Photocatalytic Functionalization of Thin-Layer Membranes Using Monomer Truncation Strategy

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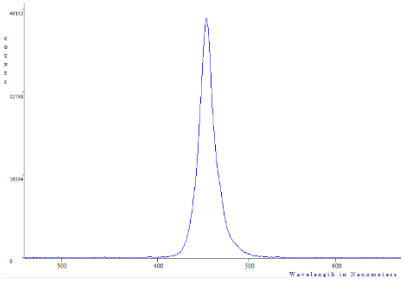
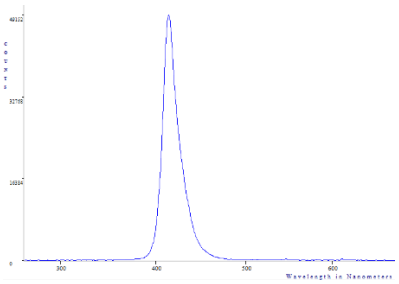
Materials and general methods.

All reagents and solvents were purchased from commercial sources and used without further purification.

Photoreactor setup: A custom-made photoreactor setup was used for the photocatalytic reactions (see Figure S1). The vial is placed inside the fitted well in which irradiation takes place at the desired wavelengths (420 nm or 450 nm were employed during this project) using single 20 mW and 15 mW blue LEDs. Reaction temperature was maintain constant at 25 ºC by a termostatic recirculating system. A spectro-radiometer equipment Stellarnet model *Blue-Wave UV-NB50* was employed to measure the emission of the Blue LEDs used (range 300-600 ƛ, integration time CR2-AP + 200 ms, intensity 21.7217 W/m2 for LED at 420 nm and).



LED Blue at 450 nm



LED Blue at 420 nm

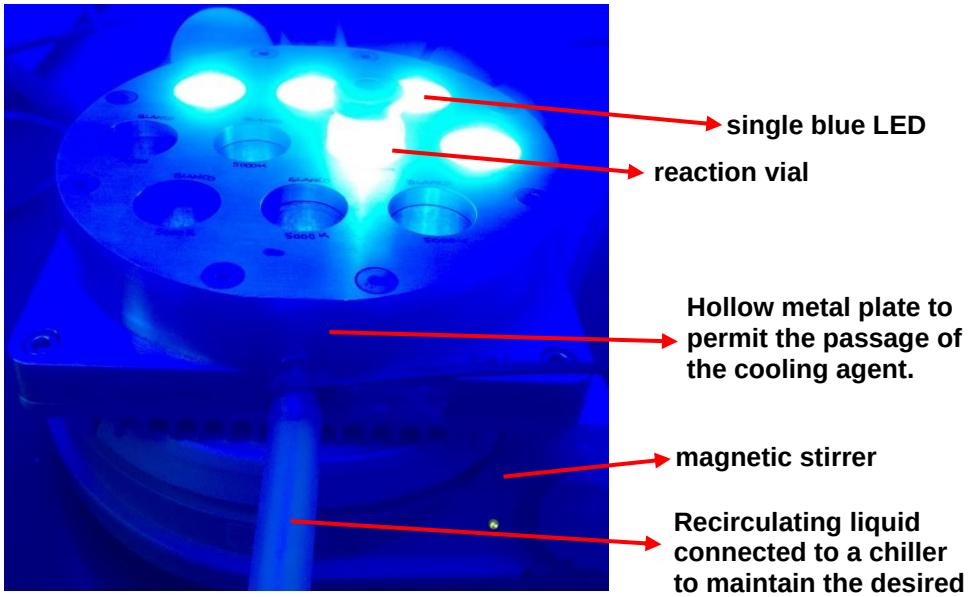


Figure S1: Photoreactor setup.

Nuclear Magnetic Resonance (NMR) spectra were acquired on a *Bruker AV-300 spectrometer*, running at 300 MHz for ^{1}H. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H-NMR). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (brs = broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz) and integration. Solid-state ^{13}C (100.61 MHz) CPMAS NMR spectra have been obtained on a *Bruker AV-400 WB spectrometer* at 300 K using a 4mm triple channel probe head (BL4 X/Y/^{1}H). Samples were carefully packed in a 4-mm diameter cylindrical zirconia rotor with Kel-F end-caps. Operating conditions involved 2.75 μs 90° ^{1}H pulses and decoupling field strength of 90.9 kHz by TPPM sequence. The rotor spin rate was set at 10 kHz. Relaxation delay of 4 s and a contact time of 3 ms. ^{13}C spectra

were originally referenced to an adamantane sample and then the chemical shifts were recalculated to the Me_4Si [for the CH_2 atom δ(adamantane)=29.5 ppm].

Elemental Chemical Analyses were obtained in an elemental analyzer *LECO CHNS-932* model number 601-800-500.

IR spectra were recorded in a *Perkin-Elmer 283* equipped with *ATR MIRacle Single Reflection Horizontal*.

Thermogravimetric analyses (TGA) tests were performed on a *TA Instruments Q500* thermobalance equipped with an EGA furnace. Pt and N_2 sample holders were used as purge gas with a flow rate of 90 mL/min. The method used is a heating ramp of 10°C/min from room temperature up to 1000 °C.

UV-Vis Diffuse Reflectance Spectroscopy was performed on a PerkinElmer Lambda850+ equipped with a spherical detector of 110 mm in the 250-800 nm range. The reflectance spectra were plotted as the Tauc plot and the Kubelka-Munk function. These analyses were carried out in solid state.

Photoluminiscence measurements were carried out in a previously prepared suspension of 1 mg of the material in 5 mL of H_2O, using a *JASCO Spectrofluorometer FP-8600* controlled by *Spectra Manager Version 2.10.01*. A 10x10 mm precision cell made of quartz was used for all emission measurements. These analyses were carried out in a suspension of water.

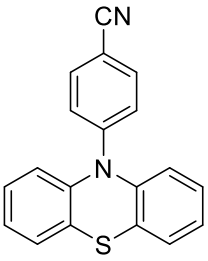
Powder X-ray difraction was obtained in a *X'Pert PRO* difractometer θ/2θ geometry from *Panalytica*l equipped with a *Johansson* monochromator for ƛ K_α, a *X'Celerator* fast detector in an alumina holder. The θ/2θ swept was performed from 4 to 45 ˚ with an angular increase of 0.0167 ˚/100 s. Simulated model structures of PXRD were carried out using Materials Studio 8.0 Program.

Scanning Electron Microscopy (SEM) images were carried out on a *Hitachi S-3000N electron microscope* with a coupled ESED detector and an analyzer from energy dispersive X-ray from *Oxford Instruments*, *INCAx-sight* model. The images were obtained in vacuum after being metallized in a *Sputter Quórum Q150T-S* with gold coating.

X Ray Photoelectron Spectroscopy (XPS) experiments reported in this paper have all been carried out under ultra-high vacuum (UHV) conditions. The experimental chamber has a base pressure of 2×10^{-10} mbar and is equipped with an X-ray source with a Mg anode whose K_α emission line produces photons of energy *hv* = 1253.6 eV which are used for X-ray photoemission spectroscopy (XPS) measurements. An He discharge lamp provides He-I (*hv* = 21.2 eV) and He-II (*hv* = 40.8 eV) photons for ultraviolet photoemission spectroscopy (UPS). For both techniques a hemispherical energy analyzer (LEYBOLD LHS10) has been used. The pass energy of the analyzer was set to 50 eV for the XPS measurements to reach a resolution of 0.7 eV and 5 eV for the UPS measurements reaching a final resolution of 0.1 eV.

Synthesis of photoactive Building Block 5-Cl.

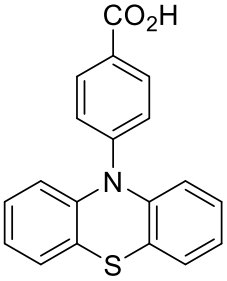
Synthesis of 4-(10*H*-phenothiazin-10-yl)benzonitrile (4)[1]



A sealed tube was charged with Phenothiazine (1.83 g, 10 mmol), 4-Bromobenzonitrile (2.00 g, 11 mmol), $Pd_2(dba)_3$ (275 mg, 0,3 mmol) and $HP^tBu_3BF_4$ (145 mg, 0,5 mmol). Then, toluene (11 mL) was added, and the mixture was stirred for 15 minutes. Finally, NaO^tBu (1.11 g, 11.5 mmol) was added, and the reaction mixture was stirred at 110 °C for 48h. After cooling to room temperature, the resulting mixture was diluted with dichloromethane (20 mL) and filtered through celite, which was washed with dichloromethane (4 x 10 mL). The filtered was evaporated under reduced pressure. The reaction crude was purified on column chromatography (99:1 cyclohexane:AcOEt), obtaining the nitrile **4** as a white solid (2.56 g, 85 % yield). Their spectroscopic data are in agreement with published data.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.44 – 7.41 (m, 2H), 7.33 – 7.26 (m, 4H), 7.22 – 7.17 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 2H).

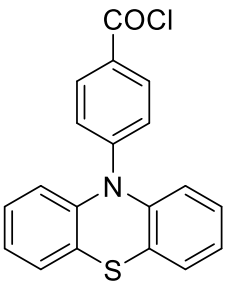
Synthesis of 4-(10*H*-phenothiazin-10-yl)benzoic acid (5)[1]



In a 250 mL round flask equipped with a magnetic stirrer, was prepared a solution of nitrile **4** (2.40, 8.0 mmol) in a mixture 7:3 of EtOH/H_2O (17 mL). Then, KOH (6.7 g, 120 mmol) was added and the reaction mixture was stirred at 100 °C for 72 h. After this time, aqueous solution of HCl (1M) was added til acidic pH, precipitating a brown solid that was filtered and washed with water until neutral pH. The acid **5** obtained was dried under vacuum, achieving 2.3 g (90 % yield). Their spectroscopic data are in agreement with published data.[1]

^{1}H NMR (300 MHz, DMSO) δ 7.98 (d, *J* = 8.7 Hz, 2H), 7.34 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.20 (td, *J* = 7.9, 1.7 Hz, 2H), 7.10 (td, *J* = 7.5, 1.4 Hz, 2H), 6.85 (dd, *J* = 8.0, 1.4 Hz, 2H).

Synthesis of 4-(10*H*-phenothiazin-10-yl)benzoyl chloride (5-Cl)



A 50 mL round flask equipped with a magnetic stirrer, was charged with acid **5** (1 g, 3.13 mmol) and 3 vacuum-nitrogen cycles were performed. Under nitrogen atmosphere, dried dichloromethane (20 mL) and a few drops of DMF were added. Then, thionyl chloride (1 mL, 13.7 mmol) was added dropwise wery slowly at 0 ºC, and the reaction mixture was stirred for 2h at the same temperature. After this time, the solvent, and the excess of thionyl chloride were removed under reduced pressure and the obtained green solid was dried under vacuum. Finally, the acid chloride **5-Cl** was stored in refrigerator and under nitrogen atmosphere. A conversion of 100 % (1.06 g) was assumed.

Synthesis of Thin-Layer Membranes

Screening of the Synthesis of Film 1

First, two solutions of each reagent were prepared. On the one hand, were prepared several solutions of variable amount of cyclen (**6**) (0.5-2.5 mmol) in distilled water (100 mL). On the other hand, fumaryl chloride **7** (54 μL, 0.5 mmol) was dissolved in the indicated solvent or in a mixture of them (100 mL) (see Table S1). Then, 20 mL of indicated cyclen solution was added into a beaker of 250 mL (6.9 cm diameter) and, successively, 20 mL of **7** solution was slowly and carefully added along the walls of the beaker. Finally, the beaker was covered with Parafilm to prevent the evaporation of the organic solvent and the reaction was allowed to progress for the time indicated in Table S1.

Table S1. Screening of reaction conditions for the preparation of film **1**.

Entry	Solvent of 5-Cl solution[a]	Ratio 6:7	Time (h)	Formation	Visual aspect
1	Hexane	1:1	288	not	-
2	Hexane	2:1	288	yes	Not uniform
3	Hexane	3:1	288	yes	Thick, regular
4	Hexane	5:1	192	yes	Thick, uniform
5	Dichloromethane	1:1	216	yes	Not uniform
6	Dichloromethane	2:1	216	yes	Thick, regular
7	Dichloromethane	3:1	216	yes	Thick, regular
8	Dichloromethane	5:1	192	yes	Not uniform
10	Hexane /DCM (4:1)	2:1	192	yes	Thick, regular
11	Hexane /DCM (4:1)	3:1	192	yes	Thick, uniform
12	Hexane /DCM (4:1)	5:1	192	yes	Thick, uniform
13	Hexane /DCM (2:1)	3:1	120	yes	Thick, uniform
14	Hexane /DCM (2:1)	5:1	120	yes	Thick, uniform
15	Hexane/AcOEt (4:1)	3:1	120	yes	Not uniform
16	Hexane/AcOEt (4:1)	5:1	120	yes	Not uniform
17	Ciclohexane/DCM (4:1)	3:1	96	yes	Thick, uniform
18	Ciclohexane/DCM (4:1)	5:1	96	yes	Thick, uniform
19[b]	**Ciclohexane/DCM (4:1)**	**5:1**	**72**	**yes**	**Thick, uniform**

[a] DCM = Dichloromethane; AcOEt = Ethyl acetate. [b] 40 mL of both reagent solutions were used.

Synthesis of Film 1

First, a solution of cyclen (**6**) (172.3 mg, 1 mmol) in distilled water (20 mL) was added into a beaker (250 mL, 6.9 cm diameter) and, successively, a solution of fumaryl chloride (**7**) (21 μL, 0.2 mmol) in a mixture of Ciclohexane/DCM (4:1) (20 mL) was slowly and carefully added along the walls of the beaker. Finally, the beaker was covered with Parafilm to prevent the evaporation of the organic solvent and the reaction was allowed to

progress for three days. Then, the solvent was removed, and the film obtained was, subsequently, rinsed several times by dichloromethane and distilled water to wash away the residual monomers and then was transferred to a watch glass and left to air dry. The film **1** was achieved as a pale yellow thick solid (18 mg).

Synthesis of Film 1-PTH

First, a solution of cyclen (**6**) (172.3 mg, 1 mmol) in distilled water (20 mL) was added into a beaker (600 mL, 8.5 cm diameter) and, successively, a solution of a mixture 1:1 of fumaryl chloride (**7**) (21 μL, 0.2 mmol) and acid chloride **5-Cl** (68 mg, 0.2 mol) in a mixture of Ciclohexane/DCM (4:1) (20 mL) was slowly and carefully added along the walls of the beaker. Finally, the beaker was covered with Parafilm to prevent the evaporation of the organic solvent and the reaction was allowed to progress for three days. Then, the solvent was removed, and the film obtained was, subsequently, rinsed several times dichloromethane and distilled water to wash away the residual monomers and then was transferred to a watch glass and left to air dry. The film **1-PTH** was achieved as a pale yellow thick solid (14.5 mg). The used of beaker smaller (250 or 400 mL, 6.9 and 7.6 cm diameter, respectively) afforded less amount of **1-PTH** (11.8 and 12.9 mg, respectively).

Extended Characterization Data of Films

PXRD Analysis

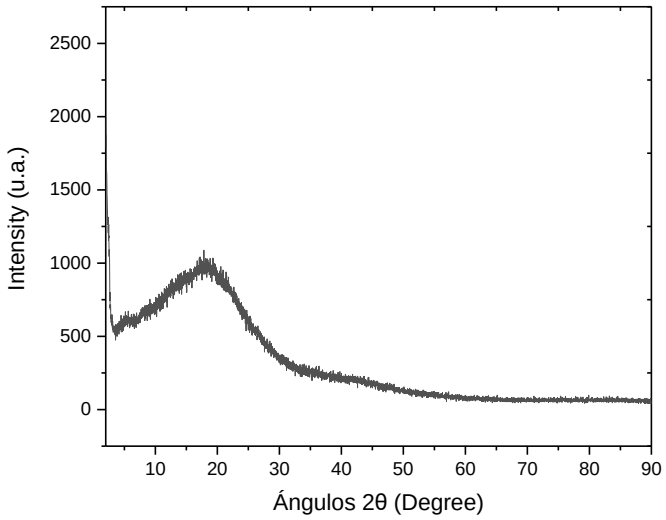


Figure S2. PXRD spectra of film **1**

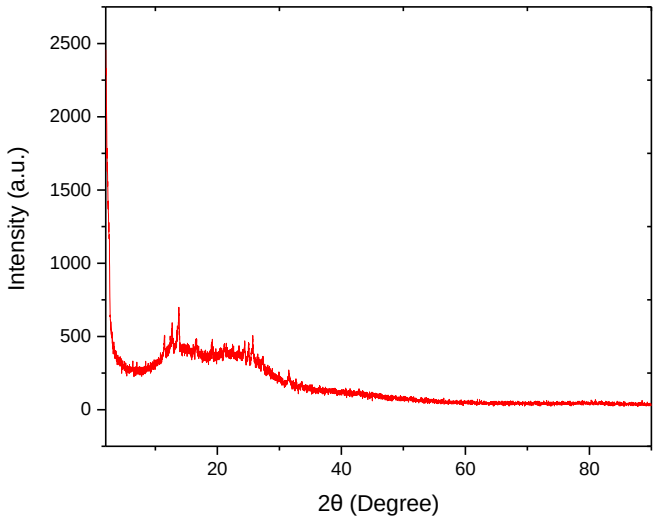


Figure S3. PXRD spectra of film **1-PTH**

BET Analysis

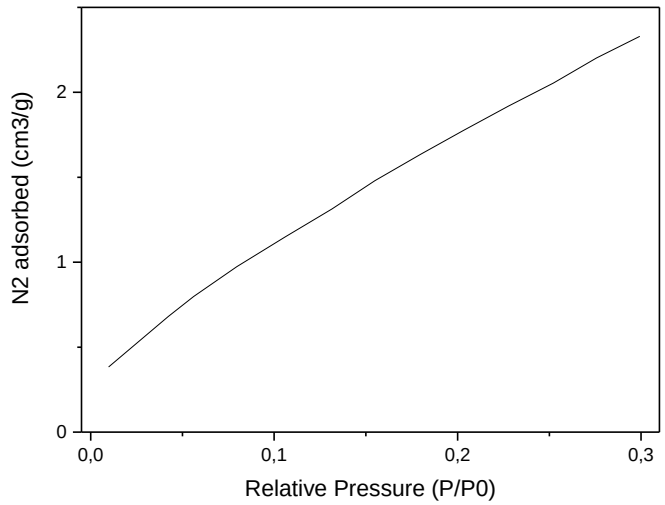


Figure S4. BET analysis of film **1-PTH**

IR Spectra

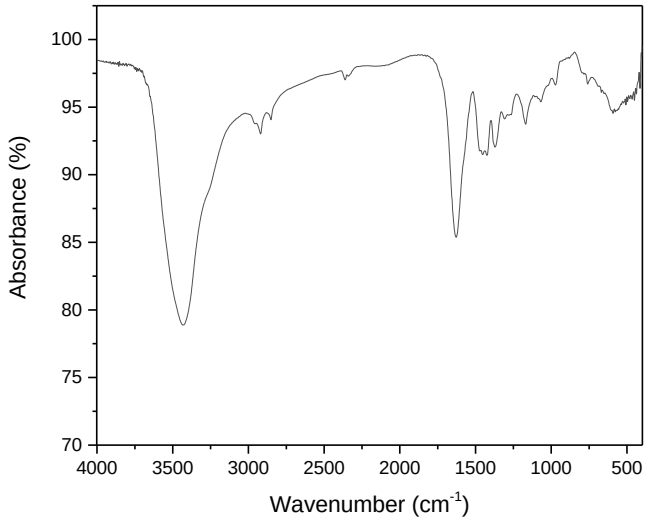


Figure S5. FT-IR spectrum of film **1**

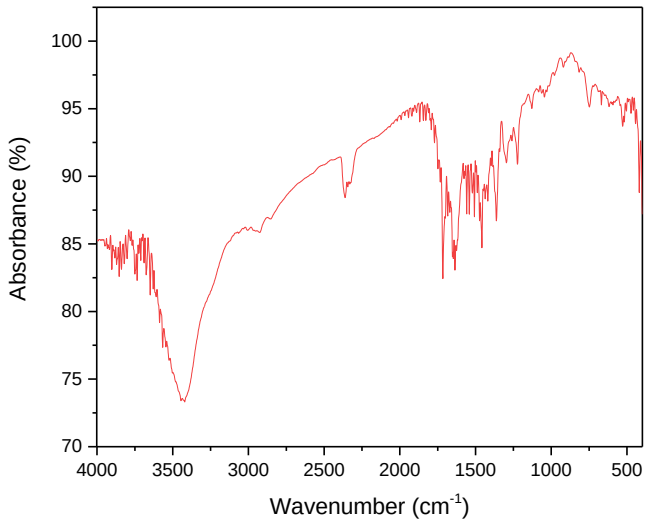


Figure S6. FT-IR spectrum of film **1-PTH**

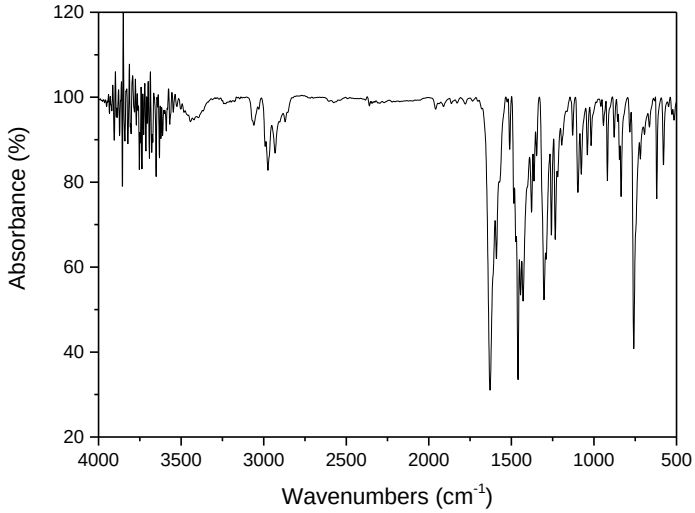


Figure S7. FT-IR spectrum of *N*,*N*-diethyl-4-(10*H*-phenothiazin-10-yl)benzamide

UV-Vis absorption and emission spectra

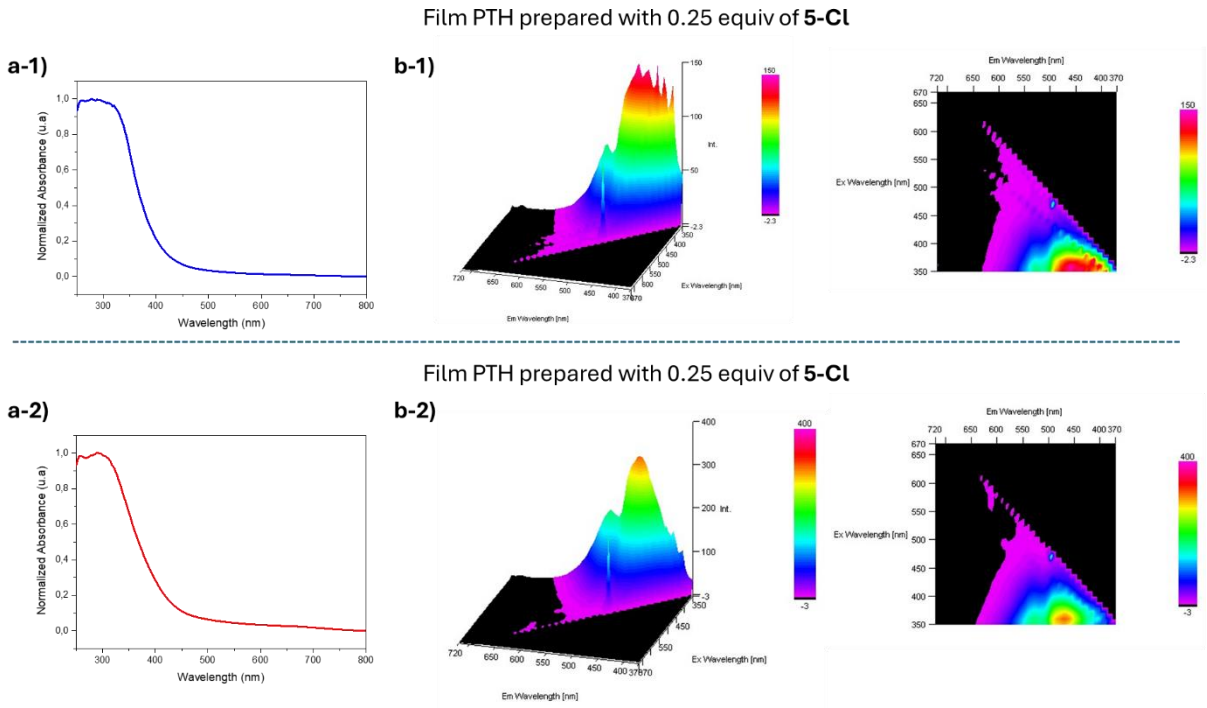


Figure S8. a) UV-Vis absorption and b) photolumiescent (PL) map spectroscopies for films obtaining using 0.25 and 0.50 equiv. of monomer **5-Cl**.

Elemental Analysis

Table S2. Elemental analysis of film prepared.

Sample	C (%wt)	H (%wt)	N (%wt)	S (%wt)
1	48.19	7.00	15.88	----
1	47.97	7.33	15.96	----
1-PTH	52.42	6.96	15.51	2.75
1-PTH	51.43	7.05	15.87	2.31
1-PTH	51.88	7.00	15.60	2.40

^{13}C NMR Spectra

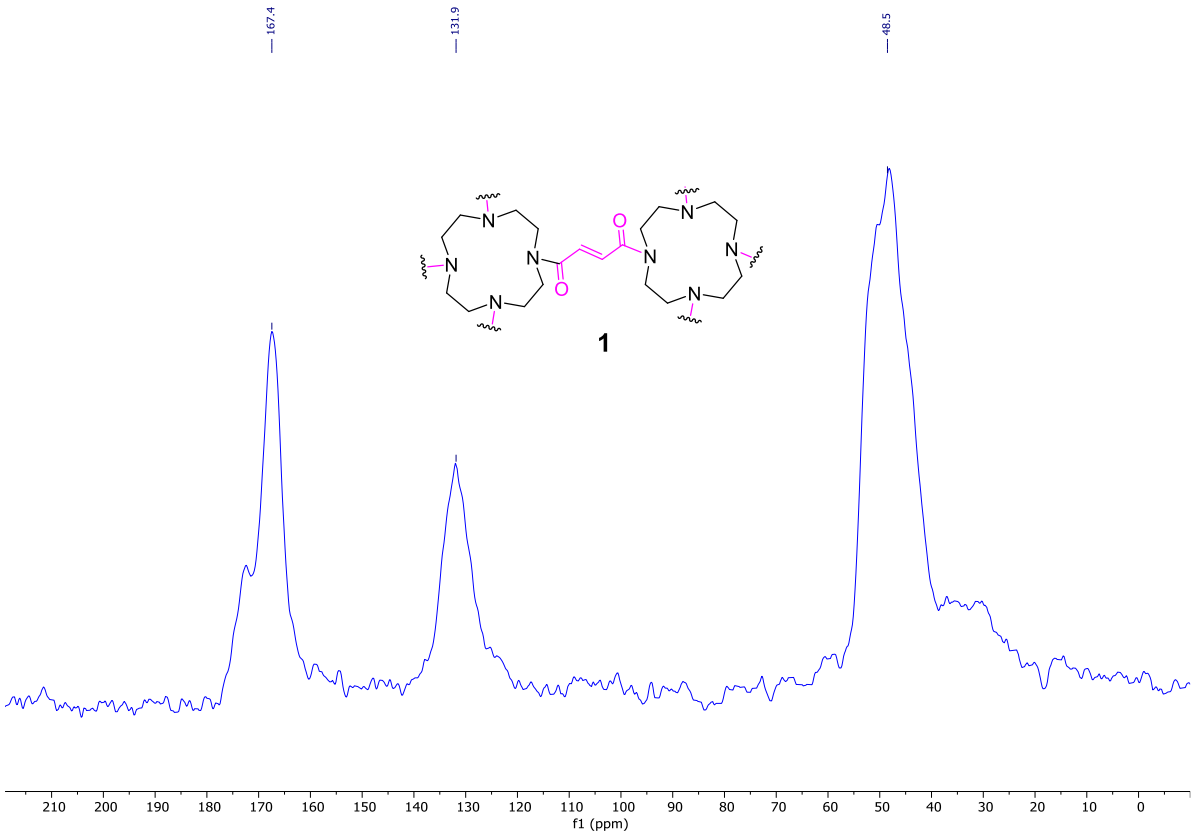


Figure S9. ^{13}C solid-state NMR spectra of film **1**

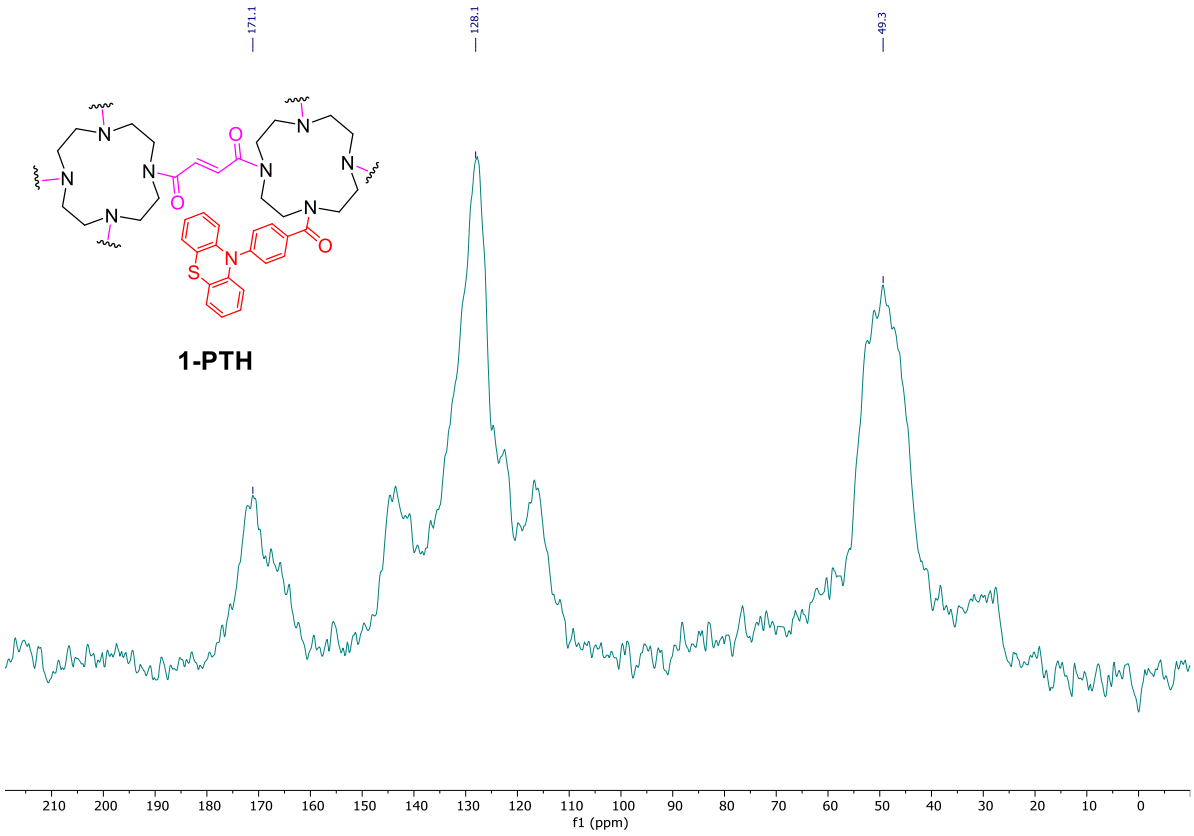


Figure S10. ^{13}C solid-state NMR spectra of film **1-PTH**

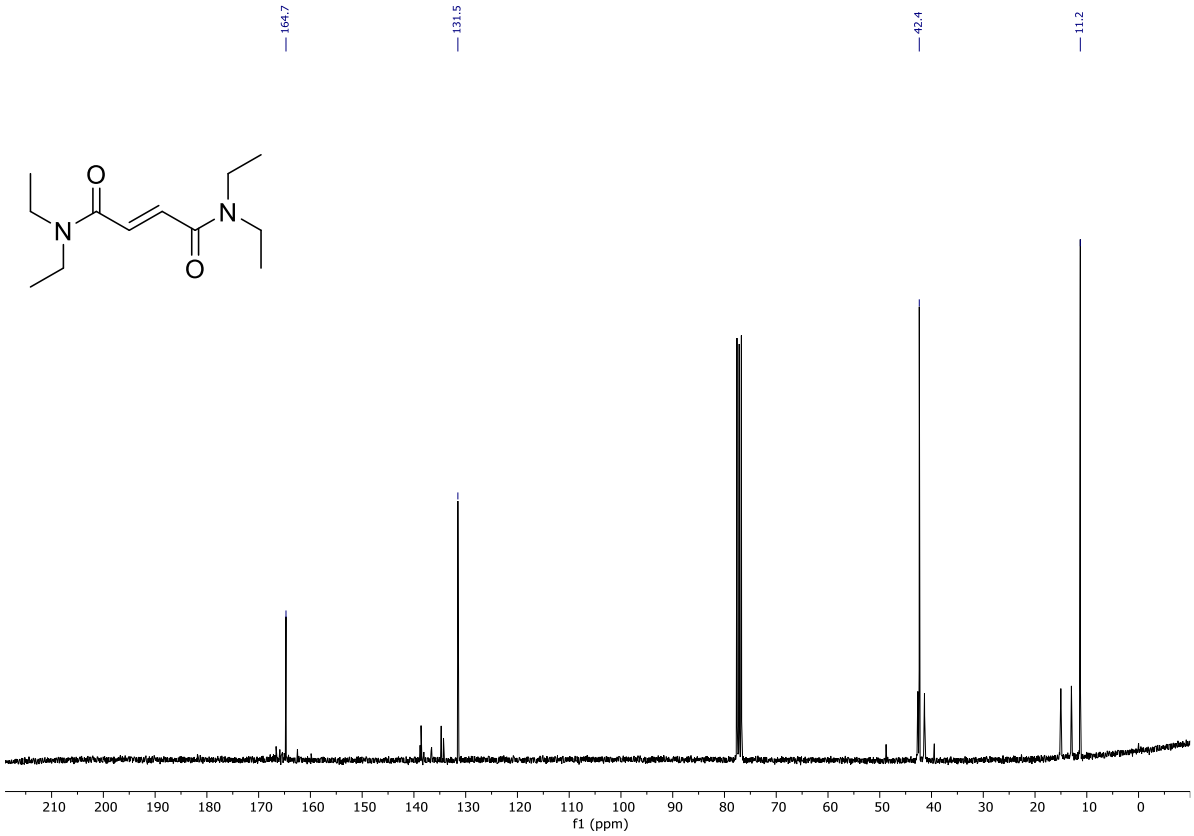


Figure S11. ^{13}C NMR spectra of *N,N*-diethyl-4-(10*H*-phenothiazin-10-yl)benzamide in $CDCl_3$

Thermogravimetric Analysis (TGA)

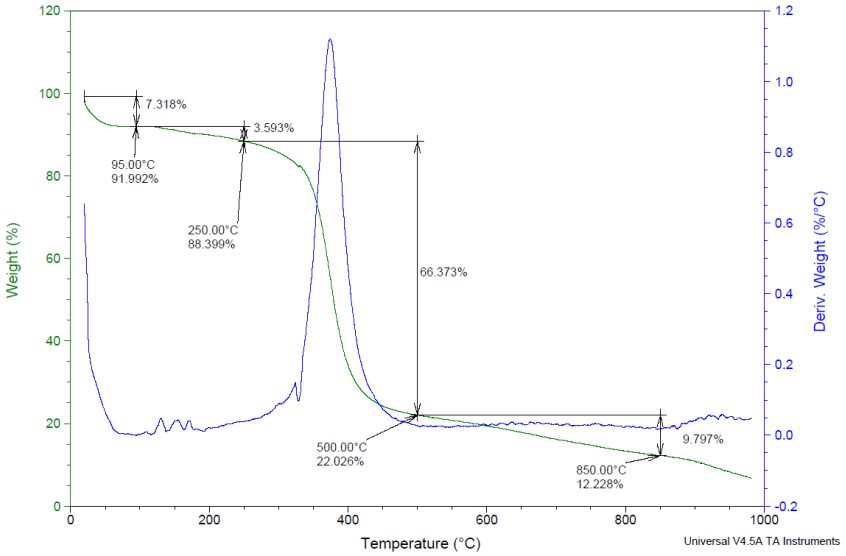


Figure S12. TGA for film **1**

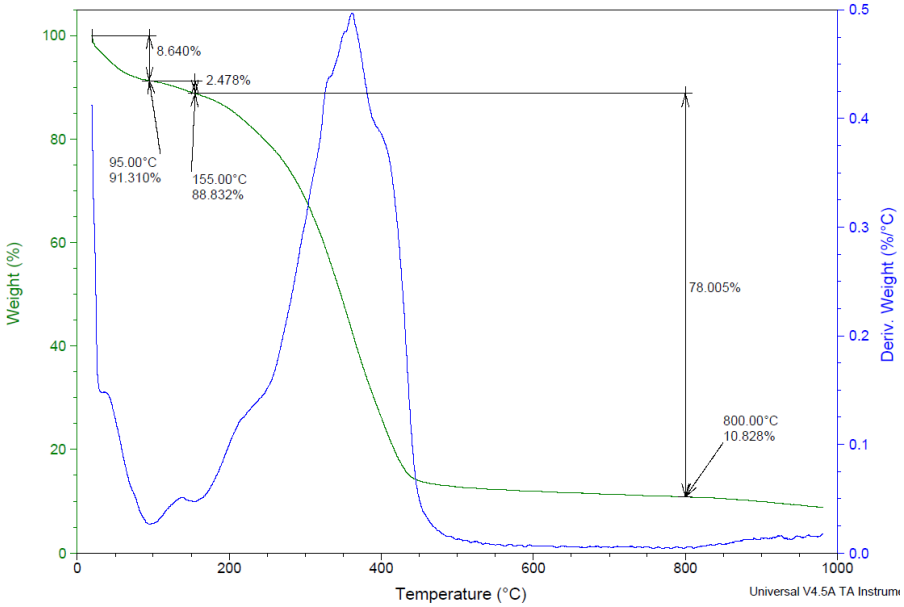


Figure S13. TGA for film **1-PTH**

SEM images

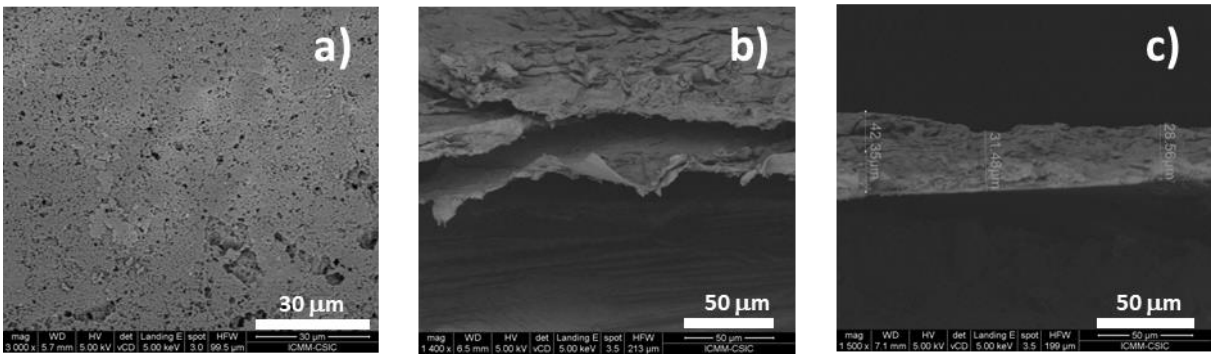


Figure S14. a) SEM image, b) and c) cross-sectional SEM images for film **1**.

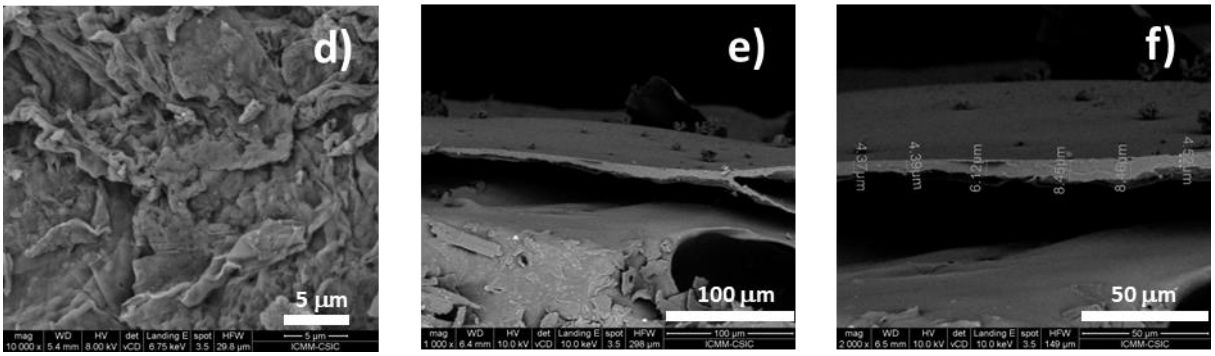


Figure S15. d) SEM image, e) and f) cross-sectional SEM images for film **1-PTH**.

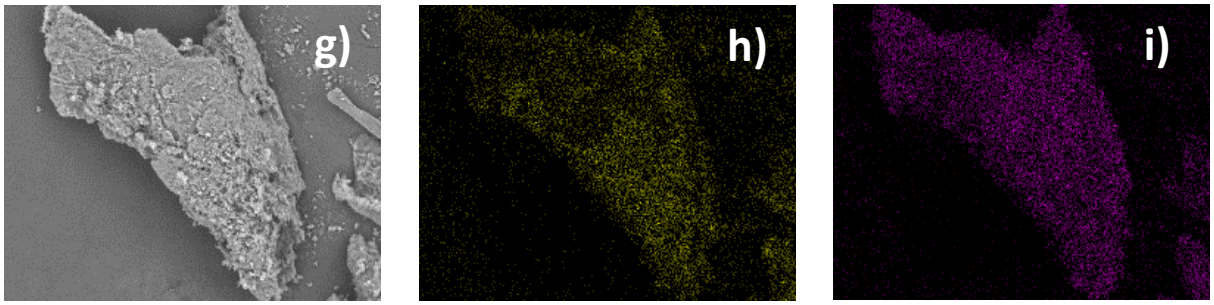


Figure S16. g) SEM image, h) Sulphur mapping, i) Chloride mapping for film **1-PTH**.

EDX Analysis

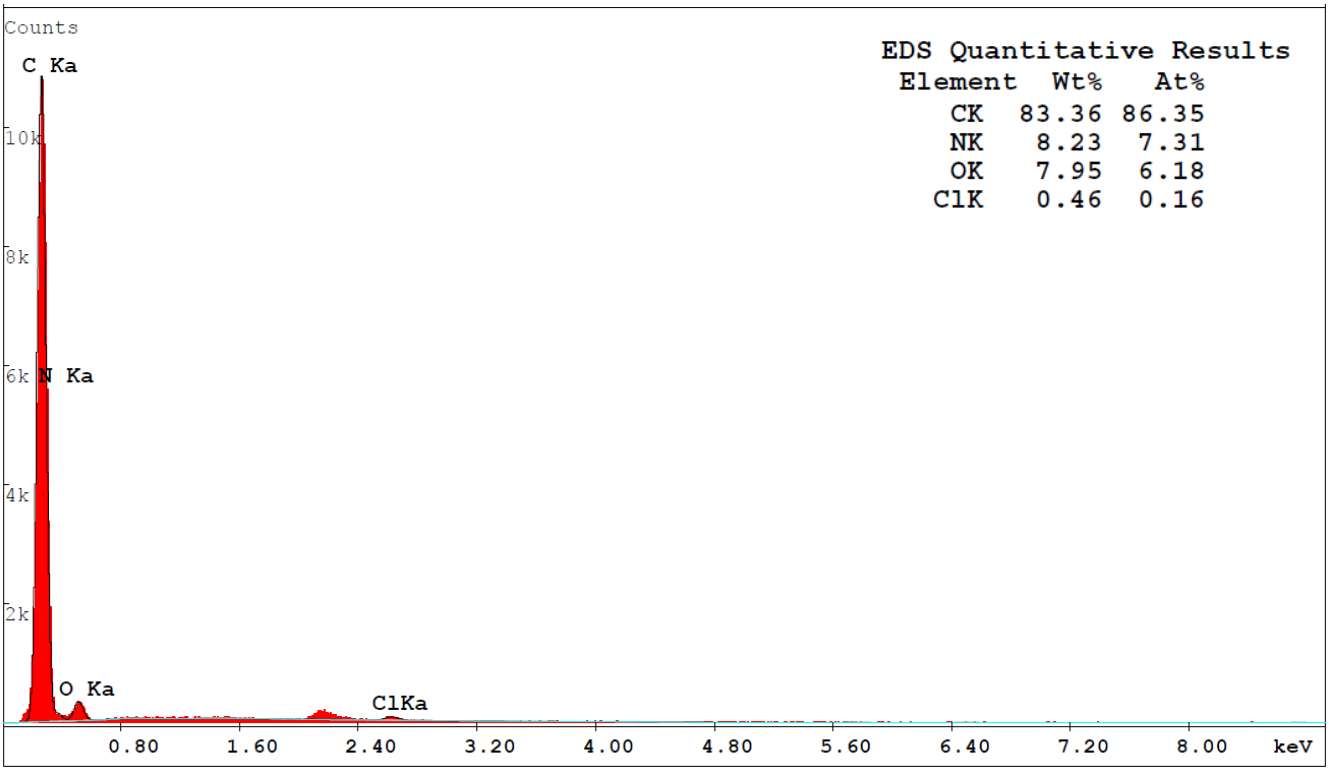


Figure S17. EDX for film **1**

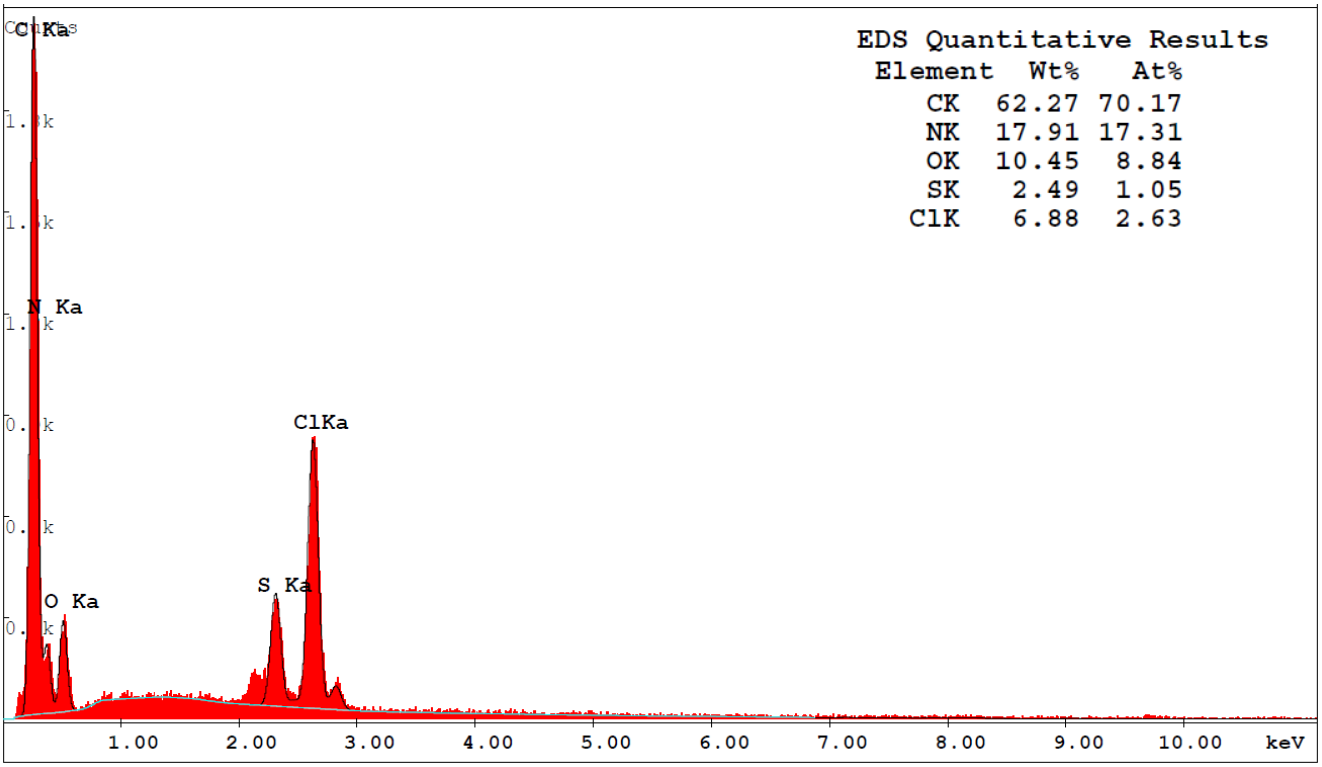


Figure S18. EDX for film **1-PTH**

XPS Analysis

The samples powder were glued using a Ag liquid colloid for the spectroscopic measurement for both; to avoid the powder fall inside the UHV chamber; and, to avoid the sample charge during the electronic measurement. Thus, all the core levels are referred to the Ag $3d_{5/2}$ core level of the Ag colloid (binding energy of 367.4 eV) which is weakly visible in the sample total XPS spectra.

The measured spectra have been deconvoluted using a Richardson–Lucy algorithm in order to eliminate the Mg K_α intrinsic line width[2] and satellites.[3] [S4] An iterative Richardson–Lucy procedure was applied until convergence, using as stopping criteria the appearance of a maximum in the Shannon entropy. In this way the information extracted is maximized, and the amplification of noise is avoided.[2] The Mg K_α satellites were removed by means of an automated algorithm based on the use of constrained penalized spline fitting. This algorithm has been used routinely for the satellite elimination for laboratory source generated X-ray diffraction patterns.[3]. The deconvoluted XPS spectra obtained in this way are equivalent to spectra acquired with a monochromatic source. The core level peaks, have been fitted, after subtraction of a Tougaard background[4] with a Doniach-Sunjic combination of Lorentzian and Gaussian lineshapes.[5]

The measured XPS intensity were corrected by the corresponding atomic sensitive factor of each edge. Thus, the corrected intensity is proportional to the average atomic composition of the films following standard procedures,[6] and using the atomic sensitivities determined previously for this spectrometer type.[7] Assuming that the films are strictly homogeneous within the escape depth of the electrons, the ratio of the intensities of two atoms core level peaks is related to the atomic density ratio (X_A/X_B) by $X_A/X_B = A\ I_A\ /I_B$ where $A = 1/S_A\ /\ 1/S_B$ and S_A and S_B are the atomic sensitive factor determined for the pure chemical elements for the specific electron analyzer used.[8]

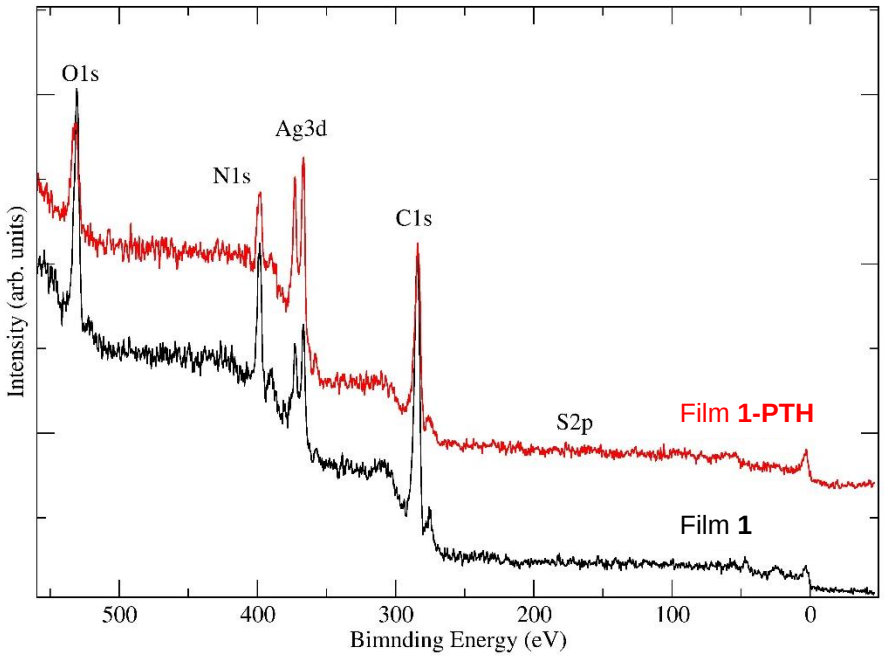
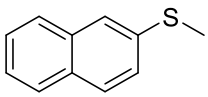


Figure S19. XPS survey spectra of samples of pristine film **1** (black line) and **1-PTH** (red line)

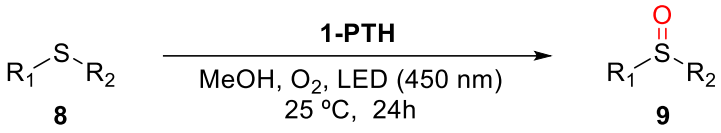
Synthesis of methyl(naphthalen-2-yl)sulfane (8d)[9]



2-Bromonaphthalene (5 mmol) was added to a round-bottom flask and three vacuum-N_2 cycles were made. Then, dry THF (20 mL) was added and stirred vigorously. The reaction mixture was cooled to -78 °C and *n*-BuLi (6 mmol) was slowly added. Finally, dimethyl disulfide (10 mmol) was added, temperature was allowed to naturally rise until room temperature and the resulting reaction mixture was stirred for 4 h. The solvent was evaporated under reduced pressure and the crude purified by flash chromatography (Cyclohexane:AcOEt (90:10)), obtained the thioether **8d** as a pale-yellow solid in 88% yield (770 mg, 4.42 mmol). Their spectroscopic data are in agreement with published data.[10]

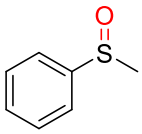
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 12.6, 8.2 Hz, 3H), 7.60 (d, *J* = 1.4 Hz, 1H), 7.51–7.34 (m, 3H), 2.59 (s, 3H).

General Procedure for the oxidation reactions of sulfides.



In a 2 ml vial without magnetic bar was prepared a mixture of sulfide **8** (0.1 mmol) and catalyst **1-PTH** (0.6 mg) in methanol (200 or 400 μl). The vial the vial was sealed with a septum and conditioned with 3 cycles of vacuum-oxygen through the septum in order to generate the oxygen-enriched atmosphere (keeping the oxygen source connected to the vial after the third cycle). Finally, the system was placed under a 450 nm blue LED lamp during 24 hours at 25 ºC. After this time, the crude was directly extracted from the vial with methanol and analyzed by ^{1}H NMR spectroscopy. The conversions to each product were calculated considering the relative integration of characteristic peaks from the sulfide and sulfoxide signals in the ^{1}HNMR spectra.

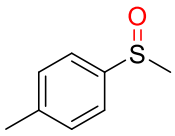
(Methylsulfinyl)benzene (9a)



The reaction of (methyl)(phenyl)sulfide (**8a**) (12 μL, 0.1 mmol) in methanol (200 μL) after 24 h afforded the sulfoxide **9a** in 80% yield (84% conversion) after purification by column chromatography (Cy:EtOAc = 50:50) as a white solid. Their spectroscopic data are in agreement with published data.[11,12]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 – 7.62 (m, 2H), 7.57 – 7.48 (m, 3H), 2.72 (s, 3H).

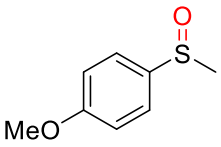
1-Methyl-4-(methylsulfinyl)benzene (9b)



The reaction of (methyl)(*p*-tolyl)sulfide (**8a**) (13.5 μL, 0.1 mmol) in methanol (200 μL) after 24 h afforded the sulfoxide **9b** in 72% yield (91% conversion) as a white solid after evaporation of the solvent and remaining thioether under vacuum. Their spectroscopic data are in agreement with published data.[11,12]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 and 7.32 (AA'BB' system, 4H), 2.70 (s, 3H), 2.41 (s, 2H).

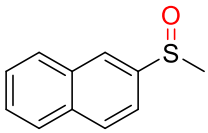
1-Methoxy-4-(methylsulfinyl)benzene (9c)



The reaction of 4-methoxythioanisole (**8c**) (15.4 mg, 0.1 mmol) in methanol (200 μL) after 24 h afforded the sulfoxide **9c** in 84% yield (91% conversion) as a white solid after evaporation of the solvent and remaining thioether under vacuum. Their spectroscopic data are in agreement with published data.[11,12]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 and 7.02 (AA'BB' system, 4H), 3.85 (s, 3H), 2.69 (s, 3H).

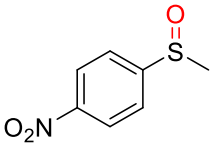
2-(Methylsulfinyl)naphthalene (9d)



The reaction of methyl(naphthalen-2-yl)sulfane (**8d**) (17.4 mg, 0.1 mmol) in methanol (400 μL) after 24 h afforded the sulfoxide **9d** in 77% yield (80% conversion) after purification by column chromatography (Cy:EtOAc = 80:20) as a white solid. Their spectroscopic data are in agreement with published data.[13]

1H NMR (300 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.03 – 7.86 (m, 3H), 7.65 – 7.54 (m, 3H), 2.79 (s, 3H).

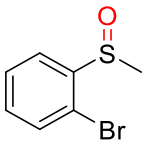
1-(Methylsulfinyl)-4-nitrobenzene (**9e**)



The reaction of methyl-4-nitrophenyl sulfide (**8e**) (16.9 mg, 0.1 mmol) in methanol (400 μL) after 24 h afforded the sulfoxide **9e** in 38% yield (45% conversion) after purification by column chromatography (Cy:EtOAc, gradient from 90:10 to 50:50) as a brown solid. Their spectroscopic data are in agreement with published data.[14]

1H NMR (300 MHz, CDCl3) δ 8.40 and 7.84 (AA'BB' system, 4H), 2.79 (s, 3H).

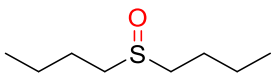
1-Bromo-2-(methylsulfinyl)benzene (9f)



The reaction of 2-bromophenyl methyl sulfide (**8f**) (13.3 μL, 0.1 mmol) in methanol (200 μL) after 24 h afforded the sulfoxide **9f** in 37% yield (41% conversion) after purification by column chromatography (Cy:EtOAc, gradient from 80:20 to 50:50) as a white solid. Their spectroscopic data are in agreement with published data.[12]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (ddd, *J* = 7.6, 1.7, 0.5 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.37 (ddd, *J* = 8.1, 7.2, 1.7 Hz, 1H), 2.82 (s, 3H).

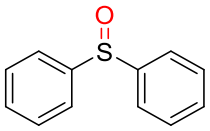
1-(Butylsulfinyl)butane (9g)



The reaction of dibutyl sulfide (**8g**) (17.5 μL, 0.1 mmol) in methanol (200 μL) after 24 h afforded the sulfoxide **9g** in 84% yield determined by ^{1}H NMR using 1,3,5-trimethoxybencene as internal standard. Their spectroscopic data are in agreement with published data.[12]

^{1}H NMR (300 MHz, CDCl3) δ 2.70 – 2.52 (m, 2H), 1.72 – 1.58 (m, 2H), 1.55 – 1.26 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

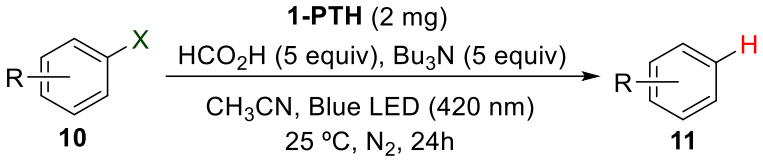
Sulfinyldibenzene (9h)



The reaction of diphenyl sulfide (**8h**) (17.1 μL, 0.1 mmol) in methanol (200 μL) after 24 h afforded the sulfoxide **9h** in 8% yield determined by ^{1}H NMR using 1,3,5-trimethoxybencene as internal standard. Their spectroscopic data are in agreement with published data.[12]

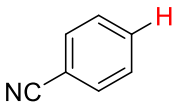
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.48 – 7.37 (m, 3H).

General Procedure for the reductive debromination reactions.



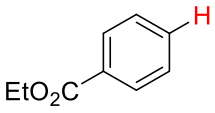
An 10 mL vial equipped with a magnetic stir bar was charged with catalyst **1-PTH** (2 mg), the corresponding aryl bromide (0.1 mmol), formic acid (19 μl, 0.5 mmol) and tributylamine (120 μl, 0.5 mmol). Then, acetonitrile (1 ml) was added and the vial sealed with a septum. Subsequently, the reaction mixture was degassed by three cycles vacuum / Ar of "freeze-pump-thaw". Finally, the system was placed under a 420 nm blue LED lamp under Argon atmosphere and stirring at 25 ºC for 24 hours. After this time, the yield was determined by ^{1}H-NMR using 1,3,5-trimethoxybencene as internal standard.

Benzonitrile (11a)



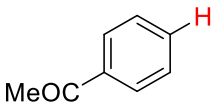
The reaction of 4-bromobenzonitrile (**10a**) (18 mg, 0.1 mmol) after 24 h afforded the benzonitrile (**11a**) in 100% conversion by ^{1}H NMR. Their spectroscopic data are in agreement with published data.[15]

Ethyl benzoate (11b)



The reaction of ethyl 4-bromobenzoate (**10b**) (16 mg, 0.1 mmol) after 24 h afforded the ethyl benzoate (**11b**) in 79% conversion by ^{1}H NMR. Their spectroscopic data are in agreement with published data.[16]

Acetophenone (11c)



The reaction of 1-(4-bromophenyl)ethan-1-one (**10c**) (20 mg, 0.1 mmol) after 24 h afforded the ethyl benzoate (**11c**) in 21% conversion by ^{1}H NMR. Their spectroscopic data are in agreement with published data.[17]

NMR Spectra

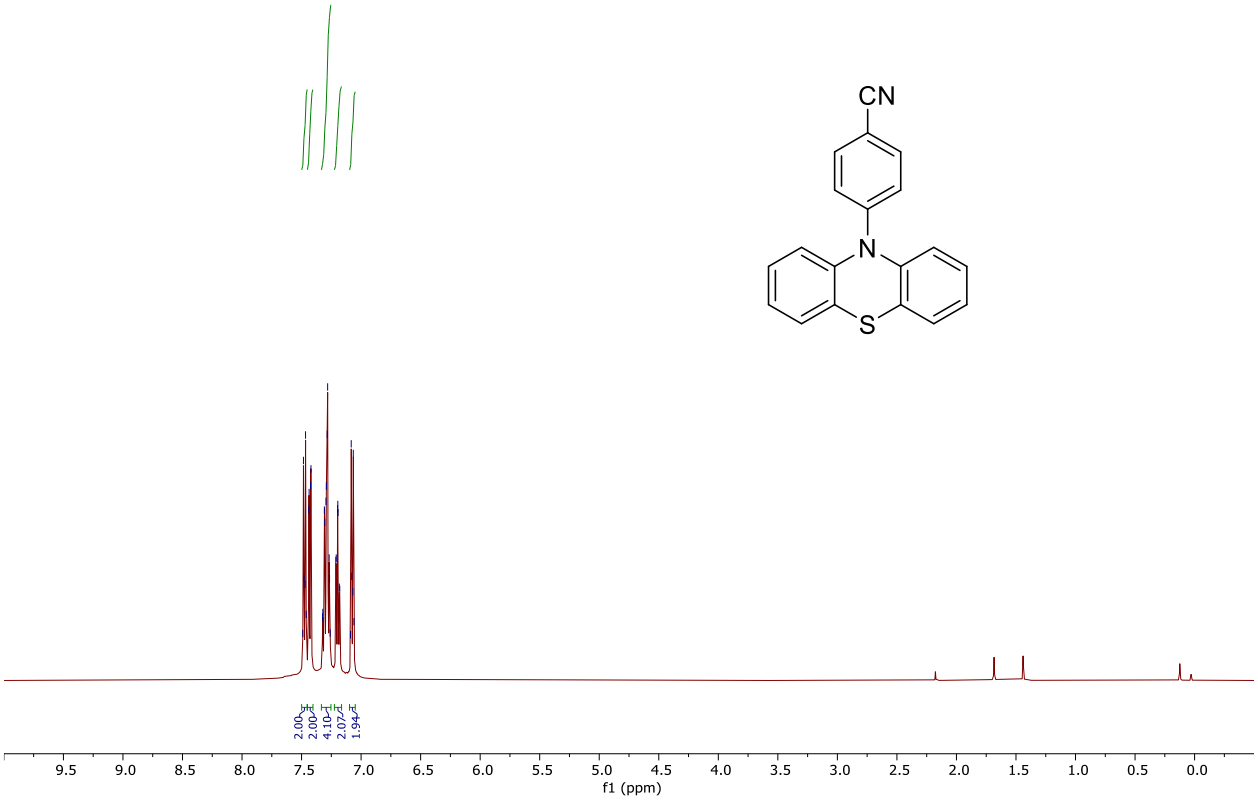


Figure S20. ^{1}H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **4**.

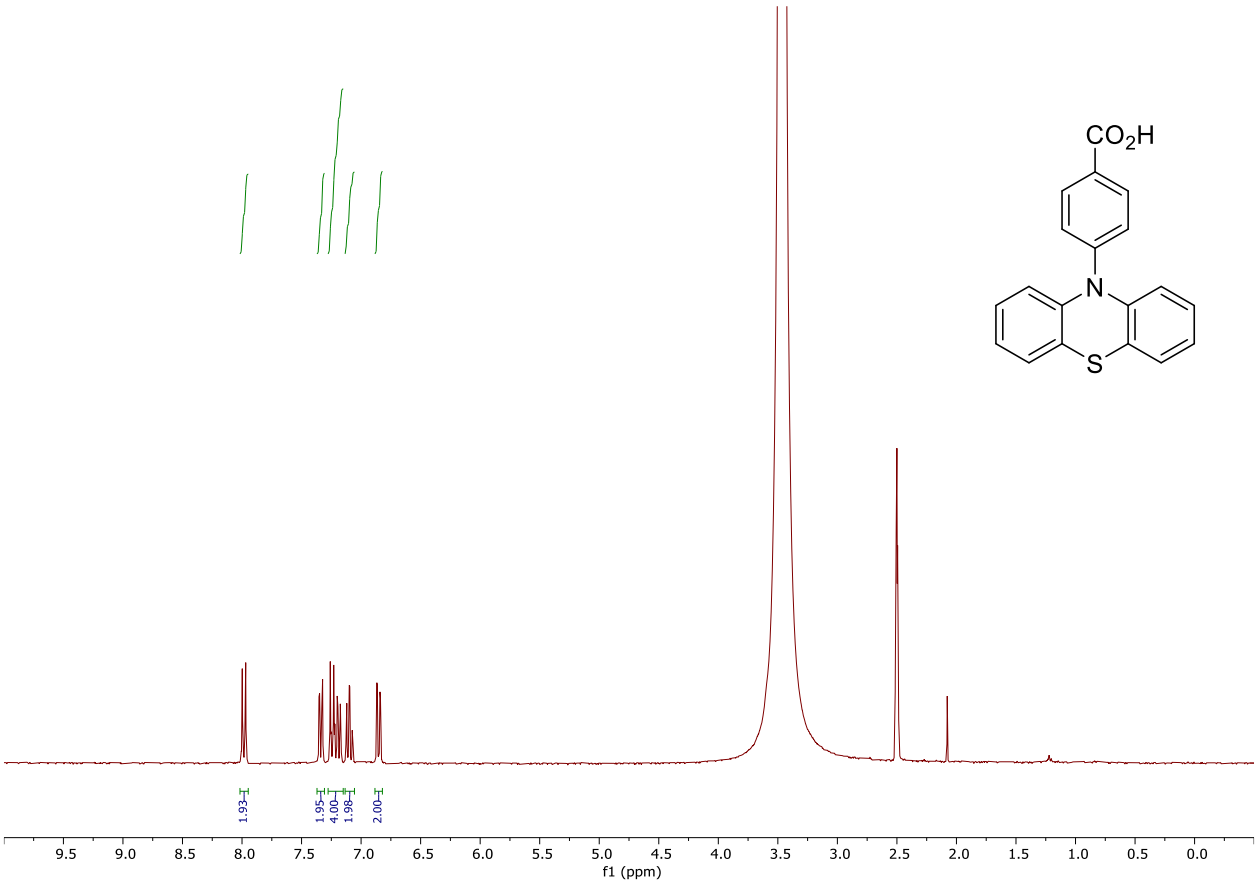


Figure S21. ^{1}H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **5**.

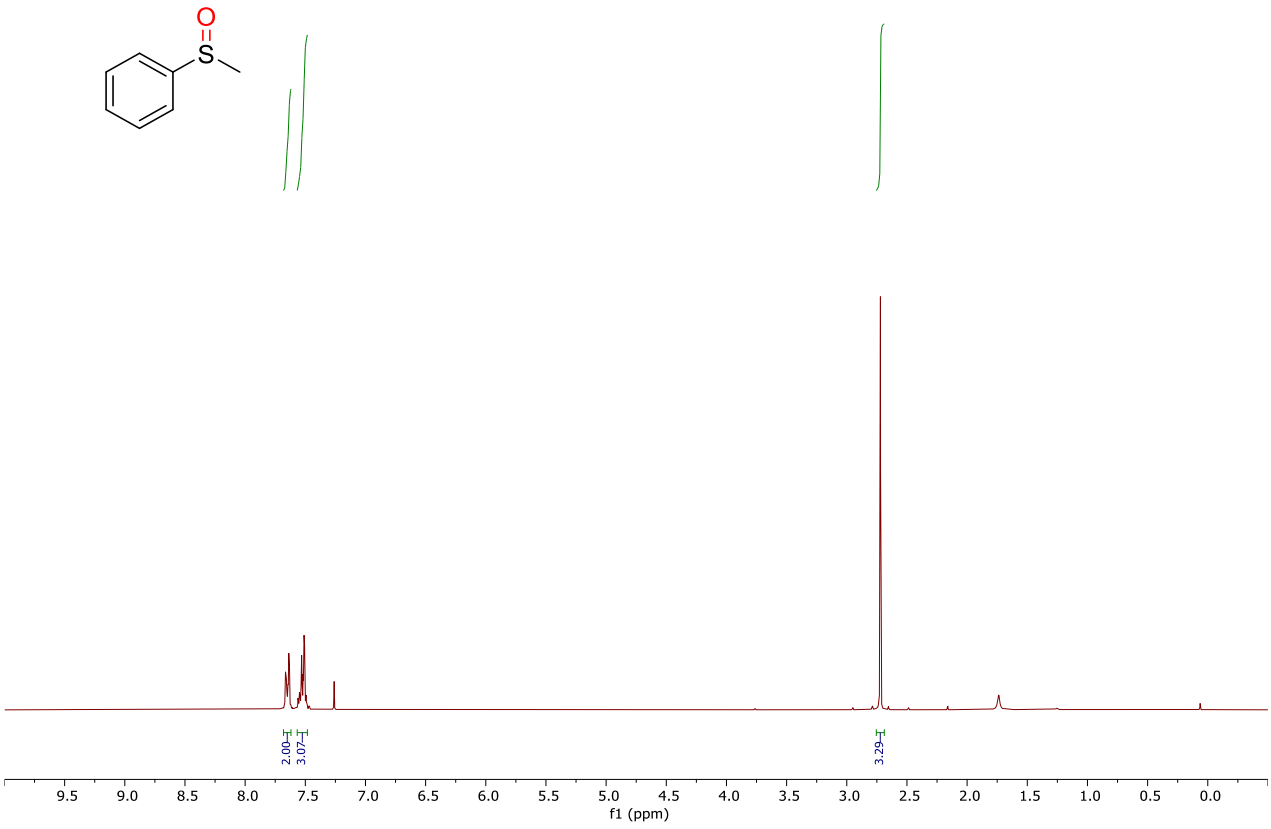


Figure S22. ^{1}H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **9a**.

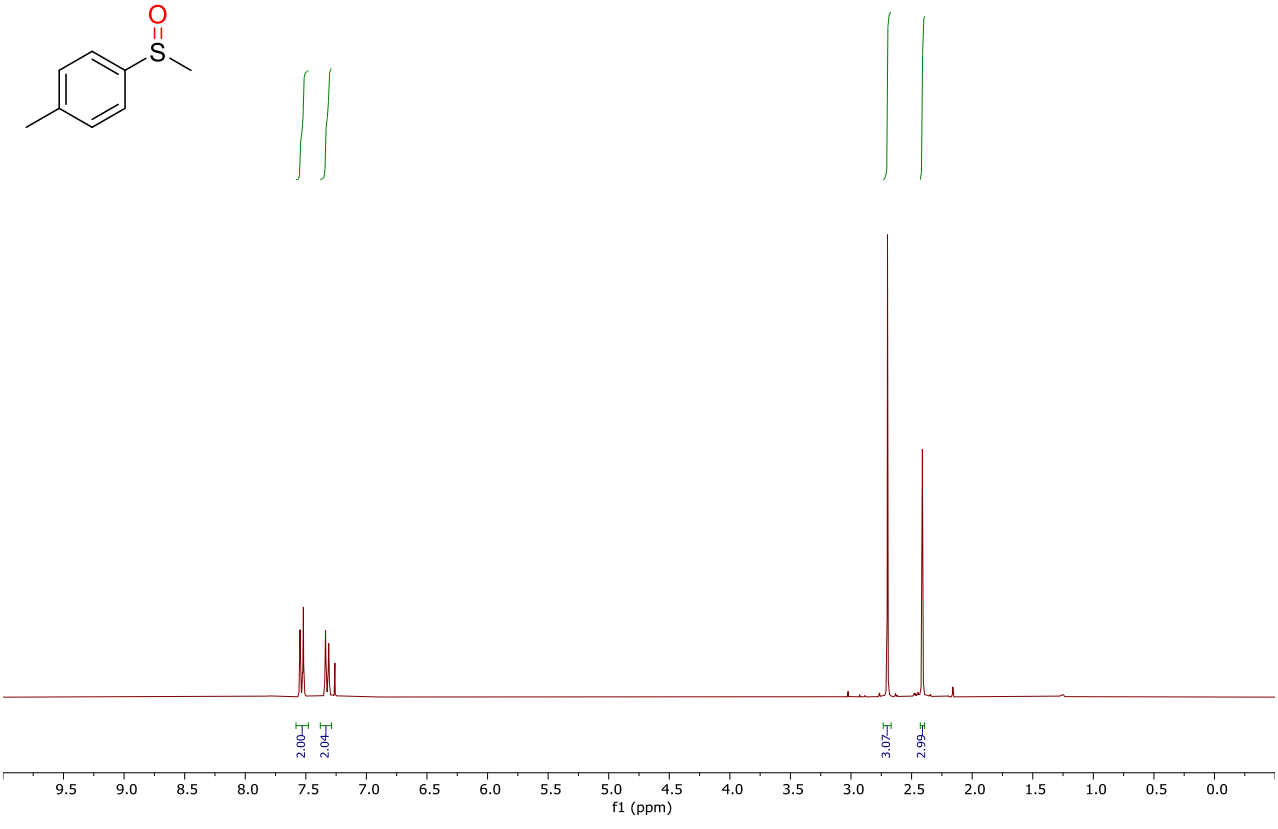


Figure S23. ^{1}H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **9b**.

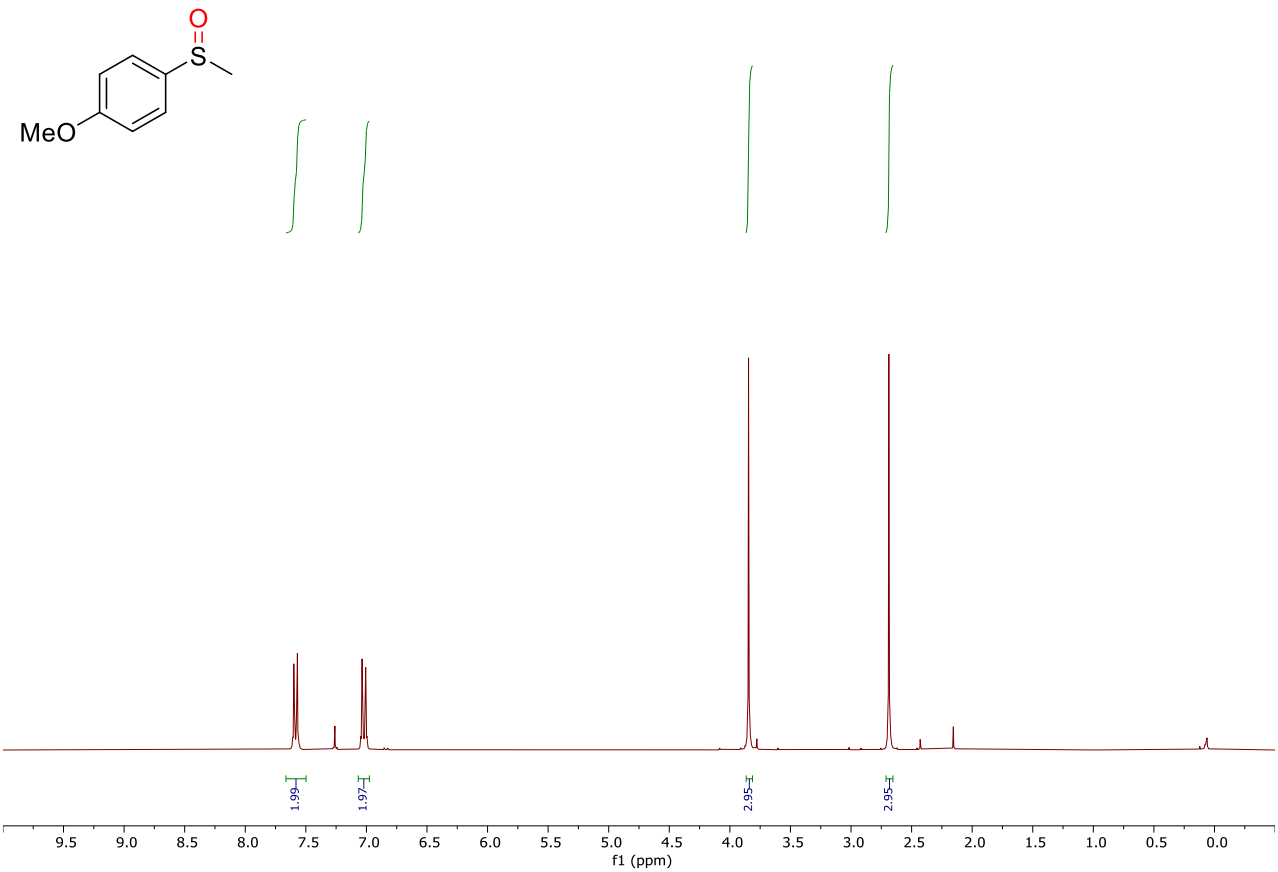


Figure S24. ^{1}H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **9c**.

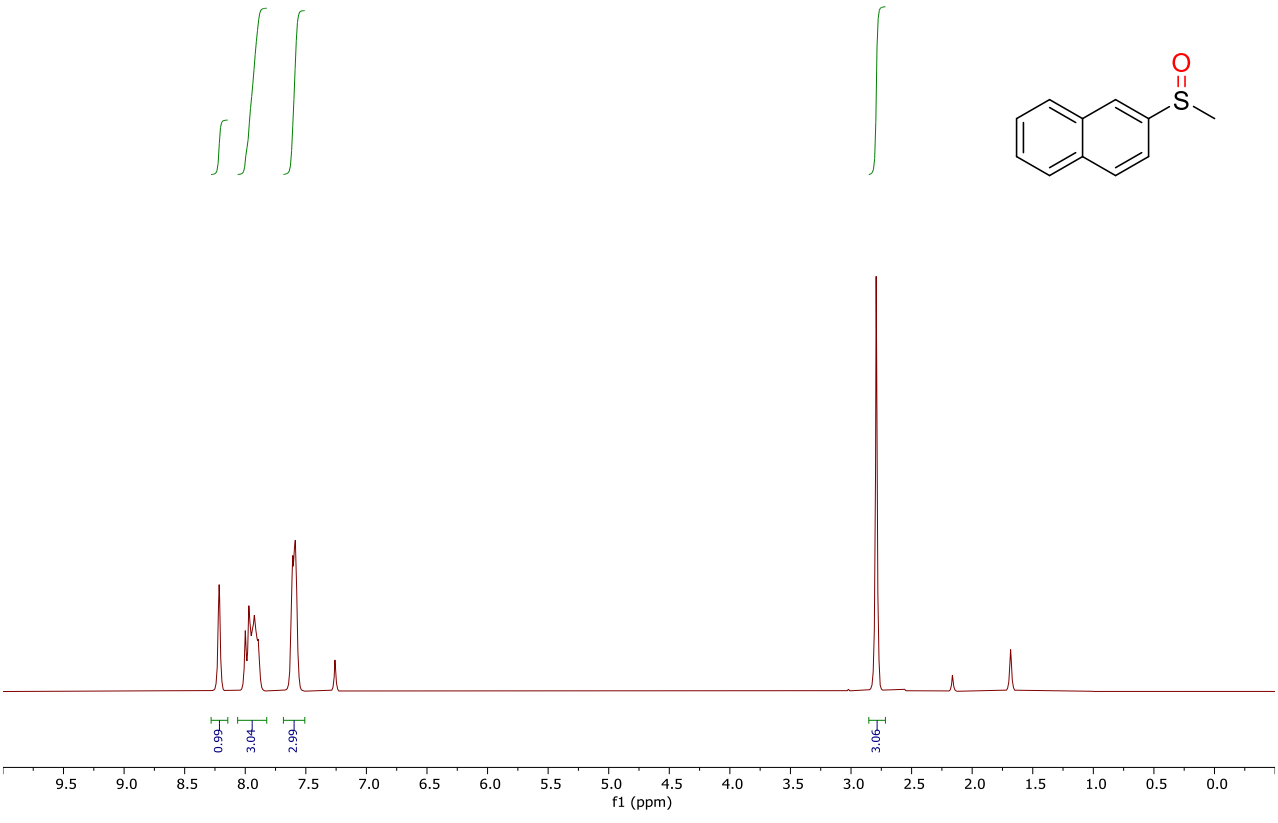


Figure S25. ^{1}H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **9d**.

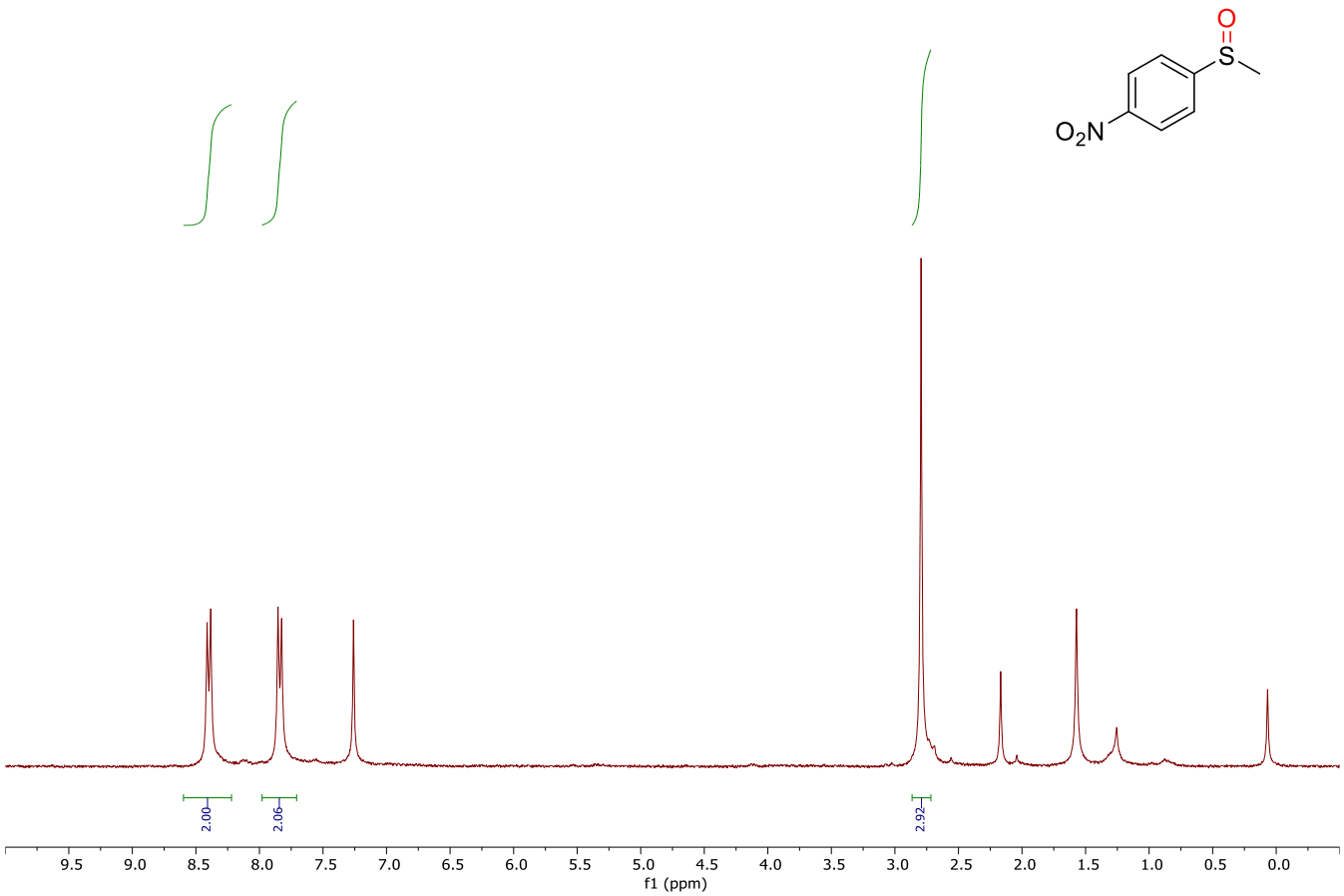


Figure S26. ^{1}H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **9e**.

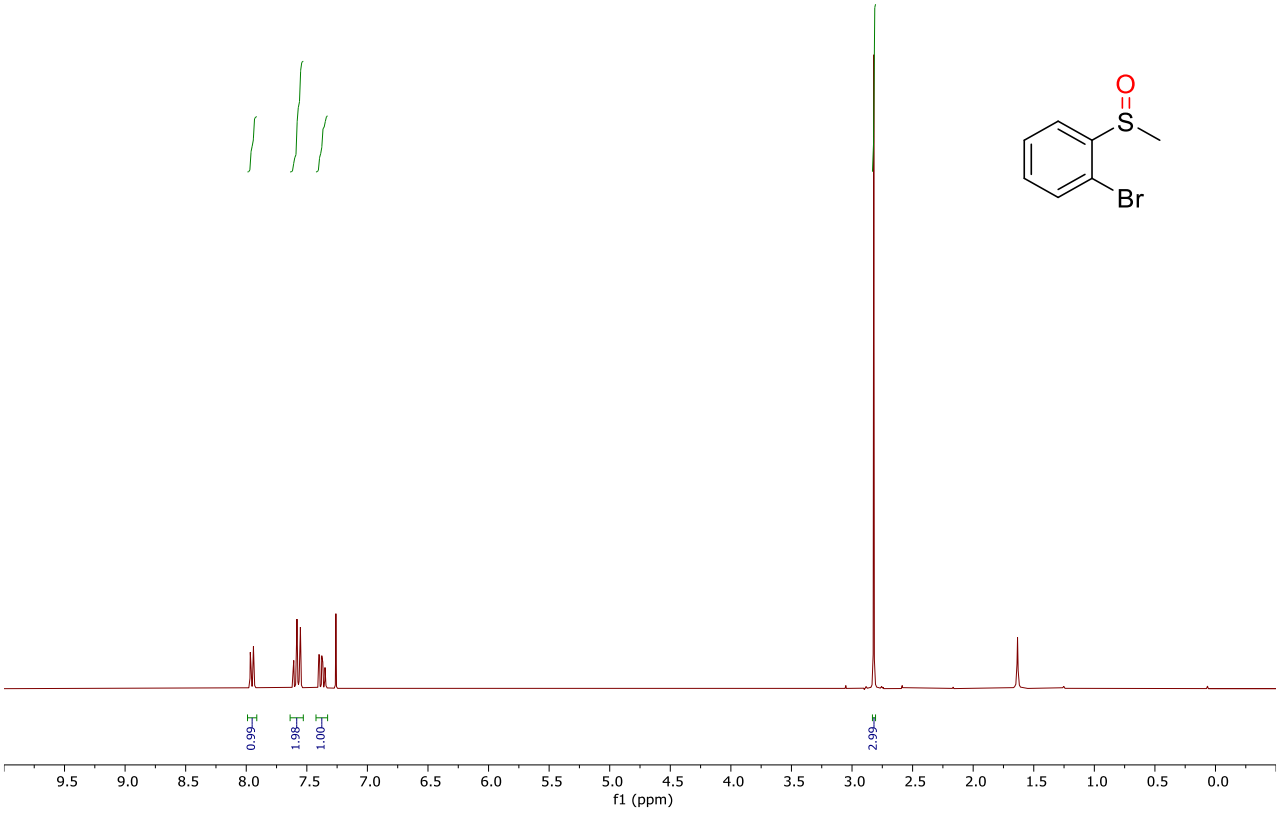


Figure S27. ^{1}H NMR spectrum (300 MHz, 298K, $CDCl_3$) of **9f**.

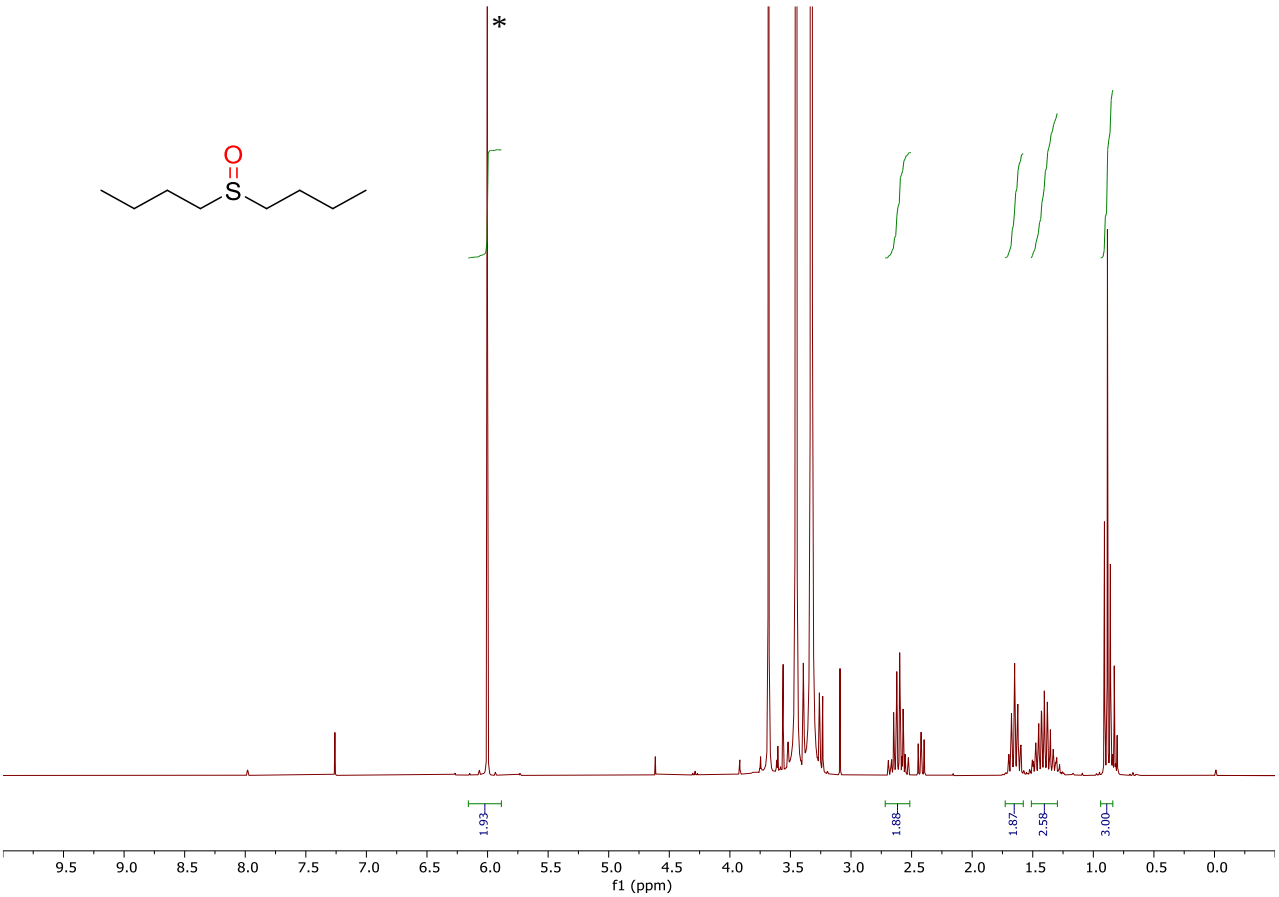


Figure S28. ^{1}H NMR spectrum of oxidation reaction crude of **8g** (300 MHz, 298K, $CDCl_3$). * Internal standard

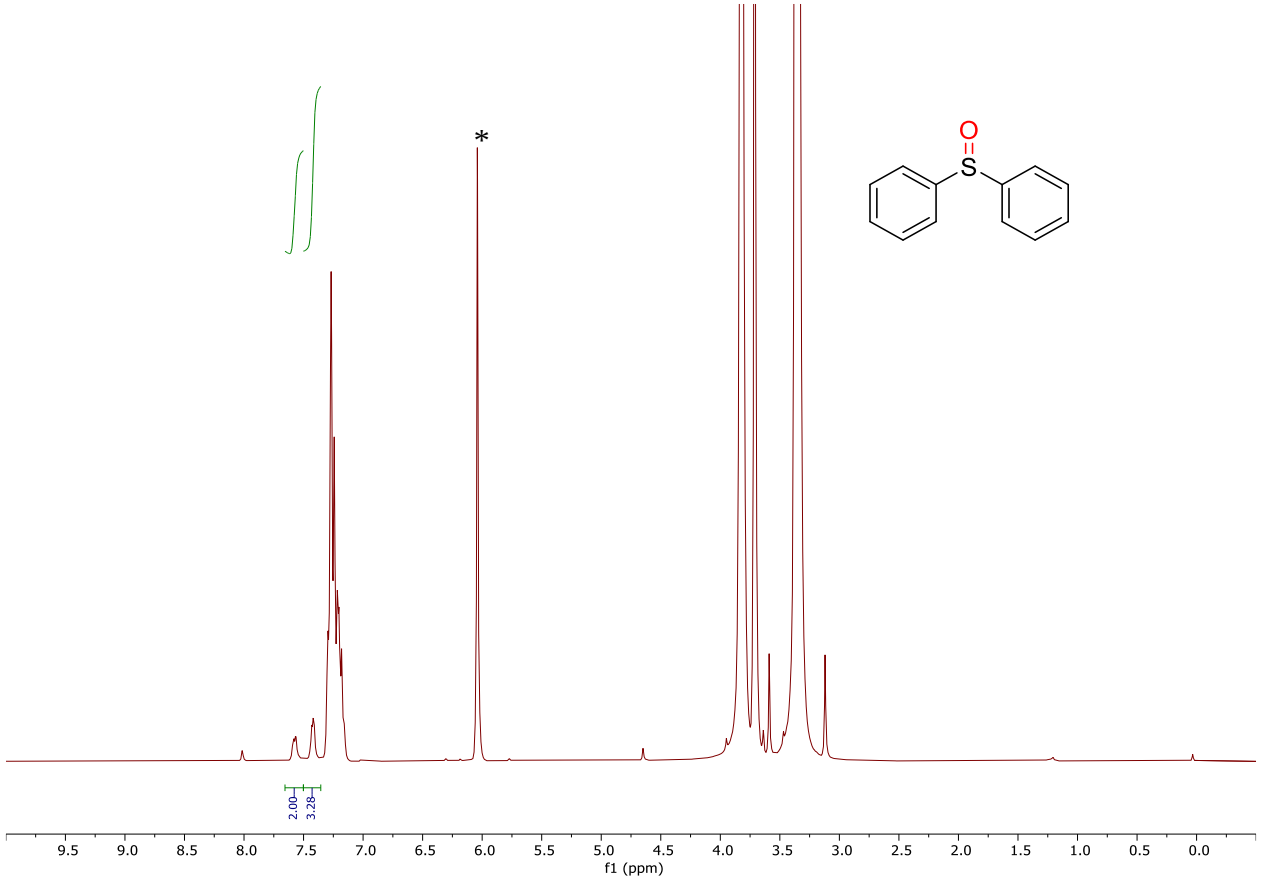


Figure S29. ^{1}H NMR spectrum of oxidation reaction crude of **8h** (300 MHz, 298K, $CDCl_3$). * Internal standard

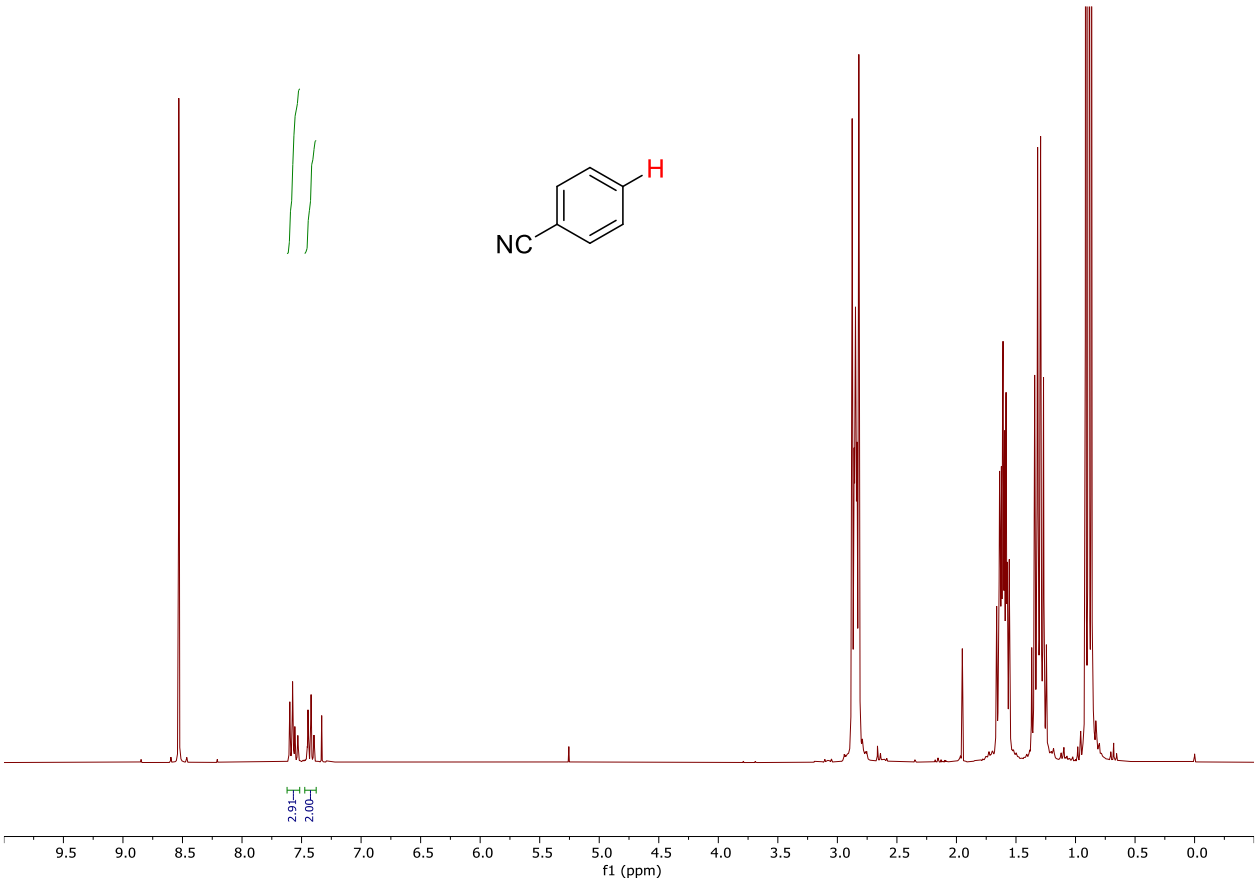


Figure S30. ^{1}H NMR spectrum of debromination reaction crude of **10a** (300 MHz, 298K, $CDCl_3$).

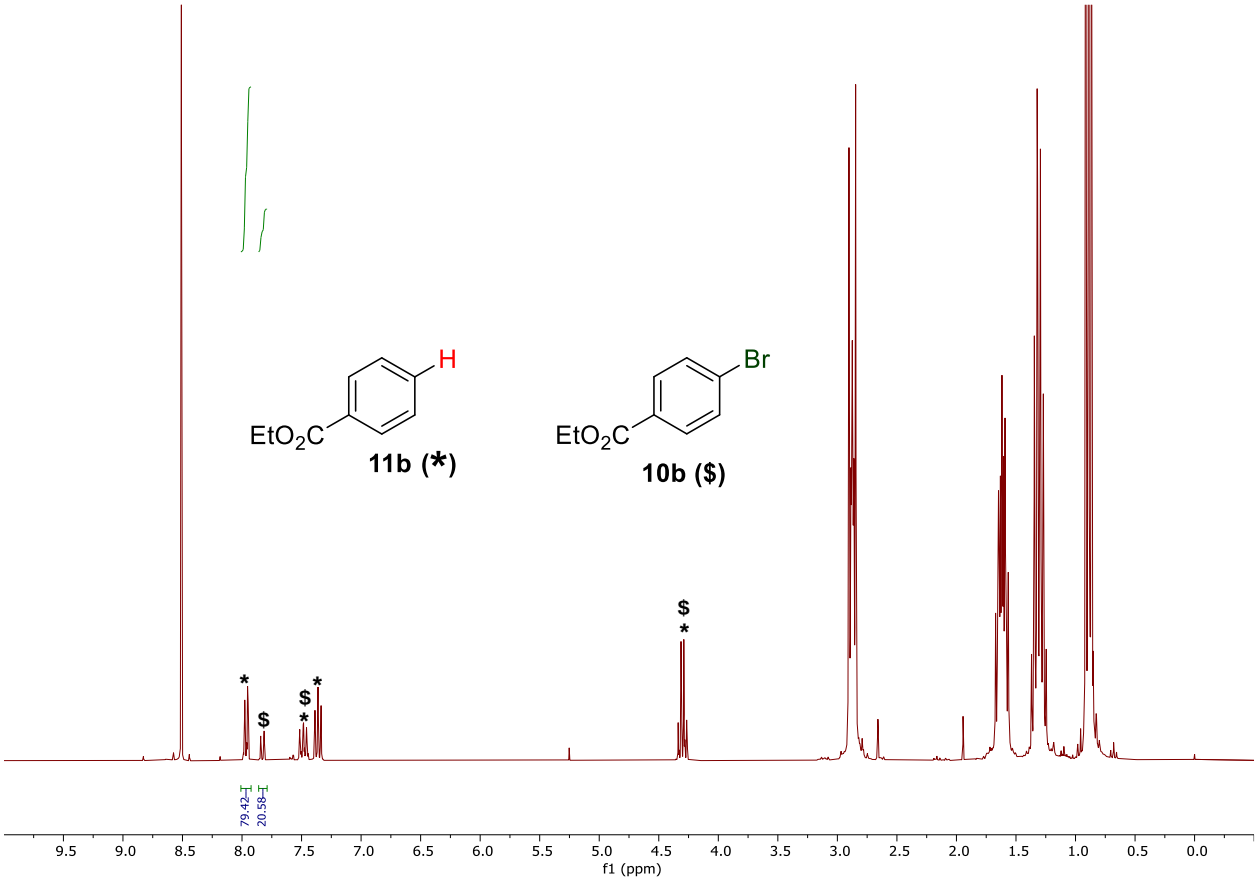


Figure S31. ^{1}H NMR spectrum of debromination reaction crude of **10b** (300 MHz, 298K, $CDCl_3$).

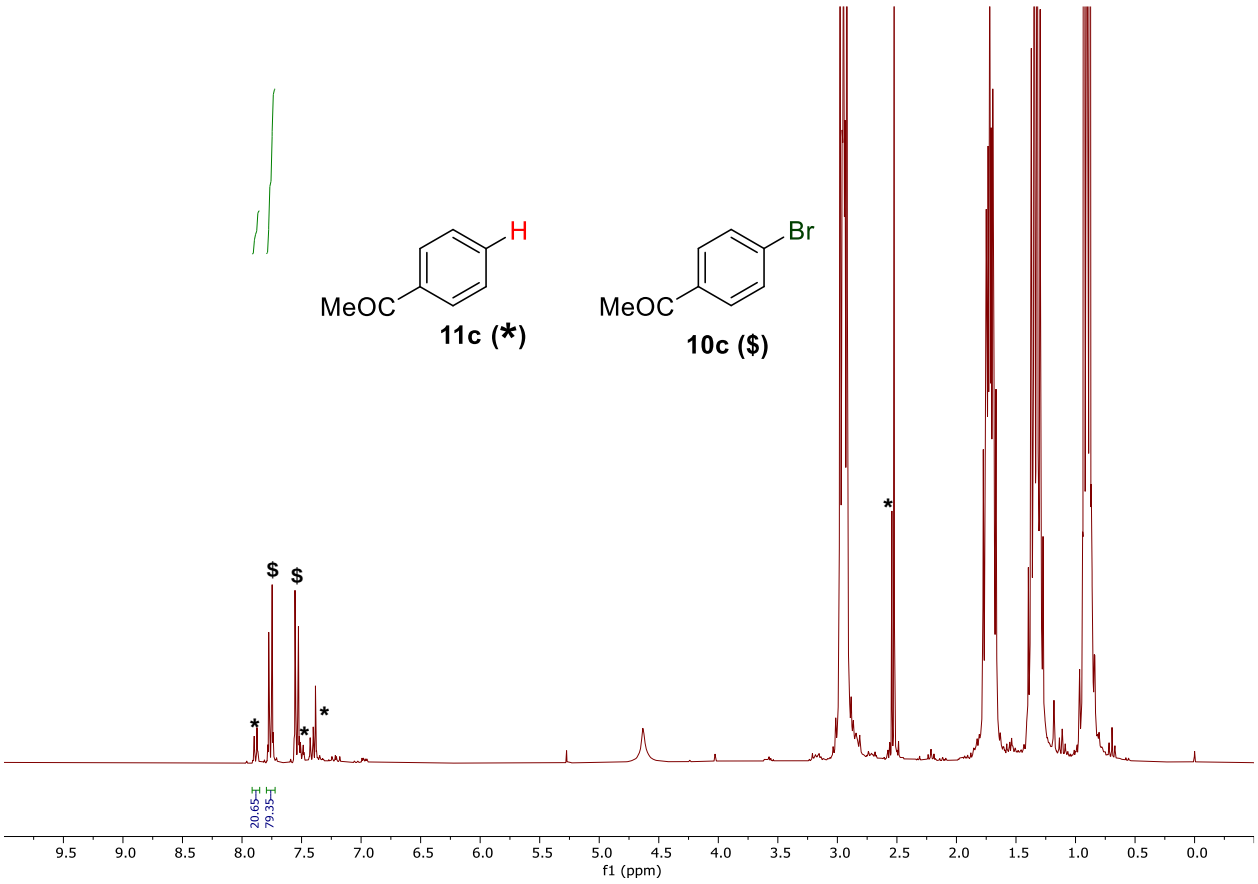


Figure S32. ^{1}H NMR spectrum of debromination reaction crude of **10c** (300 MHz, 298K, $CDCl_3$).

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