Phenothiazine redox mediators boost photocatalytic hydrogen evolution

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-Supporting Information-

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1 Materials and methods

Chemicals and Solvents

Chemicals and solvents were purchased from BLDPharm, TCI or Sigma Aldrich and used directly without purification unless specified otherwise. Moisture- or oxygen-sensitive reactions were carried out in glassware, heated under vacuo (10^{-3} mbar) using standard Schlenk techniques in a dry argon atmosphere (Argon 4.6 from MTI IndustrieGase Neu Ulm). Anhydrous solvents (toluene, DMF, THF) were obtained from an M.Braun solvent purification system (MB-SPS-800) and purged with argon before usage in synthesis. Other solvents were purchased and used in analytical grade.

Flash Colum Chromatography

Colum chromatography was carried out using Silicagel 60 (grain size 40-63 µm) from Marchery-Nagel.

Thin Layer Chromatography (TLC)

Analytical thin layer chromatography was carried out using silica gel coated aluminium plates with a fluorescence indicator (Merck 60 F_{254}). Detection was carried out by using short wave UV-light (λ_{max} = 254 nm and 366 nm).

Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR-spectra were recorded at 298 K on the following spectrometer:

BRUKER Advance 400 Neo [400.1 MHz (^{1}H), 101.6 MHz (^{13}C)]. Chemical shifts are reported in part per million (ppm, δ scale). ^{1}H-NMR spectra are referenced to tetramethylsilane as an internal standard or the residual solvent signal of the respective solvent: DMSO-d_6: δ = 2.50 ppm; $CDCl_3$: δ = 7.26 ppm, CD_2Cl_2 = 5.32 ppm. ^{13}C-NMR spectra are referenced to tetramethylsilane as an internal standard or the residual solvent signal of the respective solvent: DMSO-d_6: δ = 39.5 ppm; $CDCl_3$: δ = 77.2 ppm.

The analysis followed first order, and the following multiplicity abbreviations were used: singlet (s) doublet (d) triplet (t) multiplet (m) and combinations thereof, such as doublet of doublets (dd). Coupling constants (*J*) are given in Hertz [Hz]. Chemical shifts (*δ)* are given in parts per million [ppm].

Preparative size exclusion chromatography (SEC) - recycling GPC) was performed on a JAI *LaboACE LC-7080 Plus* recycling preparative HPLC with a set of two JAI *JAIGEL-2HR Plus* columns. HPLC grade CH_2Cl_2 (amylene stabilized) was used as eluent.

High Resolution Mass Spectroscopy (HRMS)

High-resolution mass spectrometry (HRMS) was performed using a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer solariX (Bruker Daltonik) equipped with a 7.0 T superconducting magnet and interfaced to an Apollo II Dual ESI/MALDI source.

MALDI-TOF spectrometry

Polymer masses were acquired in positive linear mode using an Ultraflex MALDI-TOF/TOF mass spectrometer (BRUKER Daltonik, Bremen, Germany). Ionisation was achieved using a smartbeam-II laser at 1-2000 Hz repetition rates at a laser power of 10 %. As internal standard a mixture of PEG 2 kDa and PEG 8 kDa was used.

MALDI-TOF sample preparation: For all MALDI measurements a DCM solution with 0.1 % TFA (stock solution) was used. For each measurement session the matrix solution was freshly prepared. For 25 samples a matrix solution consisting of DCTB (100 mg) dissolved in the stock solution (1.2 mL) was used. The polymer samples were dissolved in the stock solution (100 µL). The matrix and the sample solution were mixed in a ratio of 1:1 (30 µL each) and then pipetted onto the MALDI target (1.0 µL).

UV/Vis spectroscopy:

UV/Vis spectroscopy was performed on a Shimadzu UV-2450 spectrophotometer. All measurements were performed with standard cuvettes (d = 10.0 mm, V = 4 ml).

Emission spectroscopy:

Emission spectroscopy was performed on a Jasco FP-8500 spectrofluorometer. Standard emission cuvettes (d = 10.0 mm, V = 4 ml) were used.

Gas chromatography:

Gas-chromatography was performed on a Bruker Scion GC/MS, with a thermal conductivity detector 15 (column: molecular sieve 5A 75 m × 0.53 mm, oven temperature 40 °C, flow rate 30 ml min^{-1}, detector temperature 200 °C) with argon as carrier gas. The GC was calibrated by direct injection of known amounts of H_2 gas.

Cyclic Voltammetry (CV):

For cyclic voltammetry and differential pulse voltammetry a three-electrode single compartments cell set-up was used, and the voltage controlled using a computer-controlled Autolab PG-STAT30 potentiostat, all measurements were performed with 2 mL acetonitrile in Uvasol grade from Merck. The Pt-working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of A = 0.785 mm^2, which was polished before each measurement down to 0.25 µm using Buehler polishing paste to ensure a reproducible measurement. As counter electrode a Pt-wire was used and as reference electrode an Ag/AgCl-electrode was used. All measured potentials were internally referenced to the ferrocene/ferrocenium couple (Fc/Fc^+), and the electroactive species was prepared in a concentration of 10^{-3} M and as supporting electrolyte $TBAPF_6$, from Fluka, was used in a concentration of 0.1 M.

2 Stern-Volmer quenching experiments

For Stern-Volmer quenching experiments **solution A** was prepared containing the used photosensitizer in a concentration of $c = 1 \cdot 10^{-5}$ M. **Solution B** was prepared containing the used photosensitizer in a concentration of $c = 1 \cdot 10^{-5}$ M and the used PT derivative as quencher with $c = 1 \cdot 10^{-2}$ M. Both solutions were prepared as solvent mixture of MeOH/H_2O in 9/1 (v:v) ratio to mimic the used conditions in the catalysis.

Measurements were performed by addition of 0 µL ($\mathbf{I_0}$), 50 µL, 100 µL, 150 µL, 200 µL, 250 µL, 300 µL, 400 µL, 500 µL and 600 µL total volume of **solution B** to **solution A** (2 mL), corresponding to 0 equiv. of PT derivative added in $\mathbf{I_0}$, to 230.7 equiv. added for the addition of 600 µL of **solution B**.

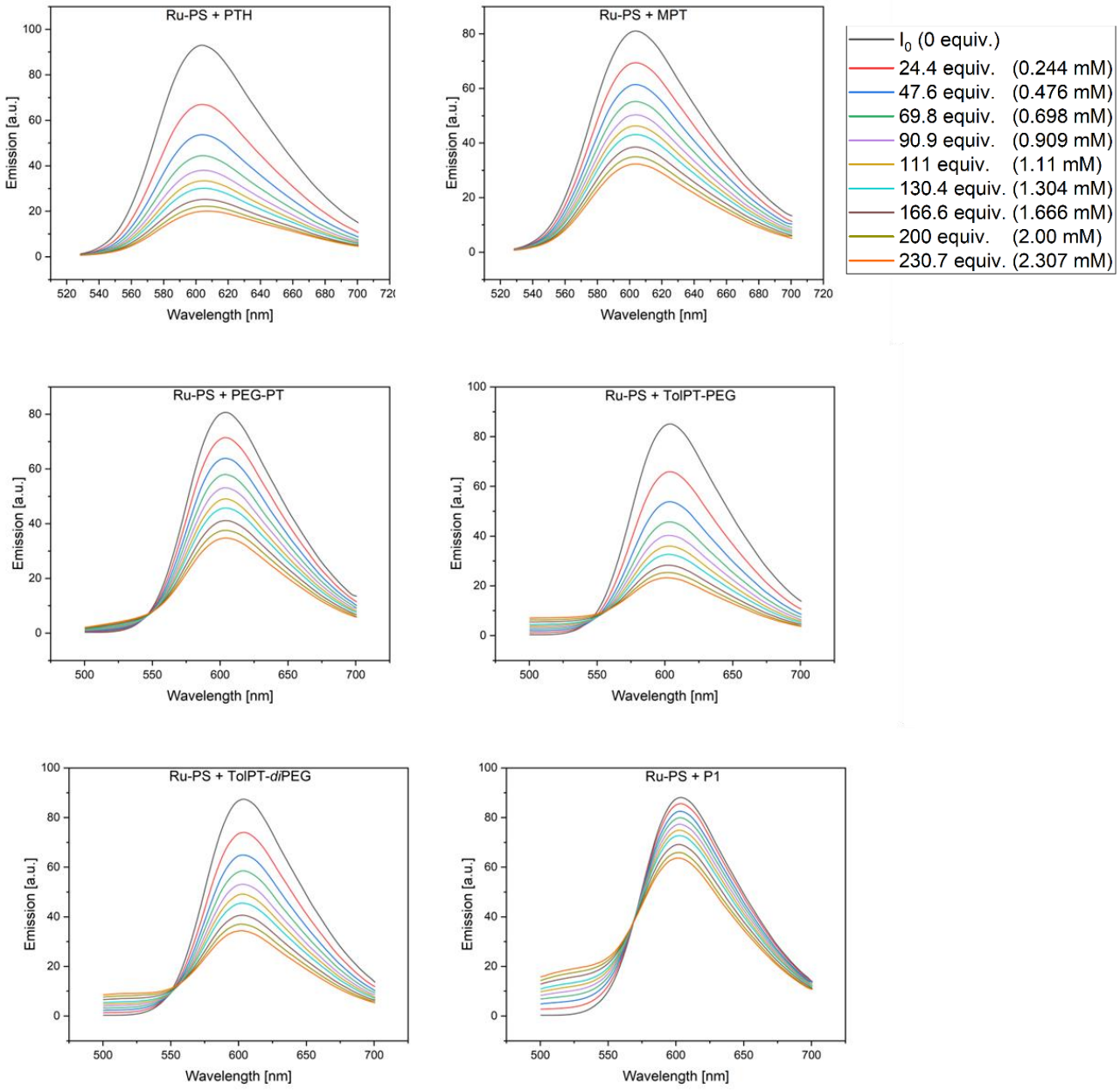


Figure S1: Stern-Volmer experiments for the emission quenching of $[Ru(bpy)_3](PF_6)_2$ in MeOH:H_2O (9:1, v:v) with different PT derivatives.

3 UV/Vis/NIR spectra of PT derivatives and radical cations

UV/Vis spectra were taken on neutral (**black curve**, $c \approx 1 \cdot 10^{-5}$ M, 240–700 nm range) and oxidized PT derivatives, oxidized by addition of 33.3 eq. of $(NH_4)_2[Ce^{(IV)}(NO_3)_6]$ = CAN (c = 0.1 M) (**red curves**, 240–1500 nm range) (Figure S2). The red curves clearly show the presence of radical cations at 500–650 nm.

Afterwards, 20 eq. (40 electron eq.) of L-ascorbic acid (ASC) ($c = 2 \cdot 10^{-2}$ M) was added to the formed radical cation solutions. The UV/Vis spectra in Figure S3 feature the diminishing of the radical cation absorption as a consequence, with absorption spectra measured every 20 seconds (for ***TolPT-diPEG*** and **P1** every 40 seconds).

In another trial the stability of formed radical cations at $c = 1 \cdot 10^{-5}$ M of the used PT derivative over the course of 14 min was tested. The radical cation was formed by addition of 33.3 eq. of CAN as oxidant (c = 0.1 M). Thereafter, UV-Vis-NIR spectra were recorded every 2 min in the 240–1500 nm range (Figure S4).

Sample preparation:

To 3 mL of a MeOH:H_2O (9:1, v:v) solution, 15 µL of a PT solution in MeOH ($c = 2 \cdot 10^{-3}$ M) were added, resulting in a concentration of $c = 1 \cdot 10^{-5}$ M. Afterwards 10 µL of a CAN-stock solution ($c = 1 \cdot 10^{-1}$ M) were added. Thereafter 30 µL of a L-ascorbic acid solution (ASC) ($c = 2 \cdot 10^{-2}$ M) were added to the mixture.

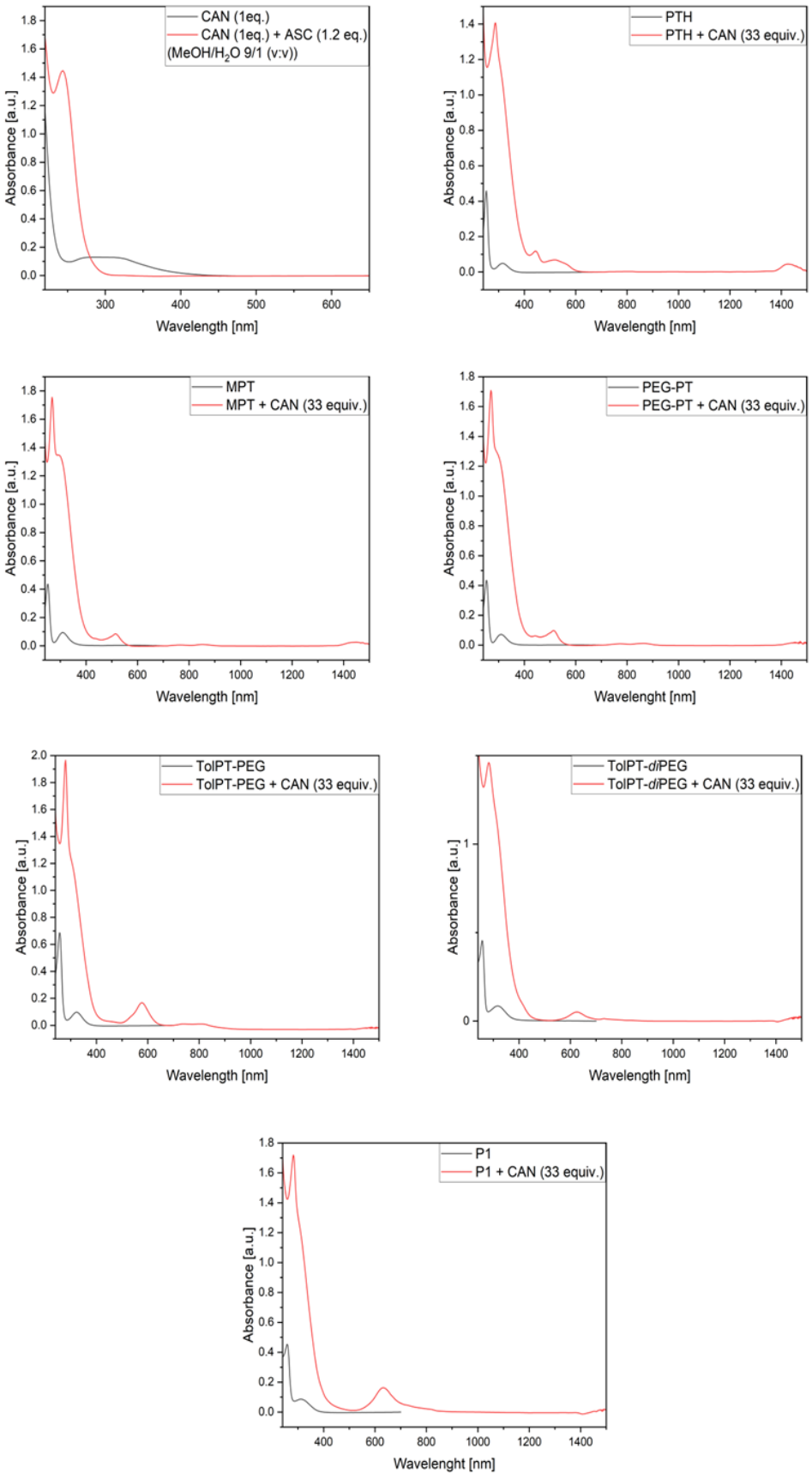


Figure S2: UV/Vis/NIR spectra of neutral and oxidized PT derivatives in MeOH:H_2O (9:1, v:v).

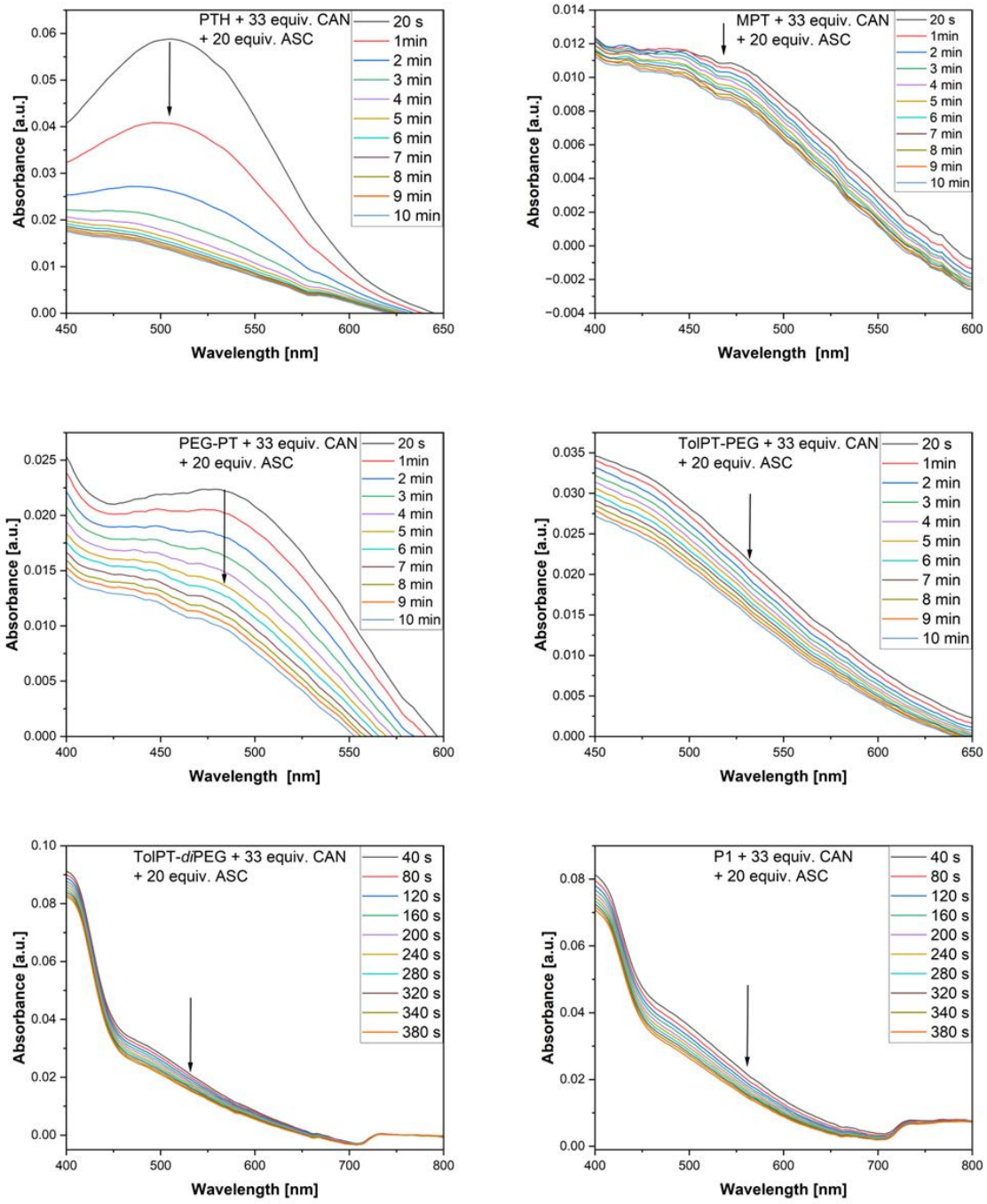


Figure S3: Time-dependent UV/Vis/NIR spectral measurements of PT radical cation treated with ascorbic acid (ASC) in MeOH:H_2O (9:1, v:v).

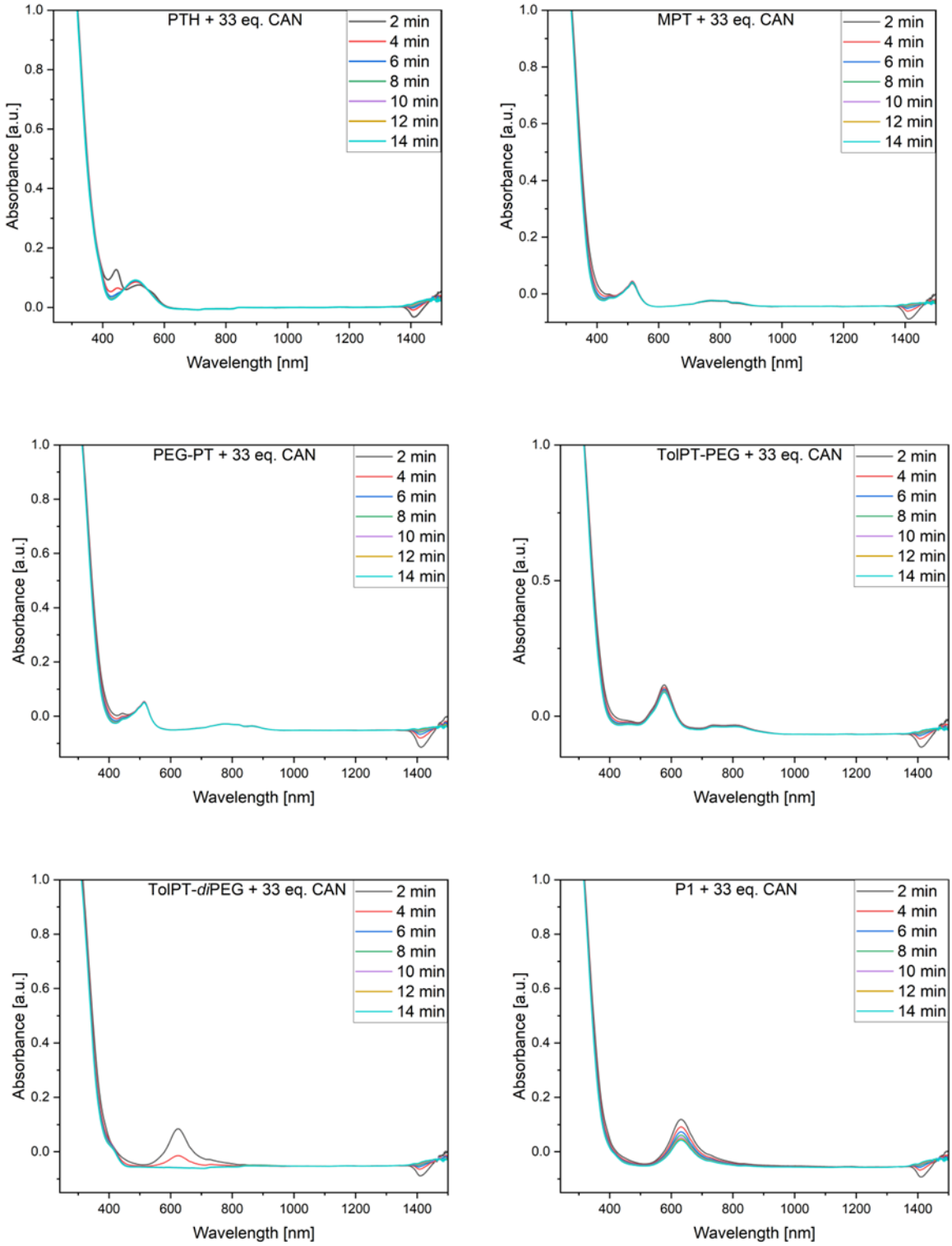


Figure S4: Time-dependent UV/Vis/NIR spectra to investigate the stability of formed PT radical cations in MeOH:H_2O (9:1, v:v).

4 Hydrogen evolution experiments

All solvents were purged with high-purity argon before each measurement to remove traces of oxygen. The samples were prepared using standard Schlenk techniques, Figure S5.

Standard reaction setup:

4.92 mL GC vials (from VWR – No. 548-0051A) were filled with 2 mL of the reaction mixture under inert conditions (containing solvent, catalyst ($(NH_4)_2[Mo_3S_{13}]$), photosensitizer ($[Ru(bpy)_3](PF_6)_2$) and sacrificial electron donor (ascorbic acid/ascorbate) at the concentrations specified.

Standard conditions: MeOH:H_2O (9:1, v:v) as solvent; c ($(NH_4)_2[Mo_3S_{13}]$) = $3.0 \cdot 10^{-7}$ M, c ($[Ru(bpy)_3](PF_6)_2$) = $2 \cdot 10^{-5}$ M, c (ascorbic acid) = 10 mM, c (PT derivative) = 1 mM (if not stated otherwise stated). The pH was adjusted to 4.0 using aqueous NH_3 (25 wt%) as NH_4^+-ion source, or $NaOH_{(s)}$. For acidic conditions the aqueous stock solution was acidified using 2.5 vol% H_3PO_4 (85 wt%) (for pH = 1.25), or 10 vol% H_3PO_4 (for pH = 0.85), until the respective pH was reached.

Afterwards, the vials were sealed with a septum cap (from VWR – 548-0511A). The samples were then irradiated with an LED light source from OSRAM LED ENGIN - LZ4-40B208 (λ_{max} = 455 nm) in a modular, air-cooled photoreactor, reported by Kowalczyk et al..[1] The GC vials were thereby placed on a height of 7 cm above the LED in the respective 3D-printed holder. Hydrogen evolution was quantified by gas-chromatography by taking 100 µL of the headspace volume of the GC vial and injecting it into the GC. Each experiment was carried out in triplicate, the values reported are the resulting average.

For Add-back experiments and time-dependent hydrogen evolution septum caps from WICOM were used (WIC 43890).

Preparation of stock solutions:

Catalyst ($(NH_4)_2[Mo_3S_{13}]$ = $(NH_4)_2\{Mo_3\}$): The stock solution of the catalyst was prepared in anhydrous and degassed DMF and kept under argon and exclusion of light at 7 °C for 3 days to fully dissolve and reach a concentration of $5 \cdot 10^{-4}$ M. Afterwards, 100 µL of that solution were used and diluted to 10 mL using anhydrous and degassed MeOH giving the final concentration of the stock solution c = $5 \cdot 10^{-6}$ M. The resulting solution was then used over the course 5 days and stored under light exclusion at 7 °C in between measurements. **Note:** Anhydrous solvents are needed to prevent the reported ligand exchange in aqueous solution.[2]

Photosensitizer ($[Ru(bpy)_3](PF_6)_2$): A stock solution with c = $5 \cdot 10^{-4}$ M was prepared in anhydrous and degassed MeOH and stored in a dark place at r.t.

Ascorbic acid/ascorbate ($HAsc/Asc^-$): Stock solutions with c = 100 mM were prepared in degassed milliQ water (R = 17–18.5 MΩ). The pH was adjusted as stated above and the resulting pH was monitored using a pH-meter. NH_3 was used as base as a source of NH_4^+ ions, or $NaOH_{(s)}$ for reference measurement at a given pH. The pH of 2.55 was achieved by using a pure 100 mM stock solution of ascorbic acid. pH 1.25 and pH 0.85 were obtained by adding 2.5 vol% H_3PO_4 (85 wt%) and 10 vol% H_3PO_4, respectively. The aqueous solutions were prepared freshly for each measurement day.

PT derivative: Solutions of phenothiazine (**PTH**) and its derivatives were prepared in anhydrous and degassed MeOH with c = $2 \cdot 10^{-2}$ M. PT derivatives served as redox mediators (RMs) in these photocatalytic HER systems.

Sample preparation:

All solvents were purged with argon before usage.

For sample preparation 80 µL of photosensitizer stock solution, 100 µL of **PTH** or PT derivative stock solution (for c = 1 mM), 1.5 mL dry and degassed MeOH as well as 200 µL of the ascorbic acid/ascorbate aqueous stock solution were placed in the GC-vial, sealed with a screw cap and degassed for 4 min. Afterwards the sample was transferred into an argon-filled flask (see Figure S5) where the screw cap was removed. After the addition of 120 µL of the catalyst stock solution, the GC-vial was closed with a new screwcap and placed in the photoreactor (within a time span of 5 min for all samples). After that, the samples were irradiated for 6 h.

Definitions: TON = $n(H_2)$ / n(catalyst)

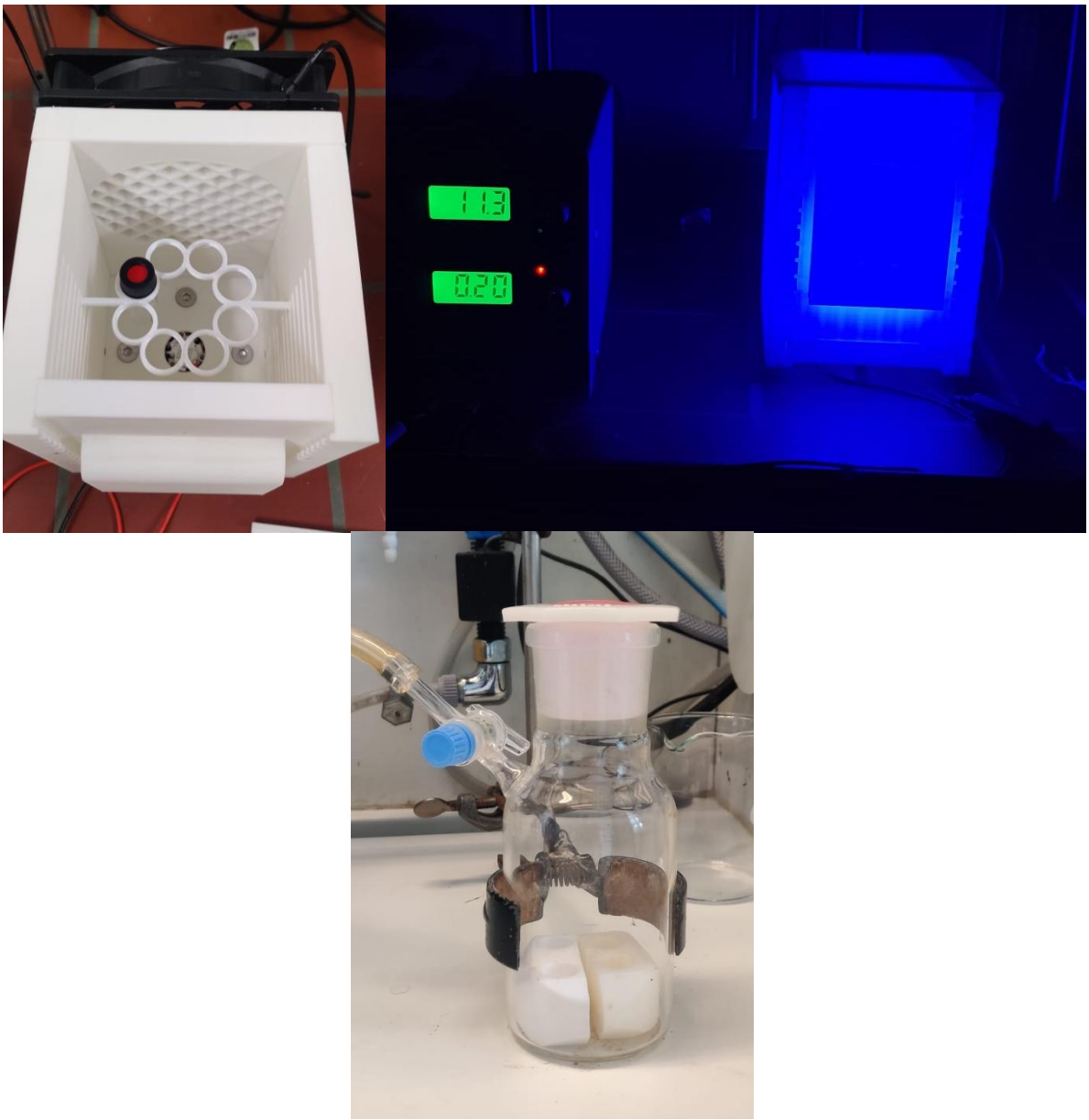


Figure S5: Top row: Used photoreactor for HER measurements. Bottom: Inert vial for opening and closing the samples under Ar counter flow.

5 Temperature dependency of HER photocatalysis

Temperature dependency of the hydrogen evolution reaction (HER) photocatalysis was measured with a Heidolph MR3001 K equipped with a temperature control sensor with experiments conducted at 20 ± 0.5 °C and 30 ± 0.5 °C with stirring set to 200 rounds per minute.

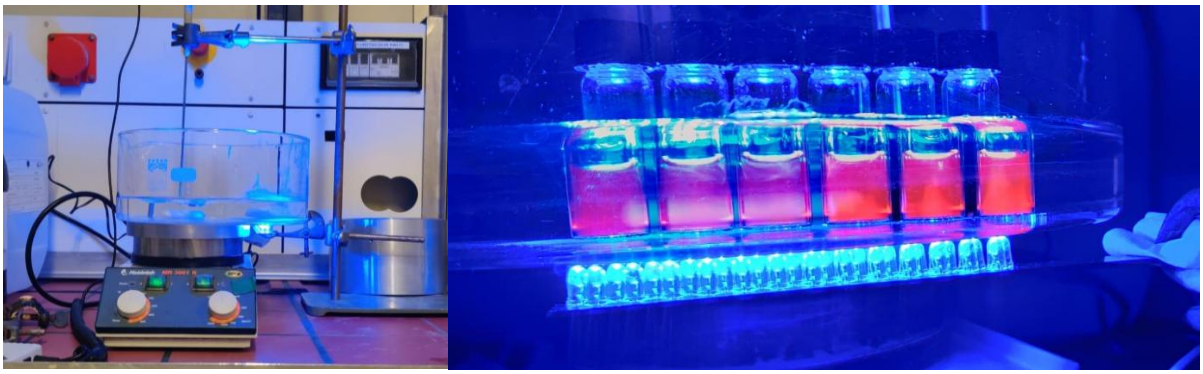


*Figure S6: Left: Water bath set-up for temperature control; right: schematic picture of HER-samples. With **PTH**: left (3x); Without PT derivative (reference): right (3x); pH = 2.55.*

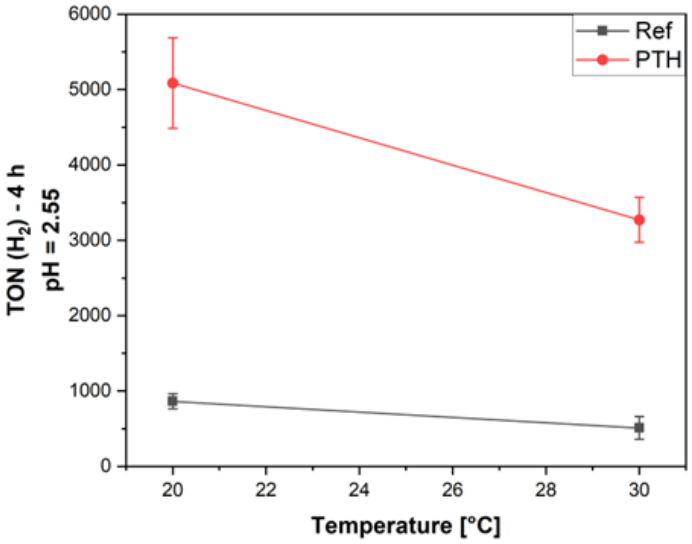


*Figure S7: Temperature dependency of HER-system. Averaged TONs after 4 h at pH = 2.55 using **PTH** or reference (with: 1 mM redox mediator (RM), 0.3 µM $(NH_4)_2\{Mo_3\}$, 20 µM $[Ru(bpy)_3](PF_6)_2$, 10 mM ascorbic acid/ascorbate in MeOH:H_2O (9:1, v:v), irradiation at 470 nm). Measured at 20 °C ± 0.5 °C and 30 °C ± 0.5 °C (each experiment carried out as triplicates).*

Table S1: Temperature dependency of HER photocatalysis

Temperature	TON (Ref.)	TON (PTH)
20 °C ± 0.5 °C	860 ± 100	5090 ± 800
30 °C ± 0.5 °C	510 ± 150	3270 ± 300

6 Effect of varying the equivalents of PT to $[Ru(bpy)_3](PF_6)_2$

The performance of **MPT** and **PEG-PT** as redox mediators at pH 1.25 was tested for different molar ratios with respect to the PS $[Ru(bpy)_3](PF_6)_2$, within a range from 12.5 eq. up to 200 eq.

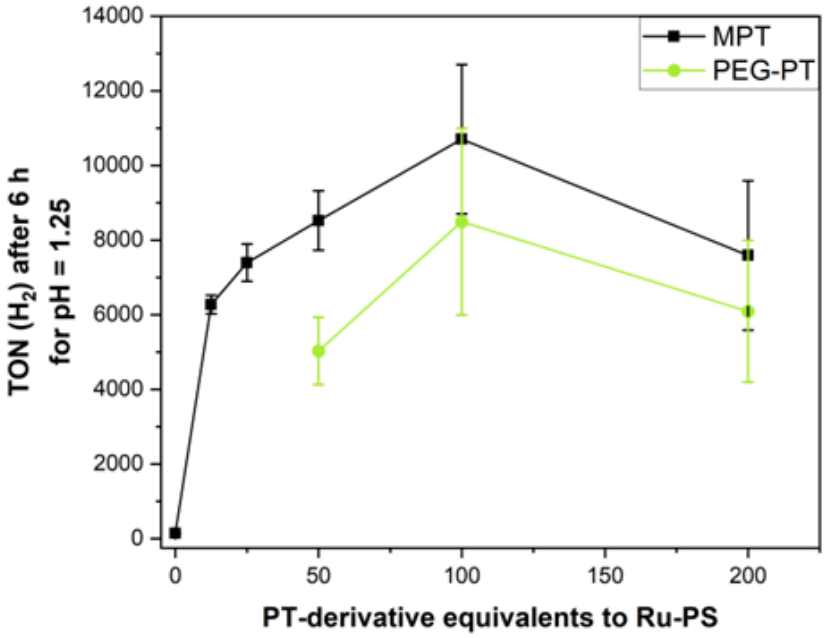


*Figure S8: Effect of varying the equivalents of PT derivative to $[Ru(bpy)_3](PF_6)_2$. Averaged TONs after 6 h at pH = 1.25 using **MPT** or **PEG-PT** (with 0.25 mM/0.5 mM/1 mM/2 mM or 4 mM of RM, 0.3 µM $(NH_4)_2[Mo_3S_{13}]$, 20 µM $[Ru(bpy)_3](PF_6)_2$, 10 mM ascorbic acid/ascorbate in MeOH:H_2O (9:1, v:v), irradiation at 470 nm). Varying from 12.5 equiv. to 200 equiv. RM vs. $[Ru(bpy)_3](PF_6)_2$ (each experiment was carried out as triplicates).*

Table S2: Obtained TONs(H_2) when utilizing different equiv. of PT derivative vs. $[Ru(bpy)_3](PF_6)_2$.

Equiv. used vs $[Ru(bpy)_3](PF_6)_2$ at pH = 1.25 Equiv./ (Conc. [mM])	**TON (MPT)**	**TON (PEG-PT)**
12.5 / (0.25 mM)	6270 ± 250	-
25 / (0.5 mM)	7390 ± 500	-
50 / (1 mM)	8520 ± 800	5030 ± 900
100 / (2 mM)	**10700 ± 2000**	**8490 ± 2500**
200 / (4 mM)	7590 ± 2000	6090 ± 1900

7 Time-dependent hydrogen evolution

The time dependency of the H_2 evolution was monitored by measuring H_2 after time intervals of 1 h each over a total time of 6 hours. For this, the reference system and an entry with 50 eq. **PTH** as RM to the PS was used.

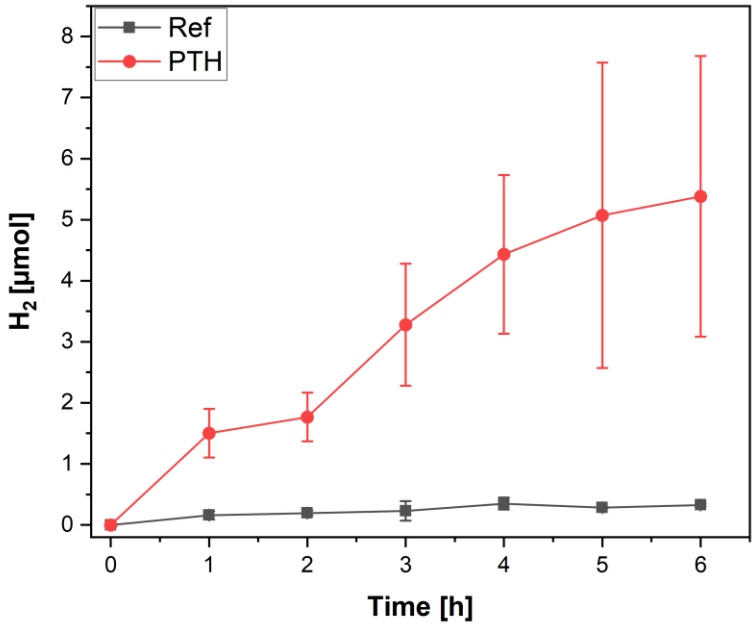


*Figure S9: Time dependency of the H_2 evolution for the reference system and with **PTH** (50 eq.) at pH = 2.55 using 0.3 µM $(NH_4)_2[Mo_3S_{13}]$, 20 µM $[Ru(bpy)_3](PF_6)_2$, 10 mM ascorbic acid/ascorbate in MeOH:H_2O (9:1, v:v), irradiation at 455 nm. (each experiment was carried out in triplicate). Note: The used septa show after piercing a slight leakage of H_2.*

Table S3: Time-dependence of H_2 evolution.

Time [h]	H_2 [µmol] (Ref.)	H_2 [µmol] (PTH 50 eq.)
1	0.16 ± 0.07	1.50 ± 0.4
2	0.20 ± 0.04	1.77 ± 0.4
3	0.23 ± 0.16	3.28 ± 1.0
4	0.35 ± 0.1	4.43 ± 1.3
5	0.28 ± 0.02	5.07 ± 2.5
6	0.33 ± 0.03	5.38 ± 2.3

8 Add-back experiments

Additionally add-back experiments were performed. For this, photocatalysis was carried out as previously described (see **4 Hydrogen evolution experiments**). After an irradiation time of 6 h, H_2 was measured, afterwards again the same amount of photosensitizer $[Ru(bpy)_3](PF_6)_2$ (80 µL) and catalyst $(NH_4)_2[Mo_3S_{13}]$ (120 µL) were added through the septa into the catalytic solution under inert atmosphere using the Argon chamber shown in Figure S5. A second H_2 measurement was performed after an additional 4.5 h (10.5 h total irradiation) to check for further activity of the used RM (**PTH**).

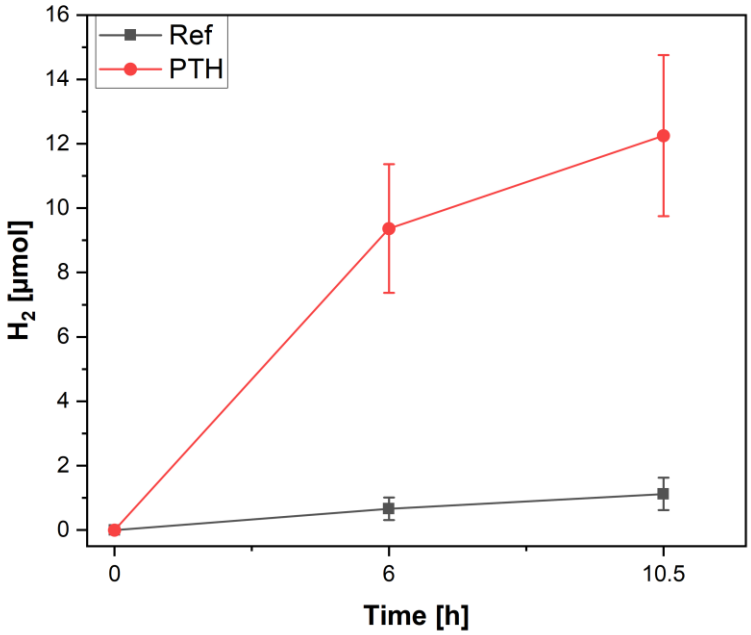


*Figure S10: Add-back experiment of the H_2 evolution for the reference system and with **PTH** (50 eq.) at pH = 2.55 using 0.3 µM $(NH_4)_2[Mo_3S_{13}]$, 20 µM $[Ru(bpy)_3](PF_6)_2$, 10 mM ascorbic acid/ascorbate in MeOH:H_2O (9:1, v:v), irradiation at 455 nm. After an irradiation time of 6 h, H_2 was measured, afterwards again the same amount of photosensitizer $[Ru(bpy)_3](PF_6)_2$ (80 µL) and catalyst $(NH_4)_2[Mo_3S_{13}]$ (120 µL) were added to the catalytic solution and hydrogen was measured after an additional 4.5 h (10.5 h total) (each experiment was carried out in triplicate). Note: The used septa show after piercing a slight leakage of H_2.*

Table S4: Add-back experiments for HER photocatalysis.

Time [h]	H_2 [µmol] (Ref.)	H_2 [µmol] (PTH 50 eq.)
6	0.66 ± 0.35	9.37 ± 2
10.5	1.12 ± 0.5	12.25 ± 2.5

For a comparison of produced hydrogen (conversion of TON to produced µmol H_2) of table 2 and add-back-experiments/time-dependent measurements see table S5. TON calculated for [catalyst] = 0.3 µM.

Table S5: Conversion table for furnished µmol H_2 to TON (for [catalyst] = 0.3 µM)

H_2 [µmol]	TON (for catalyst = 0.3 µM; $(NH_4)_2\{Mo_3\}$)
0	0
1	1666.7
2	3333.3
5	8333.3
7	11666.6
9	15000.0
11	18333.2
13	21666.6

Note: The two-electron oxidation product of ascorbic acid (**HAsc**), namely, dehydroascorbic acid (**DHA**), shows the capability to interfere with the catalytic cycle. This could lead to a slower formation of H_2 as the chance for unwanted side reactions increases with rising **DHA** concentration yielding an intrinsic poisoning of the catalytic cycle, as shown by Scandola et. al..[3]

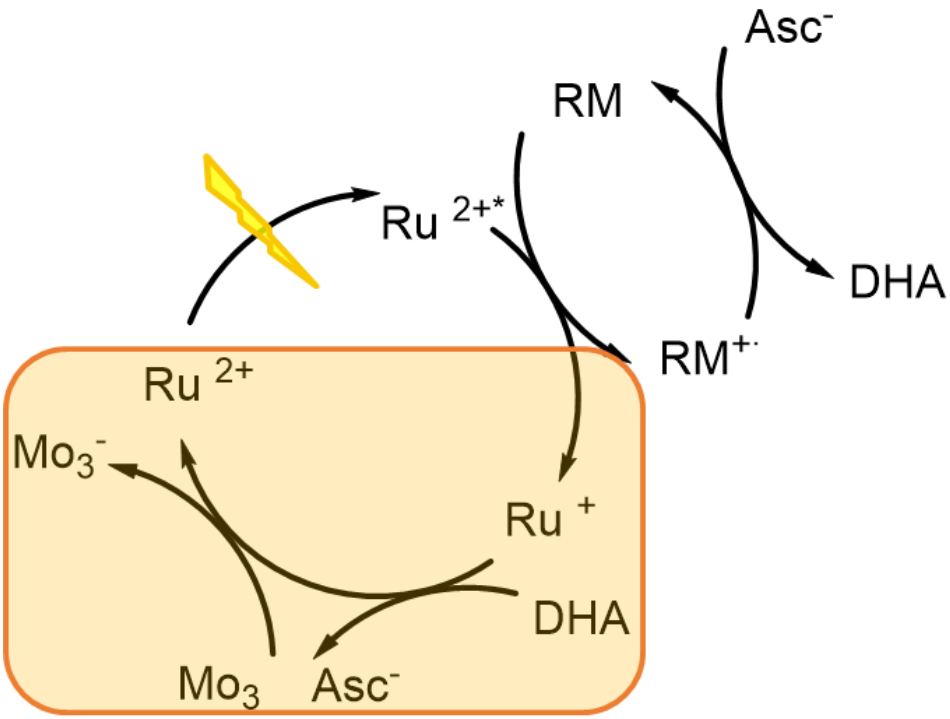


Figure S11: Schematic representation of intrinsic poisoning by produced DHA within the catalytic cycle.

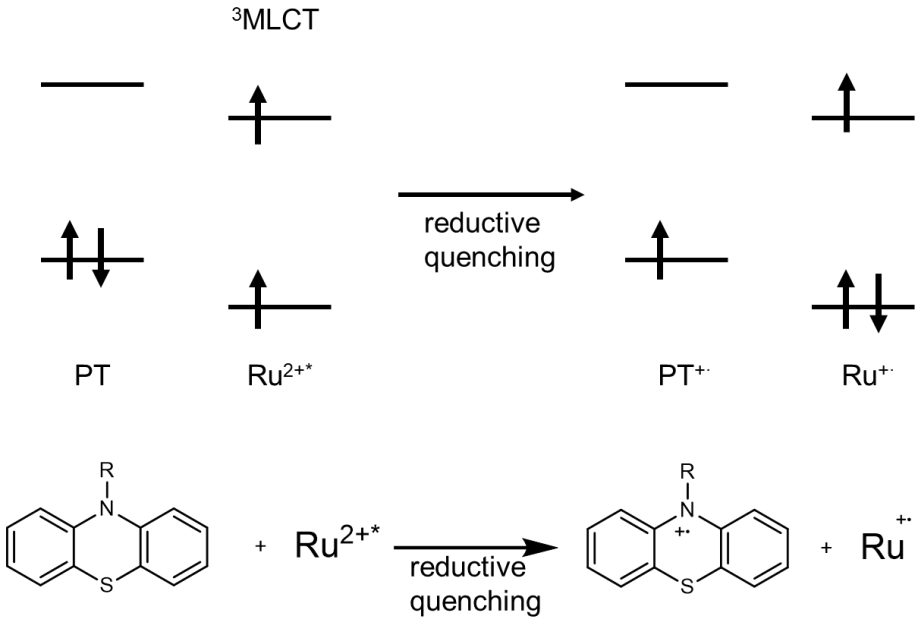
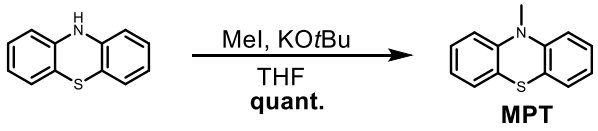


Figure S12: Schematic representation of the interaction between the RM (PT derivative) and photosensitizer (Ru-PS).

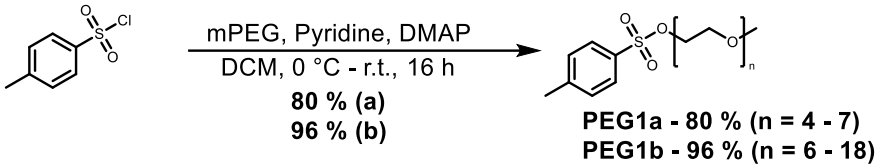
9 Synthetic procedures

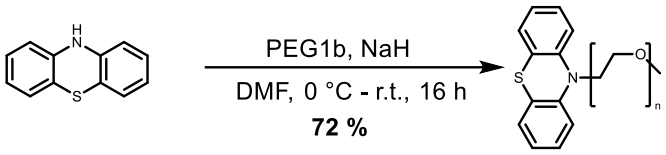
Overview of synthetic manipulations:

Synthesis of MPT:

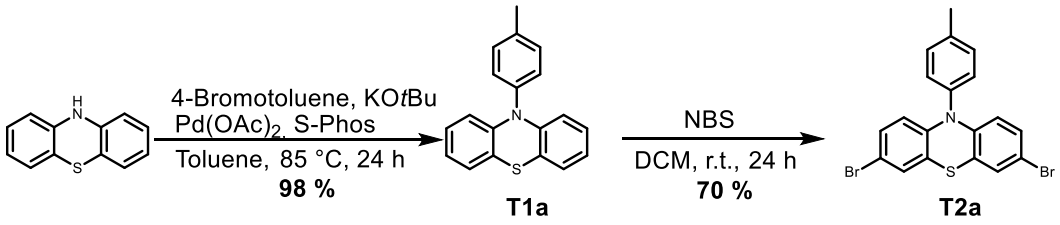


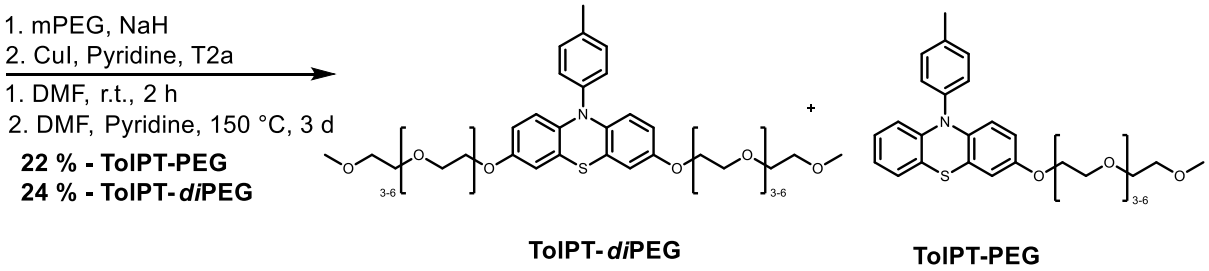
Synthesis of PEG-PT:



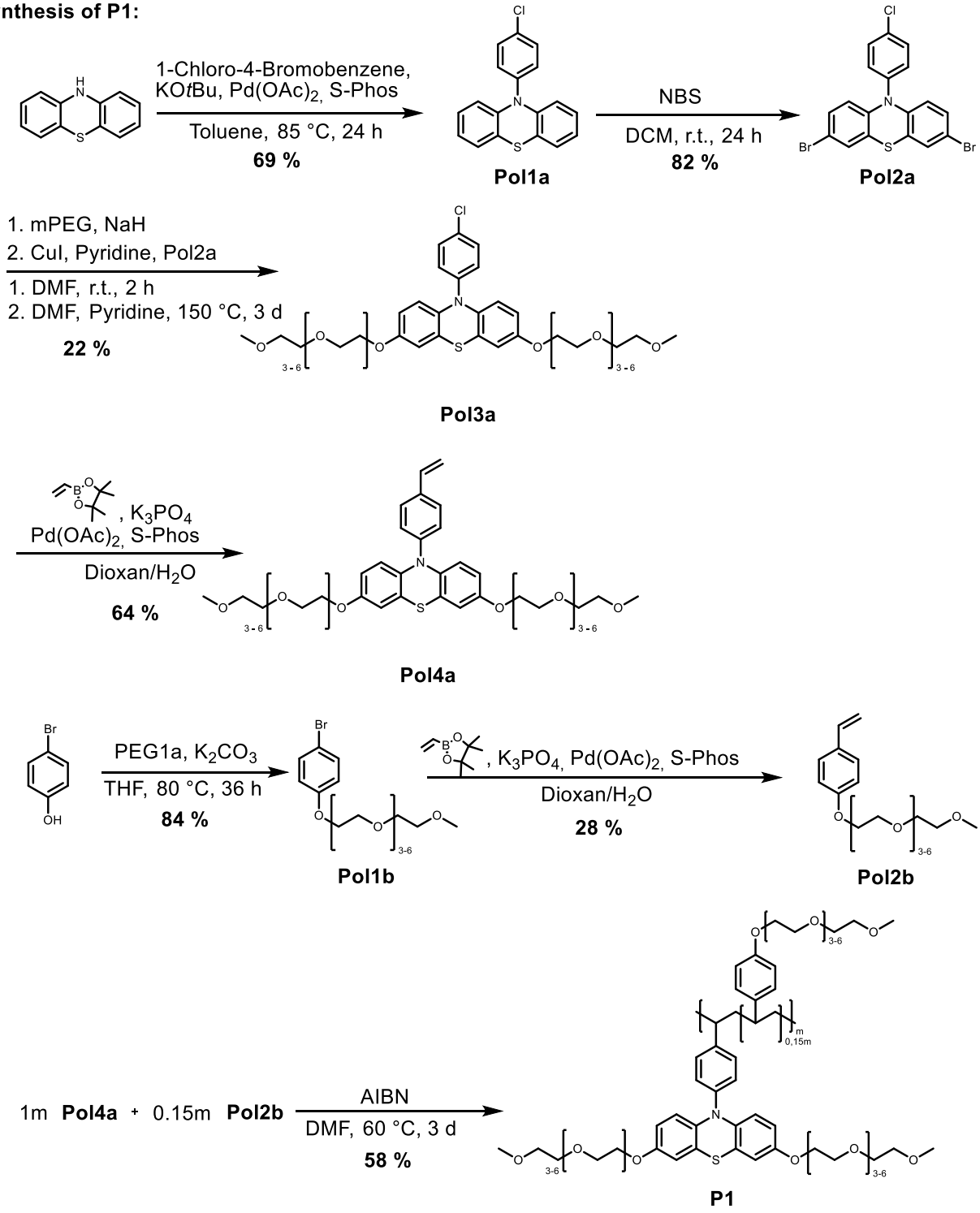


Synthesis of TolPT-PEG + TolPT-*di*PEG:





Synthesis of P1:



Synthesis of $(NH_4)_2[Mo_3S_{13}] \cdot 2\ H_2O$

$(NH_4)_2[Mo_3S_{13}] \cdot 2\ H_2O$ was synthesized according to a literature procedure.[2] The analytical data obtained fits the reported literature.

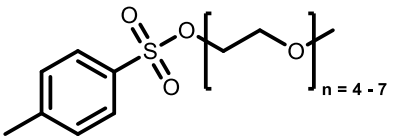
Synthesis of MPT (10-methyl-10H-phenothiazine)

MPT was prepared according to a literature procedure.[4] The analytical data obtained fits the reported literature.

Synthesis of PEG1a/PEG1b:

The synthesis of **PEG1a/PEG1b** was performed following an adapted procedure by CIBOTARU et al.[5]

PEG1a (2-methoxy poly(ethylene glycol)$_{220}$ 4-methylbenzenesulfonate)



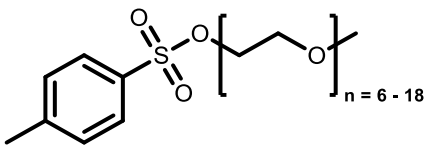
DMAP (8.54 g, 69.90 mmol, 2.05 eq.), m-PEG_{220} (7.50 g, 34.09 mmol, 1.0 eq) and pyridine (6.05 ml, 75.00 mmol, 2.2 eq.) were dissolved in CH_2Cl_2 (150 ml) and stirred at 0 °C for 1.5 h. After that a suspension of tosyl chloride (9.74 g, 51.10 mmol, 1.5 eq.) in CH_2Cl_2 (25 ml) was added during a period of 1 h. The mixture was then stirred at room temperature overnight. The organic phase was separated and washed with HCl (0.5 M, 3 × 150 ml), and the aqueous phase was extracted with CH_2Cl_2 (3 × 150 ml). The combined organic phases were dried over anh. $MgSO_4$, and volatiles were removed under reduced pressure to yield the final product as a light brown oil PEG1a (10.18 g, 27.22 mmol, 80%).

^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.78 (d, J = 8.3, 2H), 7.49 (d, J = 8.0, 2H), 4.12–4.10 (m, 2H), 3.74–3.65 (m, 2H), 3.58–3.55 (m, 2H), 3.54–3.43 (m, 14H), 3.43–3.40 (m, 2H), 3.23 (s, 3H), 2.42 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ = 145.0, 133.1, 129.9, 128.1, 72.0, 70.8, 70.7, 70.7, 70.6, 69.3, 68.8, 59.1, 21.7.

HRMS (pos. MALDI): *m/z* calcd. $C_{16}H_{26}O_7SNa$ $[M+Na]^+$ (n=4) 385.1297, found 385.1293

PEG1b (2-methoxy poly(ethylene glycol)$_{550}$ 4-methylbenzenesulfonate)



DMAP (1.56 g, 12.70 mmol, 2.05 eq.), m-PEG_{550} (3.42 g, 6.21 mmol, 1.0 eq) and pyridine (1.10 ml, 13.67 mmol, 2.2 eq.) were dissolved in CH_2Cl_2 (30 ml) and stirred at 0 °C for 1 h. After that a suspension of tosyl chloride (1.776 g, 9.3 mmol, 1.5 eq.) in CH_2Cl_2 (15 ml) was added during a period of 1 h. The mixture was then stirred at room temperature overnight. The organic phase was separated and washed with HCl (0.5 M, 2 × 150 ml), and the aqueous phase was extracted with CH_2Cl_2 (3 × 100 ml). The combined organic phases were dried over anh. $MgSO_4$, and volatiles were removed under reduced pressure to yield the final product as a light brown oil PEG1b (4.19 g, 5.95 mmol, 96%).

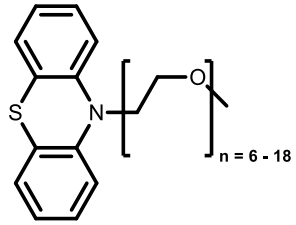
1H-NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 4.16–4.14 (m, 2H), 3.69–3.37 (m, 48H), 3.35 (s, 3H), 2.44 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ = 144.9, 133.1, 130.0, 128.1, 72.1, 70.9, 70.8, 70.7, 70.7, 69.4, 68.9, 59.2, 21.8.

HRMS (pos. MALDI): *m/z* calcd. for $C_{36}H_{66}O_{17}SNa$ $[M+Na]^+$ (n=14) 825.3918, found 825.3935.

The synthesis of **PEG-PT** was performed following an adapted procedure by CIBOTARU et al.[5]

Synthesis of PEG-PT (10-(methoxy poly(ethylene glycol)$_{550}$)-10H-phenothiazine)



In a dried Schlenk flask NaH (60% on mineral oil; 72 mg, 3 mmol, 2 eq.) was dissolved in 13 mL dry DMF, and phenothiazine (**PTH**, 250 mg, 1.25 mmol, 1 eq.) was added at 0 °C and stirred for 30 min at this temperature. To this solution, a solution of **PEG1b** (965 mg, 1.37 mmol, 1.1 eq.) in 7 mL dry DMF was added slowly over 30 min, and the reaction mixture was stirred for 16 h at r.t. After this, the DMF was removed, and the crude mixture was extracted with CH_2Cl_2 and washed with water and brine. The crude product was purified by column chromatography (CH_2Cl_2:MeOH 10:1 (v:v)) to yield the product as dark red liquid PEG-PT (660 mg, 0.9 mmol, 72%).

R_f 0.5 (CH_2Cl_2/MeOH 10:1)

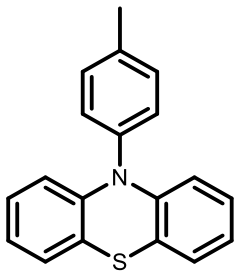
^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.19 (ddd, *J* = 8.5, 7.3, 1.6 Hz, 2H), 7.14 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.05 (dd, *J* = 8.3, 1.2 Hz, 2H), 6.94 (ddd, *J* = 7.4, 1.2 Hz, 2H), 4.05 (t, *J* = 5.8 Hz, 2H), 3.74 (t, *J* = 5.8 Hz, 2H), 3.60 – 3.45 (m, 46H), 3.23 (s, 3H).

^{13}C-NMR (101 MHz, DMSO-d_6) δ = 144.6, 127.7, 127.1, 123.3, 122.6, 115.7, 71.3, 69.9, 69.8, 69.6, 67.5, 58.1, 47.1.

HMRS (pos. MALDI) m/z calcd. for $C_{33}H_{51}NO_{10}S$ $[M]^+$ (n=10) 653.3234, found 653.3228.

The synthesis of **T1a** was performed following a adapted procedure by WESSLING et al.[6]

Synthesis of T1a (10-(p-tolyl)-10H-phenothiazine)



Phenothiazine (**PTH**, 8.00 g, 40.10 mmol, 1.0 eq.), 1-bromo-4-methylbenzene (8.24 g, 48.20 mmol, 1.2 eq.), KO^{t}Bu (5.41 g, 48.20 mmol,1.2 eq.), $Pd(OAc)_2$ (90.0 mg, 401 µmol, 1.0 mol-%) and SPhos (165 mg, 401 µmol, 1.0 mol-%) were dissolved in anh. toluene (150 ml) in a screwcap Schlenk tube and heated at 85 °C for 24 h. The crude mixture was filtered through a

short pad of SiO_2 and washed with toluene (200 ml). The solvent was removed under reduced pressure, and the product was recrystallized from ^{i}PrOH (60 ml) to yield the final compound as an off-white solid T1a (11.31 g, 39.10 mmol, 98%).

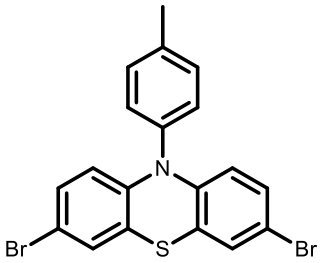
^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.48–7.46 (d, 2H), 7.31–7.26 (d, 2H), 7.08 (dd, *J* = 7.5, 1.6 Hz, 2H), 6.93–6.81 (m, 4H), 6.15 (dd, *J* = 8.2, 1.3 Hz, 2H), 2.42 (s, 3H).

^{13}C-NMR (101 MHz, DMSO-d_6) δ 143.8, 138.1, 137.5, 131.6, 130.4, 127.2, 126.6, 122.5, 118.9, 115.7, 20.8.

HRMS (pos. MALDI): *m/z* calcd. for $C_{19}H_{15}NS$ 289.0925 $[M]^+$, found 289.0920.

The synthesis of **T2a** was performed following a adapted procedure by WESSLING et al.[6]

Synthesis of T2a (3,7-dibromo-10-(*p*-tolyl)-10H-phenothiazine)



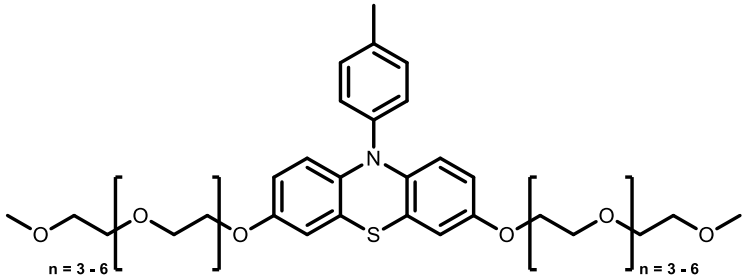
The reaction was carried under the exclusion of light by wrapping the flask in aluminium foil. 10-(p-tolyl)-10H-phenothiazine (**T1a**, 5.80 g, 20.07 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (150 ml) and purged with argon. Afterwards NBS (7.46 g, 42.00 mmol, 2.1 eq.) was added in three portions over a period of 0.5 h. The reaction mixture was stirred at rt for 24 h. Afterwards the reaction mixture was quenched with sat. aq. $Na_2S_2O_3$ (150 ml) and washed with water (150 ml) and brine (150 ml). The aqueous phase was extracted with CH_2Cl_2 (3 × 150 ml). The organic phase was dried over anh. $MgSO_4$ and volatiles were removed under reduced pressure. The crude mixture was dissolved in CH_2Cl_2 and purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 10:0.2) to yield the final compound as an off-white solid T2a (6.23 g, 14.03 mmol, 70%).

^{1}H-NMR (400 MHz, DMSO-d_6) 7.48 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 2.3 Hz, 2H), 7.08 (dd, *J* = 8.8, 2.4 Hz, 2H), 5.99 (d, *J* = 8.8 Hz, 2H), 2.42 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 143.4, 139.0, 137.5, 131.9, 130.6, 129.8, 128.9, 121.2, 117.1, 114.7, 21.4.

HRMS (pos. MALDI): *m/z* calcd. for $C_{19}H_{13}{}^{(79)}Br_2NS$ 444.9135 $[M]^+$, found 444.9132.

Synthesis of TolPT-PEG and TolPT-*di*PEG (3,7-(di-m-PEG$_{220}$)-10-(*p*-tolyl)-10H-phenothiazine)



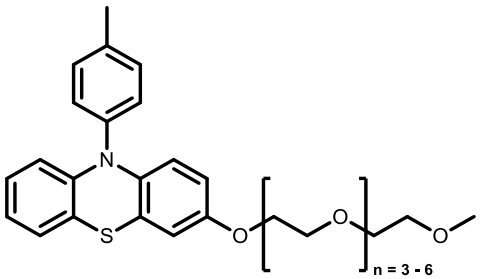
m-PEG$_{220}$ (1.38 g, 6.27 mmol, 4.1 eq.) and NaH (60 wt.% in mineral oil, 150 mg, 6.27 mmol, 4.1 eq.) were dissolved in anhydrous and degassed DMF (5 ml) in a screwcap Schlenk tube. The mixture was stirred at room temperature for 2 h. Afterwards CuI (1.31 g, 6.88 mmol, 4.5 eq.), **T2a** (608 mg, 1.52 mmol, 1.0 eq.) and anhydrous degassed pyridine (2.5 ml) were added under an argon flow. The mixture was stirred at 150 °C for 3 d. The crude mixture was diluted with ethyl acetate and washed with HCl (3 × 100 ml) as well as a saturated aq. NH_4OH-solution (25 wt%) (2 × 150 ml). The organic phase was dried over anh. $MgSO_4$ and volatiles were removed under reduced pressure. The organic phase was filtered over a short plug of silica using CH_2Cl_2 as the eluent. The product was then purified by a recycling GPC-System with CH_2Cl_2 as the eluent to yield TolPT-*di*PEG as a dark oil (256 mg, 350 µmol, 24%).

^{1}H-NMR (400 MHz, CD_2Cl_2) δ = 7.33 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 2.8 Hz, 2H), 6.51 (d, *J* = 6.2 Hz, 2H), 6.34 (d, *J* = 9.0 Hz, 2H), 4.02 (t, *J* = 4.7 Hz, 4H), 3.77 (m, 4H), 3.65–3.56 (m, 25H), 3.50 (m, 4H), 3.33 (s, 6H), 2.41 (s, 3H).

^{13}C-NMR (101 MHz, CD_2Cl_2) δ 154.9, 140.4, 138.7, 137.1, 131.4, 128.6, 123.5, 118.8, 113.4, 72.3, 71.1, 70.9, 70.9, 70.9, 70.8, 70.0, 68.4, 59.0, 21.2.

HRMS (pos. MALDI): *m/z* calcd. for $C_{39}H_{55}NO_{11}S$ 745.3496 $[M]^+$ (n_1=3; n_2=4), found 745.3490.

(3-(m-PEG$_{220}$)-10-(*p*-tolyl)-10H-phenothiazine)



In addition, a second compound featuring the mono-PEG substituted building block was isolated by using the recycling GPC-system TolPT-PEG (180 mg, 333 µmol, 22%).

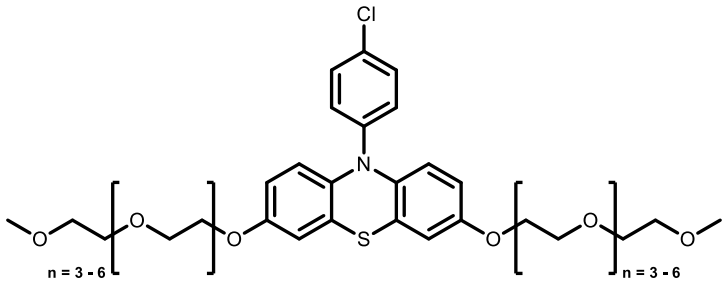
^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.44 (dd, *J* = 8.1, 6.2 Hz, 2H), 7.32–7.18 (m, 2H), 7.14–7.01 (m, 1H), 6.92 (ddd, *J* = 8.5, 7.3 Hz, 1.7 Hz, 1H), 6.82 (ddd, *J* = 7.4, 1.3 Hz, 1H), 6.72 (d, *J* = 2.8 Hz, 1H), 6.55 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.19 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.11 (m, 2H), 3.98 (m, 2H), 3.73–3.61 (m, 2H), 3.58–3.46 (m, 12H), 3.40 (m, 2H), 3.22 (s, 3H), 2.41 (s, 3H).

^{13}C-NMR (101 MHz, DMSO-d_6) δ 154.2, 144.1, 138.2, 137.3, 131.4, 130.0, 129.8, 127.2, 126.6, 122.2, 119.8, 119.1, 117.1, 116.0, 113.2, 112.6, 71.3, 69.9, 69.8, 69.8, 69.6, 68.9, 68.9, 67.5, 58.0, 20.7, 20.7.

HRMS (pos. MALDI): *m/z* calcd. for $C_{30}H_{37}NO_6S$ 539.2342 $[M]^+$ (n=4), found 539.2342.

The synthesis of **Pol1a** and **Pol2a** was performed following a procedure by WESSLING et al.[6] The analytical data obtained fits the reported literature.

Synthesis of Pol3a (3,7-(di-m-PEG$_{220}$)-10-(4-chlorophenyl)-10H-phenothiazine)



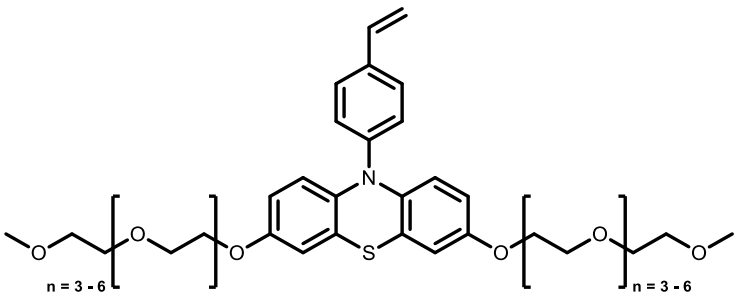
m-PEG$_{220}$ (2.97 g, 12.00 mmol, 4.1 eq.) and NaH (60 wt.% in mineral oil, 288 mg, 12.0 mmol, 4.1 eq.) were dissolved in anhydrous and degassed DMF (9 ml) in a screwcap Schlenk tube. The mixture was then stirred at room temperature for 2 h. Afterwards CuI (2.57 g, 13.50 mmol, 4.5 eq.), **P2a** (1.39 g, 3.00 mmol, 1.0 eq.) and anhydrous degassed pyridine (3 ml) were added under a flow of argon. The mixture was then stirred at 150 °C for 3 days. The crude mixture was diluted with ethyl acetate and washed with HCl (3 × 100 ml) as well as an aq. NH_4OH-solution (25 wt%) (2 × 150 ml). The organic phase was dried over anh. $MgSO_4$ and volatiles were removed under reduced pressure. Afterwards the mixture was filtered over a short plug of silica gel using CH_2Cl_2 as the eluent. The product was purified by a recycling GPC-System with CH_2Cl_2 as the eluent to yield the final product as a dark oil Pol3a (496 mg, 660 µmol, 22%).

^{1}H-NMR (600 MHz, DMSO-d_6) δ = 7.38–7.34 (m, 2H), 7.01–6.98 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.83 (dd, *J* = 8.8, 2.8 Hz, 2H), 4.08–4.07 (m, 4H), 3.72–3.71 (m, 4H), 3.58–3.56 (m, 4H), 3.54–3.48 (m, 20H), 3.41–3.40 (m, 4H), 3.22 (s, 6H).

^{13}C-NMR (151 MHz, DMSO-d_6) δ 155.5, 144.0, 135.6, 129.6, 129.3, 127.3, 124.0, 122.5, 113.9, 113.3, 71.3, 69.9, 69.8, 69.8, 69.6, 68.8, 67.65, 58.0.

HRMS (pos. MALDI): *m/z* calcd. for $C_{36}H_{48}ClNO_{10}S$ (n=3) $[M]^+$ 721.2687, found 721.2679.

Synthesis of Pol4a (3,7-(di-m-PEG$_{220}$)-10-(p-styryl)-10H-phenothiazine)

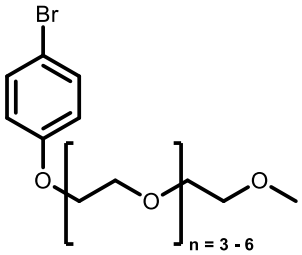


Pol3a (709 mg, 0.95 mmol, 1 eq.), 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (1.47 g, 9.52 mmol, 10 eq.), K_3PO_4 (1.62 g, 7.61 mmol, 8 eq.), $Pd(OAc)_2$ (43 mg, 0.19 mmol, 0.2 eq.) and SPhos (156 mg, 0.38 mmol, 0.4 eq.) were dissolved in degassed dioxane/water (9.6/0.9 ml) in an oven dried Schlenk tube. The mixture was then stirred at 90 °C for 24 h. Afterwards the crude reaction mixture was filtered over a short plug of celite (3 cm) with CH_2Cl_2 (300 ml) as the eluent, and the solvent was removed under reduced pressure. The mixture was dissolved in ethyl acetate (50 ml), and the organic phase was washed with water (3 × 50 ml). The organic phase was dried over anh. $MgSO_4$, and the solvent was removed under reduced pressure. The mixture was dissolved in CH_2Cl_2 (20 ml) and filtered through a short plug of silica gel (3 cm) with CH_2Cl_2 (500 ml) and then CH_2Cl_2/MeOH (5:1, 250 ml) as the eluent. The product was then purified by a recycling GPC-system with CH_2Cl_2 as the eluent to yield the final product as a dark oil Pol4a (446 mg, 604 µmol, 64%).

^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.49–7.47 (m, 2H), 7.05–7.02 (m, 2H), 6.93 (d, *J* = 1.6 Hz, 2H), 6.76 (d, *J* = 2.3 Hz, 4H), 6.76–6.67 (m, 1H), 5.77 (dd, *J* = 17.7, 1.0 Hz, 1H), 5.22 (dd, *J* = 10.9, 1.0 Hz, 1H), 4.08–4.04 (m, 4H), 3.72 (m, 4H), 3.58–3.51 (m, 4H), 3.49-3.47 (m, 22H), 3.41-3.39 (m, 4H), 3.22 (s, 6H).

^{13}C-NMR (101 MHz, DMSO-d_6) δ 155.1, 143.9, 136.2, 135.9, 133.2, 129.6, 127.7, 127.6, 122.6, 122.6, 113.7, 113.2, 71.3, 69.9, 69.8, 69.8, 69.8, 69.6, 68.9, 67.6, 58.0.

Synthesis of Pol1b (1-m-PEG$_{220}$-4-bromobenzene)



4-Bromophenol (2.14 g, 12.30 mmol, 1.1 eq.), **PEG1b** (4.19 g, 11.21 mmol, 1 eq.), and K_2CO_3 (5.11 g, 37.00 mmol, 3.3 eq.) were dissolved in THF (110 ml) and stirred at 80 °C for 36 h. The solvent was removed under reduced pressure, and the mixture was purified by column chromatography (SiO_2; CH_2Cl_2, then CH_2Cl_2/MeOH 9:1) to yield the final product as a light-brown oil Pol1b (3.54 g, 9.4 mmol, 84%).

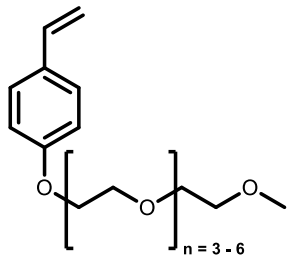
R_f 0.7 (CH_2Cl_2/MeOH 10 :1)

^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.45–7.41 (m, 2H), 6.94–6.90 (m, 2H), 4.08–4.06 (m, 2H), 3.74–3.61 (m, 2H), 3.59–3.40 (m, 17H), 3.23 (s, 3H).

^{13}C-NMR (101 MHz, DMSO-d_6) δ 157.8, 132.1, 116.8, 111.94, 71.3, 70.5, 69.9, 69.8, 69.8, 69.77, 69.7, 69.6, 68.8, 67.4, 58.0, 43.6.

HRMS (pos. MALDI): *m/z* calcd. for $C_{15}H_{23}BrO_5Na$ (n = 3) $[M+Na]^+$ 385.0729, found 385.0624.

Synthesis of Pol2b: (1-m-PEG$_{220}$-4-vinylbenzene)



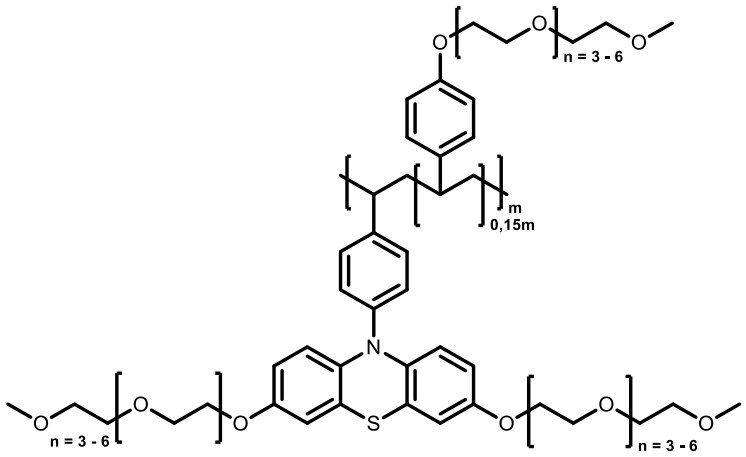
Pol1b (938 mg, 2.50 mmol, 1 eq.), 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (1.54 g, 10.00 mmol, 4 eq.), K_3PO_4 (4.24 g, 19.81 mmol, 8 eq.), $Pd(OAc)_2$ (112 mg, 0.50 mmol, 0.2 eq.) and SPhos (411 mg, 1.00 mmol, 0.4 eq.) were dissolved in degassed dioxane/water (9.6/0.9 ml) in an oven dired Schlenk tube. The mixture was then stirred at 90 °C for 24 h. Afterwards the crude reaction mixture was filtered over a short plug of celite (3 cm) with CH_2Cl_2 (300 ml) as the eluent, and the solvent was removed under reduced pressure. The mixture was then dissolved in ethyl acetate (50 ml), and the organic phase was washed with water (3 × 50 ml). The organic phase was dried over anh. $MgSO_4$, and the solvent was removed under reduced pressure. The mixture was then dissolved in CH_2Cl_2 (20 ml) and filtered through a short plug of silica gel (3 cm) with CH_2Cl_2 (500 ml) and then CH_2Cl_2/MeOH (5:1, 250 ml) as the eluent. The product was purified by a recycling GPC-system with CH_2Cl_2 as the eluent to yield the final product as a light brown oil Pol2b (229 mg, 708 µmol, 28%).

^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.41–7.37 (m, 2H), 6.93–6.89 (m, 2H), 6.70–6.62 (dd, *J* = 11.0, 17.7 Hz, 1H), 5.69 (dd, *J* = 17.7, 1.1 Hz, 1H), 5.12 (dd, *J* = 10.9, 1.1 Hz, 1H), 4.10–4.07 (m, 2H), 3.75–3.72 (m, 2H), 3.59–3.49 (m, 12H), 3.43 (m, 2H), 3.23 (s, 3H).

^{13}C-NMR (101 MHz, DMSO-d_6) δ 158.3, 136.1, 129.9, 127.4, 114.5, 111.7, 71.3, 69.9, 69.8, 69.8, 69.8, 69.6, 68.9, 67.1, 58.0.

HRMS (pos. MALDI): *m/z* calcd. for $C_{17}H_{26}O_5$ (n = 3) $[M]^+$ 310.1780, found 310.1777.

Synthesis of P1 (Poly(N-styryl-3,7-di-m-PEG$_{220}$-phenothiazine-stat-1-m-PEG$_{220}$-4-vinylbenzene (15% Comonomer))



Pol4a (200 mg, 271 µmol, 1 eq.), **Pol2b** (13 mg, 41 µmol, 0.15 eq.) and a solution of AIBN in dry and degassed DMF (0.31 ml, 0.05 M, 16 µmol, 0.05 eq.) were placed in a screwcap vial under a flow of argon and dissolved in dry and degassed DMF (1.7 ml). The screwcap vial was then placed in a preheated metal block and stirred at 60 °C for 3 days. After completion of the reaction, the residue was washed with *n*-hexane (2 × 15 ml) and Et_2O (2 × 15 ml; 2 × 5 ml). Removing volatiles under reduced pressure yielded the desired product as dark-brown wax P1 (120 mg, 157 µmol, 58%).

^{1}**H-NMR** (400 MHz, CD_2Cl_2) δ = 7.21–6.00 (m, 11H), 4.11–3.38 (m, 36H), 3.35–3.22 (m, 7H).

10 NMR spectra

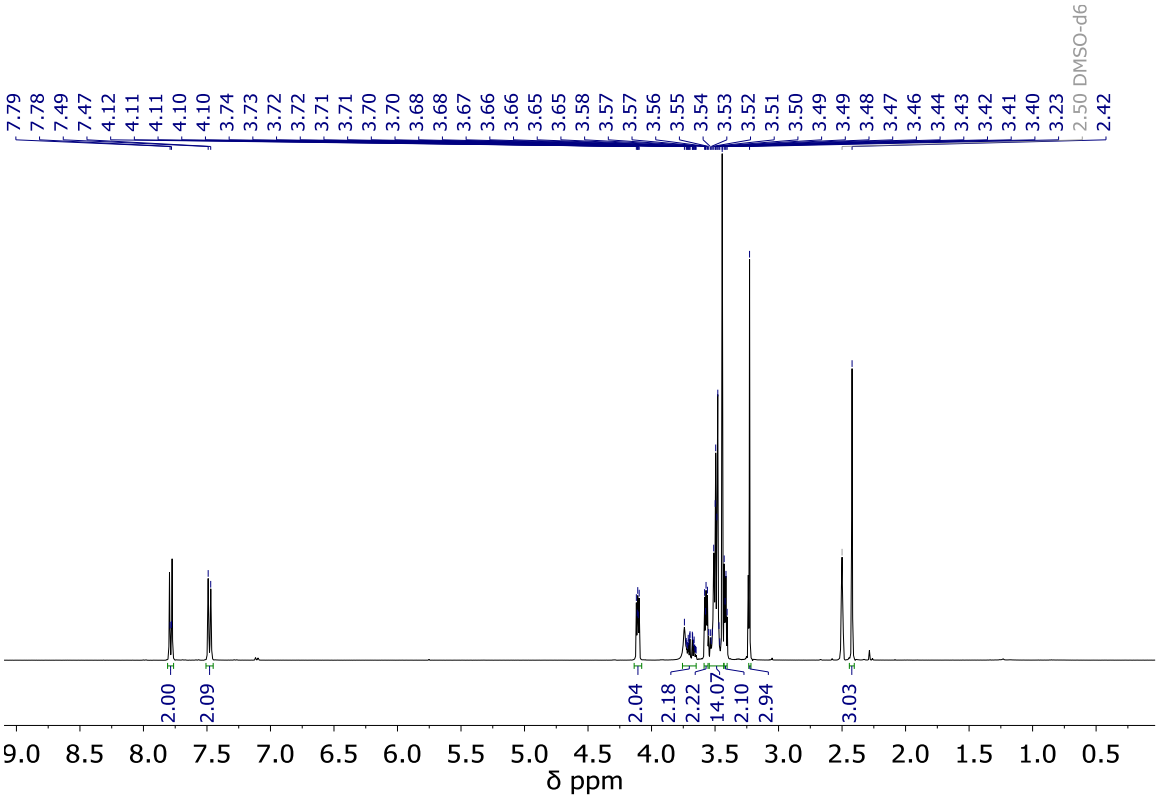


*Figure S13: [1]H-NMR spectrum of **PEG1a** in DMSO-d_6 (400 MHz).*

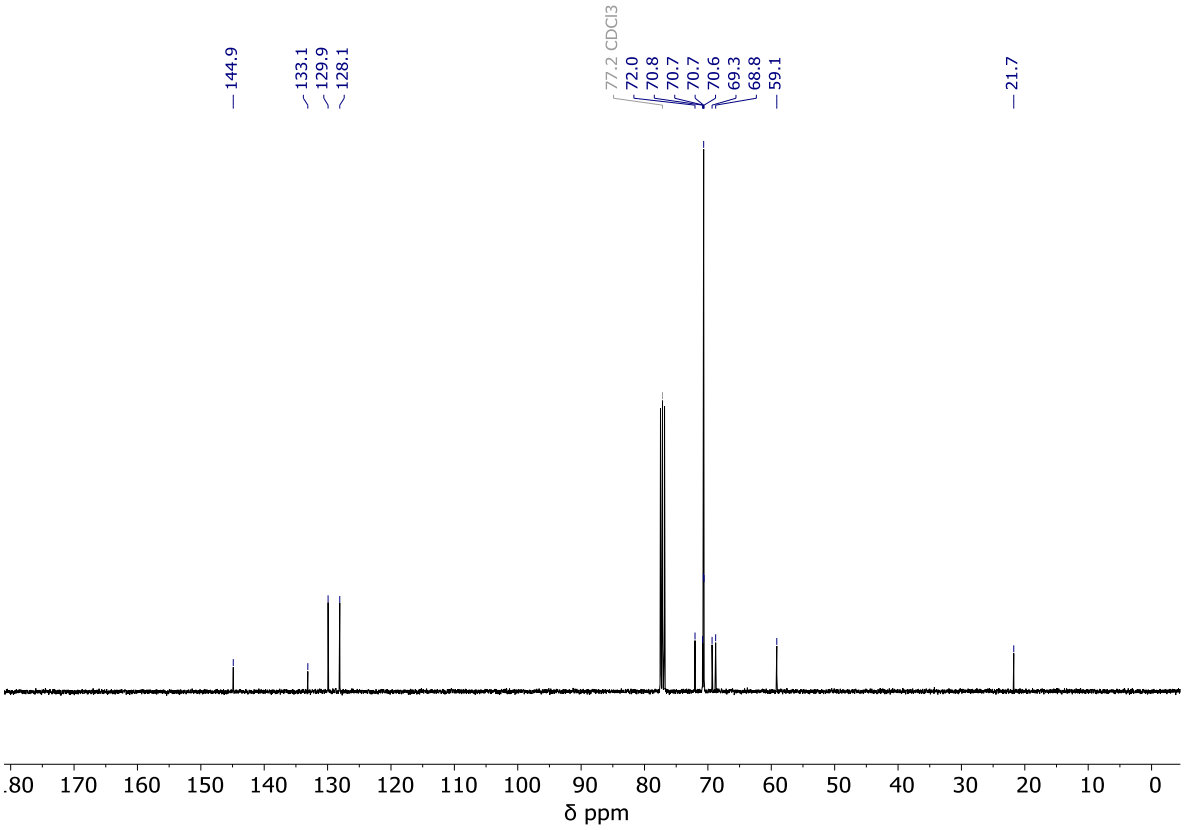


*Figure S14: [13]C-NMR spectrum of **PEG1a** in $CDCl_3$ (101 MHz).*

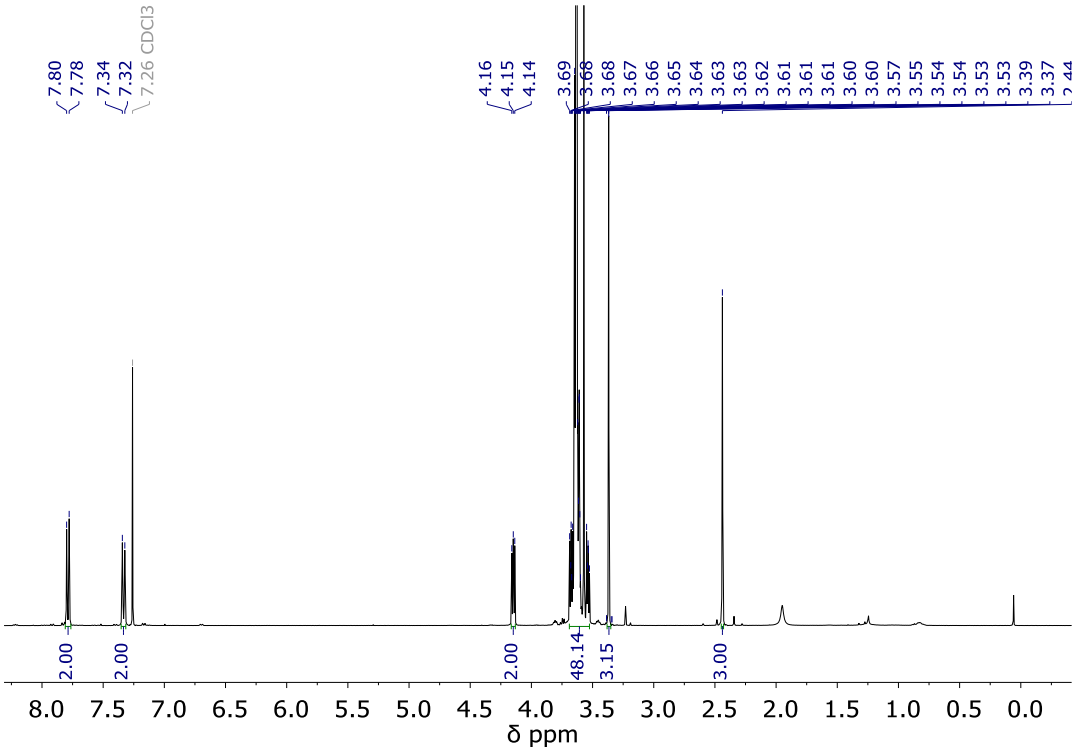


*Figure S15: ^{1}H-NMR spectrum of **PEG1b** in $CDCl_3$ (400 MHz)*

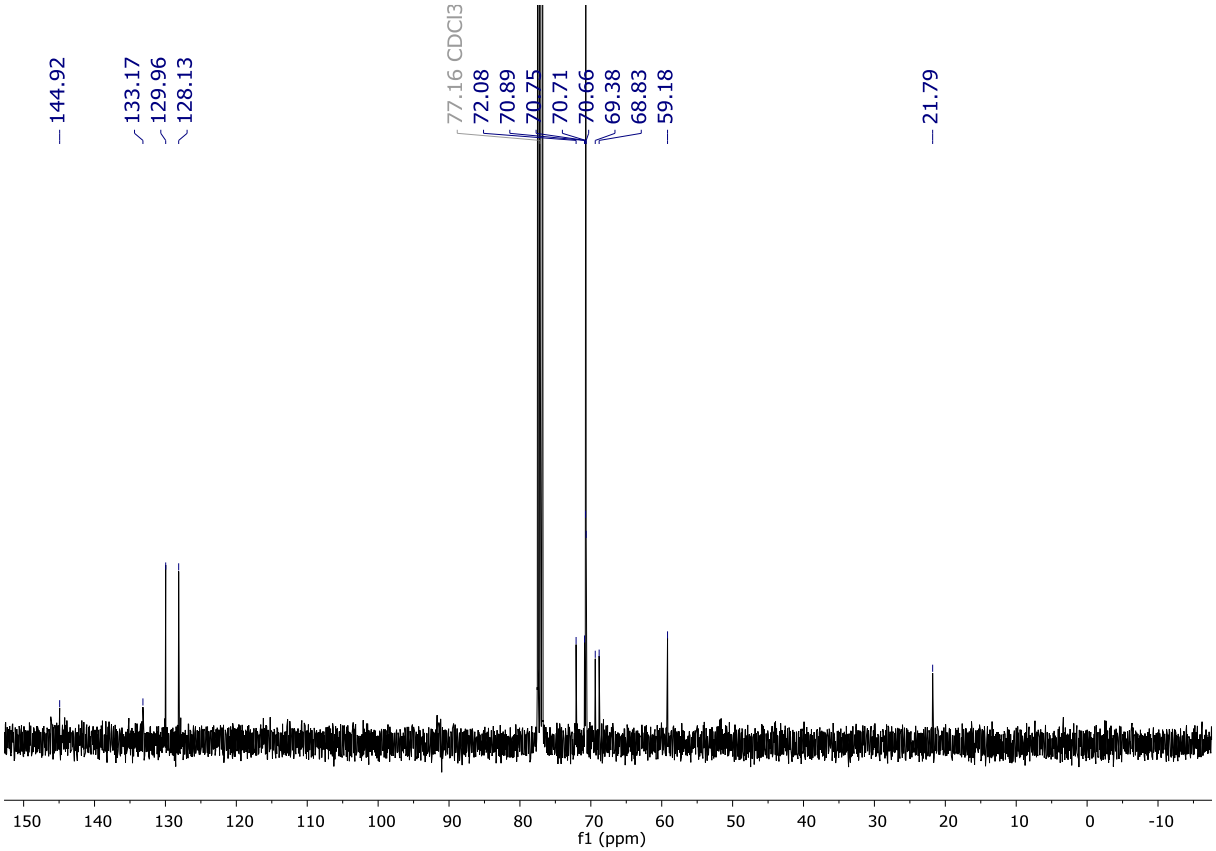


*Figure S16: ^{13}C-NMR spectrum of **PEG1b** in $CDCl_3$ (101 MHz).*

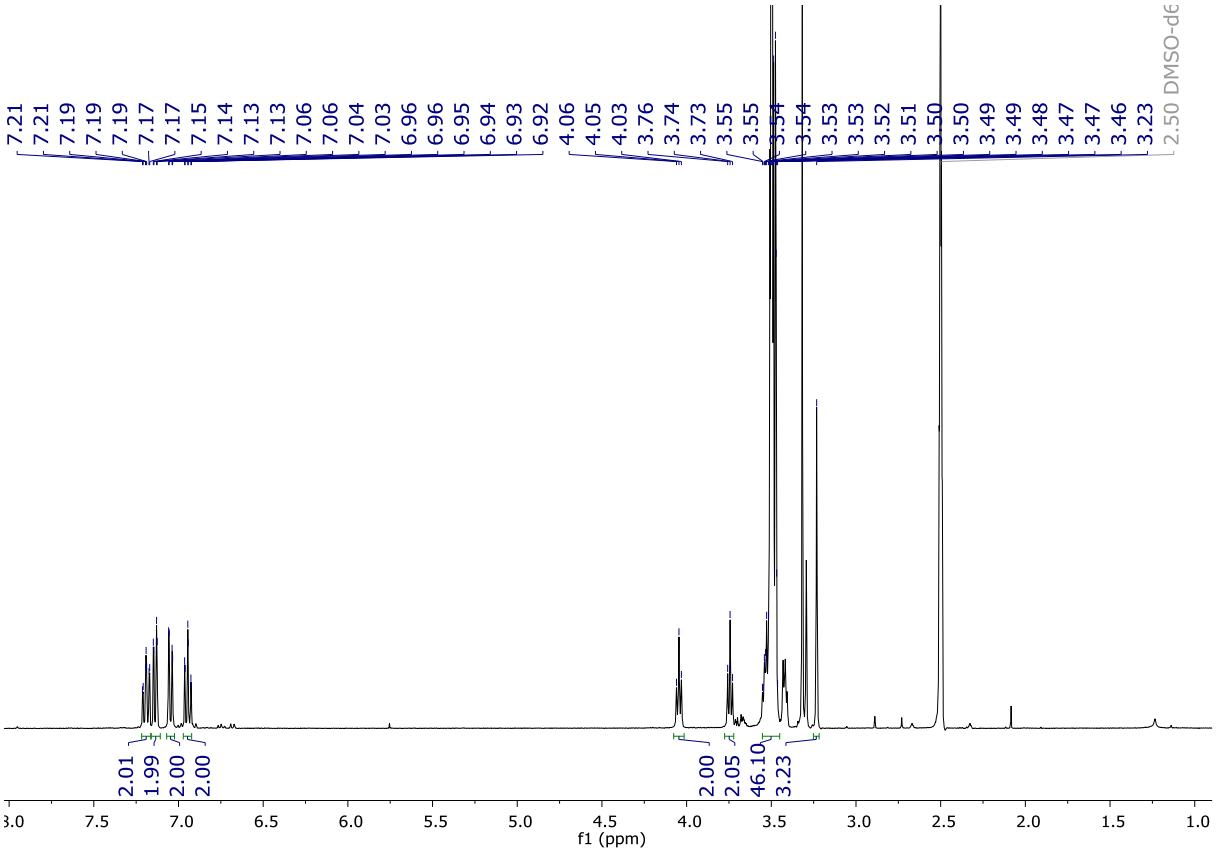


*Figure S17: [1]H-NMR spectrum of **PEG-PT** in DMSO-d_6 (400 MHz).*

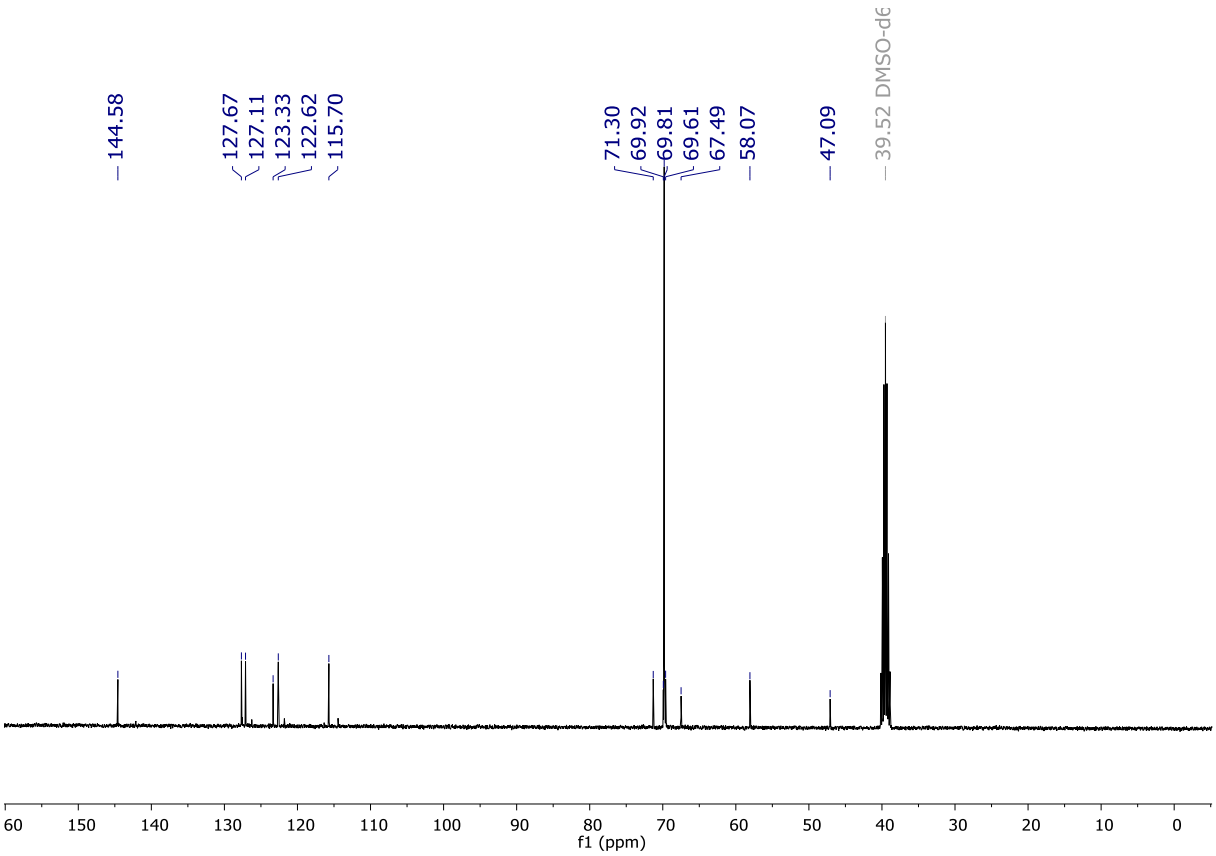


*Figure S18: [13]C-NMR spectrum of **PEG-PT** in DMSO-d_6 (101 MHz).*

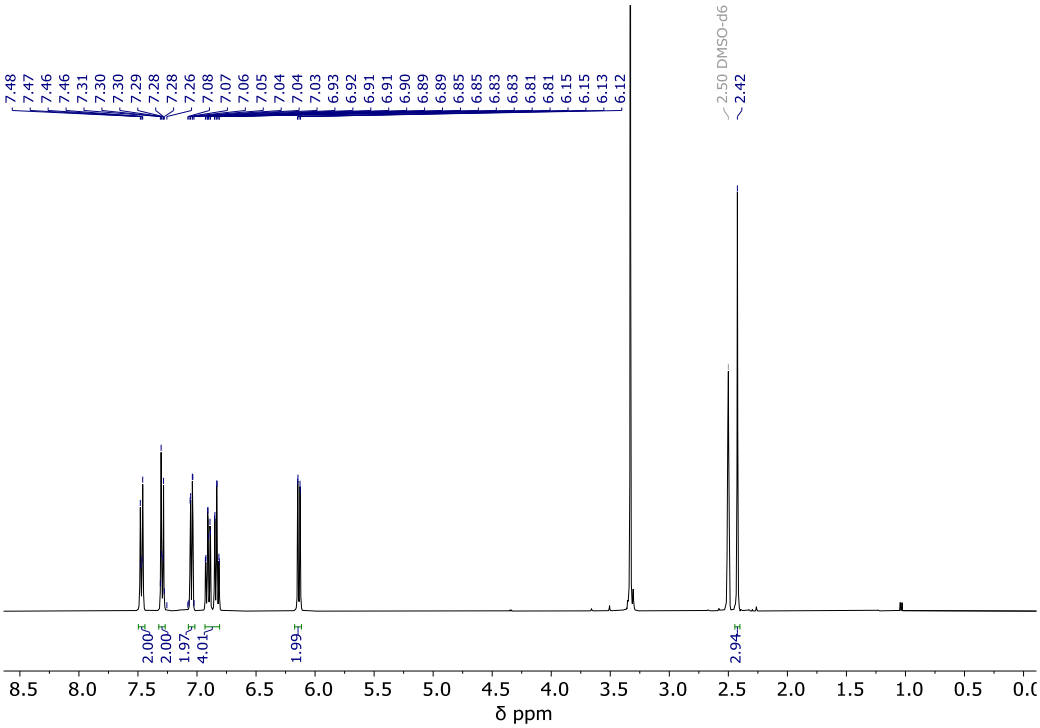


*Figure S19: [1]H-NMR spectrum of **T1a** in DMSO-d_6 (400 MHz).*

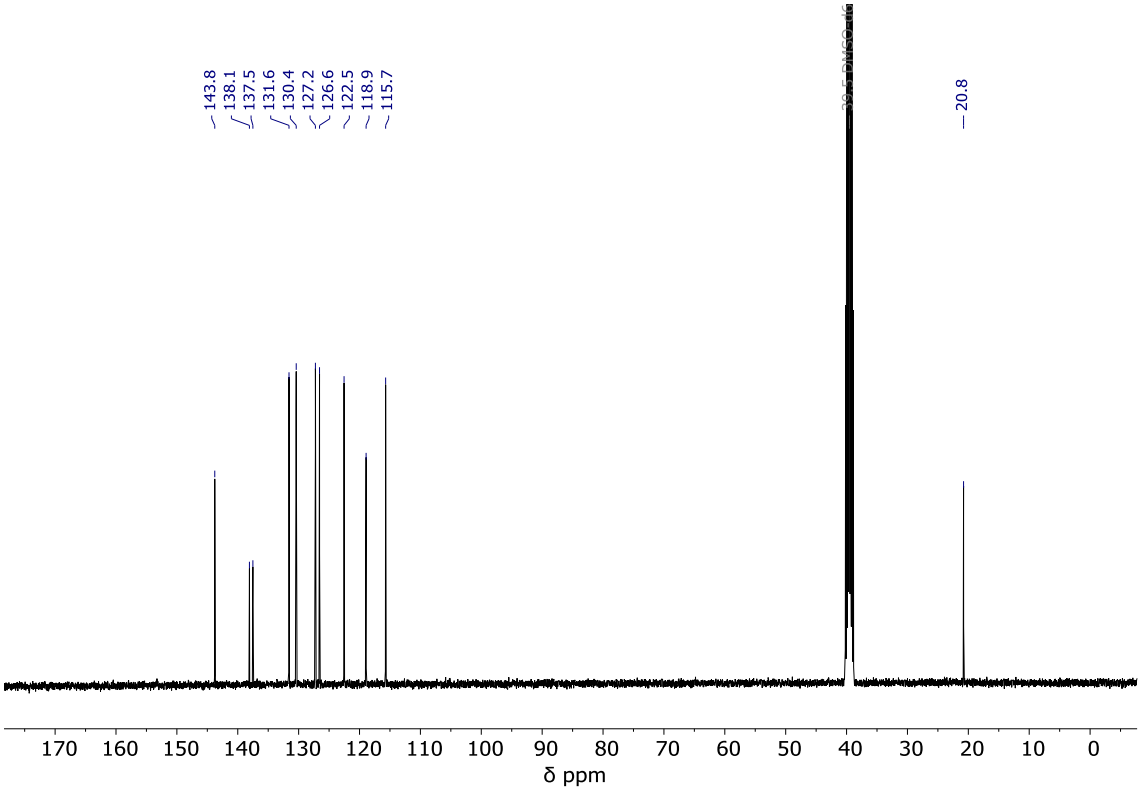


*Figure S20: [13]C-NMR spectrum of **T1a** in DMSO-d_6 (101 MHz).*

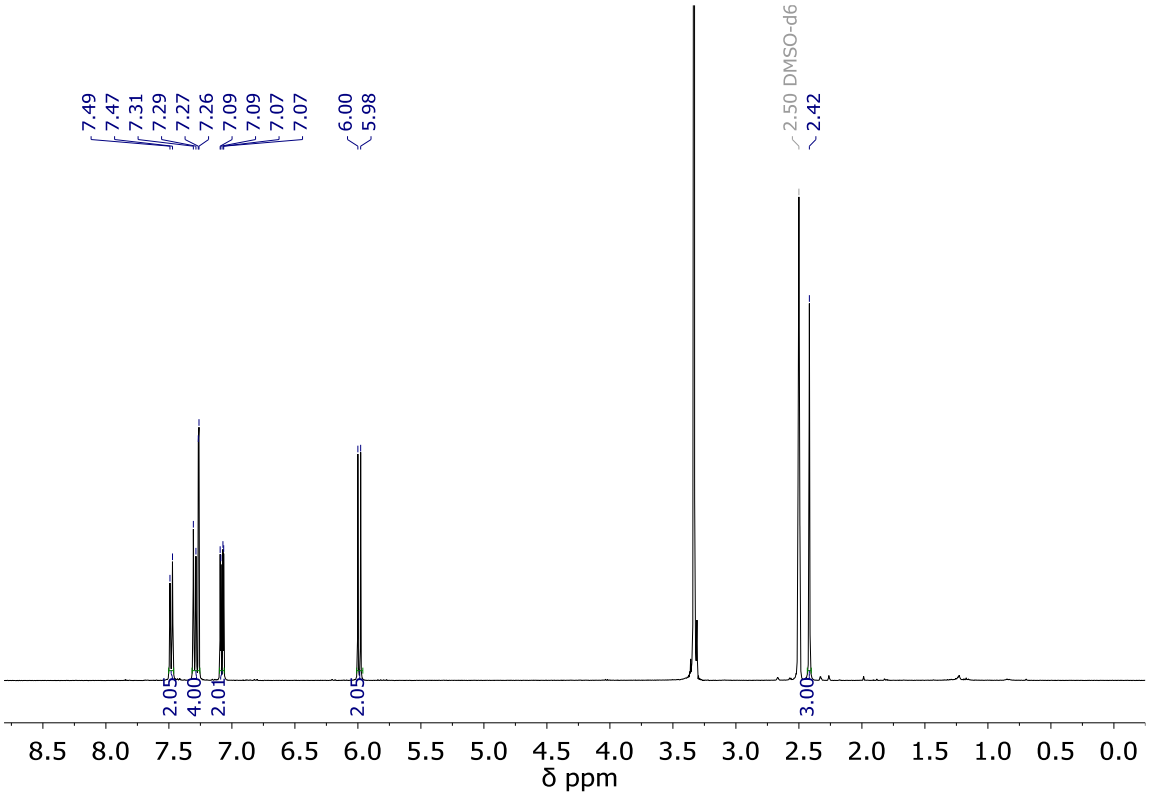


*Figure S21: ^{1}H-NMR spectrum of **T2a** in DMSO-d6 (400 MHz).*

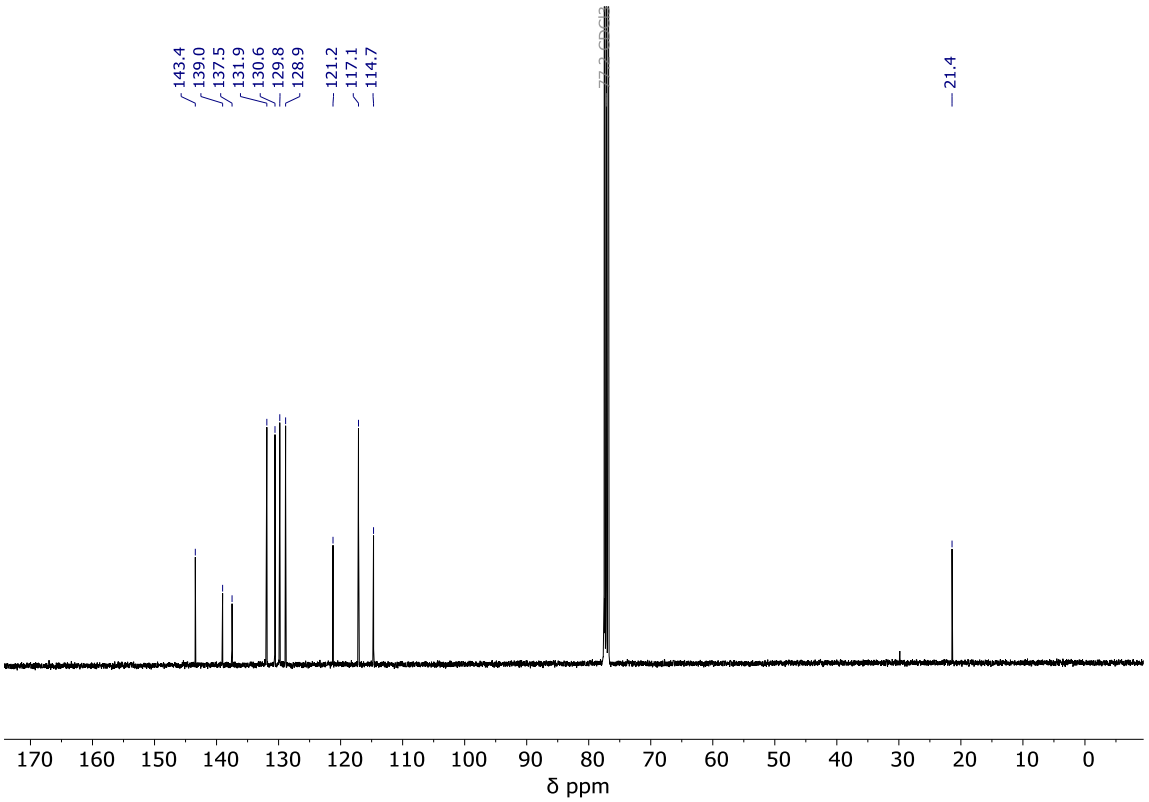


*Figure S22: ^{13}C-NMR spectrum of **T2a** in $CDCl_3$ (101 MHz).*

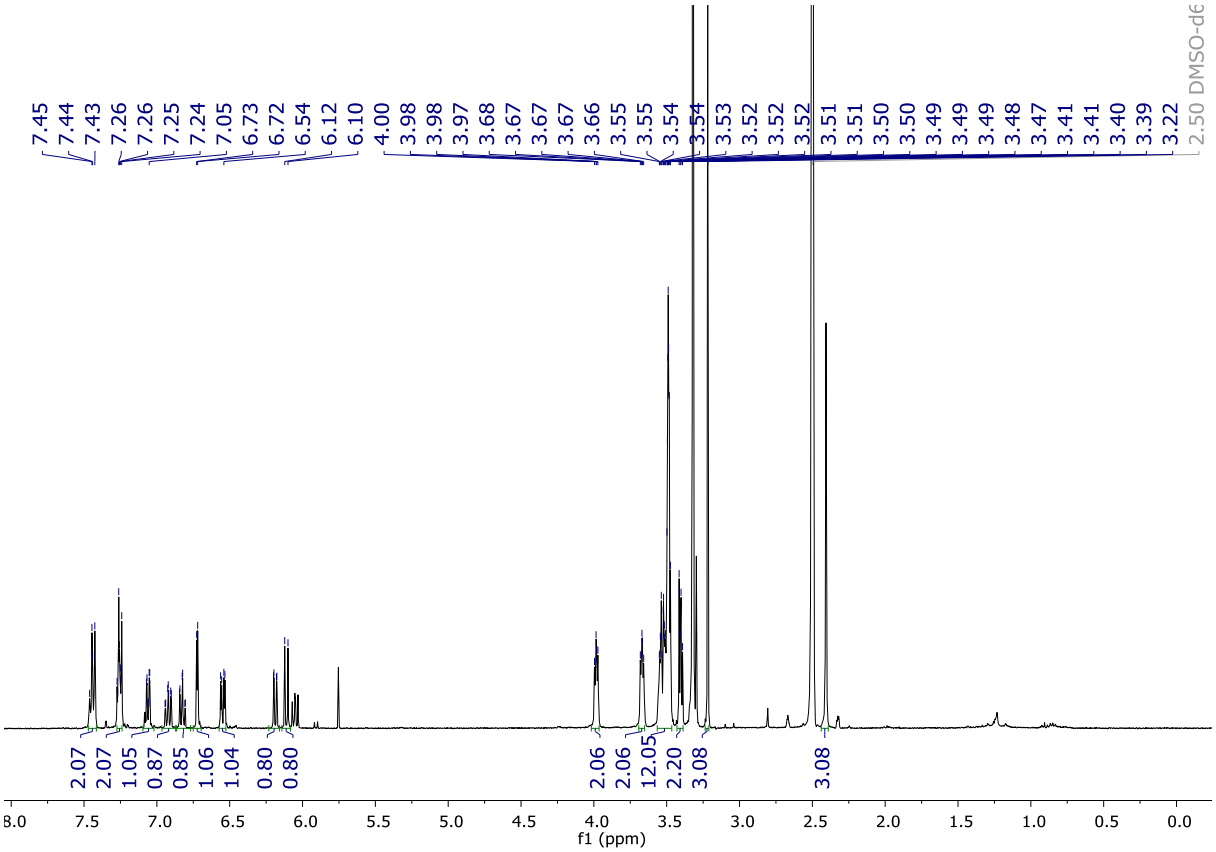


*Figure S23: [1]H-NMR spectrum of **TolPT-PEG** in DMSO-d_6 (400 MHz).*

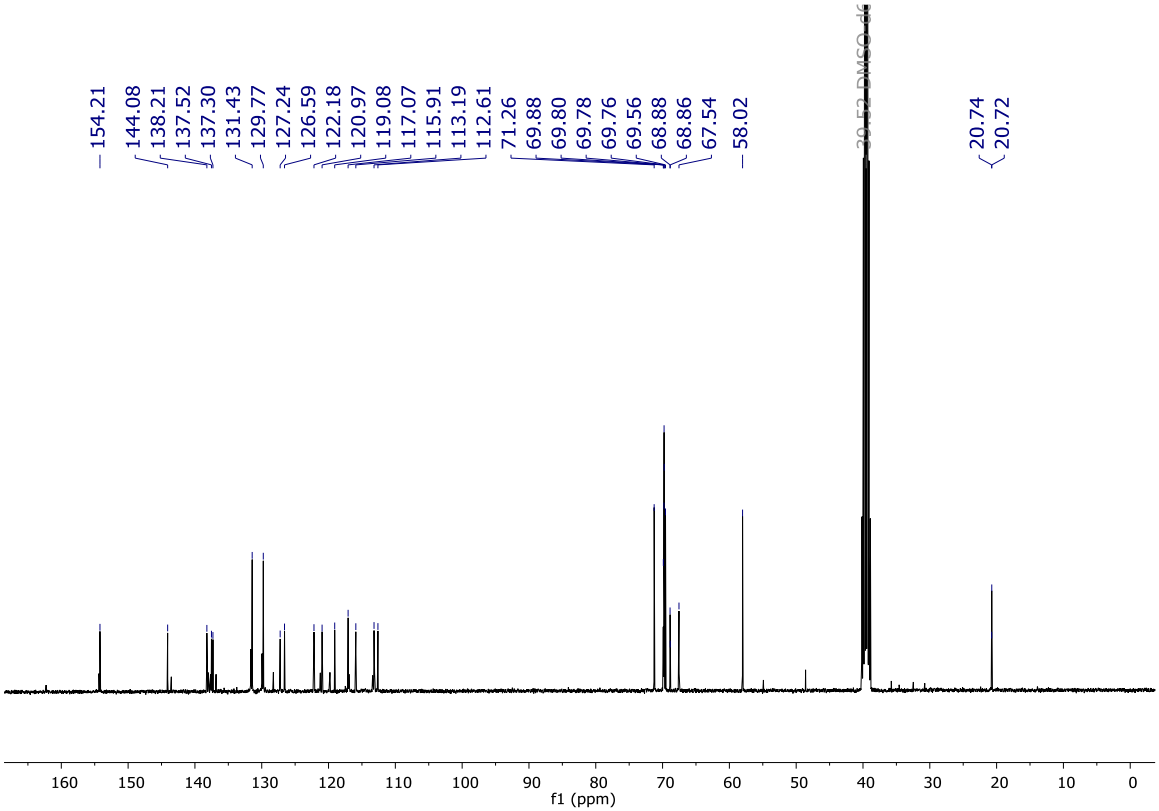


*Figure S24: [13]C-NMR spectrum of **TolPT-PEG** in DMSO-d_6 (101 MHz).*

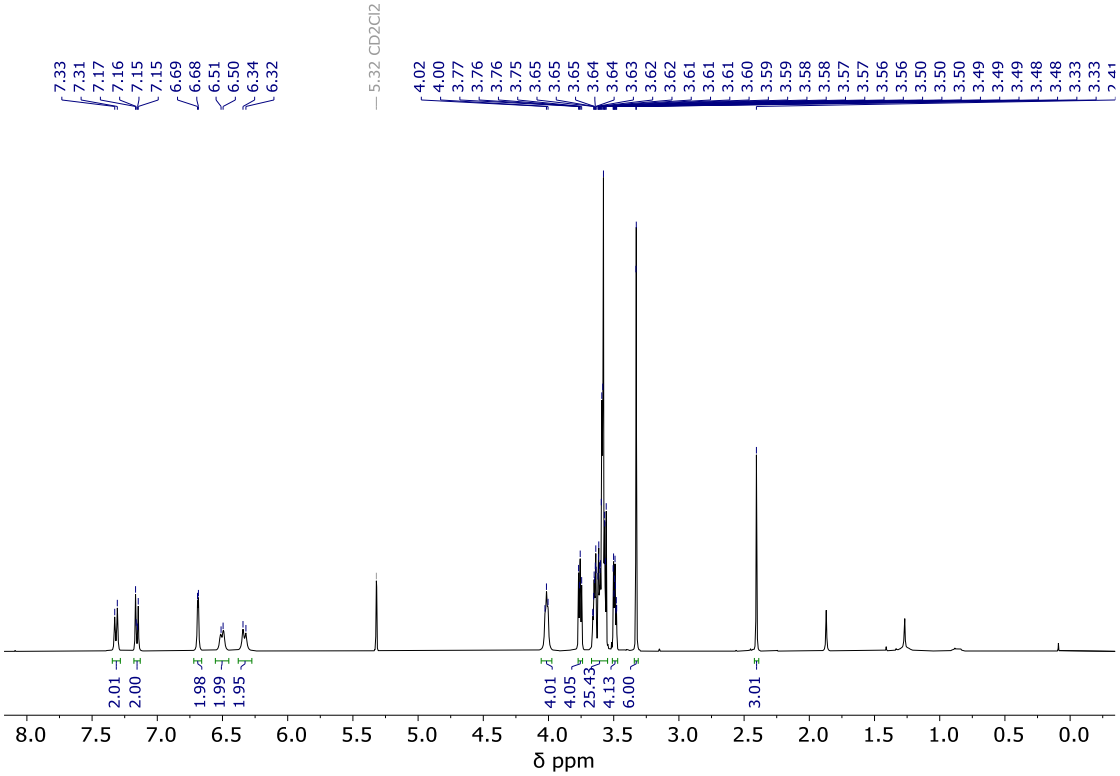


*Figure S25: [1]H-NMR spectrum of **TolPT-diPEG** in CD_2Cl_2 (400 MHz).*

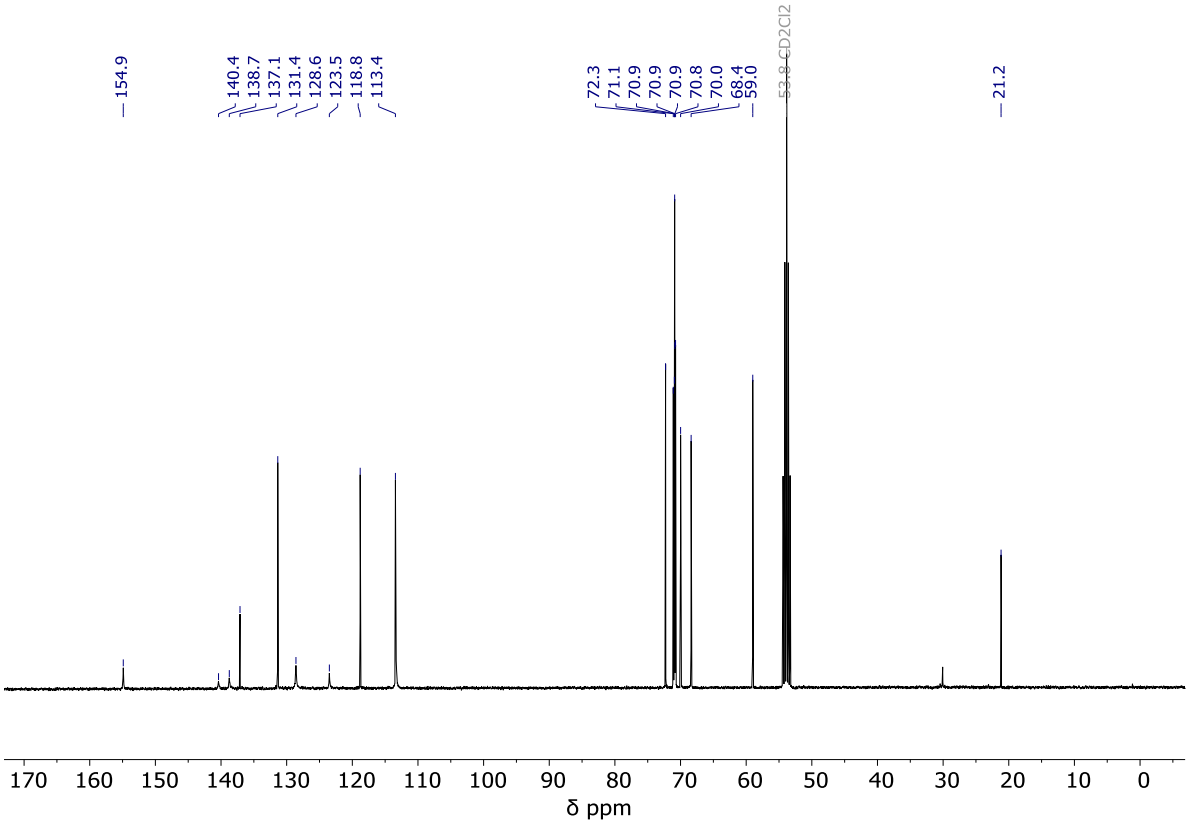


*Figure S26: [13]C-NMR spectrum of **TolPT-diPEG** in CD_2Cl_2 (101 MHz).*

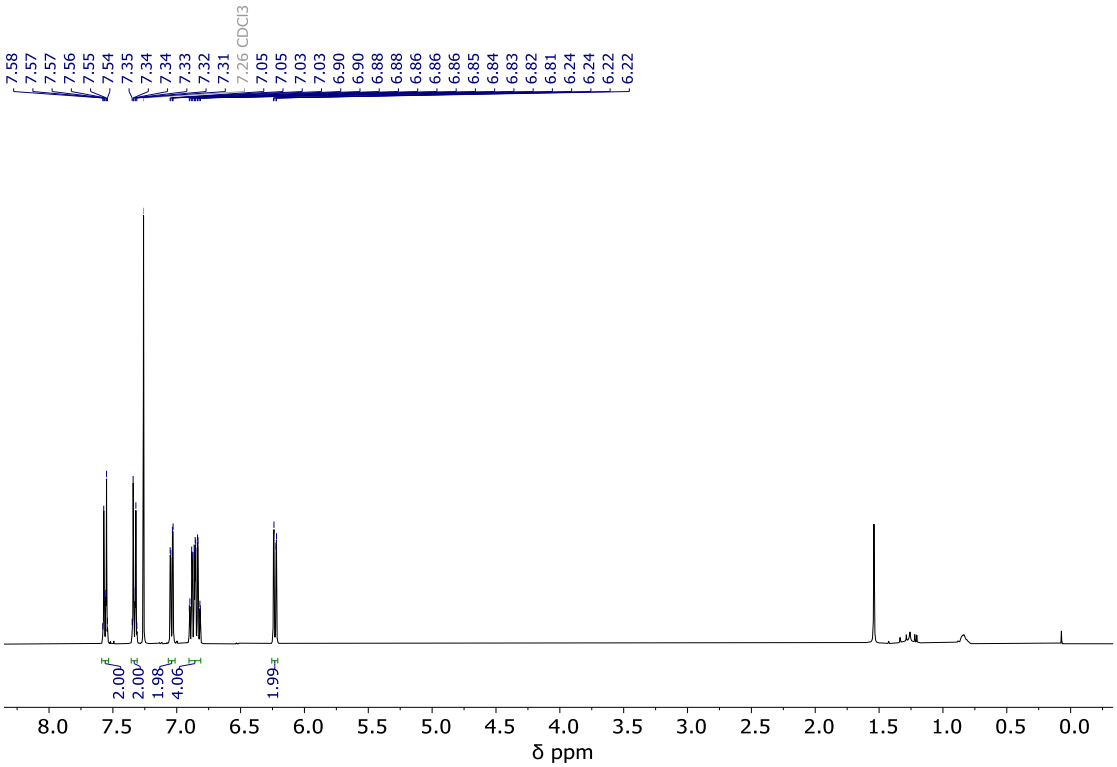


*Figure S27: ^{1}H-NMR spectrum of **Pol1a** in $CDCl_3$ (400 MHz).*

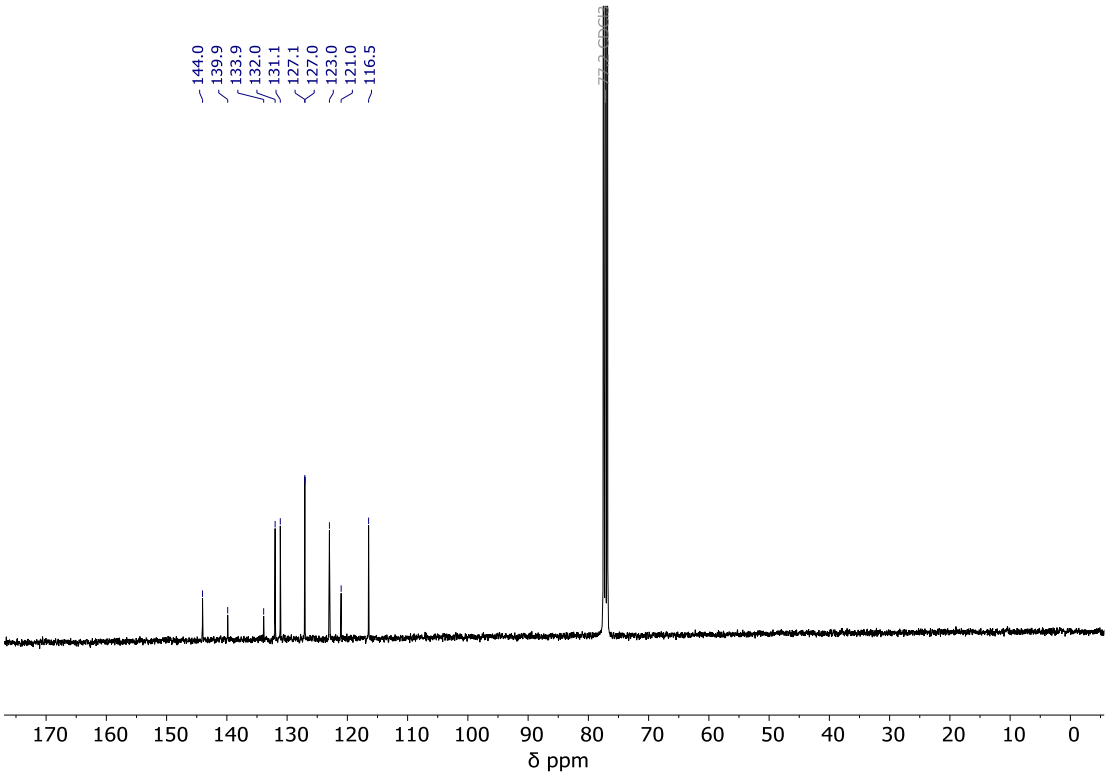


*Figure S28: ^{13}C-NMR spectrum of **Pol1a** in $CDCl_3$ (101 MHz).*

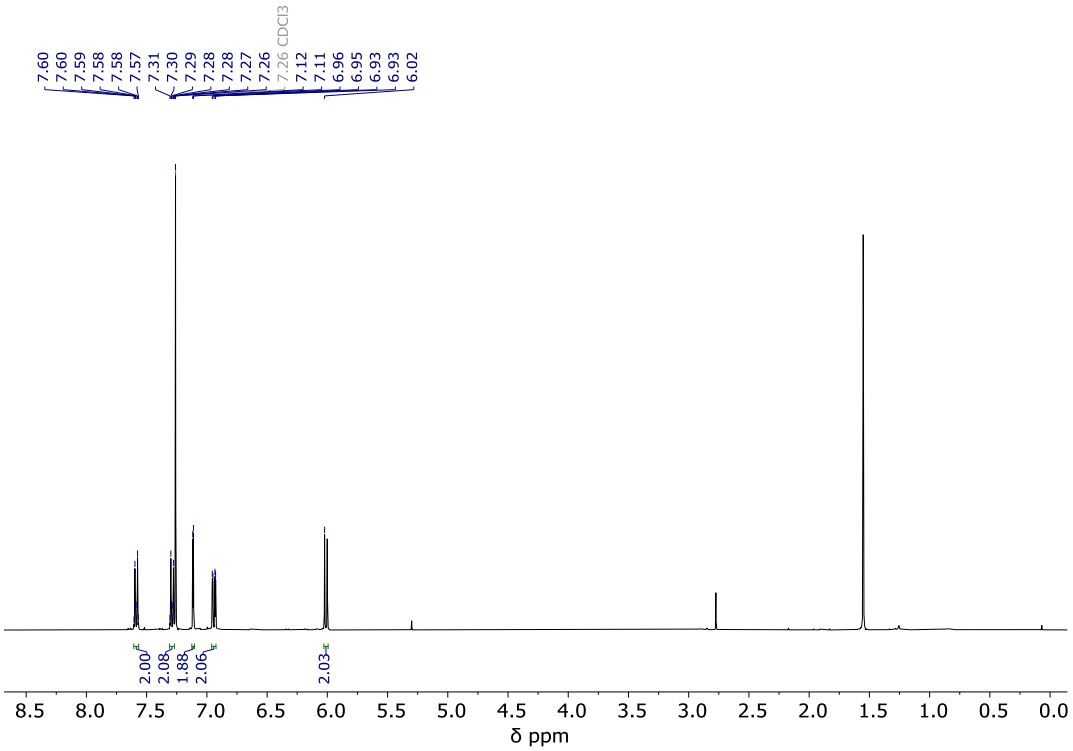


*Figure S29: ^{1}H-NMR spectrum of **Pol2a** in $CDCl_3$ (400 MHz).*

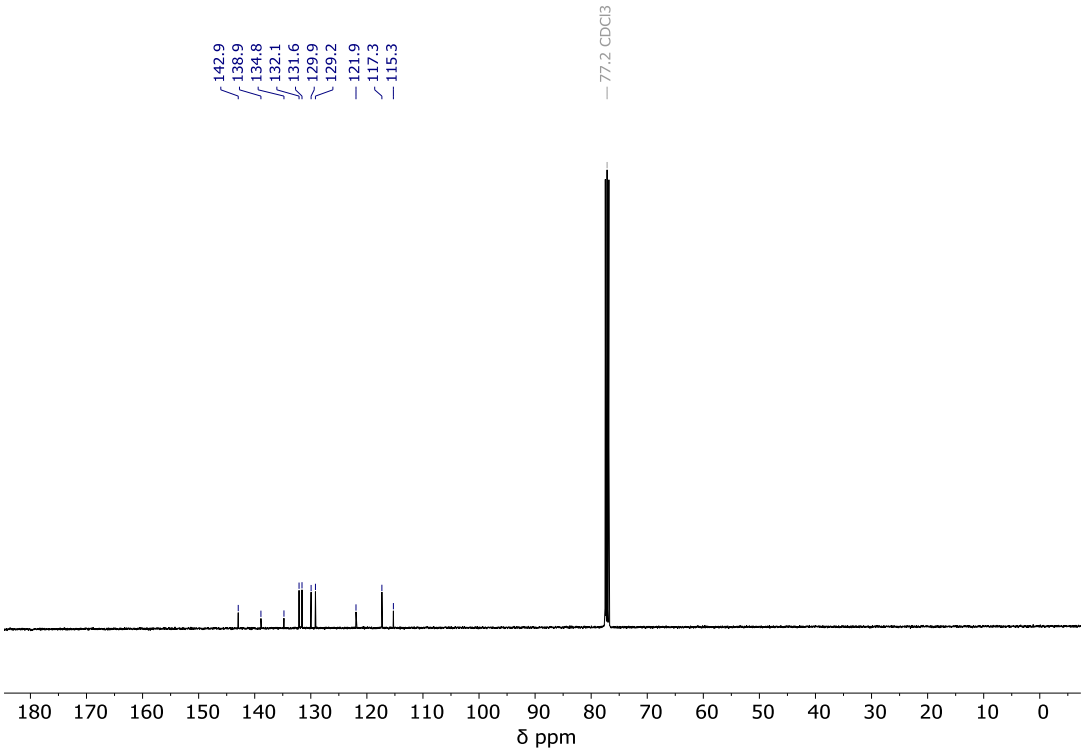


*Figure S30: ^{13}C-NMR spectrum of **Pol2a** in $CDCl_3$ (101 MHz).*

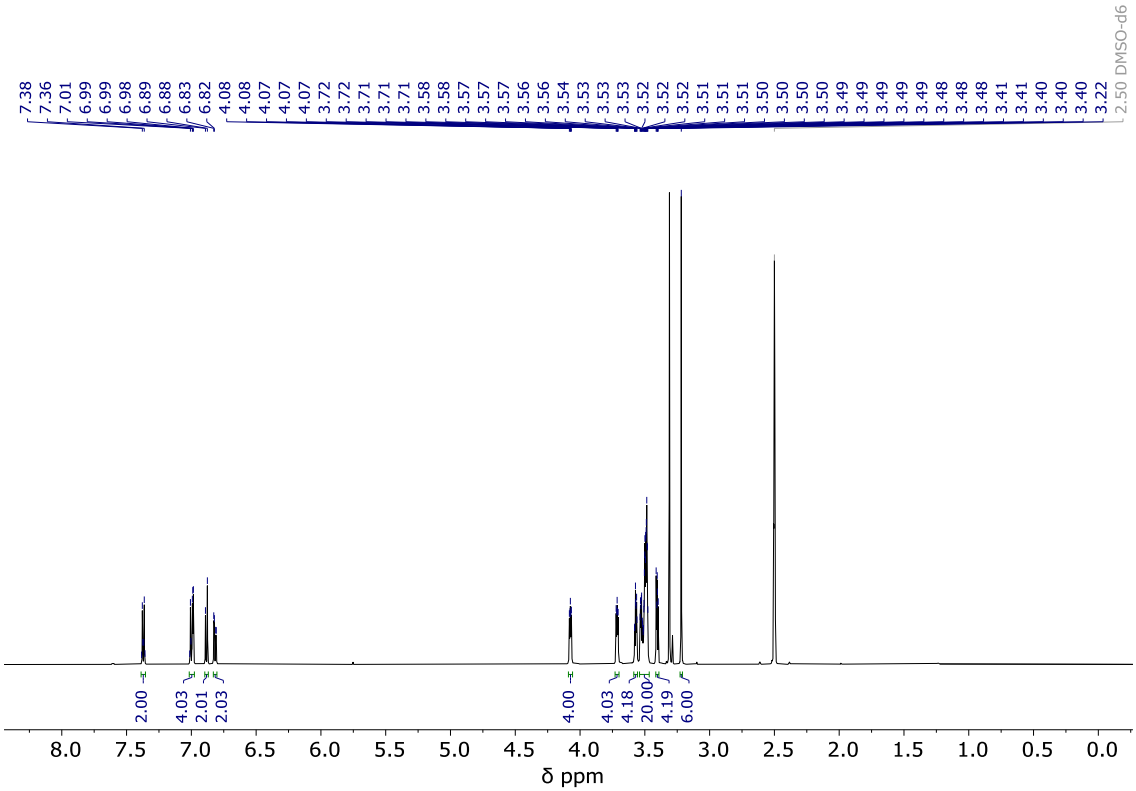


*Figure S31: [1]H-NMR spectrum of **Pol3a** in DMSO-d_6 (400 MHz).*

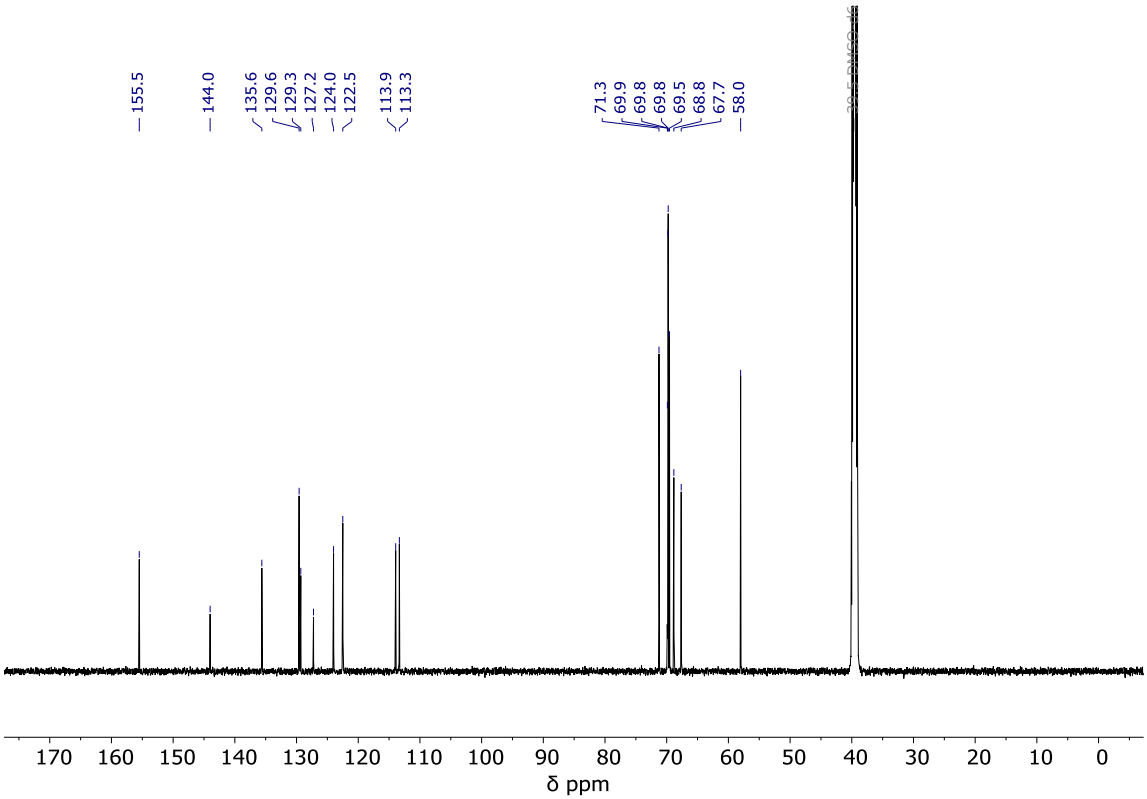


*Figure S32: [13]C-NMR spectrum of **Pol3a** in DMSO-d_6 (101 MHz).*

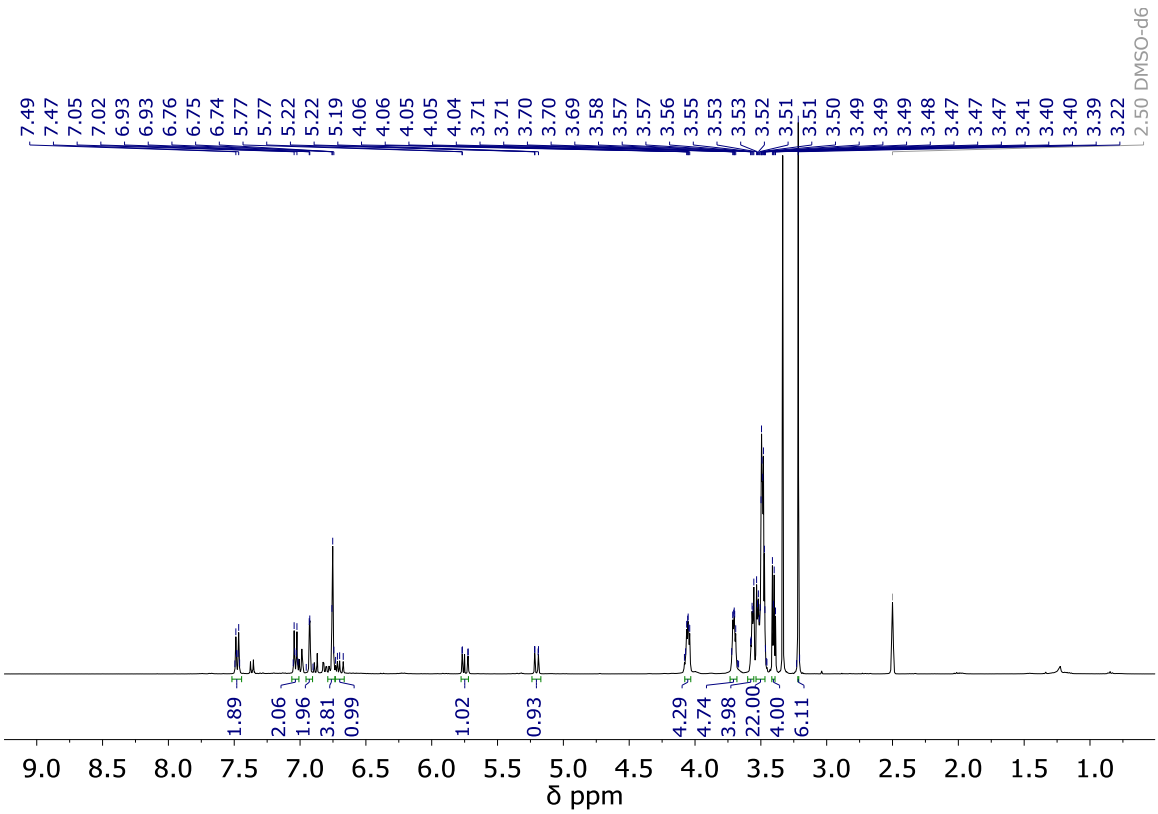


*Figure S33: [1]H-NMR spectrum of **Pol4a** in DMSO-d₆ (400 MHz).*

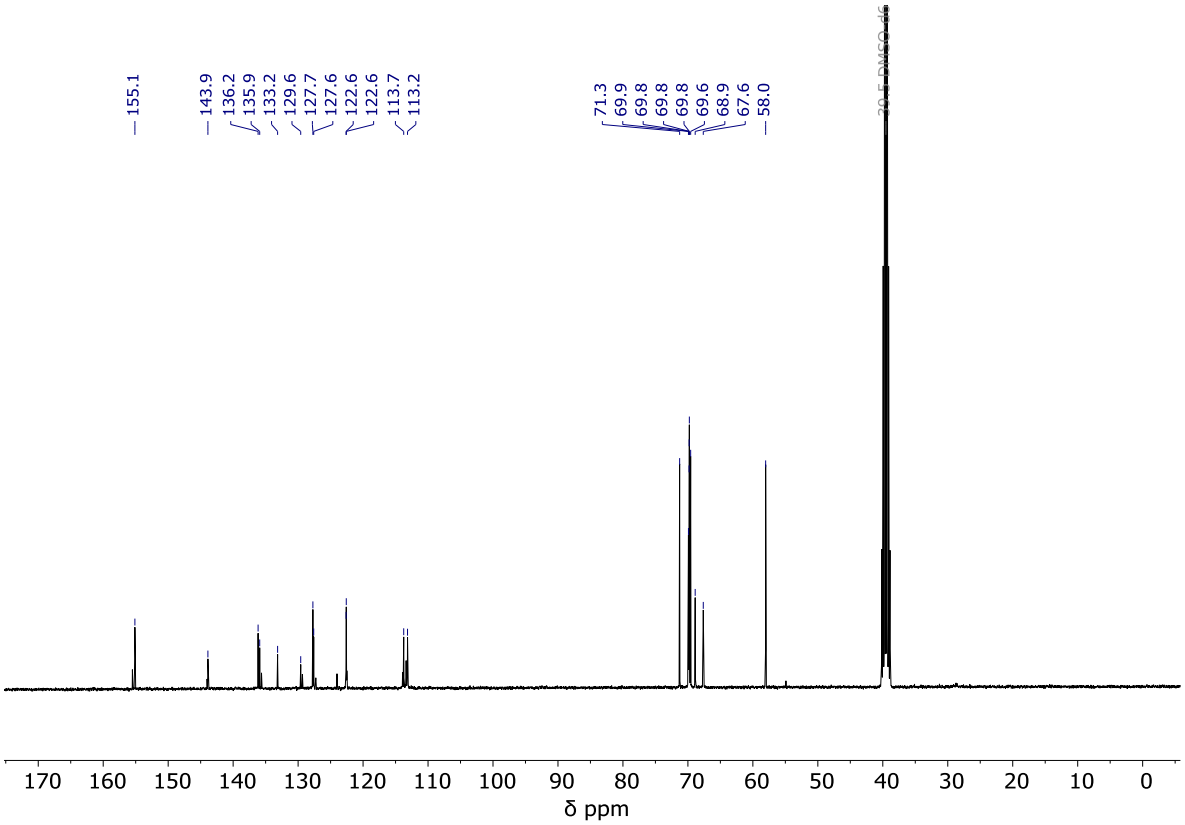


*Figure S34: [13]C-NMR spectrum of **Pol4a** in DMSO-d₆ (101 MHz).*

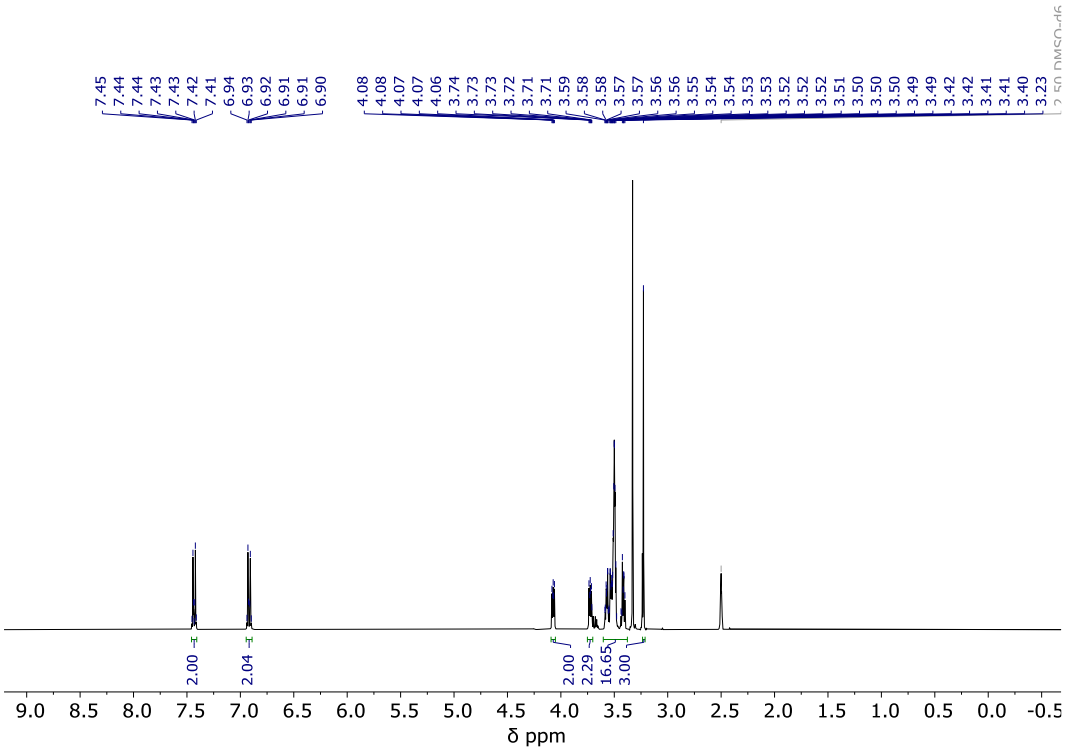


*Figure S35: [1]H-NMR spectrum of **Pol1b** in DMSO-d_6 (400 MHz).*

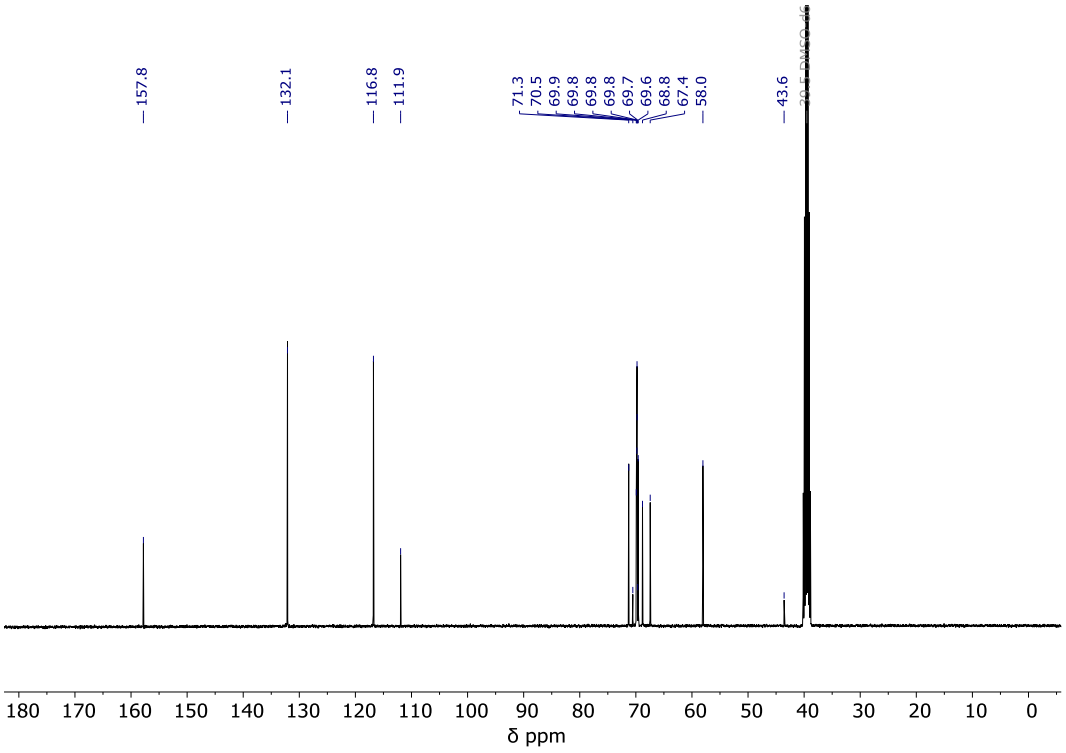


*Figure S36: [13]C-NMR spectrum of **Pol1b** in DMSO-d_6 (101 MHz).*

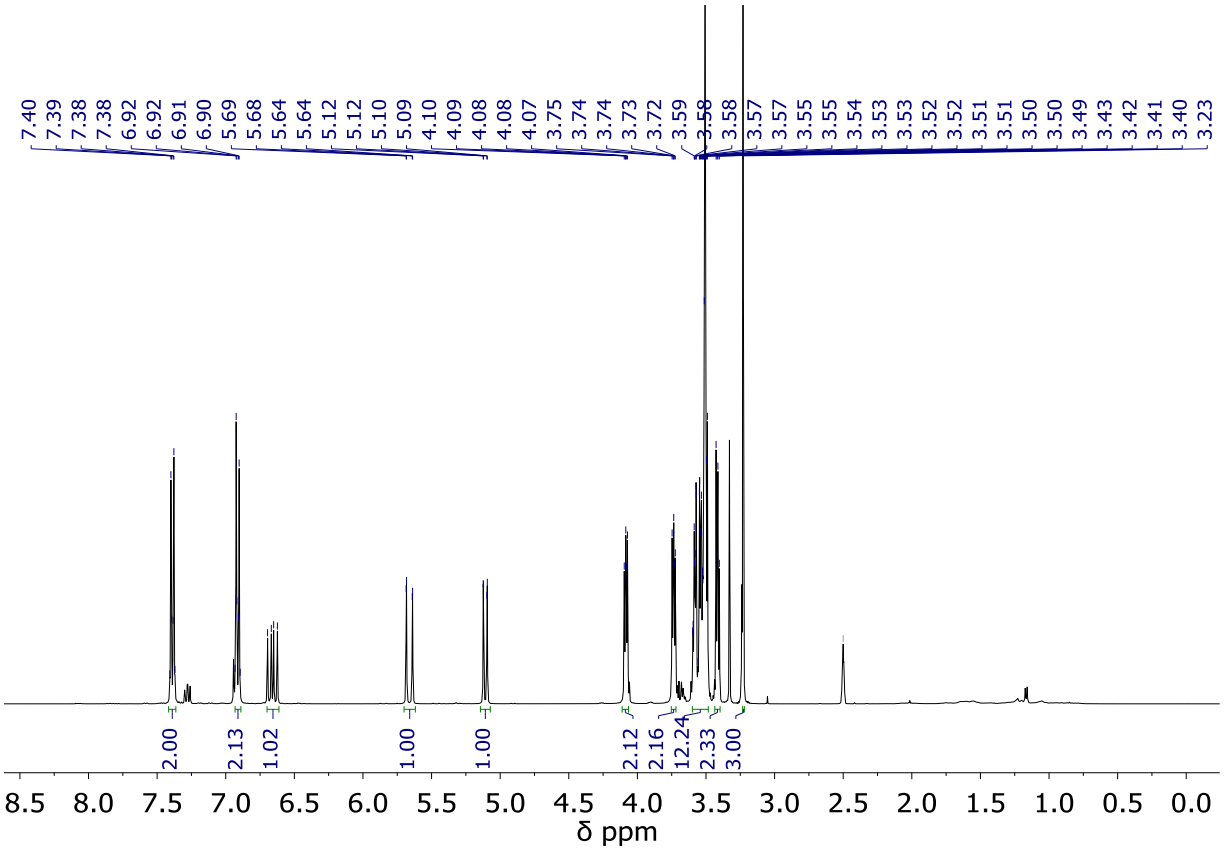


*Figure S37: [1]H-NMR spectrum of **Pol2b** in DMSO-d_6 (400 MHz).*

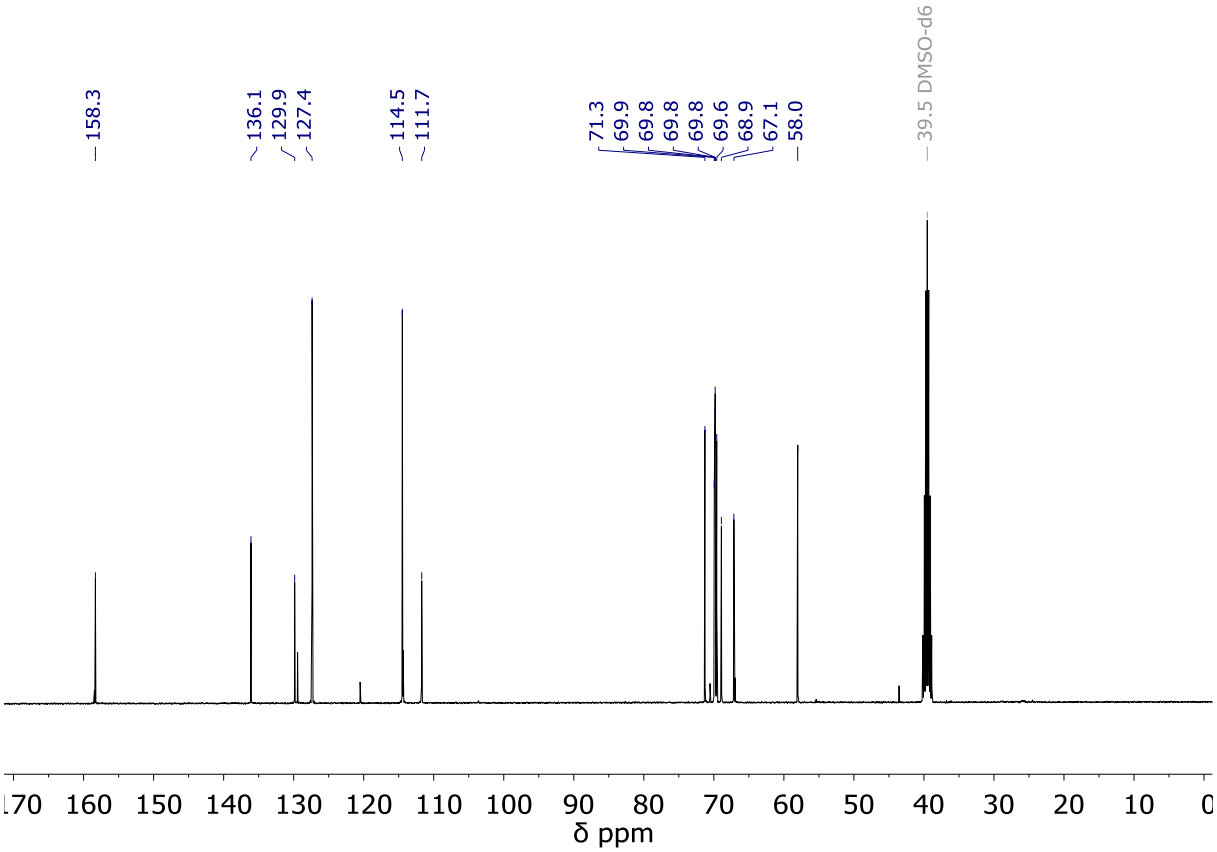


*Figure S38: [13]C-NMR spectrum of **Pol2b** in DMSO-d_6 (101 MHz).*

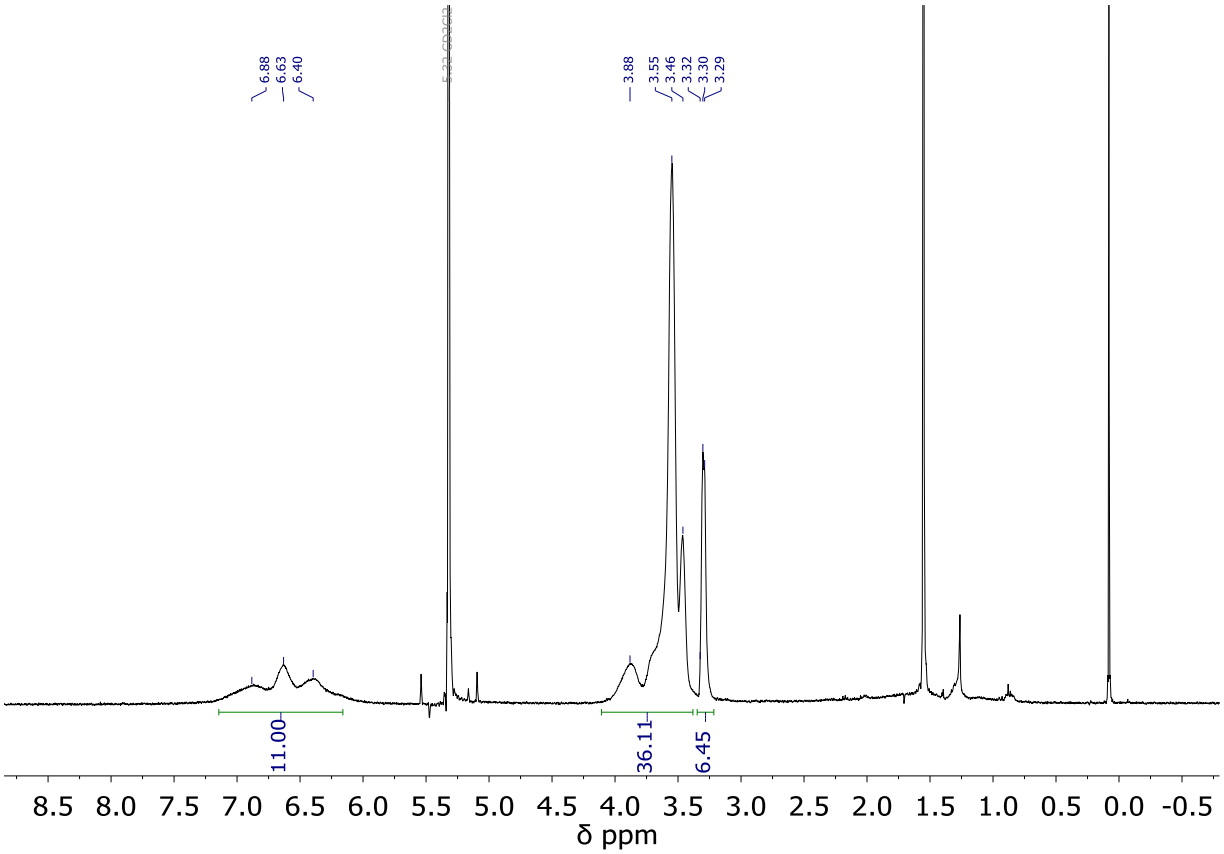


*Figure S39: ^{1}H-NMR spectrum of **P1** in CD_2Cl_2 (400 MHz).*

11 “Post-mortem” analyses

PTH:

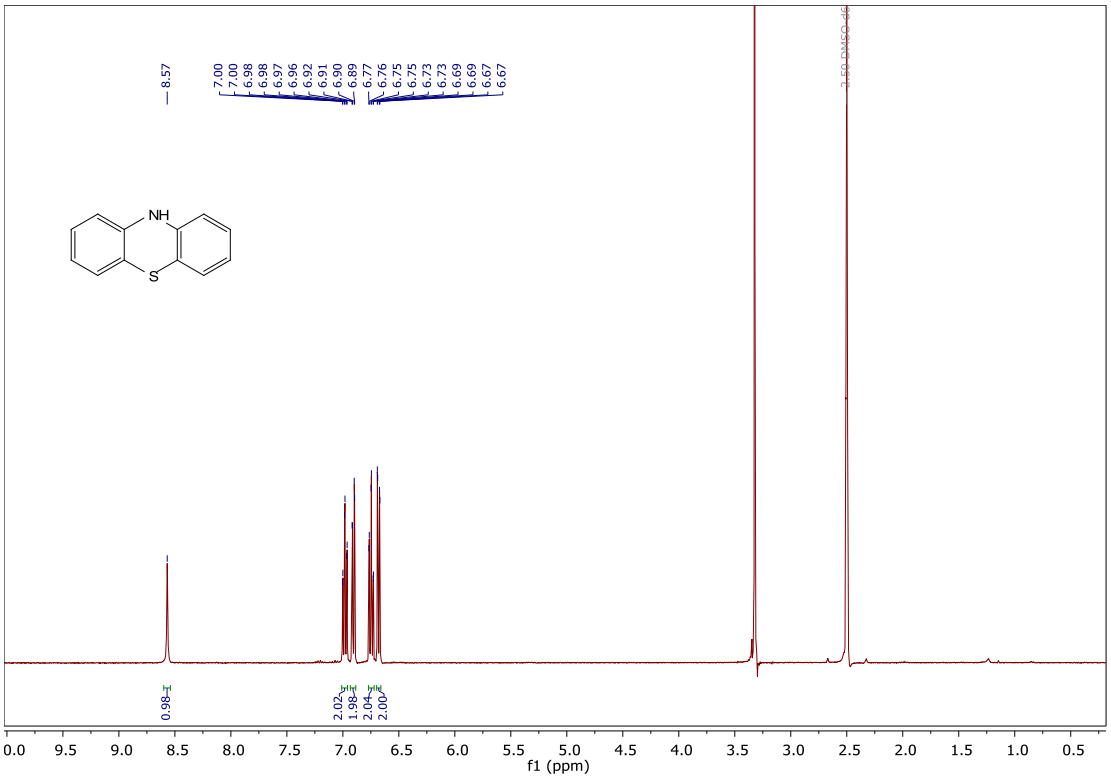


*Figure S40: ^{1}H-NMR spectrum of **PTH** in DMSO-d_6 (stock solution or back-up sample) (400 MHz).*

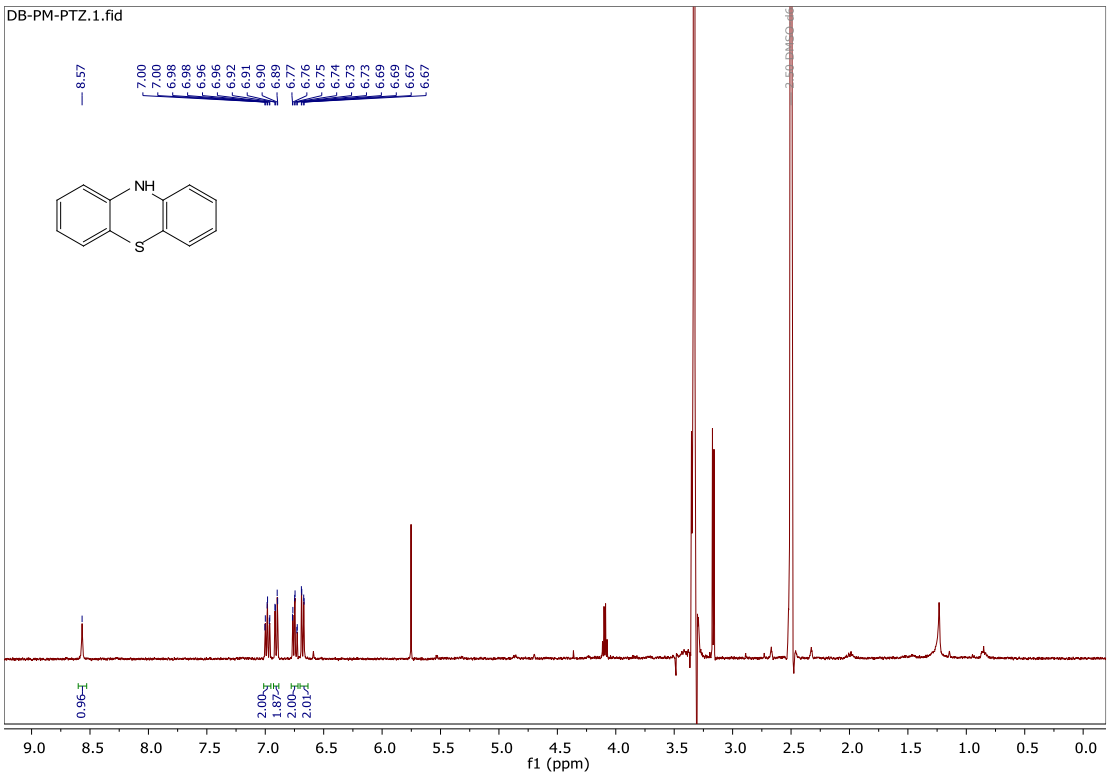


*Figure S41: ^{1}H-NMR spectrum of **PTH** in DMSO-d_6 (400 MHz), extracted with DCM from the crude photocatalysis mixture (pH = 1.25/ 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$) after 6 h irradiation.*

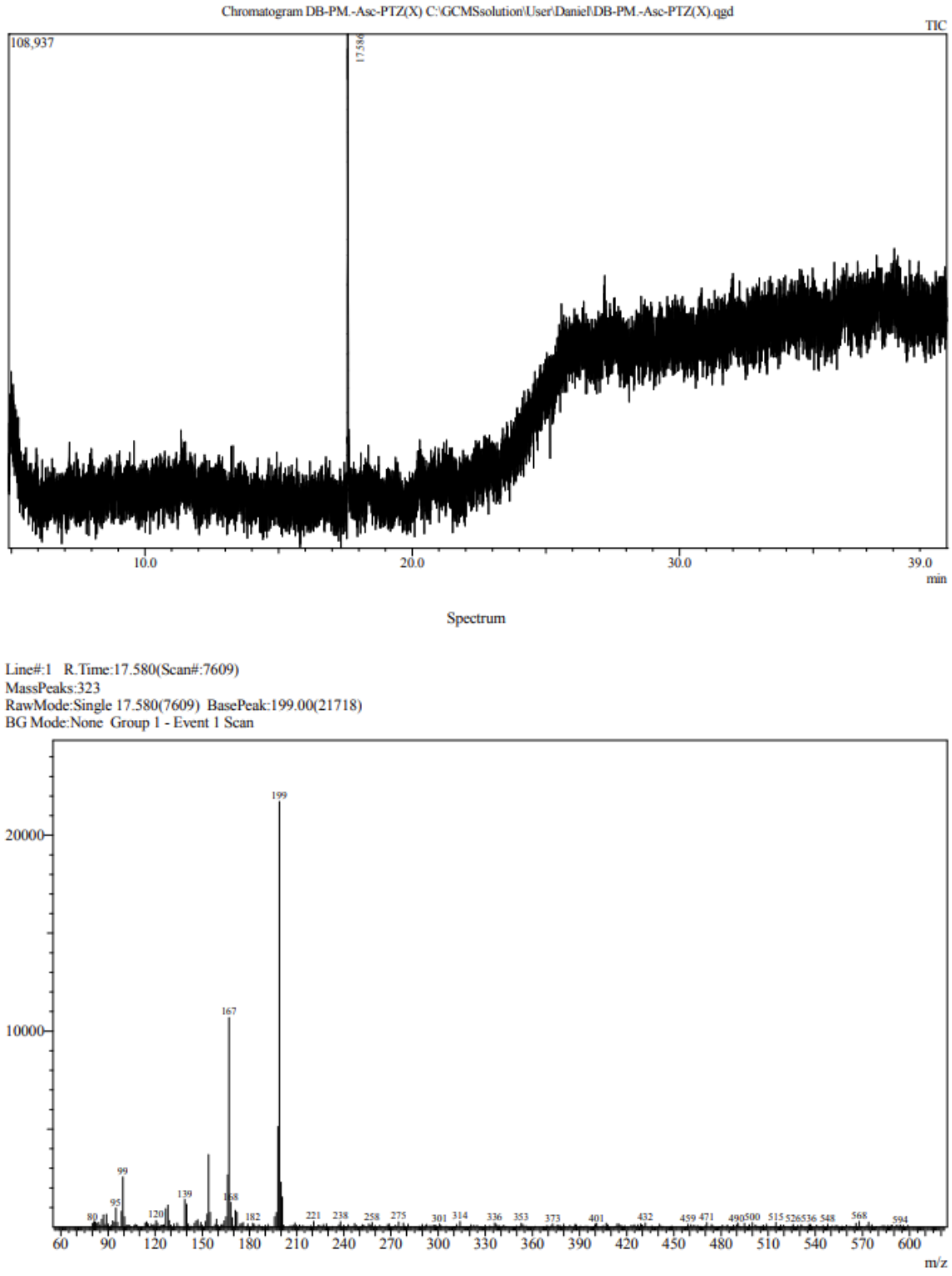


*Figure S42: GC-MS measurement of crude post-mortem catalysis (pH = 2.55, 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$) (**PTH**).*

MPT:

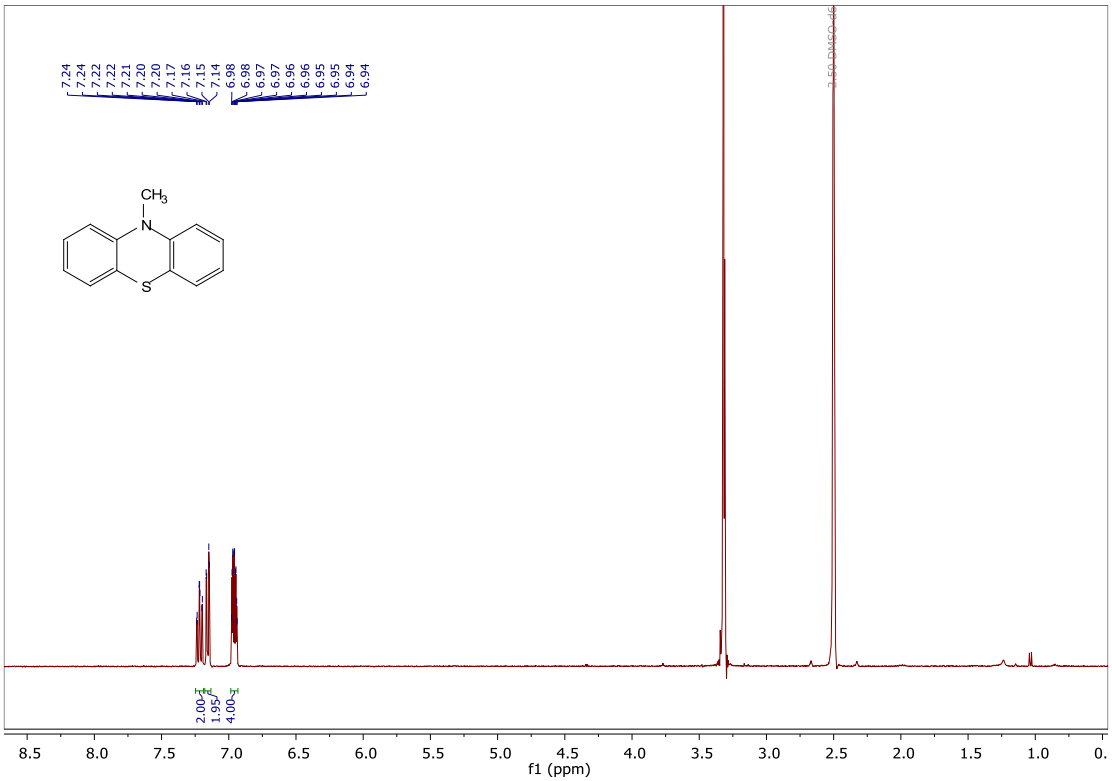


*Figure S43: ^{1}H-NMR of **MPT** in DMSO-d_6 (stock solution or back-up sample) (400 MHz).*

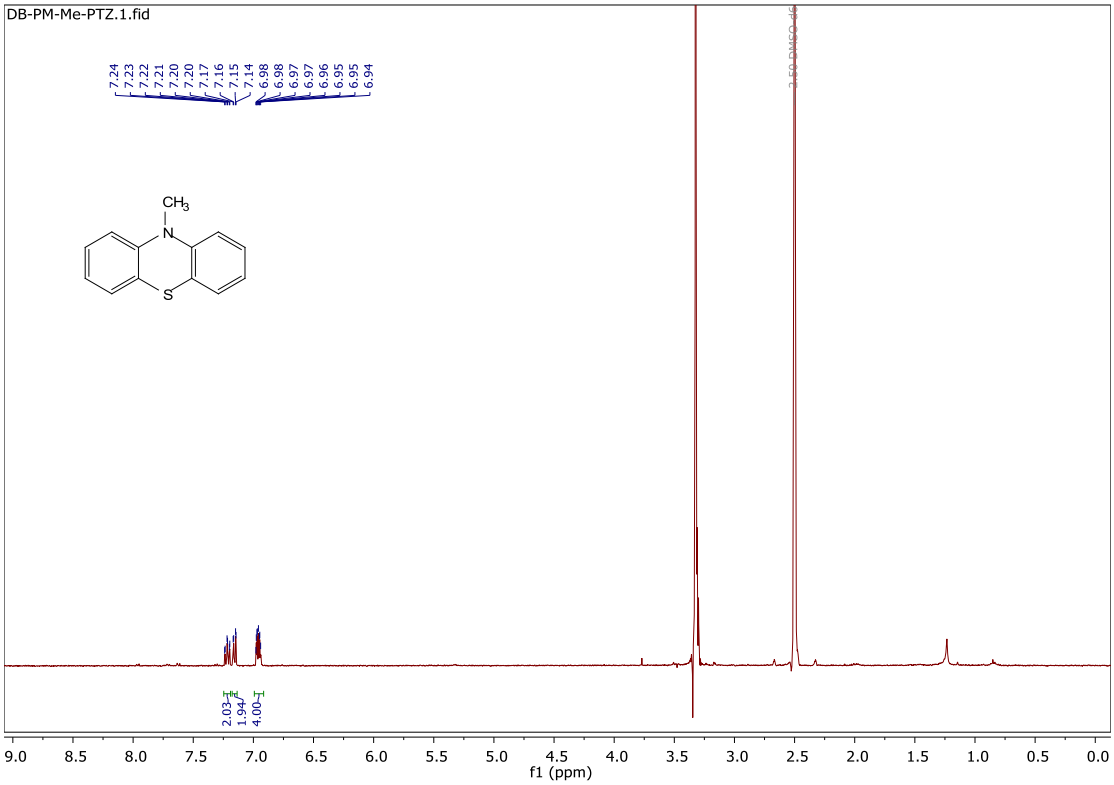


*Figure S44: ^{1}H-NMR of **MPT** in DMSO-d_6 (400 MHz), extracted with DCM from crude photocatalysis (pH = 1.25, 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$) after 6 h irradiation.*

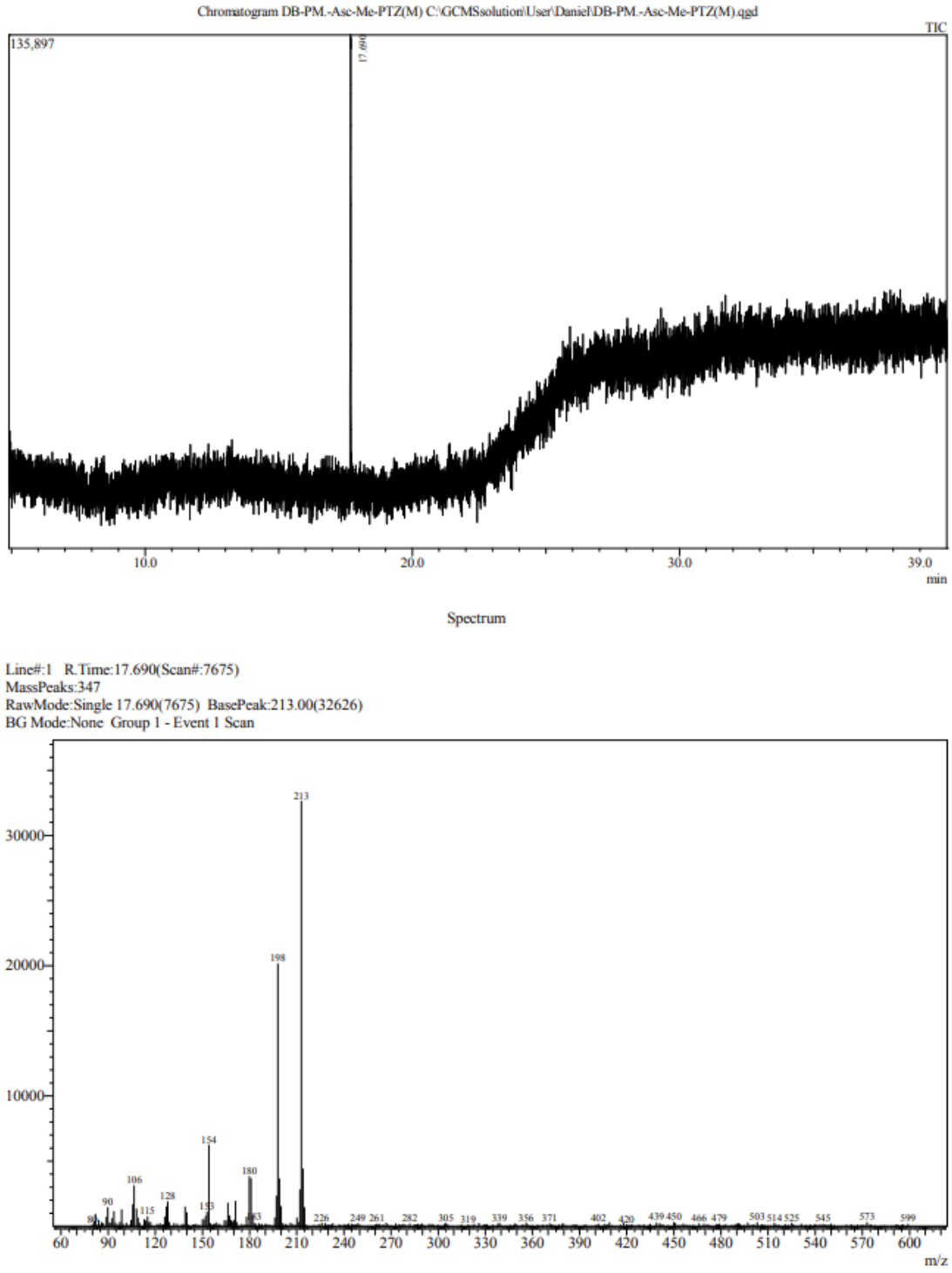


*Figure S45: GC-MS measurement of crude post-mortem catalysis (pH = 2.55, 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$) (**MPT**).*

PEG-PT:

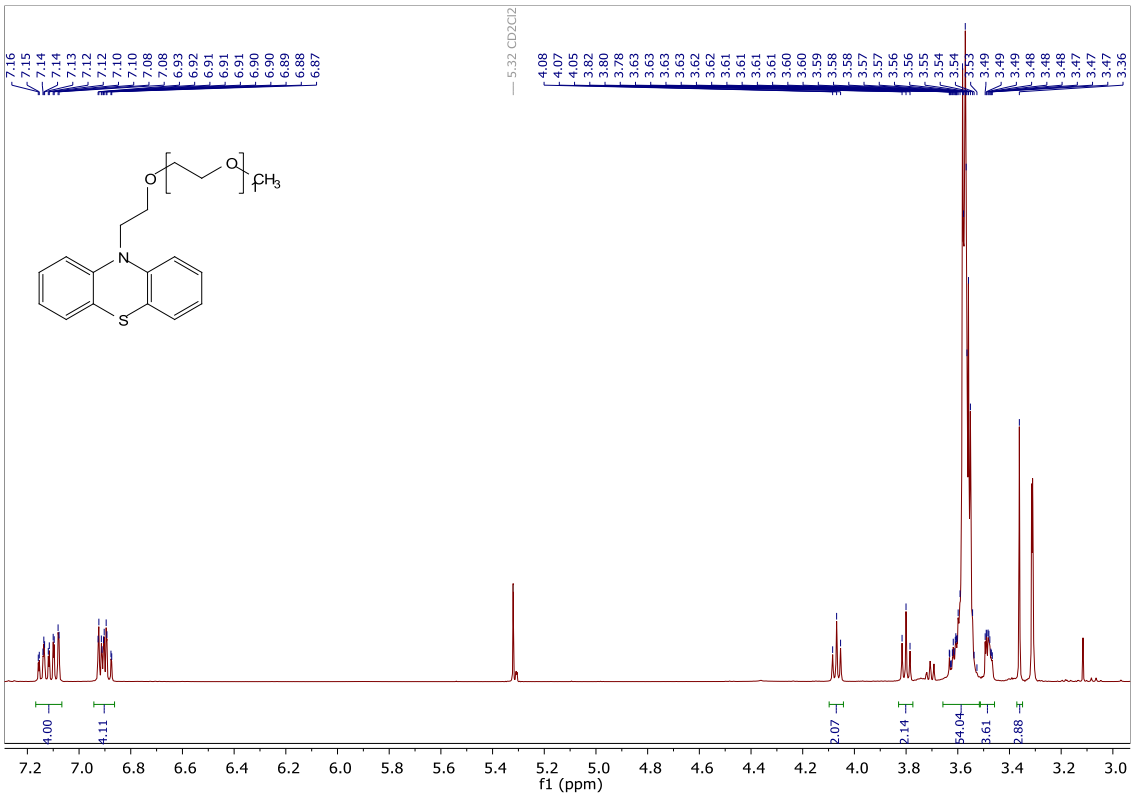


*Figure S46: ^{1}H-NMR of **PEG-PT** in CD_2Cl_2 (stock solution or back-up sample) (400 MHz).*

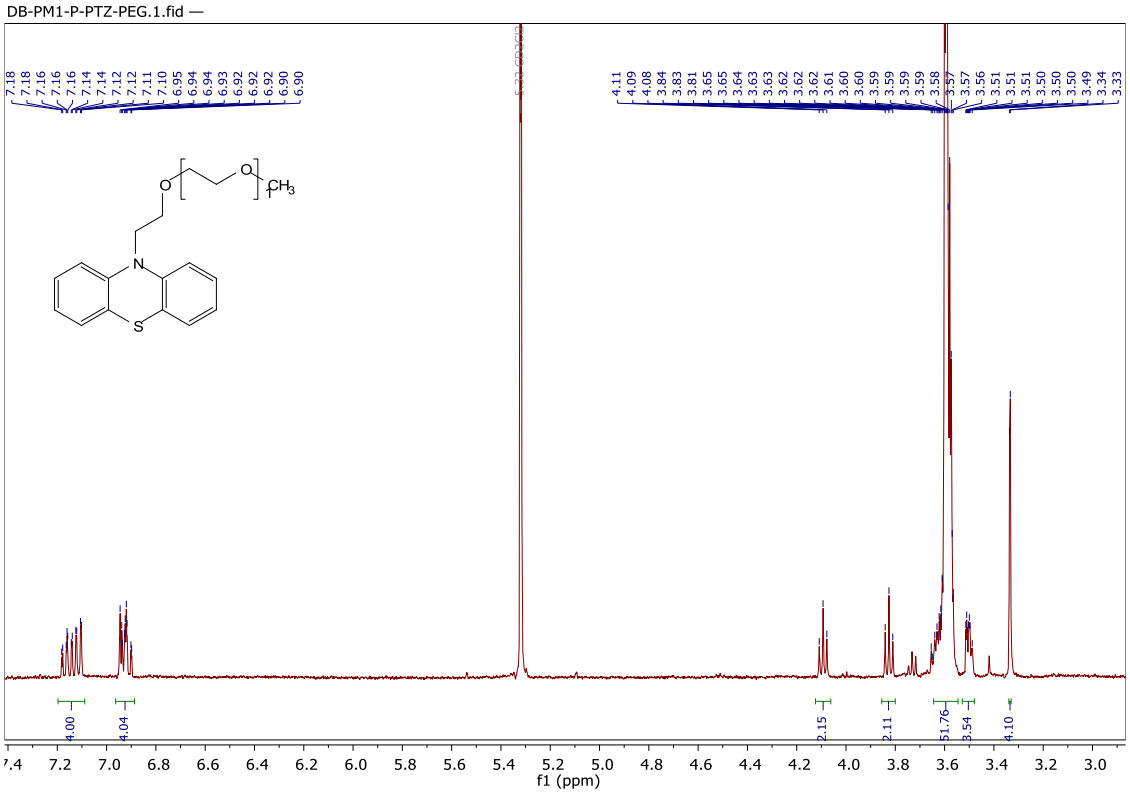


*Figure S47: ^{1}H -NMR of **PEG-PT** in CD_2Cl_2 (400 MHz), extracted with DCM from crude catalysis (pH = 1.25, 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$) after 6 h irradiation.*

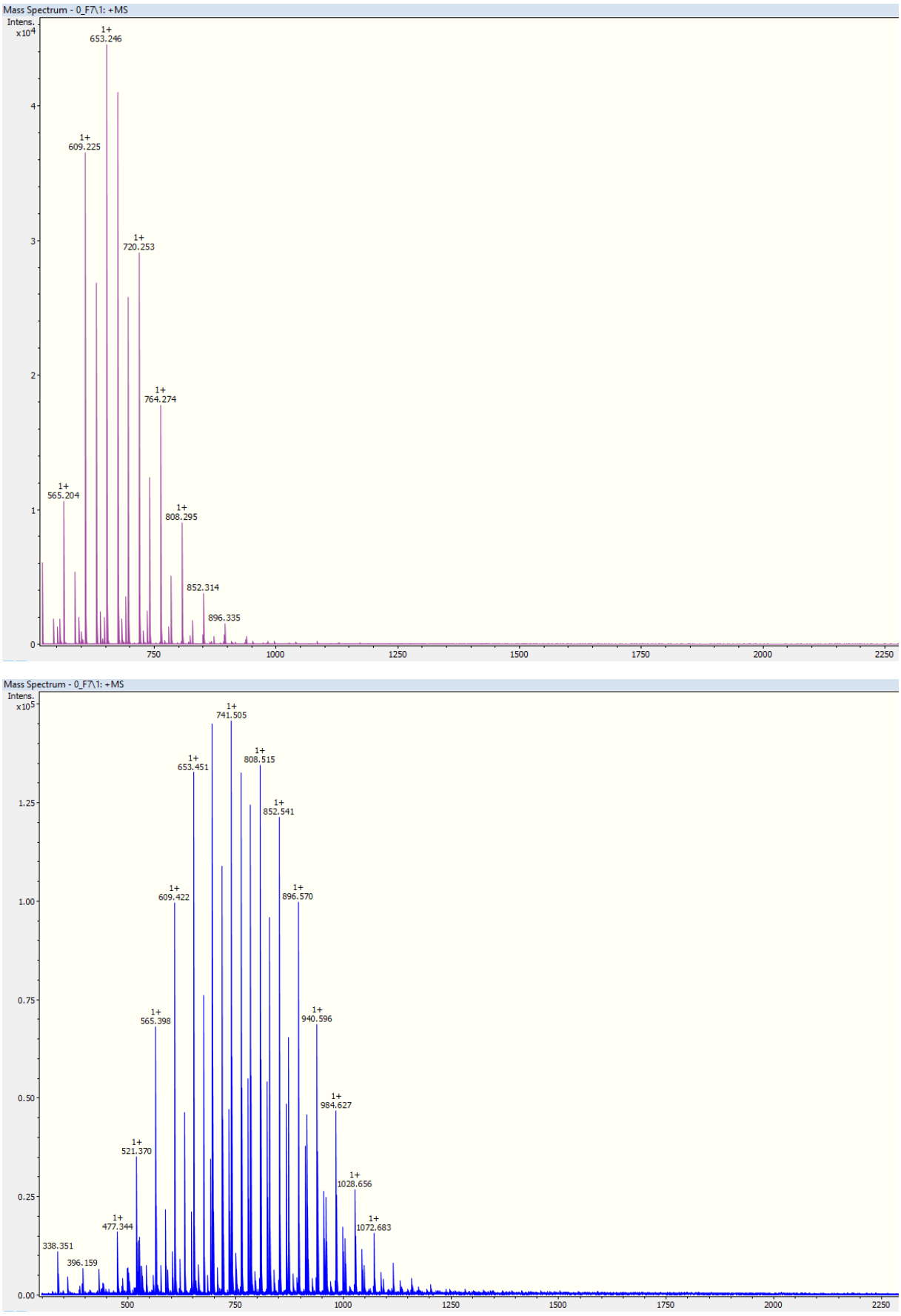


*Figure S48: MALDI-TOF measurements of **PEG-PT**; Top: Stock-solution; Bottom: Post-mortem analysis (pH = 1.25, 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$).*

TolPT-PEG:

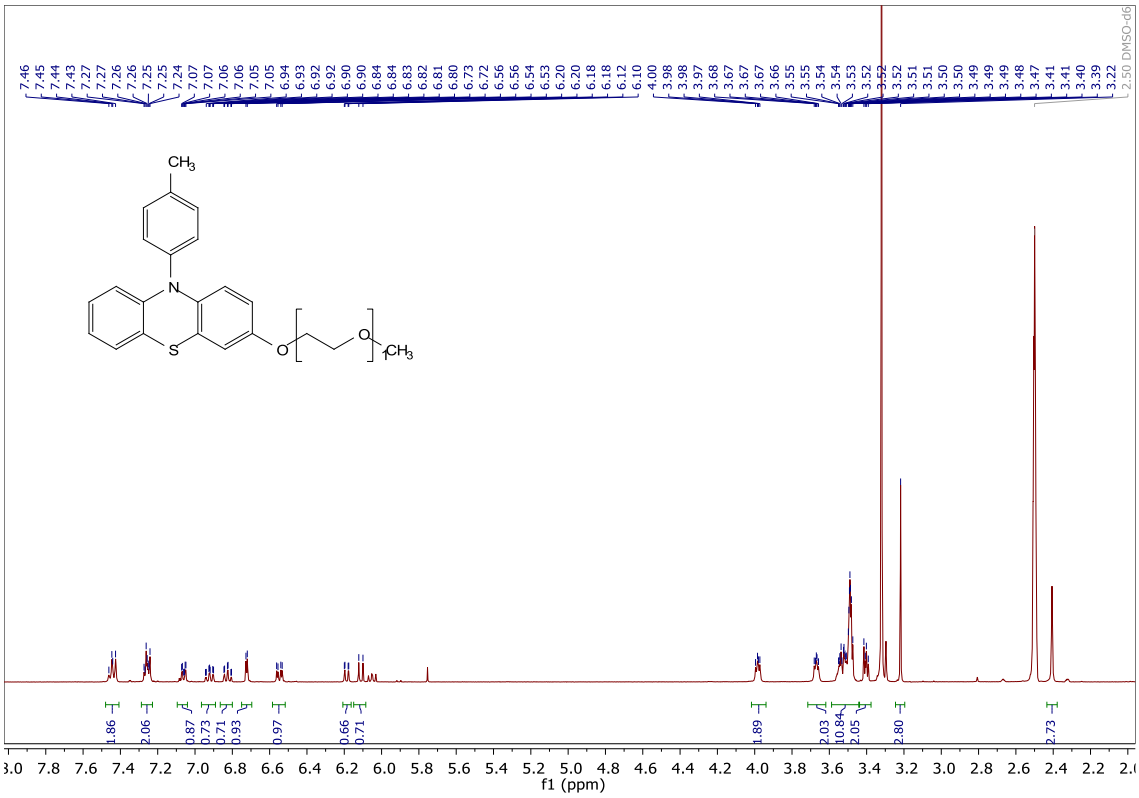


*Figure S49: ^{1}H-NMR spectrum of **TolPT-PEG** in DMSO-d_6 (stock solution or back-up sample) (400 MHz).*

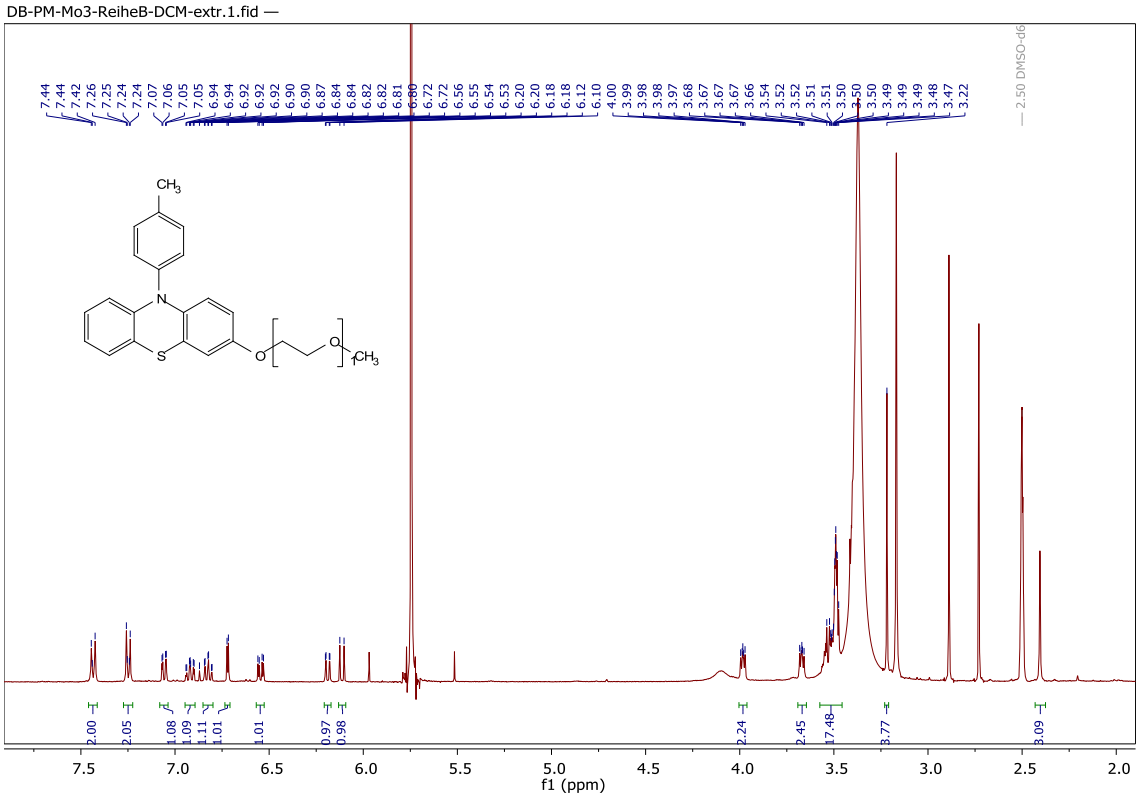


*Figure S50: ^{1}H-NMR spectrum of **TolPT-PEG** in DMSO-d_6 (400 MHz), extracted with DCM from crude catalysis (pH = 1.25, 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$) after 6 h irradiation.*

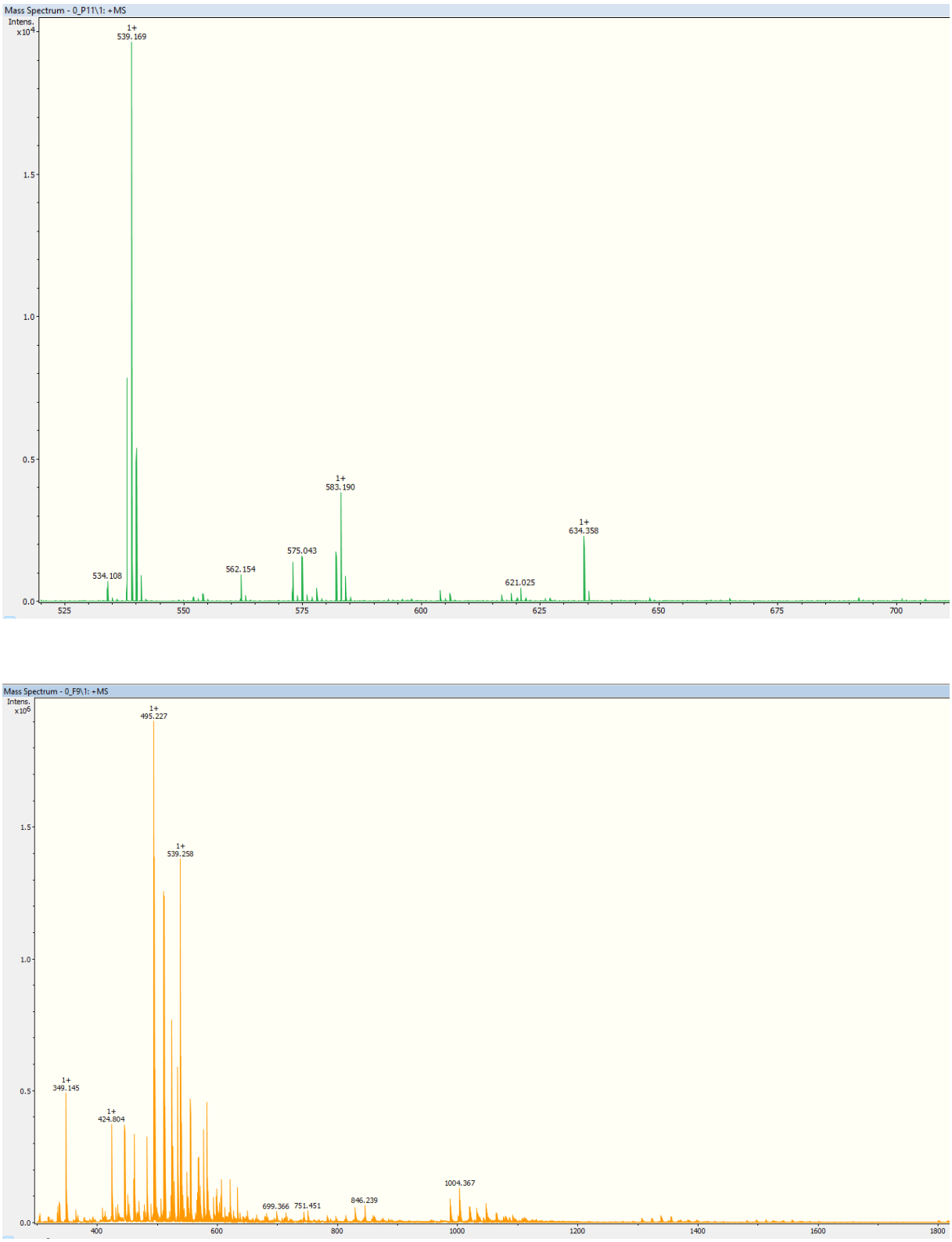


*Figure S51: MALDI-TOF measurements of **TolPT-PEG** (n = 4; [M⁺] = 539.234); Top: Stock-solution; Bottom: Post-mortem analysis (pH = 1.25/ 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$); (n = 3, $[M]^+$ = 495.234; n = 4, $[M]^+$ = 539.238).*

TolPT-*di*PEG:

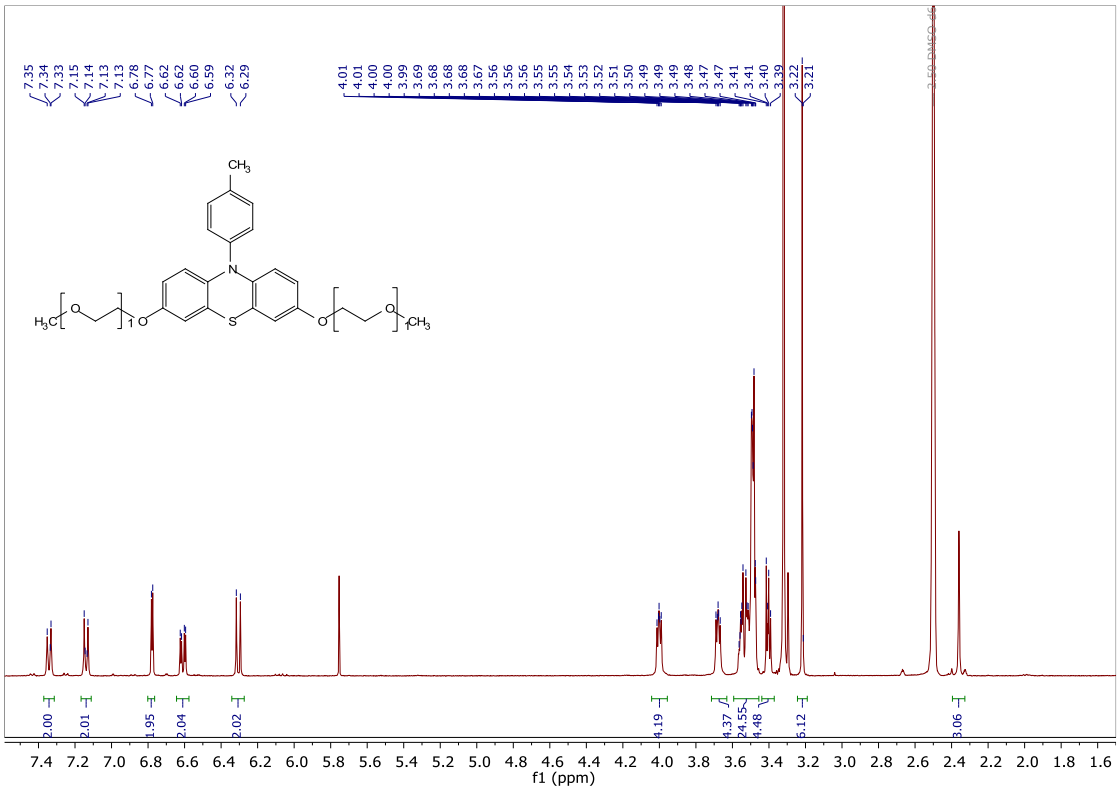


*Figure S52: ^{1}H-NMR spectrum of **TolPT-diPEG** in DMSO-d_6 (stock solution or back-up sample) (400 MHz).*

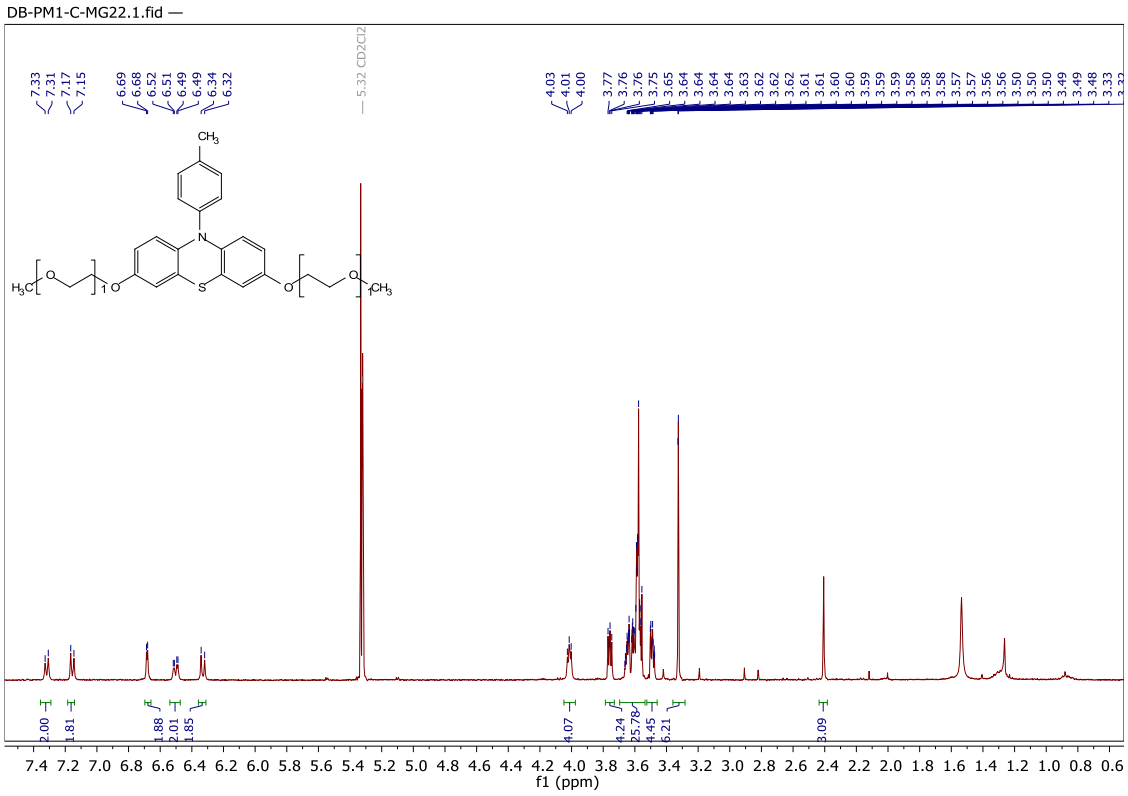


*Figure S53: ^{1}H-NMR spectrum of **TolPT-diPEG** in CD_2Cl_2 (400 MHz), extracted with DCM from crude catalysis (pH = 1.25, 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$) after 6 h irradiation.*

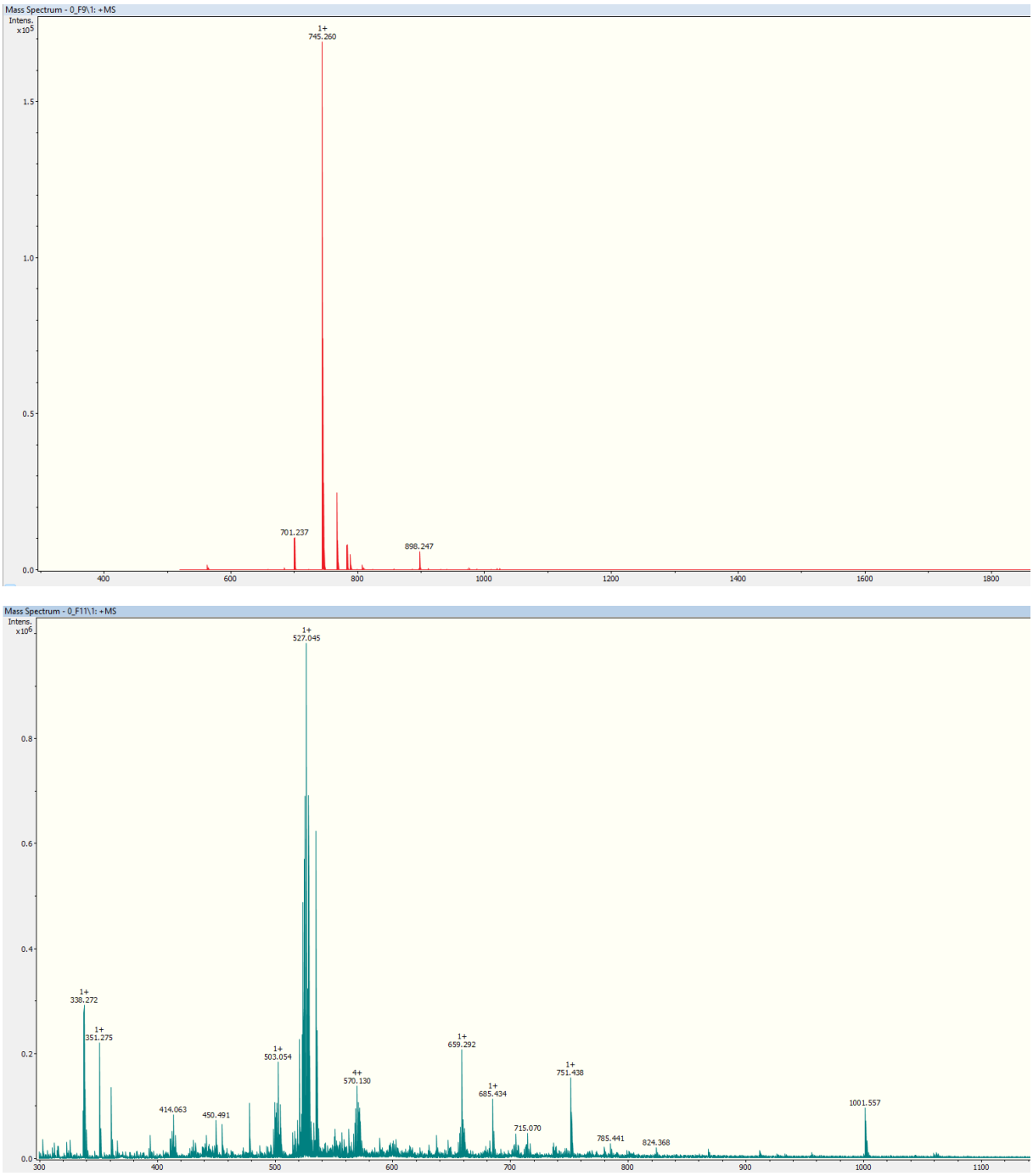


*Figure S54: MALDI-TOF measurements of **TolPT-diPEG** (n_1 = 3, n_2 = 4, $[M]^+$ = 745.349); Top: Stock-solution; Bottom: Post-mortem analysis (pH = 1.25, 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$).*

P1:

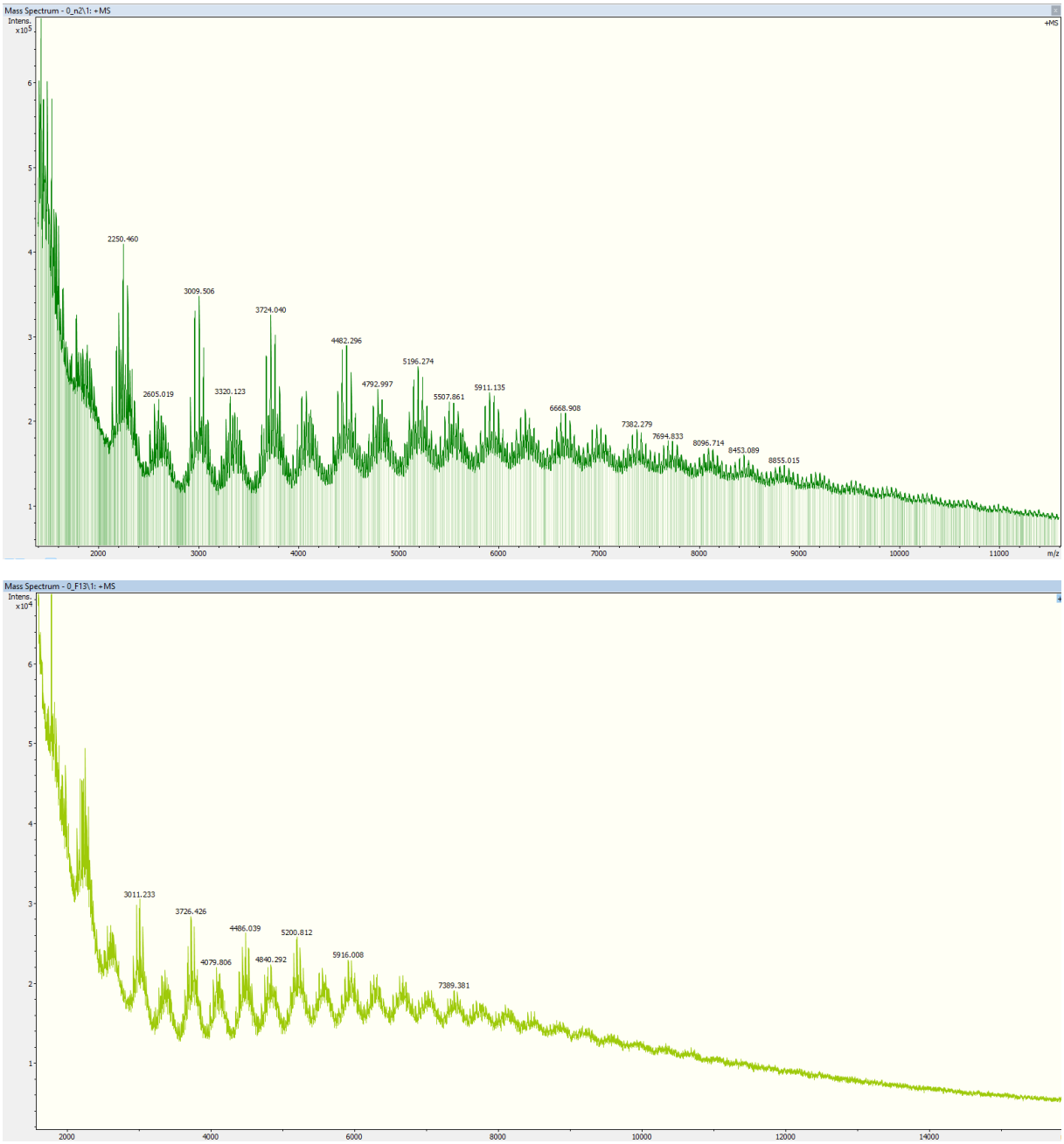
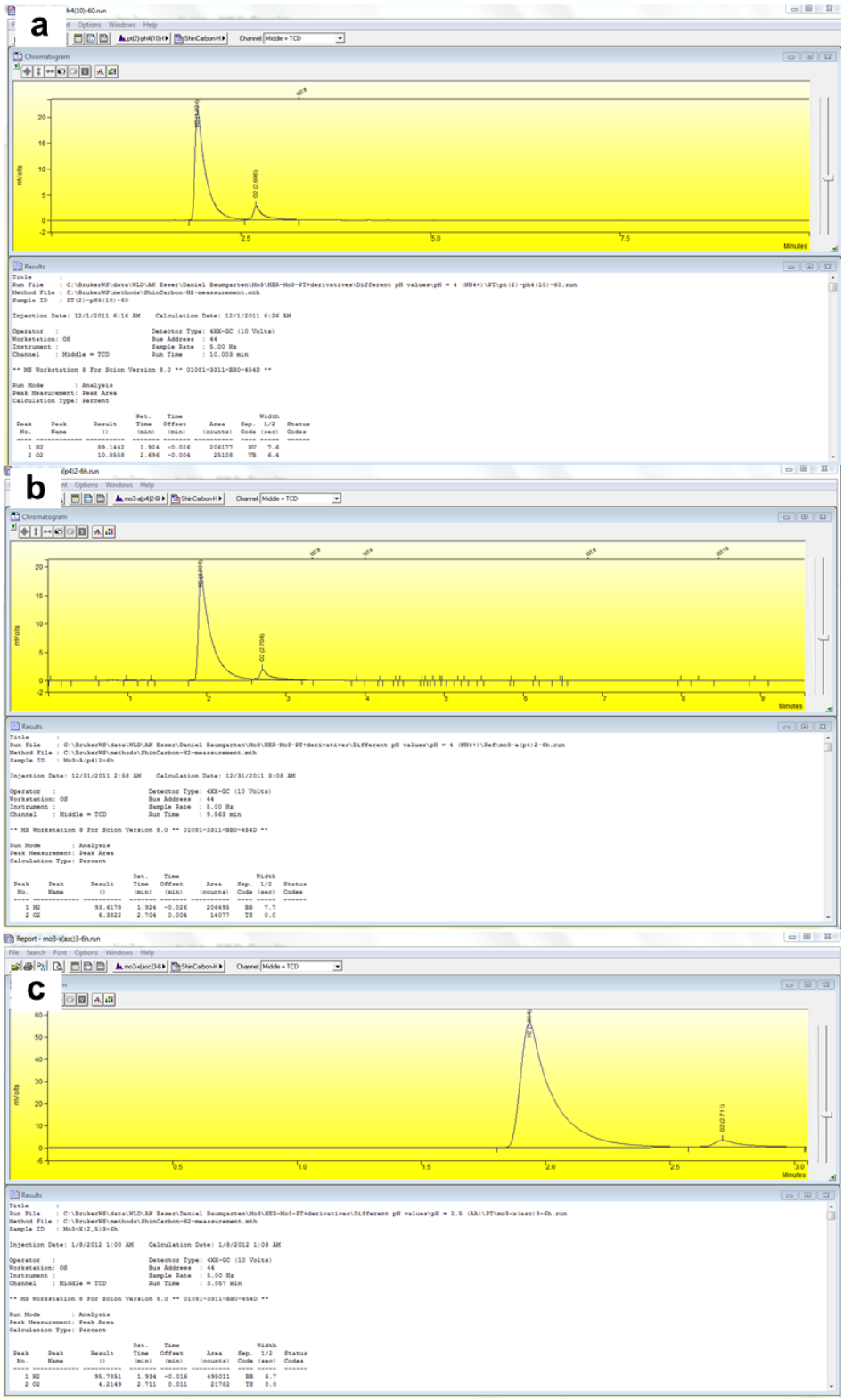


*Figure S55: MALDI-TOF measurements of **P1** Top: Stock-solution; Bottom: Post-mortem analysis (pH = 1.25/ 50 equiv. RM to $[Ru(bpy)_3](PF_6)_2$); Note: **P1** could not be extracted with DCM from the solvent mixture.*

12 Exemplary GC-traces of H_2 detection

Exemplary GC-traces of H_2 detection are shown in Figure S52. The peak measured at ca. 1.92 min shows the H_2 peak, the signal at ca. 2.70 min shows the signal for air (O_2 and N_2). The measurement was performed by taking 100 µL of the headspace of the GC-vial (with a Hamilton syringe gastight #1710) and direct injection into the Bruker Scion GC/MS. For all data, please refer to the uploaded data: 10.5281/zenodo.17799373



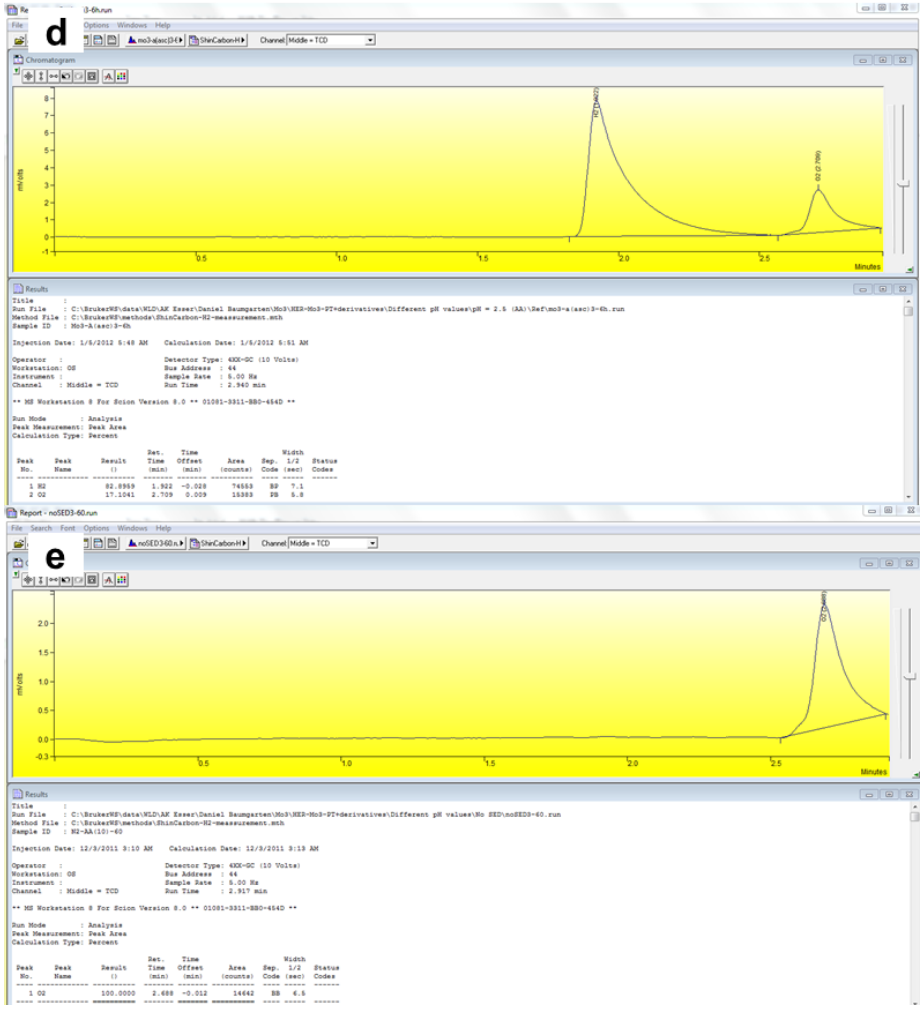


Figure S56: Exemplary GC-traces (recorded: Bruker Scion GC/MS) of the head space of HER photocatalytic reactions after 6 h reaction times using a) ***PTH*** *(50 equiv.); pH = 4; using NH_4^+;as counter ion b) Reference pH = 4; using NH_4^+;as counter ion; c)* ***PTH*** *(50 equiv.); pH = 2.55; d) Reference (no PT derivative); pH = 2.55; e) no ascorbic acid;* ***PTH*** *(50 equiv.). Standard conditions: 1 mM* ***PTH*** *or derivatives, 0.3 µM $(NH_4)_2[Mo_3S_{13}]$, 20 µM $[Ru(bpy)_3](PF_6)_2$, 10 mM ascorbic acid/ascorbate in MeOH:H_2O (9:1, v:v).*

13 Literature

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