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Supporting Information

Catalyst Free Visible Light Induced Cycloaddition as an Avenue for Polymer Ligation

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Contents

1. General

Materials

Air-sensitive reactions were carried out under an atmosphere of ultrahigh purity argon. 1-(2-hydroxyethyl)-1H-pyrrole-2,5-dione **2** was synthesized according to the literature.[1] 2-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-epoxyisoindol-2-yl)ethyl 2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoate **5** was synthesized according to the literature.[2] All other reagents were purchased from commercial suppliers and used without further purification.

Characterisation

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer and referenced to the relevant solvent peak. Solvent used is listed in the spectra description.

ESI-high-resolution mass spectra were obtained using a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) with an HESI II probe. The instrument calibration was carried out in the *m*/*z* range 74-1822 using calibration solutions from Thermo Scientific. A constant spray voltage of 4.7 kV and a dimensionless sheath gas of 5 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62.0, respectively. The samples were dissolved in THF:MeOH mixture (3:2) containing 100 µmol of sodium triflate and injected with a flow of 5 µL·min^{-1}.

Molecular weight determination was performed on a GPC system (PL-GPC 50 Plus, Polymer Laboratories) consisting of an auto injector, a guard column (PLgel Mixed C, 50 × 7.5 mm), three linear columns (PLgel Mixed C, 300 × 7.5 mm, 5 µm bead-size) and a differential refractive index detector using THF as the eluent at 35 °C and a flow rate of 1 mL·min^{-1}. The system was calibrated using narrow PMMA standards (Polymer Standard Service) ranging from 160 to 6 × 10^{6} g·mol^{-1}. Samples were injected from solutions in THF (2 mg·mL^{-1}) and molecular weight distributions were referenced versus polystyrene (PS) standards.

Absorption spectra were recorded using the 300 UV/Vis Spectrometer (Varian Cary) in MeCN ($c_{\text{target compound}}$ = 20 µmol·L^{-1}).

Fluorescense spectra were recorded using the Fluorescence Spectrometer (Carry Eclipse) in MeCN ($c_{\text{target compound}}$ = 20 µmol·L^{-1}).

Fluorescence quantum yield was recorded using Hamamatsu Quantaurus QY in MeCN (c = 2.5 µM, λ_{ex} = 365 nm, emission range: 400-800 nm).

Irradiation

All samples were irradiated in a 250 mL round bottom flask with 3 blue light diodes (Avonec, 410-420 nm, 3 W, actinic blue with an emission angle of 120° grafted on cooling elements (Fischer, SK577-25SA - 50 mm × 25 mm)) set up triangularly on top of a magnetic stirrer.

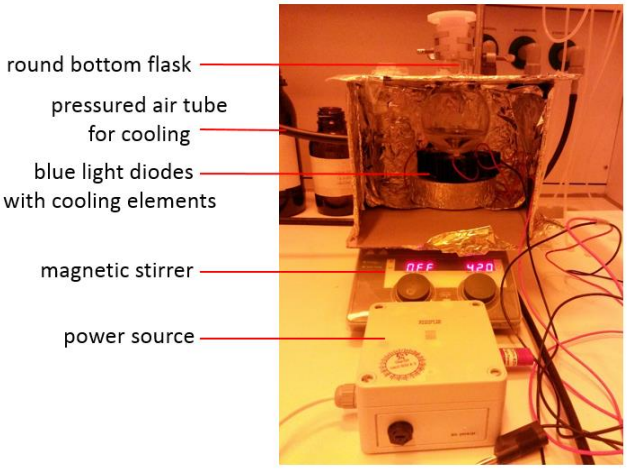


Figure S1 Set up for the photo reactions. A paper box covered with aluminum foil inside was used as reactor.

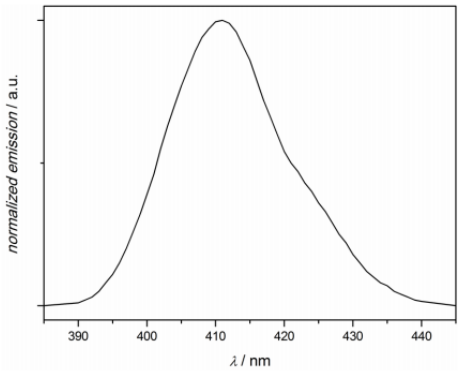
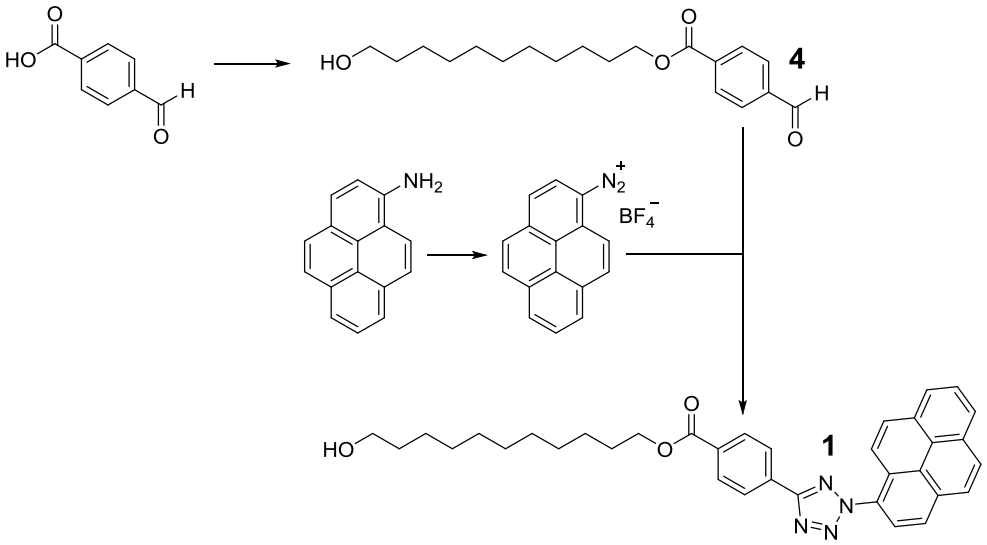


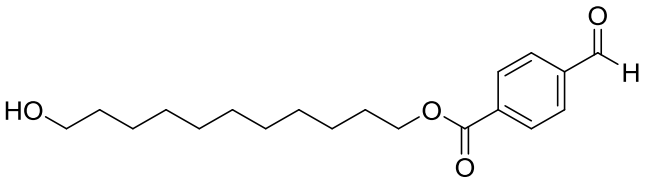
Figure S2 Emission spectra of Avonec, 410-420 nm, 3 W, actinic blue.

2. Synthesis of pyrene functional aryl tetrazole containing compounds

Scheme S1 **Synthesis of pyrene functionalized aryl tetrazole (1).**



11-hydroxyundecyl 4-formylbenzoate (4)



4-formylbenzoic acid (414 mg, 2.76 mmol) and 11-bromoundecan-1-ol (800 mg, 3.20 mmol) were dissolved in 5 mL dry DMF under argon and $NaHCO_3$ (463 mg, 5.51 mmol) was added. The reaction mixture was stirred for 1 h at 125 °C. After cooling down to room temperature the reaction mixture was diluted with 100 mL ethyl acetate washed with 1 M HCl (3 x 100 mL) and dried over $NaSO_4$. Ethyl acetate was removed under reduced pressure. The crude product was purified via column chromatography on silica gel using cyclohexane/ethyl acetate (1:1, v/v R_f 0.62) as the eluent. After drying under high vacuum the title compound **4** was obtained as white solid (781 mg, 88%). ^{1}H NMR (400 MHz , $CDCl_3$) δ = 10.11 (s, 1 H), 8.23 – 8.18 (m, 2 H), 7.98 – 7.93 (m, 2 H), 4.38 – 4.33 (m, 2 H), 3.66 – 3.63 (m, 2 H), 1.84 – 1.80 (m, 2 H), 1.59 – 1.54 (m, 2 H), 1.40 -1.25 (m, 14 H); ^{13}C NMR (100 MHz , $CDCl_3$) δ = 191.7, 165.7, 139.1, 135.5, 130.2, 129.5, 65.8, 63.1, 32.8, 29.6, 29.5, 29.4, 29.2, 28.6, 26.0, 25.7; HRMS $[M+Na]^+$ m/z: calcd for $C_{19}H_{28}NaO_4$ 343.1885 fond 343.1828.

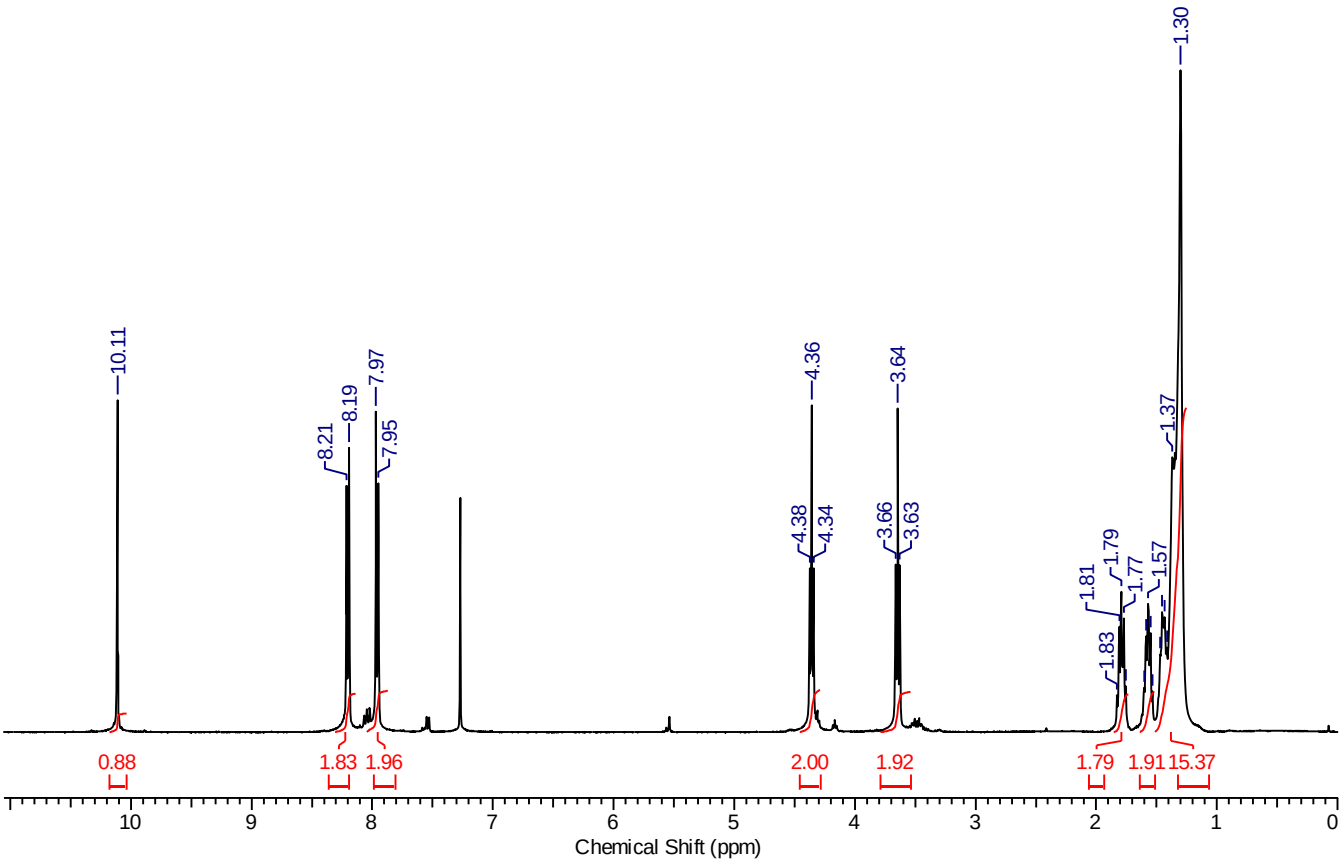


Figure S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 11-hydroxyundecyl 4-formylbenzoate **4**.

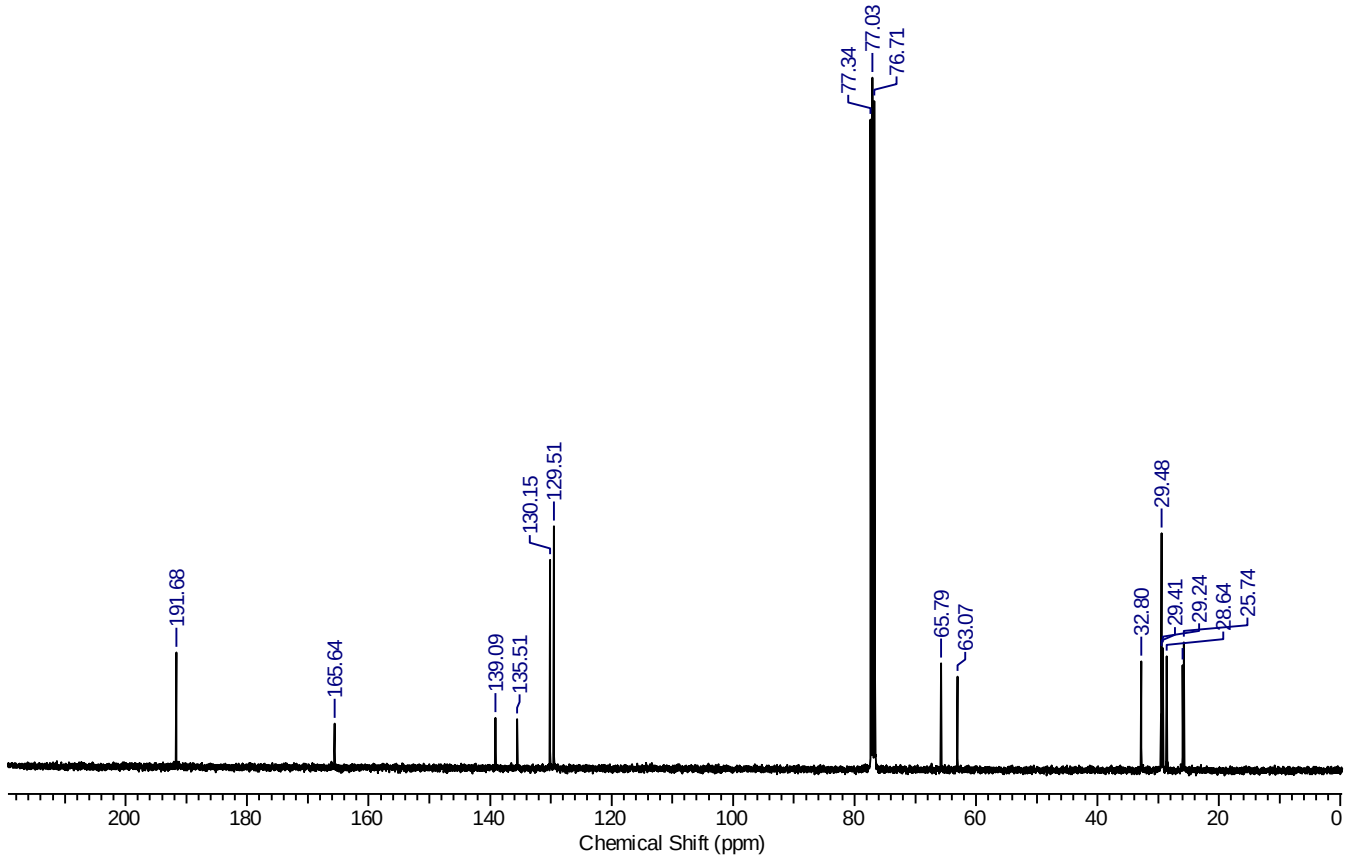
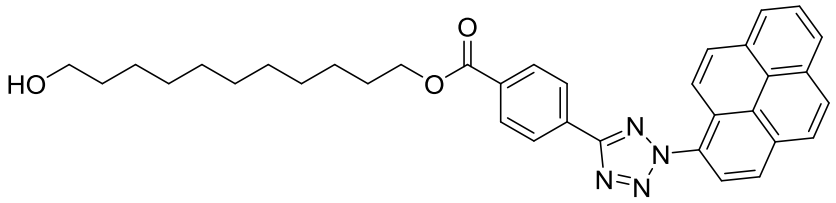


Figure S4 ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 11-hydroxyundecyl 4-formylbenzoate **4**.

11-hydroxyundecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate (1)



A mixture of 11-hydroxyundecyl 4-formylbenzoate **4** (472.6 mg, 1.48 mmol) and benzenesulfonohydrazide (254.0 mg, 1.48 mmol) in 15 mL EtOH was stirred at ambient temperature for 3 h. The solvent was removed under reduced pressure. The obtained solid was dissolved in 8 mL pyridine (solvent A). In parallel 1-aminopyrene (258.0 mg, 1.19 mmol) was dissolved in 30 mL THF under argon and cooled to -21 °C. A solution of $NaBF_4$ (1050 mg, 9.55 mmol) in 10.5 mL HBF_4 (50%) and 4.5 mL H_2O was added. The reaction mixture was stirred for 20 min at -21 °C. $NaNO_2$ (94.2 mg, 1.37 mmol) in 2 mL H_2O was added. An orange precipitate was formed after stirring at -21 °C for additional 20 min. The solid was collected and added to solution A at 0 °C. The reaction mixture was stirred for 1 h at room temperature, diluted in 80 mL ethyl acetate, extracted with 1 M hydrochloric acid (2×100 mL) and dried over $NaSO_4$. Ethyl acetate was removed under reduced pressure. The crude product was purified via recrystallization in EtOH (3×30 mL). After drying under high vacuum the title compound **1** was obtained as pink solid (181 mg, 32%). ^1H NMR (400 MHz , $CDCl_3$) δ = 8.40 - 8.06 (m, 13 H), 4.43 – 4.35 (m, 2 H), 3.70 – 3.63 (m, 2 H), 1.79 – 1.70 (m, 2 H), 1.55 - 1.22 (m, 16 H); ^{13}C NMR (100 MHz , $CDCl_3$) δ = 166.1, 164.6, 132.8, 132.3, 131.2, 131.1, 130.5, 130.3, 130.1, 129.4, 127.1, 127.0, 126.9, 126.7, 126.3, 125.1, 125.0, 124.8, 124.1, 122.7, 121.4, 65.5, 63.1, 32.8, 29.6, 29.5, 29.4, 29.3, 28.7, 26.1, 25.8; HRMS $[M+Na]^+$ m/z: calcd for $C_{35}H_{36}N_4NaO_3$ 583.2685 fond 583.2685.

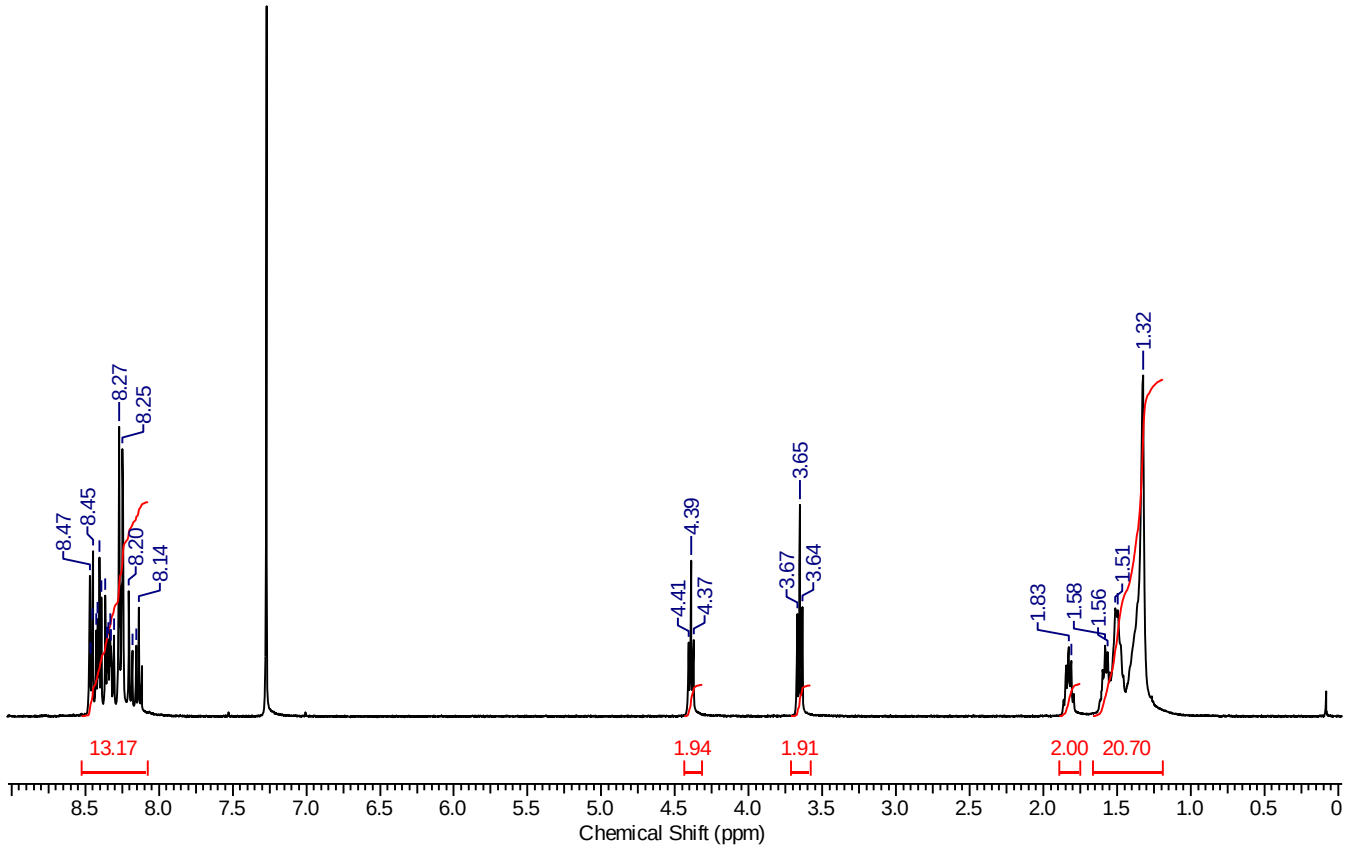


Figure S5 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 11-hydroxyundecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate **1**.

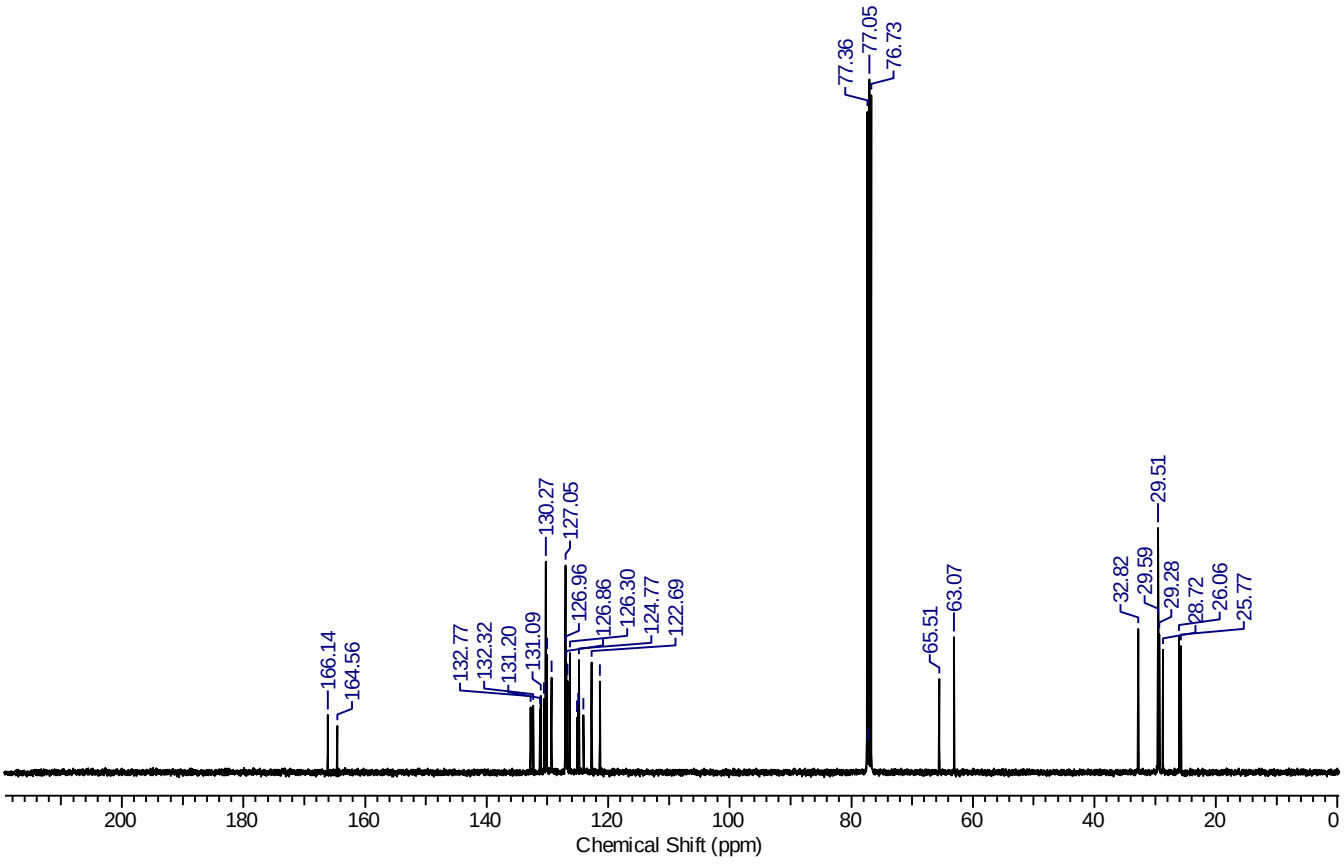
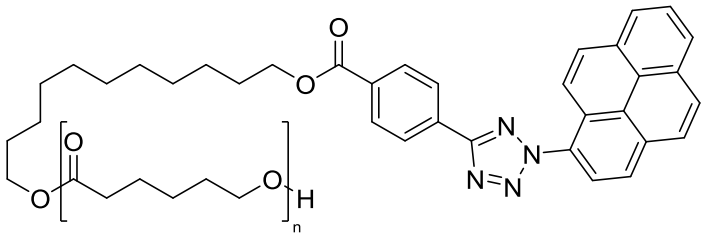


Figure S6 ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 11-hydroxyundecyl 4-formylbenzoate 11-hydroxyundecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate **1**.

Synthesis of PAT end capped PCL (A_1)



11-hydroxyundecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate **1** (98.0 mg, 0.18 mmol) and triazabicyclodecene (TBD) (24.4 mg, 0.18 mmol) were dissolved in 10 mL dry DCM under argon. ε-Caprolactone (500.0 mg, 4.38 mmol) was added. The reaction mixture was stirred at room temperature for 3 h. Benzoic acid (50.0 mg, 0.41 mmol) was added. The solvent was removed under reduced pressure. The crude product was dissolved in ethyl acetate (100 mL) and washed with 1 M HCl (3×100 mL) and saturated $NaHCO_3$ (3×100 mL). Solvent was removed under reduced pressure and the crude product was precipitated in ice cold cyclohexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.47-8.12 (m, 13 H), 4.41 – 4.37 (m, 2 H), 4.09 – 4.04 (m, polymer backbone), 3.67 – 3.63 (m, 2 H), 2.33 – 2.28 (m, polymer backbone), 1.86 - 1.79 (m, 2 H), 1.70 - 1.25 (m, 16 H + polymer backbone); M_n = 1.4 kDa (^{1}H NMR), M_n = 2.0 kDa (GPC), $Đ$ = 1.10.

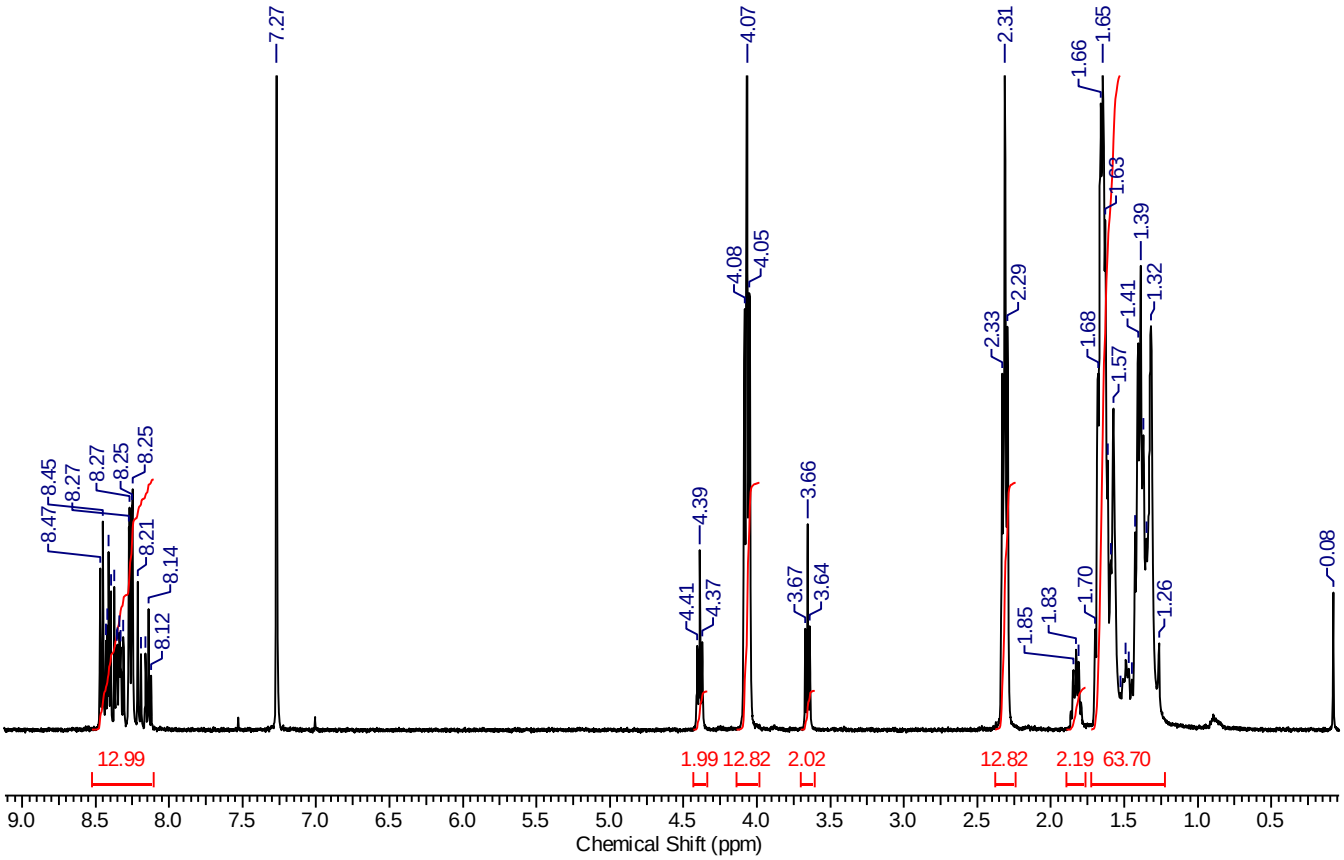


Figure S7 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of PAT end capped PCL **A_1** synthesized via ROP of hydroxyl functional PAT **1**.

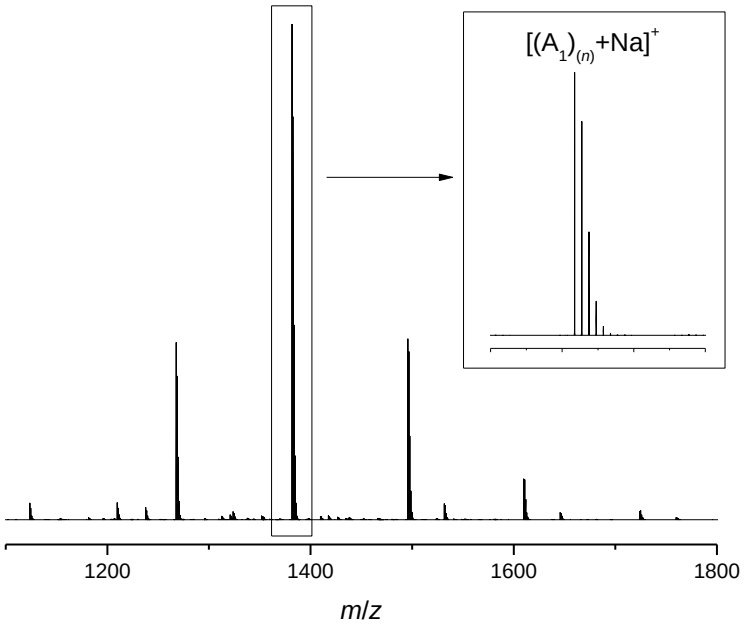


Figure S8 Magnified view into the region of 1100-1800 *m*/*z* of a ESI-MS spectrum of PAT end capped PCL $\mathbf{A_1}$ obtained in ROP polymerization employing PAT **1**. Signals repeat in intervals of 114.14 Dalton. Sodium adduct of PAT end-capped PCL, $[(A_1)_{(n)} + Na]^+$.

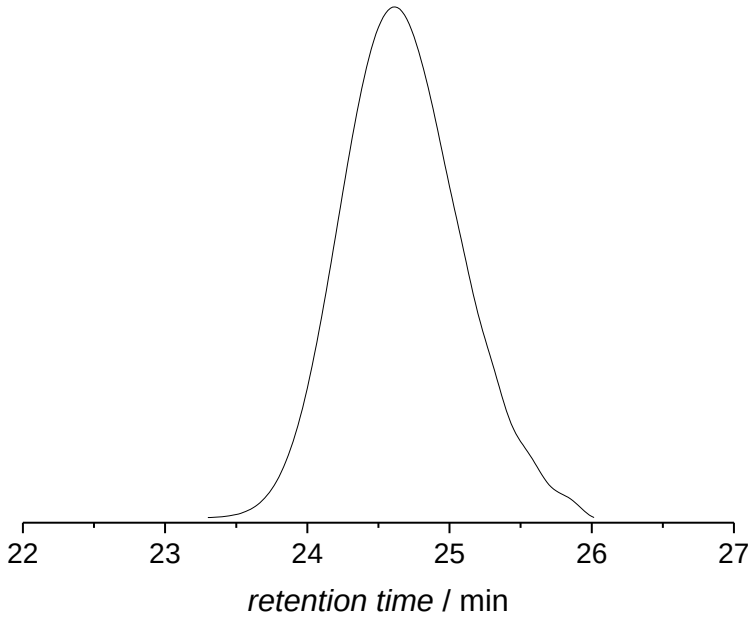


Figure S9 GPC trace of PAT end capped PCL $\mathbf{A_1}$ obtained in ROP polymerization employing PAT **1** (M_n = 1.4 kDa (^{1}H NMR), M_n = 2.0 kDa (GPC), $Đ$ = 1.10).

Synthesis of PAT end capped PCL (A_2)

11-hydroxyundecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate **1** (98.0 mg, 0.18 mmol) and triazabicyclodecene (TBD) (24.4 mg, 0.18 mmol) were dissolved in 10 mL dry DCM under argon. ε-Caprolacton (700.0 mg, 4.38 mmol) was added. The reaction mixture was stirred at room temperature for 3 h. Benzoic acid (50.0 mg, 0.61 mmol) was added. The solvent was removed under reduced pressure. The crude product was precipitated in cold cyclohexane/EtO_2 mixture (1:1). ^{1}H NMR (400MHz, $CDCl_3$) δ = 8.47-8.12 (m, 13 H), 4.41 – 4.37 (m, 2 H), 4.09 – 4.04 (m, polymer backbone), 3.67 – 3.63 (m, 2 H), 2.33 – 2.28 (m, polymer backbone), 1.86 - 1.79 (m, 2 H), 1.70 - 1.25 (m, 16 H + polymer backbone); M_n = 4.2 kDa (^{1}H NMR), M_n = 5.8 kDa (GPC), $Đ$ = 1.15.

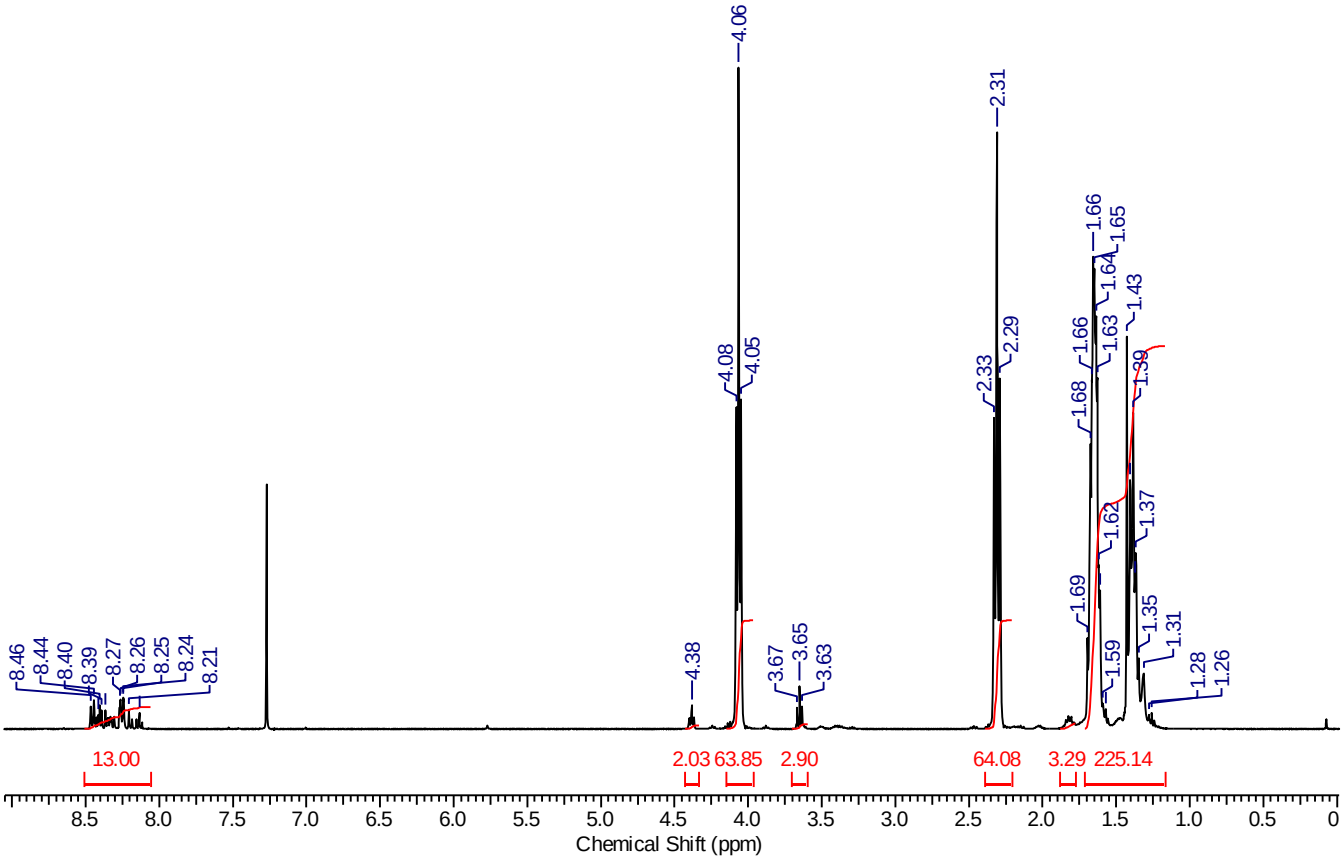


Figure S10 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of PAT end capped PCL **A_2** synthesized via ROP of hydroxyl functional PAT **1**.

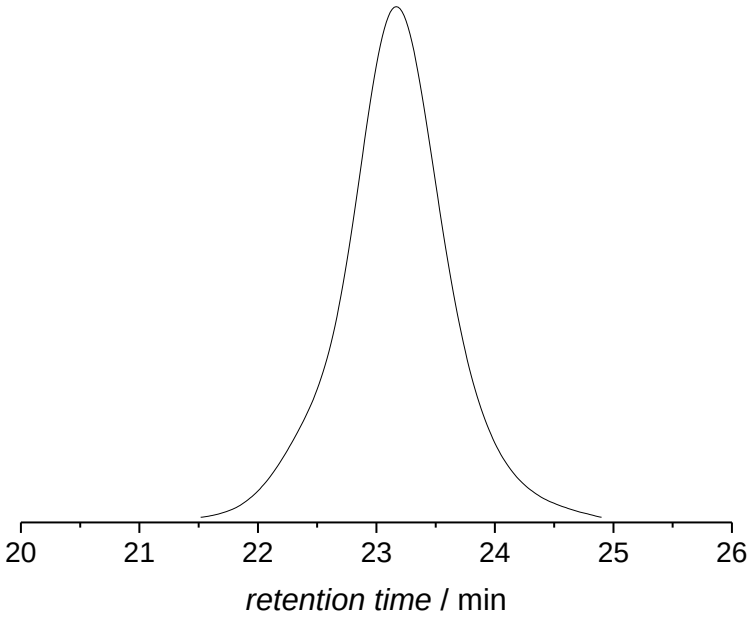
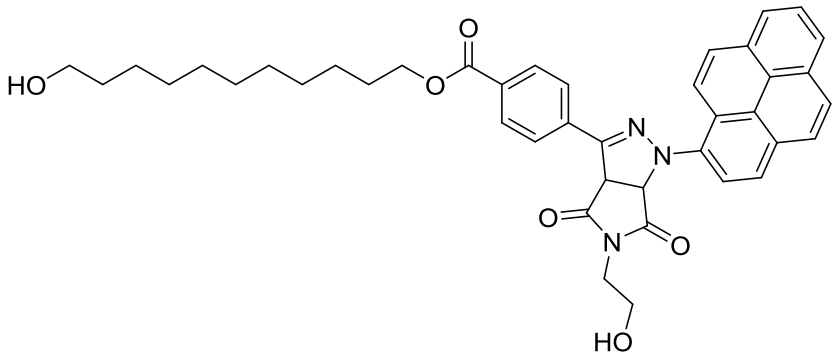


Figure S11 GPC trace of PAT end capped PCL $\mathbf{A_2}$ obtained in ROP polymerization employing PAT **1** (M_n = 4.2 kDa (^{1}H NMR), M_n = 5.8 kDa (GPC), $Đ$ = 1.15).

3. Synthesis of Cycloadducts via visible light NITEC

11-hydroxyundecyl 4-(5-(2-hydroxyethyl)-4,6-dioxo-1-(pyren-1-yl)-1,3a,4,5,6,6a-hexahydropyrrolo[3,4-c]pyrazol-3-yl)benzoate (3)



11-hydroxyundecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate **1** (10.0 mg, 0.018 mmol) and 1-(2-hydroxyethyl)-1H-pyrrole-2,5-dione **2** (5.0 mg, 0.022 mmol) were dissolved in 40 mL MeCN. The reaction mixture was irradiated at room temperature, 400 nm for 1 h. The solvent was removed under reduced pressure. The crude product was purified via column chromatography on silica gel using hexane/ethyl acetate (2:1, v/v R_f 0.26) as the eluent. After drying under high vacuum the title compound **3** was obtained as yellow solid (8.0 mg, 71%). ^{1}H NMR (400MHz, $CDCl_3$) δ = 8.47 - 7.84 (m, 13 H), , 5.50 – 5.29 (m, 1H), 4.88 – 4.68 (m, 1 H), 4.29 - 4.16 (m, 2 H), 3.74 - 3.61 (m, 4 H), 3.57 – 3.52 (m, 2 H), 1.80 - 1.68 (m, 2 H), 1.67 -1.21 (m, 16 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.6, 172.4, 166.2, 143.1, 137.6, 134.5, 131.4, 131.0, 130.7, 129.7, 129.5, 127.6, 127.2, 127.1, 126.7, 126.3, 125.8, 125.3, 125.2, 125.0, 124.7, 123.0, 120.2, 67.7, , 65.3, 63.0, 59.6, 53.2, 42.1, 32.7, 29.5, 29.4, 29.1, 28.6, 26.0, 25.7; HRMS $[M+Na]^+$ m/z: calcd for $C_{41}H_{43}N_3NaO_6$ 696.3050 fond 696.3056.

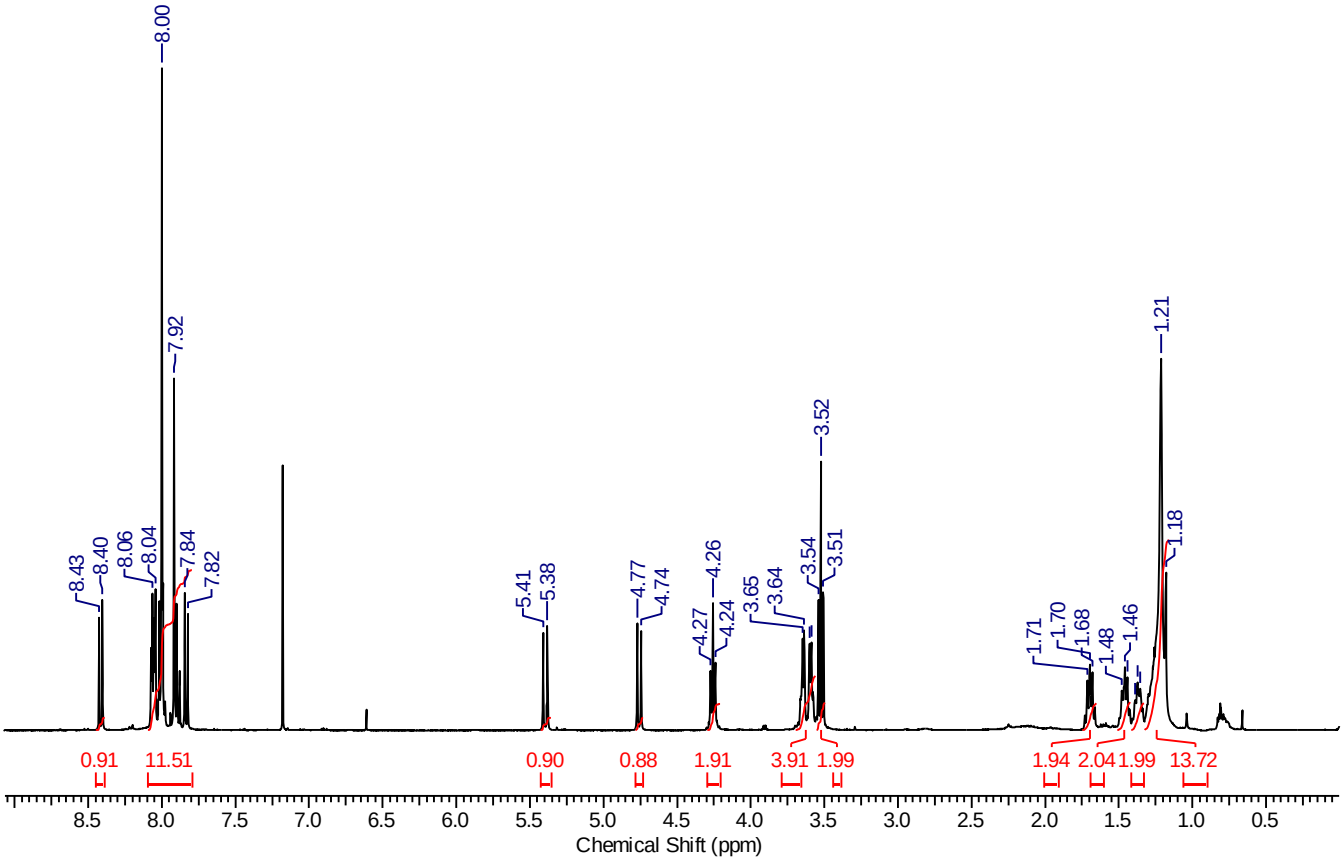


Figure S12 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 11-hydroxyundecyl 4-(5-(2-hydroxyethyl)-4,6-dioxo-1-(pyren-1-yl)-1,3a,4,5,6,6a-hexahydropyrrolo[3,4-c]pyrazol-3-yl)benzoate **3**.

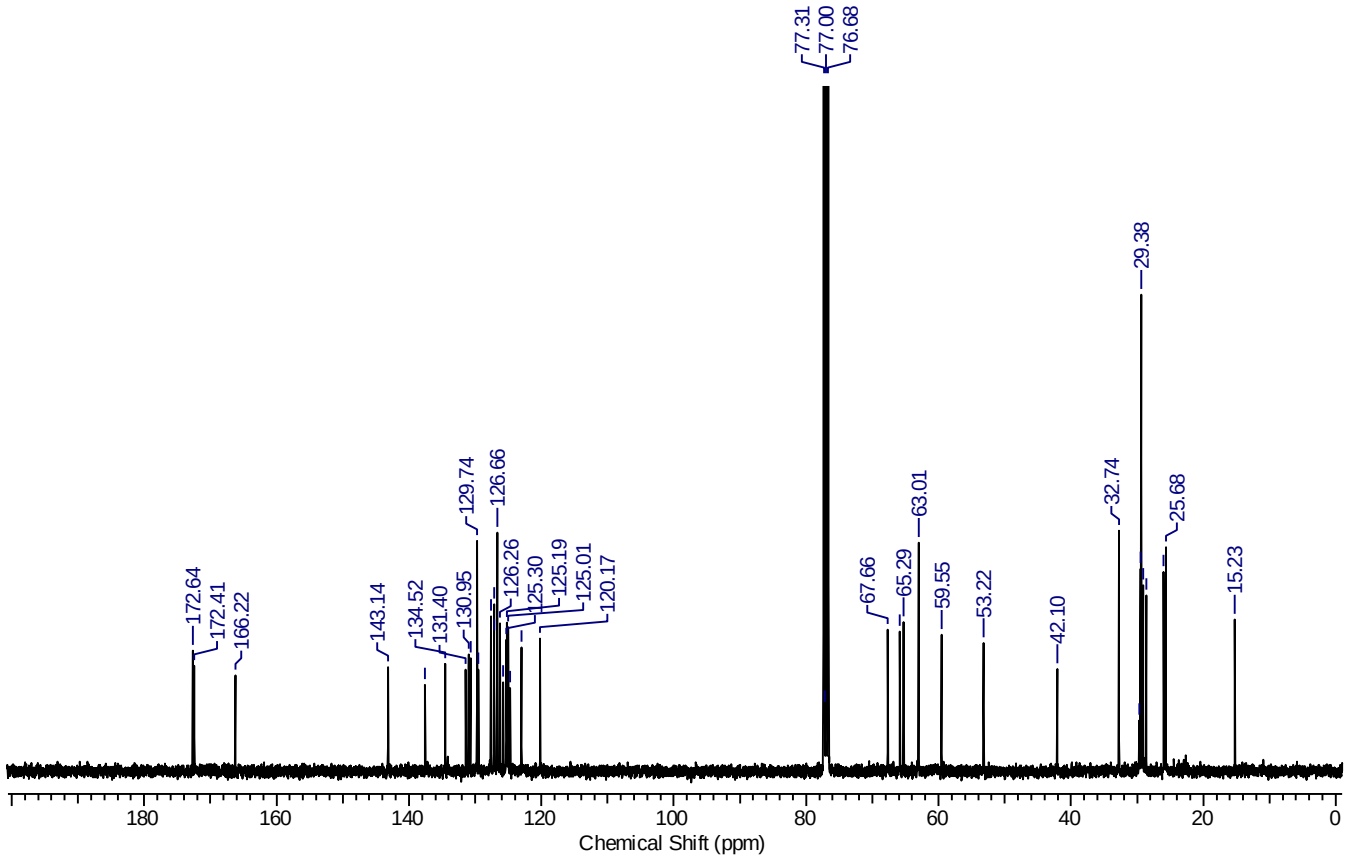
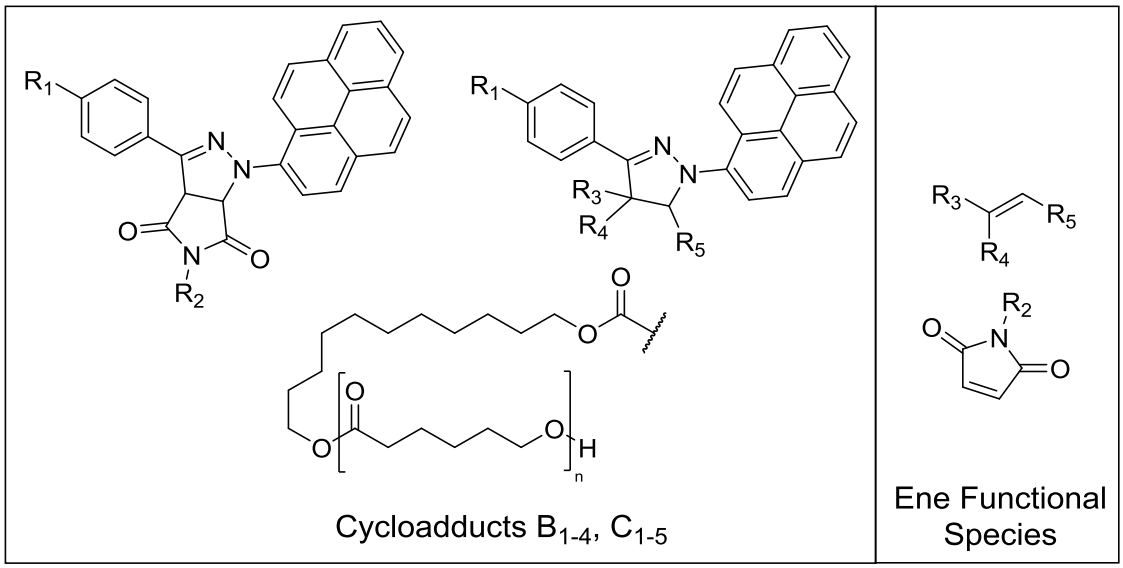


Figure S13 ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 11-hydroxyundecyl 4-formylbenzoate 11-hydroxyundecyl 4-(2-(pyren-1-yl)-2H-tetrazol-5-yl)benzoate **3**.

Polymer end group modification and formation of block copolymers.



Label	R		Label	R	
B_1	2	OH	C_1	2	
B_2	4	H	C_2	4	H
	3,5			3	
				5	
B_3	3	Me	C_3	3	Me
	5	H		5	H
	4			4	
B_4	3,5	H	C_4	3,5	H
	4			4	
			C_5	2	PNIPAM

Figure S14 Overview over synthesized cycloadducts $\mathbf{B}_{1\text{-}4}$ and $\mathbf{C}_{1\text{-}5}$. For clarity only one of two possible regioisomers for $\mathbf{B}_{3,4}$ and $\mathbf{C}_{2\text{-}4}$ is shown. See Section 4 for resolved PNIPAM structure.

PAT end capped PCL and ene functional species were dissolved in 40 mL solvent. The reaction mixture was irradiated at room temperature, 410-420 nm for 30 min. The solvent was removed under reduced pressure. See Table 1 for further details. ^{1}H NMR (400MHz, $CDCl_3$): $\mathbf{B_1}$ δ = 8.55 - 7.95 (m, 13 H), 5.70-5.59 (m, 1 H), 5.12-5.04 (m, 1 H), 4.30-4.25 (m, 2 H), 4.12-4.04 (m, polymer backbone), 3.88 - 3.64 (m, 6 H), 2.37-2.31 (m, polymer backbone), 1.86 - 1.21 (m, 18 H + polymer backbone); $\mathbf{B_2}$ δ = 8.57 - 7.94 (m, 13 H), 5.66 – 5.62 (m, 1 H), 4.88 – 4.84 (m, 1 H), 4.43 - 4.21 (m, 4 H), 4.10 – 4.03 (m,

polymer backbone), 3.92 - 3.82 (m, 2 H), 3.68 – 3.62 (m, 2 H), 2.35 – 2.27 (m, polymer backbone), 1.91 - 1.25 (m 24 H + polymer backbone); **B**$_3$ δ = 8.59 - 7.75 (m, 13 H), 4.40 – 4.32 (m, 2 H), 4.12 – 4.00 (m, 4 H + polymer backbone), 3.81 - 3.57 (m, 5 H), 3.42 – 3.36 (m, 1 H), 2.36 – 2.25 (m, polymer back bone), 1.94 - 1.08 (m, 18 H + polymer backbone); **B**$_4$ δ = 8.73 - 7.42 (m, 13 H) 6.99 (s, BHT), 5.67 - 5.14 (m, 1 H), 5.02 (s, BHT), 4.35 – 4.31 (m, 2 H), 4.12 – 4.00 (m, 1 H + polymer backbone), 3.68 – 3.63 (m, 5 H), 3.47 (s, 1 H), 2.41 - 2.24 (m, polymer back bone + BHT), 1.92 - 1.15 (m, 18 H + polymer backbone + BHT); **C**$_1$ δ = 8.69 - 7.90 (m, 13 H), 5.94 – 5.90 (m, 1 H), 5.34 – 5.29 (m, 1 H), 4.41 - 4.22 (m, 4 H), 4.05 – 3.85 (m, polymer back bone (PCL)), 3.52 – 3.45 (m, 2 H + polymer back bone (PEG)), 3.23 (s, 3 H), 3.12 – 3.05 (m, 2 H), 2.34 – 2.19 (m, polymer back bone (PCL)), 1.82 - 0.95 (m, 18 H + polymer back bone (PCL)); **C**$_2$ δ = 8.58 - 7.73 (m, 13 H), 5.74 - 5.47 (m, 1 H), 4.85 – 4.82 (m, 1 H), 4.41 - 4.17 (m, 4 H), 4.08 – 3.89 (2 H + m, polymer back bone (PCL)), 3.65 – 3.44 (m, 2 H + polymer back bone (PEG), 3.31 (s, 3 H), 2.30 – 2.11 (m, polymer back bone (PCL)), 1.80 - 1.13 (m, 24 H + polymer back bone (PCL)); **C**$_3$ δ = 8.70 - 7.84 (m, 13 H), 6.99 (s, BHT), 4.12 – 4.00 (1 H + m, polymer backbone (PCL)), 3.73 – 3.54 (m, 2 H + polymer back bone (PEG)), 3.55 – 3.43 (m, 3), 3.31 (s, 3 H), 2.40 - 2.16 (m, polymer back bone (PCL + BHT), 1.78 - 1.17 (m, 18 H + polymer back bone (PCL) + BHT); **C**$_4$ δ = 8.54 - 7.54 (m, 13 H), 4.38 – 4.31 (m, 2 H), 4.21 – 3.85 (polymer back bone (PCL)), 3.79 – 3.45(m, 2 H + polymer back bone (PEG)), 3.39 (s, 3 H), 2.35 – 2.29 (m, polymer back bone (PCL)), 1.88 - 1.14 (m, 18 H + polymer back bone (PCL)); **C**$_5$ see Figure 36.

Table 1 M_n and $Đ$ of PAT capped PCL **A**$_{1,2}$ before and after coupling with dipolarophile capped species to form **B**$_{1-4}$ or **C**$_{1-5}$.

Cycloadduct	PAT end capped PCL	c_{PCL} /mmol·L^{-1}	c_{ene} /mmol·L^{-1}	Ene capped polymer	$Đ_{ene}$	M_n[d] $_{ene}$ /kDa	solvent	$Đ_{cycload-duct}$	M_n[d] $_{cycloadduct}$ /kDa
B$_1$[a]	A$_1$	0.18	2.7	-	-	-	MeCN	1.12	2.2
B$_2$[a]	A$_1$	0.18	2.7	-	-	-	MeCN	1.11	2.1
B$_3$[a]	A$_1$	0.18	2.7	-	-	-	THF[c]	1.13	2.1
B$_4$[a]	A$_1$	0.18	2.7	-	-	-	THF[c]	1.14	2.1
C$_1$[b]	A$_2$	0.12	0.18	PEG	1.04	2.6	MeCN	1.12	8.0
C$_2$[b]	A$_2$	0.12	0.18	PEG	1.03	2.6	MeCN	1.15	8.4
C$_3$[b]	A$_2$	0.12	0.18	PEG	1.03	2.7	THF[c]	1.14	8.5
C$_4$[b]	A$_2$	0.12	0.18	PEG	1.03	2.8	THF[c]	1.15	8.7
C$_5$[b*]	A$_2$	0.12	0.14	PNIPAM	1.08	2.9	MeCN	1.24	8.8

[a] Cycloadduct was analysed without any further purification. [b] The crude product was dissolved in ethyl acetate (50 mL) extracted with 1 M hydrochloric acid (4×100 mL) and dried over $NaSO_4$. Ethyl acetate was removed under reduced pressure. The residual solid was dissolved in DCM and precipitated in cold hexane/diethyl mixture (1:1). [b*] The crude product was dissolved in ethyl acetate (50 mL) extracted with 1 M hydrochloric acid (1×100 mL) and dried over $NaSO_4$. Ethyl acetate was removed under reduced pressure. [c] BHT stabilized THF was used to avoid side products possible formed in radical involving processes (See characterisation section of B_4 for more details). [d] M_n was determined by GPC using PMMA calibration standards.

Table 2 Sum formula, the exact masses for experimental results, theoretical values and the deviation of both for PAT end capped PCL **A**$_1$ and cycloadducts **B**$_{1-4}$.

Label	Sum formula	m/z_{exp}	m/z_{theo}	Δ m/z
A$_1$	$[C_{83}H_{116}N_4NaO_{19}]^+$	1495.815	1495.813	0.002
B$_1$	$[C_{83}H_{113}N_3NaO_{20}]^+$	1494.787	1494.782	0.005
B$_2$	$[C_{83}H_{114}N_2NaO_{21}]^+$	1525.818	1525.812	0.006
B$_3$	$[C_{82}H_{114}N_2NaO_{19}]^+$	1567.862	1567.859	0.003
B$_4$	$[C_{87}H_{122}N_2NaO_{21}]^+$	1553.831	1553.844	0.013

Cycloadduct B_1

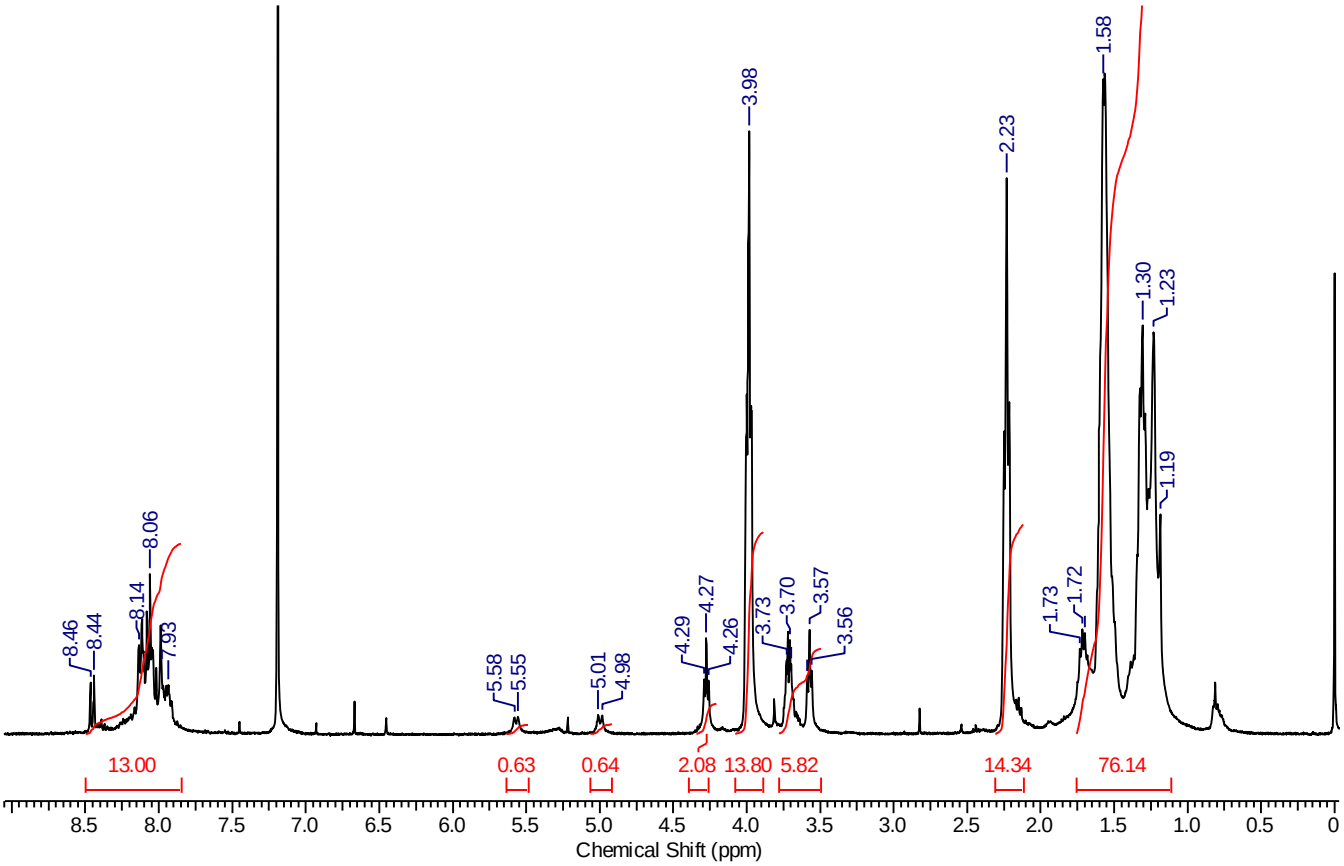


Figure S15 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of cycloadduct $\mathbf{B_1}$.

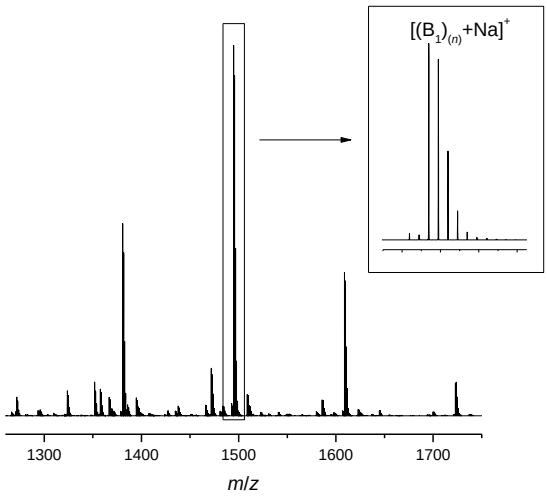


Figure S16 Magnified view into the region of 1260-1750 *m/z* of a ESI-MS spectrum of cycloadduct $\mathbf{B_1}$. Signals repeat in intervals of 114.14 Dalton. Sodium adduct of PAT end-capped PCL, $[(B_1)_{(n)} + Na]^+$.

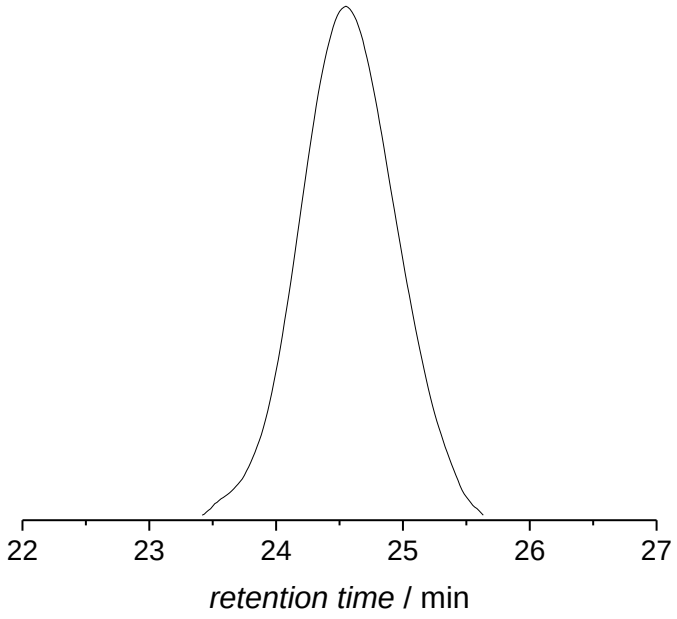


Figure S17 GPC of cycloadduct $\mathbf{B_1}$ in THF (See Table 1 for corresponding M_n and $Đ$).

Cycloadduct B_2

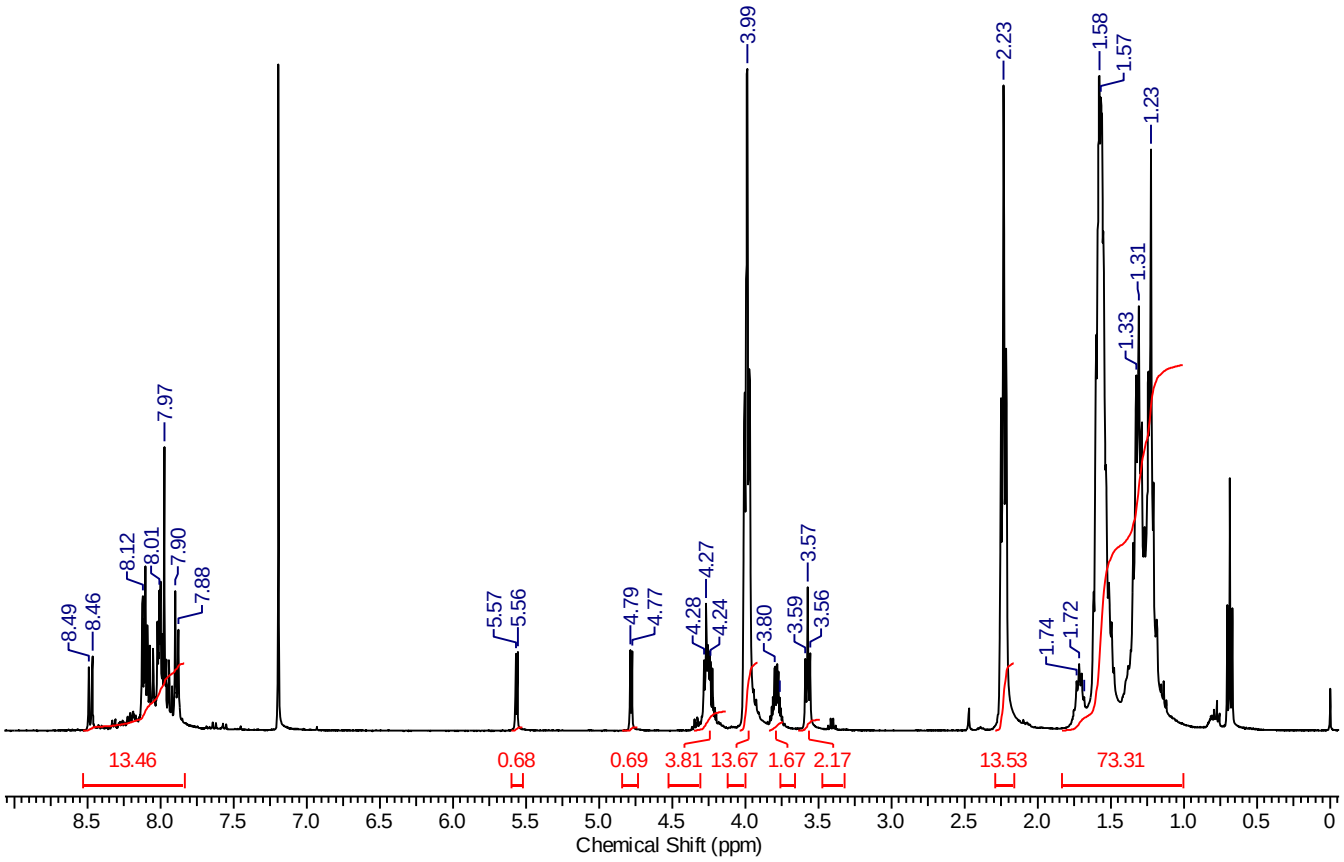


Figure S18 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of cycloadduct $\mathbf{B_2}$.

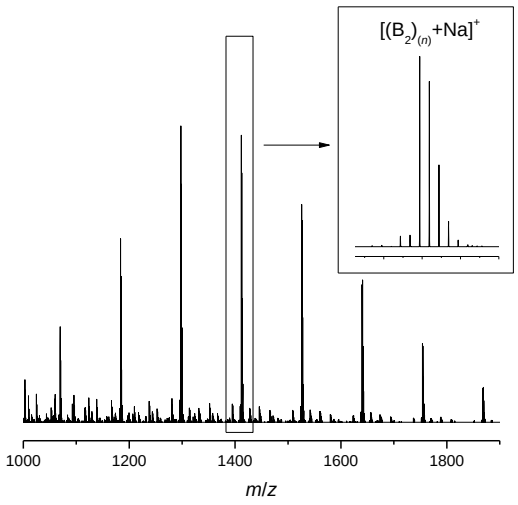


Figure S19 Magnified view into the region of 1000-1900 m/z of ESI-MS spectrum of cycloadduct $\mathbf{B_2}$. Signals repeat in intervals of 114.14 Dalton. Sodium adduct of PAT end-capped PCL, $[(B_2)_{(n)} + Na]^+$.

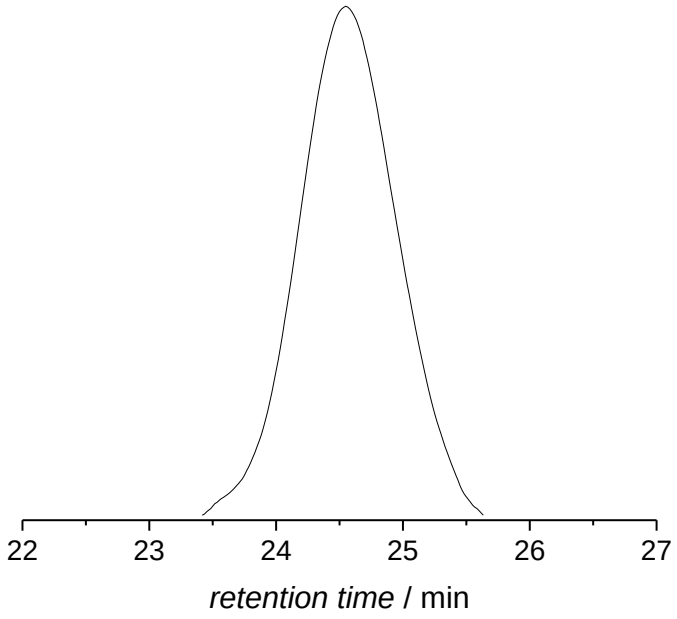


Figure S20 GPC of cycloadduct $\mathbf{B_2}$ in THF (See Table 1 for corresponding M_n and $Đ$).

Cycloadduct B_3

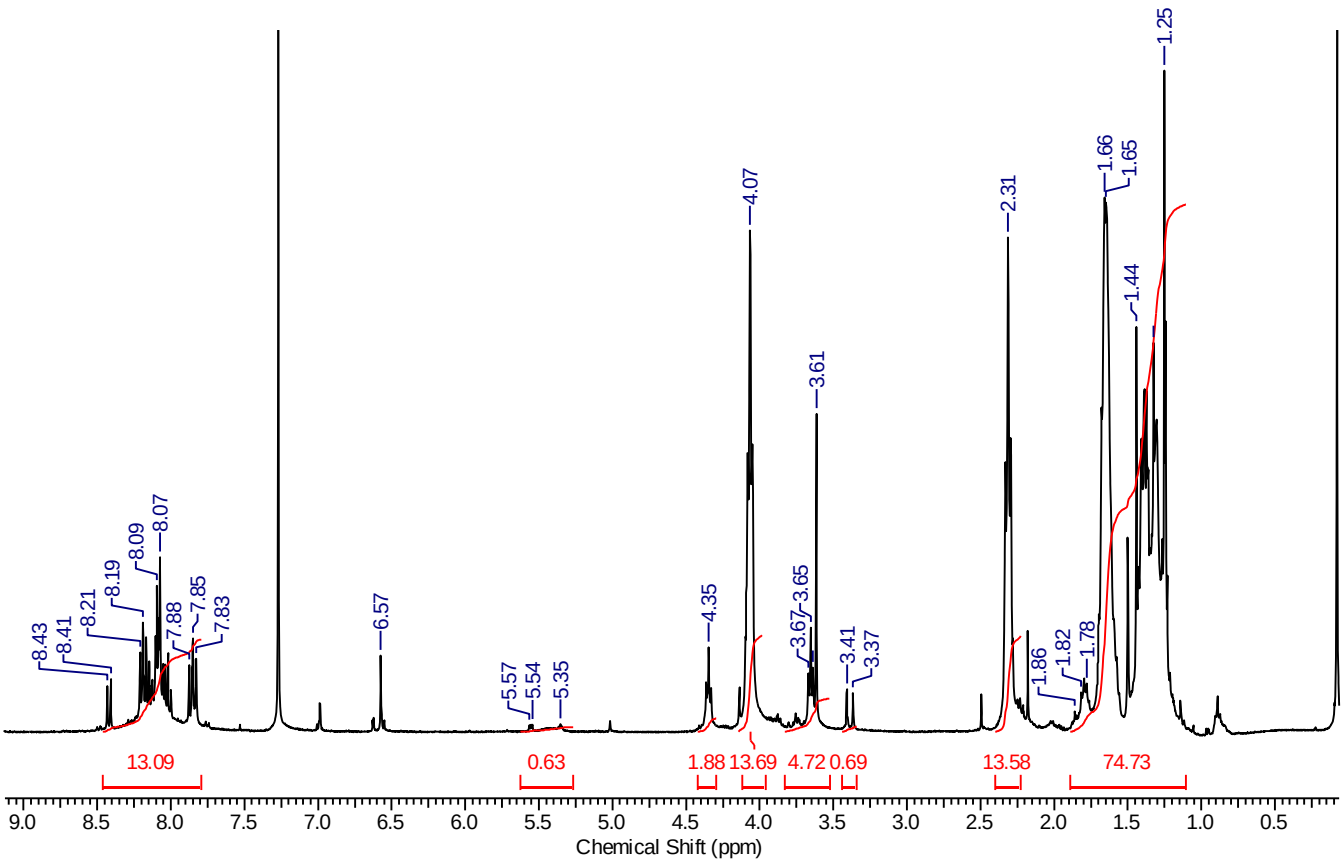


Figure S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of cycloadduct $\mathbf{B_3}$. Residual BHT can be observed, used as a radical scavenger during the formation of the $\mathbf{B_3}$ to avoid side reactions involving radical species.

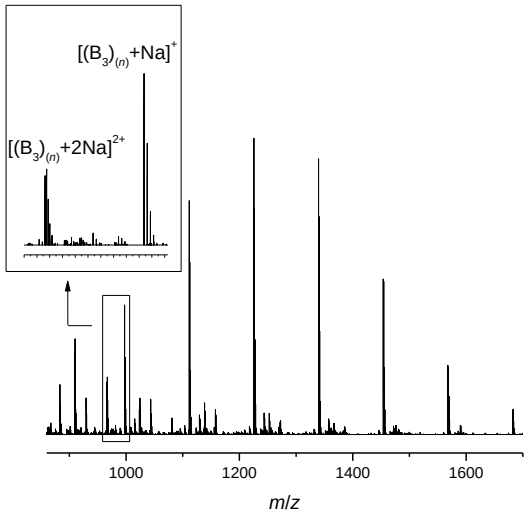


Figure S22 Magnified view into the region of 960-1700 m/z of ESI-MS spectrum of cycloadduct $\mathbf{B_3}$. Signals repeat in intervals of 114.14 Dalton. Sodium adduct of PAT end-capped PCL, $[(B_3)_{(n)} + Na]^+$ and $[(B_3)_{(n)} + 2Na]^{2+}$.

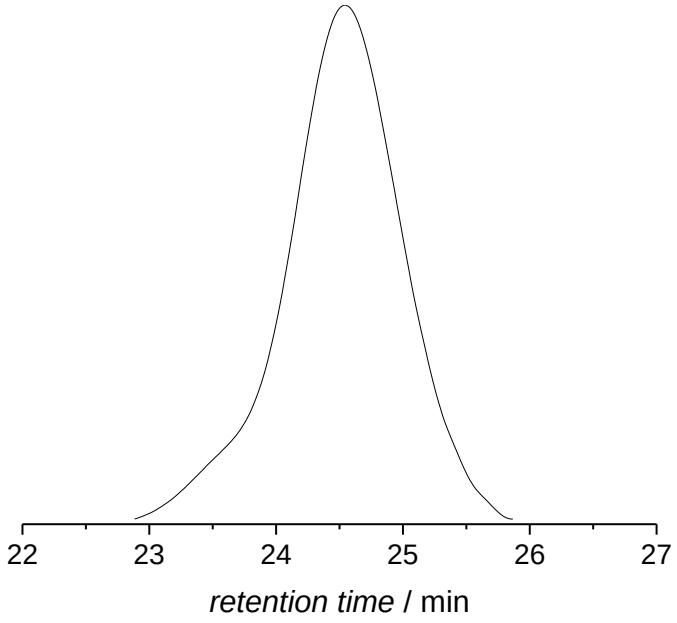


Figure S23 GPC of cycloadduct $\mathbf{B_3}$ in THF (See Table 1 for corresponding M_n and $Đ$).

Cycloadduct B_4

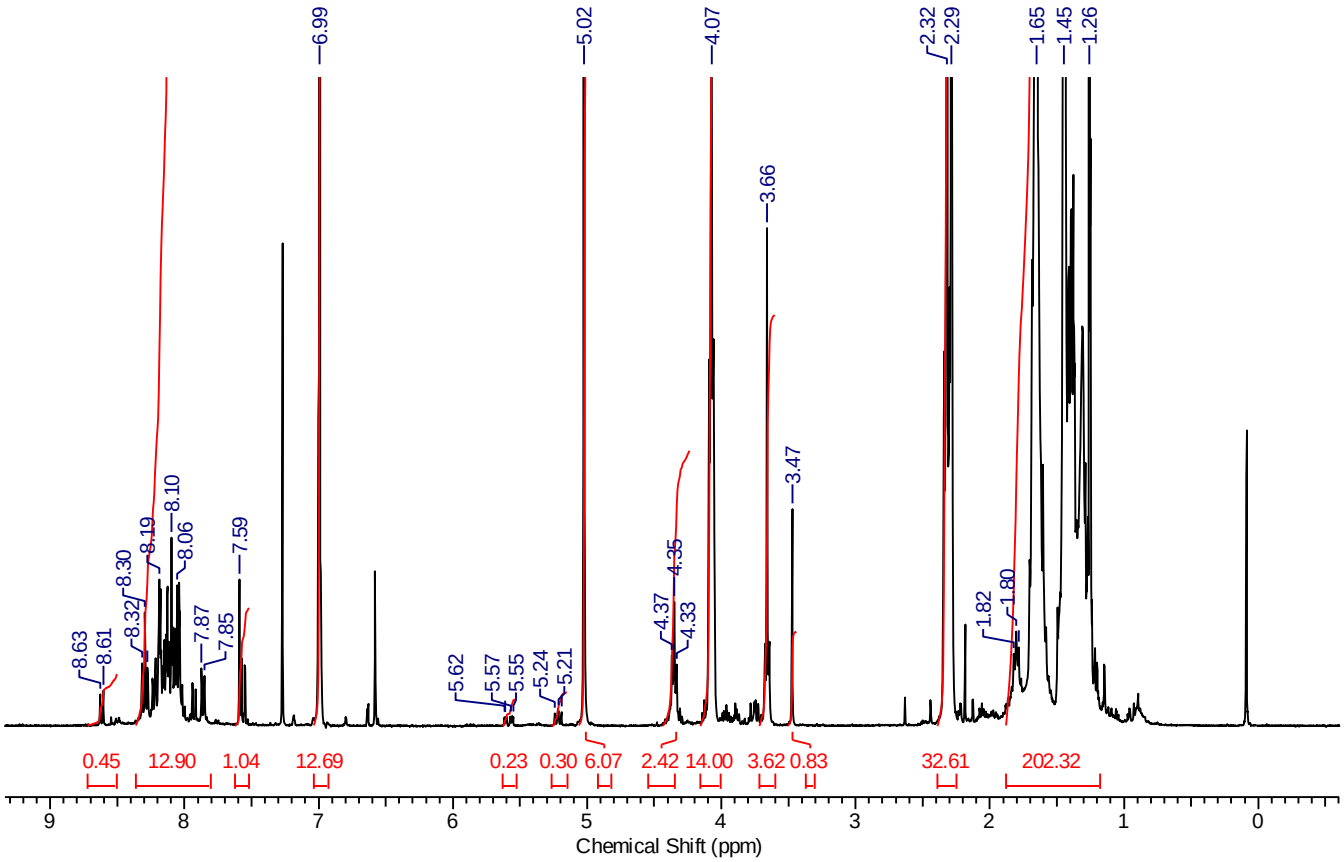


Figure S24 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of cycloadduct $\mathbf{B_4}$. Residual BHT can be observed, used as a radical scavenger during the formation of the $\mathbf{B_4}$ to avoid side reactions involving radical species.

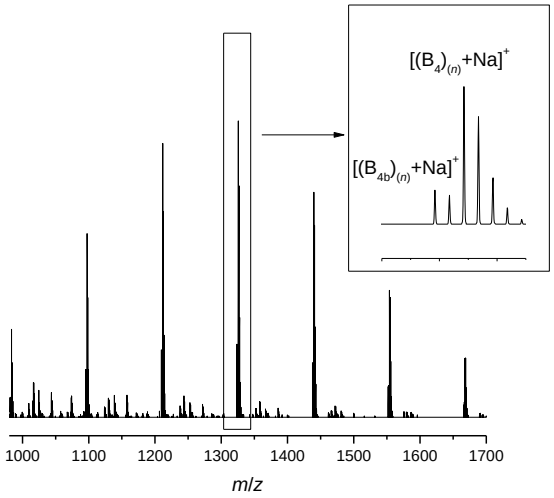


Figure S25 Magnified view into the region of 960-1700 *m/z* of ESI-MS spectrum of cycloadduct $\mathbf{B_4}$. Signals repeat in intervals of 114.14 Dalton. Sodium adduct of PAT end-capped PCL, $[(B_4)_{(n)} + Na]^+$ and $[(B_{4b})_{(n)} + Na]^+$. Side product $\mathbf{B_{4b}}$ assumed to be formed in a radical elimination reaction of $\mathbf{B_4}$ (See Figure S26 for structure).

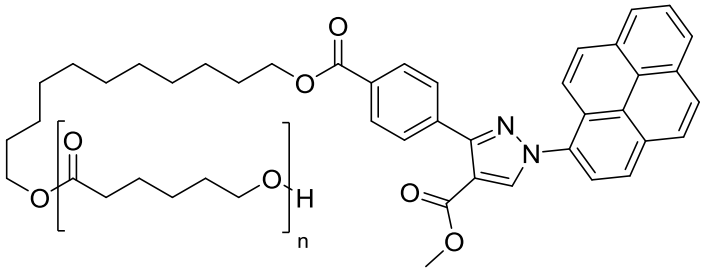


Figure S26 Structure of $\mathbf{B_{4b}}$ assumed to be radical elimination reaction product of the cycloadduct $\mathbf{B_4}$. For clarity only one of two possible regioisomer of $\mathbf{B_{4b}}$ is shown.

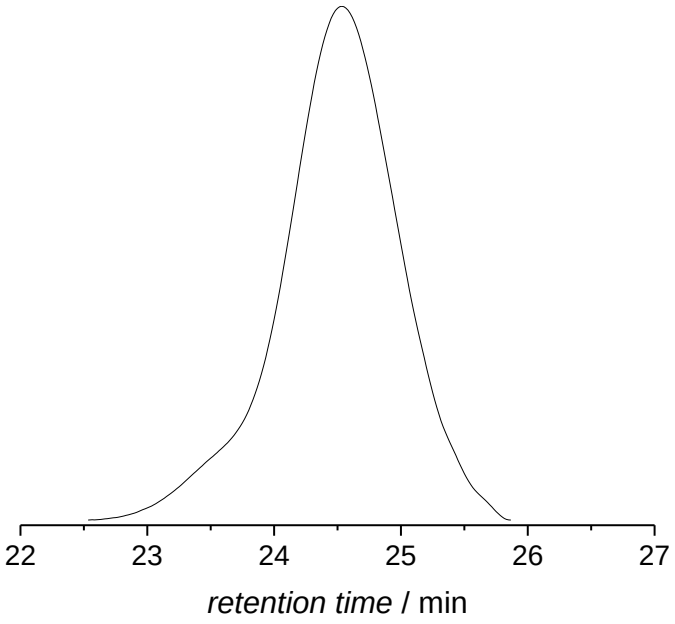


Figure S27 GPC of cycloadduct $\mathbf{B_4}$ in THF (See Table 1 for corresponding M_n and $Đ$).

Cycloadduct C_1

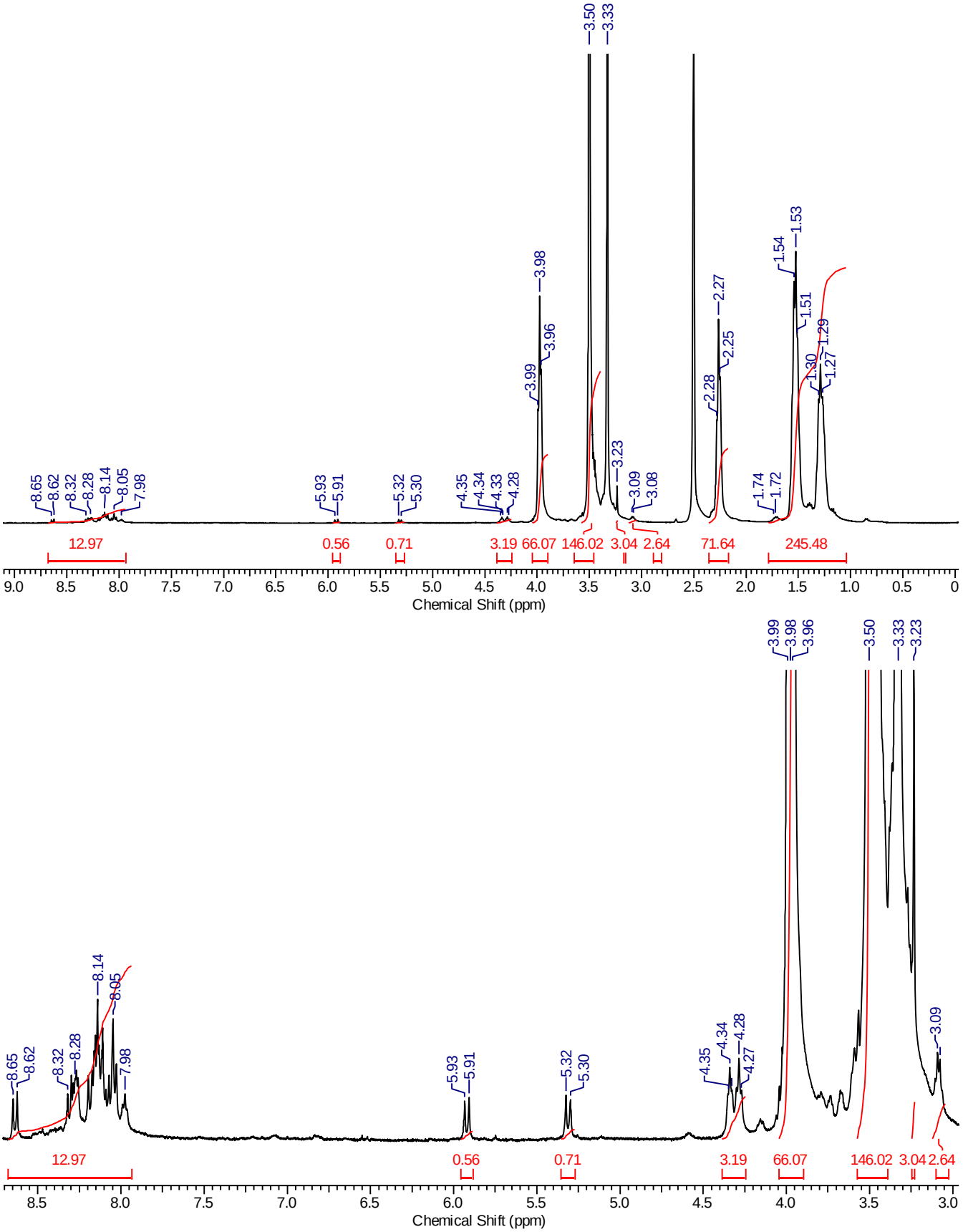


Figure S28 ^{1}H NMR (400 MHz, DMSO) spectra of cycloadduct $\mathbf{C_1}$. Full spectra of the PCL-*b*-PEG block copolymer (above), magnification of the 8.7 – 2.9 ppm region (below).

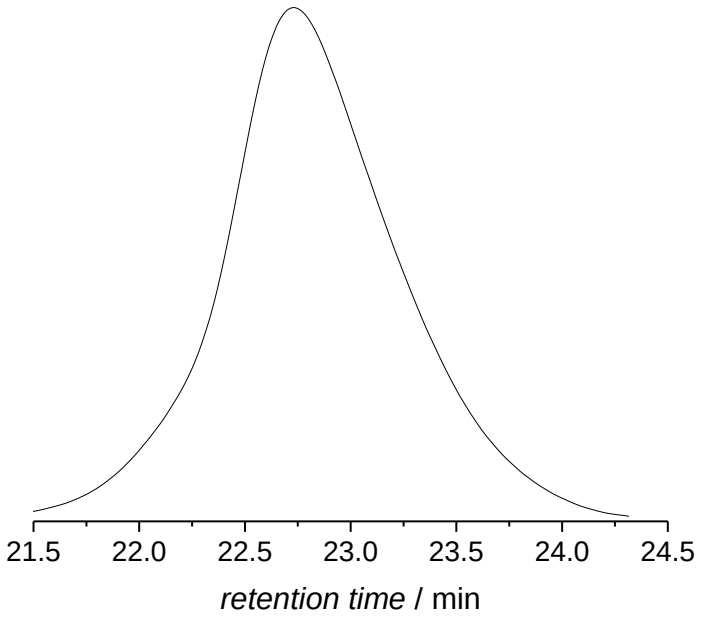


Figure S29 GPC of cycloadduct $\mathbf{C_1}$ in THF (See Table 1 for corresponding M_n and $Đ$).

Cycloadduct C_2

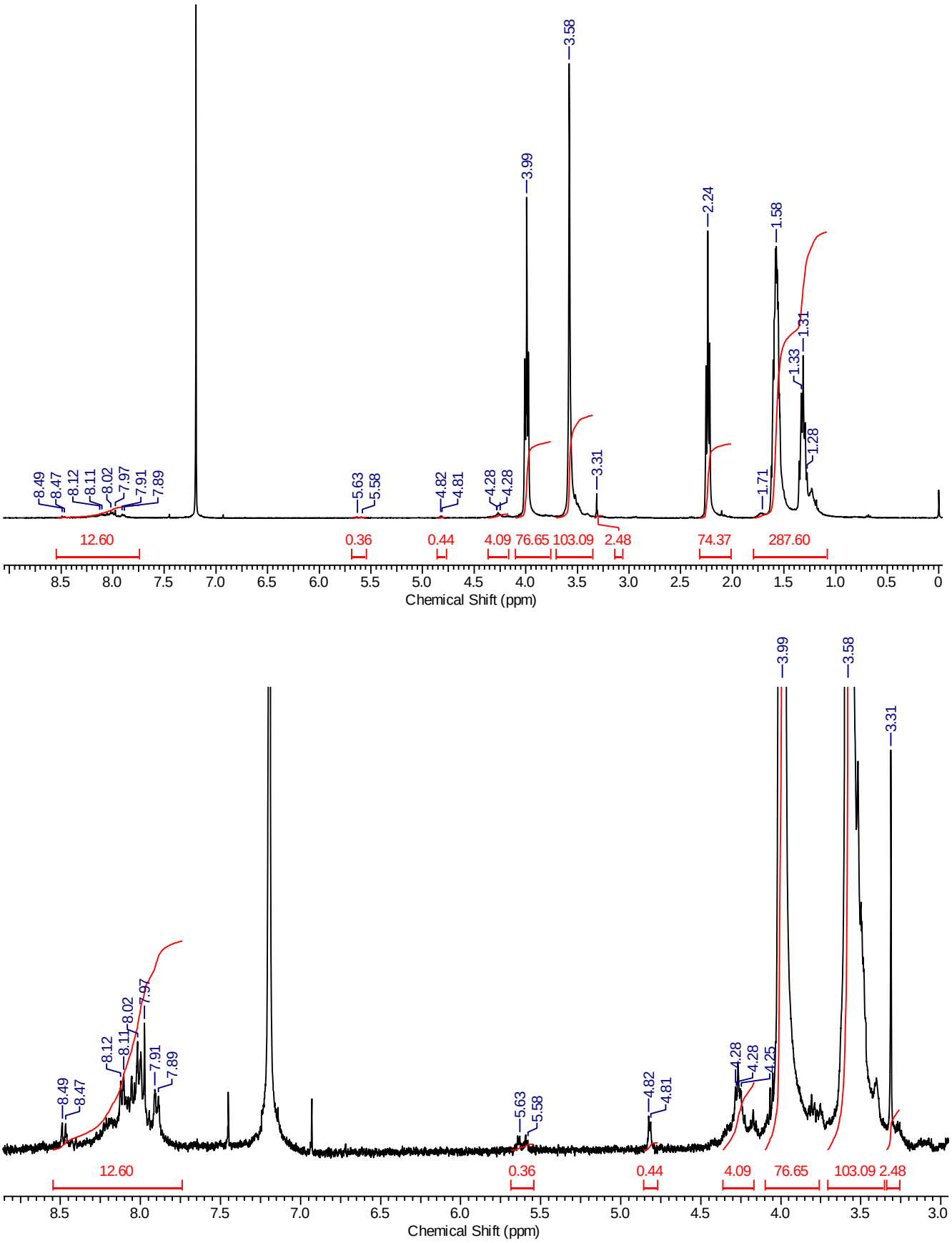


Figure S30 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of cycloadduct $\mathbf{C_2}$. Full spectra of the PCL-*b*-PEG block copolymer (above), magnification of the 8.7 – 2.9 ppm region (below).

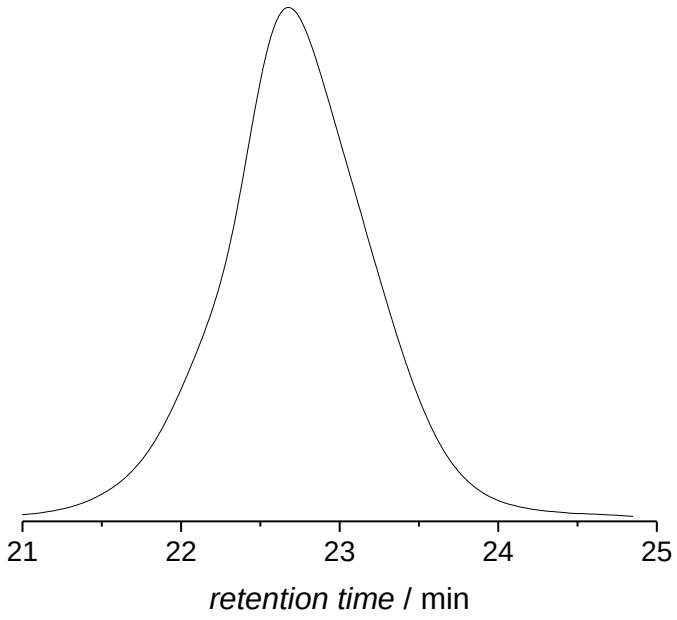


Figure S31 GPC of cycloadduct $\mathbf{C_2}$ in THF (See Table 1 for corresponding M_n and $Đ$).

Cycloadduct C_3

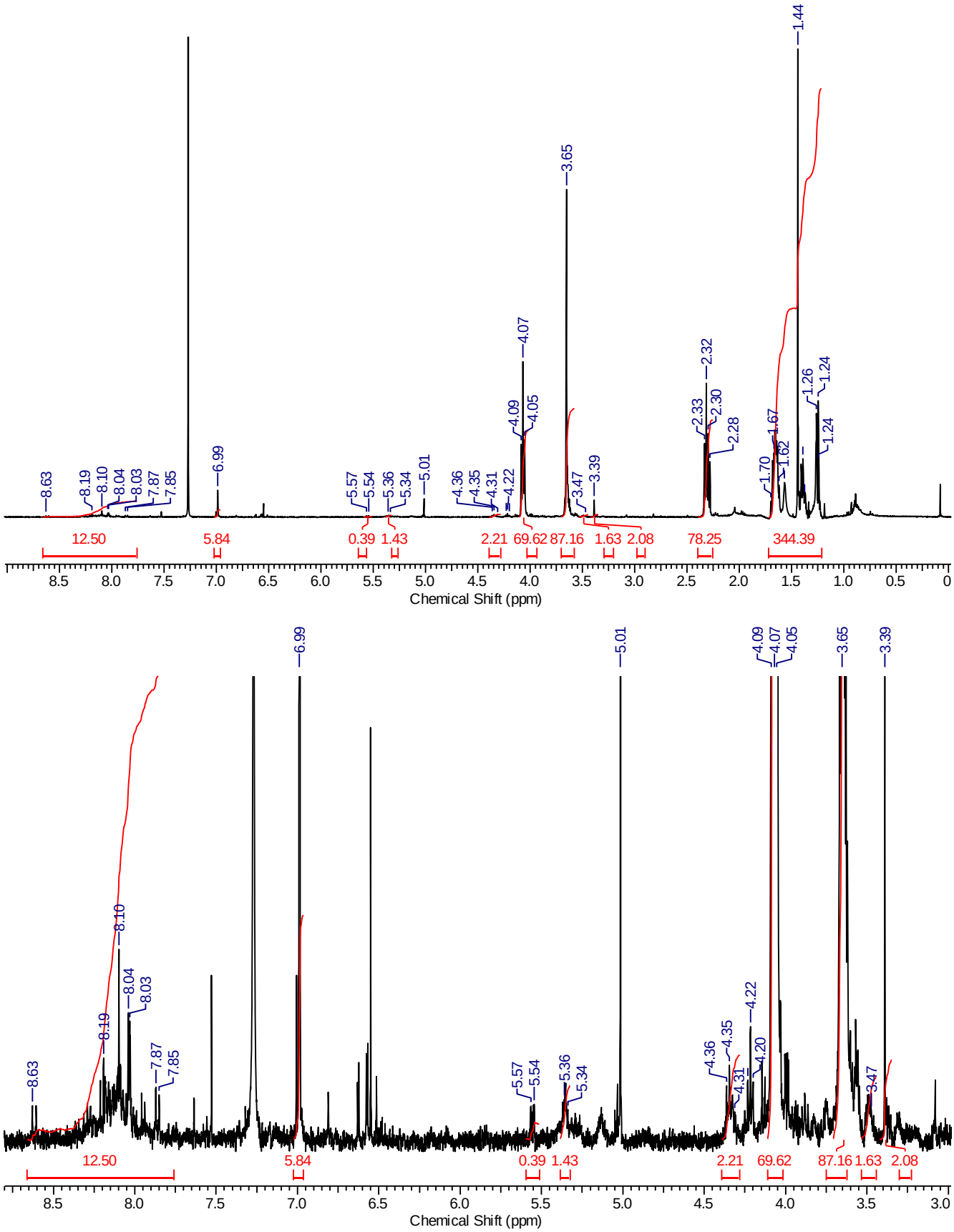


Figure S32 ^{1}H NMR (zoom, 400 MHz, $CDCl_3$) spectra of cycloadduct $\mathbf{C_3}$. Full spectra of the PCL-*b*-PEG block copolymer (above), magnification of the 8.6 – 3.0 ppm region (below). BHT can be observed, used as a radical scavenger during the formation of the $\mathbf{C_3}$ to avoid side reactions involving radical species.

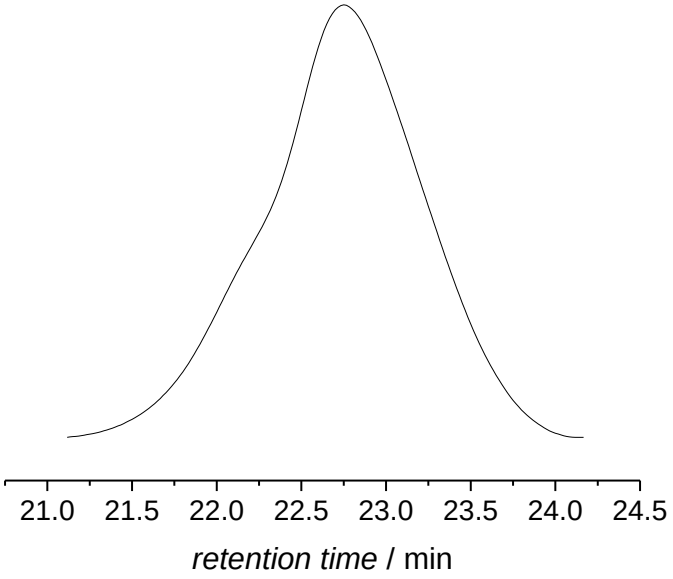


Figure S33 GPC of cycloadduct $\mathbf{C_3}$ in THF (See Table 1 for corresponding M_n and $Đ$).

Cycloadduct C_4

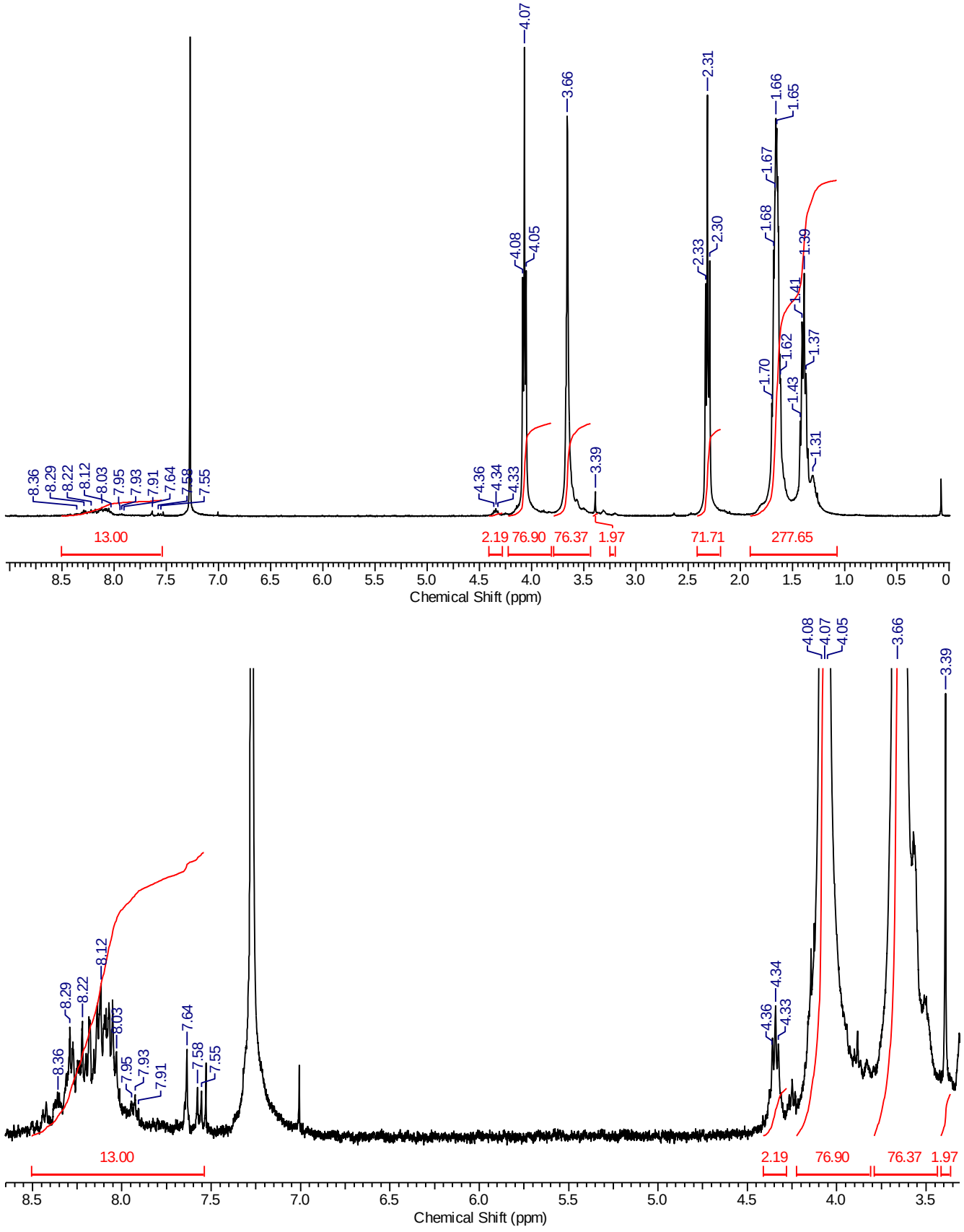


Figure S34 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of cycloadduct $\mathbf{C_4}$. Full spectra of the PCL-*b*-PEG block copolymer (above), magnification of the 8.6 – 3.0 ppm region (below).

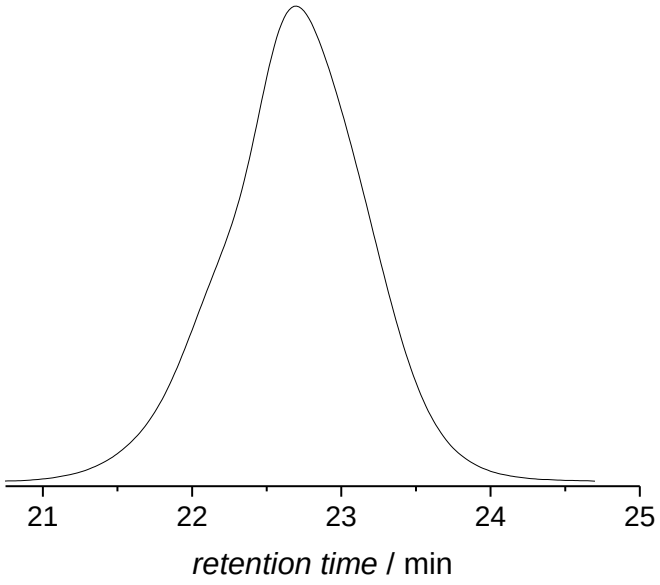


Figure S35 GPC of cycloadduct $\mathbf{C_4}$ in THF (See Table 1 for corresponding M_n and $Đ$).

Cycloadduct C_5

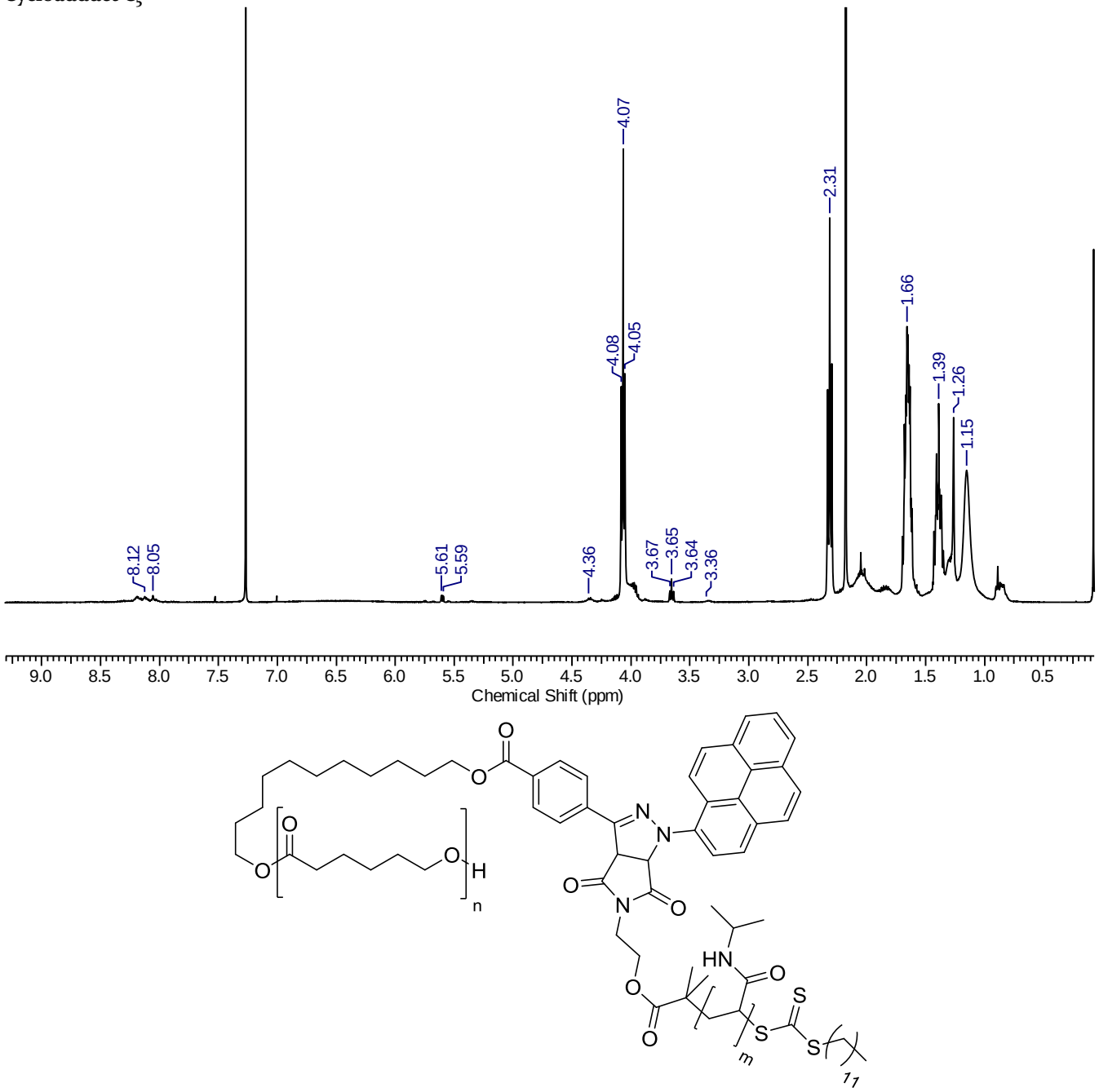
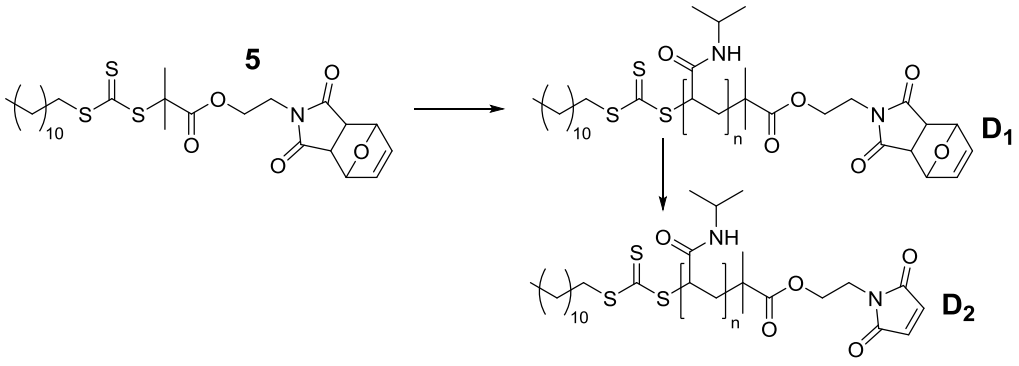


Figure S36 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of cycloadduct $\mathbf{C_5}$.

4. Synthesis of maleimide end capped species

Scheme 2 **Synthetic path for maleimide functionalized PNIPAM D_2.**



PNIPAM (D_1)

1.00 g NIPAM, **5** and AIBN (molar ratio: 1000:10:1) were dissolved in 5 mL DMF (monomer concentration = 1.77 mol·L^{-1}) and degassed *via* three consecutive freeze-pump-thaw cycles. Subsequently, the polymerization mixture was stirred at 60 °C for 8 h. The polymerization was quenched by cooling with liquid nitrogen and exposing the mixture to oxygen. The polymerization mixture was precipitated twice in diethyl ether. The obtained polymer was dried under reduced pressure to obtain a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00 – 5.81 (bs, polymer back bone + 2 H), 5.25 (s, 2 H), 3.99 (s, polymer backbone + 4 H), 3.76 (s, 2 H), 3.34 (s, 2 H), 2.90 (s, 2 H), 2.49 (s, polymer backbone), 2.34 – 0.93 (m, polymer backbone + 24 H), 0.89 – 0.84 (m, 3 H); M_n = 4.7 kDa (^{1}H NMR), M_n = 5.8 kDa (GPC), $Đ$ = 1.20.*

* GPC was measured in DMAC.

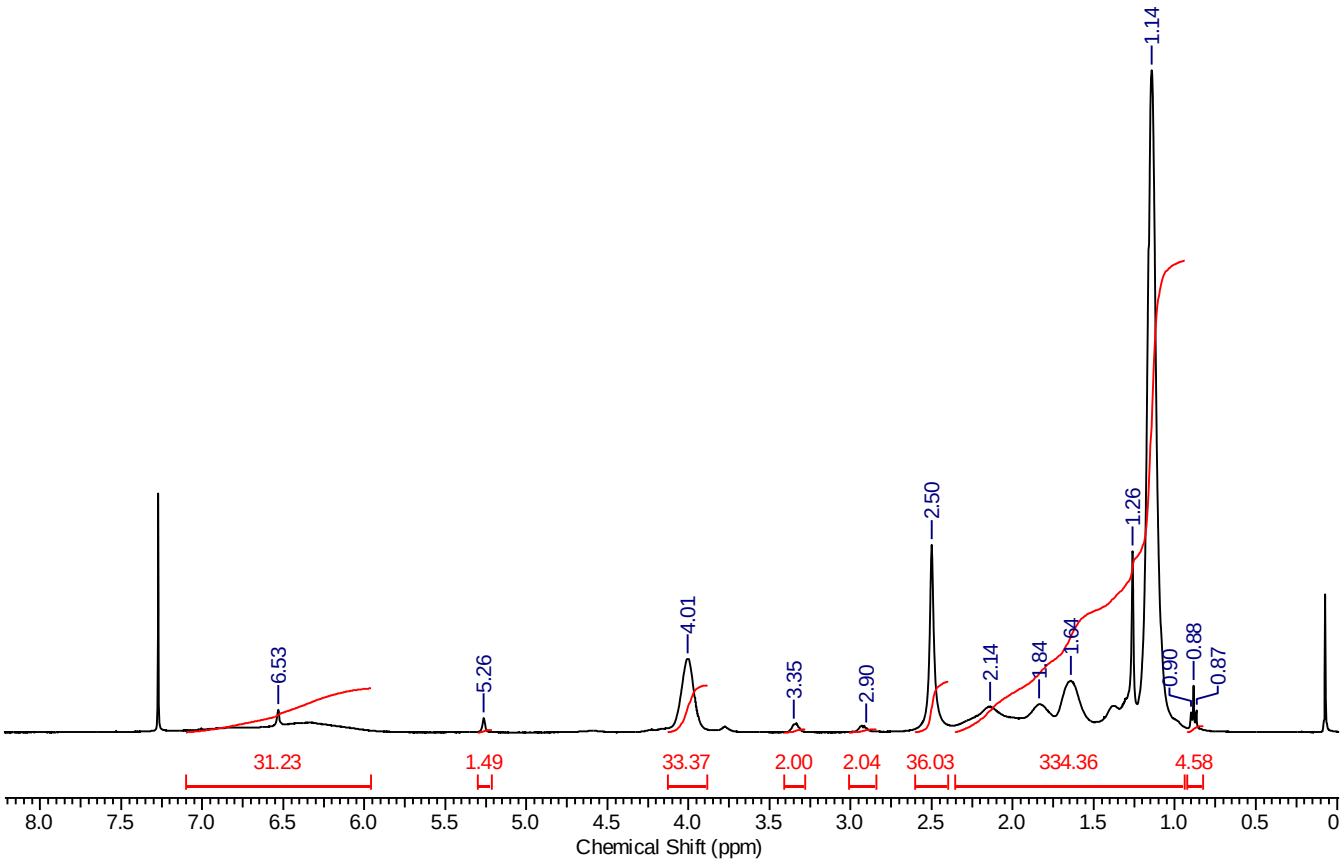


Figure S37 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of PNIPAM $\mathbf{D_1}$.

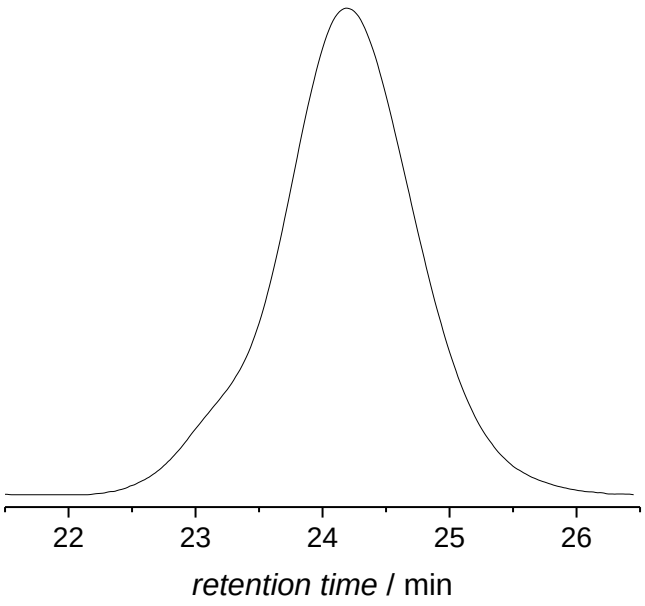


Figure S38 GPC of PNIPAM D_1 in DMAC.

PNIPAM (D_2)

The PNIPAM **D_1** was placed in a round bottom flask and heated in bulk under reduced pressure at 95 °C for 10 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00 – 5.70 (bs, polymer backbone + 2 H), 3.99 (s, polymer backbone + 4 H), 3.80 (s, 2 H), 3.33 (s, 2 H), 2.51 (s, polymer backbone), 2.34 – 0.93 (m, polymer backbone + 24 H), 0.89 – 0.85 (m 3 H) M_n = 4.7 kDa (^{1}H NMR), M_n = 2.9 kDa (GPC), $Đ$ = 1.08.

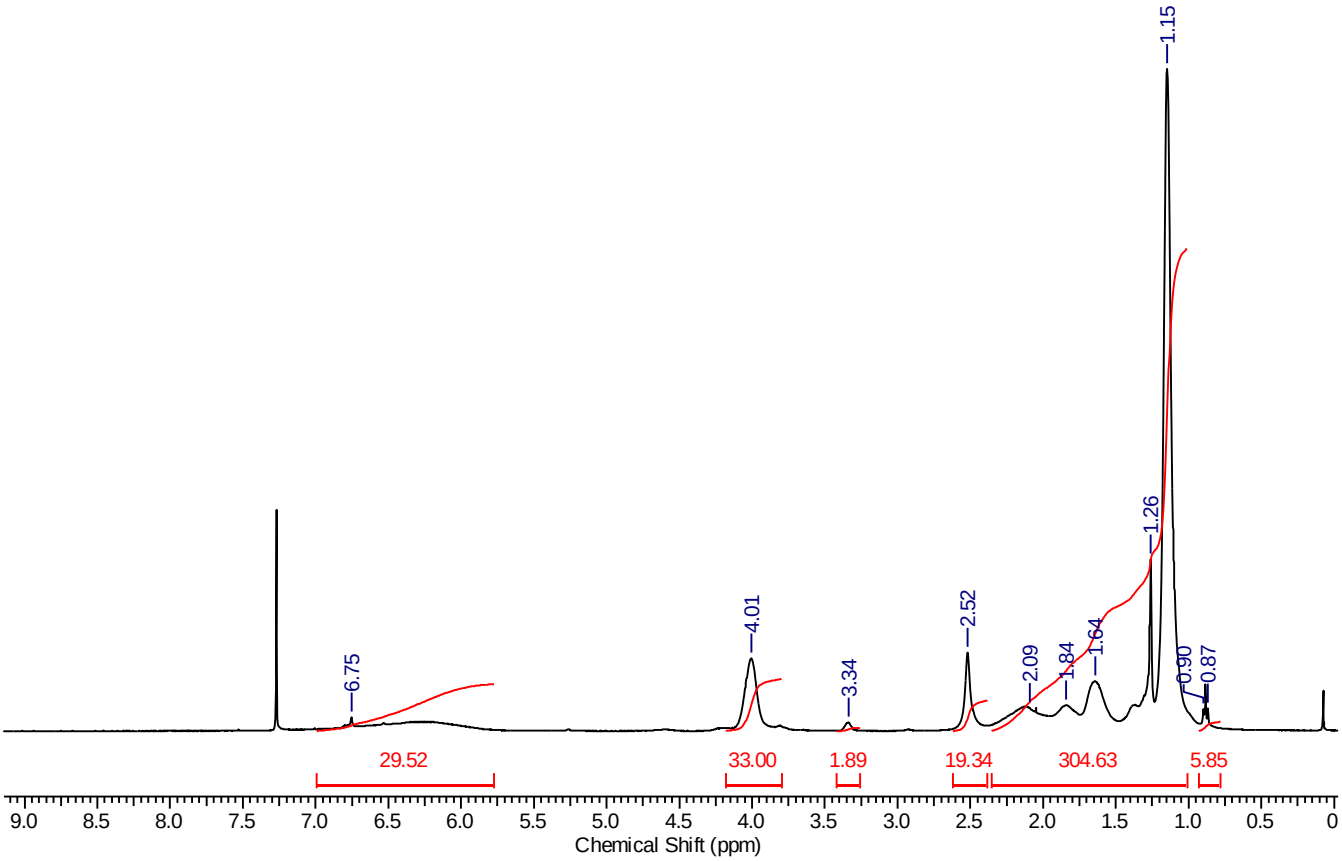


Figure S39 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of PNIPAM **D_2**.

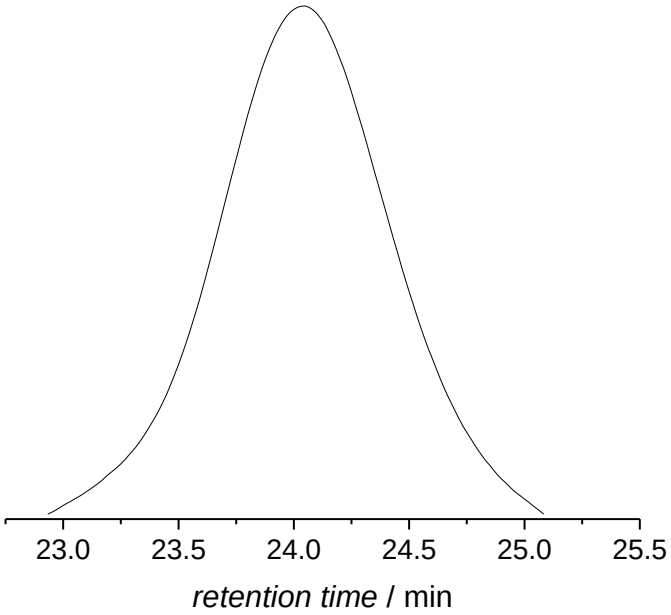


Figure 40 GPC of PNIPAM D_2 in THF.

5. Spectroscopic Data

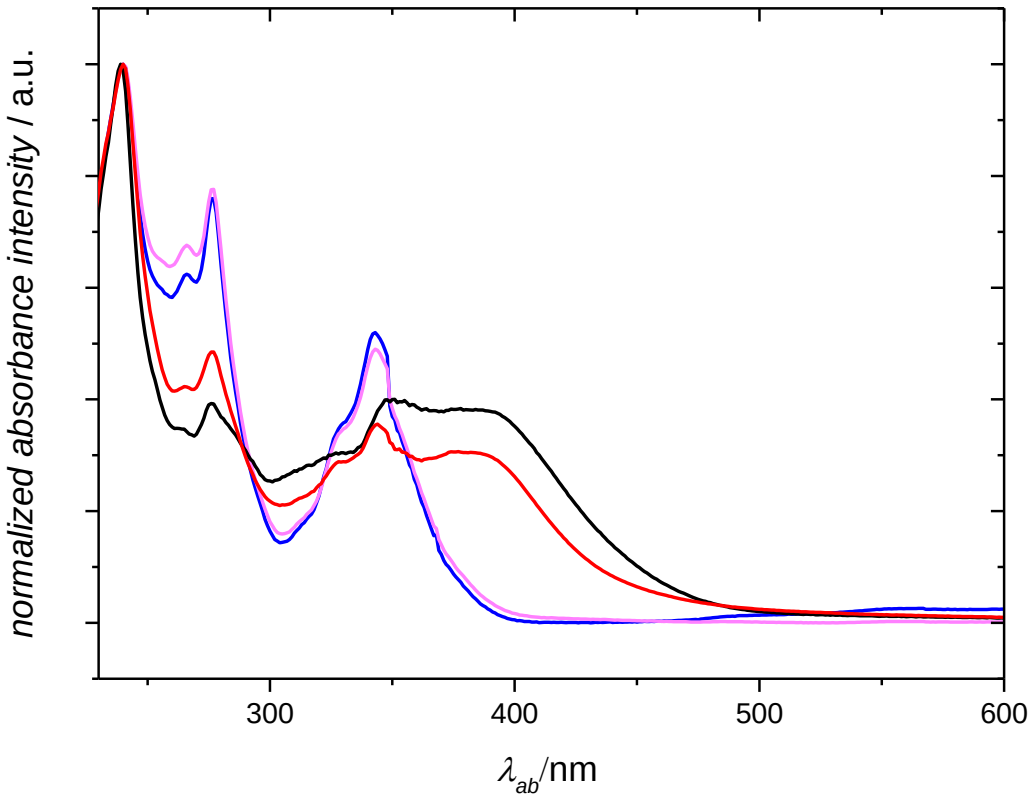


Figure S41 Normalized absorption spectra of PAT **1** (blue), pyrazoline **3** (black), PAT end-capped PCL $\mathbf{A_1}$ (pink), pyrazoline containing PEG-*b*-PCL block copolymer $\mathbf{C_1}$ (red) in MeCN.

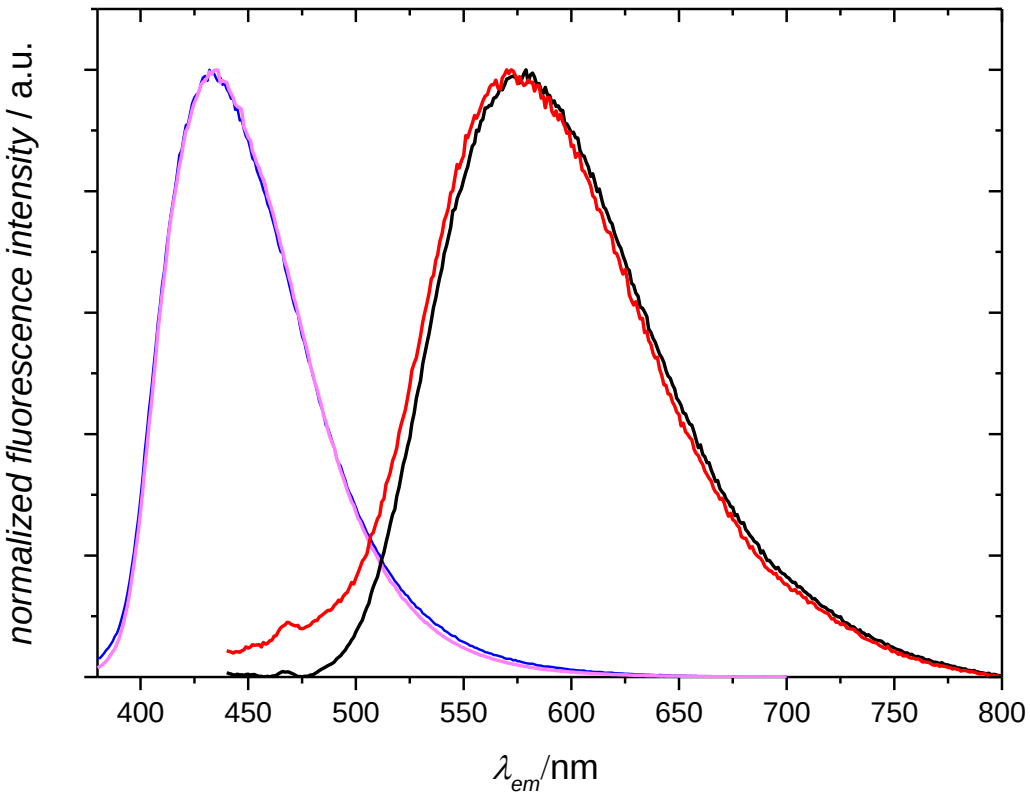


Figure S42 Normalized fluorescence spectra of PAT **1** (blue), pyrazoline **3** (black), PAT end-capped PCL $\mathbf{A_1}$ (pink), pyrazoline containing PEG-*b*-PCL block copolymer $\mathbf{C_1}$ (red) in MeCN.

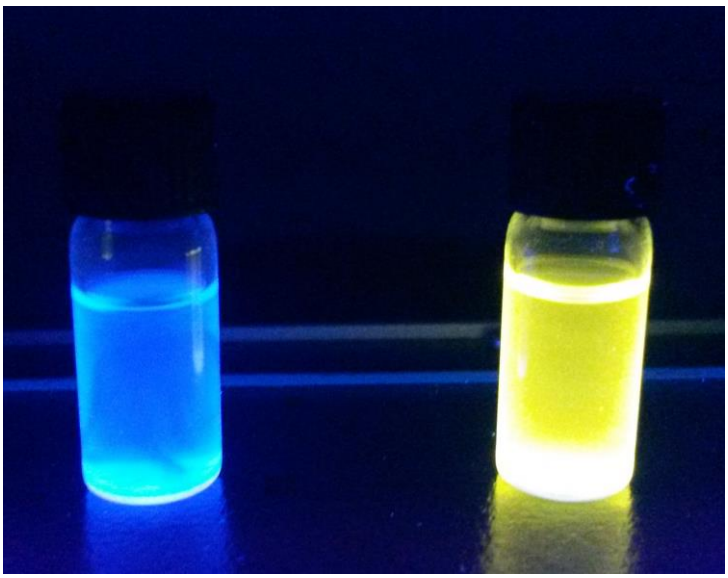


Figure S43 Fluorescence behaviour of PAT **1** (left) and pyrazoline **3** (right) irradiated with the UV hand lamp at 365 nm.

6. References

1. W. H. Heath, F. Palmieri, J. R. Adams, B. K. Long, J. Chute, T. W. Holcombe, S. Zieren, M. J. Truitt, J. L. White and C. G. Willson, *Macromolecules*, 2008, **41**, 719-726.

2. K. N. R. Wuest, V. Trouillet, A. S. Goldmann, M. H. Stenzel and C. Barner-Kowollik, *Macromolecules*, 2016, DOI: 10.1021/acs.macromol.5b02607.