Electronic Supplementary Material (ESI) for Green Chemistry.

TPPS supported on core-shell PMMA nanoparticles: the development of continuous-flow membrane-mediated electrocoagulation as photocatalyst processing method in aqueous media

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Electronic Supporting Information

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1. General Information

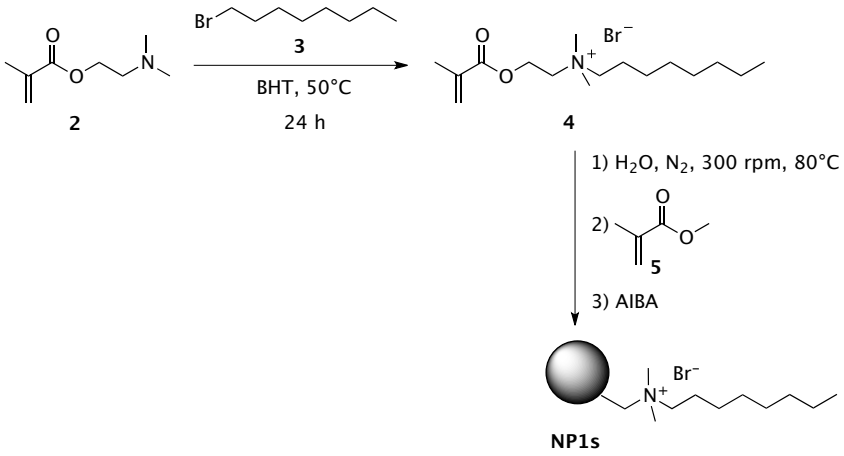
Solvents were dried over standard drying agent and freshly distilled prior to use. Deionized water was obtained with milli-Q Millipore Water Purification System and is referred as milliQ water throughout the paper. Flash chromatography was performed on Teledyne Isco CombiFlash® Rf 200 using RediSep® Normal-phase Silica Flash Columns (230-400 mesh). Reactions were monitored by TLC on silica gel 60 F254 with detection by charring with $KMnO_4$. Hydrodynamic diameters were determined by dynamic light scattering (DLS) at 25 °C using a Zetasizer 3000 HS system (Malvern, UK) equipped with a 10 mV He–Ne laser. Data were analyzed based on the viscosity and refractive index of pure water at 25°C. The instrument was calibrated with standard polystyrene latex particles of 200 nm in diameter. Zeta-potentials (Z_p) were measured at 25°C by means of the same Zetasizer 3000 HS system. The instrument calibration was checked using standard polystyrene latexes, supplied by Malvern Instruments with known Z_p. Quaternary ammonium salt loading per gram of NPs was determined by potentiometric titration of the bromide ions obtained after complete ion exchange. The ionic exchange was accomplished by dispersing the NPs sample in 1M KNO_3 at room temperature. In these conditions, a quantitative ionic exchange was achieved. The mixture was then adjusted to pH 2 with conc. H_2SO_4 and bromide ions were titrated with a 0.02 M solution of $AgNO_3$. SEM analyses were performed with a Zeiss Gemini 1530 scanning electron microscope. AFM images were performed in air and recorded using a Multimode IIIA (Bruker) scanning probe. Imaging was done in tapping mode using a silicon RTESPA probe (Bruker, frequency f0 = 270 KHz and nominal tip radius ≤ 15 nm). UV spectra were registered with a Lambda 20 Perkin Elmer spectrophotometer. NMR spectra were recorded in $CDCl_3$ or D_2O solutions at 25°C on a Mercury Varian spectrometer operating at 400 MHz (^1H) and 100.5 MHz (^{13}C). Water signal in ^1H NMR spectra of wet samples was suppressed using presat pulse sequence (optimized parameters: d_1=0, satpwr=6, satdly=4, sspul="y"). IR spectra were registered with a Perkin Elmer Spectrum BX FT-IR System. For accurate mass measurements, the compounds were analyzed in positive ion mode by Agilent 6520 HPLC-Chip Q/TOF-MS (nanospray) using a quadrupole, a hexapole, and a time-of-flight unit to produce spectra. The capillary source voltage was set at 1700 V; the gas temperature and drying gas were kept at 350°C and 5 L/min, respectively. MS analyzer was externally calibrated with ESI-L low concentration tuning mix from m/z 118 to 2700 to yield accuracy below 5 ppm. Accurate mass data were collected by directly infusing samples in 40/60 H_2O/ACN 0.1% TFA into the system at a flow-rate of 0.4 mL/min. FEP tubing, 1/16" x 1.0 mm ID and PTFE tubing, 1/16" x 1.0 mm ID were purchased from VICI Jour. UV CLEO 15 W lamp was produced by Philips. 11 W 6400 K CFL (Compact Fluorescent Lamp) was produced by Lexman. PowerChrome Pure Actinic 24 W T5 lamp was produced by Giesemann. The emission spectra of the lamps were registered using an Edinburgh FLS920 spectrometer equipped with a Peltier-cooled Hamamatsu R 928 photomultiplier tube (sensitive in the 185–850 nm range). The excitation source was off during the acquisition. Photoinduced reactions were carried out open to air in a glass vial (diameter: 1 cm [4 mL] or 2.5 cm [20 mL]; wall thickness: 0.65 mm) directly lied on lamps. Faber-Castell TK9071 2B leads (Φ = 2 mm, length = 13 cm) were used as graphite rods. (Copper rods (Φ = 2 mm, length = 25 cm, copper welding rods) was produced by KEMPER GROUP. Platinum rod (Φ = 1 mm, length = 25 cm) were purchased from Metalli Preziosi SpA. DC-current was supplied by a QJE QJ3005C 0-30VDC/0-5A, stabilized DC power supply. Voltage was measured with a

EXITV EX-845 cod. 85001030 auto-range digital multimeter. Current intensity was measured with an Electraline 4-digit 59002 digital multimeter. The dialysis membranes (Medicell International Ltd dialysis Visking tubing; Φ = 6.3 mm or Φ = 28.6 mm; MWCO = 12-14 KDa) were washed in running water for 3 - 4 hours before using. A Mettler Toledo SevenMulti pH-meter was used for pH measurements. In continuous-flow experiments reagents and washing water were fed using an Harvard Apparatus 22 syringe pump. All chemicals were purchased from Sigma-Aldrich.

Caution: the membrane-mediated electrocoagulation method results in the generation of a small amount of hydrogen gas, which is a potential fire hazard.

2. NP1s: synthesis and characterization

As depicted in Scheme S1, positively charged **NP1s** were obtained by emulsion polymerization of methyl methacrylate in the presence of the ionic comonomer 2-(dimethyloctyl) ammonium ethylmethacrylate bromide **4** as emulsion stabilizer. The comonomer **4** was obtained as previously described.[1,2] Characterization data of prepared **4** were in accordance with those previously published.



Scheme S1: Strategy for the synthesis of nanoparticles **NP1s**.

2.1 Synthesis of the starting comonomer 4

2-(dimethyloctyl) ammonium ethylmethacrylate bromide (4): 2 (dimethylamino)ethylmethacrylate (**2**, DMAEMA) (26.1 g, 0.166 mol) was mixed with neat 1-bromooctane (**3**) (16.0 g, 0.083 mol) and BHT (2,6-di-tert-butyl-4-methylphenol) (8 mg, 0.036 mmol). The mixture was

then stirred at 50°C. After 24 h, the obtained solid product was washed with dry diethyl ether, crystallized in acetone, and dried under vacuum to obtain 17.7 g (0.051 mol, 61% yield) of the title compound.

^{1}H NMR ($CDCl_3$): δ = 6.12 (t, J = 1.1 Hz, 1 H), 5.63 - 5.70 (m, 1 H), 4.58 - 4.70 (m, 2 H), 4.11 - 4.21 (m, 2 H), 3.57 - 3.67 (m, 2 H), 3.51 (s, 6 H), 1.93 (dd, J = 1.5, 0.9 Hz, 3 H), 1.66 - 1.81 (m, 2 H), 1.13 - 1.43 (m, 10 H), 0.80 - 0.91 (m, 3 H) ppm

^{13}C NMR ($CDCl_3$): δ = 166.5, 135.4, 127.6, 65.7, 62.4, 58.3, 52.1, 31.8, 29.4, 29.2, 26.5, 23.2, 22.8, 18.5, 14.2 ppm

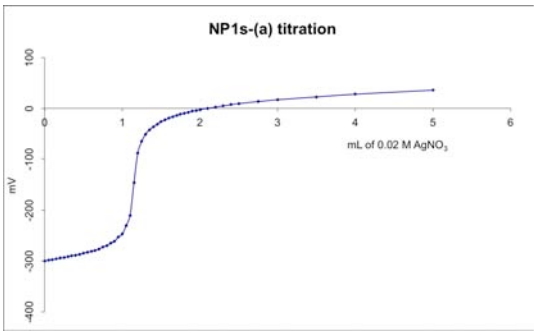
2.2 NP1s-(a) and NP1s-(b): synthesis and characterization

General procedure for NP1s synthesis. See Table S1 for: *i)* the reagent amounts utilized for the preparation of **NP1s-(a)** and **NP1s-(b)**; *ii)* their characterization. **NP1s-(a)** differed from **NP1s-(b)** in terms of morphological and electrokinetic parameters, bromide loading and concentration.

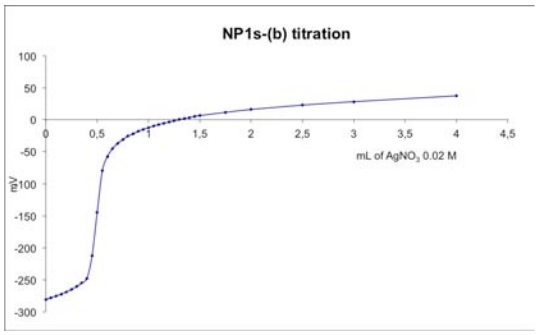
A 4-necked 250 mL round bottomed flask equipped with a mechanical stirrer, a thermometer, a nitrogen inlet and a condenser, was charged with 2-(dimethyloctyl) ammonium ethylmethacrylate bromide **4** and distilled water (100 mL). The mixture was then heated. Upon reaching 80°C, nitrogen was bubbled in the solution bulk for 10 min. Methyl methacrylate (**5**, MMA) was then added dropwise into the stirred reaction mixture under nitrogen atmosphere. After 15 min, 2,2′-azobis (isobutyramidine) dihydrochloride (AIBA) was added thereto. The obtained white suspension was stirred at 80°C for additional 4 h. After cooling at room temperature, the milky suspension was dialyzed for 15 days changing the outer water 2 times a day (dialysis Visking tubing; Φ = 28.6 mm; MWCO = 12-14 KDa). The obtained **NP1s** were characterized as detailed in Table S1, Graphs S1-S2 and Figure S1-S2.

Table S1: NP1s synthesis and characterization.

Sample	MMA	Compound **4**	AIBA	d_h [nm]	Polydispersity [nm]	Z_p [mV]	Br^- [µmol/g]	[NPs] [mg/mL]
NP1s-(a)	5.0 mL 53 mmol	1.016 g 2.90 mmol	13 mg 0.048 mmol	169±2	0.11±0.04	57.2±0.4	381	30.3
NP1s-(b)	2.0 mL 19 mmol	1.022 g 2.92 mmol	15 mg 0.055 mmol	74.0±0.3	0.10±0.01	32±14	688	14.6



Graph S1: NP1s-(a) potentiometric titration (2 mL of a 30.3 mg/mL colloid)



Graph S2: NP1s-(b) potentiometric titration (1 mL of a 14.6 mg/mL colloid)

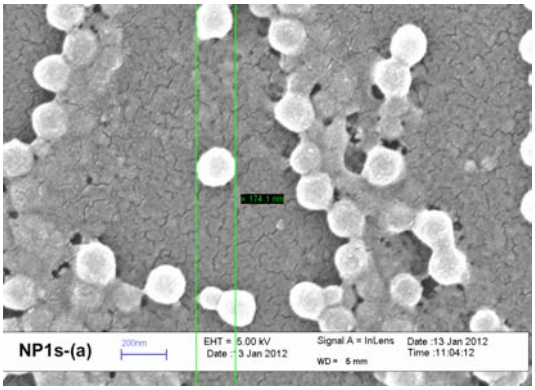
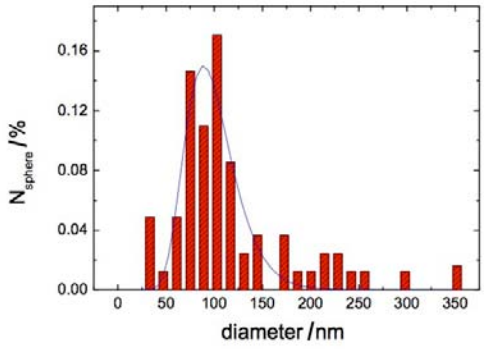


Figure S1: SEM image of **NP1s-(a)**.



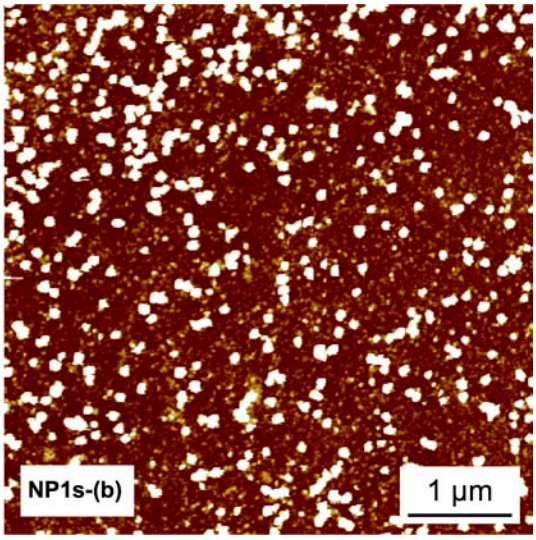


Figure S2: AFM diameter distribution and image of **NP1s-(b)**: radius = 35±15 nm (Z-range = 30 nm)

3. Preliminary observations: coagulation *vs.* EPD of NP1s-(a)

A graphite anode and a copper cathode (Φ = 2 mm, length = 13 cm) were directly immersed into the white, eye-visible aqueous colloid of **NP1s-(a)** (10 mL of a 2.0 mg/mL aqueous colloid). A DC was supplied for 30 min at constant current or constant voltage. Pictures in Table S2 show the concomitant electrophoretic deposition (EPD) and NPs coagulation as function of voltage across the electrodes (or of the current in the electrolytic cell). The effect of water electrolysis on the colloid clarification and the beneficial effect of the dialysis membrane on NPs coagulation are also evidenced.

Table S2: Water electrolysis, EPD,[a] and coagulation of **NP1s-(a)** in preliminary experiments.

5 min (1.0 mA)[b]	15 min (1.0 mA)[b]	30 min (1.0 mA))[b]	30 min (2.5 V)	30 min (1.9 V)	40 min (15.0 V, membrane)
					

[a] The EPD was evidenced by the whitish film deposited on the copper cathode and on the membrane; [b] A voltage of 3.76 V was measured across the electrodes at the beginning of the experiment operated at the constant DC of 1.0 mA.

4. Systematic study of the membrane-mediated electrocoagulation of NP1s-(a)

4.1 Electrolytic cell and separating apparatus

Electrolytic cell (Figure S3a): ***i)*** a copper rod (Φ = 2 mm) and ***ii)*** a platinum rod (Φ = 1 mm), separated by ***iii)*** a dielectric spacer (polypropylene [PP], thickness = 0.8 mm) and aligned at the distance of 3 mm, were inserted into ***iv)*** a bottom-end sealed dialysis membrane (Visking tubing, MWCO = 12-14 KDa, Φ = 6.3 mm). The membrane was filled with 2.0 mL of milliQ water. When connected to the DC power supply, the copper rod worked as the cathode and the platinum rod worked as the anode.

A **custom made cap** (Figures S3b) equipped with a ***v)*** 29/32 cone on the bottom, ***vi)*** two eccentric inlet on the top, ***vii)*** one coaxial, and ***viii)*** two perpendicular pipes on the body, was used as holder for the electrolytic cell.

A custom made dropping funnel (Figure S3c) equipped with a ***ix)*** thermostatic jacket, ***x)*** a Rotaflow Stopcock on the bottom, ***xi)*** an overflow pipe, and a ***xii)*** 29/32 socket on the top was used as **settling device**.

The **final separating apparatus** (Figure S3d) was assembled when the electrodes holder was fixed on the top of the settling device.

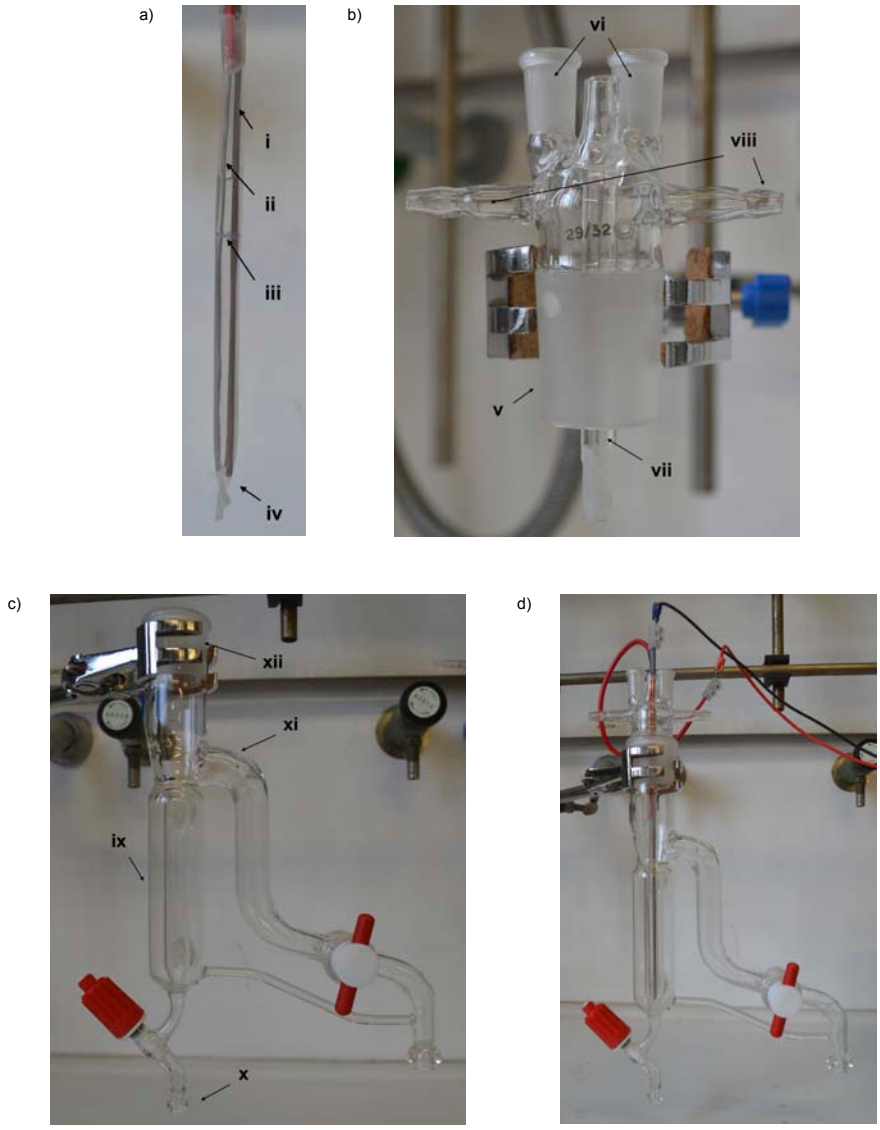


Figure S3: Separating apparatus: a) electrolytic cell; b) custom made cap: front view; c) settling device; d) assembled separating apparatus

4.2 General procedure for NP1s-(a) electrocoagulation

Electrocoagulation procedure: A 5.05 mg/mL suspension of **NP1s-(a)** was obtained diluting 3.0 mL of **NP1s-(a)** starting colloid in 15.0 mL of milliQ water. 6.0 mL of the diluted colloid were placed into the settling device. The electrolytic cell was immersed therein and DC was supplied. All experiments were run at constant DC or constant voltage. During each run, the following parameters were monitored: the current flowing in the electrolytic cell, the voltage across the electrodes, the up-front height of the settling colloid and, starting from when it became recognizable, the thickness of the settling area (Figure S4). After 60 min, and with the power still on, the clarified liquor was withdrawn from the top of the separating apparatus at the flow-rate of 1.4 mL/min. This was an optimized procedure to limit NP remixing during the separation of the two phases. All recovered clarified liquors were diluted at the final volume of 5.0 mL. The settled colloids of coagulated **NP1s-(a)** were recovered and diluted at the final volume of 9.0 mL. The pH of both recovered **NP1s-(a)** and clarified liquors were finally measured.

Gravimetric analysis: after each experiment, two portions of an exactly known volume of both recovered **NP1s-(a)** and clarified liquors were freeze-dried in pre-tared vials (see Table S3 for experimental outcomes).

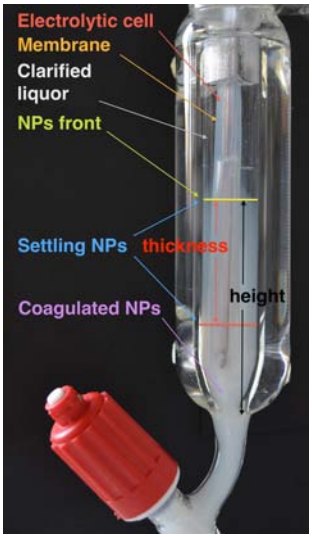
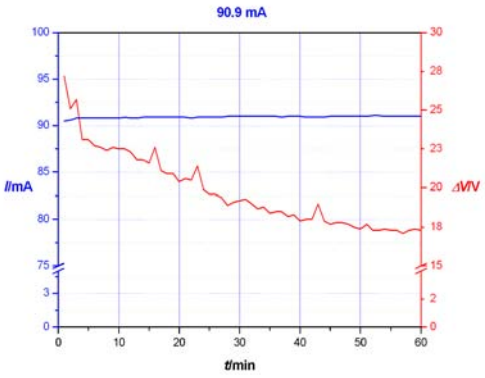


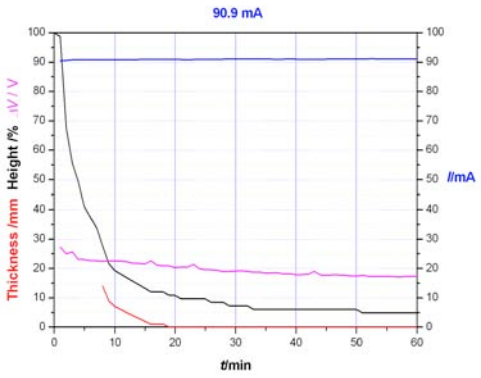
Figure S4: A picture of **NP1s-(a)** electrocoagulation and the relevant parameters evaluated.

4.3 Constant DC NP1s-(a) electrocoagulation

Five electrocoagulation experiments were performed at the following constant DCs: 36.5 mA, 52.2 mA, 73.7 mA, 90.9 mA, and 150.1 mA. The time-course of the measured currents and the corresponding measured voltages are reported in Graph S3 for the experiment at 90.9 mA. All measured parameters are reported as function of time in Graph S4 (selected experiment at 90.9 mA).

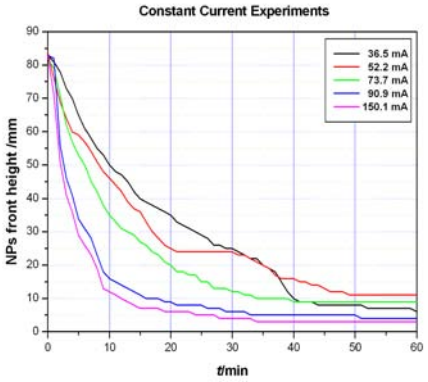


Graph S3: Measured current and voltage in the experiment at 90.9 mA.

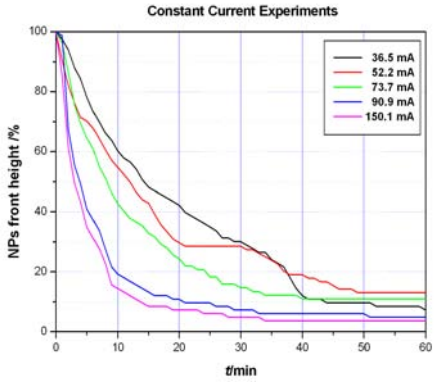


Graph S4: Time-course of the measured parameters in the experiment at 90.9 mA.

The front heights of coagulating **NP1s-(a)**, measured in mm (Graph S5) or expressed as height % (Graph S6), are collectively reported as function of time for all constant DC electrocoagulation experiments.



Graph S5: Time-course of the coagulating **NP1s-(a)** front height (mm) for all constant DC experiments.



Graph S6: Time-course of the coagulating **NP1s-(a)** front height (%) for all constant DC experiments.

In the experiments at 36.5 mA and 52.2 mA, a portion of **NP1s-(a)** in the settling region of the colloid slowly collapsed on the membrane instead of coagulating on the bottom of the settling device. This phenomenon accounts for the significant deviation from the exponential-like time-course of the measured NPs front height reported in Graphs S5/S6. The pictures taken at 18 min, 21 min and 29 min (Figure S5 a/b/c, respectively) of the electrocoagulation experiment at 52.2 mA clearly show the collapse of **NP1s-(a)** on the membrane together with their electrocoagulation. Therefore, this experimental evidence confirms that constant DCs lower than ca. 70 mA are not suitable for the electrocoagulation process.

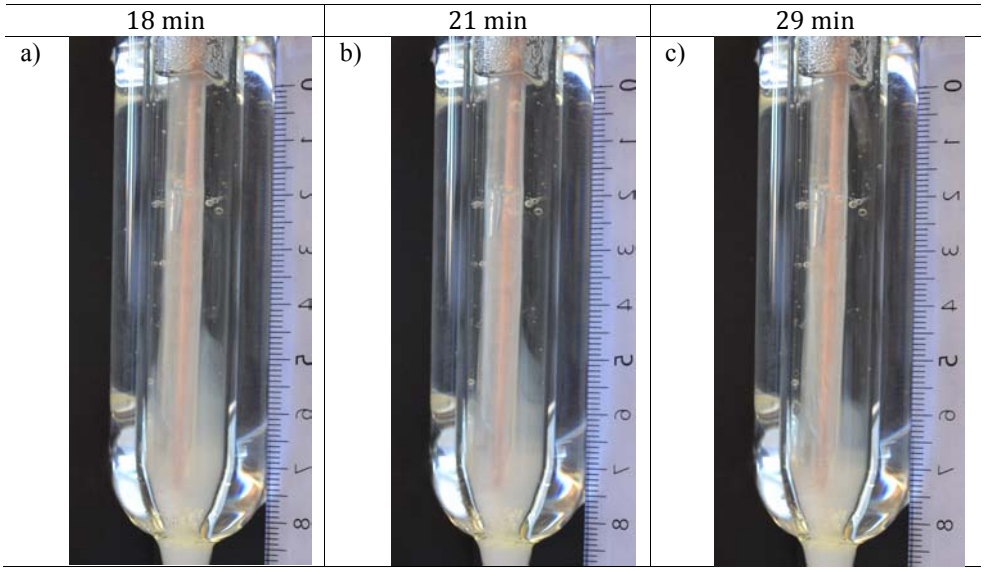
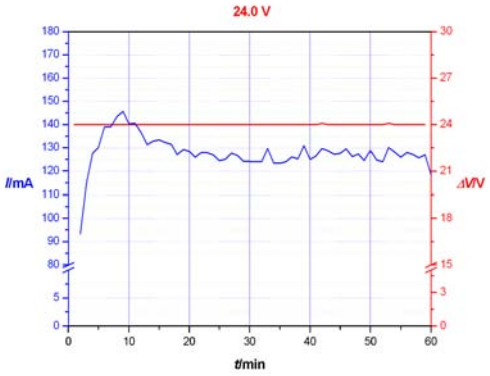


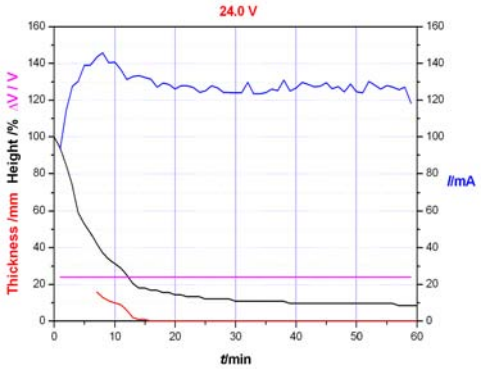
Figure S5: Pictures of **NP1s-(a)** electrocoagulation experiment at 52.2 mA evidencing the decrease of NPs front height and their collapse on the membrane.

4.4 Constant voltage NP1s-(a) electrocoagulation

Five electrocoagulation experiments were performed at the following constant voltages: 8.71 V, 11.98 V, 18.06 V, 24.0 V, and 30.0 V. The time-course of the measured currents and the corresponding measured voltages are reported in Graph S7 for the experiment at 24.0 V. All measured parameters are reported as function of time in Graph S8 (selected experiment at 24.0 V).

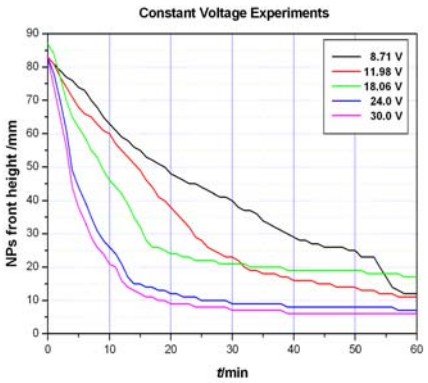


Graph S7: Measured current and voltage in the experiment at 24.0 V.

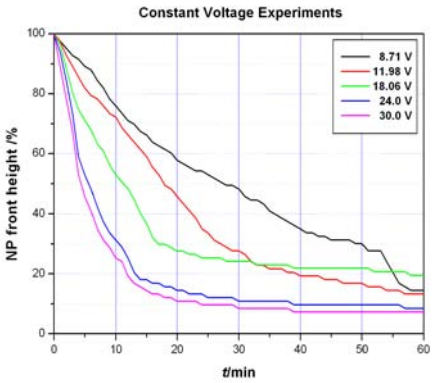


Graph S8: Time-course of the measured parameters in the experiment at 24.0 V.

The front heights of coagulating **NP1s-(a)**, measured in mm (Graph S9) or expressed as height % (Graph S10), are collectively reported as function of time for all constant voltage coagulation experiments.



Graph S9: Time-course of the coagulating **NP1s-(a)** front height (mm) for all constant voltage experiments.



Graph S10: Time-course of the coagulating **NP1s-(a)** front height (%) for all constant voltage experiments.

Mass recoveries along with characterization data of coagulated/redispersed **NP1s-(a)** and **NP1s-(a)** left in the clarified liquor are summarized in Table S3. Entry 1 reports data of starting **NP1s-(a)** for comparison.

Table S3: Experimental outcomes of electrocoagulation experiments at constant DC or voltage.[a]

Entry	Current/voltage	$t_{50\%}$ [min][b]	pH	Mass Recovery [w/w %]	d_h [nm][c]	Zp [mV]
1	**NP1s-(a)**	/	/	/	169±2 (0.110)	57.2±0.4
2	36.5 mA	14.2	3.41	3.1	/	/
			8.91	96.9	170.3±0.8 (0.043)	54.6±0.5
3	52.2 mA	12.0	3.58	4.2	/	/
			8.99	95.8	211±2 (0.028)	53.1±0.7
4	73.7 mA	8.2	3.38	5.3	/	/
			8.99	94.7	210±2 (0.085)	53.7±0.6
5	90.9 mA	3.9	3.72	4.3	/	/
			8.85	95.7	212.6±0.9 (0.040)	60.9±0.7
6	150.1 mA	3.0	3.56	16.2	/	/
			8.91	91.5	215±1 (0.082)	53±1
7	8.71 V	27.5	3.48	2.5	/	/
			9.36	97.5	215±1 (0.056)	65±2
8	11.98 V	17.8	3.66	1.3	/	/
			9.22	98.7	208±2 (0.066)	55±1
9	18.06 V	11.2	3.58	3.2	/	/
			9.47	96.8	213±2 (0.059)	53.9±0.9
10	24.0 V	5.6	3.64	2.4	/	/
			9.67	97.6	205±1 (0.078)	53.8±0.6
11	30.0V	4.5	3.59	8.5	/	/
			9.19	83.8	211.4±0.7 (0.058)	53.1±0.7

[a] Blank: **NP1s-(a)** in the clarified liquor. Shaded: coagulated/redispersed **NP1s-(a)**; [b] Time to reach 50% of the initial NPs front height; [c] Bracketed: polydispersity.

4.5 Electrocoagulation *vs.* membrane EPD of NP1s-(a)

During the electrocoagulation experiment, NPs coagulation and membrane EPD of NPs are concomitant phenomena that cooperate in the complete clarification of the colloid. NPs that are reversibly deposited on the membrane are then dragged back into the clarified liquor when this latter is withdrawn from the top of the settling device by a syringe. Those dragged NPs account for the residual NPs recovery in the clarified liquor. Our experiments showed that membrane EPD is minimized below 100 mA or 25 V applied constant DC or voltage, respectively, while becoming significant above those limits. Figure S6 shows **NP1s-(a)** deposited on the membrane and their dragging back into solution during withdrawal of the clarified liquor in the experiment at 30.0 V constant voltage.

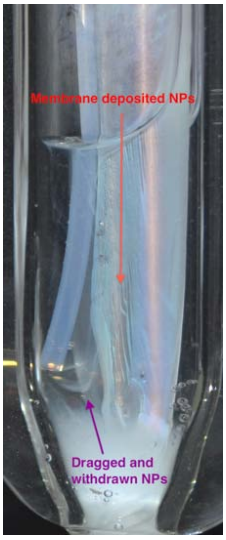


Figure S6: **NP1s-(a)** deposited on the membrane and dragged back into the clarified liquor during withdrawal (experiment at 30.0 V constant voltage).

4.6 Evidencing the ions flow through the membrane

The ions flow through the membrane was unequivocally confirmed by two experiments carried out with the electrolytic cell immersed in milliQ water in the absence of NPs. In the first experiment, the universal pH indicator was exclusively added within the cell (Figure S7 a/b). In the second experiment, the universal pH indicator was only added outside the membrane (Figure S7 c/d). The color changes observed when a constant voltage of 8 V was applied across the electrodes accounted for the ions produced in the electrolytic cell (Figure S7 a/b) and their flow in the bulk solution (Figure S7 c/d).

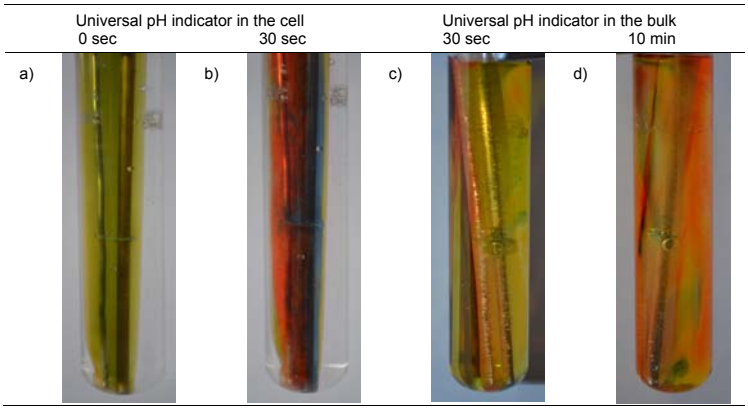
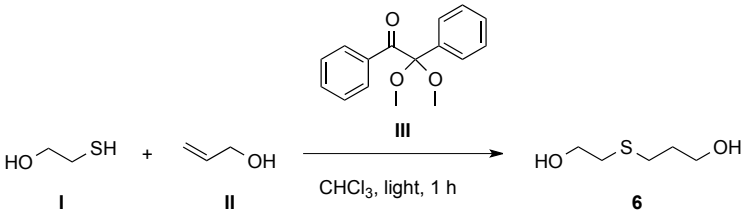


Figure S7. Ions produced inside the membrane and their flow through the membrane as evidenced by the color changes of the universal pH indicator (green: neutral; blue: basic; red: acid).

5. Synthesis of sulfide 6 and sulfone 8

5.1 Synthesis of the starting sulfide 6



Scheme S2: Synthesis of sulfide **6**.

3-((2-hydroxyethyl)thio)propan-1-ol (6): A mixture of 2-mercaptoethanol (**I**) (360 µL, 5.12 mmol), prop-2-en-1-ol (**II**) (350 µL, 5.12 mmol), 2,2-dimethoxy-2-phenyl-acetophenone (**III**, DMPA) (66 mg, 0.26 mmol), and chloroform (8.0 mL) was vigorously stirred, degassed under vacuum, and saturated with argon (by an Ar-filled balloon) three times. The mixture was irradiated (Philips CLEO 15W tube) at room temperature for 1 h under magnetic stirring, then 3.0 g of silica were added to the reaction mixture and the solvent was evaporated affording a white powder. This latter was charged on the top of a silica gel

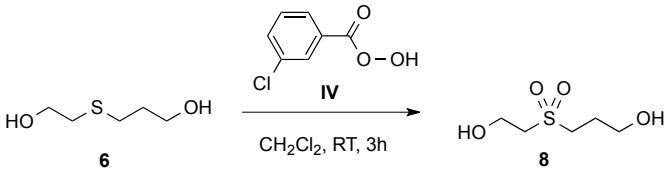
column and was purified by flash chromatography (stationary phase: 40 g of silica gel; eluting flow-rate: 40 mL/min; Collect wavelength 1: 254 nm; Collect wavelength 2: 280 nm). Elution gradient: from 30% to 100% of EtOAc in Cyclohexane for 5 CV; then neat EtOAc for 20 CV. Recovered 403 mg (2.9 mmol; yield: 57%) of 3-((2-hydroxyethyl)thio)propan-1-ol **6**.

^{1}H NMR ($CDCl_3$): δ = 3.70 – 3.78 (m, 4 H), 2.73 (t, J = 6.0 Hz, 2 H), 2.66 (t, J = 7.1 Hz, 2 H), 2.34 (br. S, 2 H), 1.78 – 1.90 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 61.6, 60.8, 35.4, 32.3, 28.6 ppm

^{1}H NMR (D_2O): δ = 3.62 (t, J = 6.4 Hz, 2 H), 3.55 (t, J = 6.3 Hz, 2 H), 2.61 (t, J = 6.3 Hz, 2 H), 2.49 – 2.55 (m, 2 H), 1.65 – 1.75 (m, 2 H) ppm. ^{13}C NMR (D_2O): δ = 60.5, 60.4, 33.5, 31.5, 27.7 ppm

HRMS (ESI/Q-TOF): calcd *m/z* for $C_5H_{12}O_2SNa$ $[M+Na]^+$: 159.0456; found: 159.0428.

5.2 Synthesis of sulfone 8



Scheme S3: Synthesis of sulfone **8**.

3-((2-hydroxyethyl)sulfonyl)propan-1-ol (8): In a 25 mL round bottomed flask, 48.9 mg (0.36 mmol) of sulfide **6** were dissolved in 5 mL of CH_2Cl_2. Under vigorous magnetic stirring, 192 mg (1.11 mmol) of 3-chlorobenzoperoxoic acid (**IV**) were added portion-wise to the reaction mixture. CAUTION: vigorous gas evolution was observed. After 1.5 h, additional 192 mg (1.11 mmol) of **IV** were added thereto. After 3 h, the reaction mixture was extracted with water (3 x 5 mL). The collected aqueous phases were free-dried to obtain 46 mg (0.27 mmol; yield 76%) of 3-((2-hydroxyethyl)sulfonyl)propan-1-ol **8**.

^{1}H NMR ($CDCl_3$): δ = 4.13 – 4.19 (m, 2 H), 3.83 (t, J = 5.9 Hz, 2 H), 3.23 – 3.35 (m, 4 H), 2.08 – 2.20 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 60.8, 56.7, 55.5, 51.8, 25.0 ppm

^{1}H NMR (D_2O): δ = 3.93 (t, J = 5.6 Hz, 2 H), 3.59 (t, J = 6.3 Hz, 2 H), 3.32 (t, J = 5.5 Hz, 2 H), 3.18 – 3.24 (m, 2 H), 1.86 – 1.98 (m, 2 H) ppm. ^{13}C NMR (D_2O): δ = 59.7, 55.0, 54.6, 51.0, 24.0 ppm

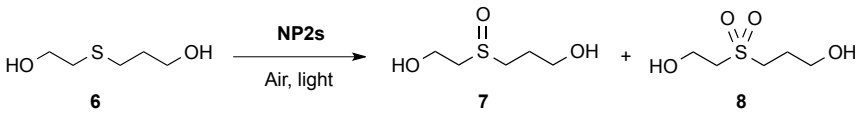
HRMS (ESI/Q-TOF): calcd *m/z* for $C_5H_{13}O_4S$ $[M+H]^+$: 169.0529; found: 169.0533.

6. Photo-sulfoxidation of sulfide 6 with NP2s: control experiments

NP1s-(b) nanoparticles were used as solid support for TPPS **1** in all photo-sulfoxidation.

6.1 Control oxidation reactions and characterization data of sulfoxide 7

Control experiments were carried out to exclude any catalytic activity of unloaded **NP1s-(b)** and any reactivity in the dark and/or without dissolved oxygen using **NP2s**.



Scheme S4: Photo-sulfoxidation of sulfide **6** promoted by **NP2s**.

Preparation of TPPS 1 mother solution: 5.9 mg of TPPS **1** were dissolved in 1.0 mL of milliQ water.

3-((2-hydroxyethyl)sulfinyl)propan-1-ol (**7**). A solution of sulfide **6** (22 mg, 0.16 mmol) in milliQ water (0.50 mL) was diluted with the **NP1s-(b)** mother solution (0.50 mL of a 14.6 mg/mL colloid). Then, the TPPS **1** mother solution (248 μL of a 5.9 mg/mL solution) was added portion-wise to the resulting colloid, vortexing the mixture after each addition. The obtained reaction mixture was irradiated (Philips CLEO 15W tube) at room temperature while compressed air was bubbled therein. In respect with this procedure, a series of experiments were performed in the absence of either TTPS **1**, **NP1s-(b)**, air, and/or irradiation (Table S4). All these experiments were monitored by ^{1}H NMR; the products distribution is detailed for each experiment in Section 6.2.

^{1}H NMR (D_2O): δ = 3.83 - 3.95 (m, 2 H), 3.62 (t, J = 6.5 Hz, 2 H), 2.97 - 3.07 (m, 1 H), 2.78 - 2.96 (m, 3 H), 1.83 - 1.93 (m, 2 H) ppm.

^{13}C NMR (D_2O): δ = 60.2, 54.9, 53.8, 48.0, 25.0 ppm.

HRMS (ESI/Q-TOF): calcd *m/z* for $C_5H_{13}O_3S$ $[M+H]^+$: 153.0585; found: 153.0612.

Table S4: Summary of the performed control experiments.

Entry	NP1s-(b)[a]	TPPS **1**[a]	Light[a]	Air[a]
1				
2				
3				
4				
5				
6				N[b]
7				A[b]
8				C[b]

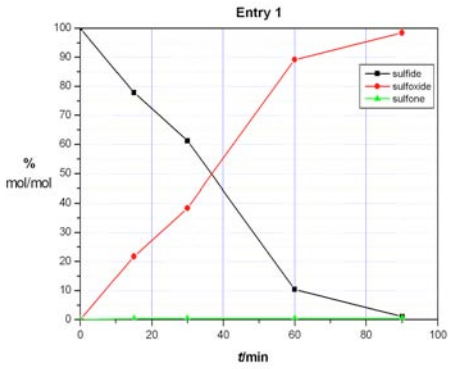
[a] Green color: present; red color: absent. [b] N = nitrogen flush (reaction mixture not previously degased); A = argon flush (reaction mixture previously degased); C = closed vial (reaction mixture not previously degased)

6.2 Products distribution in control oxidation reactions

In the following tables and graphs the time-course of the control reactions are reported in terms of distribution of products (mol % of sulfide **6**, sulfoxide **7**, and sulfone **8**) as determined by ^{1}H NMR analysis. Tables and graphs are referred to the entries of Table S4.

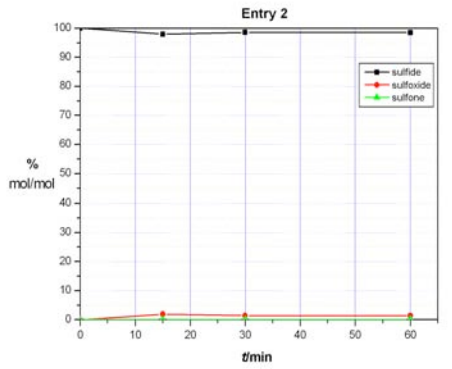
NPs	TPPS	Light	Air

Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
1	0	100.00	0.00	0.00
	15	77.87	21.78	0.35
	30	61.28	38.40	0.32
	60	10.48	89.16	0.36
	90	1.11	98.44	0.44



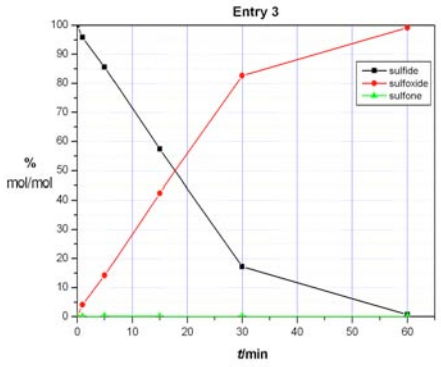
NPs	TPPS	Light	Air

Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
2	0	100.00	0.00	0.00
	15	97.99	1.91	0.10
	30	98.57	1.39	0.04
	60	98.52	1.37	0.11



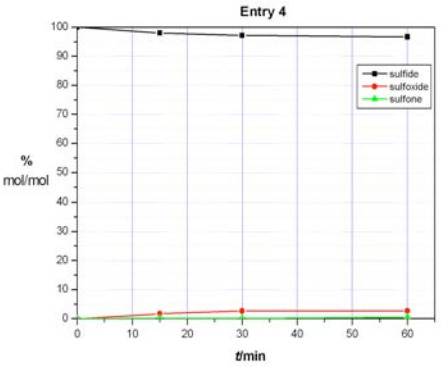
NPs	TPPS	Light	Air

Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
3	0	100.00	0.00	0.00
	1	95.87	4.11	0.02
	5	85.57	14.22	0.21
	15	57.42	42.45	0.13
	30	17.27	82.65	0.08
	60	0.72	99.14	0.14



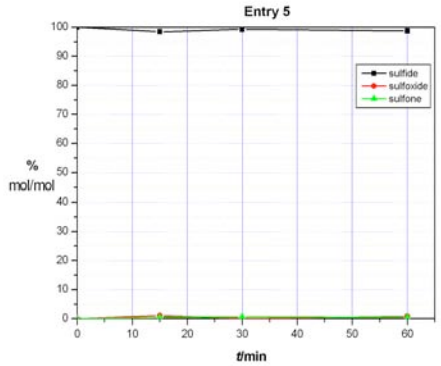
NPs	TPPS	Light	Air

Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
4	0	100.00	0.00	0.00
	15	98.04	1.70	0.26
	30	97.21	2.67	0.12
	60	96.68	2.73	0.59



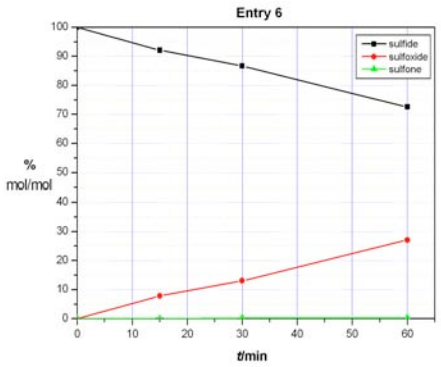
NPs	TPPS	Light	Air

Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
5	0	100.00	0.00	0.00
	15	98.46	1.10	0.43
	30	99.30	0.05	0.65
	60	98.70	0.83	0.46



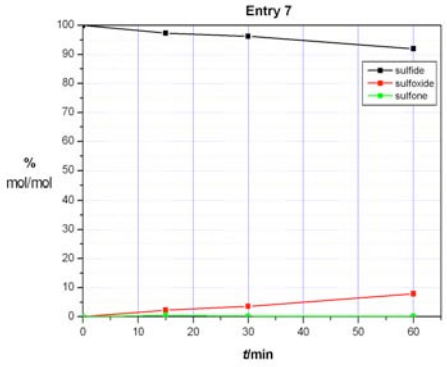
NPs	TPPS	Light	N

Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
6	0	100.00	0.00	0.00
	15	92.11	7.88	0.01
	30	86.71	13.04	0.25
	60	72.58	27.10	0.32



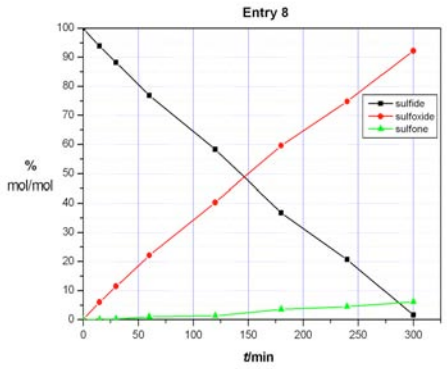
NPs	TPPS	Light	A

Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
7	0	100.00	0.00	0.00
	15	97.30	2.24	0.46
	30	96.24	3.56	0.20
	60	91.93	7.91	0.16

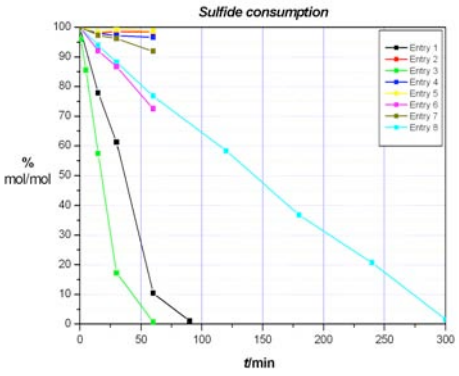


NPs	TPPS	Light	C

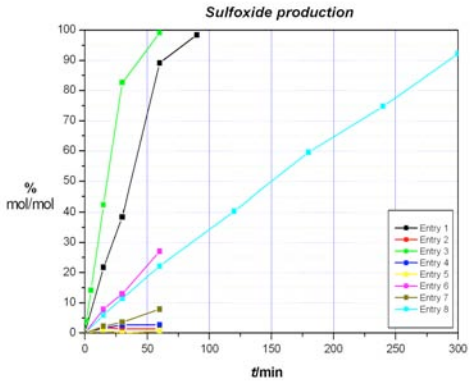
Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
8	0	100.00	0.00	0.00
	15	93.88	6.04	0.08
	30	88.20	11.49	0.30
	60	76.83	22.18	0.99
	120	58.34	40.33	1.34
	180	36.81	59.58	3.61
	240	20.70	74.79	4.50
	300	1.62	92.23	6.15



6.3 Comparison of control reactions



Graph S11: Sulfide **6** consumption in control reactions.



Graph S12: Sulfoxide **7** production in control reactions.

7. Photo-sulfoxidation of sulfide 6 with NP2s: optimized procedure

7.1 Nanocatalyst NP2: synthesis and characterization

Synthesis of NP2s. A 0.1 mg/mL solution of TPPS **1** was initially prepared by dissolving 0.86 mg of TPPS **1** in 8.6 mL of milliQ water. Under vigorous magnetic stirring, 4.50 mL of the TPPS **1** solution (449 μg, 0.44 μmol) were added drop-wise to the **NP1-(b)** starting colloid [1.23 mL of a 14.6 mg/mL colloid corresponding to 18.0 mg of **NP1s-(b)**]. 0.47 mL of additional milliQ water were added to the purple colored colloid to obtain the final nanocatalyst **NP2** [concentration = 2.9 mg/mL; TPPS **1** loading = 0.024 (μmol **1**/mg **NP1s-(b)**)]. See entry 3 of Table S5 for hydrodynamic diameter and Zeta potential.

The above procedure resulted from a brief optimization study aimed at limiting **NP2s** aggregation. Indeed, the addition of concentrated TPPS **1** solutions to the **NP1s-(b)** starting colloid (14.6 mg/mL) caused **NP2s** aggregation (entries 1-2, Table S5) even with portion-wise additions accompanied with vortexing or sonication.

Table S5: Hydrodynamic diameter and Zeta potential of **NP2s** as function TPPS **1** solution concentration.[a]

Entry	TPPS **1** solution [mg/mL]	d_h [nm][b]	Z_p [mV]
1	0.288	153.0±2.8 (0.566)	/
2	0.244	123.9±0.9 (0.427)	54.6±0.5
3	0.100	109.9±1.0 (0.341)	54±11

[a] Starting colloid of **NP1s-(b)** (14.6 mg/mL; d_h = 74±0.3 nm; Z_p = 32±14 mV. [b] Polydispersity in brackets.

In the optimized procedure for the preparation of **NP2s**, all TPPS **1** was electrostatically loaded on **NP1s-(b)**. This was proved by the direct comparison of the UV/Vis absorption spectra of freshly-prepared **NP2s** colloid and the filtrate obtained by centrifugation of the same colloid in a 100 KDa Millipore Filter (Figure S8).

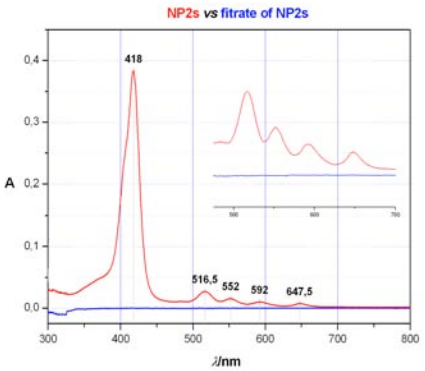


Figure S8: Comparison of the UV/Vis absorption spectra of freshly-prepared **NP2s** (red curve) *vs.* the corresponding filtrate (blue curve).

7.2 Optimized oxidation procedure

1.25 mL of a **NP2** colloid was freshly prepared as described in Section 7.1: [**NP2**] = 2.9 mg/mL; TPPS **1** loading = 0.024 [μmol **1**/mg **NP1s-(b)**].

In a 4 mL vial, the obtained colloid was added to sulfide **6** (23.5 mg, 0.17 mmol). The obtained reaction mixture was irradiated (Giesemann PowerChrome Pure Actinic 24 W T5 lamp) at room temperature while compressed air was bubbled therein. After 1 h, ^{1}H NMR analysis of the crude reaction mixture indicated the following products distribution: sulfide **6**, 0.73 mol %; sulfoxide **7** 98.78 mol %; sulfone **8**, 0.48 mol % (entry 7 of Table S6).

7.3 Maximizing the Chemical Efficiency (CE)

The above optimized procedure resulted from a study aimed at maximizing the Chemical Efficiency (CE) of the photo-sulfoxidation process as defined in the main text (Equation 1). In this study, it was evaluated the use of three different light sources and variation of three main reaction parameters, namely TPPS **1** mol % (μmol of **1** per μmol of **6**), TPPS **1** loading (μmol of **1** per mg of **NP1s-(b)**), and NP weight % (mg of **NP1s-(b)** per mg of **6**). The results of this study are summarized in Table S6 (see entry 7 for the optimal reaction conditions that afforded the final product distribution detailed in Section 7.2).

Table S6: Optimization study for the photo-sulfoxidation of **2**.

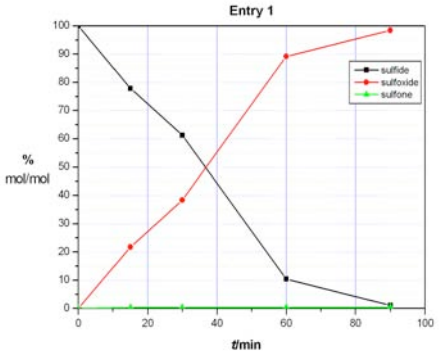
Entry	lamp[a]	[**NP2**][b] [mg/mL]	TPPS **1** mol % [μmol **1**/μmol **6**]	TPPS **1** loading [μmol **1**/mg NPs]	**NP1s-(b)** weight % [mg **NP1s-(b)**/mg **6**]	$t_{50\%}$ [min]	Conversion[c] [μmol $\mathbf{6}_{fin}$/μmol $\mathbf{6}_{in}$]	Selectivity[c] [μmol **7**/μmol $\mathbf{6}_{fin}$]	CE[c]
1	C	5.85	0.875	0.196	32.88	36.75	0.989	0.995	0.01
2	C	5.85	0.444	0.098	33.33	33.32	0.992	0.996	0.02
3	C	5.85	0.239	0.049	35.96	27.28	0.986	0.994	0.09
4	C	5.85	0.117	0.024	35.10	25.12	0.990	0.997	0.39
5	L	5.85	0.120	0.024	36.14	18.56	0.994	0.993	0.50
6	G	5.85	0.125	0.024	37.63	29.78	0.988	0.963	0.28
7	G	2.90	0.050	0.024	15.14	27.16	0.993	0.995	1.95
8	G	2.90	0.099	0.049	14.89	24.40	0.939	0.984	0.52
9	G	2.00	0.051	0.049	7.61	34.48	0.789	0.995	1.21
10	G	2.00	0.033	0.049	4.97	94.17	0.363	0.994	0.48

[a] C = Philips UV CLEO 15 W; Lexman 11 W 6400 K CFL; Giesemann PowerChrome Pure Actinic 24 W T5; [b] concentration of the nanocatalyst **NP2s** in the final reaction mixture; [c] CE = Chemical Efficiency as defined in the equation 1 of the main text; [c] determined by ^{1}H NMR analysis (D_2O).

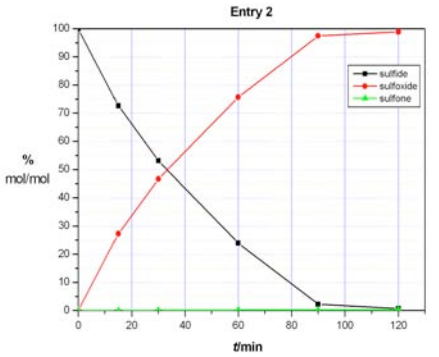
7.4 Products distribution in oxidation reactions

The evolution over the time of the product distribution, as determined by ^{1}H NMR analysis, for the experiments reported in Table S6 is described in the following graphs and tables.

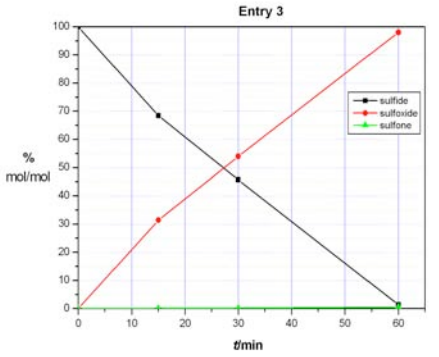
Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
1	0	100.00	0.00	0.00
	15	77.87	21.78	0.35
	30	61.28	38.40	0.32
	60	10.48	89.16	0.36
	90	1.11	98.44	0.44



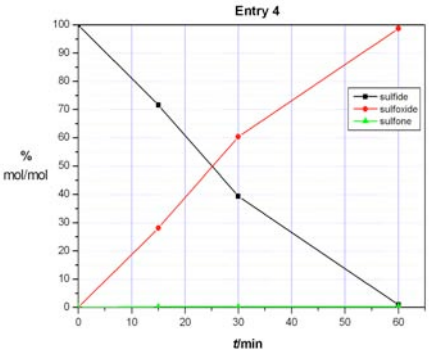
Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
2	0	100.00	0.00	0.00
	15	72.66	27.34	0.00
	30	53.16	46.72	0.12
	60	24.02	75.70	0.27
	90	2.28	97.47	0.25
	120	0.76	98.88	0.36



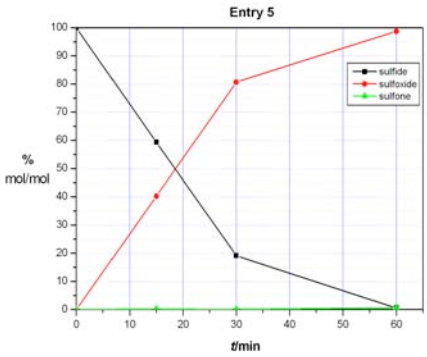
Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
3	0	100.00	0.00	0.00
	15	68.49	31.40	0.11
	30	45.77	53.99	0.24
	60	1.39	98.01	0.60



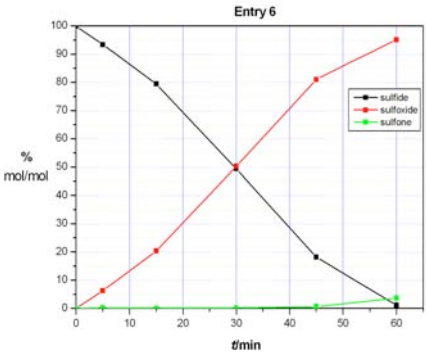
Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
4	0	100.00	0.00	0.00
	15	71.64	28.14	0.22
	30	39.41	60.37	0.22
	60	0.96	98.74	0.30



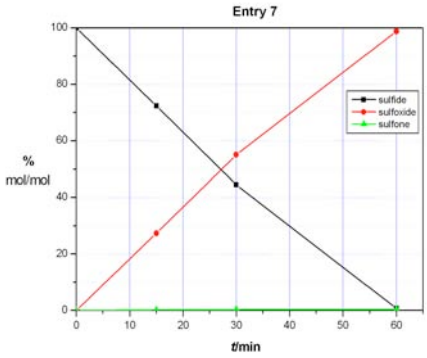
Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
5	0	100.00	0.00	0.00
	15	59.43	40.28	0.29
	30	19.21	80.71	0.08
	60	0.61	98.70	0.68



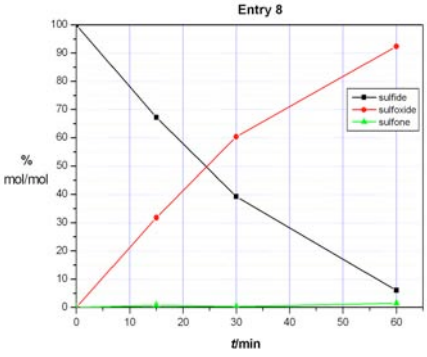
Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
6	0	100.00	0.00	0.00
	5	93.42	6.33	0.25
	15	79.49	20.38	0.13
	30	49.46	50.33	0.21
	45	18.25	81.05	0.70
	60	1.17	95.15	3.68



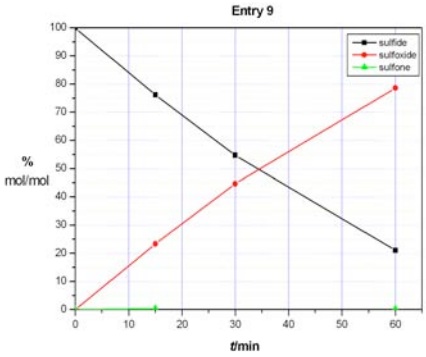
Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
7	0	100.00	0.00	0.00
	15	72.36	27.34	0.30
	30	44.53	55.07	0.40
	60	0.73	98.78	0.48



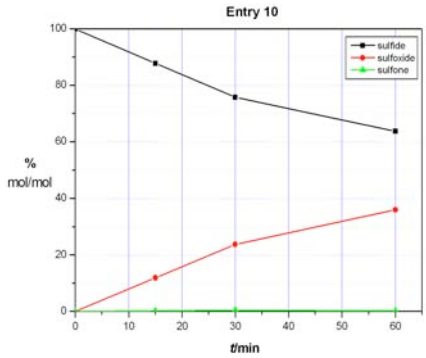
Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
8	0	100.00	0.00	0.00
	15	67.29	31.82	0.89
	30	39.26	60.39	0.35
	60	6.11	92.40	1.49



Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
9	0	100.00	0.00	0.00
	15	76.18	23.39	0.43
	30	54.75	44.65	0.59
	60	21.07	78.57	0.36



Entry	Time [min]	Sulfide **6** [mol %]	Sulfoxide **7** [mol %]	Sulfone **8** [mol %]
10	0	100.00	0.00	0.00
	15	87.82	11.94	0.24
	30	75.76	23.78	0.46
	60	63.73	36.05	0.22



8. UV/Vis absorption spectra of TPPS 1 and NP2s

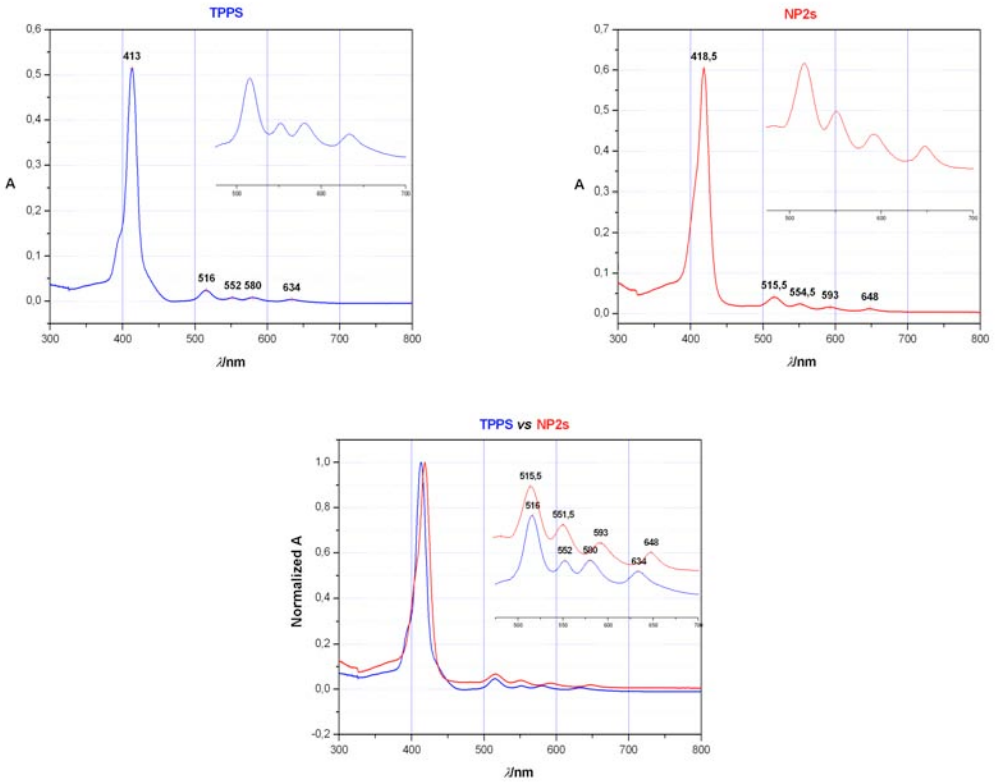


Figure S9: UV/Vis absorption spectra of TPPS **1**, **NP2s**, and their comparison.

9. UV/Vis lamps emission spectra

The UV/Vis emission spectra of the lamps[3] utilized in this study were compared with the UV/Vis absorption spectrum of **NP2s**. On the basis of this comparison, the Giesemann PowerChrome Pure Actinic 24 W T5 lamp was selected as the best light source.

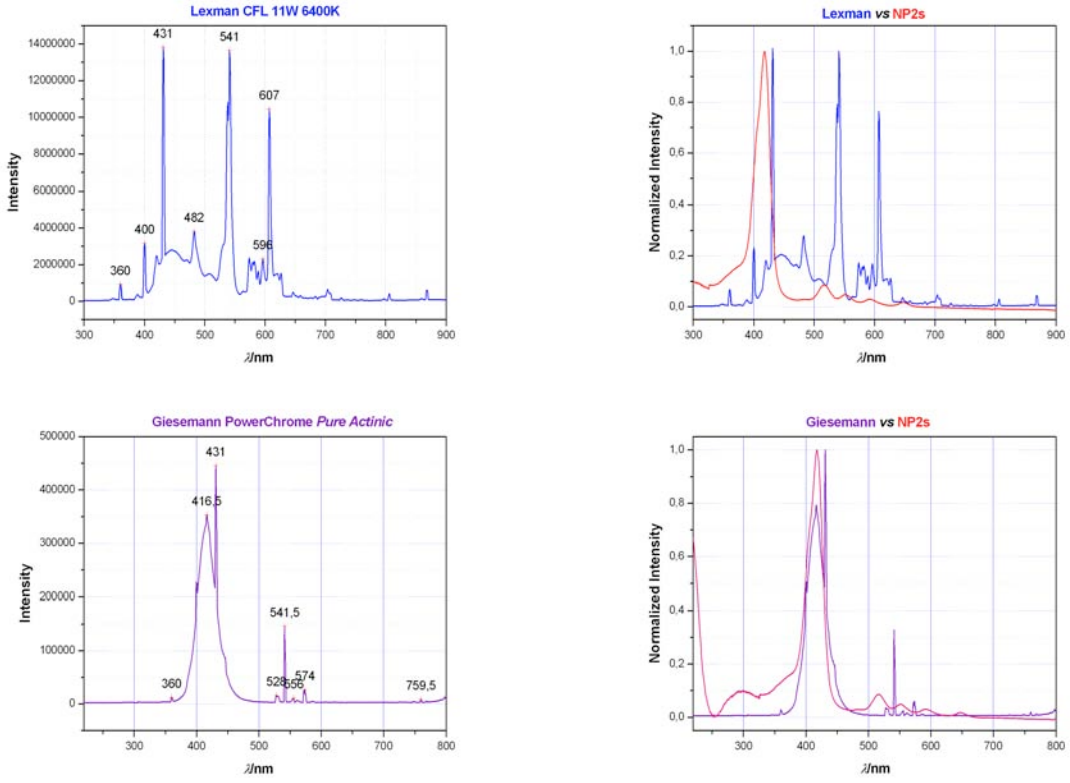


Figure S10: Comparison of lamp UV/Vis emission spectra with **NP2s** UV/Vis absorption spectrum.

10. NP2s electrocoagulation under batch conditions

10.1 Separation procedure

6.0 mL of freshly prepared **NP2s** (Section 7.1) were placed into the settling device ([**NP2**] = 2.9 mg/mL; TPPS **1** loading = 0.024 [μmol **1**/mg **NP1s-(b)**]). The electrolytic cell was immersed therein and a constant voltage of 24.0 V was supplied. After 1 h and with the power still on, the clarified liquor was withdrawn from the top of the separating apparatus at the flow-rate of 1.4 mL/min. The recovered clarified liquor was diluted at the final volume of 5.0 mL. The settled colloid of coagulated **NP2s** was recovered and diluted at the final volume of 9.0 mL. The pH of both coagulated **NP2s** and clarified liquor were finally

measured. Two portions of an exactly known volume of both recovered **NP2s** and clarified liquor were freeze-dried in pre-tared vials. Experimental outcomes are reported in entry 2 of Table S7.

The efficiency of the electrocoagulation procedure was also tested with colloids of **NP2** displaying various loading of TPPS **1** and **NP2** concentration. The results of this study are summarized in Table S7.

Table S7: Electrocoagulation of **NP2s** with different loadings of TPPS **1** under batch conditions.[a]

Entry	[**NP2s**] [mg/mL]	TPPS **1** loading [μmol **1**/mg **NP1s-(b)**]	pH[b]	Mass Recovery [w/w %]	**NP2s** d_h [nm] Starting	**NP2s** d_h [nm] Coagulated	**NP2s** Zp [mV] Starting	**NP2s** Zp [mV] Coagulated
1	5.8	25	3.30	7.0	/	/	/	/
			9.74	93.0	123.9±0.9	137±3	54.6±0.5	67±8
2	2.9	25	3.95	2.8	/	/	/	/
			9.40	97.2	110±1	104.7±0.5	54±11	47±13
3	2.9	50	3.56	14.3	/	/	/	/
			8.86	85.7	153.0±2.8	160±5	/	44±3
4	2.0	50	3.34	15.8	/	/	/	/
			8.27	84.2	146.5±0.8	155±2	/	56±1

[a] Blank: **NP2s** in the clarified liquor. Shaded: coagulated/redispersed **NP2s**.

10.2 Nanocatalyst stability during electrocoagulation

The integrity of **NP2** nanocatalyst was not affected by the electrocoagulation. This was proved by the direct comparison of the UV/Vis absorption spectrum of freshly-prepared **NP2s** with that of recovered **NP2s** (Figure S11).

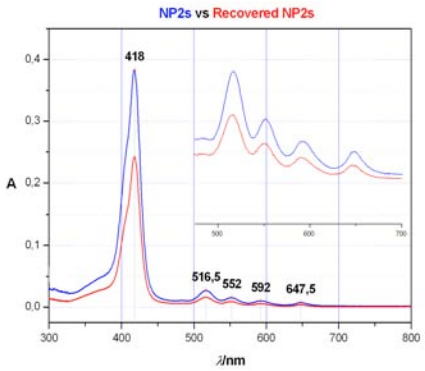


Figure S11: Direct comparison of the UV/Vis absorption spectra of freshly-prepared **NP2s** *vs.* recovered **NP2s**

No release of TPPS **1** was observed in the clarified liquor during the electrocoagulation. This was proved by the direct comparison of the UV/Vis absorption spectrum of the clarified liquor and that of the filtrate obtained by centrifugation of the same colloid in a 100 KDa Millipore Filter (Figure S12).

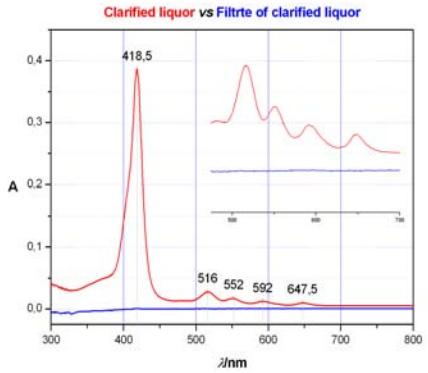


Figure S12: Direct comparison of UV/Vis absorption spectra: clarified liquor (red trace) *vs.* the corresponding filtrate (blue trace) .

11. Batch synthesis of 7/Batch electrocoagulation of NP2s

6.2 mL of a **NP2** colloid were freshly prepared as described in Section 7.1: ([**NP2**] = 2.9 mg/mL; TPPS **1** loading = 0.024 [μmol **1**/mg **NP1s-(b)**].

In a 20 mL vial, the obtained colloid was added to sulfide **6** (121.9 mg, 0.896 mmol). The resulting reaction mixture was irradiated (Giesemann PowerChrome Pure Actinic 24 W T5) at room temperature while compressed air was bubbled therein (air flow-rate: 240 mL/min).

After 120 min, ^{1}H NMR analysis of the crude reaction mixture indicated the following products distribution: sulfide **6**, 2.11 mol %; sulfoxide **7**, 97.73 mol %; sulfone **8**, 0.16 mol %. The crude mixture was then charged into the settling device and the electrolytic cell was immersed therein. The power was turned on at the constant DC of 100.0 mA. After 1 h and with the power still on, the clarified liquor was withdrawn from the top of the separating apparatus at the flow-rate of 1.4 mL/min. The recovered clarified liquor (5.4 mL), the water in the membrane and the coagulated **NP2s** were freeze-dried to evaluate the distribution of product **7** in these phases (Table S8). The amount of **7** in coagulated **NP2s** was determined by difference and confirmed by ^{1}H NMR analysis of this phase using methanol as the internal standard. The longer reaction time of this experiment compared with that of the optimization study was due to change of scale.[4]

Table S8: Mass recoveries of **7** in the Batch reaction/Batch electrocoagulation experiment.

Isolated **7** [w/w %]	**7** in **NP2s**[a] [w/w %]	**7** in membrane [w/w %]	partition of **7** clarified liquor/membrane	Recovered **NP2s**[b] [w/w %]
65.8	18.5	15.7	4.19	97.3

[a] Calculated value: theoretical amount of **7** fed in the separating apparatus – **7** in the purified solution – **7** in the membrane. This value was confirmed by ^{1}H NMR analysis of coagulated **NP2s** using methanol as the internal standard. [b] Determined by difference on the basis of the known amount of **7**.

12. Nanocatalyst integrity in a batch reaction/batch electrocoagulation sequence and recycle experiment

The integrity of **NP2** nanocatalyst was also proved in a batch reaction/batch electrocoagulation sequence followed by a recycle experiment. Accordingly, the UV/Vis absorption spectra of **NP2s** were registered, and d_h and Zp measured after each step of the whole reaction/electrocoagulation/recycle/electrocoagulation sequence (Table S10 and Figure S13).

1st cycle: the first cycle was performed following the procedure described in the previous paragraph (section 11).

The reaction mixture was monitored over the time by ^{1}H NMR by sampling 50 μL of the colloid at 15 min, 100 min, and 120 min. All samples were diluted with 500 μL of D_2O before ^{1}H NMR analysis. The products distribution after 120 min is reported in entry 1 of Table S9.

The crude mixture was then charged into the settling device and the electrolytic cell was immersed therein. The power was turned on at the constant DC of 100.0 mA. After 1 h, and with the power still on, the clarified liquor was withdrawn from the top of the separating apparatus at the flow-rate of 1.4 mL/min. The recovered **NP2s** were analyzed (Table S10 and Figure S13) and used for the recycle experiment.

2nd cycle: the above coagulated **NP2s** were transferred in a 20 mL vial, diluted to 6.2 mL with milliQ water, and added to sulfide **6** (120.9 mg, 0.911 mmol).

The recycle experiment was performed as described before.

The products distribution after 120 min is reported in entry 2 of Table S9.

The crude mixture was then charged into the settling device and the electrolytic cell was immersed therein. The power was turned on at the constant DC of 100.0 mA. After 1 h, and with the power still on, the clarified liquor was withdrawn from the top of the separating apparatus at the flow-rate of 1.4 mL/min. The recovered **NP2s** were collected and analyzed (Table S10 and Figure S13).

Table S9: Product distribution after 120 min in the first and the second cycle of the batch reaction.[a]

cycle	sulfide **6** [mol %]	sulfoxide **7** [mol %]	sulfone **8** [mol %]
1	3.74	96.11	0.15
2	3.26	96.30	0.44

[a] Determined by ^{1}H NMR analysis (D_2O).

The **NP2** nanocatalyst was not significantly affected during the whole sequence investigated. In Table S10 and Figure S13 are reported **NP2** characterization data for each step of the whole recycle experiment.

Table S10: Features of **NP2s** during reaction/electrocoagulation/recycle/electrocoagulation batch sequence.

NP2s	UV/Vis spectrum [a]	d_h [nm]	Zp [mV]
starting colloid	Blue line	94±3	38±5
after 1st cycle reaction	Red line	89.1±0.4	61±4
after 1st cycle electrocoagulation	Magenta line	79.1±0.7	21±2
after 2nd cycle reaction	Green line	83±3	30.5±0.8
after 2nd cycle electrocoagulation	Black line	83±3	24±6

[a] See spectra in Figure S13.

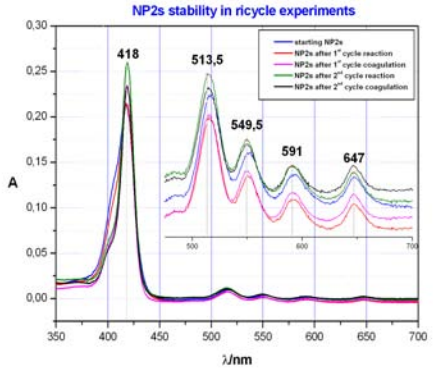


Figure S13: UV/Vis absorption spectra of **NP2s** in each step of the recycle experiment.

13. Flow synthesis of 7/flow electrocoagulation of NP2s: selection of operative parameters

An effective continuous-flow reaction/separation sequence for the synthesis of **7** required the optimization of three main parameters: *i)* the flow-rate of the overall input (reaction mixture + washing water) inside the separating apparatus; *ii)* the washing water/reaction mixture flow-ratio; and *iii)* the residence time of the continuous photo-oxidation of sulfide **6**.

The parameter at the point *i)* was identified by electrocoagulation experiments performed under flow conditions (without washing water) using neat **NP2s**. In this study the mass recovery of coagulated **NP2s** was evaluated at various flow-rates (Section 13.1).

The parameter at the point *ii)* was identified in combined batch-reaction/flow-electrocoagulation experiments performed with colloids resulting from the optimized batch reaction. In this study the mass recovery of purified **7** was evaluated at various water/reaction mixture flow-ratios (Section 13.2).

The parameter at the point *iii)* was identified in flow-reaction experiments where the residence time of reactants was related to the conversion of starting sulfide **6** (Section 13.3).

13.1 Selection of the overall input flow-rate: electrocoagulation of neat NP2s under flow conditions

The best overall input flow-rate resulted that of entry 1 in Table S11.

13.1.1 Setup of the separating apparatus

The settling device was charged with 6.0 mL of milliQ water and the electrolytic cell was immersed therein. The inlet of a PTFE tubing (OD 1/16" x 1.00 mm ID) was connected to a 10.0 mL gastight syringe filled with the **NP2** colloid. The outlet of the same PTFE tubing was immersed in the separating apparatus, below the bottom of the membrane.

13.1.2 Experimental procedure and recovery of coagulated NP2s

6.0 mL of the **NP2** colloid were freshly prepared as described in Section 7.1: ([**NP2**] = 2.9 mg/mL; TPPS **1** loading = 0.024 [μmol **1**/mg **NP1s-(b)**].

The obtained colloid was charged in the 10.0 mL gastight syringe. The power in the electrolytic cell was turned on at constant voltage (24.0 V). The **NP2** colloid was fed into the separating apparatus by a syringe pump (Table S11 for flow-rate and fed time). During these experiments, the NPs remained trapped below the bottom of the membrane. At the end of each experiment, the clarified liquor, which was recovered from the overflow, and the coagulated **NP2s** were freeze-dried. The mass recoveries of these experiments are reported in Table S11.

Table S11: Electrocoagulation of neat **NP2s** under flow-conditions.[a]

Entry	Flow-rate [μl/min]	Fed time [min]	pH	Mass Recovery [%]
1	180	34	4.22	3.9
			9.76	96.1
2	110	56	4.41	13.9
			9.79	86.1

[a] Blank: clarified liquor; Shaded: recovered **NP2s**.

13.2 Selection of the best water/reaction mixture flow-ratio: batch synthesis of 7 /flow electrocoagulation of NP2s

The best water/reaction mixture flow-ratio resulted that of entry 1 in Table S12.

13.2.1 Setup of the separating apparatus

The settling device was charged with 6.0 mL of milliQ water and the electrolytic cell was immersed therein. The inlet of a first PTFE tubing (OD 1/16" x 1.00 mm ID) was connected to a 10.0 mL gastight syringe filled with the crude resulting from the optimized batch reaction. The outlet of the same PTFE tubing was immersed in the separating apparatus, below the bottom of the membrane.

The inlet of a second PTFE tubing (OD 1/16" x 1.00 mm ID) was connected to a 50.0 mL gastight syringe filled with milliQ water. The outlet of the same PTFE tubing was immersed in the separating apparatus, below the first PTFE tubing (Figure S14).

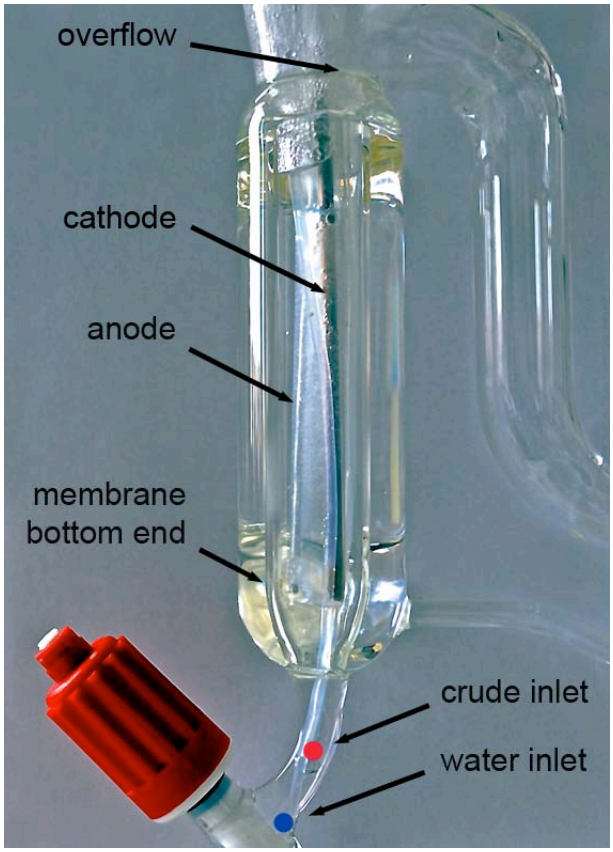


Figure S14: Details of the continuous-flow separating apparatus.

13.2.2 Experimental procedure and recovery of sulfoxide 7

6.2 mL of the **NP2** colloid were freshly prepared as described in Section 7.1: [**NP2**] = 2.9 mg/mL; TPPS **1** loading = 0.024 [μmol **1**/mg **NP1s-(b)**].

In a 20 mL vial, the obtained colloid was added to sulfide **6** (120.4 mg, 0.885 mmol). The resulting reaction mixture was irradiated (Giesemann PowerChrome Pure Actinic 24 W T5 lamp) at room temperature while compressed air was bubbled therein (air flow-rate: 240 mL/min).

After 120 min, ^{1}H NMR analysis of the crude reaction mixture indicated the following products distribution: sulfide **6**, 1.49 mol %; sulfoxide **7**, 98.51 mol %; sulfone **8** not detected.

The above crude mixture was then charged in the 10 mL gastight syringe.

The separating apparatus, assembled as described in the previous Section 13.2.1, was used to separate the sulfoxide **7** from **NP2s**. To the scope, the power in the electrolytic cell was turned on at constant DC (100.0 mA) and both the crude reaction mixture and the washing water were fed into the separating apparatus at the overall flow-rate of 180 μL/min by a dual syringe pump. The water/reaction mixture flow-ratio was regulated as reported in Table S12. Once the addition of the crude reaction mixture was completed, pure water was pumped inside the separating apparatus at 180 μL/min for 15 min.

At the end of the experiments, the purified solution of **7**, which was collected from the overflow, the coagulated **NP2s** trapped below the membrane, and the water contained in the membrane were

independently freeze-dried in pre-tared vials. The mass recoveries of these experiments are reported in Table S12. The amount of **7** in coagulated **NP2s** was determined by difference and confirmed by ^{1}H NMR analysis of this phase using methanol as the internal standard. A dedicated experiment (see Section 13.2.3) was also performed to further validate the obtained values of recovered **NP2s**.

Table S12: Mass recoveries of **7** in the Batch reaction/Flow electrocoagulation experiments.

Entry	Water flow-rate [μL/min]	reaction mix flow-rate [μL/min]	Water/reaction mix ratio [Vol/Vol]	Isolated **7** [w/w %]	**7** in **NP2s**[a] [w/w %]	**7** in membrane [w/w %]	Recovered **NP2s**[b] [w/w %]
1	150	30	5:1	91.1	6.2	2.7	91.9
2	135	45	3:1	85.4	8.6	6.0	94.1

[a] Calculated value: theoretical amount of **7** fed in the separating apparatus – **7** in the purified solution – **7** in the membrane. This value was confirmed by ^{1}H NMR analysis of coagulated **NP2s** using methanol as the internal standard. [b] Determined by difference on the basis of the known amount of **7**. See also Section 13.2.3.

13.2.3 Control experiment to validate NP2s mass recovery

*The presence of a small portion of sulfoxide **7** in coagulated **NP2s** may affect the accurate evaluation of **NP2** recovery efficiency. Thus, this parameter (column eight, Table S12) was further confirmed by a dedicated flow electrocoagulation experiment with neat **NP2s** performed at the optimized water and colloid flow-rates (water flow-rate = 150 μL/min; colloid flow-rate = 30 μL/min).*

7.0 mL of the **NP2** colloid were freshly prepared as described in Section 7.1: [**NP2**] = 2.9 mg/mL; TPPS **1** loading = 0.024 [μmol **1**/mg **NP1s-(b)**].

The obtained colloid was charged in the 10.0 mL gastight syringe; in parallel, 35.0 mL of milliQ water were charge in the 50.0 mL gastight syringe.

The power in the electrolytic cell was turned on at constant voltage (24.0 V). Using a syringe pump, both the **NP2** colloid (flow-rate: 30 μL/min) and the washing water (flow-rate: 150 μL/min) were fed into the separating apparatus (overall flow-rate: 180 μL/min). During electrocoagulation, **NP2s** remained trapped below the bottom of the membrane, while the clarified liquor was collected through the overflow. After 233 min (3 h 53 min) 42.0 mL of clarified liquor were collected. The trapped and washed **NP2s** were diluted with milliQ water to obtain 13.0 mL of the colloid. Both the clarified liquor and the recovered colloid were freeze-dried in pre-tared vials. The results of this experiment are reported Table S13.

Table S13: Results of flow-electrocoagulation performed with neat **NP2s** in the presence of washing water.[a]

Overall flow-rate [μL/min]	Water flow-rate [μL/min]	**NP2s** flow-rate [μL/min]	water/**NP2s** ratio [Vol/Vol]	Volume [mL]	pH	Recovered **NP2s** [%]
180	150	30	5:1	42.0	4.38	7.9
				13.0	9.71	92.1

[a] Blank: clarified liquor; Shaded: recovered **NP2s**.

13.3 Selection of the optimal residence time for the flow oxidation of sulfide 6

Complete conversion of sulfide **6** into sulfoxide **7** was achieved at the optimal residence time indicated in entry 4 of Table S14.

13.3.1 Setup of the flow reactor

10 m of FEP tubing (OD 1/16" x 1.0 mm ID; 7.85 mL) was wrapped in a single layer around the quartz tube holding the Giesemann PowerChrome Pure Actinic 24 W T5 lamp to build-up the photo-reactor. Additional 0.50 m of FEP tubing were used for connection with a 10.0 mL gastight syringe (inlet) and for collection in an appropriate vessel (outlet). The photo-reactor was coaxially inserted into a glass tube covered with an aluminum sheet. The whole system was covered with a black sheet of cardboard and maintained at room temperature by air flowing with a cooling fun (Figure S15).

Figure S15: Details of the photo-reactor and of the whole reacting system.

13.3.2 Experimental procedure

7.85 mL of the **NP2** colloid were freshly prepared as described in Section 7.1: [**NP2**] = 2.9 mg/mL; TPPS **1** loading = 0.024 [μmol **1**/mg **NP1s-(b)**].

In a 10 mL vial, the obtained colloid was added to sulfide **6** (151.9 mg, 1.116 mmol). The resulting reaction mixture was charged into the 10.0 mL gastight syringe and fed in the FEP photo-reactor at the flow-rate indicated in Table S14. Instant conversions at the outlet of the photo-reactor were determined by ^{1}H NMR analysis.

Table S14: Conversion efficiencies at different residence times in the flow oxidation of sulfide **6**.

Entry	flow-rate [μL/min]	residence time [min]	conversion[a] [%]
1	87	90	35.24
2	44	180	54.51
3	26	300	91.13
4	22	360	98.23

[a] Determined by ^{1}H NMR analysis (D_2O).

14. Flow synthesis of 7/flow electrocoagulation of NP2s and recycle experiment

14.1 Experimental set-up

The settling device was charged with 6.0 mL of milliQ water and the electrolytic cell was immersed therein.

13.8 m of FEP tubing (OD 1/16" x 1.0 mm ID; 10.8 mL) was wrapped in a single layer around a quartz tube holding the Giesemann PowerChrome Pure Actinic 24 W T5 lamp to build-up the photo-reactor. Additional 1.50 m of FEP tubing were used for the connection with a 10.0 mL gastight syringe (inlet) and for the collection in the separating apparatus (outlet) below the bottom of the membrane.

The inlet of a second PTFE tubing (OD 1/16" x 1.00 mm ID) was connected to a 50.0 mL gastight syringe filled with milliQ water, while the outlet was immersed in the separating apparatus below the outlet of tubing coming from the photo-reactor. Both syringes were placed in the dual syringe pump apparatus.

The flow reactor/separating apparatus was assembled as in Figure S16.

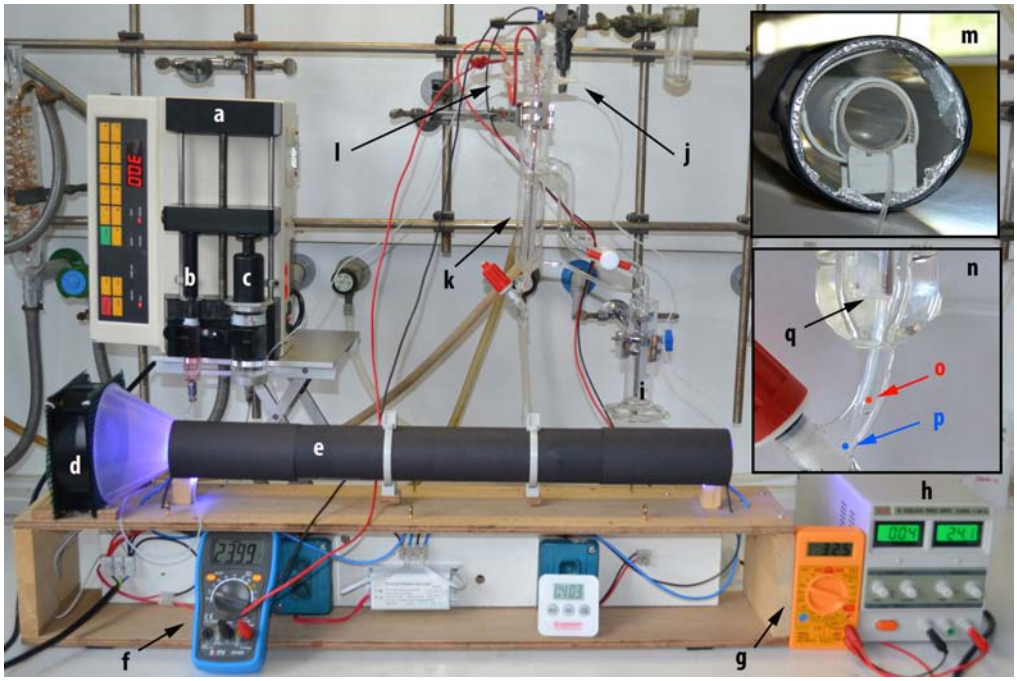


Figure S16: Flow reactor/separator design: a) dual syringe pump apparatus; b) 10 mL gastight syringe filled with the mixture of reactants; c) 50 mL gastight syringe filled with the washing milliQ water; d) cooling fan; e) protected photo-reactor; f) voltage-measuring unit; g) current-measuring unit; h) DC power supply; i) cylinder collecting the purified product **7**; j) inlet of the crude reaction mixture into the separating apparatus; k) separating apparatus; l) inlet of the washing water into the separating apparatus; m) details of the photo-reactor; n) details of the separating apparatus; o) outlet of the crude reaction stream; p) outlet of the washing water stream; q) bottom of the membrane.

14.2 Experimental procedure

6.0 mL of the **NP2** colloid were freshly prepared as described in Section 7.1: [**NP2**] = 2.9 mg/mL; TPPS **1** loading = 0.024 [μmol **1**/mg **NP1s-(b)**].

In a 20 mL vial, the obtained colloid was added to sulfide **6** (121.1 mg, 0.889 mmol). The resulting reaction mixture was charged into the 10.0 mL gastight syringe and fed in the FEP photo-reactor at the flow-rate of 30 μL/min (residence time: 360 min).

When the crude mixture started to flow inside the separating apparatus, the power in the electrolytic cell was turned on (100 mA constant DC) and the washing water was fed in the separating apparatus at the flow-rate of 150 μL/min. Once the addition of the crude reaction mixture was completed, pure water was pumped inside the separating apparatus at 180 μL/min for 15 min.

At the end of the experiment, the purified solution of **3**, which was collected from the overflow, the water contained in the membrane, and **NP2s** trapped below the membrane were independently freeze-dried. The mass recoveries of this experiment are reported in Table S15 (entry 1). The amount of **7** in coagulated **NP2s** was determined by difference and confirmed by ^{1}H NMR analysis of this phase using methanol as the internal standard.

14.3 Continuous-flow recycle experiment

NP2s trapped below the membrane after the first flow-reaction/flow-electrocoagulation cycle were transferred in a 20 mL vial, diluted to 6.0 mL with milliQ water, and added to sulfide **6** (120.6 mg, 0.885 mmol). The recycle experiment was performed and analyzed as described in Section 14.2 (Table S15, entry 2).

Table S15: Continuous-flow reaction/separation sequence and recycle.

Cycle	Overall flow [μL/min]	water/colloid ratio [Vol/Vol]	Isolated **7** [w/w %]	**7** in **NP2s** [w/w %][a]	**7** in membrane [w/w %]	Recovered **NP2s**[b] [w/w %]
1	180	5:1	92.1	4.9	3.0	86.8
2	180	5:1	89.2	7.7	3.1	75.2[c]

[a] Calculated value: theoretical amount of **7** fed in the separating apparatus – **7** in the purified solution – **7** in the membrane. This value was confirmed by ^{1}H NMR analysis of coagulated **NP2s** using methanol as the internal standard. [b] Determined by difference on the basis of the known amount of **7**. [c] Based on **NP2s** recovered after the 1st cycle.

[1] M. Laus, K. Sparnacci, M. Lelli, R. Vannini, L. Tondelli, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 1110.

[2] S. M. Hamid, D. C. Sherrington, *Polymer*, 1987, **28**, 325.

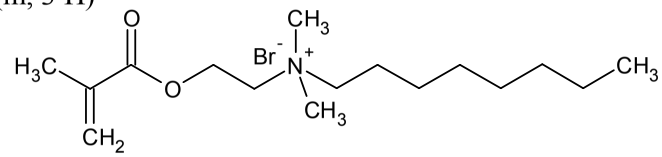
[3] Emission spectrum of the Philips Cleo lamp was reported by J. Narbutt, B. Cebula, A. Lesiak, A. Sysa-jedrzejowska, M. Norval, T. Robak, P. Smolewski, *Arch. Dermatol.*, 2009, **145**, 133.

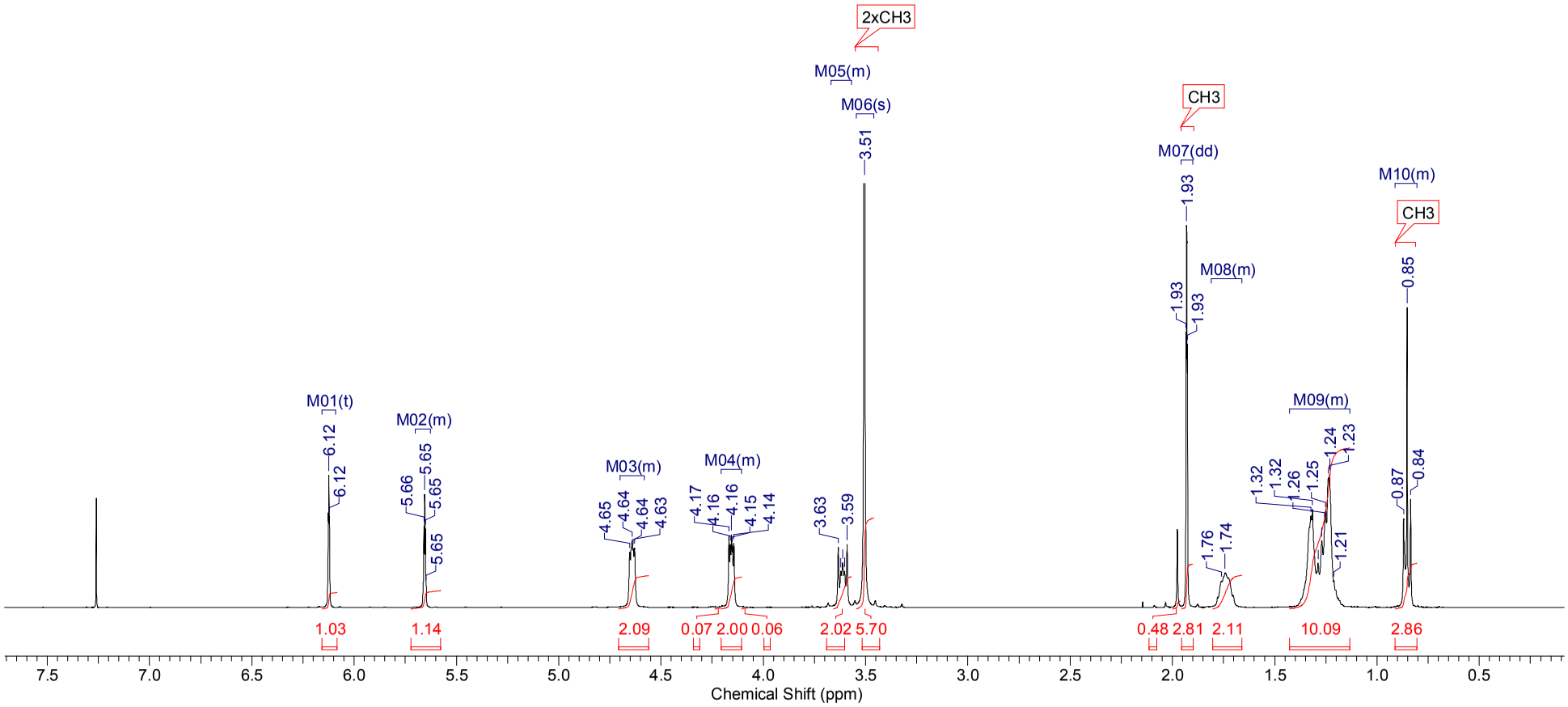
[4] R. S. Andrews, J. J. Becker, M. R. Gagnè, *Angew. Chem. Int. Ed.*, 2012, **51**, 4140.

15. NMR Spectra

2-(dimethyloctyl) ammonium ethylmethacrylate bromide

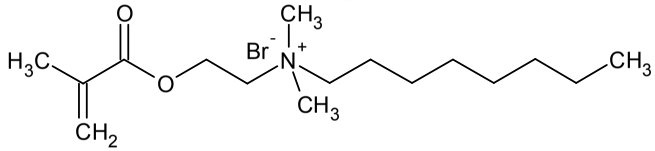
^{1}H NMR (CHLOROFORM-d ,400MHz): δ = 6.12 (t, *J*=1.1 Hz, 1 H), 5.63 - 5.70 (m, 1 H), 4.58 - 4.70 (m, 2 H), 4.11 - 4.21 (m, 2 H), 3.57 - 3.67 (m, 2 H), 3.51 (s, 6 H), 1.93 (dd, *J*=1.5, 0.9 Hz, 3 H), 1.66 - 1.81 (m, 2 H), 1.13 - 1.43 (m, 10 H), 0.80 - 0.91 ppm (m, 3 H)

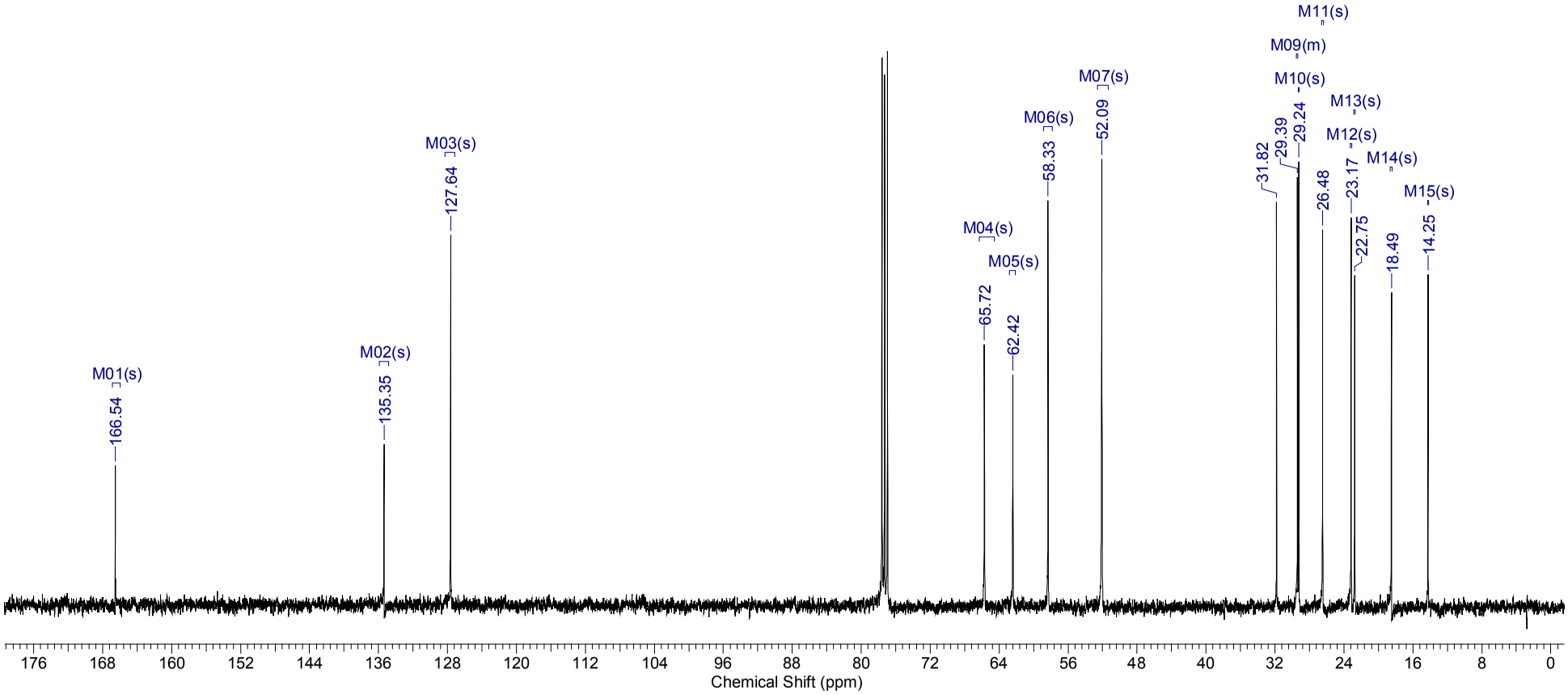




2-(dimethyloctyl) ammonium ethylmethacrylate bromide

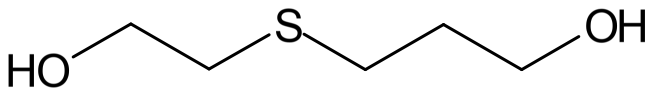
^{13}C NMR (CHLOROFORM-d ,101MHz): δ = 166.5, 135.4, 127.6, 65.7, 62.4, 58.3, 52.1, 31.8, 29.4, 29.2, 26.5, 23.2, 22.8, 18.5, 14.2 ppm

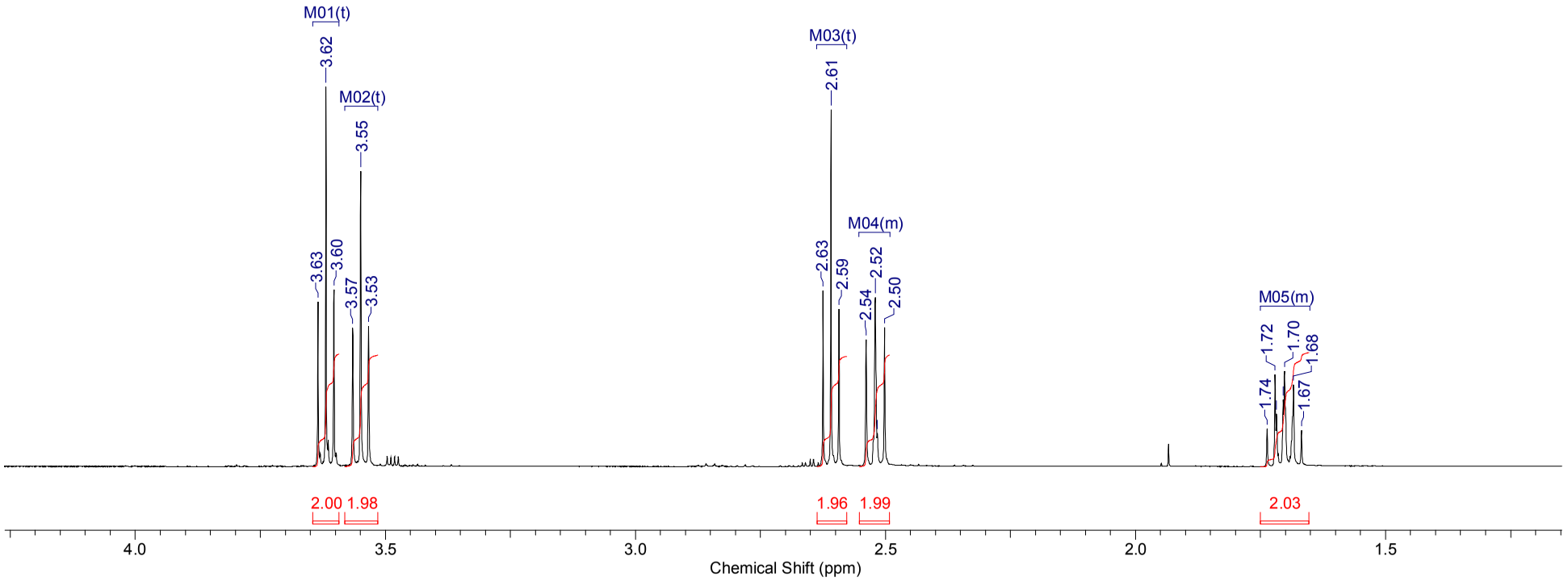




Sulfide 6 - 1H NMR in deuterium oxide

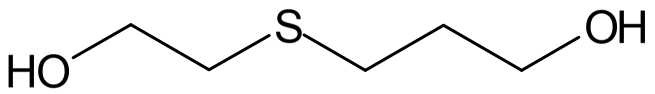
^{1}H NMR (DEUTERIUM OXIDE ,400MHz): δ = 3.62 (t, *J*=6.4 Hz, 2 H), 3.55 (t, *J*=6.3 Hz, 2 H), 2.61 (t, *J*=6.3 Hz, 2 H), 2.49 - 2.55 (m, 2 H), 1.65 - 1.75 ppm (m, 2 H)

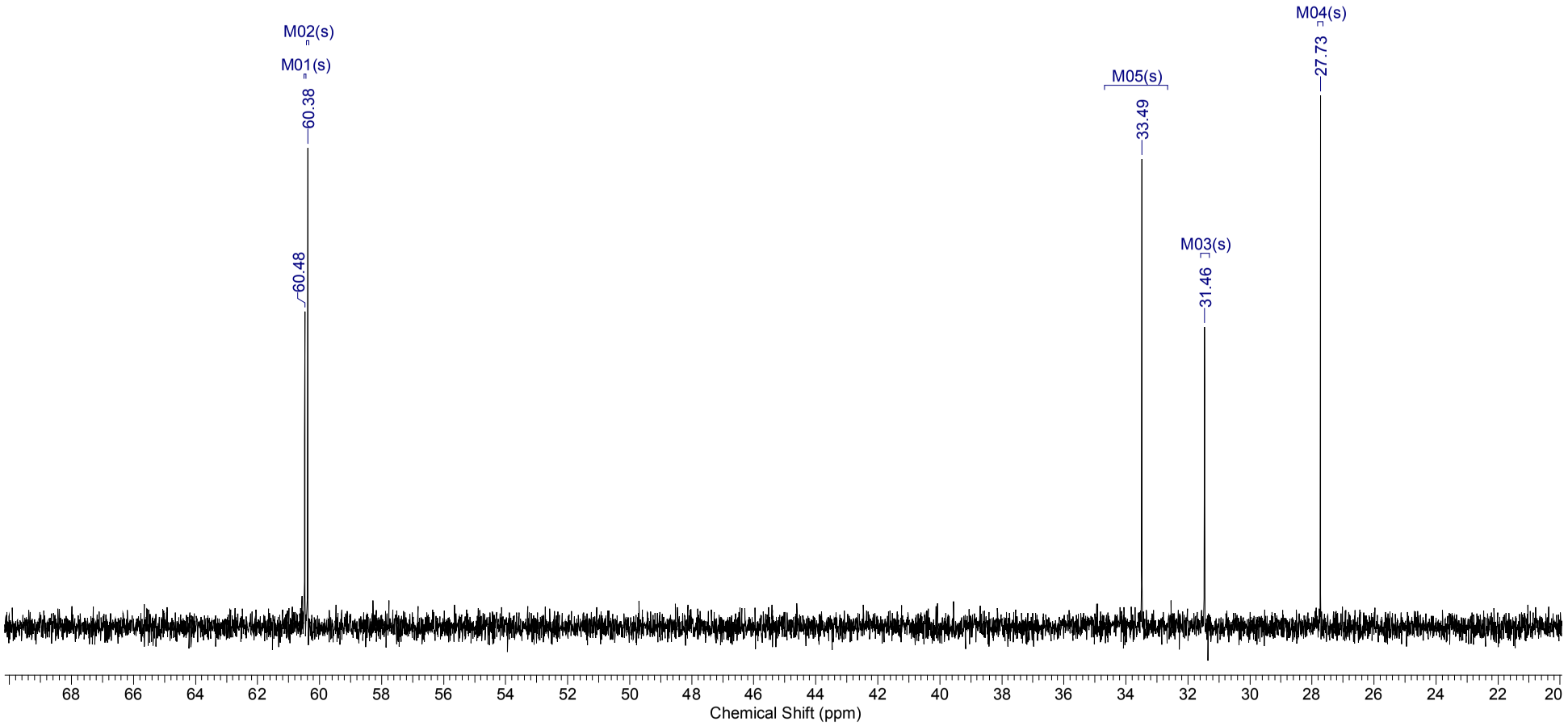




Sulfide 6 - 13C NMR in deuterium oxide

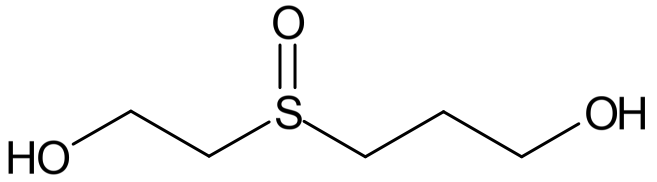
^{13}C NMR (DEUTERIUM OXIDE ,101MHz): δ = 60.5, 60.4, 33.5, 31.5, 27.7 ppm

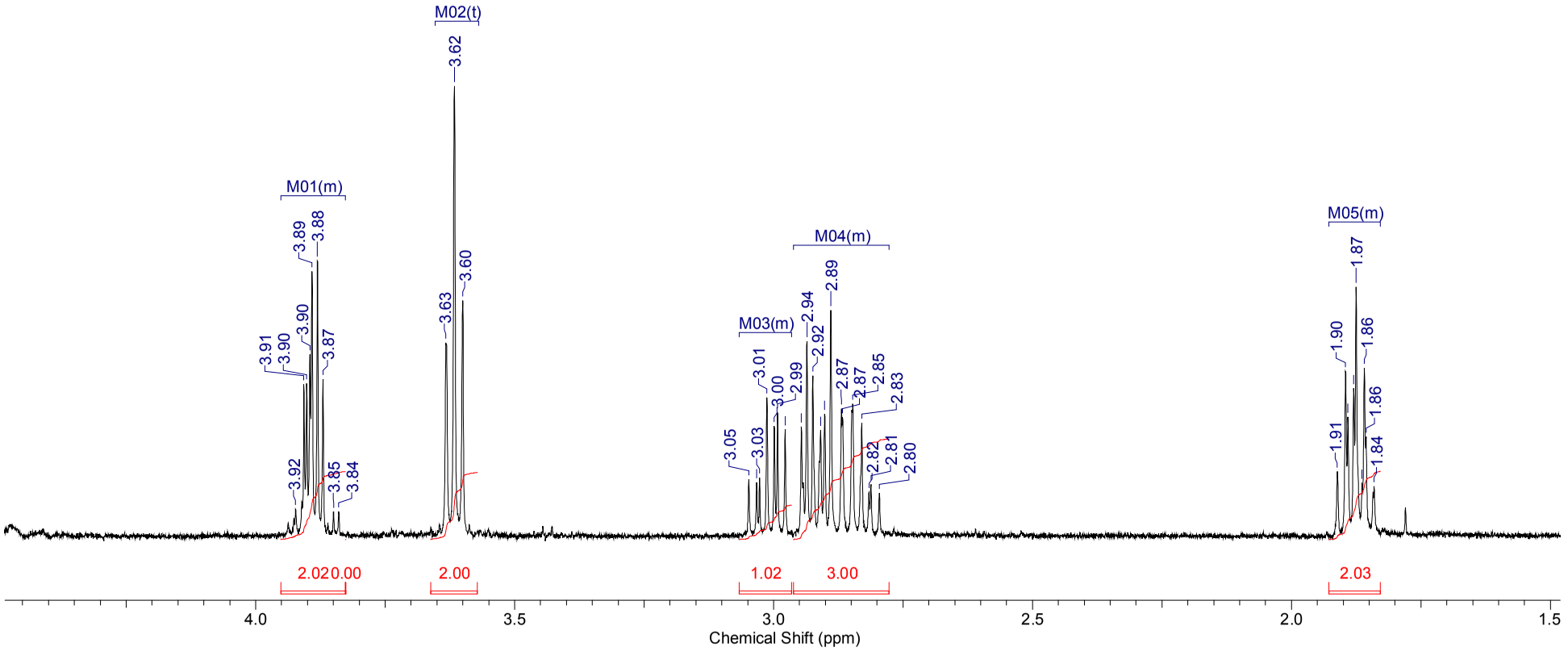




Sulfoxide 7 - 1H NMR - before coagulation

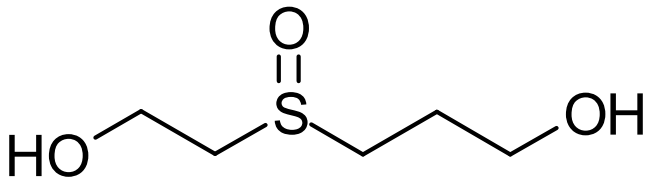
^{1}H NMR (DEUTERIUM OXIDE ,400MHz): δ = 3.83 - 3.95 (m, 2 H), 3.62 (t, *J*=6.5 Hz, 2 H), 2.97 - 3.07 (m, 1 H), 2.78 - 2.96 (m, 3 H), 1.83 - 1.93 ppm (m, 2 H)

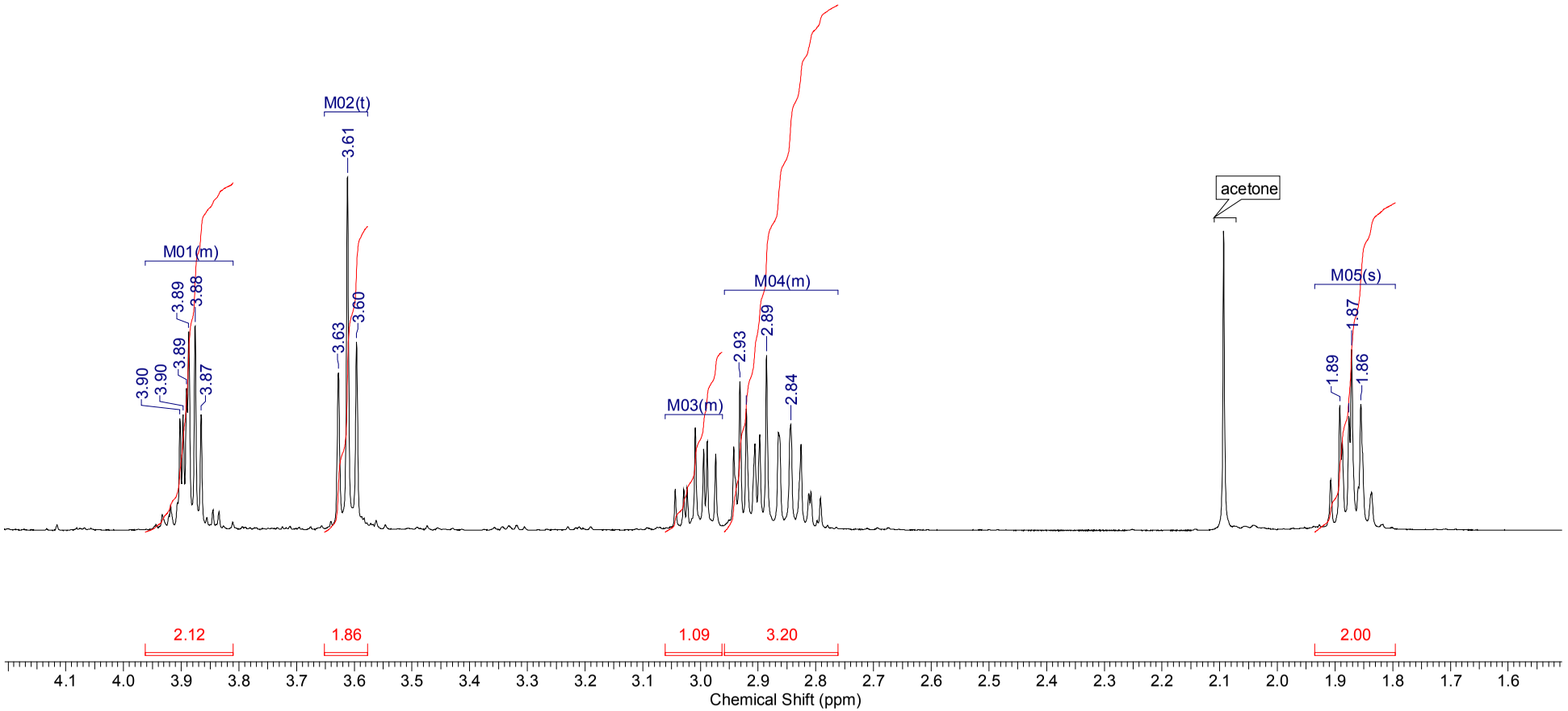




Sulfoxide 7 - 1H NMR - after coagulation

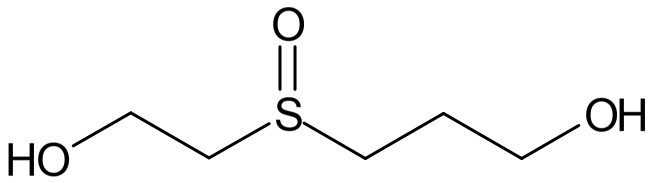
^{1}H NMR (DEUTERIUM OXIDE ,400MHz): δ = 3.81 - 3.96 (m, 2 H), 3.61 (t, *J*=6.3 Hz, 2 H), 2.96 - 3.06 (m, 1 H), 2.76 - 2.96 (m, 3 H), 1.87 ppm (s, 2 H)

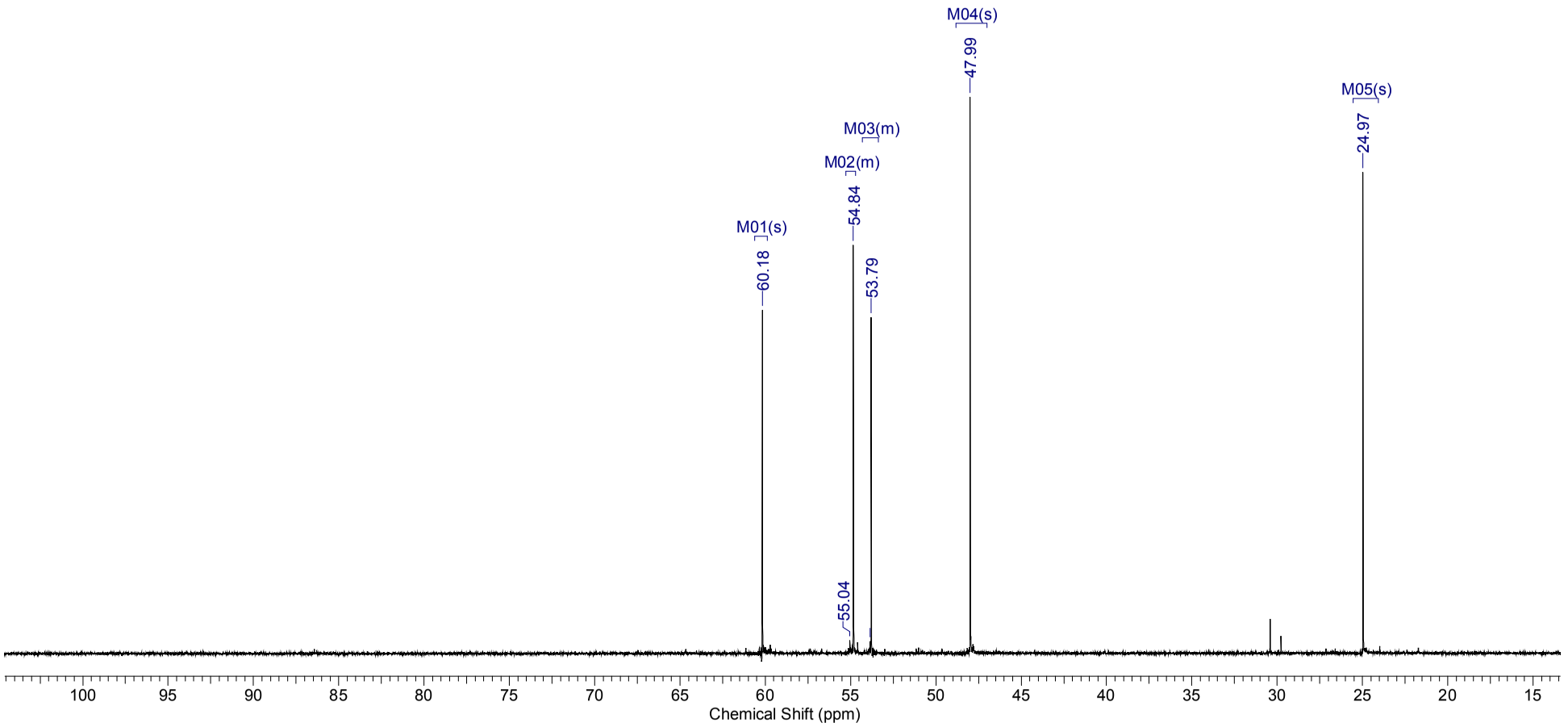




Sulfoxide 7 - 13C NMR - after coagulation

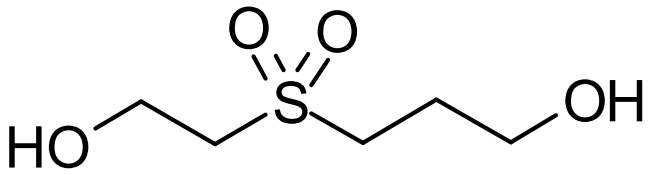
^{13}C NMR (DEUTERIUM OXIDE ,101MHz): δ = 60.2, 54.9, 53.8, 48.0, 25.0 ppm

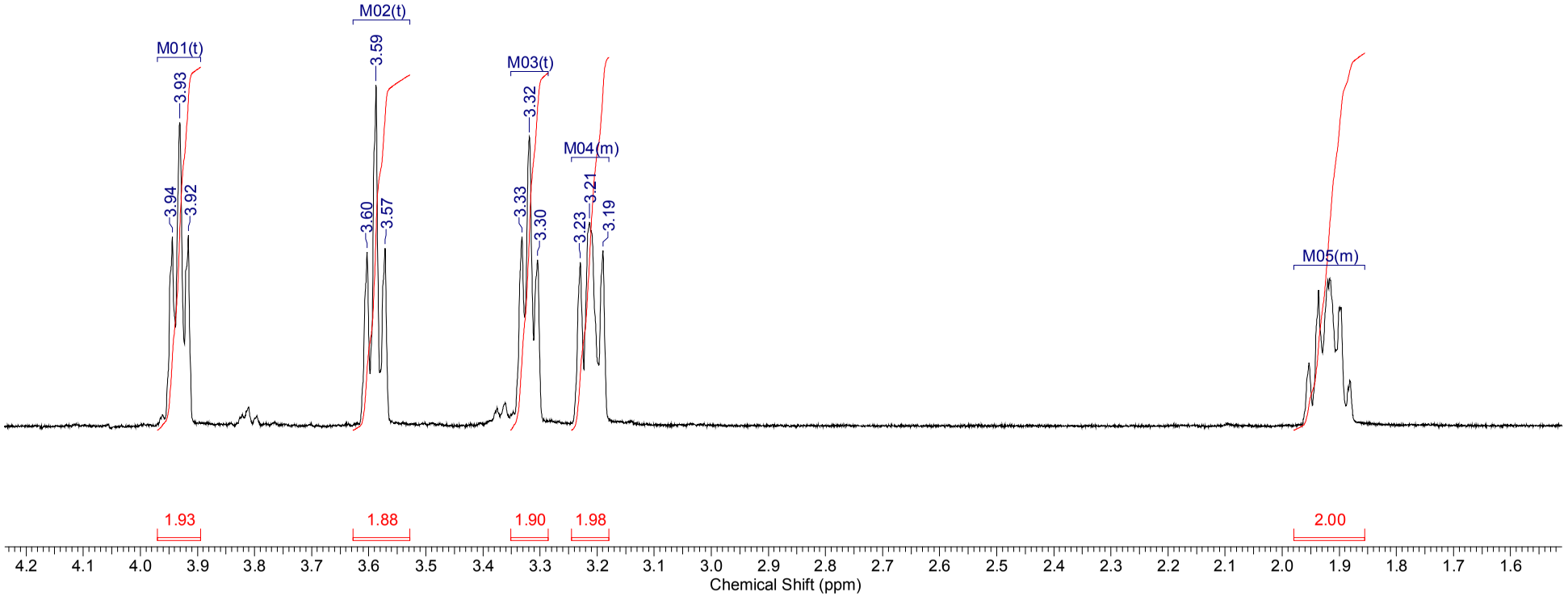




Sulfone 8 - 1H NMR in deuterium oxide

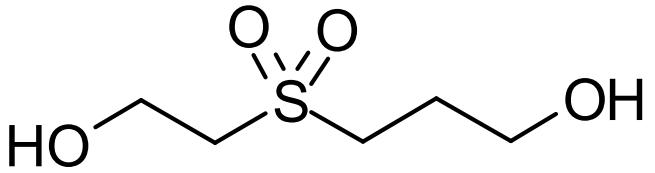
^{1}H NMR (DEUTERIUM OXIDE ,400MHz): δ = 3.93 (t, *J*=5.6 Hz, 2 H), 3.59 (t, *J*=6.3 Hz, 2 H), 3.32 (t, *J*=5.5 Hz, 2 H), 3.18 - 3.24 (m, 2 H), 1.86 - 1.98 ppm (m, 2 H)





Sulfone 8 - 13C NMR in deuterium oxide

^{13}C NMR (DEUTERIUM OXIDE ,101MHz): δ = 59.7, 55.0, 54.6, 51.0, 24.0 ppm



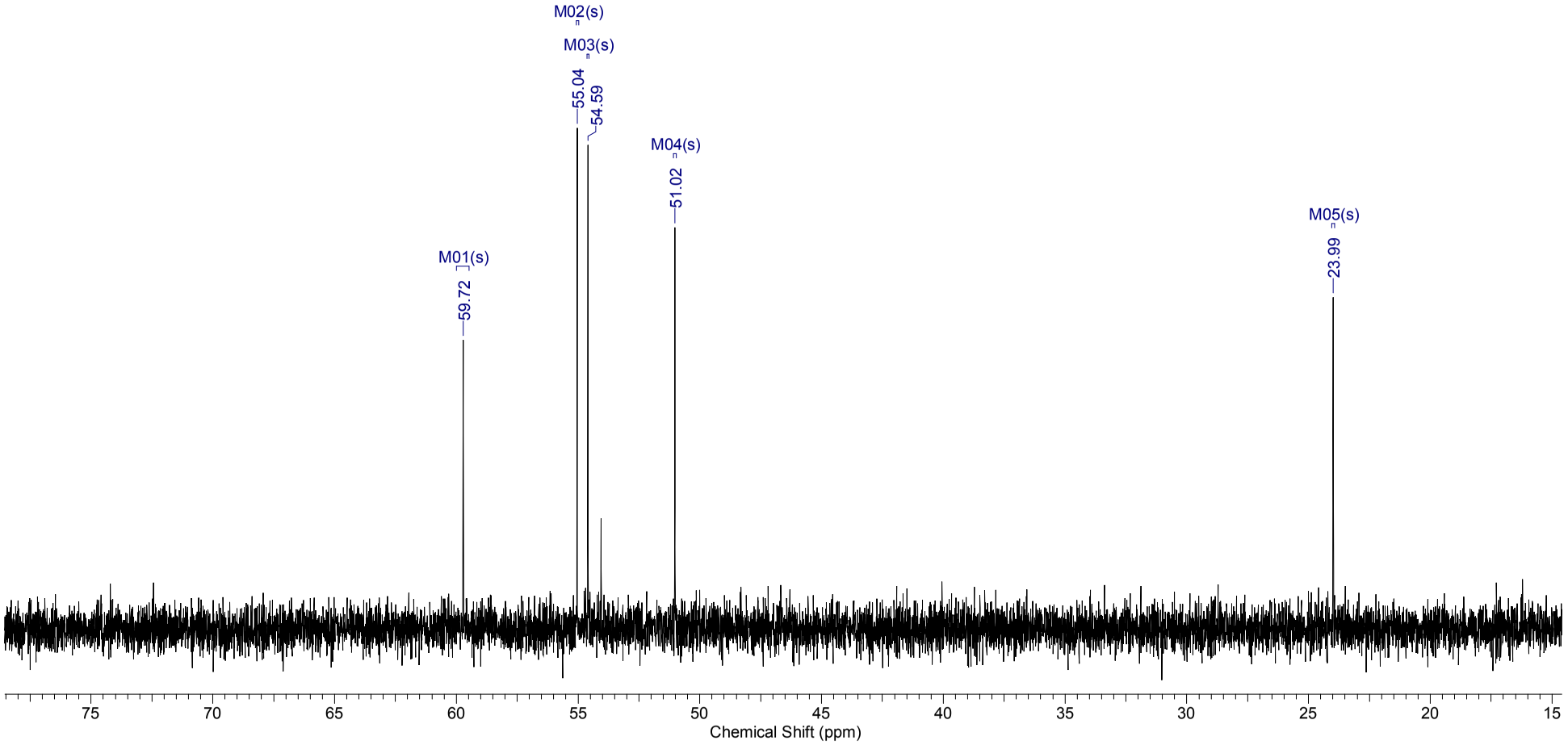


Table S6 - Entry 7 - 15 min

sulfide 6 / sulfoxide 7 - 1H NMR in deuterium oxide

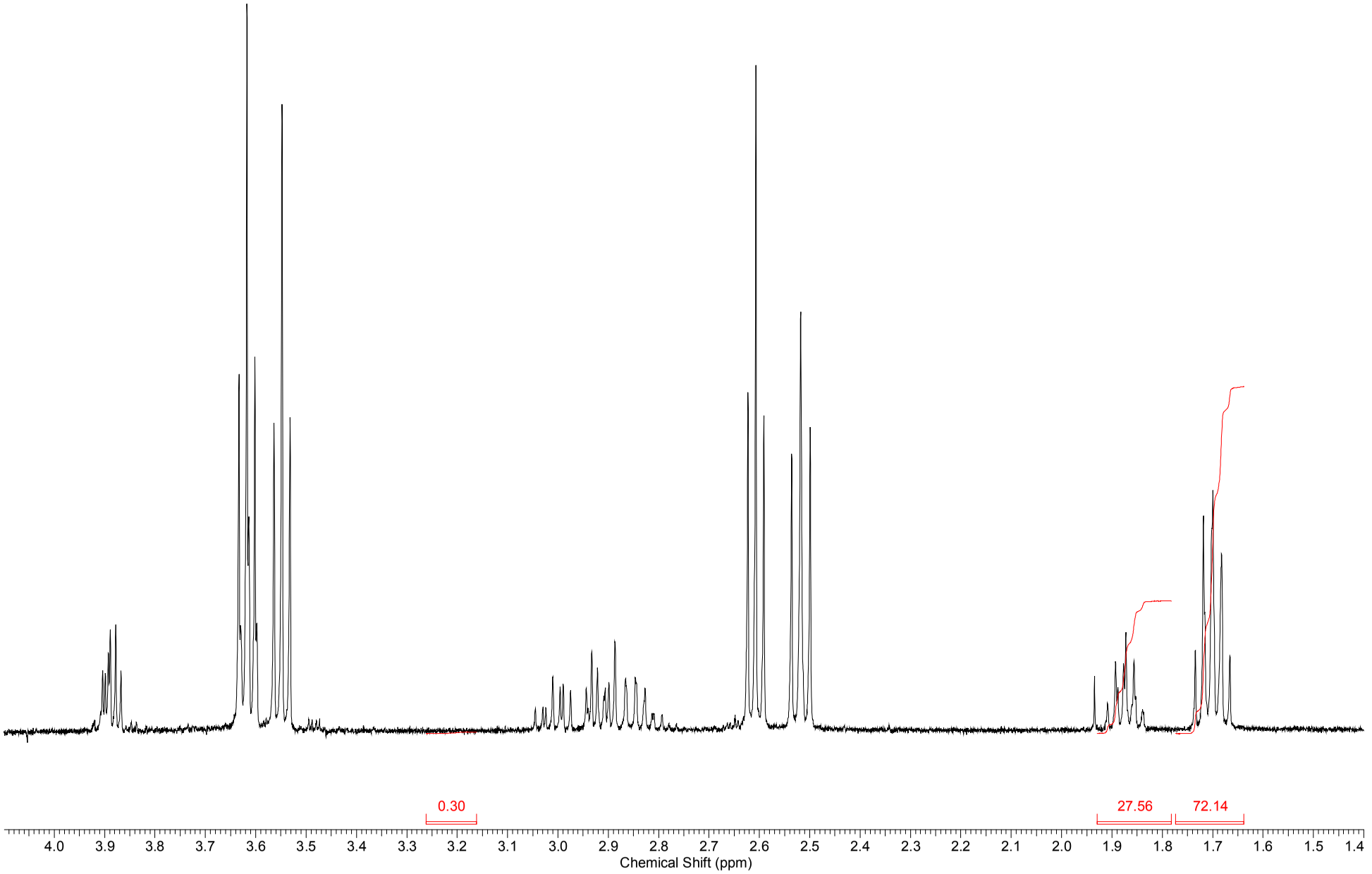


Table S6 - Entry 7 - 30 min

sulfide 6 / sulfoxide 7 - 1H NMR in deuterium oxide

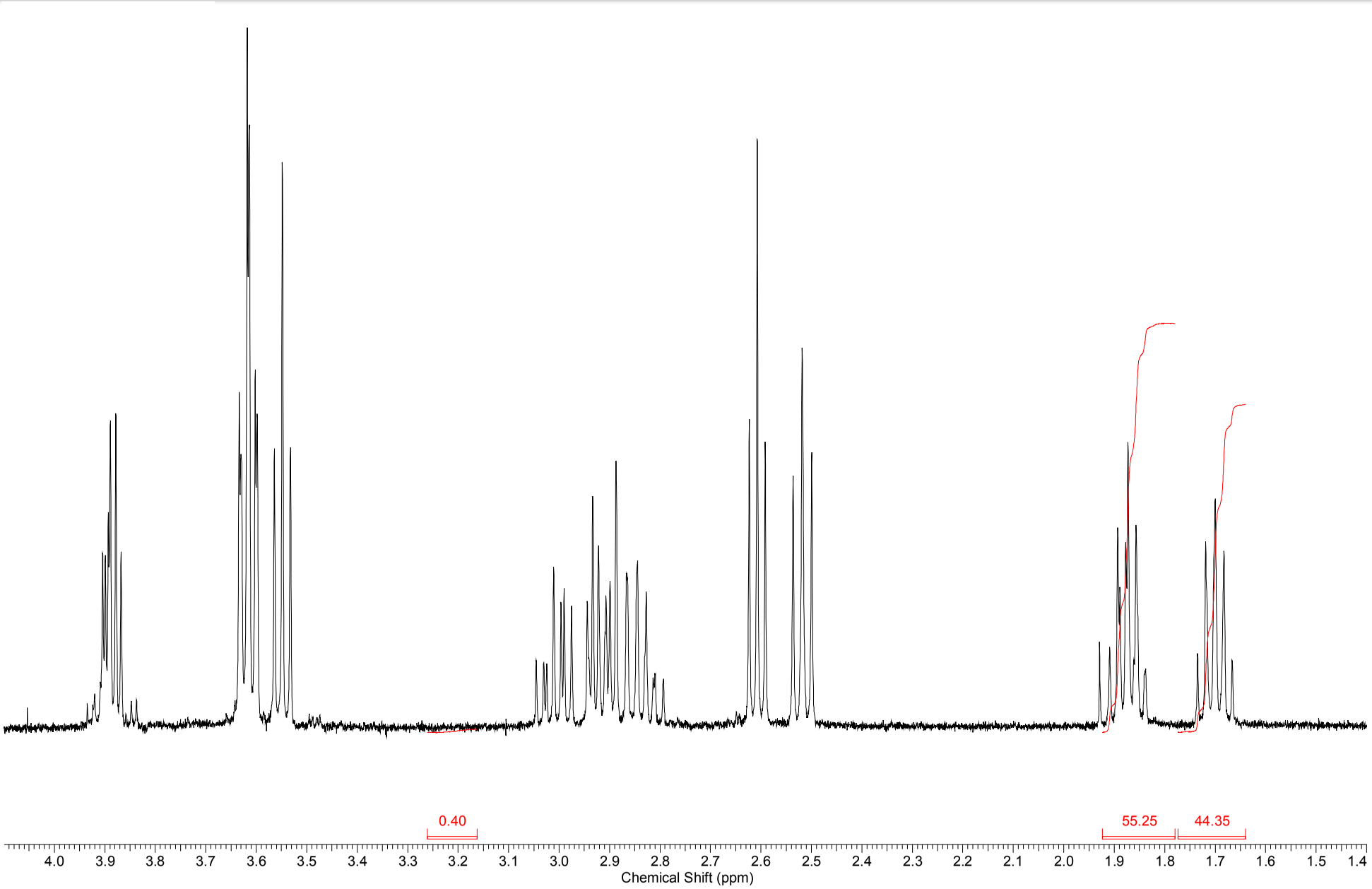


Table S6 - Entry 7 - 60 min

sulfide 6 / sulfoxide 7 - 1H NMR in deuterium oxide

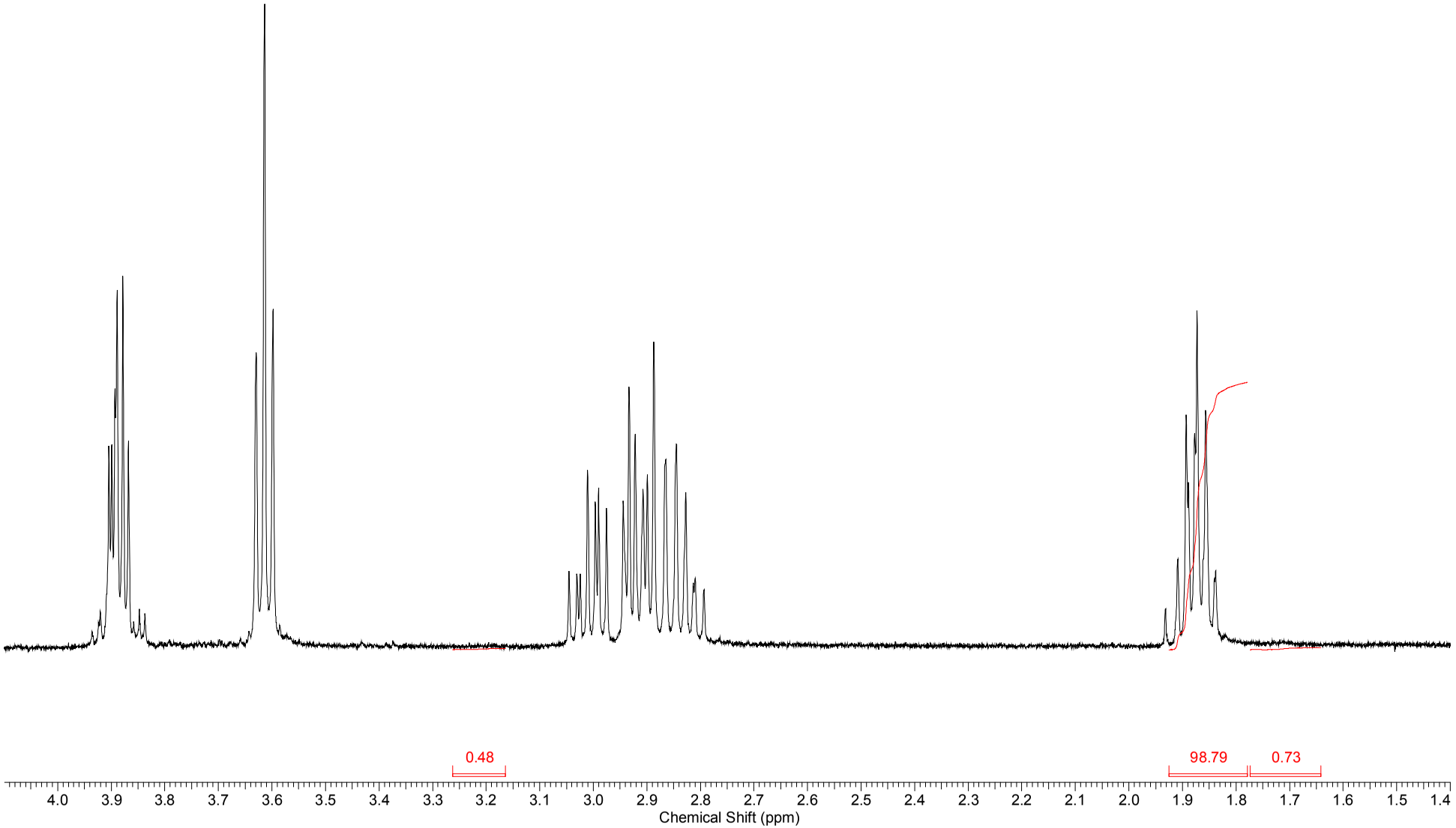
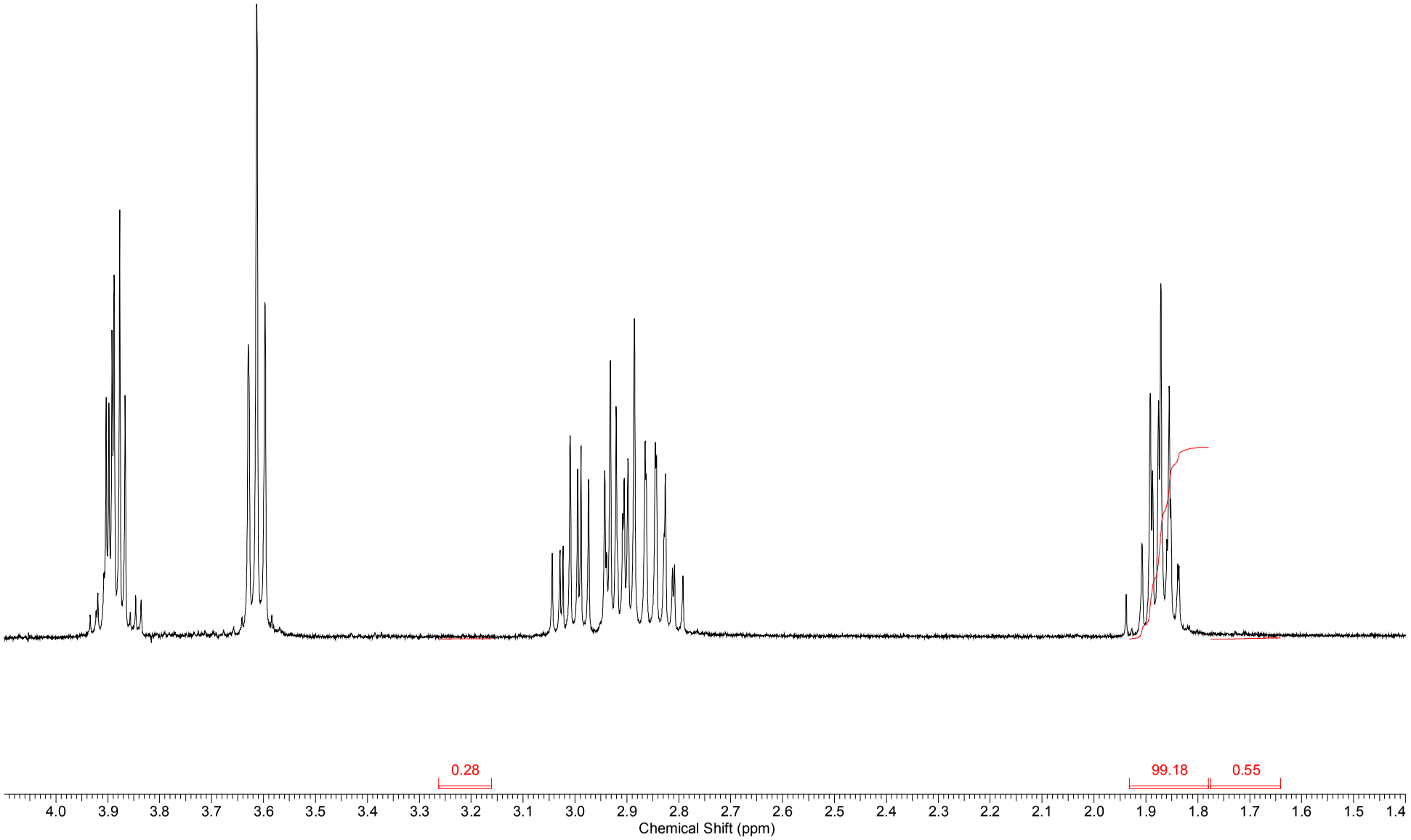
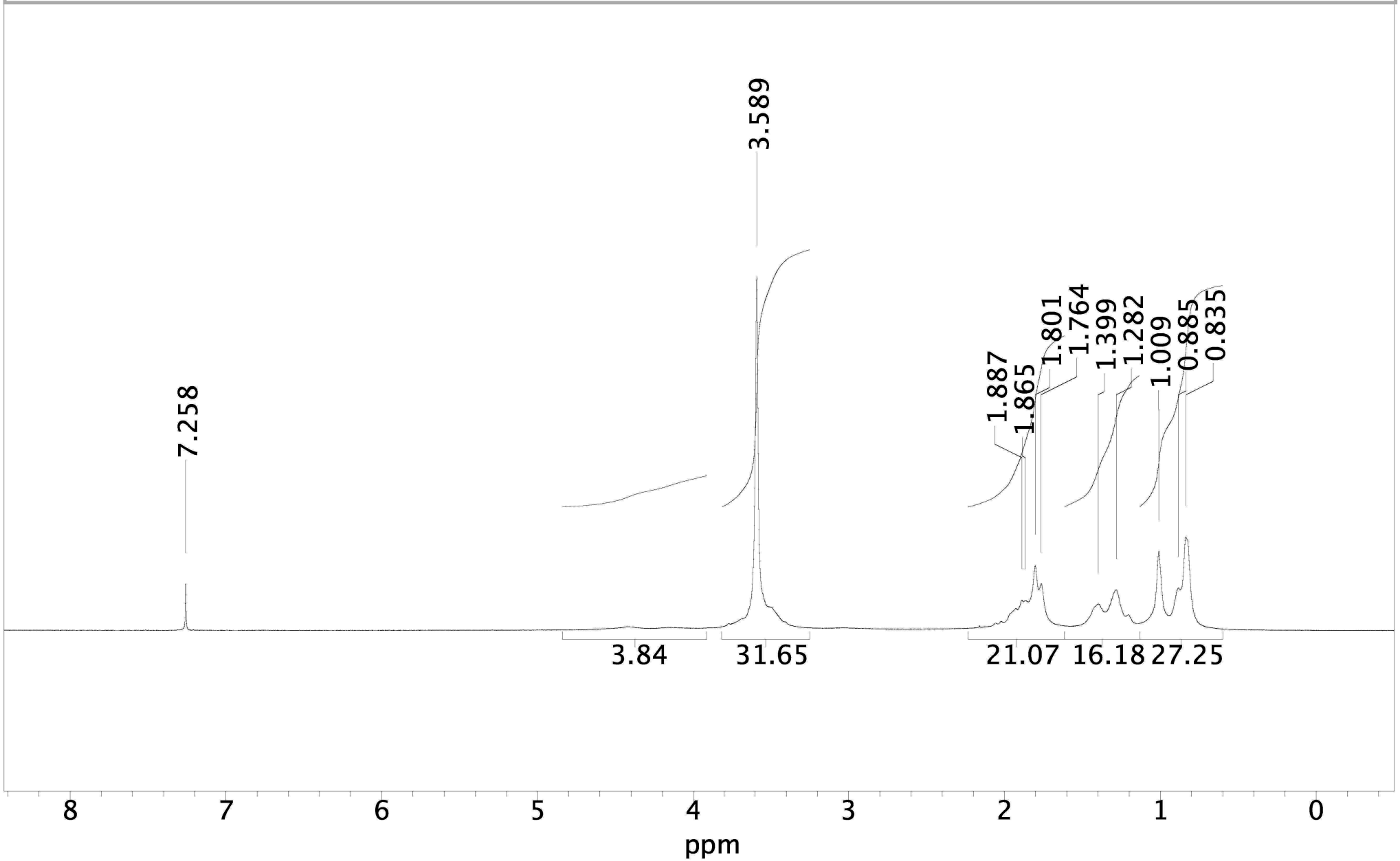


Table S6 - Entry 7 - 90 min

sulfide 6 / sulfoxide 7 - 1H NMR in deuterium oxide



NP1s-(a) - 1H NMR - freeze-dried sample dissolved in CDCl3



NP1s-(a): Overlapped 1H NMR, edHSQC (blue/red) and HMBC (green)