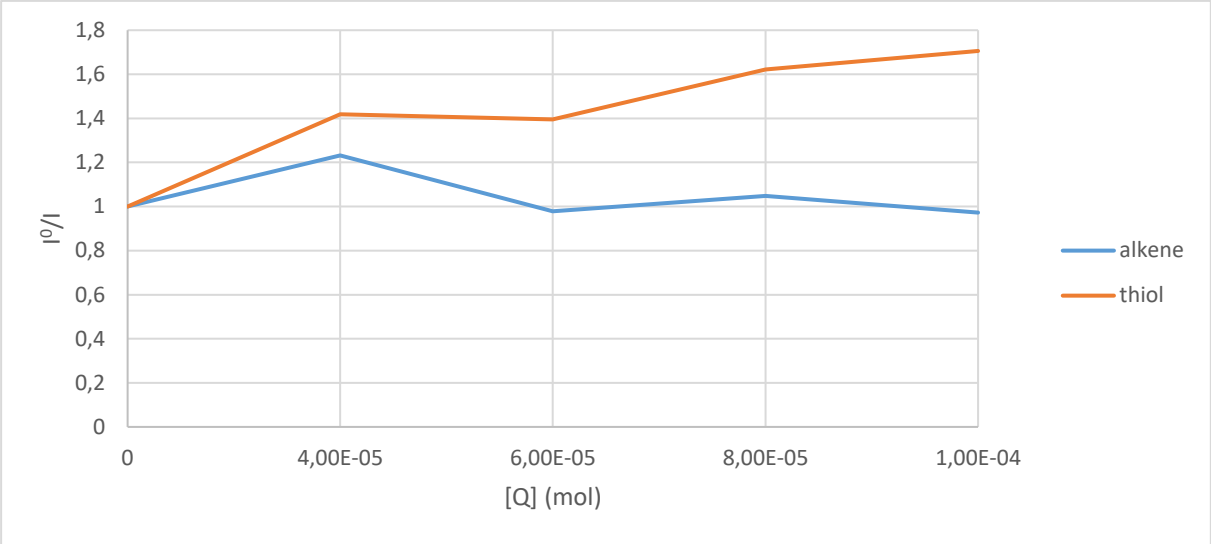


Figure S5. Stern-Volmer quenching plots.

11.- Experiment in the absence of light

The reaction with the photocatalyst Eosin Y **3h** (3.2 mg, 0.0050 mmol) was placed in a vial, followed by 2-bromostyrene **1j** (26 µL, 0.2 mmol) and 4-methylbenzenethiol (0.075 mg, 0.6 mmol) in 720 µL of CH_2Cl_2. A needle was set into the vial to let the oxygen pass through the reaction mixture and the green light was switched on. Every hour the light was switched off and an aliquot was taken from the reaction and analyzed by ^{1}H-NMR in $CDCl_3$.

Plotting the conversion versus the time that the reaction has been irradiated we can say that is a process dependent on light, because the conversion does not change when the light is off (**Figure S6**).

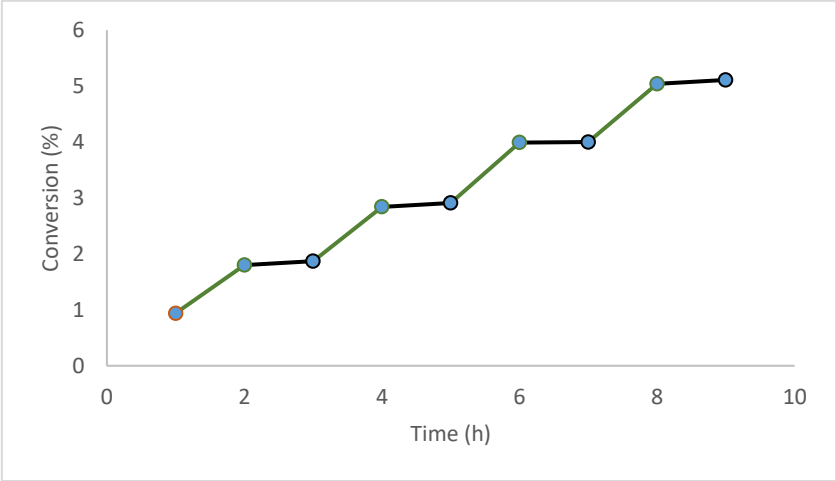


Figure S6. Experiment in the absence of light.

12.- Potassium Iodide/Starch Indicator Test:

To a photoxidation reaction mixture of sulfoxide **4j**, KI was added and stored in the dark. After 2 hours, starch indicator was added and no turned dark-blue colour was observed.