Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Photo- and Halochromism of Spiropyran-based Main-chain Polymers

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Contents

1. Materials and Characterization

1.1. Chemicals

2,3,3-Trimethylindolenine (Sigma-Aldrich), 2-bromoethanol (Sigma-Aldrich), 2,3-dihydroxybenzalde hyde (Combi-Blocks), 2,4-dihydroxybenzaldehyde (Combi-Blocks), 2,5-dihydroxy benzaldehyde (Combi-Blocks), 2,6-dihydroxybenzaldehyde (Combi-Blocks), 10-undecenoyl chloride (Sigma-Aldrich), acryloyl chloride (Sigma-Aldrich), triethylamine (Sigma-Aldrich), methanesulfonic acid (MsOH) (Sigma-Aldrich), trifluoroacetic acid (TFA) (Alfa Aesar), 10-undecenoic acid (Sigma-Aldrich), N,N'-dicylohexylcarbodiimide (DCC) (Sigma-Aldrich), 4-(dimethylamino)pyridine (DMAP) (Sigma-Aldrich), Hoveyda-Grubbs 2nd generation catalyst (Sigma-Aldrich), ethyl vinyl ether (Sigma-Aldrich). All solvents and chemicals, unless specified, were purchased and used without further purification.

1.2. Flash chromatography

Flash chromatography was performed on a Interchim XS420+ flash chromatography system consisting of a SP-in-line filter 20-µm, an UV-VIS detector (200-800 nm) and a SofTA Model 400 ELSD (55 °C drift tube temperature, 25 °C spray chamber temperature, filter 5, EDR gain mode) connected via a flow splitter (Interchim Split ELSD F04590). The separations were performed using an Interchim dry load column (liquid injection) and an Interchim Puriflash Silica HP 30 µm column.

1.3. Size-Exclusion Chromatography (SEC)

The SEC measurements were conducted on a PSS SECurity2 system consisting of a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven (35 °C), PSS SDV Column Set (8 x 150 mm 5 µm Precolumn, 8 x 300 mm 5 µm Analytical Columns, 100000 Å, 1000 Å and 100 Å) and an Agilent 1260 Infinity Isocratic Pump, Agilent 1260 Infinity Standard Autosampler, Agilent 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), Agilent 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL·min^{-1}. Narrow disperse linear poly(styrene) (M_n: 266 g·mol^{-1} to 2.52·106 g·mol^{-1}) and poly(methyl methacrylate) (M_n: 202 g·mol^{-1} to 2.2·106 g·mol^{-1}) standards (PSS ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in PSS WinGPC UniChrom software (version 8.2).

1.4. Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H and ^{13}C NMR spectra were recorded on a Bruker System 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient (^{1}H: 600.13 MHz, ^{13}C 150.90 MHz). Resonances are reported in parts per

million (ppm) relative to tetramethylsilane (TMS). The *d*-scale was calibrated to the respective solvent resonance of $CHCl_3$ or CH_2Cl_2 or toluene for ^1H spectra and for ^{13}C spectra on the middle resonance of the $CDCl_3$ triplet and the CD_2Cl_2 pentet.

1.5. UV-vis spectroscopy

Solution UV-vis spectra were recorded on a Shimadzu UV-2700 spectrophotometer equipped with a CPS-100 electronic temperature control cell positioner. For studies in solution, samples were prepared in a solvent (dichloromethane (DCM), toluene, and dimethylacetamite (DMAc)) and measured in quartz cuvettes (Hellma Analytics high precision cell cuvettes) at 25 °C.

1.6. Liquid Chromatography-Mass Spectrometry (LC-MS)

LC-MS measurements were performed on an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SZ), autosampler (WPS 3000TSL) and a temperature-controlled column compartment (TCC 3000). Separation was performed on a C_{18} HPLC column (Phenomenex Luna 5µm, 100 Å, 250 × 2.0 mm) operating at 40 °C. Water (containing 5 mmol·L^{-1} ammonium acetate) and acetonitrile were used as eluents. A gradient of acetonitrile: H_2O, 5:95 to 100:0 (v/v) in 7 min at a flow rate of 0.40 mL·min^{-1} was applied. The flow was split in a 9:1 ratio, where 90% of the eluent was directed through a DAD UV-detector (VWD 3400, Dionex) and 10% was infused into the electrospray source. Spectra were recorded on an LTQ Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the *m*/*z* range 74-1822 using premixed calibration solutions (Thermo Scientific). A constant spray voltage of 3.5 kV, a dimensionless sheath gas, and a dimensionless auxiliary gas flow rate of 5 and 2 were applied, respectively. The capillary temperature was set to 300 °C, the S-lens RF level was set to 68, and the aux gas heater temperature was set to 100 °C.

1.7. Electrospray Ionization-Mass Spectrometry (ESI-MS)

(Direct Injection) ESI-MS spectra were recorded on a Q Exactive Plus (Orbitrap) mass spectrometer (Thermo Fisher Scientific*,* San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the *m*/*z* range 74-1822 using premixed calibration solutions (Thermo Scientific) and for the high mass mode in the m/z range of 600-8000 using ammonium hexafluorophosphate solution. A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 5 and 3 were applied, respectively.

1.8. Dynamic Light Scattering (DLS)

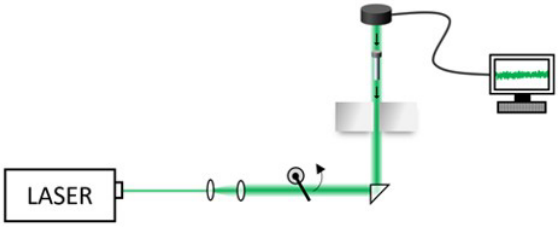
DLS experiments were performed on a Malvern Zetasizer Nano Z at 25 °C. A quartz cuvette (10 x 2 mm) was used for the experiment in DCM solvent.

1.9. Fourier Transform Infrared (FT-IR) spectroscopy

Infrared (IR) spectra were recorded in the region 4000–400 cm^{-1} with a resolution of 4 cm^{-1} on a Bruker Alpha-P FTIR spectrometer equipped with a room temperature DLaTGS detector, and a diamond attenuated total reflection (ATR) unit. The background was recorded prior to each experiment and subtracted from acquired data using the OPUS software. For all spectra (samples and background), 64 scans were averaged.

Laser Experiments

All laser experiments were conducted using the apparatus shown in Figure S1.[1] The light source was an Opotek Opolette 355 OPO, producing 7 ns, 20 Hz pulses with a flattop spatial profile. The output beam was initially passed through a beam expander (-50 mm and 100 mm lens combination) to ensure it is sufficiently large to uniformly irradiate the entire sample volume. The beam subsequently passes through an electronic shutter and is directed upwards using a UV silica right angle prism. Finally, the beam enters the sample, suspended in an aluminum block, from below. The laser energy deposited into the sample was measured above the aluminum block before and after experiments using a Coherent EnergyMax thermopile sensor (J-25MB-LE) to account for any power fluctuations during irradiation.



***Scheme S1**. Schematic diagram of apparatus used for laser experiments.*

For laser measurements, samples were prepared in suitable solvents (e.g.,DCM) in either a 10 mm x 10 mm quartz cuvette capped with a PTFE septum or laser vials (8 mm in diameter). Precise photons numbers were determined from the laser pulse energy using the following relation:

$$N_{\mathrm{p}} = \frac{P\lambda t}{hc} \quad (\mathrm{Eq\ S1})$$

Where:

P (W): actual laser power passing through the substrate. $P = E_{pulse} f_{rep} T_{\lambda}$, where E_{pulse} is the pulse energy recorded above the sample holder (without sample container), f_{rep} is the laser repetition rate (20 Hz), and T_{l} is the wavelength dependent transmission of the sample container (e.g., UV-vis cuvette or glass vial). The T_{λ} values for the glass vials used in the current study can be found in our previous work.[1, 2]

λ (m): wavelength of the incident radiation.

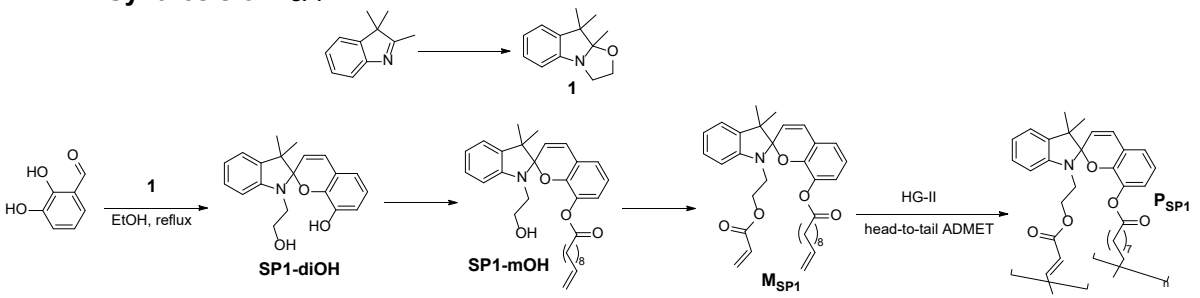
t (s): irradiation time.

h: Planck's constant ($6.626 \cdot 10^{-34}$ J·s).

c: speed of light ($\approx 3.0 \cdot 10^{8}$ m·s^{-1}).

2. Synthesis protocol

2.1. Synthesis of P_{SP1}



***Scheme S2**. Synthesis route for M_{SP1} and P_{SP1}.*

2.1.1. Synthesis of compound 1

A solution of 2,3,3-trimethylindolenine (5.0 g, 31.4 mmol, 1.0 eq) and 2-bromoethanol (4.9 mL, 47.1 mmol, 1.2 eq) in 40 mL acetonitrile (ACN) was refluxed overnight. Upon completion, the solvent was removed under reduced pressure and a solution of KOH (120 mL, 0.32 M) was added to the residue. After stirring for approximately 30 minutes, the mixture was extracted with DCM and brine. The organic phase was dried over Na_2SO_4, followed by evaporation, yielding compound **1** as purple oil. The product was used for the next reaction without further purification. The ^{1}H NMR spectrum of the compound matches with the literature spectrum.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (td, *J* = 7.7, 1.3 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 3.87 – 3.81 (m, 1H), 3.76 – 3.69 (m, 1H), 3.62 – 3.54 (m, 1H), 3.54 – 3.48 (m, 1H), 1.43 (s, 3H), 1.39 (s, 3H), 1.18 (s, 3H).

LC-MS: calculated *m*/*z* for $C_{13}H_{18}NO^+$ $[M+H]^+$ = 204.1383, found 204.1385.

2.1.2. Synthesis of SP1-diOH

Compound **1** (1500 mg, 7.4 mmol, 1.0 eq) and 2,3-dihydroxybenzaldehyde (1020 mg, 7.4 mol, 1.0 eq) was added to 15 mL ethanol and the resulting mixture was refluxed overnight. The solvent was subsequently removed under reduced pressure. The product was obtained by crystallization in ACN:H_2O (7/3, v/v) as gray solid (1400 mg, 60% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (td, *J* = 7.7, 1.3 Hz, 1H), 7.08 (dd, *J* = 7.2, 1.3 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.79 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.75 (t, *J* = 7.7 Hz, 1H), 6.66 – 6.62 (m, 2H), 5.71 (d, *J* = 10.3 Hz, 1H), 3.79 (ddd, *J* = 11.0, 7.3, 5.1 Hz, 1H), 3.70 (dt, *J* = 11.1, 5.5 Hz, 1H), 3.50 (ddd, *J* = 14.8, 7.4, 5.7 Hz, 1H), 3.31 (dt, *J* = 14.9, 5.2 Hz, 1H), 1.30 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.34, 143.42, 140.53, 136.36, 129.79, 127.85, 122.09, 120.93, 120.76, 119.75, 119.67, 118.88, 118.31, 116.03, 106.96, 105.74, 61.15, 52.30, 46.02, 20.01.

LC-MS: calculated *m*/*z* for $C_{20}H_{22}NO_3^+$ $[M+H]^+$ = 324.1595 , found 324.1596.

2.1.3. Synthesis of SP1-mOH

SP1-diOH (1 000 mg, 3.09 mmol, 1.0 eq) was dissolved in 15 mL $CHCl_3$ at 50 °C, followed by triethylamine (Et_3N) (0.43 mL, 3.09 mmol, 1.0 eq). 10-Undecenoyl chloride (0.66 mL, 3.09 mmol, 1.0 eq) was added slowly to the mixture. After 18 h, the mixture was washed with water and brine and the organic phase was dried over Na_2SO_4. The crude product was purified by flash column chromatography (cyclohexane/ethyl acetate, 7/3, v/v). The product was obtained as an oil (822 mg, 55% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.94 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.89 (d, *J* = 10.3 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.83 – 6.78 (m, 2H), 6.60 (d, *J* = 7.7 Hz, 1H), 5.88 – 5.79 (m, 1H), 5.74 (d, *J* = 10.3 Hz, 1H), 5.01 (d, *J* = 17.0 Hz, 1H), 4.95 (d, *J* = 10.2 Hz, 1H), 3.77 – 3.65 (m, 2H), 3.42 – 3.34 (m, 1H), 3.33 – 3.26 (m, 1H), 2.06 (ddt, *J* = 17.9, 13.0, 9.3 Hz, 4H), 1.39 (q, *J* = 7.6 Hz, 2H), 1.32 – 1.21 (m, 7H), 1.20 – 1.12 (m, 7H), 1.08 (q, *J* = 6.8 Hz, 2H).

LC-MS: calculated *m*/*z* for $C_{31}H_{40}NO_4$+ $[M+H]^+$ = 490.2952, found 490.2962.

2.1.4. Synthesis of M_{SP1}

To a solution of **SP1-mOH** (800 mg, 1.63 mmol, 1.0 eq) and Et_3N (0.25 mL, 1.82 mmol, 1.12 eq) in DCM (2.5 mL) acryloyl chloride (0.15 mL, 1.80 mmol, 1.1 eq) was slowly added at 0 °C. After 18 h, the reaction mixture was washed with water and brine, and the organic phase was dried over Na_2SO_4. Pure product was obtained by flash column chromatography (cyclohexane:Ethyl acetate, 9/1, v/v) as an oil (700 mg, 79% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.7 Hz, 1H), 7.03 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.94 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.89 – 6.84 (m, 2H), 6.83 – 6.78 (m, 2H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.37 (dd, *J* = 17.4, 1.4 Hz, 1H), 6.08 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.87 – 5.82 (m, 1H), 5.81 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.75 (d, *J* = 10.3 Hz, 1H), 5.01 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.95 (dd, *J* = 10.2, 1.0 Hz, 1H), 4.27 (t, *J* = 6.3 Hz, 2H), 3.46 – 3.40 (m, 1H), 3.38 – 3.32 (m, 1H), 2.09 – 1.99 (m, 4H), 1.39 (q, *J* = 7.6 Hz, 2H), 1.34 – 1.20 (m, 7H), 1.19 – 1.11 (m, 7H), 1.10 – 1.03 (m, 2H).

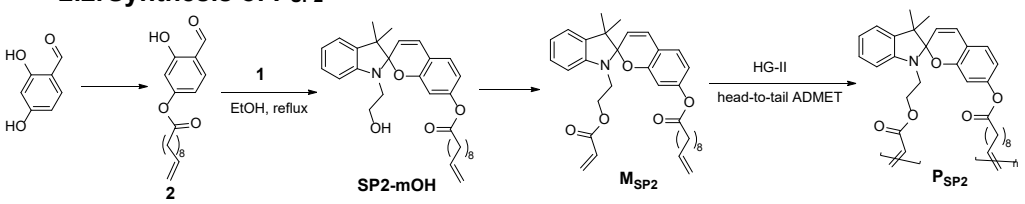
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.81, 166.13, 147.14, 145.04, 139.34, 138.04, 136.51, 130.97, 129.47, 128.50, 127.53, 126.96, 124.20, 123.01, 121.53, 119.89, 119.85, 119.51, 119.39, 63.00, 51.73, 42.51, 34.11, 33.96, 33.88, 33.87, 29.43, 29.23, 29.21, 29.07, 29.03, 25.96, 24.66, 19.67.

LC-MS: calculated *m*/*z* for $C_{34}H_{42}NO_5^+$ $[M+H]^+$ = 544.3058, found 544.3068.

2.1.5. Synthesis of P_{SP1}

Monomer $\mathbf{M_{SP1}}$ (200 mg, 0.37 mmol) was dissolved in CH_2Cl_2 in a crimp vial. The solution was heated to 40 °C upon addition of Hoveyda-Grubbs 2nd generation (HG-II) (4.6 mg, 2 mol%) and a needle was pierced into the septum to allow the ethylene gas generated from the reaction to escape. After 18 h, ethyl vinyl ether (0.05 mL) was injected into the mixture and the solution was stirred for 30 min. The polymer was precipitated in methanol and collected via centrifugation and dried under vacuum at 40 °C.

2.2. Synthesis of P_{SP2}



***Scheme S3**. Synthesis route for monomer M_{SP2} and polymer P_{SP2}.*

2.2.6. Synthesis of compound 2

2,4-Dihydroxybenzaldehyde (2 000 mg, 14.48 mmol, 1.0 eq), 10-undecenoic acid (2668 mg, 14.48 mmol, 1.0 eq) and DMAP (354 mg, 2.9 mol, 0.2 eq) were dissolved in $CHCl_3$ at 50 °C. DCC (3017 mg, 14.6 mmol, 1.05 eq) was added in portion to the reaction mixture. The reaction was stirred overnight at 50 °C. After 18 h, the precipitate was filtered out and the residue was purified by flash column chromatography (cyclohexane:ethyl acetate, 95-80/5-20, v/v), yielding the product as an oil (2 500 mg, 56% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.21 (s, 1H), 9.85 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.74 (d, *J* = 2.1 Hz, 1H), 5.81 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.00 (ddt, *J* = 17.1, 2.2, 1.6 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.08 – 2.02 (m, 2H), 1.78 – 1.71 (m, 2H), 1.41 – 1.29 (m, 10H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.59, 171.38, 163.28, 157.60, 139.30, 135.04, 118.74, 114.33, 114.07, 110.82, 34.54, 33.91, 29.40, 29.30, 29.17, 29.15, 29.02, 27.06, 24.91.

LC-MS: calculated *m*/*z* for $C_{18}H_{23}O_4^-$ $[M-H]^-$ = 303.1601, found 303.1601.

2.2.7. Synthesis of SP2-mOH

Compound **1** (1255 mg, 4.90 mol, 1.0 eq) and compound **2** (1500 mg, 4.90 mmol, 1.0 eq) were dissolved in ethanol (10 mL) and the solution was refluxed overnight. The solvent was subsequently removed and the product (1 500 mg, 62% yield) was obtained by column chromatography (cyclohexane/ethyl acetate, 95-50/50, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (td, *J* = 7.7, 1.3 Hz, 1H), 7.07 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.86 (td, *J* = 7.4, 0.9 Hz, 1H), 6.82 (dd, *J* = 10.3, 0.7 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.57 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.45 (dd, *J* = 2.2, 0.7 Hz, 1H), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.66 (d, *J* = 10.2 Hz, 1H), 5.01 – 4.96 (m, 1H), 4.92 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 3.75 (ddt, *J* = 35.3, 11.1, 6.0 Hz, 2H), 3.49 (ddd, *J* = 14.9, 7.4, 5.3 Hz, 1H), 3.31 (dt, *J* = 15.0, 5.1 Hz, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.06 – 2.01 (m, 2H), 1.69 (p, *J* = 7.5 Hz, 2H), 1.40 – 1.34 (m, 4H), 1.30 (d, *J* = 5.7 Hz, 9H), 1.17 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.13, 154.78, 151.87, 147.46, 139.32, 136.52, 129.04, 127.72, 127.36, 121.97, 119.60, 119.15, 116.55, 114.29, 113.77, 108.83, 106.84, 105.10, 61.06, 52.39, 46.26, 34.50, 33.91, 29.39, 29.32, 29.18, 29.15, 29.01, 26.02, 25.04, 20.40.

LC-MS: calculated *m*/*z* for $C_{31}H_{40}NO_4^+$ $[M+H]^+$ = 490.2951 , found 490.2952.

2.2.8. Synthesis of M_{SP2}

To a solution of **SP2-mOH** (600 mg, 1.22 mmol, 1.0 eq) and Et_3N (0.22 mL, 1.37 mmol, 1.12 eq) in DCM (2.5 mL) acryloyl chloride (0.11 mL, 1.37 mmol, 1.12 eq) was slowly added at 0 °C. After 18 h, the reaction mixture was washed with water and brine, and the organic phase was dried over Na_2SO_4. Pure product was obtained by flash column chromatography (cyclohexane:ethyl acetate, 9/1, v/v) as an oil (400 mg, 60% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (td, *J* = 7.7, 1.3 Hz, 1H), 7.07 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.85 (td, *J* = 7.4, 0.9 Hz, 1H), 6.82 (d, *J* = 10.3 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.56 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.45 – 6.44 (m, 1H), 6.38 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.08 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.84 – 5.77 (m, 2H), 5.67 (d, *J* = 10.2 Hz, 1H), 4.99 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.92 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.31 (t, *J* = 6.4 Hz, 2H), 3.57 (dt, *J* = 15.1, 6.7 Hz, 1H), 3.40 (dt, *J* = 15.1, 6.1 Hz, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 2.05 – 2.01 (m, 2H), 1.70 (p, *J* = 7.5 Hz, 2H), 1.40 – 1.34 (m, 4H), 1.33 – 1.22 (m, 9H), 1.14 (s, 3H).

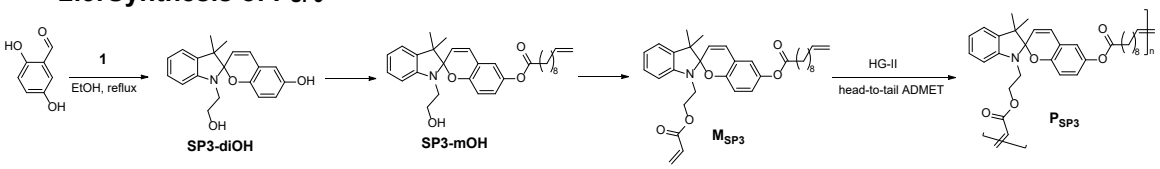
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.13, 166.14, 154.95, 151.85, 147.21, 139.30, 136.40, 131.09, 129.02, 128.41, 127.72, 127.31, 121.86, 119.50, 119.05, 116.42, 114.28, 113.60, 108.82, 106.60, 104.93, 62.90, 52.35, 42.57, 34.49, 33.91, 29.38, 29.31, 29.17, 29.15, 29.01, 25.99, 25.04, 20.15.

LC-MS: calculated *m*/*z* for $C_{34}H_{42}NO_5^+$ $[M+H]^+$ = 544.3058, found 544.3057.

2.2.9. Synthesis of P_{SP2}

Monomer $\mathbf{M_{SP2}}$ (200 mg, 0.37 mol) was dissolved in 1,2-dichlorobenzene (DCB) in a vial which can be attached to the vacuum pump. After HG-II catalyst (4.6 mg, 2 mol%) was added, the mixture was heated to 50 °C at 200 mbar. After 2 h, the pressure was reduced to 100 mbar for 1 h, after which the pressure was further reduced to 50 mbar for 30 minutes. The total reaction time was 3.5 h. Upon completion, ethyl vinyl ether (0.05 mL) was added, and the solution was stirred at ambient pressure for 30 minutes. The polymer was precipitated twice in MeOH and collected via centrifugation and dried under vacuum at 40 °C.

2.3. Synthesis of P_{SP3}



***Scheme S4**. Synthesis route for M_{SP3} and P_{SP3}.*

2.3.10. Synthesis of SP3-diOH

Compound **1** (1 800 mg, 8.82 mmol, 1.0 eq) and 2,5-dihydroxybenzaldehyde (1 217 mg, 8.82 mol, 1.0 eq) were added to 18 mL ethanol and the resulting mixture was refluxed overnight. The solvent was subsequently removed under reduced pressure. The product was obtained by crystallization in ACN:H_2O (7/3, v/v) as gray solid (1000 mg, 35% yield). ^{1}H NMR spectrum matches with the literature spectrum.[4]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (td, *J* = 7.7, 1.3 Hz, 1H), 7.07 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.84 (td, *J* = 7.4, 0.9 Hz, 1H), 6.71 (d, *J* = 10.2 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.55 – 6.51 (m, 3H), 5.66 (d, *J* = 10.2 Hz, 1H), 3.80 (ddd, *J* = 11.2, 6.2, 4.8 Hz, 1H), 3.73 (ddd, *J* = 11.2, 6.6, 4.5 Hz, 1H), 3.54 (ddd, *J* = 15.1, 6.7, 4.9 Hz, 1H), 3.37 (ddd, *J* = 15.0, 6.2, 4.5 Hz, 1H), 1.29 (s, 3H), 1.14 (s, 3H).

LC-MS: calculated *m*/*z* for $C_{20}H_{22}NO_3^+$ $[M+H]^+$ = 324.1595 , found 324.1587.

2.3.11. Synthesis of SP3-mOH

SP3-diOH (500 mg, 1.54 mmol, 1.0 eq) was dissolved in 18 mL $CHCl_3$ at 50 °C, followed by triethylamine (Et_3N) (0.22 mL, 1.54 mmol, 1.0 eq). 10-undecenoyl chloride (0.33 mL, 1.54 mmol, 1.0 eq) was slowly added to the mixture. After 18 h, the mixture was washed with water and brine, and the organic phase was dried over Na_2SO_4. The crude product was purified by flash column chromatography (cyclohexane/ethyl acetate, 7/3, v/v). The product was obtained as an oil (490 mg, 65% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (td, *J* = 7.7, 1.3 Hz, 1H), 7.09 – 7.07 (m, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.78 (tt, *J* = 5.0, 2.5 Hz, 3H), 6.70 – 6.66 (m, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.72 (d, *J* = 10.2 Hz, 1H), 5.02 – 4.97 (m, 1H), 4.93 (ddt, *J* = 10.2, 2.3, 1.3 Hz, 1H), 3.79 – 3.71 (m, 2H), 3.53 – 3.46 (m, 1H), 3.37 – 3.28 (m, 1H), 2.52 (s, 2H), 2.08 – 2.02 (m, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.41 – 1.36 (m, 4H), 1.36 – 1.28 (m, 9H), 1.17 (s, 3H).

LC-MS: calculated *m*/*z* for $C_{31}H_{40}NO_4^+$ $[M+H]^+$ = 490.2952 , found 490.2946.

2.3.12. Synthesis of M_{SP3}

To a solution of **SP3-mOH** (500 mg, 1.02 mmol. 1.0 eq) and Et_3N (0.17 mL, 1.23 mmol, 1.2 eq) acryloyl chloride (0.10 mL, 1.23 mmol, 1.2 eq) was slowly added at 0 °C. After 18 h, the reaction mixture was washed with water and brine, and the organic phase was dried over Na_2SO_4. Pure product was obtained by flash column chromatography (cyclohexane/ethyl acetate, 9/1, v/v) as an oil (500 mg, 80% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.81 – 6.74 (m, 3H), 6.66 (d, *J* = 8.1 Hz, 2H), 6.38 (d, *J* = 17.3 Hz, 1H), 6.07 (dd, *J* = 17.4, 10.4 Hz, 1H), 5.85 – 5.78 (m, 2H), 5.72 (d, *J* = 10.1 Hz, 1H), 5.00 (d, *J* = 16.8 Hz, 1H), 4.94 (d, *J* = 9.8 Hz, 1H), 4.30 (t, *J* = 6.3 Hz, 2H), 3.61 – 3.55 (m, 1H), 3.40 (dt, *J* = 15.0, 6.1 Hz, 1H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.05 (td, *J* = 8.7, 4.2 Hz, 2H), 1.73 (q, *J* = 7.5 Hz, 2H), 1.42 – 1.28 (m, 13H), 1.14 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.79, 166.13, 151.66, 147.21, 143.83, 139.29, 136.39, 131.10, 129.09, 128.39, 127.74, 122.66, 121.88, 120.53, 119.52, 119.47, 118.88, 115.75, 114.31, 106.58, 104.75, 62.90, 52.44, 42.55, 34.45, 33.91, 29.41, 29.33, 29.21, 29.18, 29.02, 25.96, 25.09, 20.22.

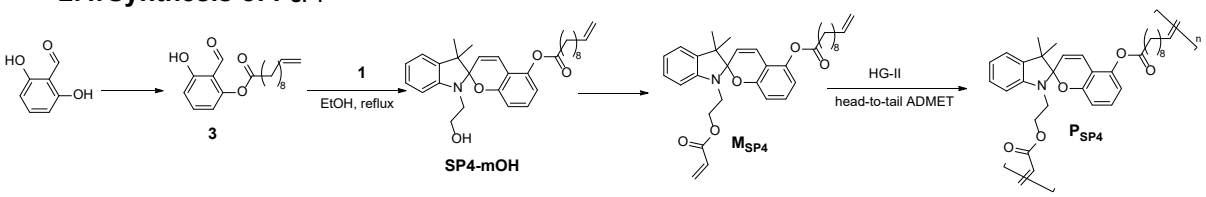
LC-MS: calculated *m*/*z* for $C_{34}H_{42}NO_5^+$ $[M+H]^+$ = 544.3058, found 544.3053.

2.3.13. Synthesis of P_{SP3}

Monomer $\mathbf{M_{SP3}}$ (200 mg, 0.37 mol) was dissolved in CH_2Cl_2 in a crimp vial. The solution was heated to 40 °C upon addition of Hoveyda-Grubbs 2nd generation (HG-II) (4.6 mg, 2 mol%) and a needle was pierced into the septum to allow the ethylene gas generated from the reaction to escape. After 18 h, ethyl vinyl ether (0.05 mL) was injected into the mixture and the solution was stirred for 30 min. The

polymer was precipitated in methanol and collected via centrifugation and dried under vacuum at 40 °C.

2.4. Synthesis of P_{SP4}



***Scheme S5**. Synthesis route for M_{SP4} and P_{SP4}.*

2.4.14. Synthesis of compound 3

2,6-Dihydroxybenzaldehyde (1 500 mg, 10.86 mmol, 1.0 eq), 10-undecenoic acid (2 000 mg, 10.86 mmol, 1.0 eq) and DMAP (265 mg, 2.17 mol, 0.2 eq) was dissolved in $CHCl_3$ at 50 °C. DCC (2260 mg, 10.97 mmol, 1.01 eq) and added in portions to the reaction mixture. The reaction was stirred overnight at 50 °C. After 18 h, the precipitate was filtered off and the residue was purified by flash column chromatography (cyclohexane/ethyl acetate, 95-80/5-20, v/v), yielding the product as an oil (1 700 mg, 51% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.21 (s, 1H), 9.85 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.74 (d, *J* = 2.1 Hz, 1H), 5.81 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.00 (ddt, *J* = 17.1, 2.2, 1.6 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.08 – 2.02 (m, 2H), 1.78 – 1.71 (m, 2H), 1.41 – 1.29 (m, 10H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.59, 171.38, 163.28, 157.60, 139.30, 135.04, 118.74, 114.33, 114.07, 110.82, 34.54, 33.91, 29.40, 29.30, 29.17, 29.15, 29.02, 24.91.

LC-MS: calculated *m*/*z* for $C_{18}H_{25}O_4^+$ $[M+H]^+$ = 303.1601, found 303.1602.

2.4.15. Synthesis of SP4-mOH

Compound **1** (1 000 mg, 4.93 mmol, 1.0 eq) and compound **3** (1 700 mg, 4.93 mmol, 1.0 eq) was dissolved in ethanol (10 mL) and the solution was refluxed overnight. The solvent was subsequently removed and the product (1 600 mg, 66% yield) was obtained by column chromatography (cyclohexane/ethyl acetate, 95-50/50, v/v).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (td, *J* = 7.7, 1.3 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.88 – 6.83 (m, 2H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.60 (ddd, *J* = 8.1, 2.8, 0.9 Hz, 2H), 5.83 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.73 (d, *J* = 10.4 Hz, 1H), 5.01 (ddd, *J* = 17.1, 2.1, 1.5 Hz, 1H), 4.95 (ddt, *J* = 10.2, 2.3, 1.3 Hz, 1H), 3.77 (ddd, *J* = 11.2, 7.2, 5.0 Hz, 1H), 3.72 (dt, *J* = 11.2, 5.5 Hz, 1H), 3.50 (ddd, *J* = 14.9, 7.3, 5.5 Hz, 1H), 3.32 (dt, *J* = 15.0, 5.2 Hz, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.14 – 2.02 (m, 2H), 1.80 (p, *J* = 7.6 Hz, 2H), 1.42 – 1.28 (m, 13H), 1.17 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.11, 154.84, 147.38, 146.80, 139.26, 136.43, 129.69, 127.75, 123.38, 121.96, 120.41, 119.57, 114.33, 113.95, 112.92, 112.08, 106.79, 104.63, 60.99, 52.43, 46.19, 34.41, 33.92, 29.43, 29.34, 29.30, 29.19, 29.03, 25.99, 25.14, 20.40.

LC-MS: calculated *m*/*z* for $C_{31}H_{40}NO_4^+$ $[M+H]^+$ = 490.2952, found 490.2949.

2.4.16. Synthesis of M_{SP4}

To a solution of **SP4-mOH** (600 mg, 1.22 mmol, 1.0 eq) and Et_3N (0.22 mL, 1.31 eq) acryloyl chloride (0.13 mL, 1.60 mmol, 1.30 eq) was slowly added at 0 °C. After 18 h, the reaction mixture was washed with water and brine, and the organic phase was dried over Na_2SO_4. Pure product was obtained by flash column chromatography (cyclohexane/ethyl acetate, 9/1, v/v) as an oil (450 mg, 68% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (td, *J* = 7.7, 1.3 Hz, 1H), 7.09 – 7.04 (m, 2H), 6.90 – 6.82 (m, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 8.2 Hz, 2H), 6.37 (dd, *J* = 17.4, 1.4 Hz, 1H), 6.07 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.89 – 5.78 (m, 2H), 5.72 (d, *J* = 10.4 Hz, 1H), 5.01 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.94 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.60 (dt, *J* = 13.9, 6.6 Hz, 1H), 3.41 (dt, *J* = 15.1, 6.2 Hz, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.10 – 2.03 (m, 2H), 1.80 (p, *J* = 7.6 Hz, 2H), 1.51 – 1.32 (m, 12H), 1.29 (s, 3H), 1.13 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.05, 166.14, 155.04, 147.22, 146.77, 139.27, 136.34, 131.08, 129.64, 128.39, 127.74, 123.39, 121.89, 120.35, 119.51, 114.34, 113.78, 112.92, 111.86, 106.64, 104.63, 62.91, 52.52, 42.52, 34.42, 33.92, 29.43, 29.34, 29.30, 29.19, 29.03, 25.88, 25.15, 20.17.

LC-MS: calculated *m*/*z* for $C_{34}H_{42}NO_5^+$ $[M+H]^+$ = 544.3058, found 544.3062.

2.4.17. Synthesis of P_{SP4}

Monomer **M_{SP4}** (100 mg, 0.183 mol) was dissolved in CH_2Cl_2 in a crimp vial. The solution was heated to 40 °C upon addition of Hoveyda-Grubbs 2nd generation (HG-II) (2.3 mg, 2 mol%) and a needle was pierced into the septum to allow the ethylene gas generated from the reaction to escape. After 18 h, ethyl vinyl ether (0.02 mL) was injected into the mixture and the solution was stirred for 30 min. The polymer was precipitated in methanol and collected via centrifugation and dried under vacuum at 40 °C.

3. Dynamic Light Scattering (DLS)

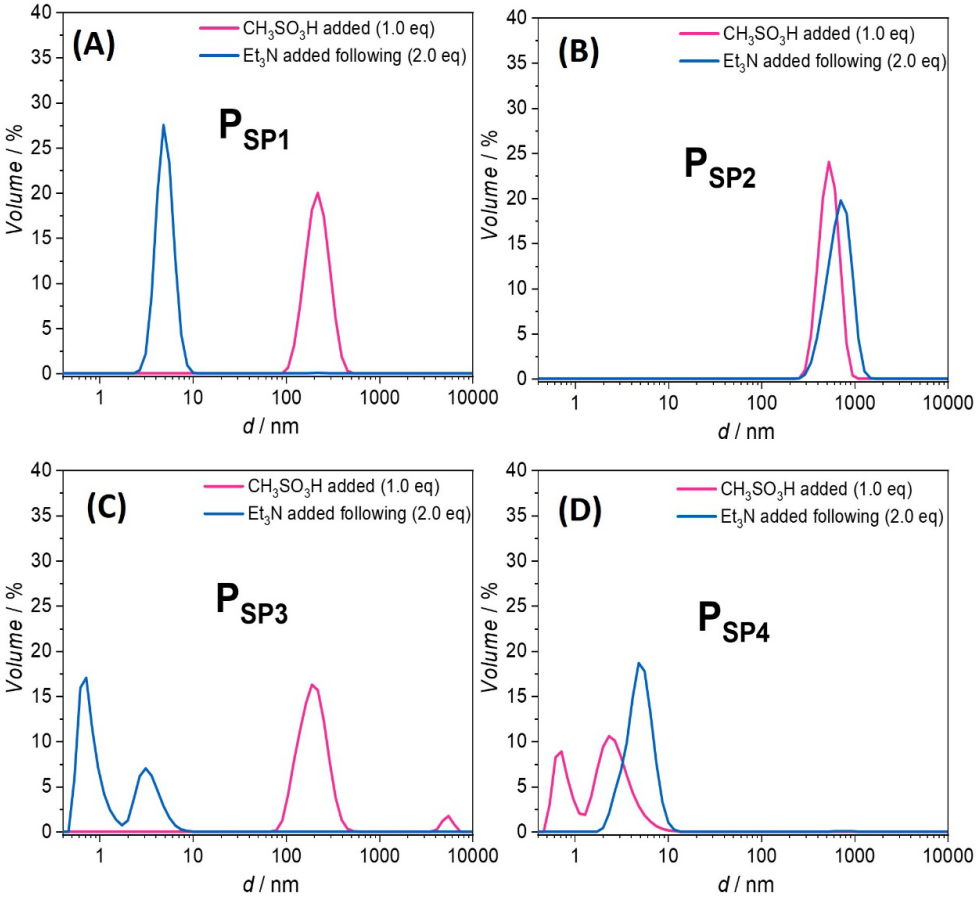


Figure S1. *DLS size distribution (Volume%) recorded for four polymers after addition of MsOH (1.0 eq) acid in DCM at 25 °C. The polymer solutions were kept in the dark overnight before the measurement.*

4. UV-vis spectra of PSP2 polymer film on quart slide

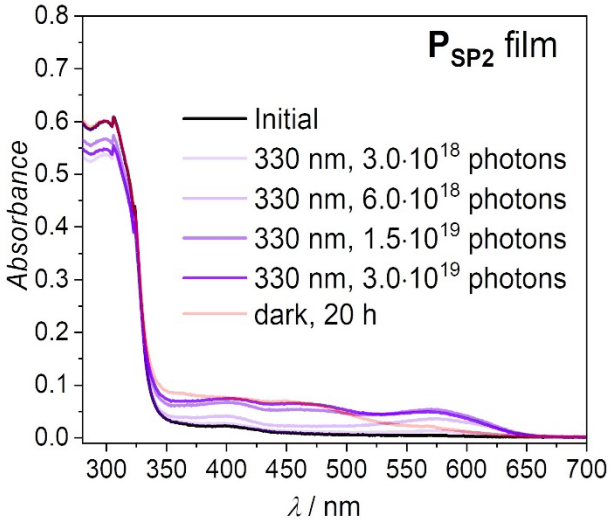


***Figure S2**. UV-vis spectra of **P_{SP2}** polymer film on a quart slide before and after 330 nm irradiation. The film was generated by spin-coating of the **P_{SP2}** solution (60 mg·mL^{-1}) in toluene and subsequently dried at reduced vacuum for 24h before the irradiation experiment (330 nm irradiation, P = 6.5 mW ± 6.5%).*

5. ^{1}H NMR spectra and SEC traces of acid-added polymer solutions

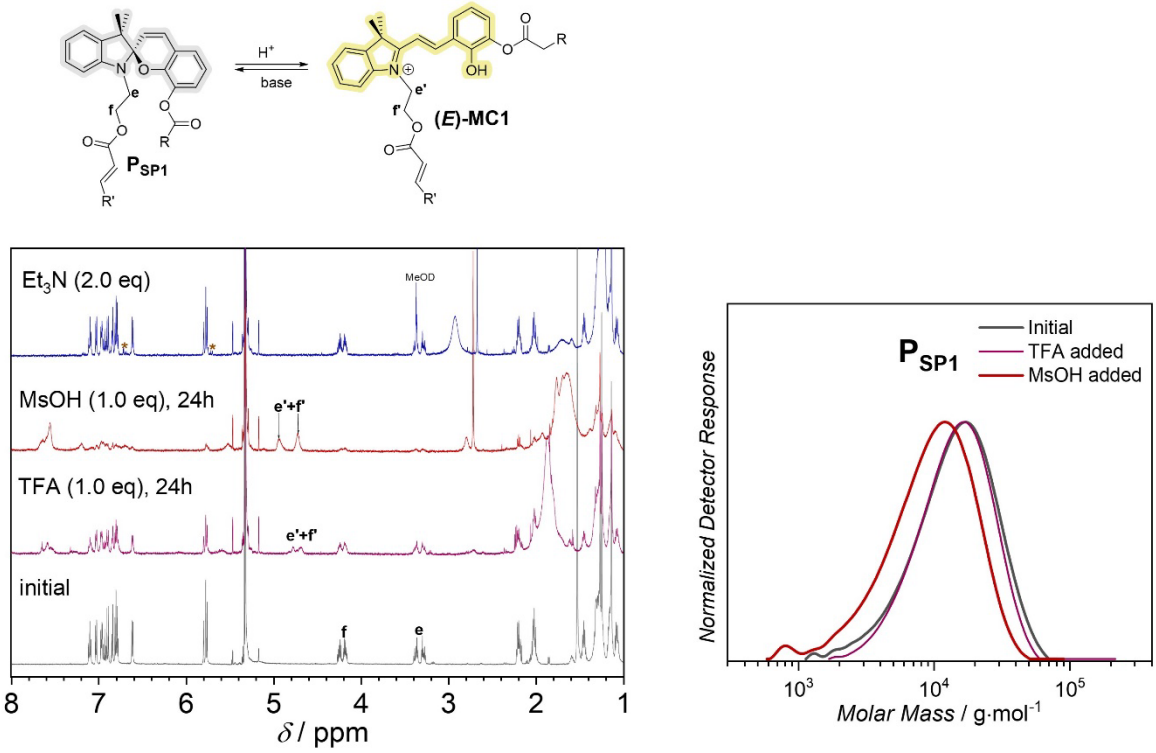


***Figure S3**. ^{1}H NMR spectra (left) and DMAc-SEC traces (right) of **P_{SP1}** solution before and after addition of TFA (1.0 eq) and MsOH (1.0 eq). The MsOH-added solution was subsequently quenched with 2.0 eq Et_3N. As can be seen in the NMR spectrum of the Et_3N-quenched polymer solution (top, blue), a small degree of degradation (most likely hydrolysis) was observed (signals marked with an asterisk). The breakage of one bond in the main chain can cause significant shift in the SEC traces. In addition, side reactions arising from the internal acrylate C=C double bonds (e.g., [2+2]-cyclization) and the damage of the chromophore can be excluded as there is no change in the corresponding resonances of the acrylate C=C double bonds and the chromophore in the Et_3N-quenched polymer solution and the pristine solution.*

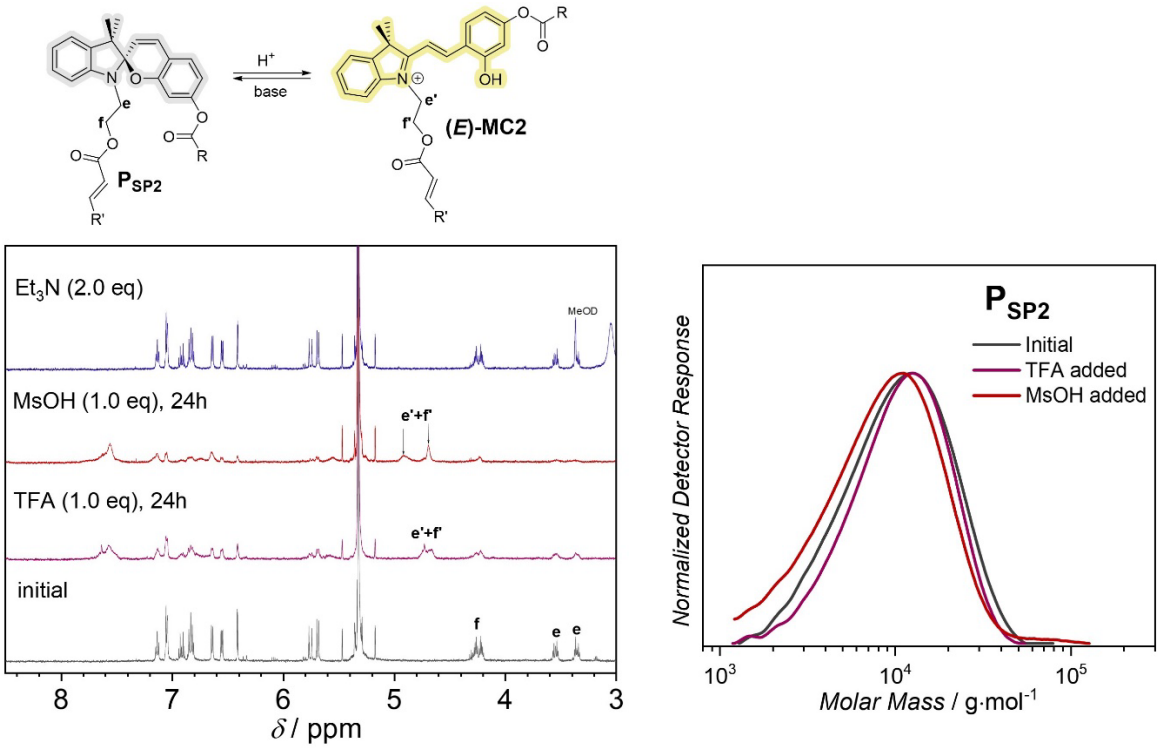


Figure S4. *^{1}H NMR spectra (left) and DMAc-SEC traces (right) of* $\mathbf{P_{SP2}}$ *solution before and after addition of TFA (1.0 eq) and MsOH (1.0 eq). The MsOH-added solution was subsequently quenched with 2.0 eq Et_3N. Insignificant damage was shown in the NMR spectrum of the Et_3N-quenched polymer solution and the corresponding SEC traces.*

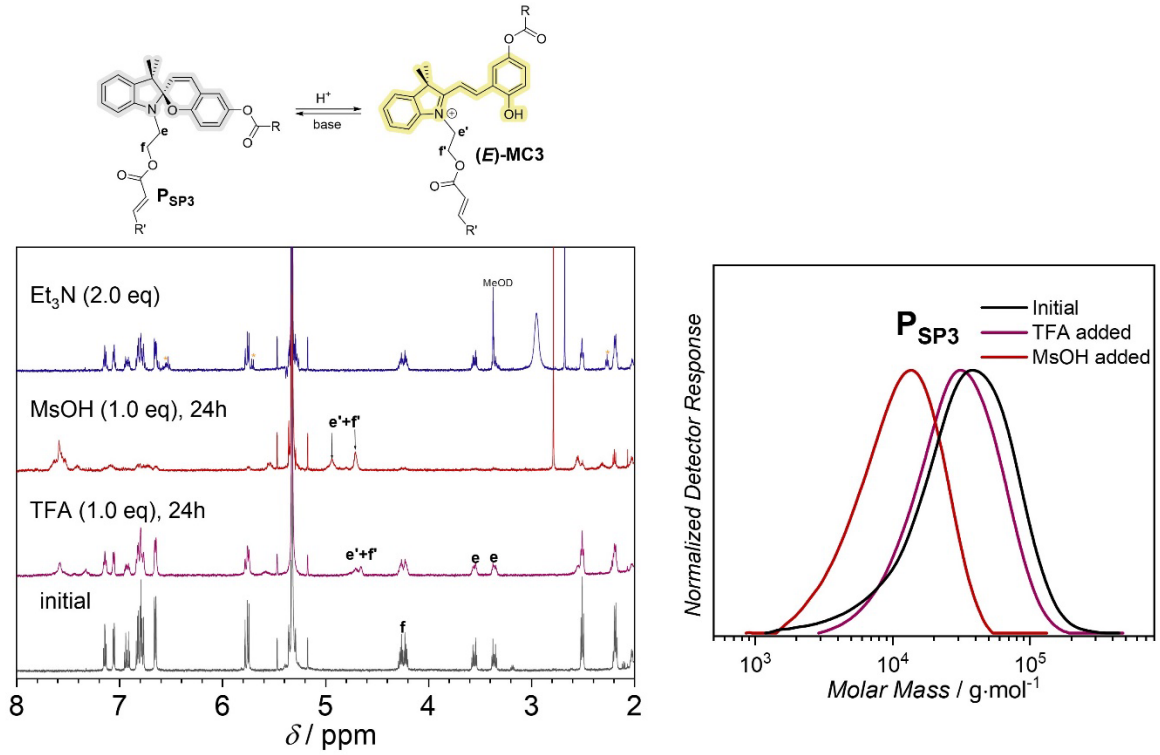


Figure S5. *^{1}H NMR spectra (left) and DMAc-SEC traces (right) of* $\mathbf{P_{SP3}}$ *solution before and after addition of TFA (1.0 eq) and MsOH (1.0 eq). The MsOH-added solution was subsequently quenched with 2.0 eq Et_3N. Significant degradation (due to hydrolysis of ester bonds) was observed in the MsOH-added solution. The NMR spectrum of the MsOH-added solution quenched with Et_3N (top, blue) also indicates significant degradation (resonances marked with an asterisk). The chromophore and the internal acrylate C=C double bonds remain intact as shown in the NMR spectrum (top, blue).*

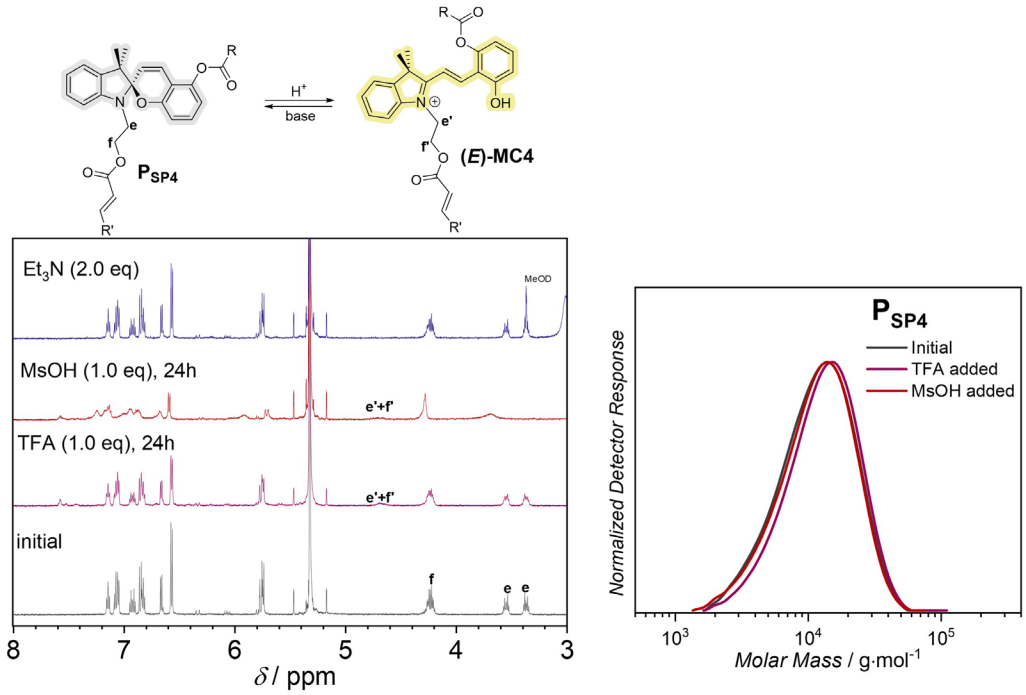


***Figure S6**. [1]H NMR spectra (left) and DMAc-SEC traces (right) of **P_{SP4}** solution before and after addition of TFA (1.0 eq) and MsOH (1.0 eq). The MsOH-added solution was subsequently quenched with 2.0 eq Et_3N. Both NMR spectrum and SEC traces confirm the resistance of the polymer solution against hydrolysis induced upon MsOH addition.*

6. UV-vis spectra of polymer solution in DMAc and Toluene

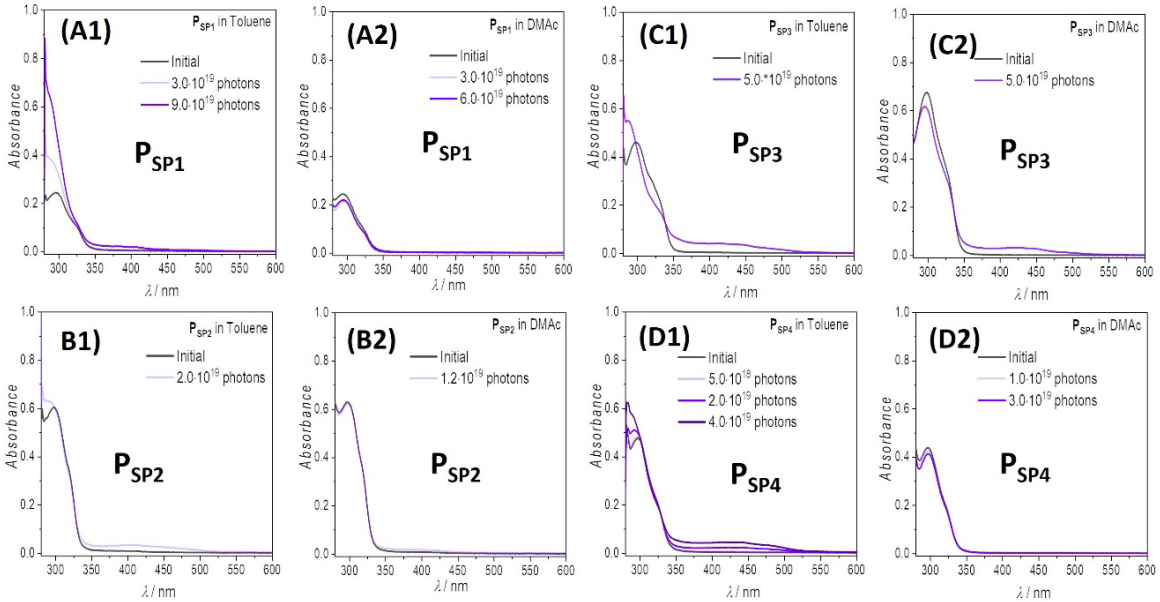


***Figure S7**. UV-vis spectra recorded for **P_{SP1}**, **P_{SP2}**, **P_{SP3}** and **P_{SP4}** before and after 330 nm irradiation in either toluene or DMAc solvent. Molar concentrations are between 50 and 150 µM.*

7. Photoirradiation of polymer solutions in DCM and control experiments

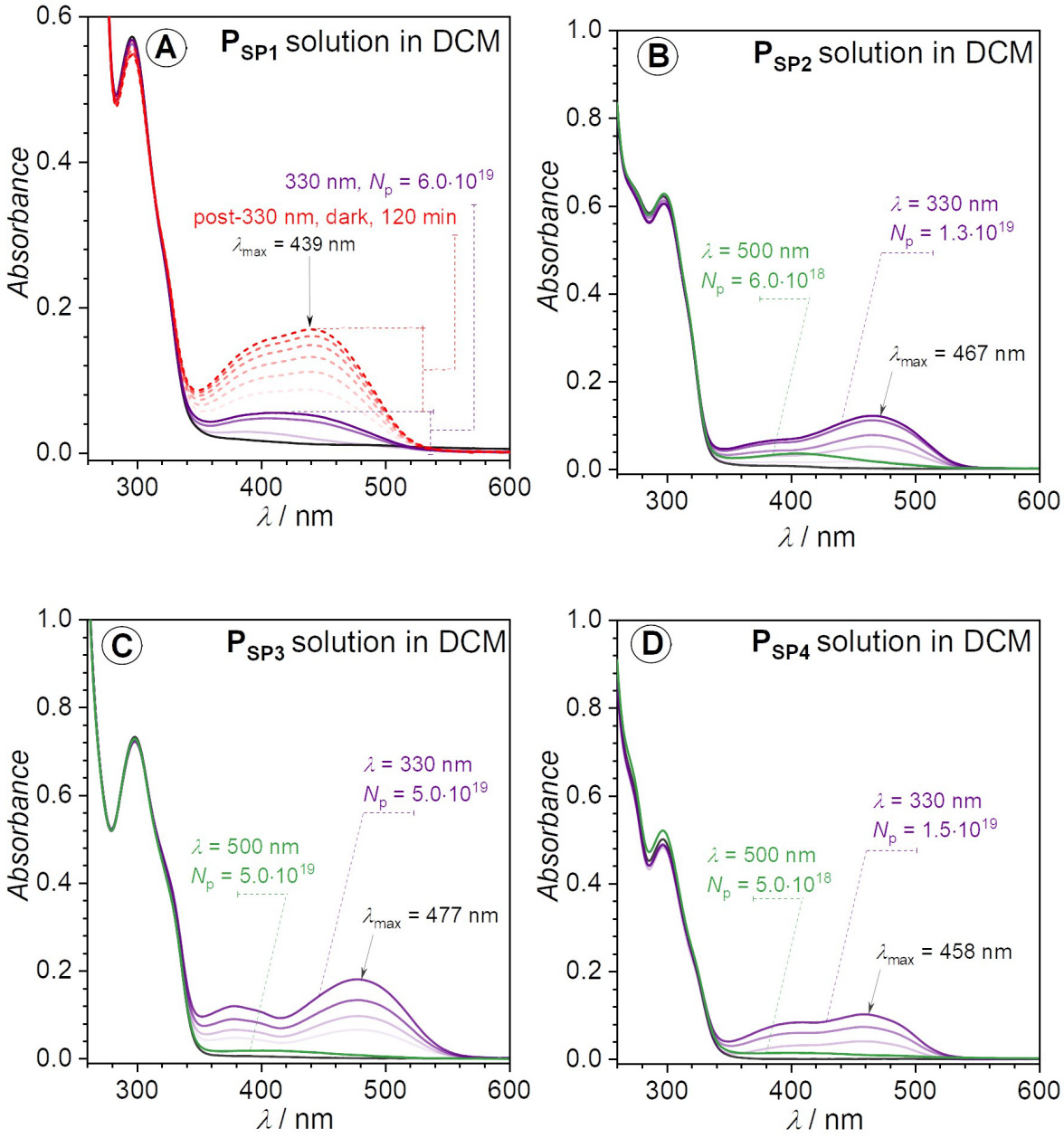


Figure S8 (continued below). *UV-vis spectra of polymer solutions in DCM upon 330 nm- irradiation (enlargement of the spectra 3A-D shown in the main text).*

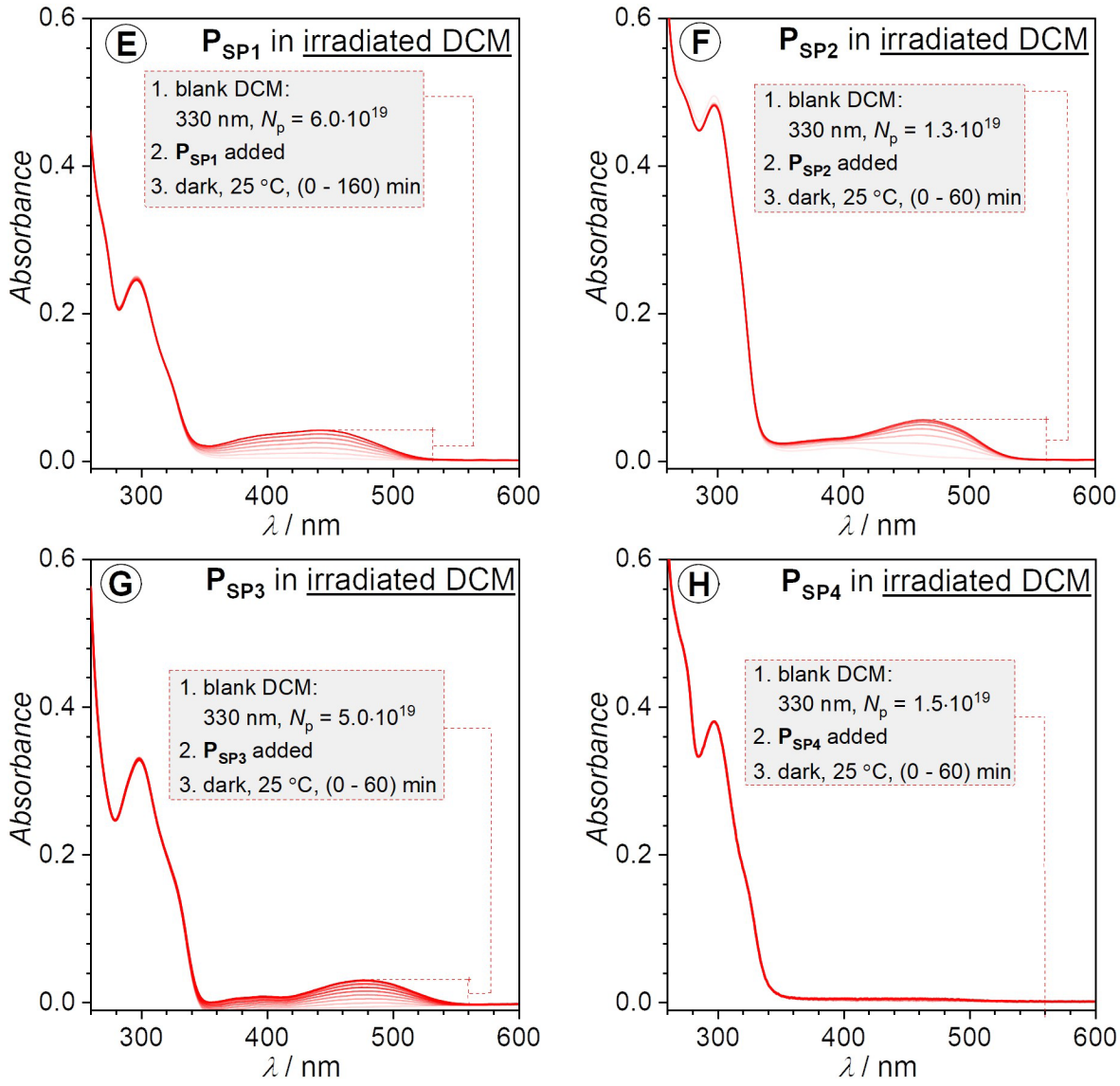


Figure S8 (continued). *UV-vis spectra of polymer solutions in DCM upon 330 nm- irradiation (enlargement of the spectra 3E-H shown in the main text).*

8. FT-IR spectra of P_{SP3}

P_{SP3}

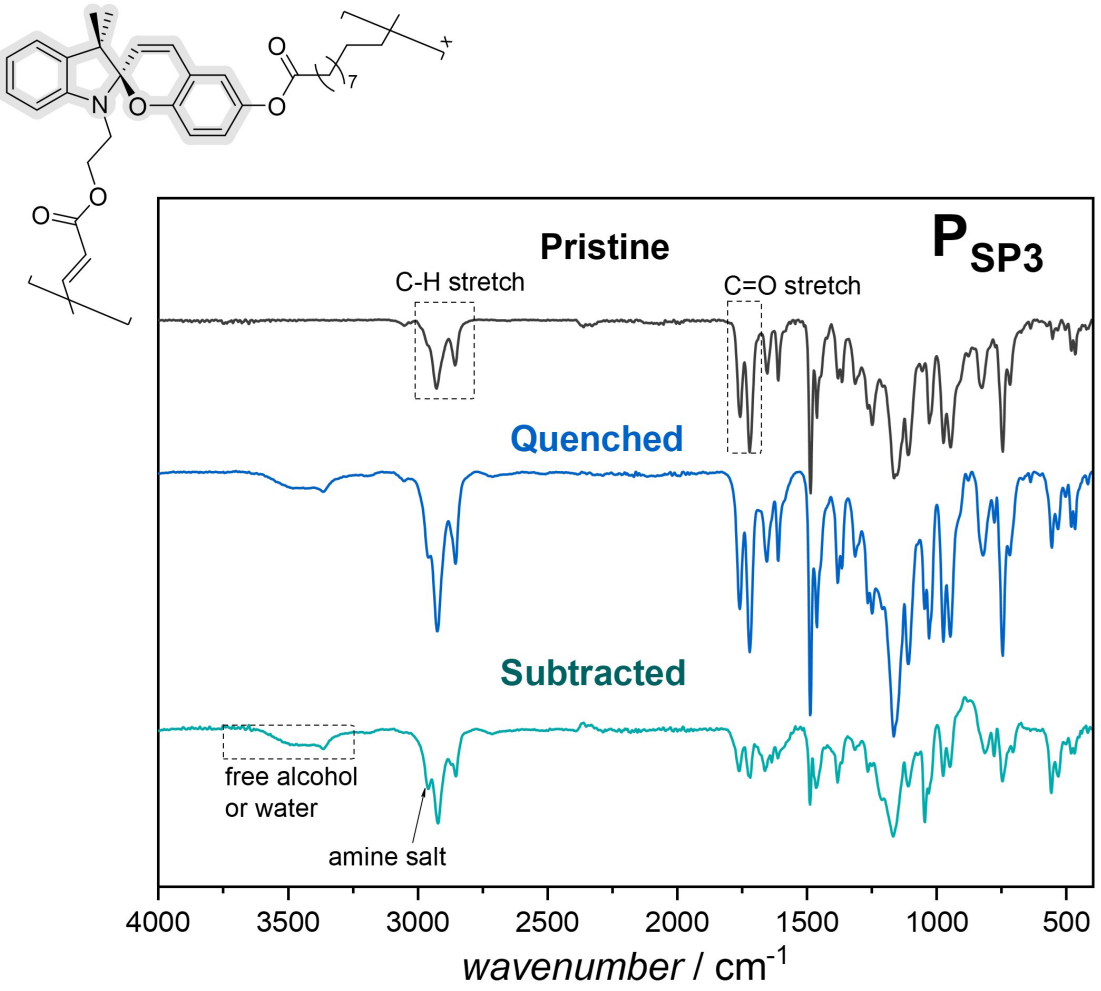


***Figure S9**. FT-IR spectra of **P_{SP3}** polymer before and after MsOH-addition (quenched with Et_3N). The MsOH-added polymer solution in DCM was quenched with Et_3N, followed by blow-drying prior to the FT-IR measurement.*

9. 1D and 2D NMR spectra of precusors, monomers and polymers

9.1. Compound 1

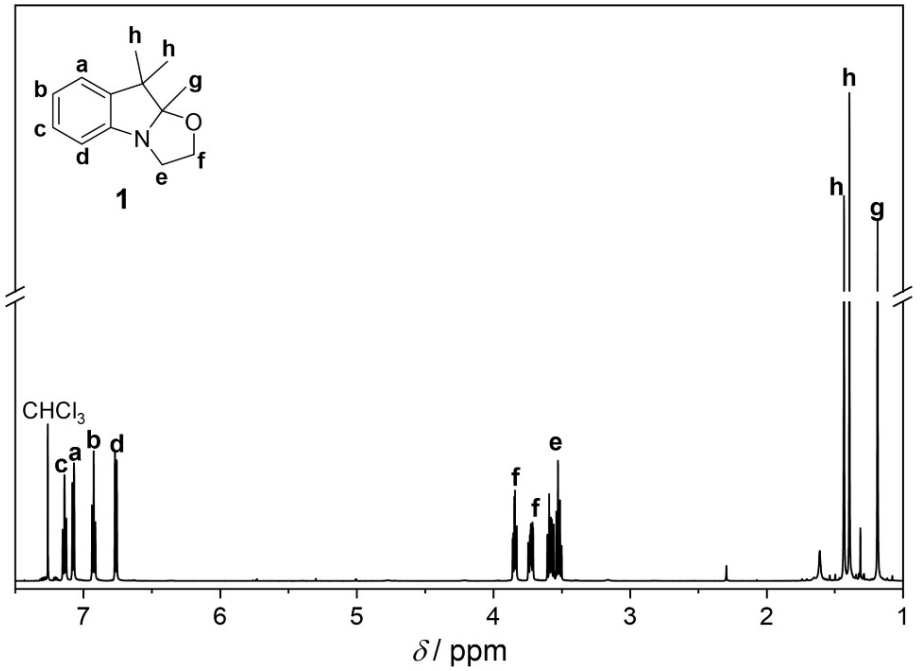


Figure S10. *^{1}H NMR spectrum (600 MHz, 16 scans) of compound **1** recorded in $CDCl_3$.*

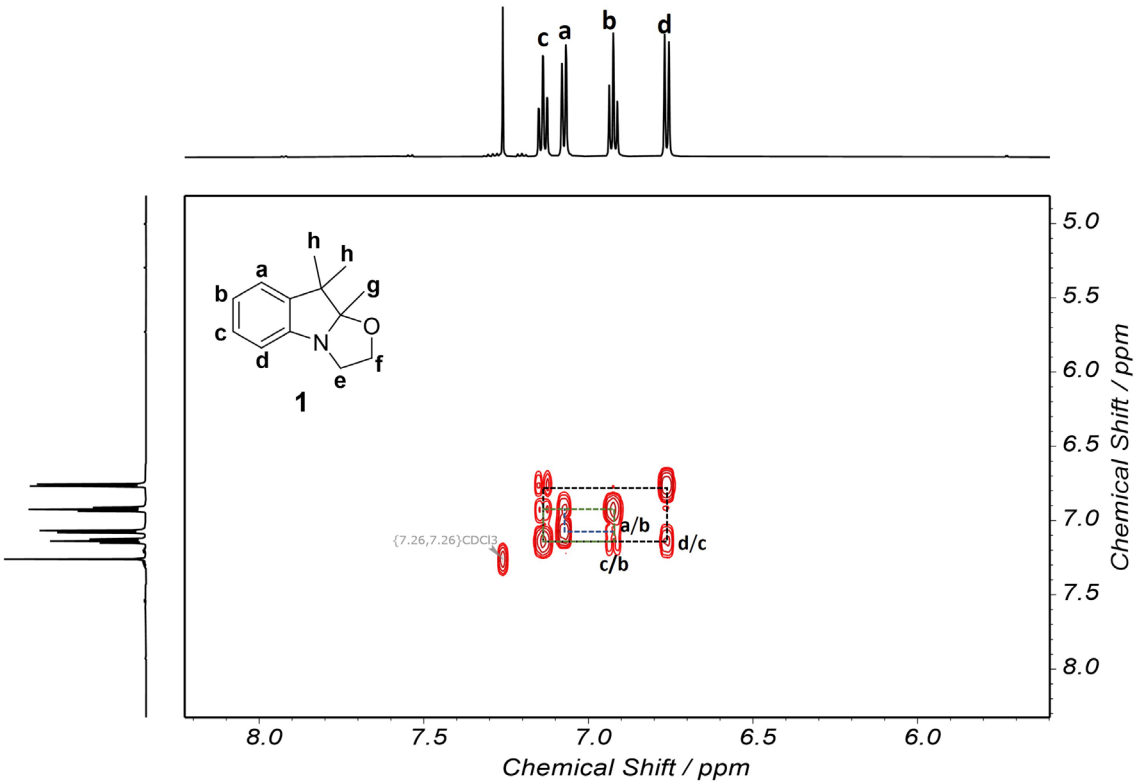


Figure S11. *COSY sectional spectrum of compound **1** recorded in $CDCl_3$.*

9.2. SP1-diOH

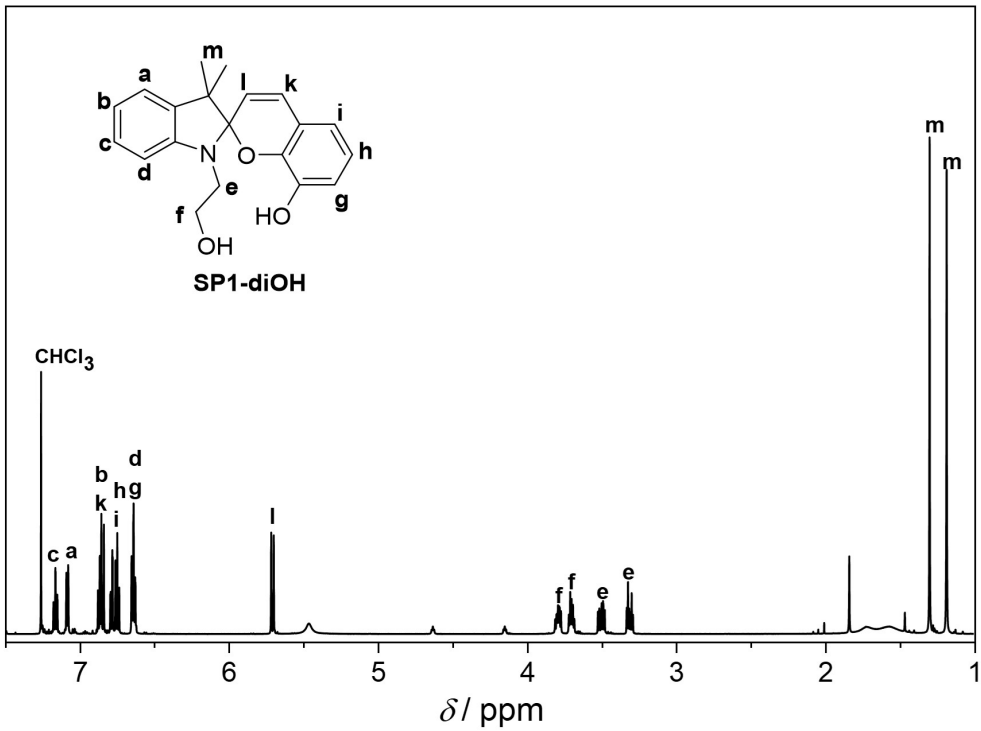


Figure S12. *^{1}H NMR spectrum (600 MHz, 16 scans) of* ***SP1-diOH*** *recorded in $CDCl_3$.*

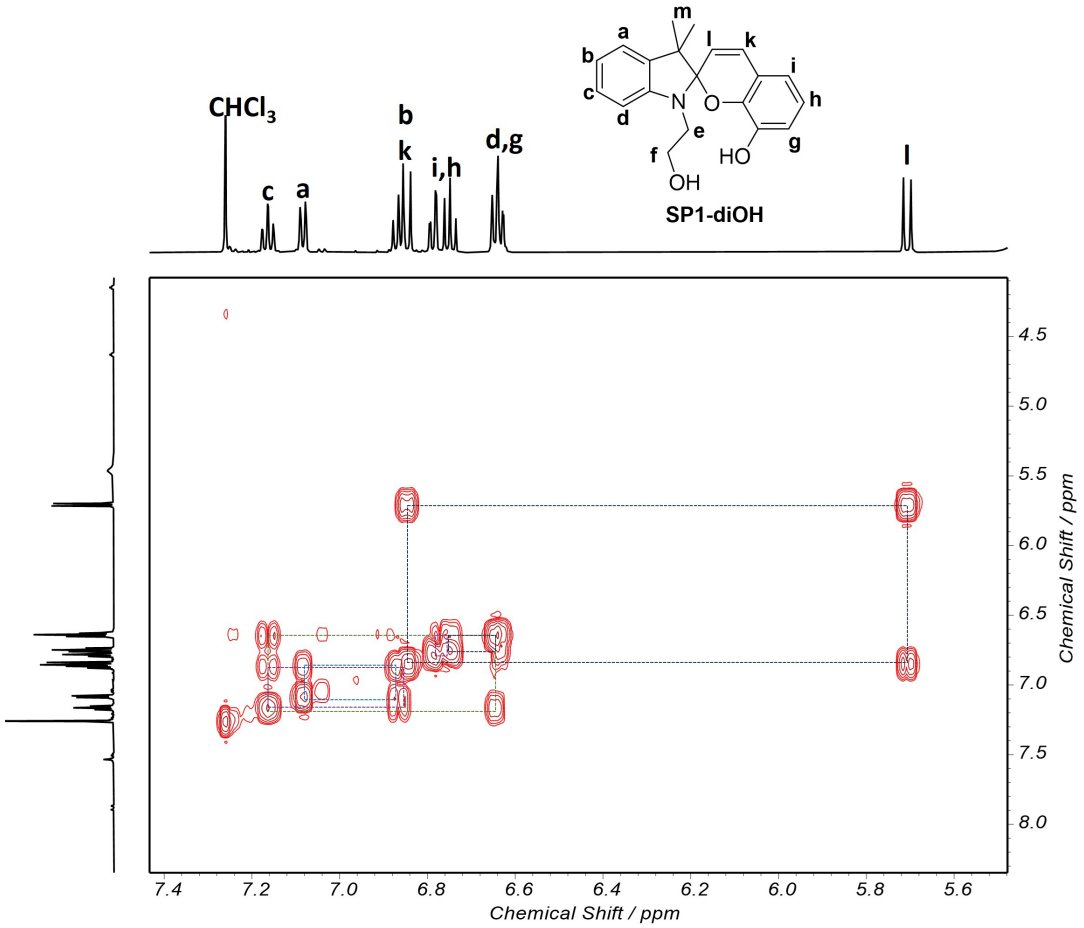


Figure S13. *COSY sectional spectrum of compound* ***SP1-diOH*** *recorded in $CDCl_3$.*

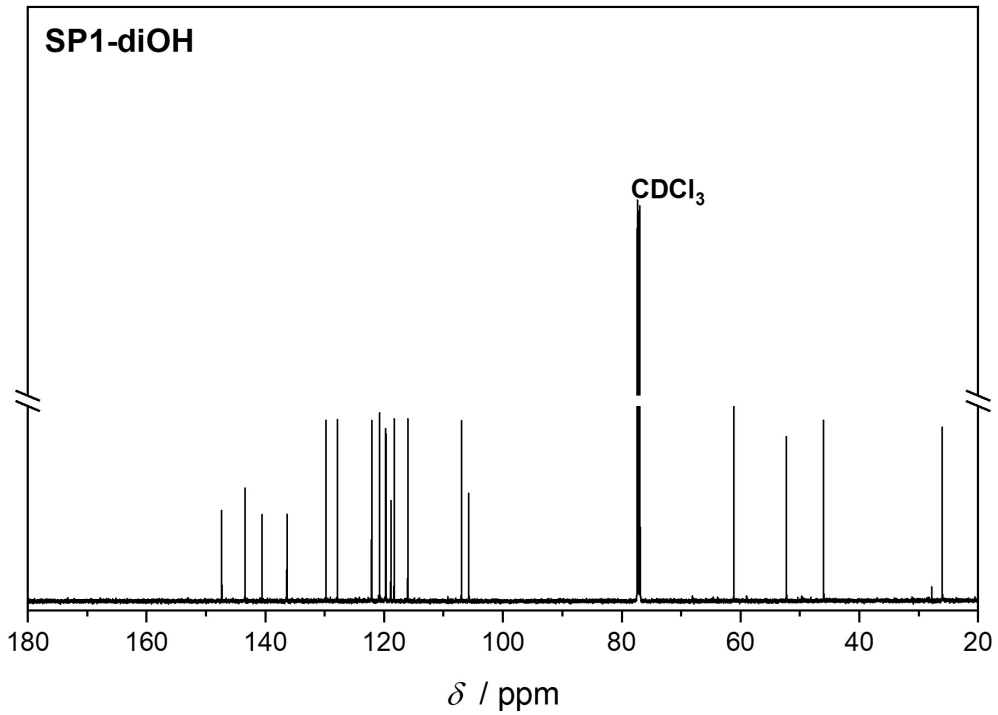


Figure S14. *^{13}C (151 MHz) NMR spectrum of* ***SP1-diOH*** *in $CDCl_3$*

9.3. SP1-mOH

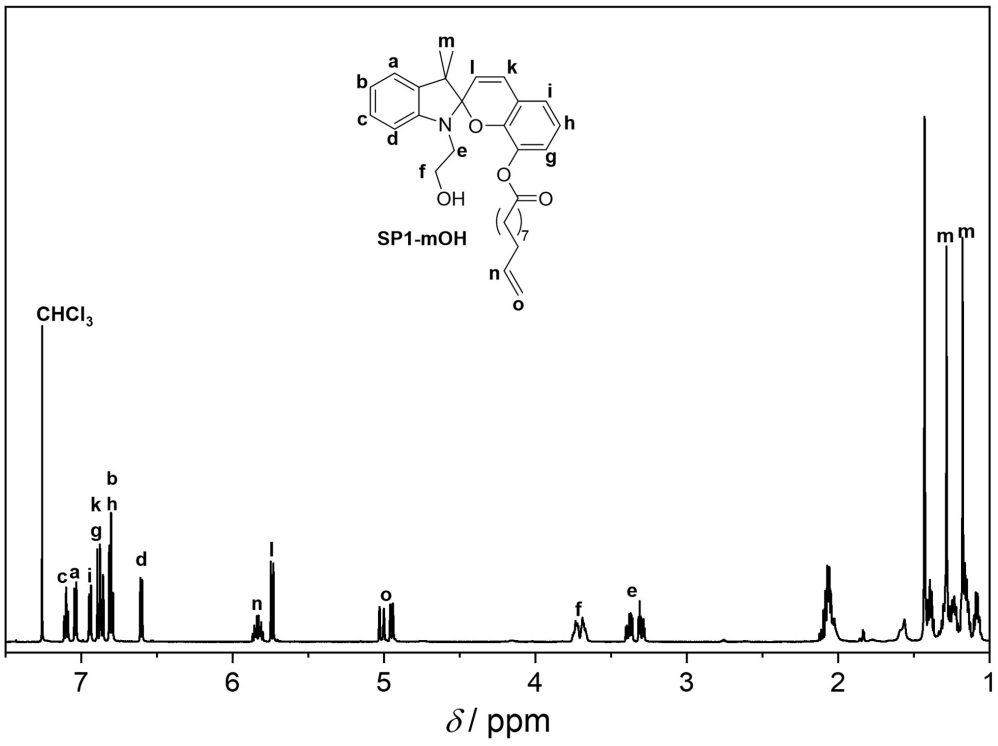


Figure S15. *^{1}H NMR spectrum (600 MHz, 16 scans) of* ***SP1-mOH*** *recorded in $CDCl_3$.*

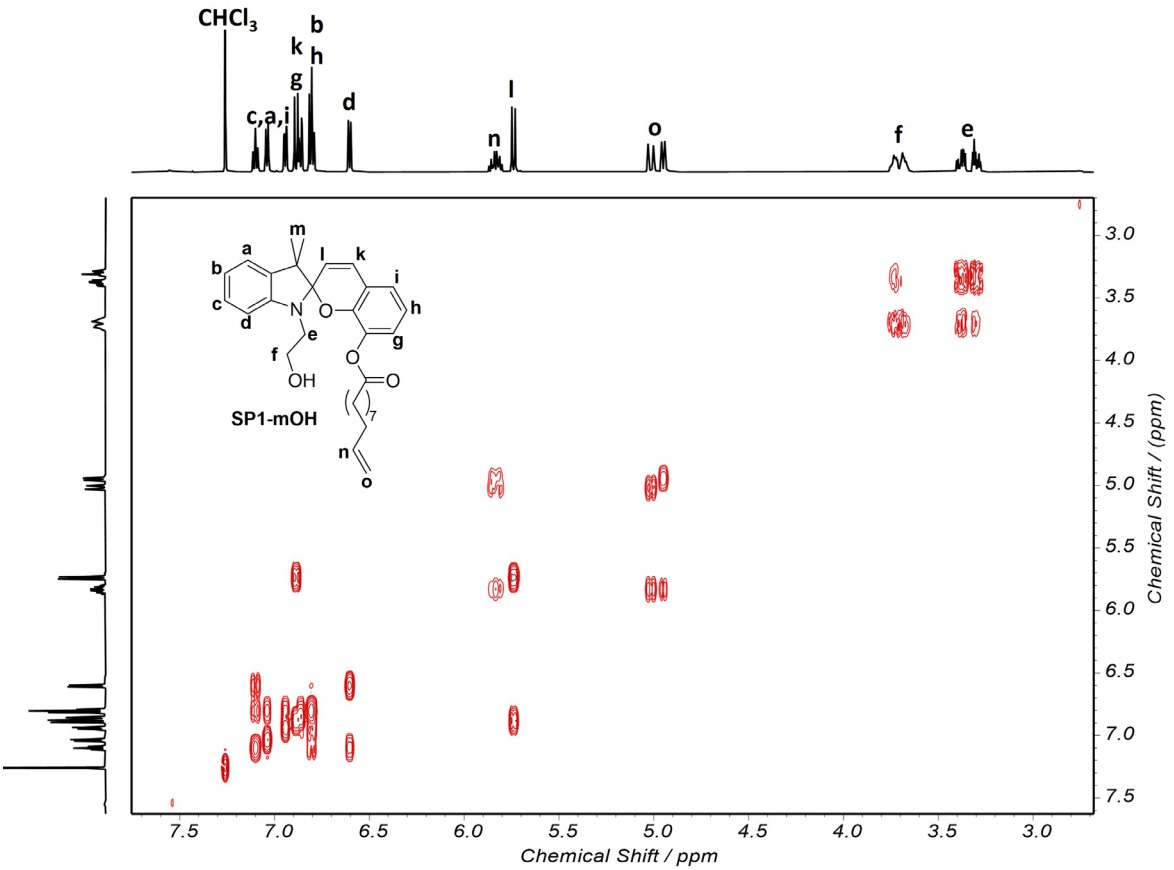


Figure S16. *COSY sectional spectrum of compound* ***SP1-mOH*** *recorded in* $CDCl_3$.

9.4. M_{SP1}

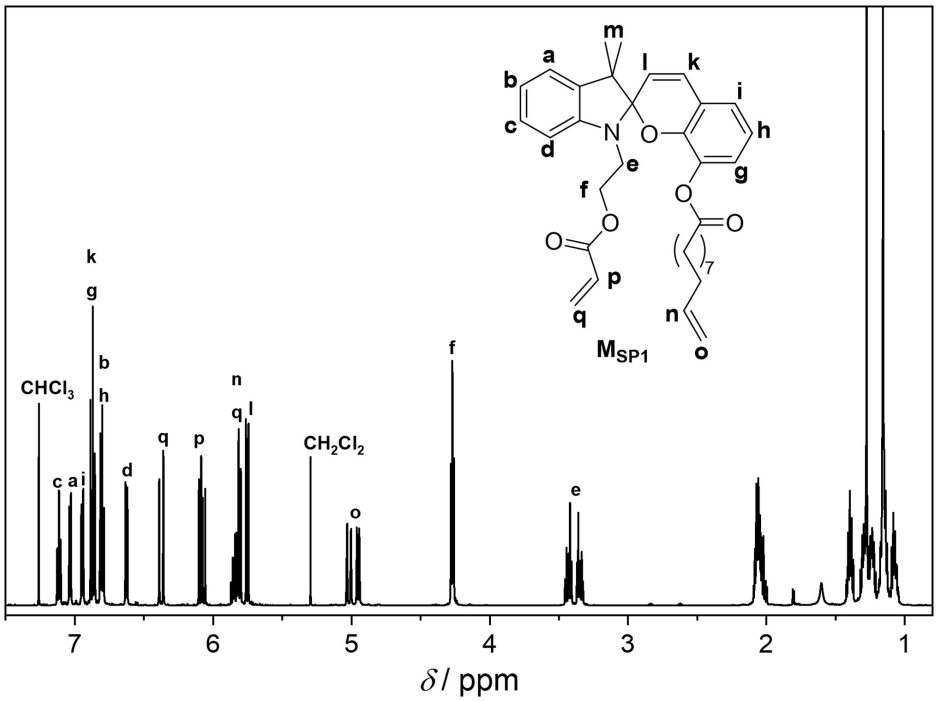


Figure S17. *^{1}H NMR spectrum (600 MHz, 16 scans) of* M_{SP1} *recorded in* $CDCl_3$.

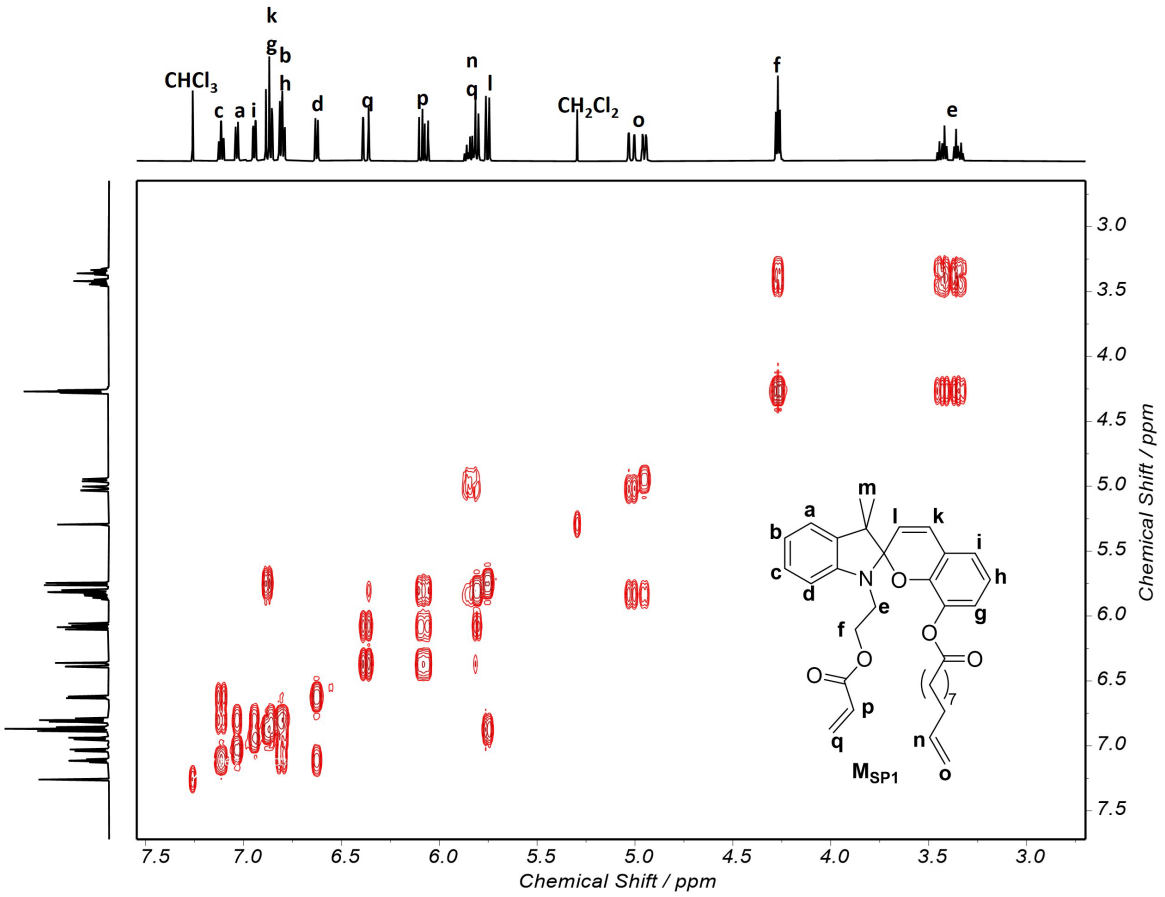


Figure S18. *COSY sectional spectrum of compound* ***M*** *recorded in* $CDCl_3$.

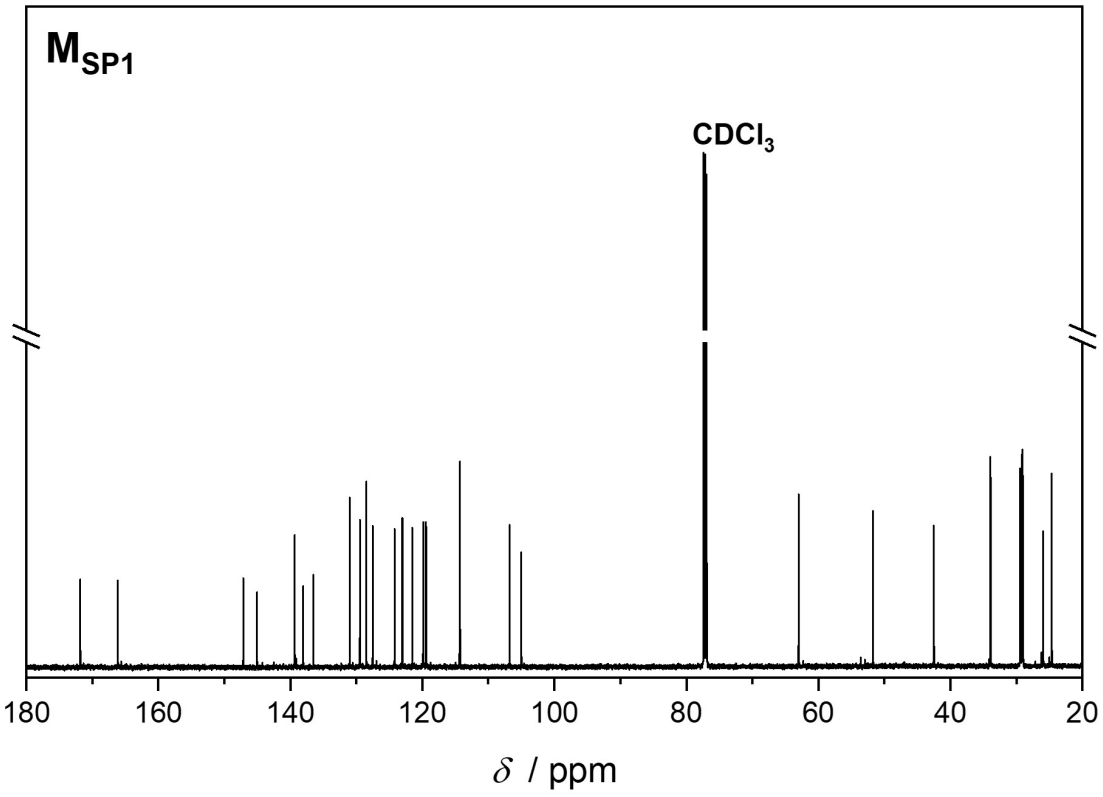


Figure S19. ^{13}C *(151 MHz) NMR spectrum of* ***M*** *in* $CDCl_3$.

9.5. P_{SP1}

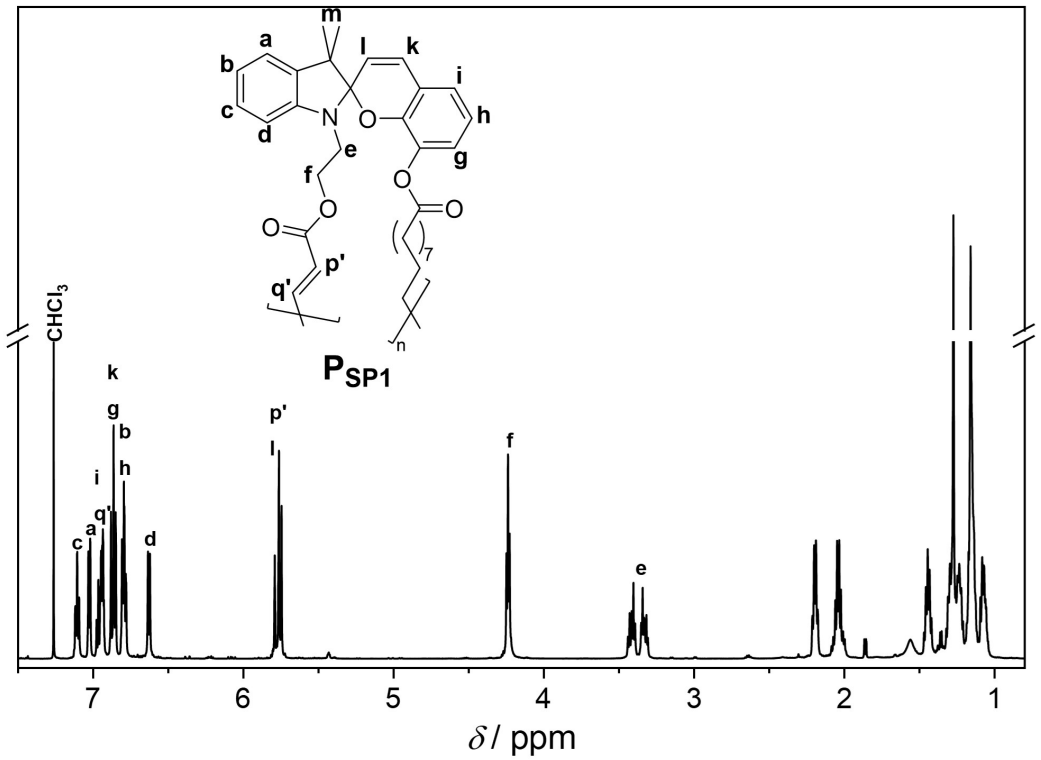


Figure S20. *^{1}H NMR spectrum (600 MHz, 32 scans) of **P_{SP1}** recorded in $CDCl_3$.*

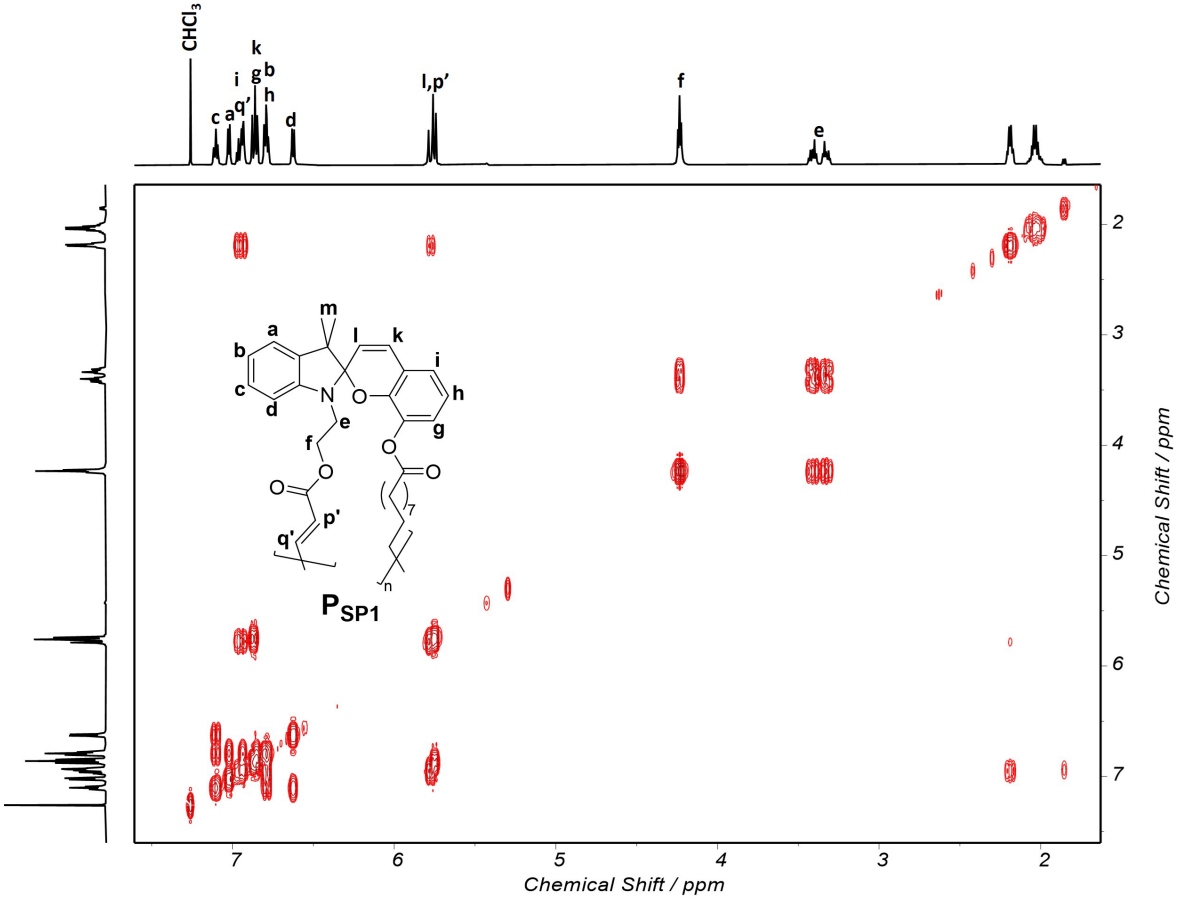


Figure S21. *COSY sectional spectrum of compound **P_{SP1}** recorded in $CDCl_3$.*

9.6. Compound 2

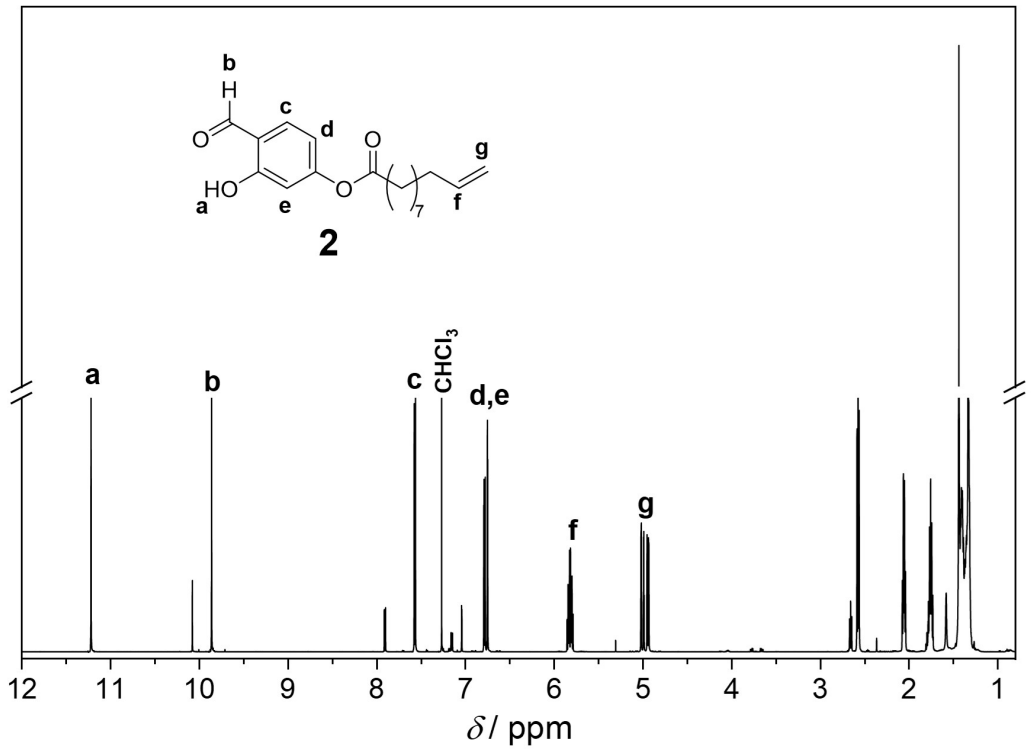


Figure S22. *^{1}H NMR spectrum (600 MHz, 16 scans) of compound **2** recorded in $CDCl_3$.*

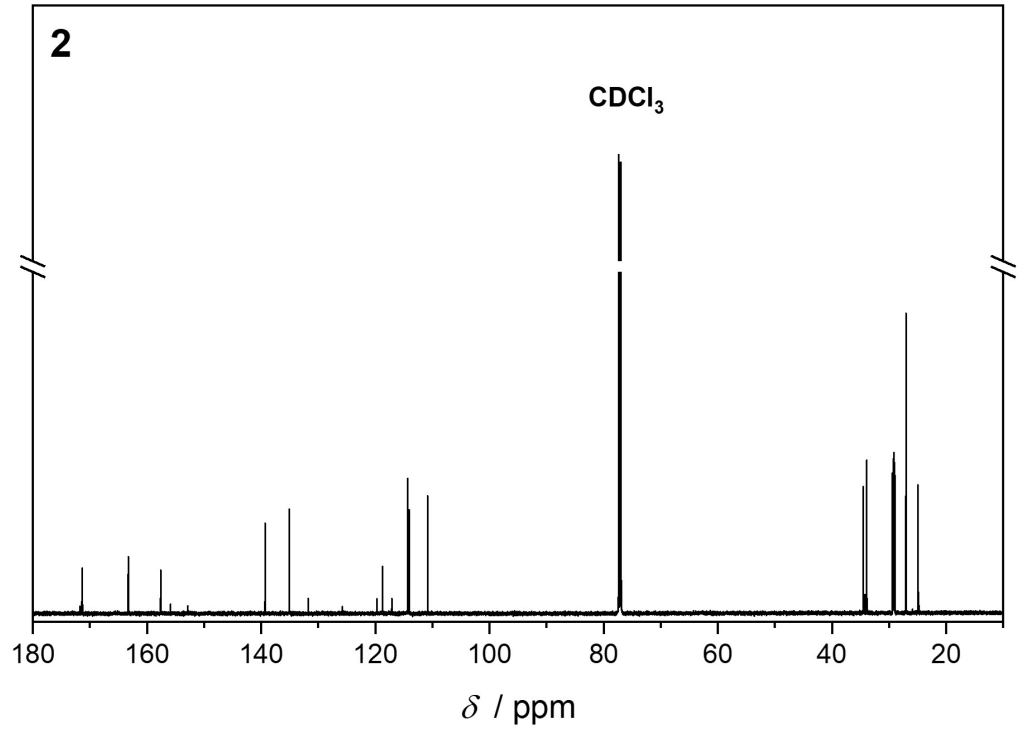


Figure S23. *^{13}C (151 MHz) NMR spectrum of compound **2** in $CDCl_3$*

9.7. SP2-mOH

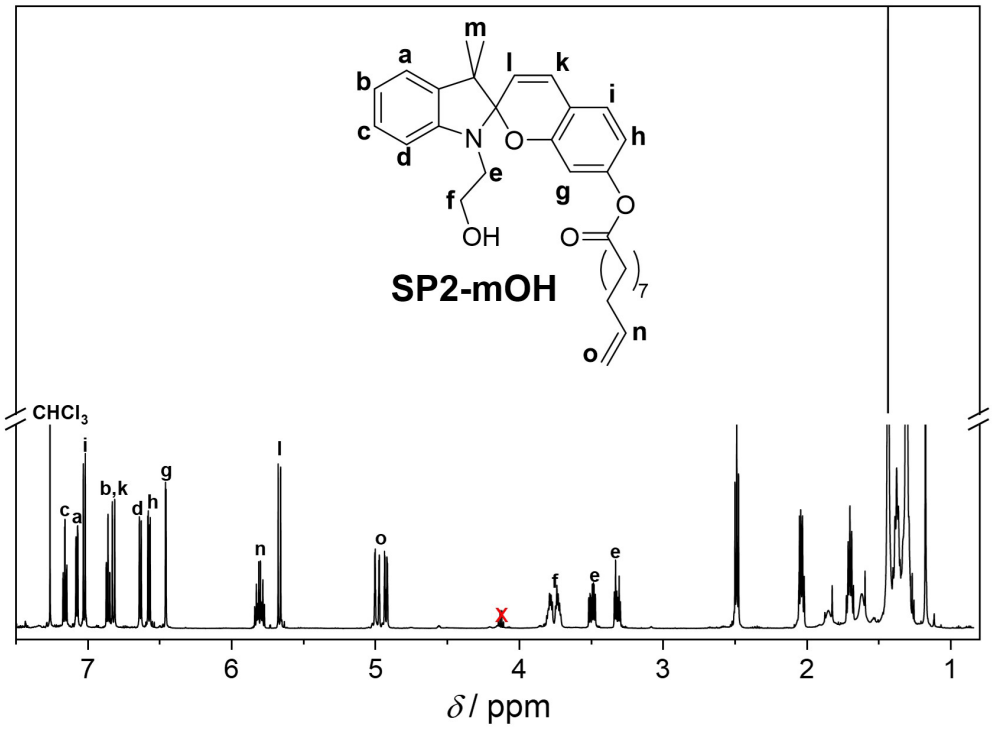


Figure S24. *^{1}H NMR spectrum (600 MHz, 16 scans) of **SP2-mOH** recorded in $CDCl_3$.*

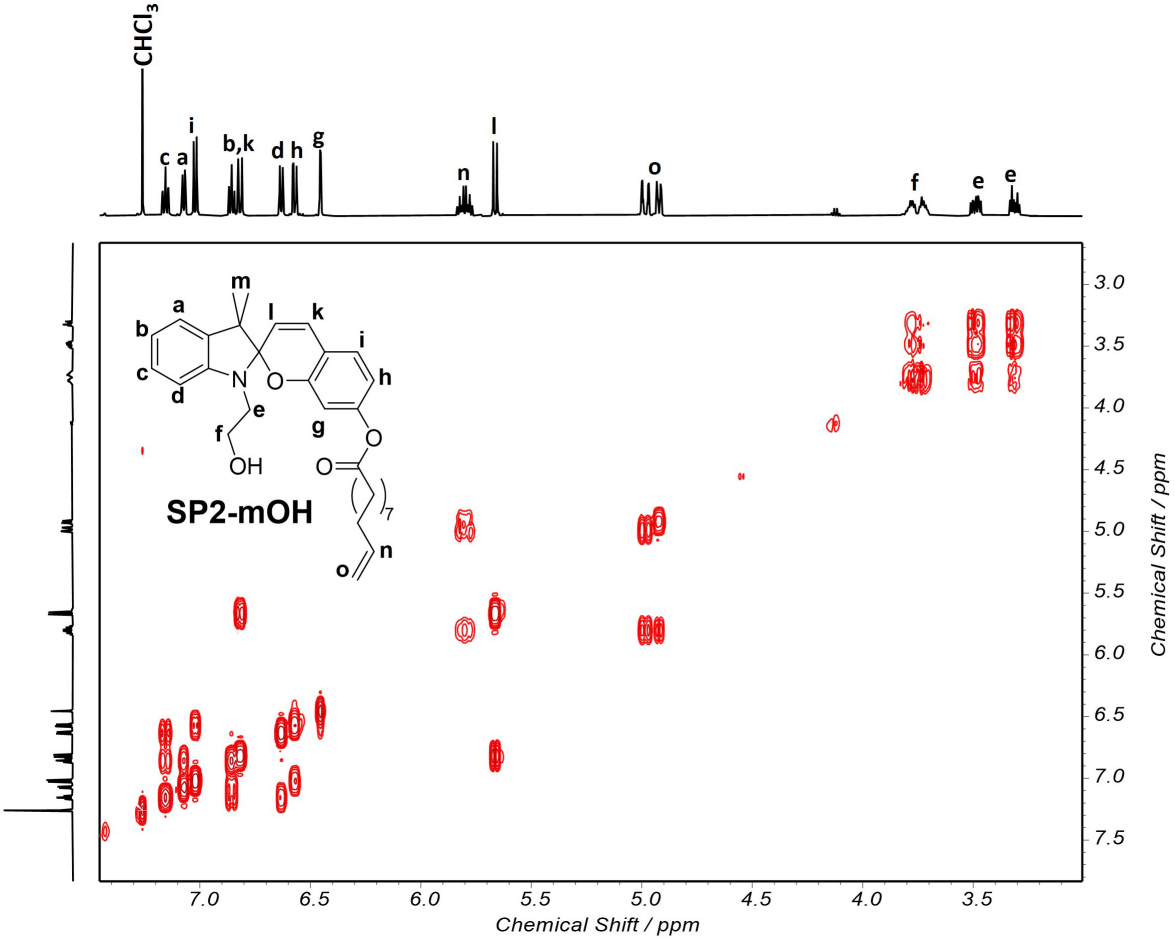


Figure S25. *COSY sectional spectrum of compound **SP2-mOH** recorded in $CDCl_3$.*

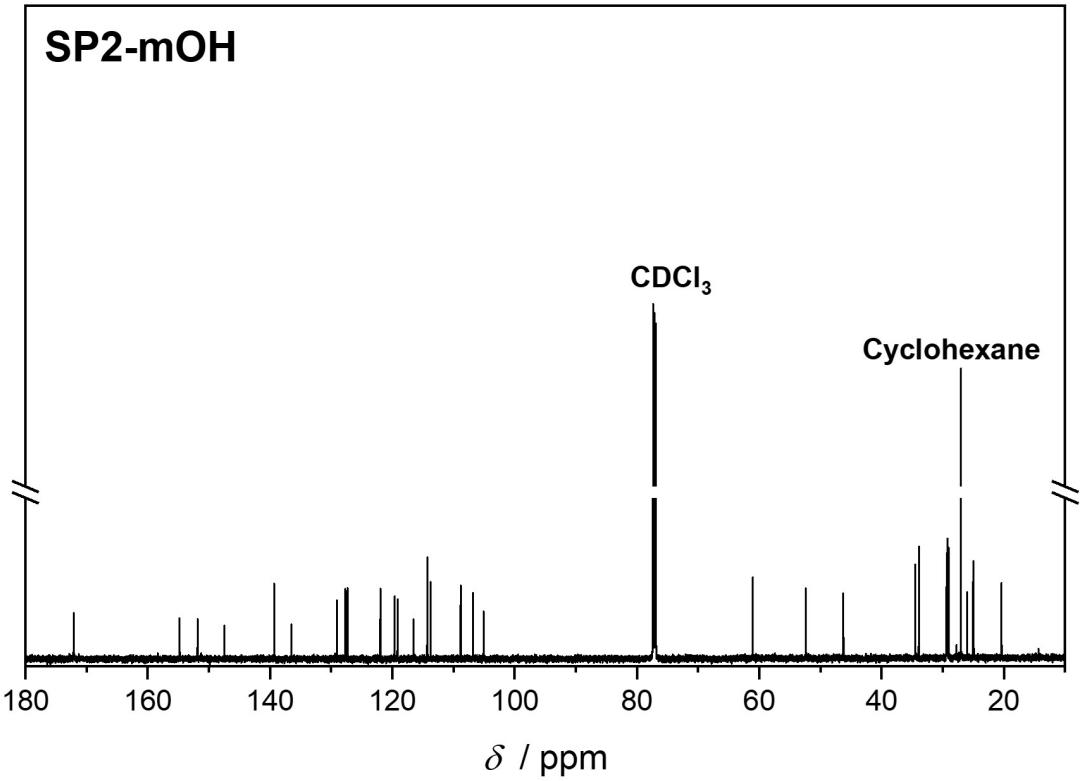


Figure S26. *^{13}C (151 MHz) NMR spectrum of **SP2-mOH** in $CDCl_3$.*

9.8. M_{SP2}

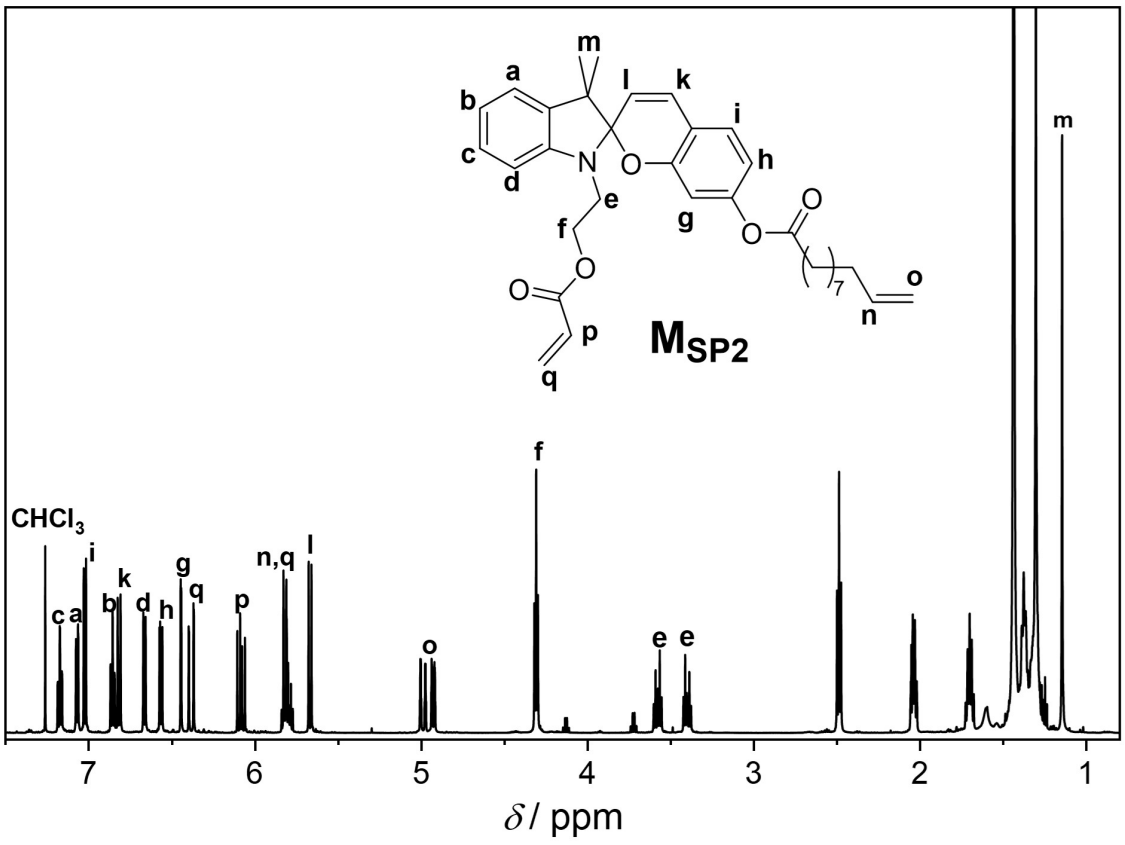


Figure S27. *^{1}H NMR spectrum (600 MHz, 16 scans) of **M_{SP2}** recorded in $CDCl_3$.*

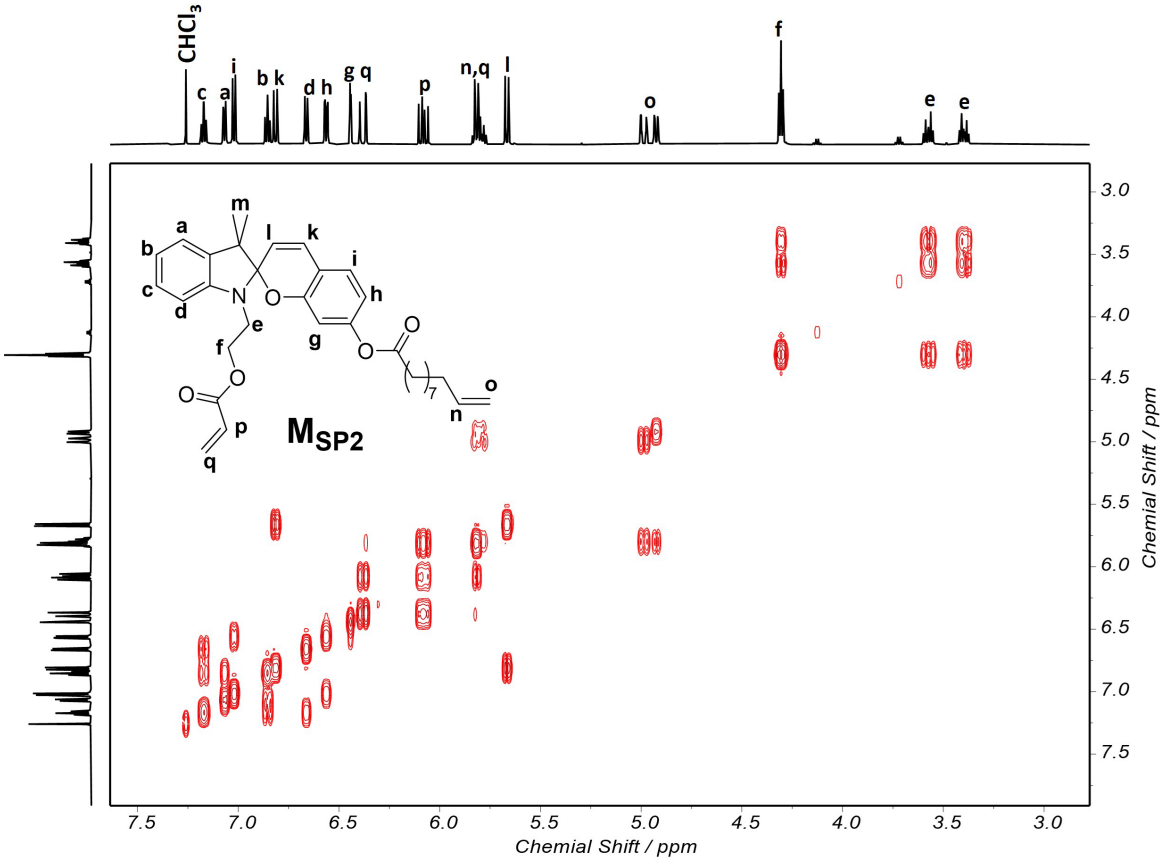


Figure S28. *COSY sectional spectrum of compound* ***M_{SP2}*** *recorded in* $CDCl_3$.

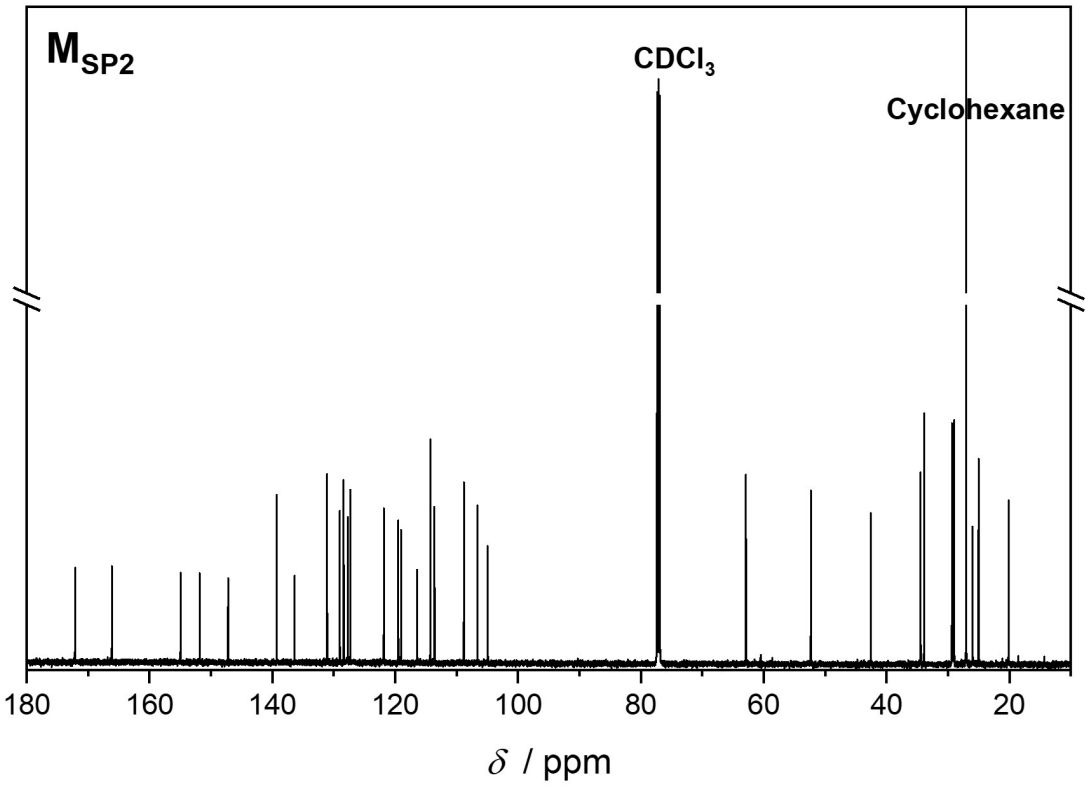


Figure S29. ^{13}C *(151 MHz) NMR spectrum of* ***M_{SP2}*** *in* $CDCl_3$.

9.9. P_{SP2}

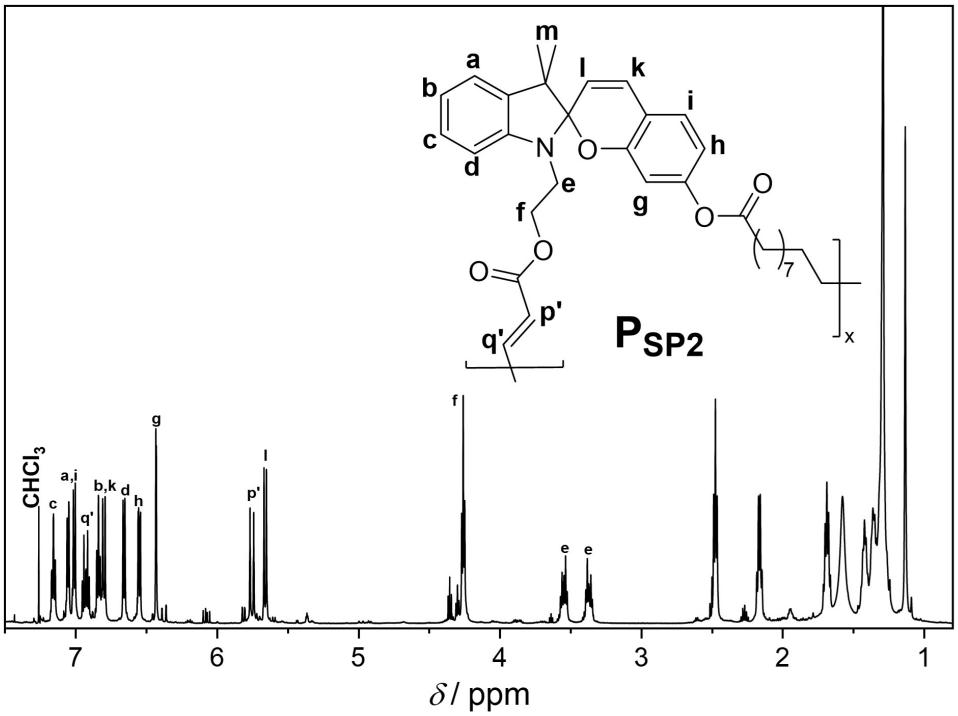


Figure S30. *^{1}H NMR spectrum (600 MHz, 32 scans) of **P_{SP2}** recorded in $CDCl_3$.*

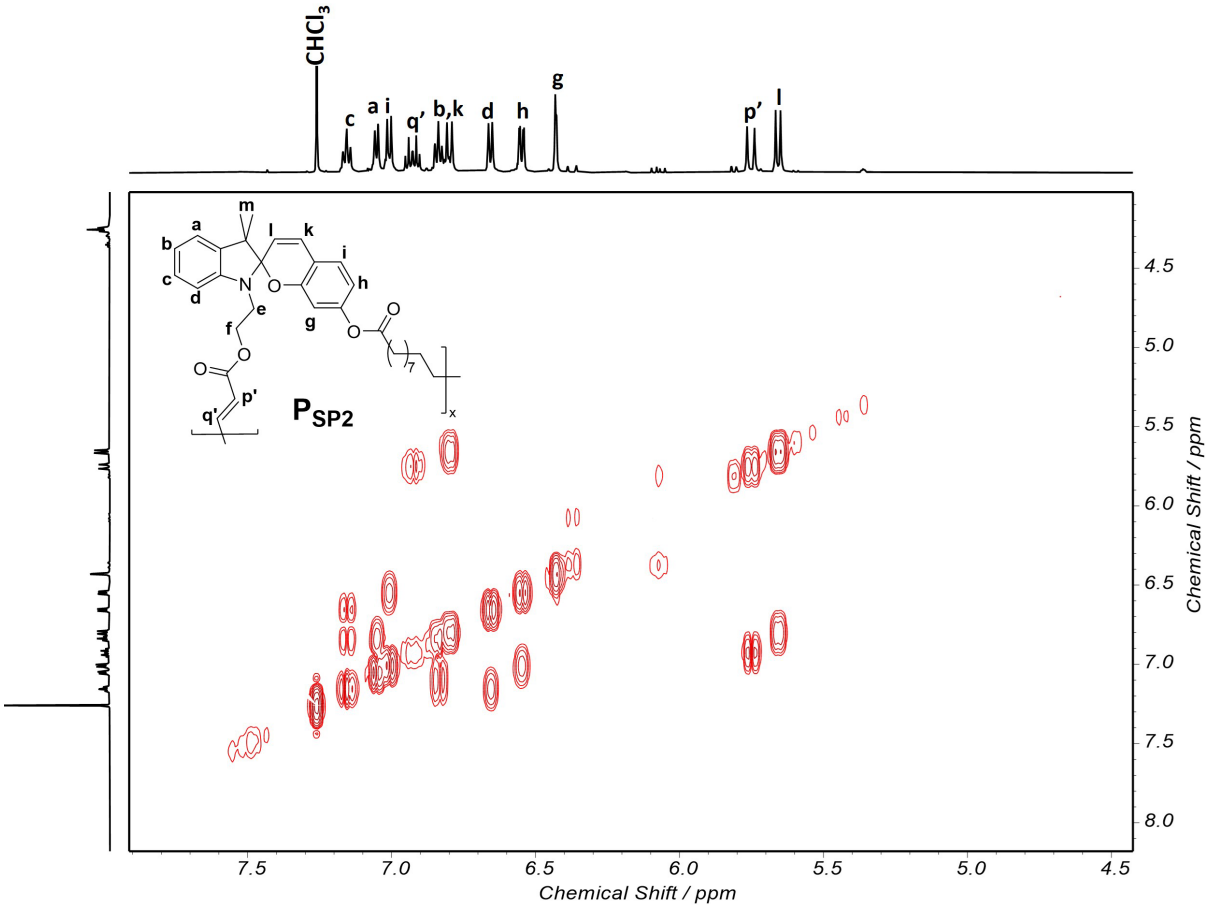


Figure S31. *COSY sectional spectrum of compound **P_{SP2}** recorded in $CDCl_3$.*

9.10. SP3-diOH

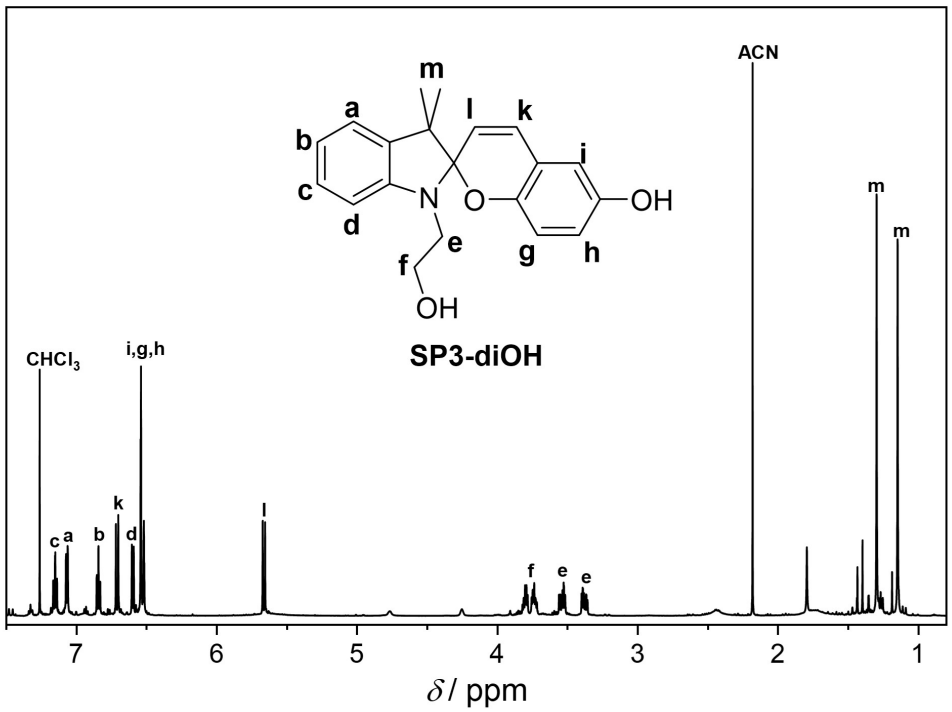


Figure S32. *^{1}H NMR spectrum (600 MHz, 16 scans) of* ***SP3-diOH*** *recorded in $CDCl_3$.*

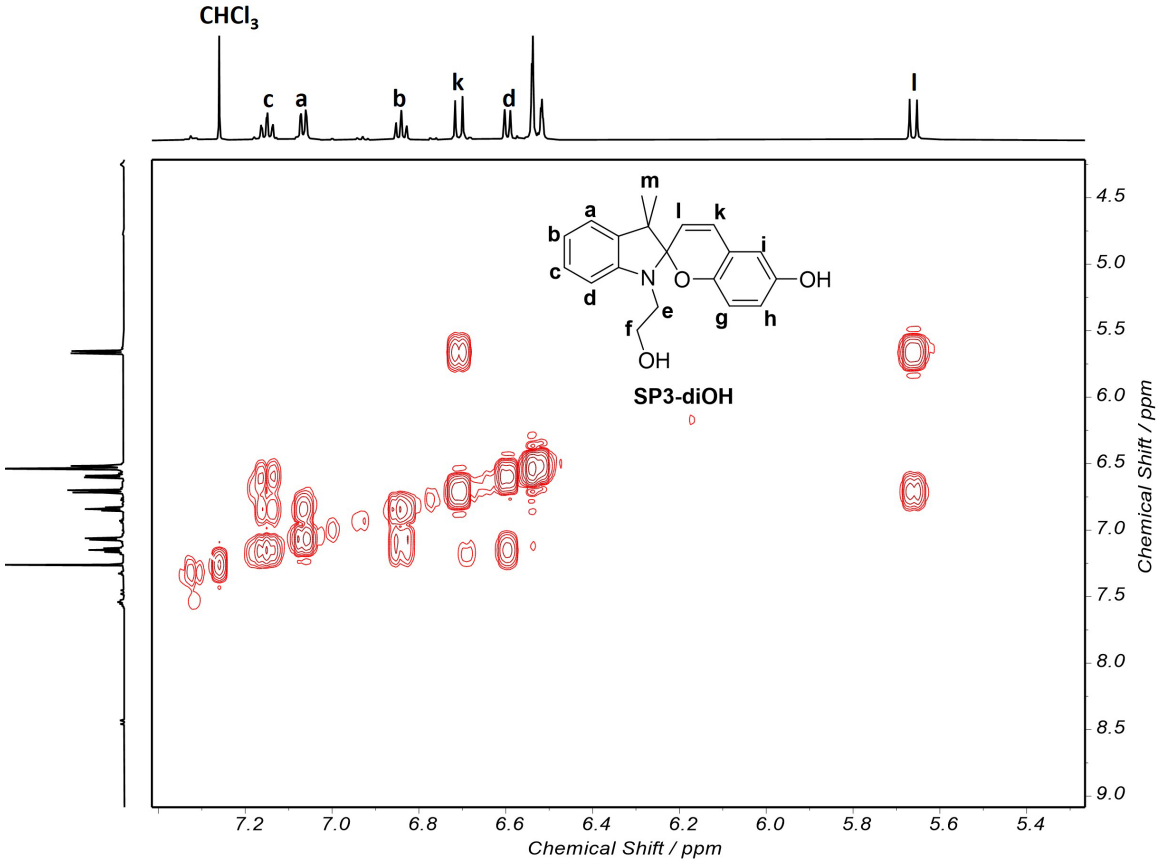


Figure S33. *COSY sectional spectrum of compound* ***SP3-diOH*** *recorded in $CDCl_3$.*

9.11. SP3-mOH

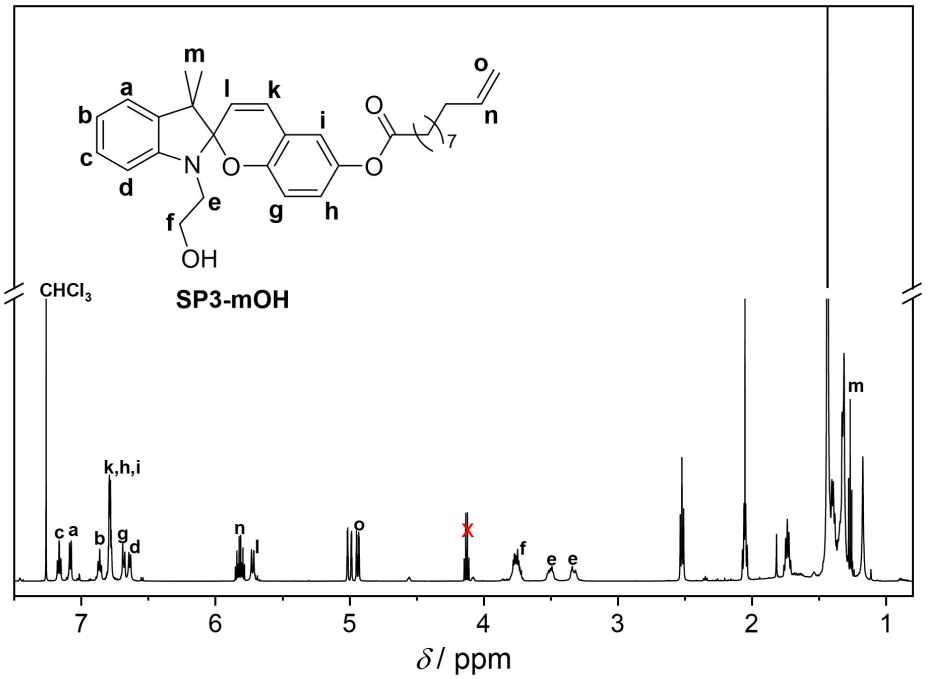


Figure S34. *^{1}H NMR spectrum (600 MHz, 16 scans) of **SP3-mOH** recorded in $CDCl_3$.*

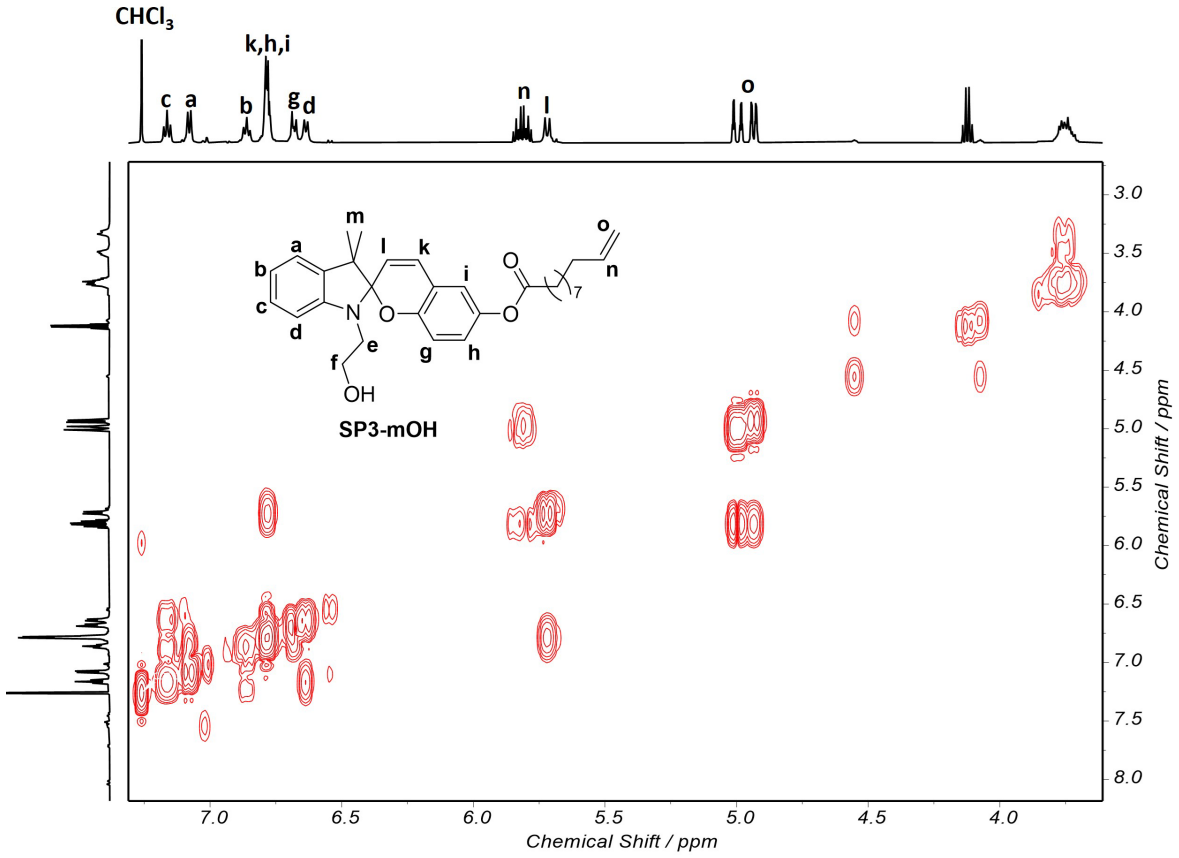


Figure S35. *COSY sectional spectrum of compound **SP3-mOH** recorded in $CDCl_3$.*

9.12. M_{SP3}

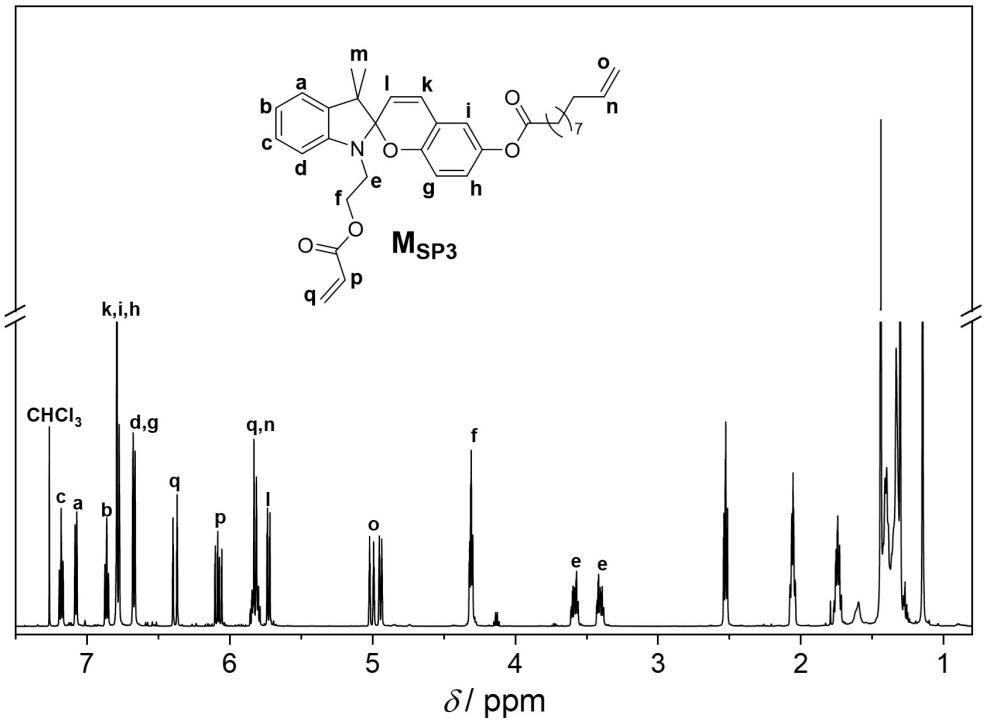


Figure S36. *^{1}H NMR spectrum (600 MHz, 16 scans) of* ***M_{SP3}*** *recorded in $CDCl_3$.*

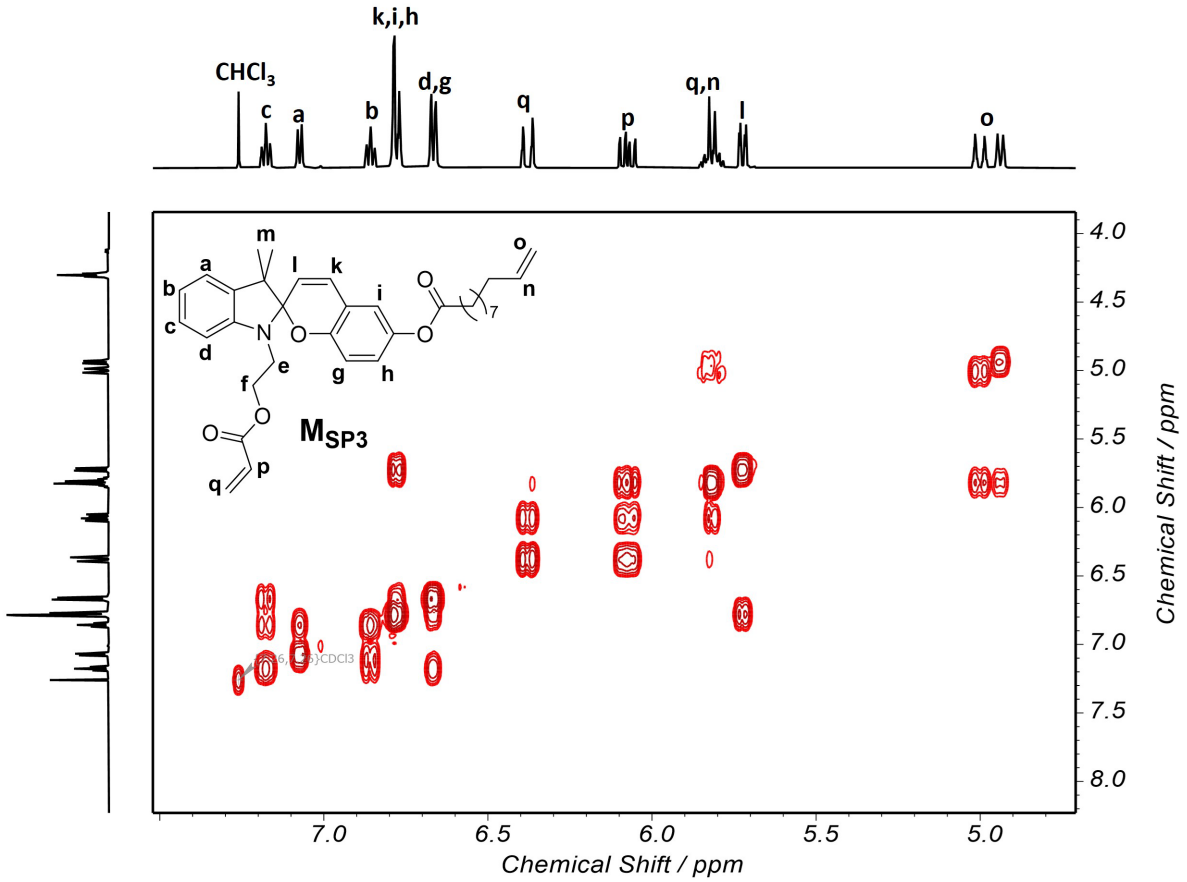


Figure S37. *COSY sectional spectrum of compound* ***M_{SP3}*** *recorded in $CDCl_3$.*

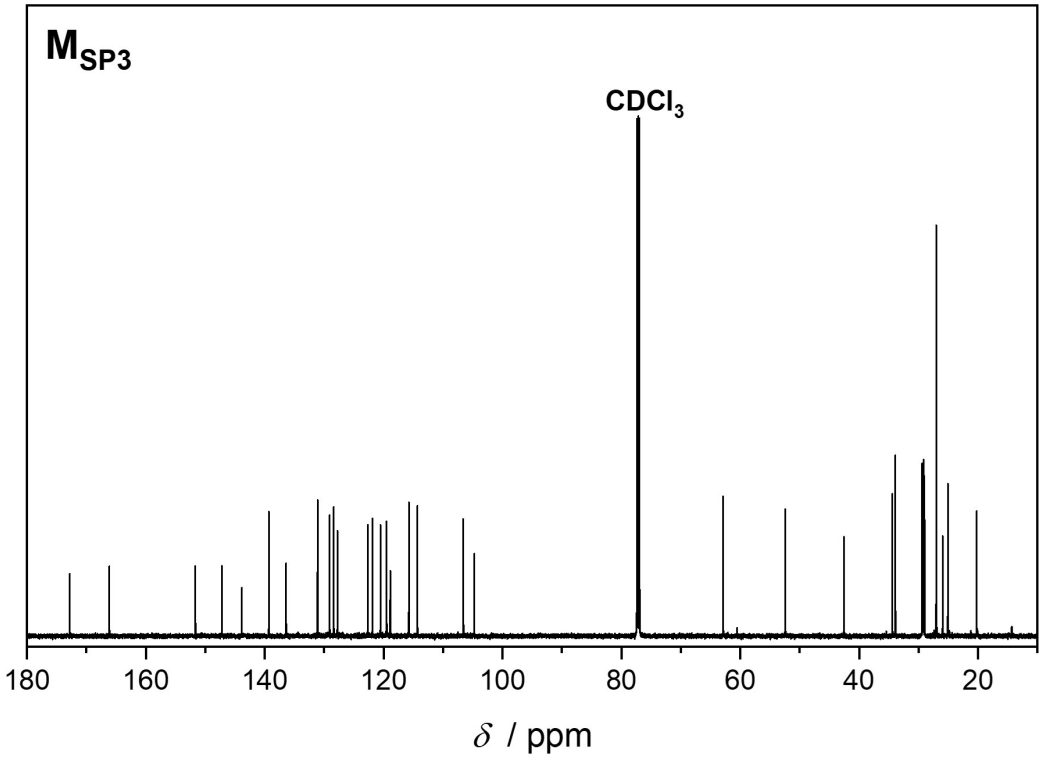


Figure S38. *^{13}C (151 MHz) NMR spectrum of **M_{SP3}** in $CDCl_3$.*

9.13. P_{SP3}

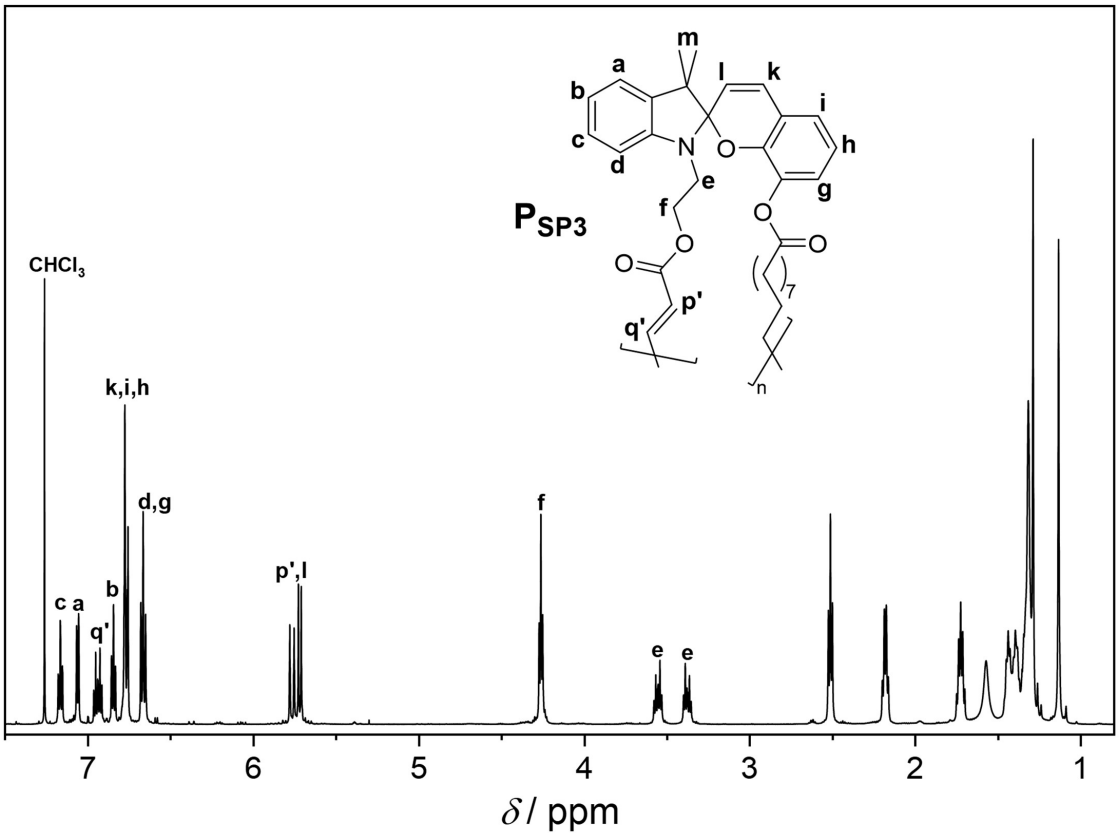


Figure S39. *^{1}H NMR spectrum (600 MHz, 32 scans) of **P_{SP3}** recorded in $CDCl_3$.*

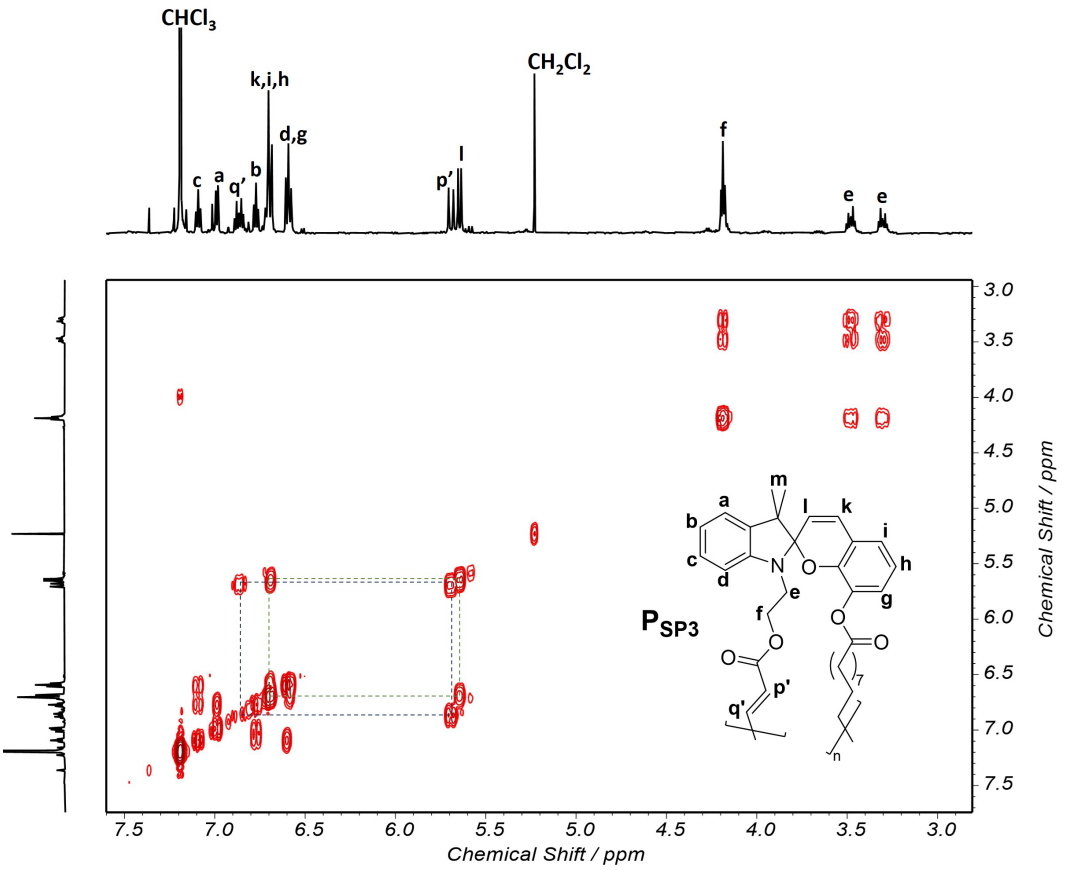


Figure S40. *COSY sectional spectrum of compound* ***P*****$_{SP3}$** *recorded in* $CDCl_3$.

9.14. Compound 3

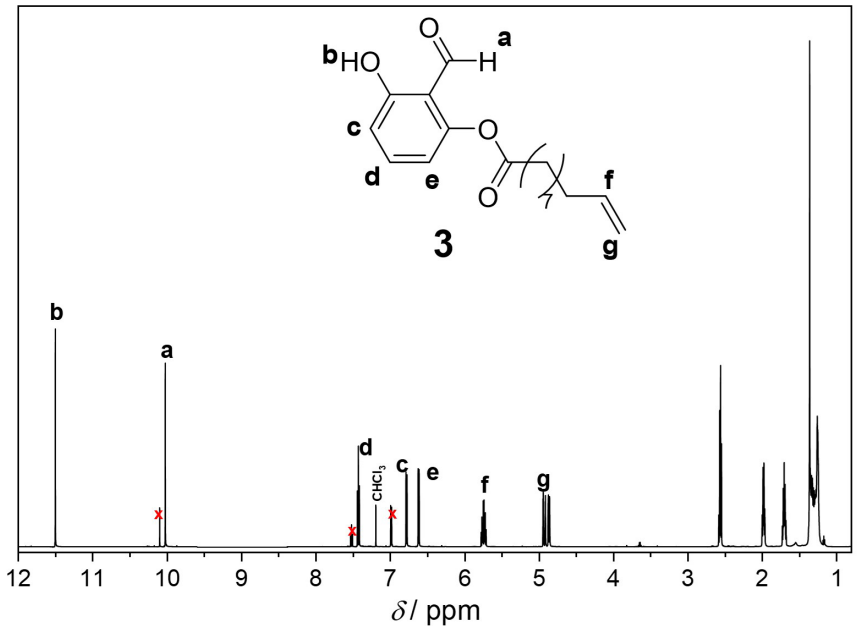


Figure S41. ^1H *NMR spectrum (600 MHz, 16 scans) of compound* ***3*** *recorded in* $CDCl_3$. *By-products are marked with a cross.*

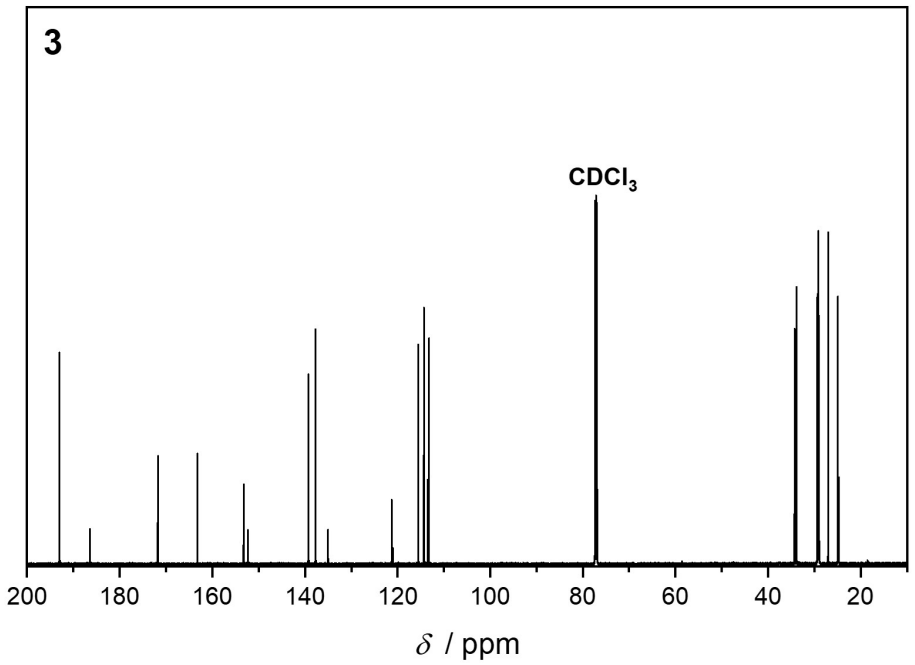


Figure S42. *^{13}C (151 MHz) NMR spectrum of compound **3** in $CDCl_3$.*

9.15. SP4-mOH

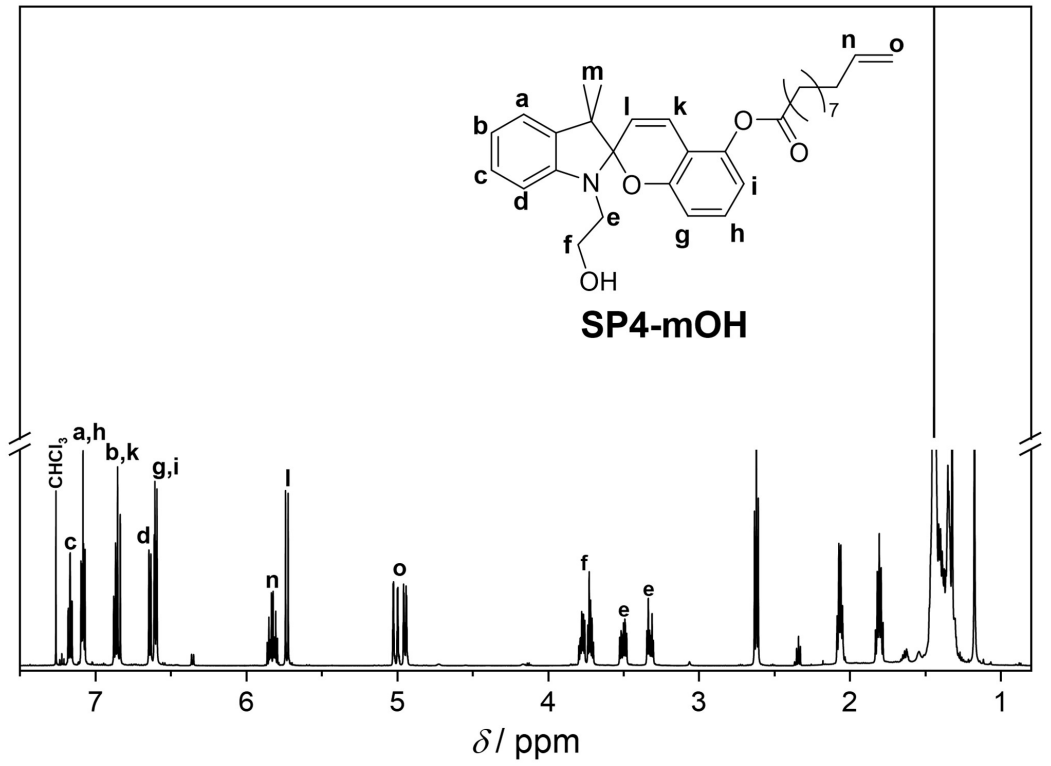


Figure S43. *^{1}H NMR spectrum (600 MHz, 16 scans) of **SP4-mOH** recorded in $CDCl_3$.*

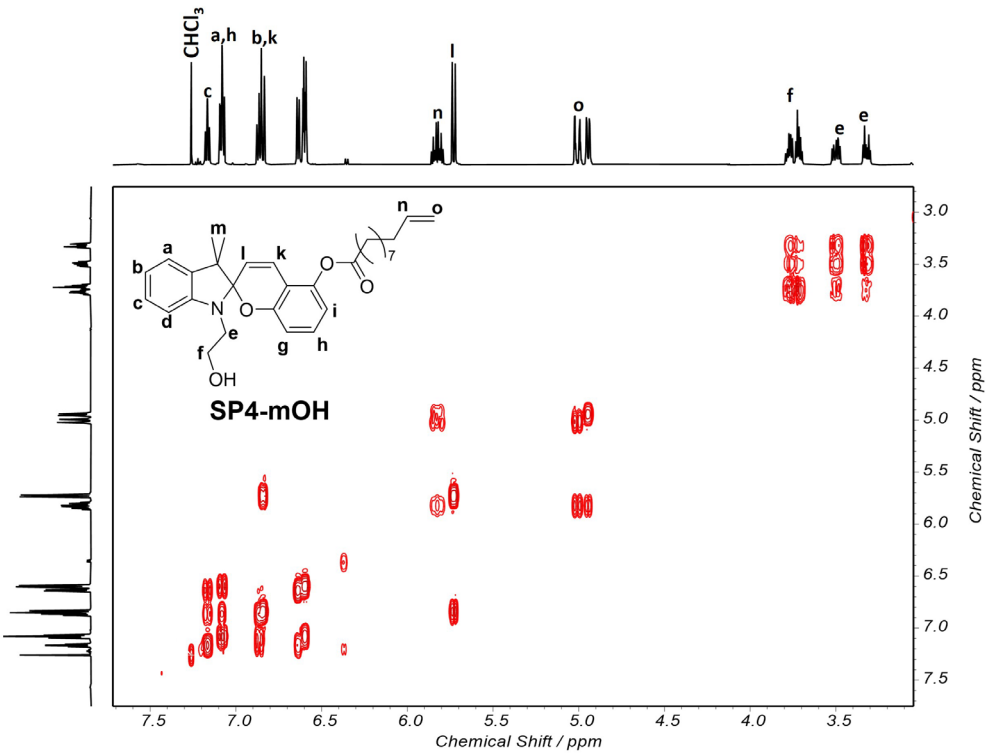


Figure S44. *COSY sectional spectrum of compound* ***SP4-mOH*** *recorded in* $CDCl_3$.

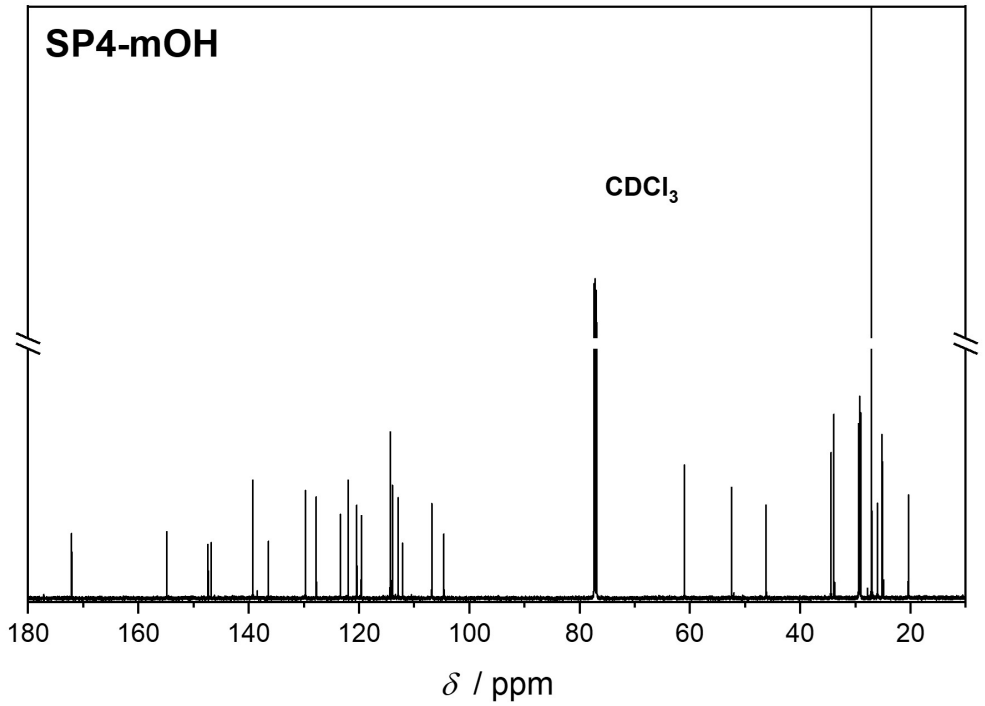


Figure S45. ^{13}C *(151 MHz) NMR spectrum of* ***SP4-mOH*** *in* $CDCl_3$.

9.16. M_{SP4}

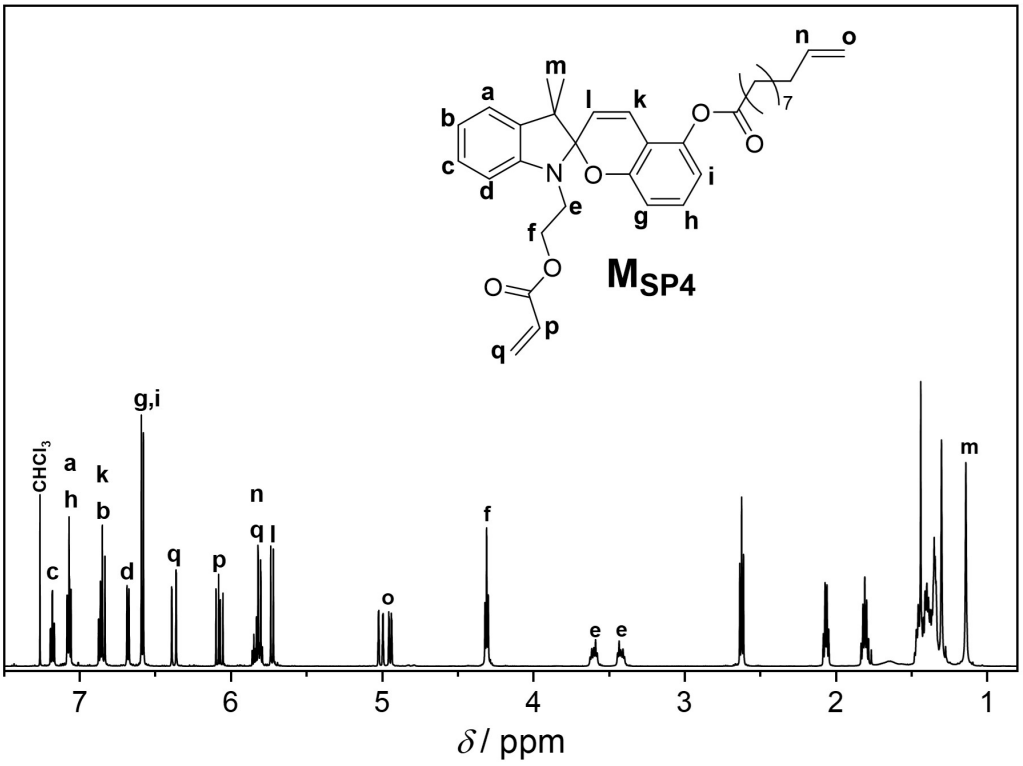


Figure S46. *^{1}H NMR spectrum (600 MHz, 16 scans) of **M_{SP4}** recorded in $CDCl_3$.*

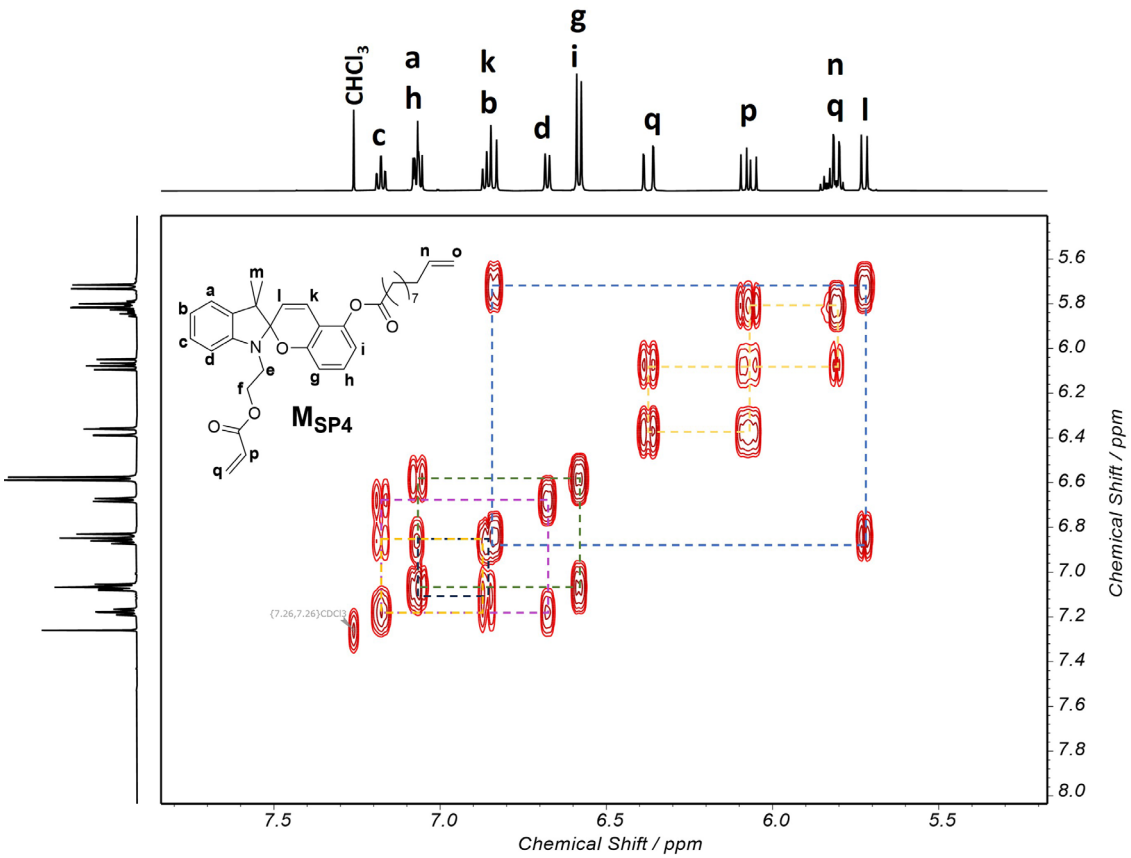


***Figure S47**. COSY sectional spectrum of compound **M_{SP4}** recorded in $CDCl_3$.*

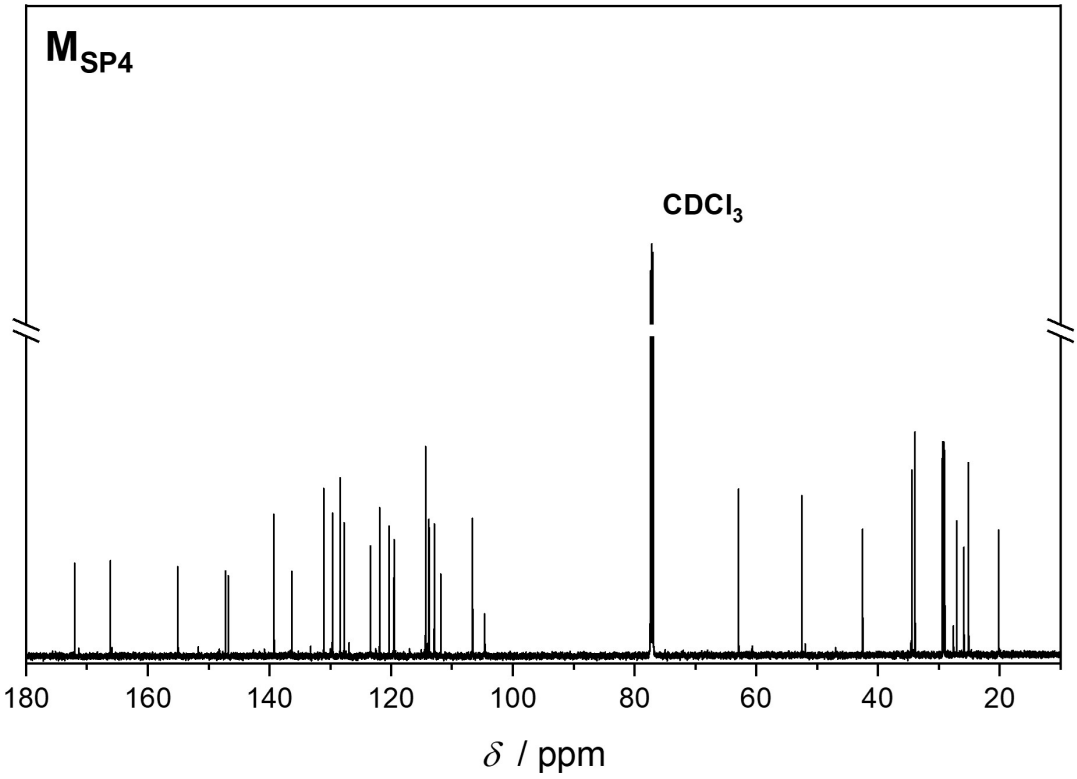


Figure S48. *^{13}C (151 MHz) NMR spectrum of **M_{SP4}** in $CDCl_3$.*

9.17. P_{SP4}

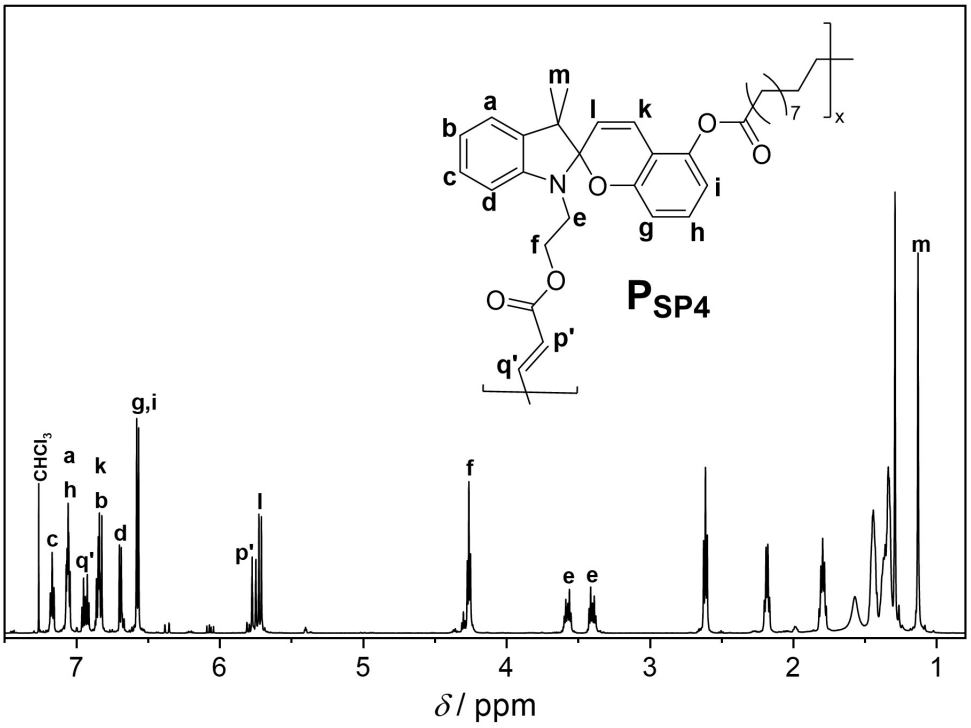


Figure S49. *^{1}H NMR spectrum (600 MHz, 32 scans) of **P_{SP4}** recorded in $CDCl_3$.*

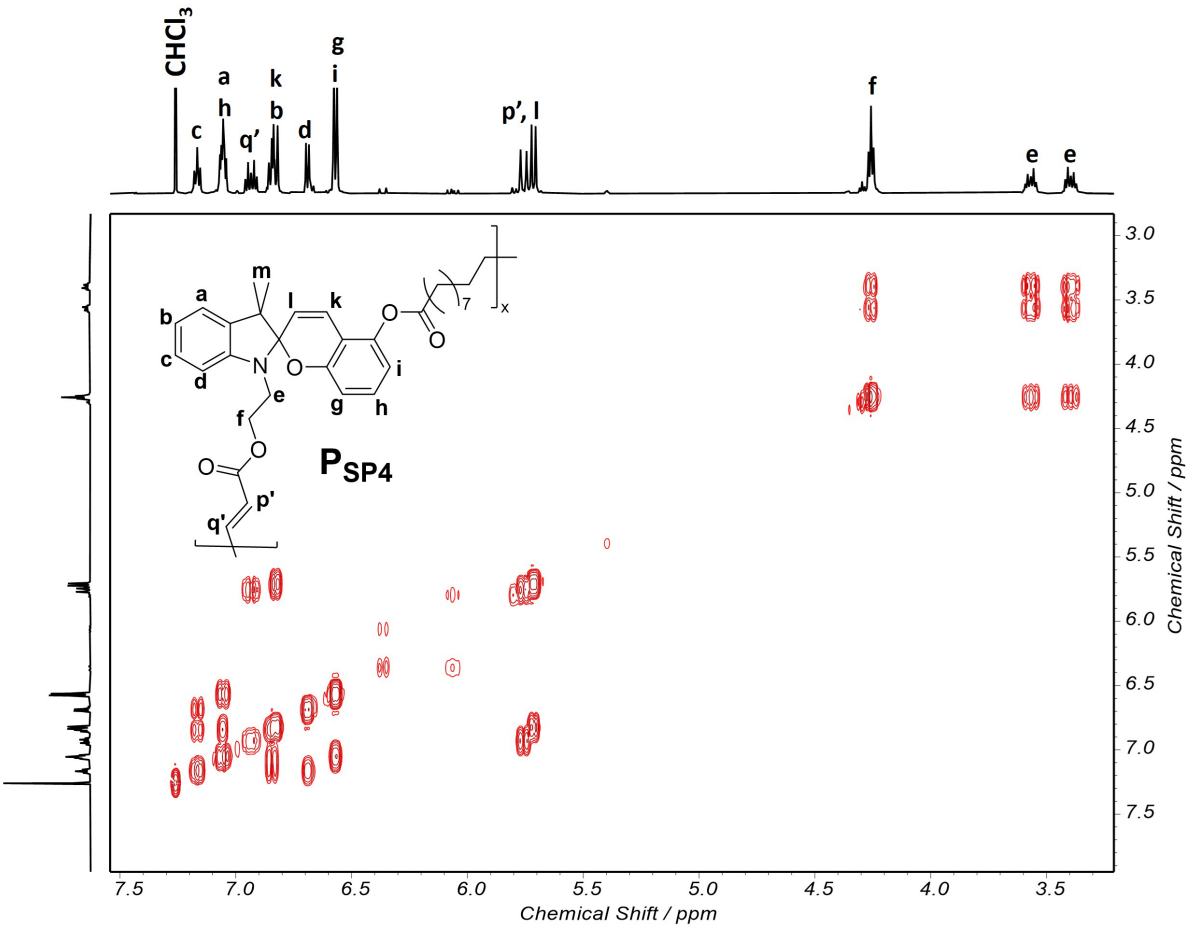


Figure S50. *COSY sectional spectrum of compound* $\boldsymbol{P_{SP4}}$ *recorded in* $CDCl_3$.

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