Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supporting Information

Light- and Mechanic Field Controlled Dynamic Soft Matter Materials

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1 Experimental details

1.1 Bruker 600 MHz 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 δ-scale was calibrated to the respective solvent signal of $CHCl_3$,DCM, or DMSO for ^{1}H spectra and for ^{13}C spectra on the middle signal of the $CDCl_3$ triplet or the CD_2Cl_2 singlet, or the $(CD_3)_2SO$ quintet. The annotation of the signals is based on HSQC-, COSY- and DEPT-experiments.

1.2 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 C18 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 and 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.

1.3 Size Exclusion Chromatography Mass Spectrometry SEC-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 10 and 0 were applied, respectively. The capillary temperature was set to 320 °C, the S-lens RF level was set to 150 and the aux gas heater temperature was set to 125 °C. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a temperature-controlled column department (TCC 3000). Separation was performed on two mixed bed size exclusion chromatography columns (Agilent, Mesopore 250 × 4.6 mm, particle diameter 3 µm) with a precolumn (Mesopore 50 × 7.5 mm) operating at 30 °C. THF at a flow rate of 0.30 mL·min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to an UV-detector (VWD 3400, Dionex), and a RI-detector (RefractoMax520, ERC, Japan) in a setup

described earlier.[1] 0.27 mL·min^{-1} of the eluent were directed through the UV- and RI-detector and 30 µL·min^{-1} were infused into the electrospray source after post-column addition of a 50 µM solution of sodium iodide in methanol at 20 µL·min^{-1} by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 200 µL aliquot of a polymer solution with a concentration of 2 mg·mL^{-1} was injected into the SEC system.

1.4 Size exclusion Chromatography THF-GPC

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 (8x150 mm 5 µm Precolumn, 8x300 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}) (PSS ReadyCal) was 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).

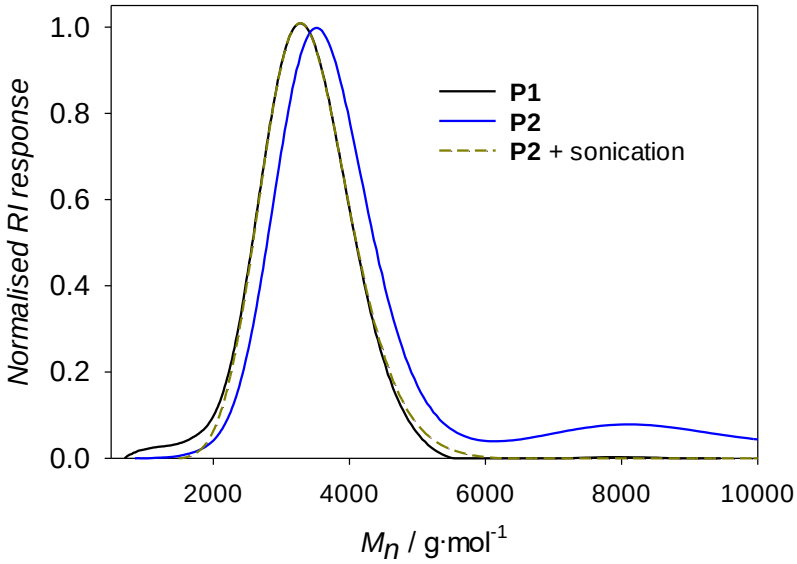


Figure S1. SEC traces (THF, refractive index detection) of **P1**, **P2** and **P2** after sonication.

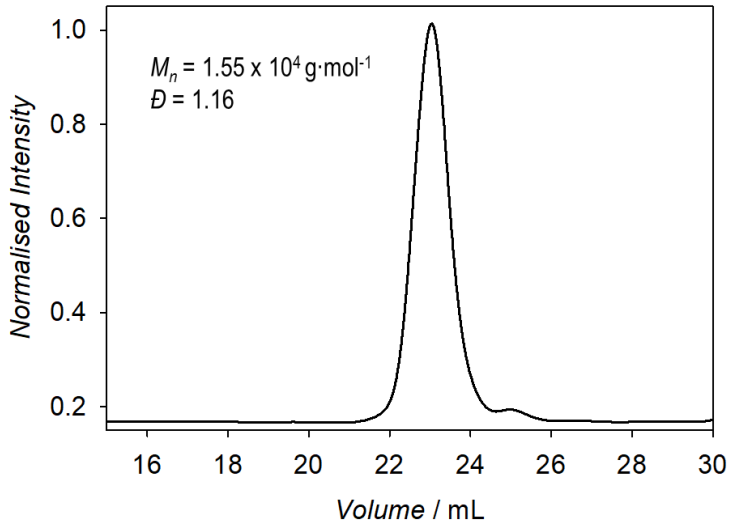


Figure S2. SEC trace (THF, refractive index detection) of **P3.**

Table S1. Assignment of the measured mass of intact **P1** and **P2** to its simulation and composition

	Assignment	$m_{experimental}$	$m_{simulated.}$	Composition
P1	$[M+Na]^+$	1860.0751	1860.0594	$C_{88}H_{161}NO_{37}Na^+$
P2	$[M+Na]^+$	1890.0850	1890.0636	$C_{92}H_{157}NO_{37}Na^+$

1.5 LED Characterization

LED emission spectra were recorded using an Ocean Insight Flame-T-UV-Vis spectrometer, with an active range of 200-850 nm and an integration time of 10 ms. LED output energies were recorded using a Thorlabs S401C thermopile sensor, with an active area of 100 mm^2 and a wavelength range of 190 nm – 20 µm, connected to a Thorlabs PM400 energy meter console. The emitted power from each LED was measured for 60 seconds at a fixed distance from the sensor, after which the mean and standard deviation of the emission could be determined. LEDs were cooled during measurement to minimise any thermal effects on the emission power or sensor performance.

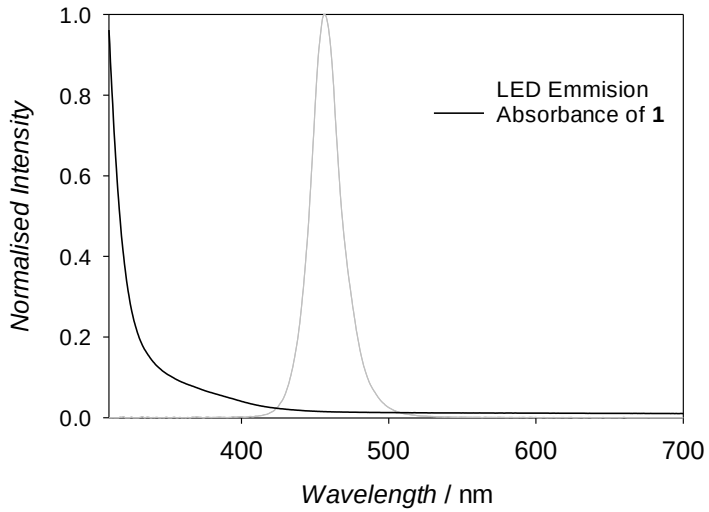


Figure S3. Emission spectrum of the blue LED light source used for ketene generation, and absorbance spectrum of diazoketone **1** in CH_2Cl_2.

1.6 Ultrasonication

Elma Ultrasonic Cleaner S60 was used for sonication with the default setting of ultrasonic power = 80 W and frequency = 37 KHz.

1.7 Rheology Assessment

Rheological experiments were measured using an Anton Paar Physica rheometer (MCR 302e) with a plate-plate configuration. The lower plate is made of quartz and the upper plate of stainless steel with a diameter of 25 mm. The LED light sources were placed below the quartz plate. In a typical experiment, a solution (50 μL) of 4-arm PEG-SH (0.5 M) and bimane dinorbornene (1 M) in acetonitrile was placed on the lo wer plate and the upper plate was lowered to a measurement gap of 0.2 mm. The measurement was started by applying a 1% strain with a frequency of 0.1 Hz on the sample. After a certain time period (ca. 5 min), the UV LED light was switched on to induce crosslinking.

After full gelation was achieved, i.e., no more increase in the G' value, the measurement was halted, and the upper plate was moved upwards. The crosslinked material was subsequently immersed in water under irradiation of a blue LED light. The storage modulus of the material was recorded after predetermined intervals of irradiation time.

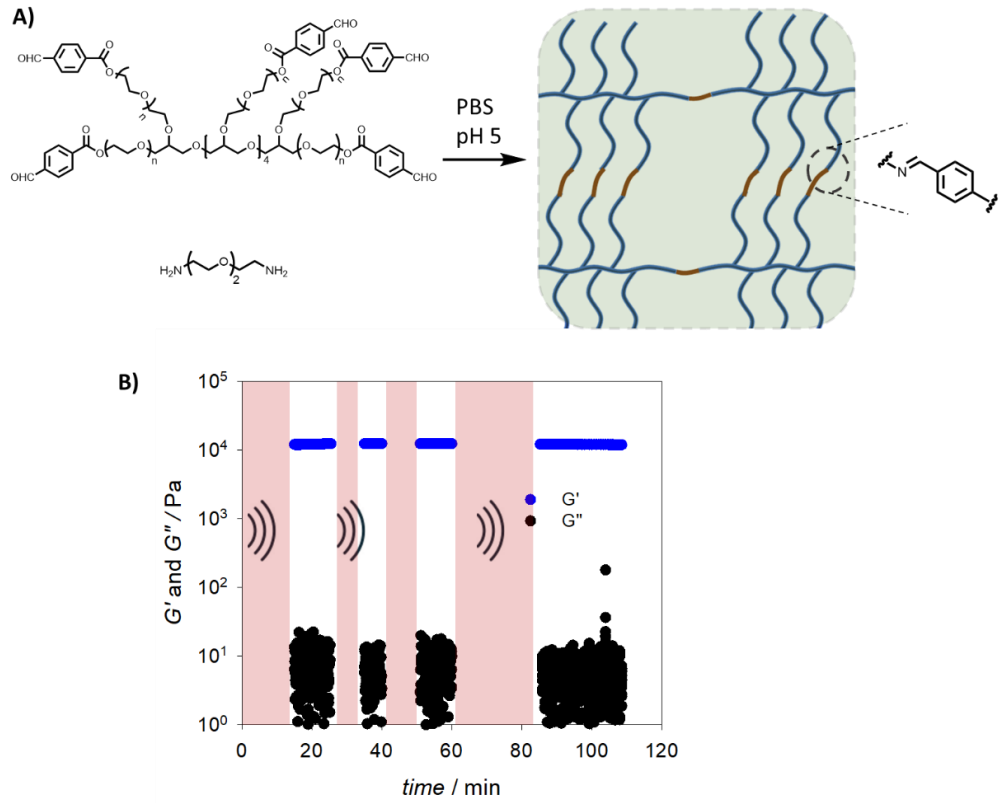
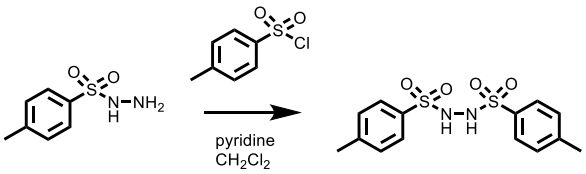


Figure S4. A) Formation of a control hydrogel by imine bond linkage; **B)** rheological assessment showing no degradation of the control hydrogels when subjected to sonication.

2 Synthesis

2.1 N,N'-ditosylhydrazine (TsNHNHTs)



Pyridine (6 mL, 75 mmol) was added dropwise to a solution of p-toluenesulfonyl hydrazide (9.32 g, 50.0 mmol) and p-toluenesulfonyl chloride (14.3 g, 75.0 mmol) in CH_2Cl_2 (50 mL). The solution was stirred for 2 h at ambient temperature during which white precipitation formed. Water (100 mL) and diethylether (200 mL) was added to the solution and the reaction mixture was cooled on an ice bath for 30 min. The solid was filtered, dried *in vacuo*, and recrystalised in methanol to give product as white crystal (yield 15.1 g, 88.4%). The NMR spectral data are identical to the previously reported data.[2]

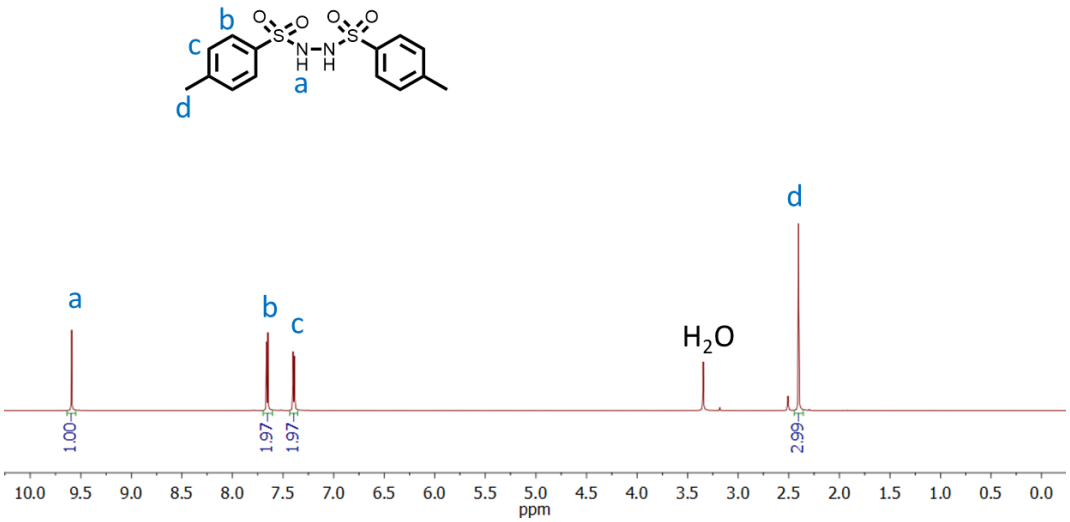
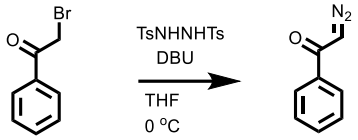


Figure S5. ^{1}H NMR spectrum of N,N'-ditosylhydrazine (DMSO-d_6, 600 MHz).

2.2 α-Diazoacetophenone



α-Bromoacetophenone (0.6 g, 3 mmol) and N,N'-ditosylhydrazine (2.04 g, 6 mmol) were dissolved in THF (20 mL) and the solution was cooled on an ice bath. DBU (2.25 mL, 15 mmol) was added dropwise to the solution, and allowed to warm to ambient temperature. The solution was stirred for 1 h at ambient temperature, quenched with saturated $NaHCO_3$ solution (50 mL), and extracted with diethyl ether (50 mL x3). The organic phases were combined, dried ($MgSO_4$), concentrated in vacuo and purified by column chromatography on SiO_2 and eluting with EtOAc:hexane (v/v = 1/4) to give product as a yellow crystal (yield: 0.37 g, 85%). The NMR spectral data are identical to the previously reported data.[2]

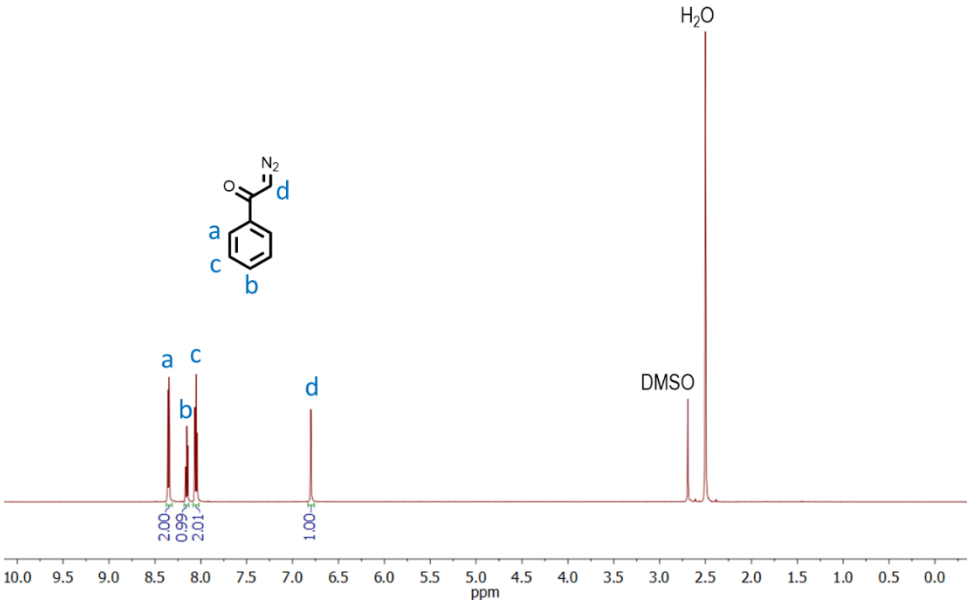


Figure S6. ^{1}H NMR spectrum of α-diazoacetophenone (DMSO-d_6, 600 MHz).

2.3 MeO-PEG-benzaldehyde

MeO-PEG-OH (4 g, 2 mmol) was dissolved in CH_2Cl_2 (20 mL) and to this solution was added 4-carboxybenzaldehyde (0.6 g, 4 mmol), EDC.HCl (0.788 g, 4 mmol), and DMAP (48 mg, 0.4 mmol). The solution was stirred for 16 h at ambient temperature and precipitated twice into diethyl ether (200 mL) to give the product as white powder (yield 3.9 g, 86.7%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 10.12 (s), 2.83-2.84 (d, J = 8.2 Hz), 7.97-7.98 (d, J = 8.6 Hz), 4.52-4.54 (t, J = 4.8 Hz), 3.7 (t, J = 4.9 Hz), 3.66 (broad s), 3.39 (s).

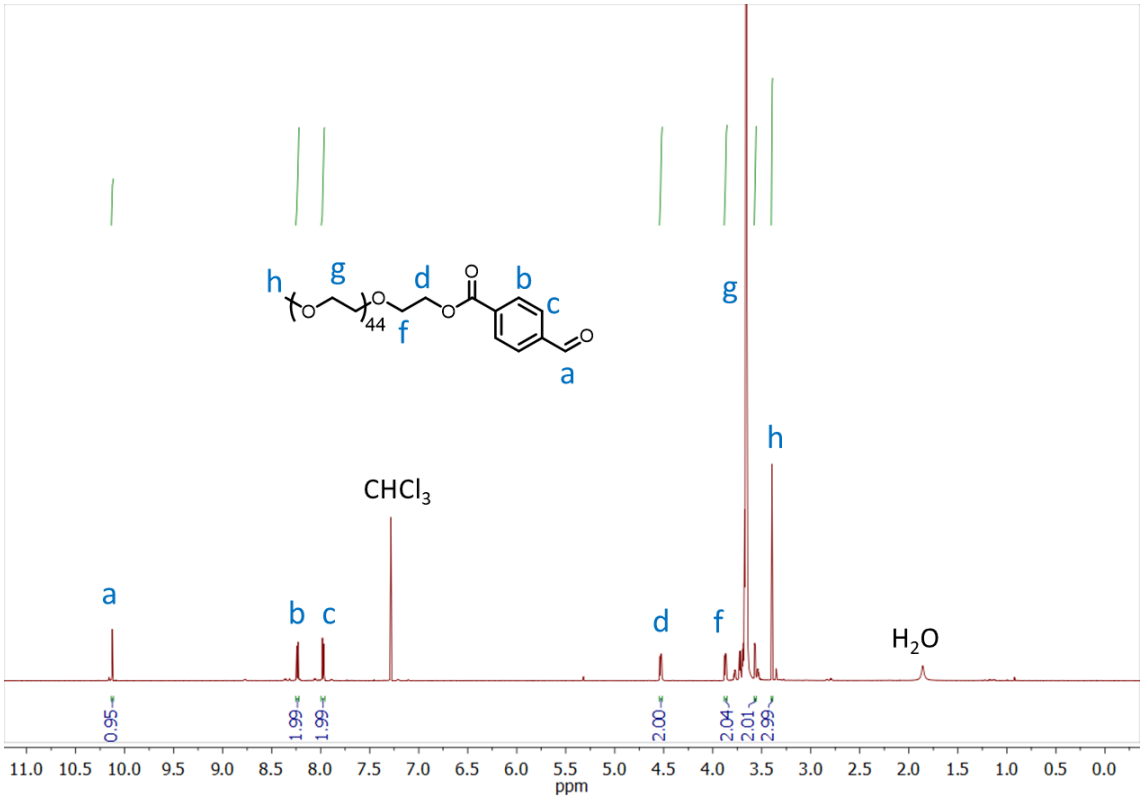
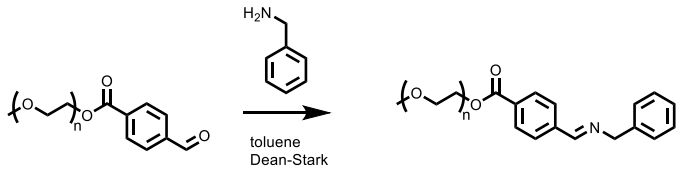


Figure S7. ^{1}H NMR spectrum of PEG-benzaldehyde ($CDCl_3$, 600 MHz).

2.4 MeO-PEG-benzyl imine (P1)



MeO-PEG-benzaldehyde (2 g, 1 mmol) and benzyl amine (0.214 g, 2 mmol) were dissolved in toluene (50 mL) and the solution was heated at 130 °C under Dean-Stark conditions for 3 h. The solvent was concentrated in vacuo and the residue was redissolved in dichloromethane (10 mL) and precipitated into diethyl ether (200 mL) to give product as a white solid (yield 2.1 g, 95%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 8.46 (s), 8.1-8.12 (d, *J* = 8.1 Hz), 7.85-7.87 (d, *J* = 8.4 Hz), 7.36-7.37 (m), 4.88 (s), 4.49-4.51 (t, *J* = 4.8 Hz), 3.85-3.87 (t, *J* = 4.8 Hz), 3.66 (broad s), 3.39 (s).

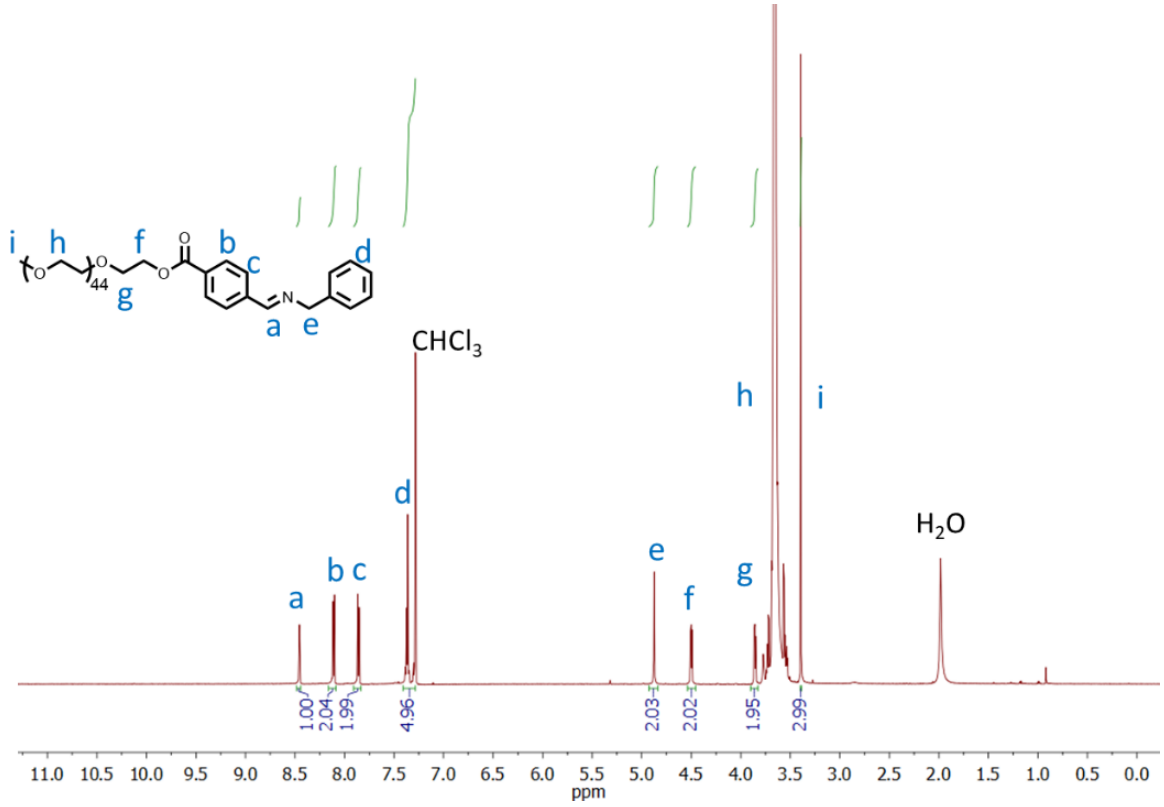
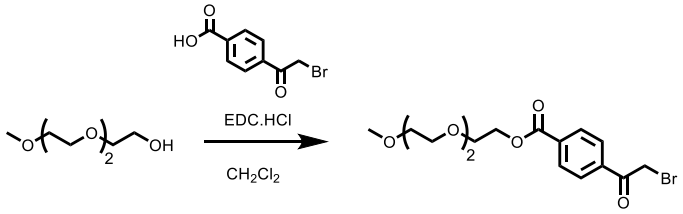


Figure S8. ^{1}H NMR spectrum of **P1** ($CDCl_3$, 600 MHz).

2.5 2-(2-methoxyethoxy)ethyl 4-(2-bromoacetyl)benzoate



Triethylene glycol monomethyl ether (3.28 g, 20 mmol) was dissolved in dichloromethane (20 mL) and 4-(2-bromoacetyl)benzoic acid (4.82 g, 20 mmol), EDC.HCl (3.94 g, 20 mmol) and DMAP (122 mg, 1 mmol) were added. The solution was stirred for 4 h at ambient temperature and concentrated into silica gel (4 g). The mixture was purified by column chromatography running on SiO_2 and eluting with EtOAc/hexane (v/v = 1/1) to give product as a clear oil (yield: 5.1 g, 75%). The product contains a small amount of solvent and bromoacetyl benzoic acid, however it was used directly in the next step.

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 8.19-8.21 (d, *J* = 8.4 Hz), 8.03-8.04 (d, *J* = 8.5 Hz), 4.74 (s), 4.53-4.54 (t, *J* = 4.5 Hz), 3.87-3.88 (t, *J* = 4.8), 3.66-3.74 (m), 3.55-3.56 (m), 3.39 (s).

^{13}C NMR (145 MHz, Chloroform-*d*) δ/ppm: 190.7, 166.4, 137.4, 134.7, 130.2, 128.9, 72, 70.7, 69.1, 64.7, 59.1, 45.9.

$C_{16}H_{21}BrO_6$ $[M]^+_{calculated}$ = 388.0522, $[M]^+_{experimental}$ = 388.0542

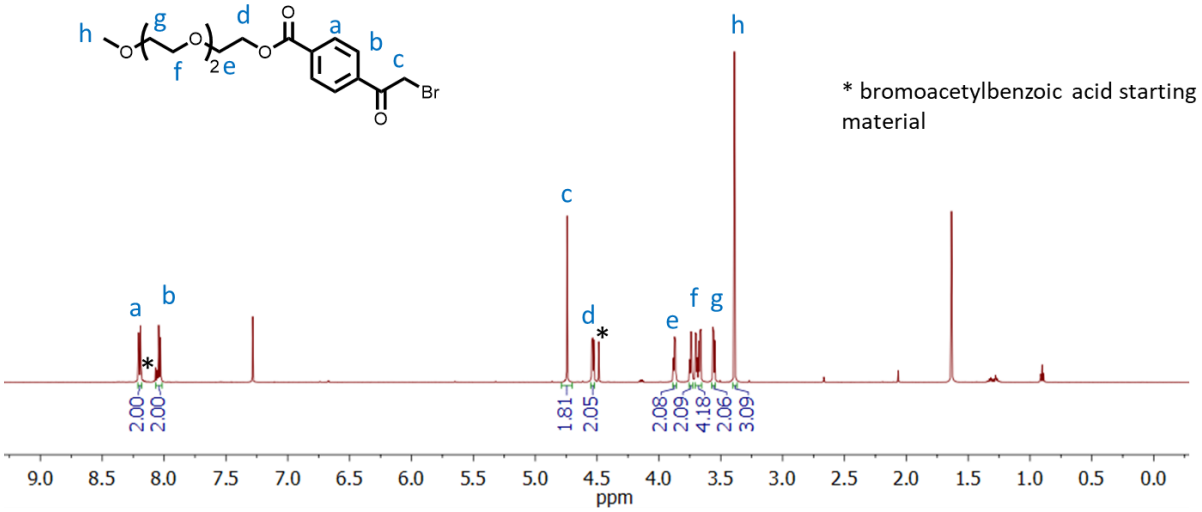


Figure S9. ^{1}H NMR spectrum of 2-(2-methoxyethoxy)ethyl 4-(2-bromoacetyl)benzoate ($CDCl_3$, 600 MHz), the compound contains a small amount of ethyl acetate and hexane solvent.

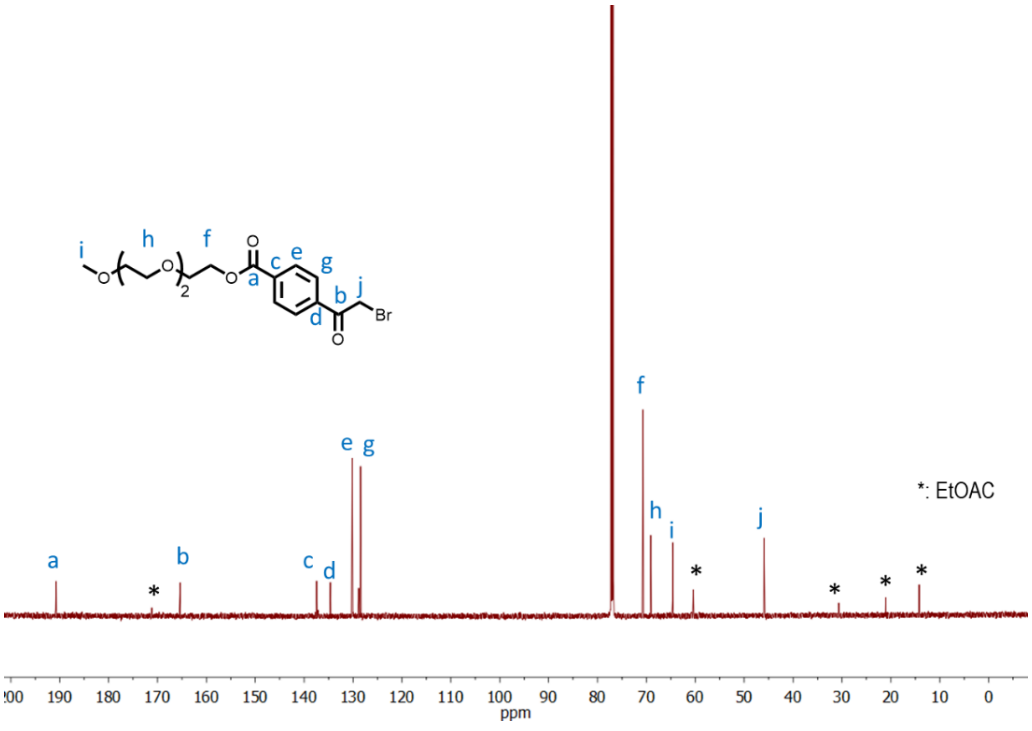
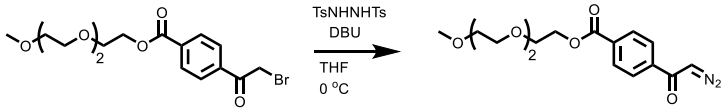


Figure S10. ^{13}C NMR spectrum of 2-(2-methoxyethoxy)ethyl 4-(2-bromoacetyl)benzoate ($CDCl_3$, 145 MHz).

2.6 2-(2-methoxyethoxy)ethyl 4-(2-diazoacetyl)benzoate (2)



2-(2-methoxyethoxy)ethyl 4-(2-bromoacetyl)benzoate (0.6 g, 3 mmol) and N,N'-ditosylhydrazine (2.04 g, 6 mmol) were dissolved in THF (20 mL) and the solution was cooled on an ice bath. DBU (2.25 mL, 15 mmol) was added dropwise to the solution, and allowed to warm to ambient temperature. The solution was stirred at ambient temperature and monitored with TLC until complete disappearance of the starting material. The mixture was quenched with saturated $NaHCO_3$ solution (50 mL), and extracted with diethyl ether (50 mL x3). The organic phases were combined, dried ($MgSO_4$), concentrated in vacuo and purified by column chromatography on SiO_2 and eluting with EtOAc:hexane (v/v = 2/1) to give product as pale yellow oil (yield: 0.37 g, 61%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 8.12-8.14 (d, *J* = 8.8 Hz), 7.81-7.83 (d, *J* = 8.6 Hz), 5.97 (s), 4.5-4.51 (t, *J* = 4.5 Hz), 3.84-3.86 (t, *J* = 4.8), 3.64-3.72 (m), 3.53-3.54 (m), 3.37 (s).

^{13}C NMR (145 MHz, Chloroform-*d*) δ/ppm: 185.4, 165.6, 140.1, 133.6, 130, 126.7, 71.9, 70.7, 69.1, 64.5, 59, 55.

$C_{16}H_{21}N_2O_6$ $[M]^+_{calculated}$ = 336.3440, $[M]^+_{experimental}$ = 336.3442

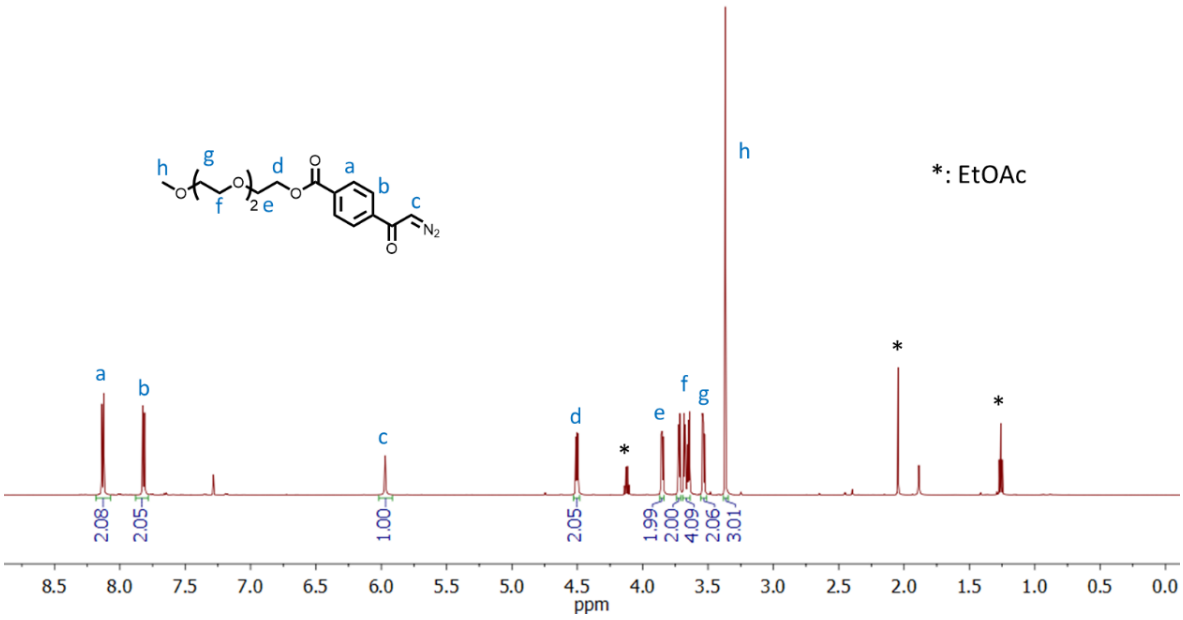


Figure S11. ^{1}H NMR spectrum of **2** ($CDCl_3$, 600 MHz).

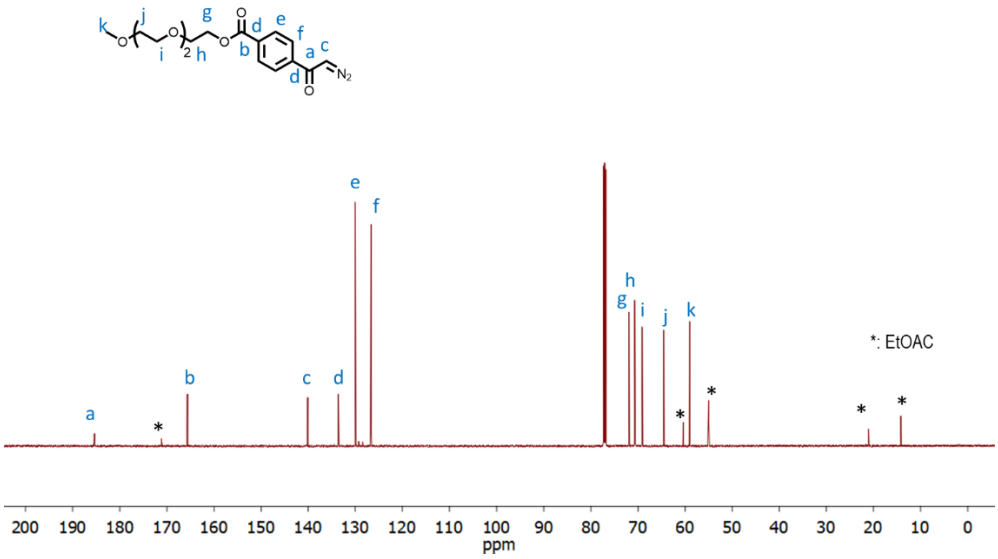


Figure S12. ^{13}C NMR spectrum of **2** ($CDCl_3$, 145 MHz).

2.7 2-(2-methoxyethoxy)ethyl 4-(2-diazoacetyl)benzoate (3)

Compound **3** was synthesized using a procedure similar to the synthesis of **2** (see above) starting from triethylene glycol to give the product (yield: 71%) as a slightly yellow oil that slowly solidified on standing at ambient temperature.

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 8.12-8.14 (d, *J* = 8.8 Hz), 7.81-7.83 (d, *J* = 8.6 Hz), 5.97 (s), 4.5-4.51 (t, *J* = 4.5 Hz), 3.84-3.86 (t, *J* = 4.8), 3.69-3.71 (m).

^{13}C NMR (145 MHz, Chloroform-*d*) δ/ppm: 185.4, 165.6, 140.1, 133.6, 130, 126.7, 71.9, 70.7, 69.1, 64.5, 59, 55.

$C_{22}H_{18}N_4O_7$ $[M]^+_{calculated}$ = 450.1175, $[M]^+_{experimental}$ = 450.1142

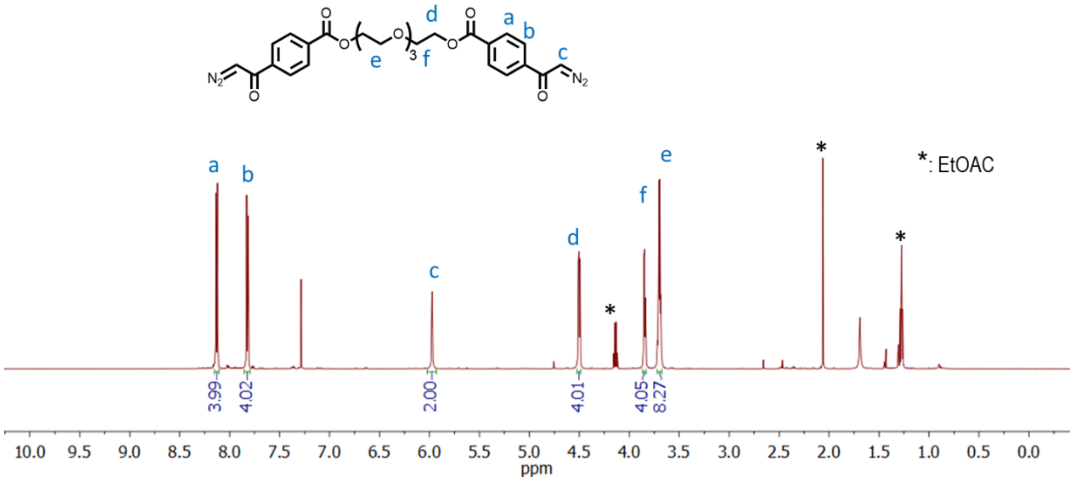


Figure S13. ^{1}H NMR spectrum of **3** ($CDCl_3$, 600 MHz).

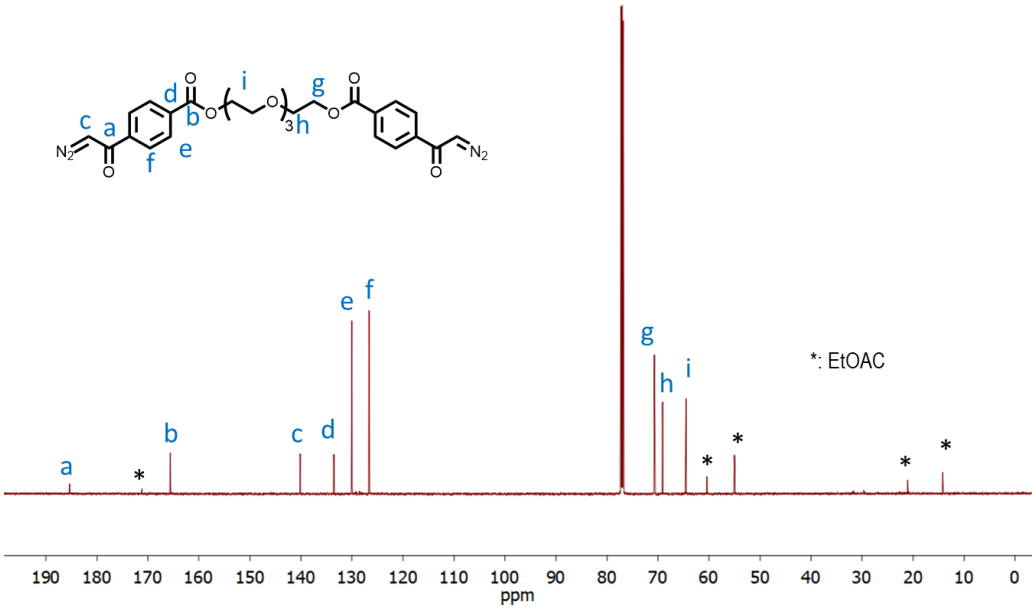


Figure S14. ^{13}C NMR spectrum of **3** ($CDCl_3$, 145 MHz).

2.8 General procedure for synthesis of esters and amides regulated by light and sonication

Trapping of the reactive ketene via β-lactam formation: **P1** (1 g, 0.5 mmol) and α-diazoacetophenone (7.5 mg, 0.51 mmol) were dissolved in dry dichloromethane (5 mL) and the solution was irradiated with

a blue LED light for 3 h in a water bath. The solution was subsequently precipitated in diethyl ether (25 mL) to give the PEG β-lactam product (**P2**) with a yield of 98%.

Release of the reactive ketene and production of ester/amide: **P2** was dissolved in dry dichloromethane (5 mL) in a glass vial and dry alcohol or amine (1 mmol) was added. The vial was sealed and sonicated in an ice-cold environment for 2 h. The solution was subsequently precipitated into diethyl ether (25 mL) and the polymer **P1** was recovered. The diethyl ether was washed with water (10 mL), saturated NH_4Cl solution (10 mL), brine (10 mL), and concentrated in vacuo and run through a short column of SiO_2 eluting with CH_2Cl_2 to give ester/amide products.

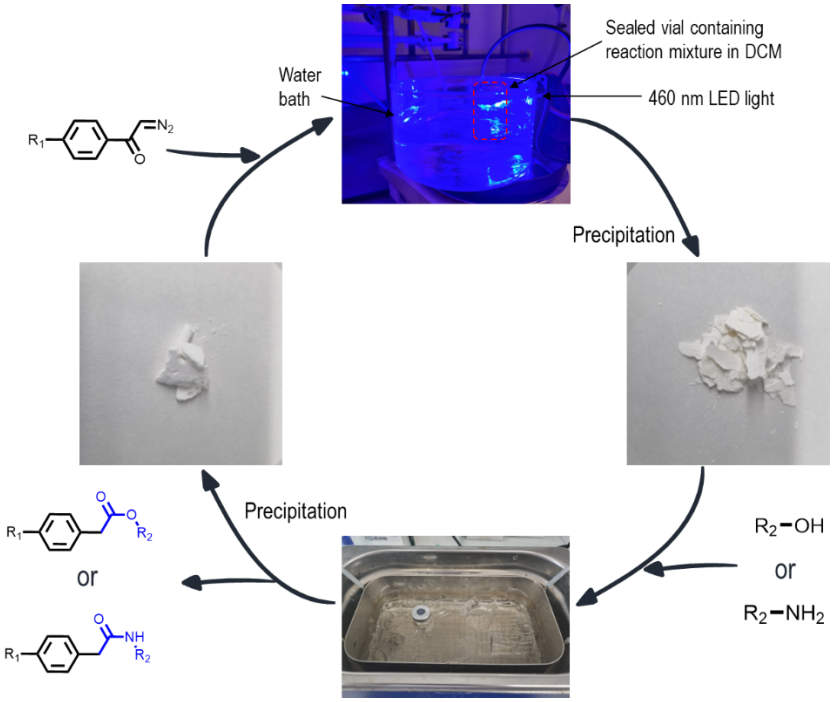


Figure S15. Photos of the process of light and mechanic field activated modification of polymer endgroups in the preparation of esters and amides. The PEG-benzyl imine and diazoketone were dissolved in dichloromethane and subjected to blue (460 nm) light irradiation for 3 h in a water bath, followed by precipitation in diethyl ether to yield PEG-β lactam. The solution of PEG-β lactam and alcohol or amine was then sonicated for 3 h in an ice bath, and precipitated in diethyl ether to produce the PEG-benzyl amine. Workup of the diethyl ether solution yields the respective ester or amine.

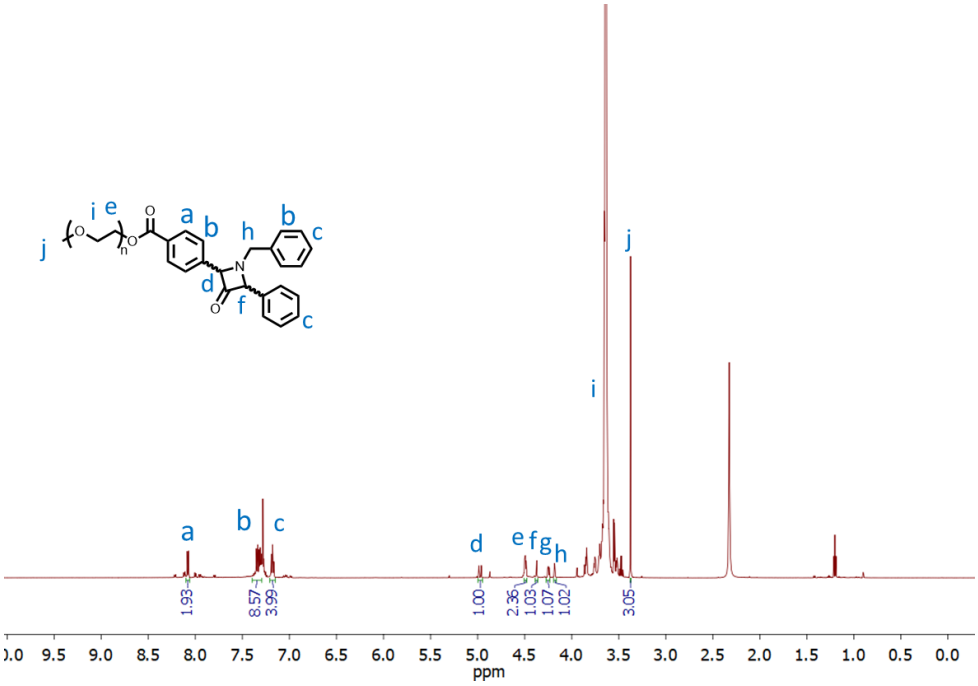


Figure S16. ^{1}H NMR spectrum of PEG-β lactam intermediate from **P1** with **1** ($CDCl_3$, 600 MHz), the material contains a small amount of diethyl ether.

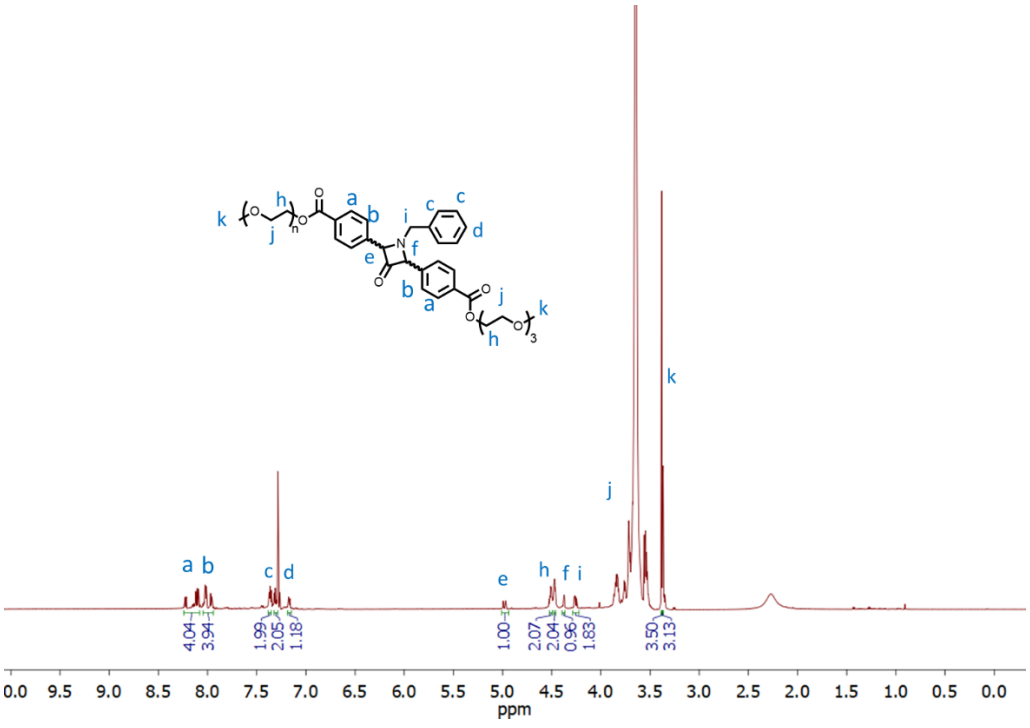
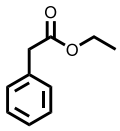


Figure S17. ^{1}H NMR spectrum of PEG-β lactam intermediate from **P1** with **2** ($CDCl_3$, 600 MHz).

1a



Yield: 86%

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 7.29-7.35 (m), 4.16-4.20 (q, *J* = 7.4 Hz, 7.2 Hz), 3.64 (s), 1.27-1.29 (t, *J* = 7.4 Hz).

^{13}C NMR (145 MHz, Chloroform-*d*) δ/ppm: 171.6, 134.2, 129.2, 128.6, 127, 60.9, 41.5, 14.2.

$C_{10}H_{12}O_2$ $[M]^+_{calculated}$ = 164.2040, $[M]^+_{experimental}$ = 164.2062

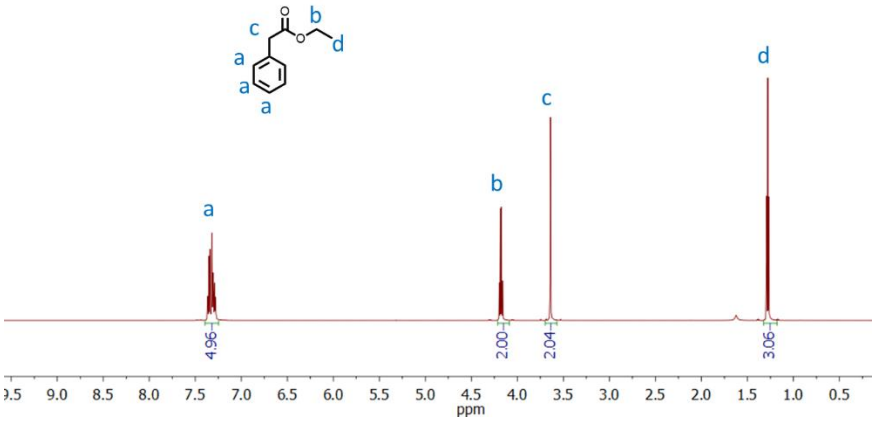


Figure S18. ^{1}H NMR spectrum of **1a** ($CDCl_3$, 600 MHz).

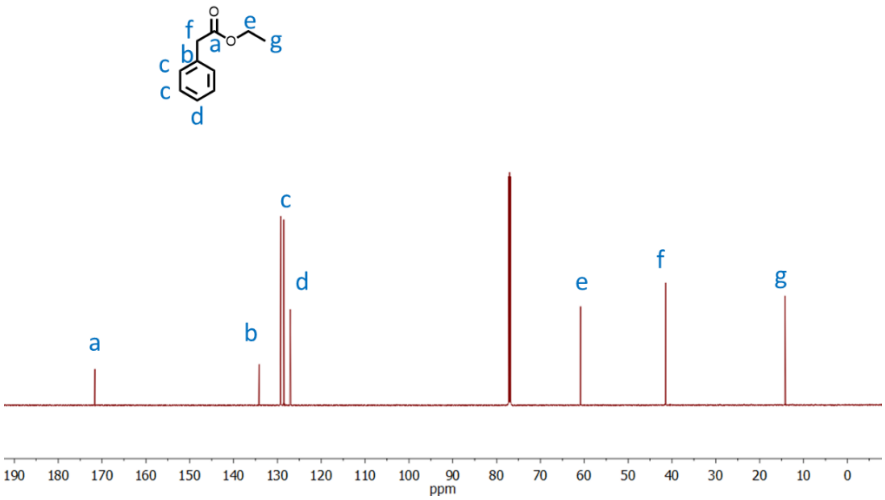
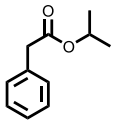


Figure S19. ^{13}C NMR spectrum of **1a** ($CDCl_3$, 145 MHz).

1b



clear oil, yield: 75%

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 7.28-7.35 (m), 5.03-5.05 (m), 3.61 (s), 1.25-1.26 (d, *J* = 6.3 Hz).

^{13}C NMR (145 MHz, Chloroform-*d*) δ/ppm: 171.2, 134.3, 129.2, 128.5, 127, 68.2, 41.7, 21.8.

$C_{11}H_{14}O_2$ $[M]^+_{calculated}$ = 178.0994, $[M]^+_{experimental}$ = 178.0951

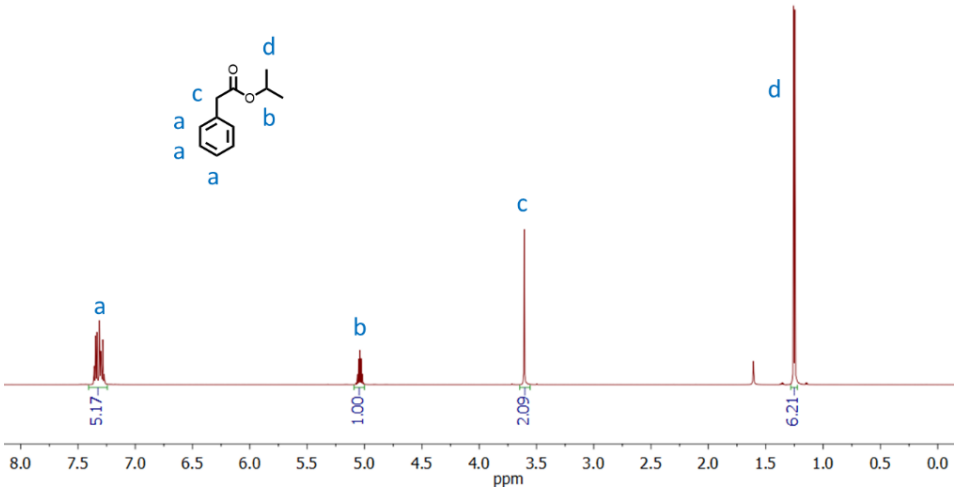


Figure S20. ^{1}H NMR spectrum of **1b** ($CDCl_3$, 600 MHz).

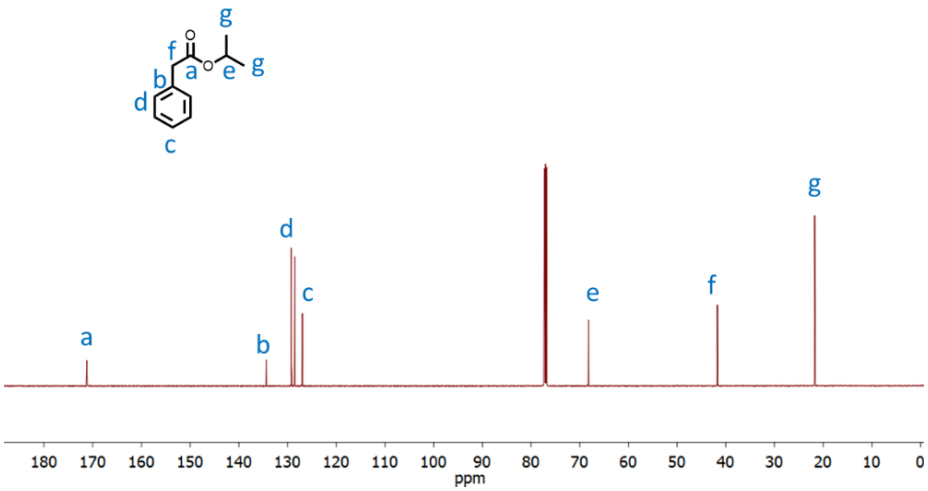
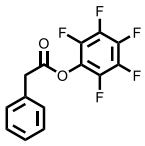


Figure S21. ^{13}C NMR spectrum of **1b** ($CDCl_3$, 145 MHz).

1c



clear oil, yield: 78%

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 7.36-7.48 (m), 4.01 (s).

^{13}C NMR (145 MHz, Chloroform-*d*) δ/ppm: 161.5, 132.1, 129.2, 129.1, 128.9, 127.8, 40.2.

$C_{14}H_7F_5O_2$ $[M]^+_{calculated}$ = 302.0366, $[M]^+_{experimental}$ = 302.0354

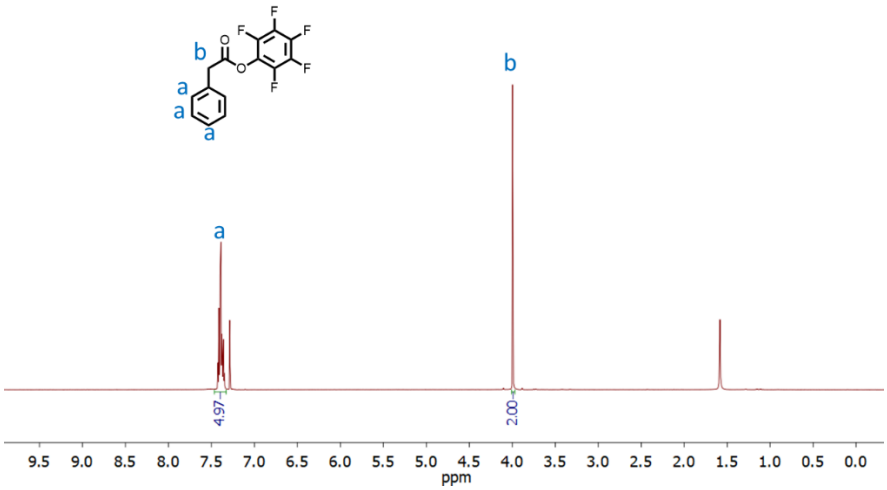


Figure S22. ^{1}H NMR spectrum of **1c** ($CDCl_3$, 600 MHz).

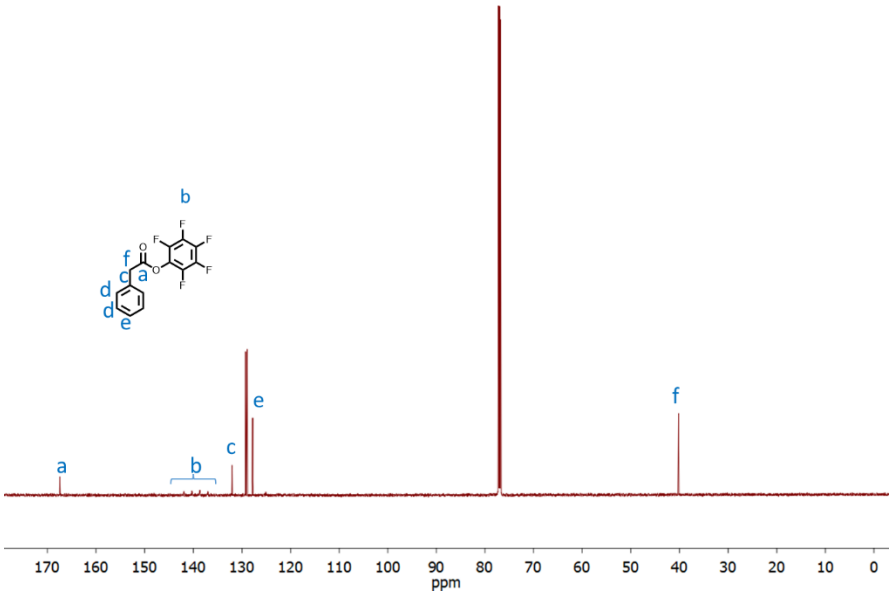
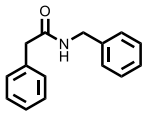


Figure S23. ^{13}C NMR spectrum of **1c** ($CDCl_3$, 145 MHz).

1d



white solid, yield: 83%

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 7.19-7.33 (m), 5.72 (s), 4.43-4.44 (d, 5.8 Hz), 3.66 (s)

^{13}C NMR (145 MHz, Chloroform-*d*) δ/ppm: 170.9, 138.1, 134.8, 128.7, 129.1, 129.5, 127.4, 43.9, 43.6.

$C_{14}H_{19}NO$ $[M]^{+}_{calculated}$ = 217.1467, $[M]^{+}_{experimental}$ = 217.1443

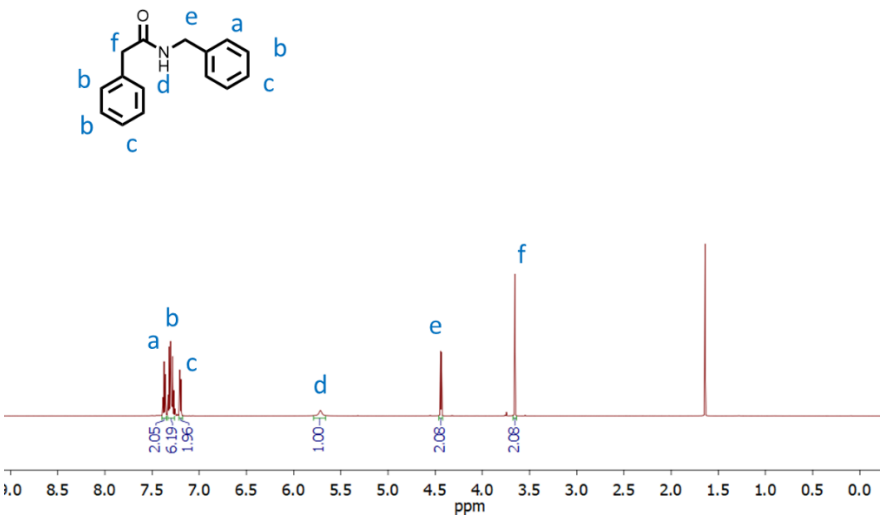


Figure S24. ^{1}H NMR spectrum of **1d** ($CDCl_3$, 600 MHz).

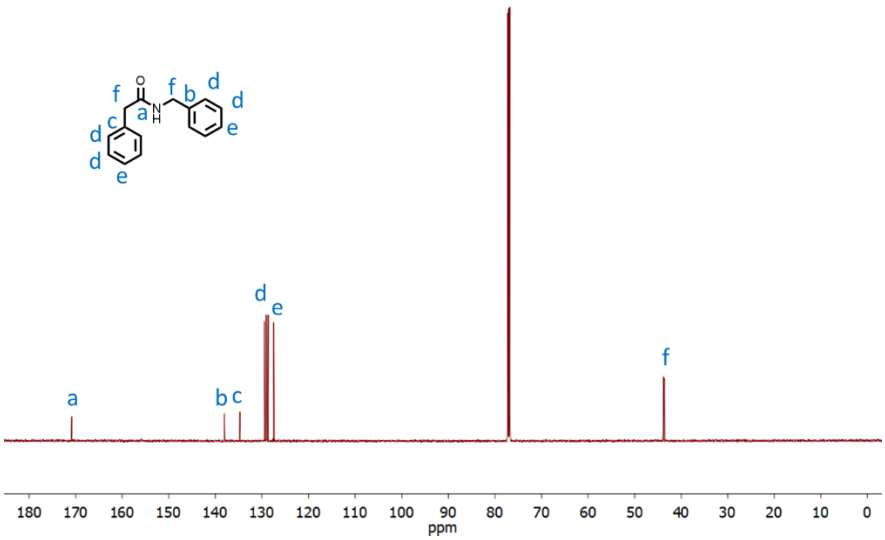
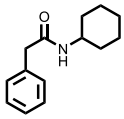


Figure S25. ^{13}C NMR spectrum of **1d** ($CDCl_3$, 145 MHz).

1e



White solid, yield: 80%

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 7.26-7.39 (m), 5.22 (s), 3.75-3.8 (m), 1.83-187 (m), 1.56-1.65 (m), 1.31-1.38 (m), 1-1.15 (m).

^{13}C NMR (145 MHz, Chloroform-*d*) δ/ppm: 170, 135.1, 129.4, 129, 127.3, 129.5, 127.4, 48.2, 44, 32.9, 25.5, 24.7.

$C_{14}H_{19}NO$ $[M]^{+}_{calculated}$ = 217.1467, $[M]^{+}_{experimental}$ = 217.1443

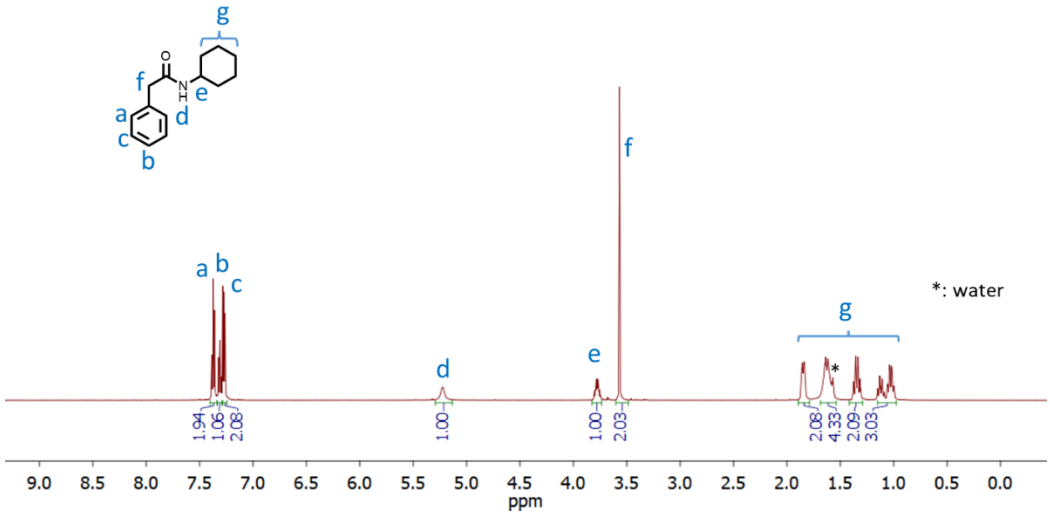


Figure S26. ^{1}H NMR spectrum of **1e** ($CDCl_3$, 600 MHz).

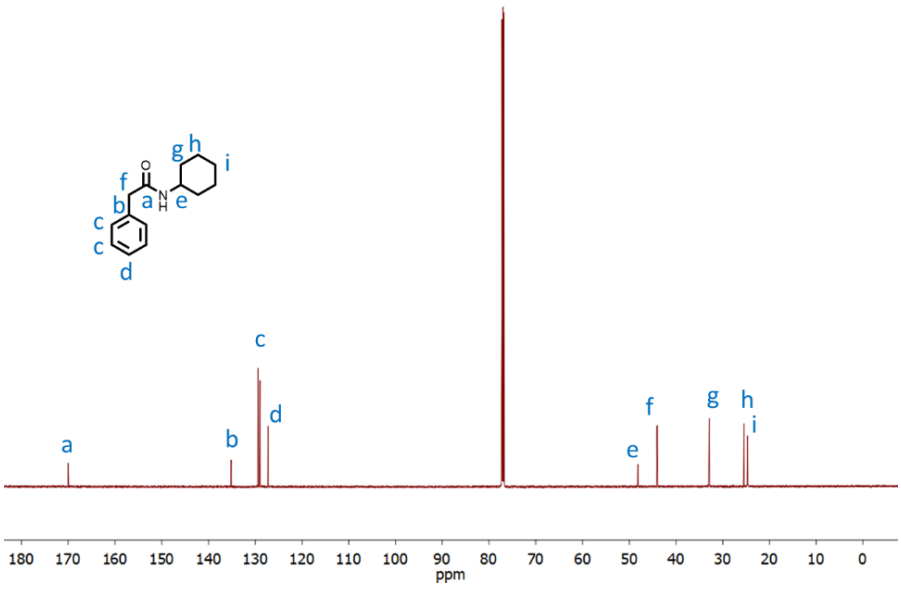
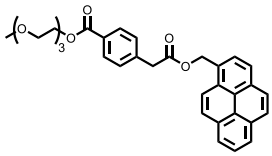


Figure S27. ^{13}C NMR spectrum of **1e** ($CDCl_3$, 145 MHz).

2a



The crude product was further purified by column chromatography running on SiO2 and eluting with CH_2Cl_2 to give the pure product as a pale-yellow wax, yield: 63%

^1H NMR (600 MHz, Chloroform-*d*) δ/ppm: δ: 8.02-8.23 (m), 8.01 (d, *J* = 8.4 Hz), 7.36 (d, *J* = 8.4 Hz), 5.87 (s), 4.48-4.5 (*J* = 4.9 Hz), 3.84-3.86 Hz (t, *J* = 4.8 Hz), 3.76 (s), 3.65-3.7 (m), 3.55 (m), 3.38 (s).

^{13}C NMR (145 MHz, Chloroform-*d*) δ/ppm: 170.8, 166.3, 139, 131.8, 131.2, 130.7, 130, 129.5, 129.4, 129.1 128.5, 128.2, 127.9, 127.8, 127.3, 126.1, 125.6, 125.5, 124.9, 124.6, 122.8, 71.9, 70.7, 70.6, 69.2, 64.2, 59, 41.4.

$C_{33}H_{32}O_7$ $[M]^+_{calculated}$ = 540.2148, $[M]^+_{experimental}$ = 540.2131

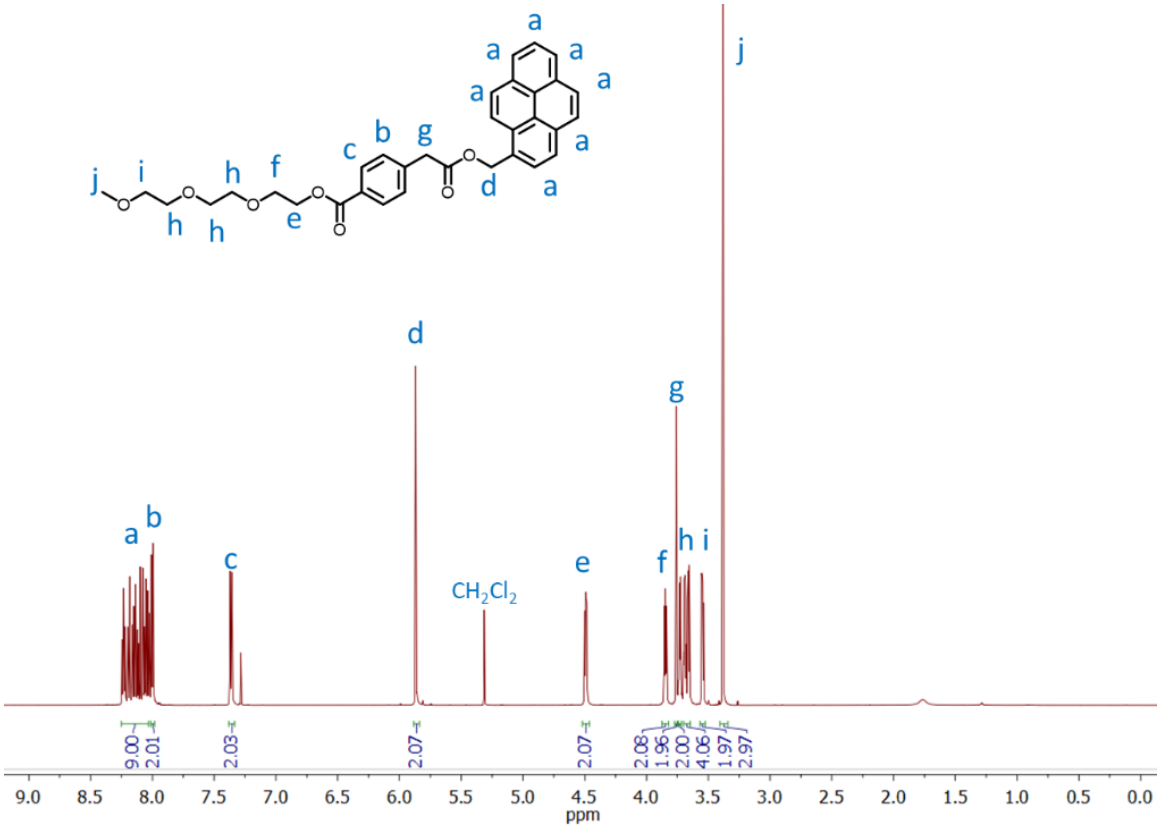


Figure S28. ^{1}H NMR spectrum of **2a** ($CDCl_3$, 600 MHz).

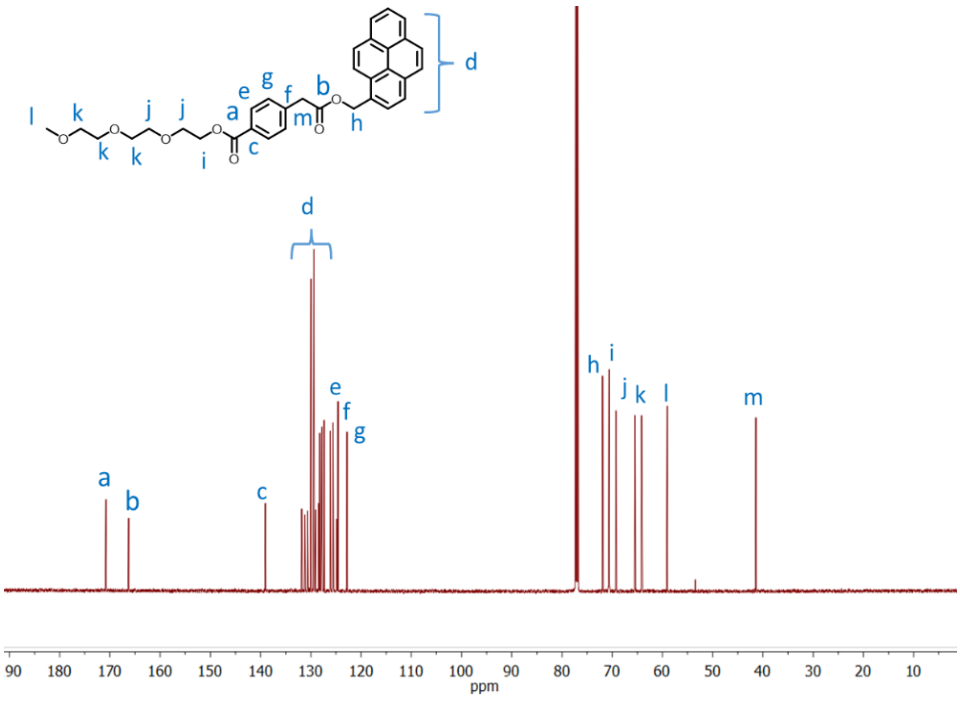


Figure S29. ^{13}C NMR spectrum of **2a** ($CDCl_3$, 145 MHz).

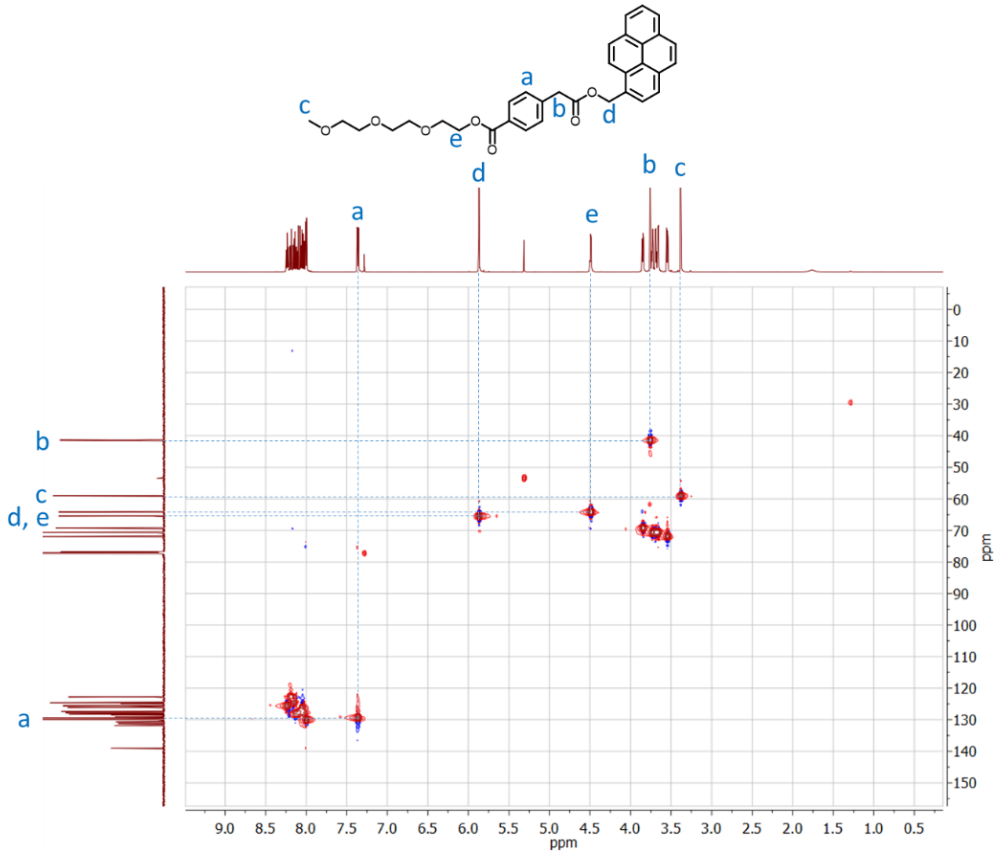
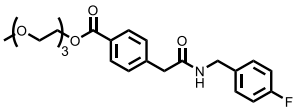


Figure S30. HSQC ^{1}H-^{13}C NMR of **2a**.

2b



The crude product was further purified by column chromatography running on SiO2 and eluting with CH_2Cl_2 to give pure product as clear wax, yield: 53%.

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 8.03 (d, *J* = 7 Hz), 7.35 (d, *J* = 7.1 Hz), 7.16-7.18 (t, *J* = 6 Hz), 6.98-7.01 (t, *J* = 7.7), 5.82 (s), 4.48 (t, *J* = 4.2 Hz), 4.38 (d, *J* = 5.2 Hz), 3.83-3.85 (t, *J* = 4.2 Hz), 3.65-3.73 (m), 3.55 (t, *J* = 3.6 Hz), 3.37 (s).

^{13}C NMR (145 MHz, Chloroform-*d*) δ/ppm: 170, 166, 163, 161, 140, 134, 130, 129, 116, 115, 77, 72, 71, 69, 64, 59, 44, 43.

$C_{23}H_{28}FNO_6$ $[M]^+_{calculated}$ = 433.1901, $[M]^+_{experimental}$ = 433.1889

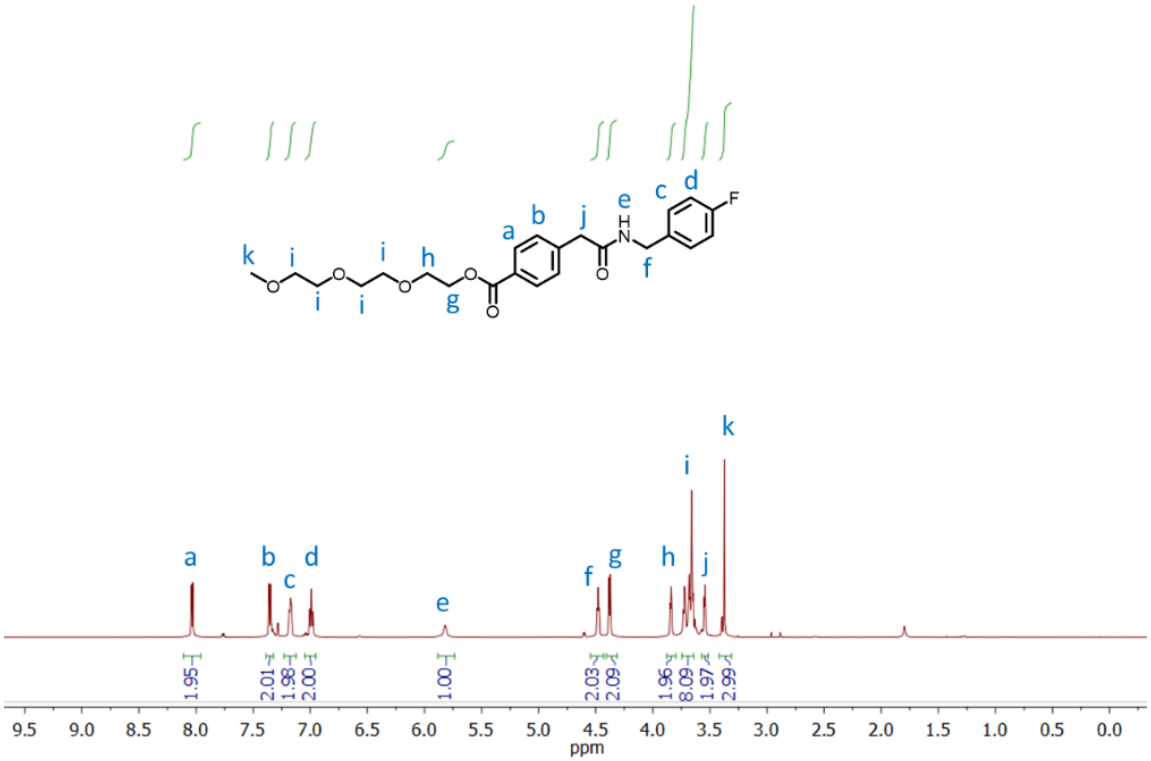


Figure S31. ^{1}H NMR spectrum of **2b** ($CDCl_3$, 600 MHz).

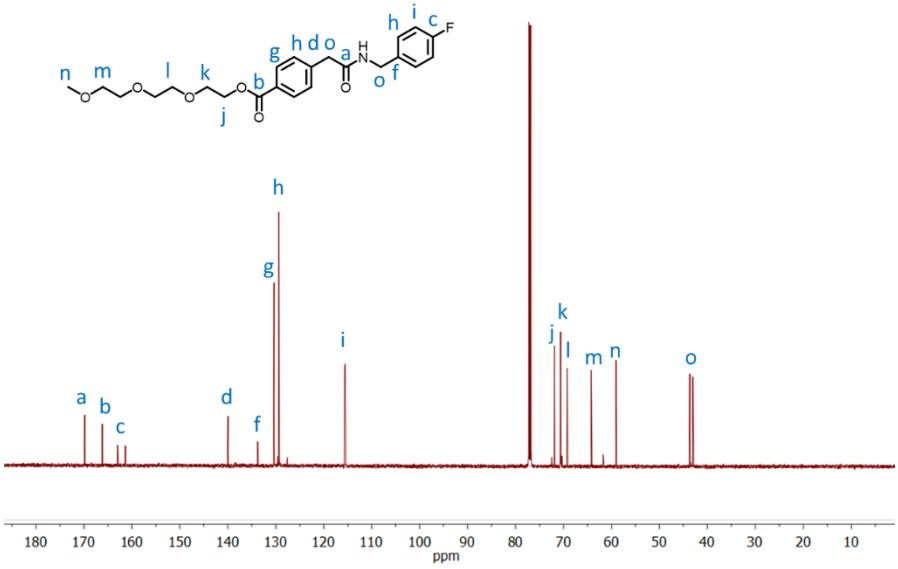


Figure S32. ^{13}C NMR spectrum of **2b** ($CDCl_3$, 145 MHz).

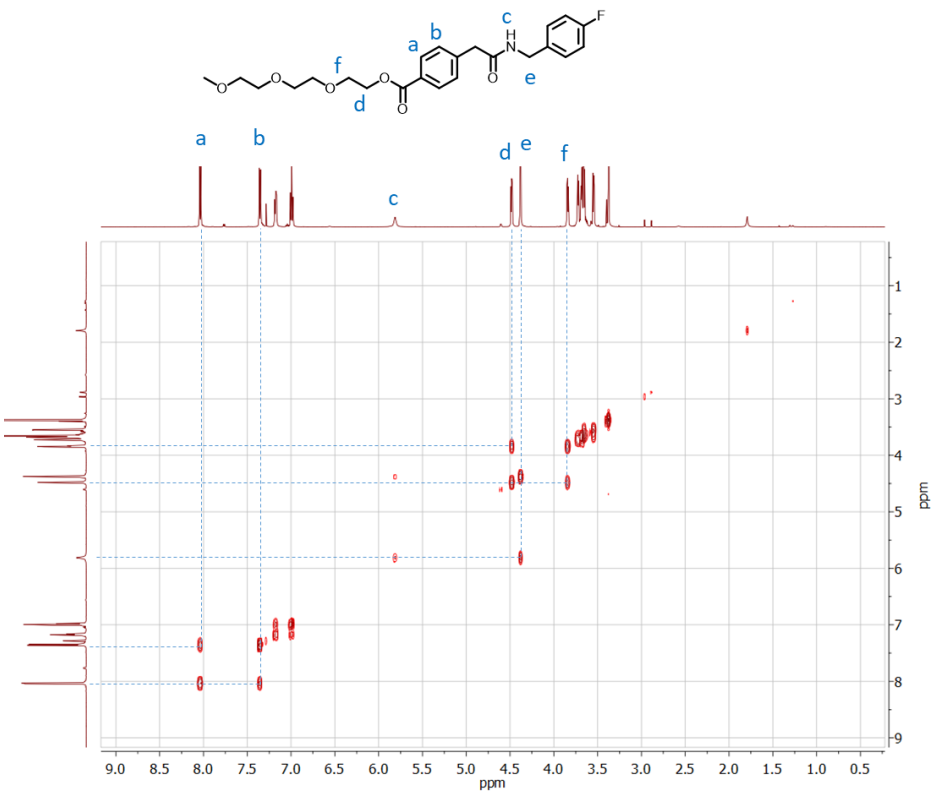


Figure S33. DOSY ^{1}H NMR of **2b** ($CDCl_3$, 600 MHz).

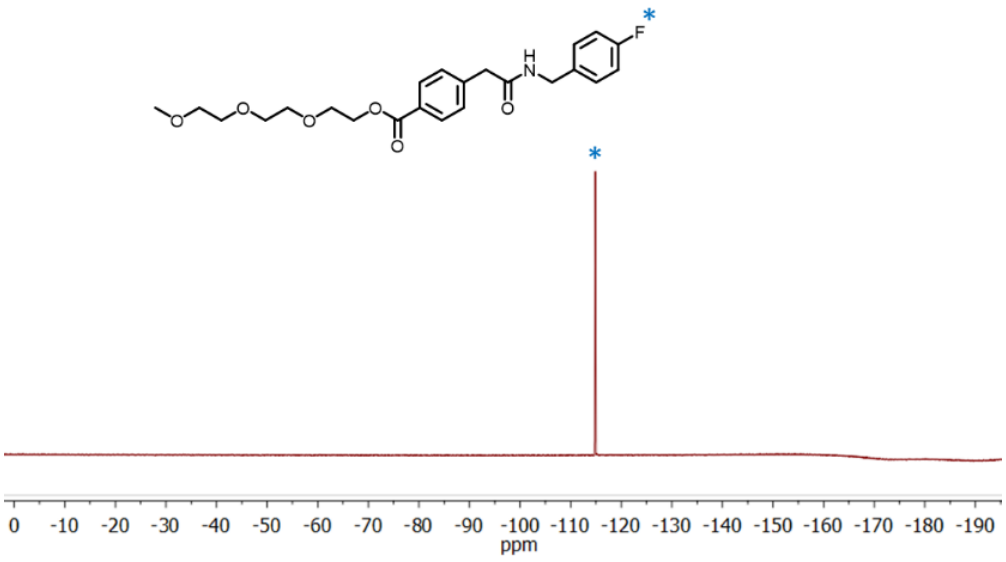


Figure S34. ^{19}F NMR of **2b** ($CDCl_3$, 564 MHz).

2.9 8-armed PEG-benzyl imine (P3)

8-armed PEG-benzyl imine was prepared from 8-armed PEG-OH (molar mass = 10,000 Da) following a procedure similar to the synthesis of MeO-PEG-benzyl imine **P1** (see **2.4**) with a total yield of 92%.

^{1}H NMR (600 MHz, Chloroform-*d*) δ/ppm: 8.46 (s), 8.1-8.12 (d, *J* = 8.1 Hz), 7.85-7.87 (d, *J* = 8.4 Hz), 7.36-7.37 (m), 4.88 (s), 4.49-4.51 (t, *J* = 4.8 Hz), 3.85-3.87 (t, *J* = 4.8 Hz), 3.66 (broad s), 3.41(s), 3.35 (s).

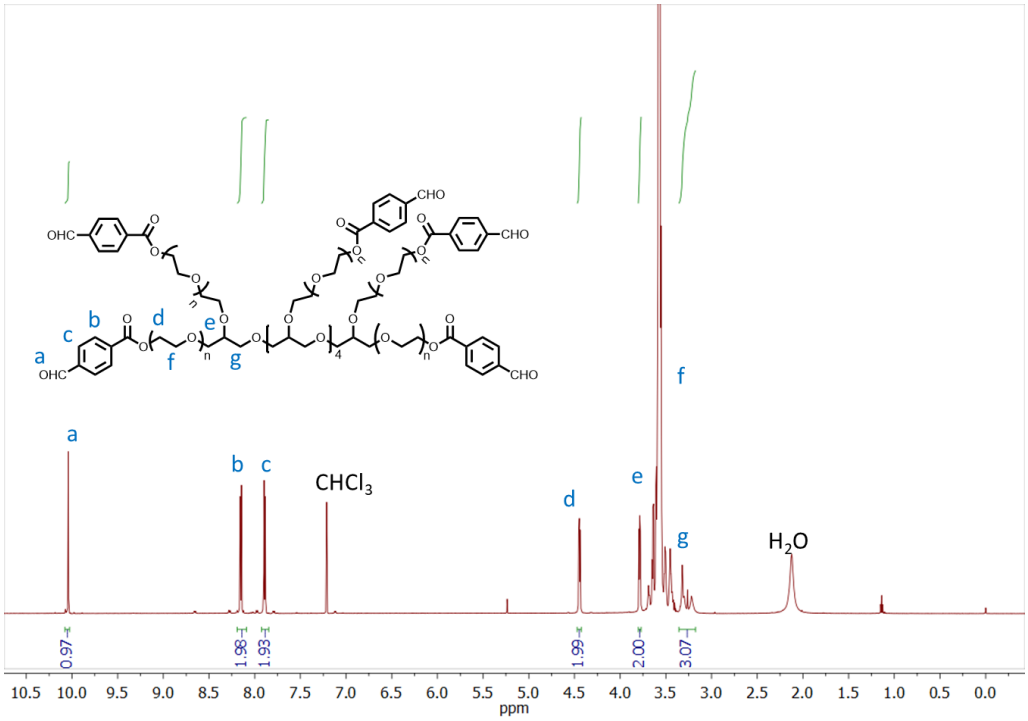


Figure S35. ^{1}H NMR spectrum of 8-armed PEG-benzaldehyde ($CDCl_3$).

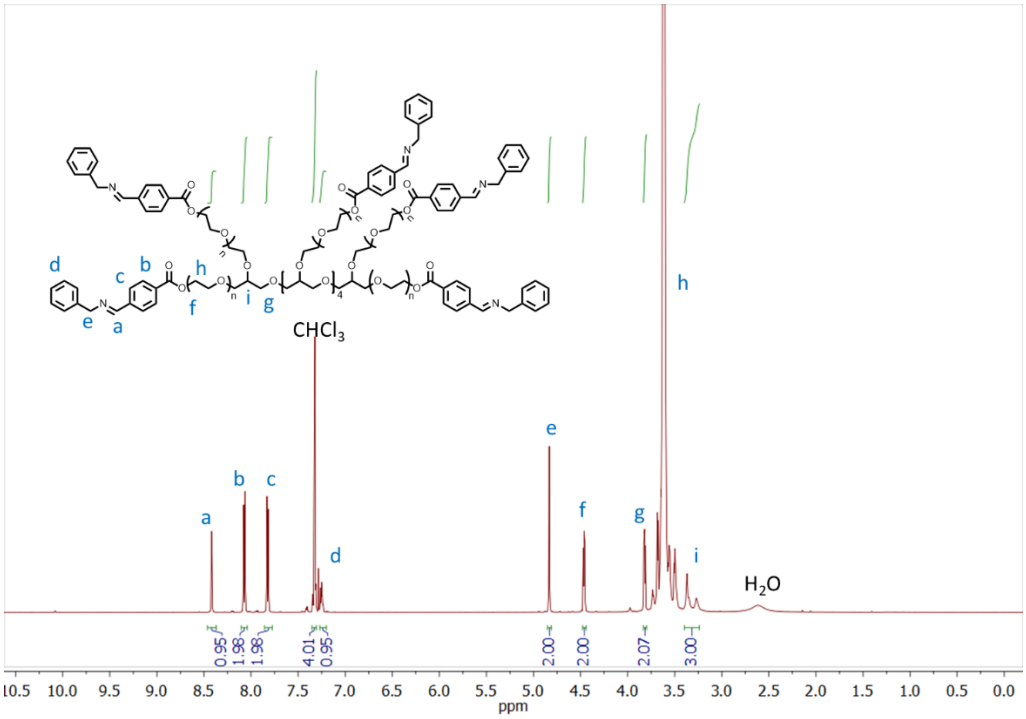


Figure S36. ^{1}H NMR spectrum of 8-armed PEG-benzyl imine (**P3**).

References

[1] K. Jovic, T. Nitsche, C. Lang, J. P. Blinco, K. De Bruycker and C. Barner-Kowollik, *Polymer Chemistry* **2019**, *10*, 3241-3256.
[2] T. Toma, J. Shimokawa and T. Fukuyama, *Organic Letters* **2007**, *9*, 3195-3197.