Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for

Strained alkyne polymers capable of SPAAC via ring-opening metathesis polymerization

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Experimental Section

Materials and Methods

4-Butoxy-9-hydroxy-6,7-dihydro-1H-dibenzo[a,e]cyclopropa[c]-[8]annulen-1-one was prepared according to a published procedure.[1] All other reagents were used as received and purchased from Sigma-Aldrich and Alfa Aesar. All common solvents and anhydrous drying agents were purchased from Caledon. Solvents were dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Mercury 400 MHz spectrometer. ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) relative to $CDCl_3$ (δ 7.27, singlet). Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), and bs (broad signal). Coupling constants are reported as *J* values in Hertz (Hz). The number of protons (n) for a given resonance is indicated as nH and is based on spectral integration values. ^{13}C{^{1}H} NMR spectra are reported as δ in units of parts per million (ppm) relative to $CDCl_3$ (δ 77.00, t).

FT-IR spectra were recorded using a Perkin Elmer Spectrum 2 ATR FT-IR spectrometer by loading sample on to diamond platform. The background was subtracted from each spectrum.

UV-Vis absorption spectra were collected using a Varian Cary 300 Bio spectrophotometer. The solvent background was subtracted from each spectrum.

Emission spectra were collected using a Photon Technology International (PTI) QM-4 SE spectrofluorometer by dissolving the sample in spectroscopic grade CH_2Cl_2.

Gel permeation chromatography was conducted in DMF containing 10 mM LiBr and 1% NEt_3 flowing at 1 mL min^{-1} for 30 min run times at 85 °C. The instrument was equipped with a Waters 515 HPLC pump and a Waters In-line Degasser AF. Materials were detected using a Wyatt Optilab Rex RI detector operating at 25 °C. The method employed two PLgel Mixed-D 5 µm (300 × 1.5 mm) columns connected to a PLgel guard column. Samples were dissolved in the above mobile phase at approximately 5 mg mL^{-1} concentration and filtered through 0.22 µm PTFE syringe filters prior to injection using a 50 µL loop. Monodisperse polystyrene samples ranging in molecular weights of 580 to 170,800 g mol^{-1} were used as calibration standards.

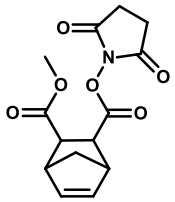
Thermal degradation studies were performed using a TA Instruments Q50 TGA. The sample was placed in a platinum pan and heated at a rate of 10 °C min^{-1} from 25 °C to 1000 °C under a

flow of nitrogen (100 mL min^{-1}). Glass transition temperatures were determined using Differential Scanning Calorimetry (DSC) on a TA Instruments DSC Q2000. The polymer samples were placed in an aluminum Tzero pan and heated/cooled at 10 °C min^{-1} in their respective stability window under a flow of nitrogen (50 mL min^{-1}). The data reported were taken from the second heating/cooling cycle.

Photolysis experiments were conducted in a Luzchem (L2C-4V) equipped with 14 8W 350 nm lamps. Under these conditions samples for unmasking were irradiated for 10 min.

Synthetic Procedures

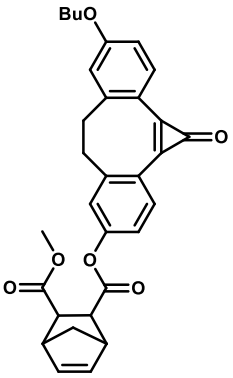
NHS-activated *endo*-monomethyl-5-norbornene-2,3-dicarboxylate



Endo-monomethyl-5-norbornene-2,3-dicarboxylate (1.00 g, 5.10 mmol), 4-dimethylaminopyridine (0.12 g, 1.02 mmol), *N*,*N*'-dicyclohexylcarbodiimide (1.26 g, 6.12 mmol), N-Hydroxysuccinimide (0.70 g, 6.1 mmol) were dissolved in dry THF (40 mL) under argon. The reaction mixture was stirred at 22 °C for 16 h. Upon completion of the reaction, the THF was evaporated, replaced with CH_2Cl_2, solids were removed by gravity filtration and the filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography (5% MeOH/CH_2Cl_2) to give NHS-activated *endo*-monomethyl-5-norbornene-2,3-dicarboxylate as a white solid. Yield = 1.30 g, 87%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.49–6.47 (dd, *J* = 5.6 & 3.1 Hz, 1H), 6.21–6.19 (dd, *J* = 5.6 & 2.9 Hz, 1H), 3.66–3.63 (dd, *J* = 10.2 & 3.5 Hz, 1H), 3.61 (s, 3H), 3.42–3.39 (m, 1H), 3.38–3.35 (dd, *J* = 10.2 & 3.3 Hz, 1H), 3.25–3.24 (m, 1H), 2.81 (s, 4H), 1.60–1.56 (dt, *J* = 8.9 Hz, 1H), 1.43–1.41 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 172.0, 169.2, 168.2, 137.3, 133.5, 52.0, 49.4, 49.0, 48.1, 45.8, 44.9, 25.8. FT-IR (ATR, cm^{-1}): 2982, 2949, 1786, 1730, 1434, 1371, 1216, 1071, 1041, 752, 649. HRMS: calculated for $[C_{12}H_{15}NO_6]^+$, $[M]^+$: 293.0899, found 293.0903.

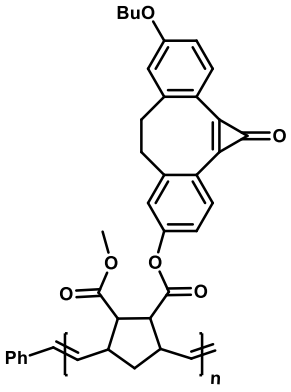
Cyclopropenone-masked monomer 1



4-Butoxy-9-hydroxy-6,7-dihydro-1H-dibenzo[a,e]cyclopropa[c]-[8]annulen-1-one[1] (0.430 g, 1.34 mmol) and K_2CO_3 (0.223 g, 1.61 mmol) were dissolved in CH_3CN (50 mL). *Endo*-monomethyl-5-norbornene-2,3-dicarboxylate (0.472 g, 1.61 mmol) was dissolved in CH_3CN (15 mL) and added to reaction mixture. The reaction mixture was stirred at 22 °C for 16 h and upon completion concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, 15% EtOAc/CH_2Cl_2) to give compound (**1**) as an off-white solid. Yield = 0.487 g, 73%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01–7.96 (m, 2H), 7.21–7.14 (m, 2H), 6.92–6.91 (m, 2H), 6.46–6.43 (m, 1H), 6.26–6.25 (m, 1H), 4.07–4.05 (t, 2H), 3.67 (s, 3H), 3.53–3.49 (m, 2H), 3.39–3.35 (t, 2H), 3.32–3.29 (d, J = 12 Hz, 2H), 2.63–2.61 (m, 2H), 1.84–1.79 (m, 2H), 1.59–1.49 (m, 3H), 1.45–1.44 (m, 1H), 1.02–0.99 (t, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 172.5, 170.6, 162.3, 153.7, 153.1, 147.9, 147.0, 144.9, 141.2, 136.0, 135.5, 134.7, 134.4, 122.9, 120.9, 120.2, 116.1, 115.8, 112.3, 67.9, 51.7, 48.6, 48.2, 47.9, 46.8, 46.1, 37.2, 36.6, 30.9, 19.0, 13.7. FT-IR (ATR, cm^{-1}): 2954, 2933, 2875, 1847, 1763, 1734, 1610, 1556, 1343, 1254, 1112. HRMS: calculated for $[C_{31}H_{30}O_6]^+$, $[M]^+$: 498.2042, found 498.2032. UV-Vis [λ_{max} = 341 (log ε = *ca.* 4.12) and 323 nm in CH_2Cl_2]

Cyclopropenone-masked polymer 2



Under a nitrogen atmosphere, monomer **1** (0.25 g, 0.50 mmol) was dissolved in dry CH_2Cl_2 (24.5 mL) in a Schlenk flask. G3 (4.4 mg, 1% mol) was also dissolved in dry and degassed CH_2Cl_2 (24.5 mL) in a separate Schlenk flask. The catalyst solution was added to the monomer solution and stirred for 8 h at 22 °C. Catalysis was terminated by the addition of ethyl vinyl ether (25 equiv.) with stirring for 30 min. The catalyst was removed by passing the reaction mixture through a plug of neutral alumina (CH_2Cl_2) to give the crude polymer. The crude polymer was dissolved in CH_2Cl_2 (10 mL) and precipitated in ice-cold pentane (50 mL) to afford polymer **2** as an off-white solid. Yield = 0.190 g, 76%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00–7.90 (bs, 2H), 7.20–7.09 (bs, 2H), 6.91–6.79 (bs, 2H), 5.91–5.35 (bs, 2H), 4.05–3.95 (bs, 2H), 3.69–3.62 (bs, 3H), 3.38–3.11 (bs, 5H), 2.60–2.39 (bs, 2H), 2.07–1.87 (bs, 2H), 1.77–1.72 (bs, 3H), 1.49–1.47 (bs, 2H), 0.98–0.96 (bs, 3H). FT-IR (ATR, cm^{-1}): 2953, 2924, 2870, 1847, 1729, 1600, 1556, 1348, 1255, 1122. UV-Vis [λ_{max} = 342 (log ε = *ca.* 4.3) and 322 nm in CH_2Cl_2]. Concentration used in UV-vis was calculated by taking mass of polymer/monomer MW and was ca 8 x 10^{-5} M. GPC (DMF vs. polystyrene standards): M_n = 41,640 g mol^{-1}, M_w = 87,190 g mol^{-1}, $Đ$ = 2.09.

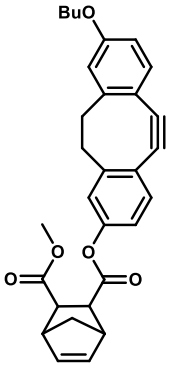
Time-dependent ROMP of cyclopropenone-masked monomer 1

According to the procedure described above, monomer **1** underwent ROMP. Aliquots were removed after 1, 2, 4, 6, and 8 h, passed through a short plug of neutral alumina and analyzed by GPC and ^{1}H NMR spectroscopy without precipitation to produce Table 1, Fig. 2a, and Fig. S14.

Variation of feed molar ratio

According to the procedure described above, a series of ROMP reactions with different molar feed ratios of monomer to catalyst were conducted. The catalyst loading was varied in each reaction (0.8, 1.0, 1.2, 2.0, and 4.0 mol%), which corresponded to monomer:catalyst ratios of 125, 100, 83, 50, and 25. After purification via passing the solution through a neutral alumina plug and precipitation, samples were analyzed by GPC to produce Fig. 2b.

Strained alkyne monomer M3

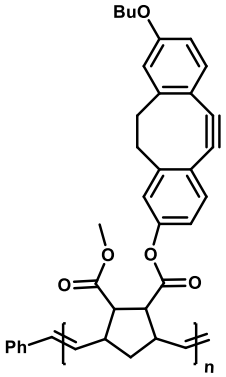


Monomer **1** (9.8 mg, 0.020 mmol) was dissolved in glass distilled CH_2Cl_2 (250 mL) and purged with argon for 15 min. The solution was irradiated in the photochemical Luzchem (L2C-4V) using 350 nm light for 10 min with stirring. Strained alkyne monomer **M3** was isolated as a pale-yellow oil and characterized without further purification. Yield = 9.3 mg, 100%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26–7.22 (dd, *J* = 10.2 & 8.3 Hz, 2H), 7.09–7.07 (dd, *J* = 5.0 & 2.3 Hz, 1H), 6.99–6.96 (dt, *J* = 8.3 Hz, 1H), 6.89–6.88 (d, *J* = 2.5 Hz, 1H), 6.79–6.76 (dd, *J* = 8.5 & 2.7 Hz, 1H), 6.44–6.40 Hz (m, 1H), 6.29–6.25 (m, 1H), 3.99 (t, *J* = 8 Hz, 2H), 3.71–3.60 (m, 3H), 3.54–3.44 (m, 2H), 3.31–3.12 (m, 4H), 2.44–2.41 (m,

2H), 1.82–1.75 (m, 1H), 1.58–1.42 (m, 3H), 1.26 (s, 2H), 0.99 (t, J = 8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 172.7, 171.0, 158.9, 155.2, 154.3, 149.8, 135.4, 134.8, 126.9, 126.3, 122.9, 121.8, 119.5, 116.7, 115.4, 111.9, 111.8, 109.5, 77.2, 67.8, 51.8, 48.7, 48.2, 46.8, 46.3, 36.5, 36.4, 31.3, 19.2, 13.8. FT-IR (ATR, cm^{-1}): 2959, 2923, 2865, 1758, 1734, 1556, 1487, 1176, 1146. HRMS: calculated for $[C_{30}H_{30}O_5]^+$, $[M]^+$: 470.2093, found 470.2082. UV-Vis (λ_{max} = 319 (log ε = *ca.* 4.1) and 304 nm in CH_2Cl_2).

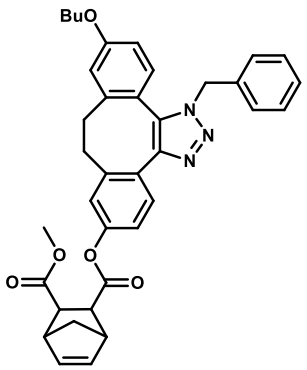
Strained alkyne polymer 3



Cyclopropenone-masked polymer **2** (10 mg, 0.020 mmol) was dissolved in glass distilled CH_2Cl_2 (250 mL) and purged with argon for 15 min. The solution was irradiated in the photochemical Luzchem (L2C-4V) using 350 nm light for 10 min with stirring. Compound (**3**) was isolated as a pale-yellow oil and characterized without further purification. Yield = 9.3 mg, 99%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20 (bs, 2H), 7.01 (bs, 1H), 6.87 (bs, 1H), 6.75 (bs, 1H), 6.00–5.42 (bs, 2H), 3.98–3.89 (bs, 2H), 3.67–3.61 (bs, 3H), 3.40–3.07 (bs, 4H), 2.45–2.28 (bs, 1H), 2.03 (bs, 1H), 1.75 (bs, 2H), 1.47 (bs, 2H), 1.32–1.20 (bs, 4H), 0.99–0.84 (bs, 6H). FT-IR (ATR, cm^{-1}): 2954, 2924, 2870, 2253, 2164, 1734, 1561, 1482, 1216, 1137, 894, 726. UV-Vis (λ_{max} = 320 and 303 nm in CH_2Cl_2).

Benzyl-functionalized monomer M4a (both regioisomers)

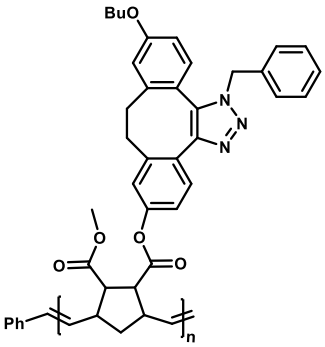


Strained alkyne monomer **M3** (10 mg, 0.021 mmol) was dissolved in glass distilled CH_2Cl_2 (2 mL). Benzyl azide (3 mg, 0.02 mmol) was added to the reaction mixture, which was stirred for 30 min. After solvent removal *in vacuo*, the crude product was purified by column chromatography (silica gel, 5% EtOAc/CH_2Cl_2) to give compound **M4a** as a yellow oil. Yield = 12 mg, 95%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53–7.50 (d, J = 8.0 Hz, 1H), 7.25–7.24 (m, 2H), 7.09–7.08 (m, 3H), 6.97–6.88 (m, 2H), 6.78–6.72 (m, 2H), 6.37–6.35 (m, 1H), 6.27–6.25 (m, 1H), 5.59–5.47 (m, 2H), 3.98–3.94 (m, 2H), 3.61 (s, 3H), 3.49–3.40 (m, 2H), 3.27–2.64 (m, 4H), 2.32–2.18 (m, 1H), 2.08–2.05 (m, 1H), 1.81–1.74 (m, 2H), 1.54–1.25 (m, 5H), 1.00–0.07 (m, 3H). $^{13}C\{^{1}H\}$ NMR

($CDCl_3$, 100 MHz): δ 172.9, 171.1, 160.5, 159.1, 150.6, 143.3, 139.2, 138.1, 136.8, 135.7, 133.2, 130.2, 129.2, 127.7, 126.3, 123.6, 118.3, 115.9, 112.7, 72.8, 70.8, 68.0, 60.7, 52.1, 48.5, 46.9, 36.8, 34.9, 31.9, 29.7, 25.6, 21.3, 20.0, 19.5, 14.4, 11.7, 1.3. FT-IR (ATR, cm^{-1}): 2934, 2865, 1739, 1610, 1516, 1343, 1245, 1201, 1146. HRMS: calculated for $[C_{37}H_{37}N_3O_5]^+$, $[M]^+$: 603.2733, found 603.2738.

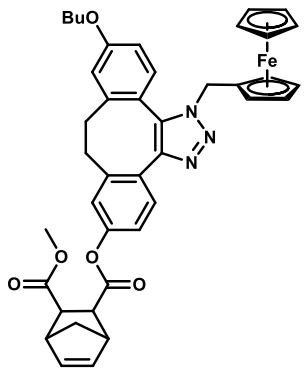
Benzyl-functionalized polymer 4a (both regioisomers)



Cyclopropenone-masked polymer **2** (33 mg, 0.067 mmol) and benzyl azide (11 mg, 0.080 mmol) and was dissolved in CH_2Cl_2 (250 mL) and purged with argon for 15 min. The solution was irradiated in the photochemical Luzchem (L2C-4V) using 350 nm light for 10 min. The reaction was monitored by UV-Vis absorption spectroscopy. After solvent removal, the crude polymer was dissolved in CH_2Cl_2 (10 mL) and precipitated in ice-cold pentane (50 mL) to afford benzyl-functionalized polymer as a yellow solid. Yield = 40 mg, 98%.

The product was characterized by ^1H NMR spectroscopy in $CDCl_3$ (Fig. S23). Because of the broadness of the signals this was done by comparing the spectrum to that of the monomer **M4a**. FT-IR (ATR, cm^{-1}): 3368, 2924, 2855, 1734, 1605, 1457, 1206, 1132. UV-Vis (λ_{max} = 257 nm in CH_2Cl_2). M_n = 44,780 g mol^{-1}, M_w = 100,900 g mol^{-1}, $Đ$ = 2.43.

Ferrocene-functionalized monomer M4b (both regioisomers)

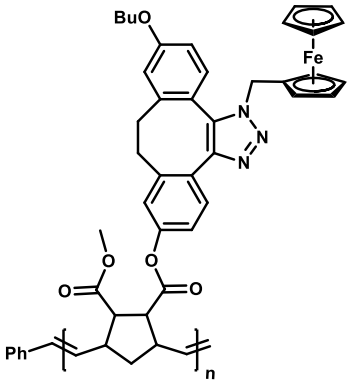


Strained alkyne monomer **M3** (10 mg, 0.021 mmol) was dissolved in glass distilled CH_2Cl_2 (2 mL). Azidomethylferrocene (5 mg, 0.02 mmol) was added to the reaction mixture, which was then stirred for 30 min. After solvent removal, the crude product was purified by column chromatography (silica gel, pure CH_2Cl_2 followed by pure EtOAc) to give compound **M4b** an orange solid (12 mg, 81% yield).

^1H NMR ($CDCl_3$, 400 MHz): δ 7.48–7.38 (m, 1H), 7.22–7.07 (m, 2H), 6.93–6.83 (m, 2H), 6.75–6.63 (m, 1H), 6.47–6.34 (m, 1H), 6.27–6.25 (m, 1H), 5.26 (s, 2H), 4.29–4.00 (m, 7H), 3.93–3.83 (m, 2H), 3.67–3.60 (m, 2H), 3.50–3.39 (m, 2H), 3.31–3.23 (m, 3H), 3.00–2.72 (m, 3H), 1.82–1.69 (m, 3H), 1.62–1.38 (m, 4H), 1.31–1.29 (m, 2H), 1.03–0.93 (m, 3H). Due to the presence

of both regioisomers, there are additional carbon signals for many of the carbon environments. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 173.0, 171.4, 171.2, 160.4, 159.0, 151.8, 150.5, 146.9, 146.2, 143.5, 143.3, 139.3, 139.2, 135.9, 135.7, 135.1, 135.0, 134.8, 133.6, 133.1, 132.7, 130.5, 130.4, 127.9, 124.5, 123.6, 123.2, 123.1, 122.5, 120.1, 120.0, 119.5, 118.7, 116.7, 115.9, 113.0, 112.6, 69.2, 68.8, 68.0, 67.8, 60.6, 53.7, 52.1, 52.0, 49.0, 48.5, 47.1, 46.9, 46.5, 36.7, 36.6, 33.2, 31.9, 31.6, 30.0, 29.6, 29.3, 25.5, 22.9, 21.3, 19.5, 14.5, 14.1. FT-IR (ATR, cm^{-1}): 3071, 2949, 2934, 2865, 1739, 1610, 1511, 1343, 1250, 1201, 1151, 1003, 820, 736. HRMS: calculated for $[C_{41}H_{41}FeN_3O_5]^+$, $[M]^+$: 711.2396, found 711.2381.

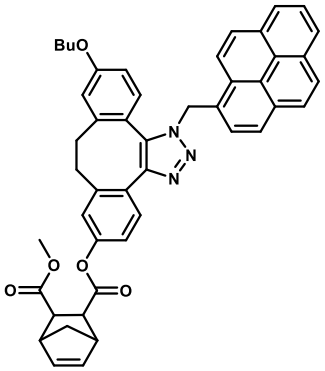
Ferrocene-functionalized polymer 4b (both regioisomers)



Cyclopropenone-masked polymer **2** (44 mg, 0.088 mmol) and azidomethylferrocene (30 mg, 0.12 mmol) and was dissolved in CH_2Cl_2 (250 mL) and purged with argon for 15 min. The solution was irradiated in the photochemical Luzchem (L2C-4V) using 350 nm light for 10 min. The reaction was monitored by UV-Vis absorption spectroscopy. After solvent removal, the crude polymer was dissolved in CH_2Cl_2 (10 mL) and precipitated in ice-cold pentane (50 mL) to afford ferrocene-functionalized polymer **4b** as a yellow solid. Yield = 60 mg, 95%. The product was characterized by ^{1}H NMR in $CDCl_3$ (Fig. S32). Because of the broadness of the signals this was done by comparing the spectrum to that of the monomer **M4b**.

FT-IR (ATR, cm^{-1}): 3437, 3092, 2959, 2924, 2865, 2242, 1739, 1605, 1511, 1206, 1137, 983, 914, 820, 721. M_n = 50,890 g mol^{-1}, M_w = 110,600 g mol^{-1}, $Đ$ = 2.17.

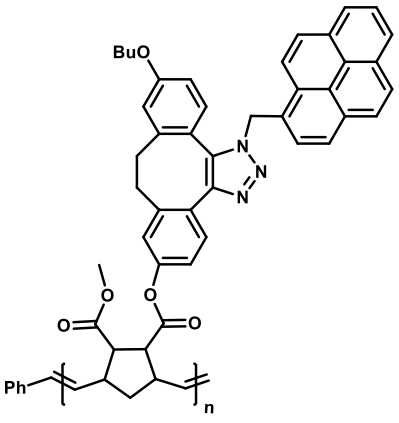
Pyrene-functionalized monomer M4c (both regioisomers)



Strained alkyne monomer **M3** (10 mg, 0.021 mmol) was dissolved in glass distilled CH_2Cl_2 (2 mL). Azidomethylpyrene (6 mg, 0.023 mmol) was added to the reaction mixture, which was stirred for 30 min. After solvent removal, the crude product was purified by column chromatography (silica gel, pure CH_2Cl_2 followed by pure EtOAc) to give compound **M4c** as a beige solid (14 mg, 90% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21–8.16 (m, 3H), 8.10–8.00 (m, 5H), 7.59–7.49 (m, 2H), 7.16–7.04 (m, 1H), 6.97–6.92 (m, 1H), 6.86–6.75 (m, 1H), 6.70–6.67 (m, 1H), 6.59 (s, 1H), 6.36–6.34 (m, 1H), 6.26–6.24 (m, 1H), 3.92–3.89 (t, 8 Hz, 2H), 3.60 (s, 3H), 3.48–3.38 (m, 2H), 3.28–3.22 (m, 2H), 3.15–3.03 (m, 1H), 2.91–2.75 (m, 1H), 2.65–2.58 (m, 1H), 1.77–1.70 (m, 2H), 1.56–1.38 (m, 5H), 1.31–1.30 (m, 1H), 0.99–0.93 (m, 3H). Due to the presence of both regioisomers, there are additional carbon signals for many of the carbon environments. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 172.6, 170.7, 160.1, 158.8, 151.6, 150.3, 146.9, 146.2, 142.8, 139.2, 139.0, 135.1, 134.8, 134.4, 133.5, 132.7, 132.6, 131.3, 131.1, 130.5, 130.2, 130.0, 128.4, 128.2, 128.1, 127.7, 127.5, 127.3, 126.4, 126.1, 125.5, 125.4, 124.7, 124.6, 124.5, 123.8, 123.2, 122.0, 119.2, 118.0, 116.3, 115.7, 112.8, 112.4, 67.7, 67.5, 60.4, 53.4, 51.7, 50.4, 48.7, 48.2, 46.7, 46.6, 46.3, 36.1, 36.0, 32.7, 31.2, 19.2, 14.2, 13.8. FT-IR (ATR, cm^{-1}): 3043, 2954, 2924, 2865, 1753, 1739, 1605, 1511, 1339, 1260, 1196, 1146, 845, 701. HRMS: calculated for $[C_{47}H_{41}N_3O_5]^+$, $[M]^+$: 727.3046, found 728.3112. UV-Vis in CH_2Cl_2 (λ_{max} = 346, 329, 315, 278 and 267 nm in CH_2Cl_2).

Synthesis of pyrene-functionalized polymer 4c (both regioisomers)



Cyclopropenone-masked polymer **2** (45 mg, 0.090 mmol) and azidomethylpyrene (25 mg, 0.097 mmol) and were dissolved in CH_2Cl_2 (250 mL) and purged with argon for 15 min. The solution was irradiated in the photochemical Luzchem (L2C-4V) using 350 nm light for 10 min. The reaction was monitored by UV-Vis absorption spectroscopy. After solvent removal, the crude polymer was dissolved in CH_2Cl_2 (10 mL) and precipitated into ice-cold pentane (50 mL) to afford pyrene-functionalized polymer **4c** as a yellow solid. Yield = 50 mg, 77%.

The product was characterized by ^{1}H NMR spectroscopy in $CDCl_3$ (Fig. S39). Because of the broadness of the signals this was done by comparing the spectrum to that of the monomer **M4c**. FT-IR (ATR, cm^{-1}): 3043, 2959, 2870, 2361, 2257, 1734, 1605, 1205, 1132, 904, 845, 726. UV-Vis in CH_2Cl_2 (λ_{max} = 346, 329, 315, 277 and 266 nm). M_n = 33,710 g mol^{-1}, M_w = 84,860 g mol^{-1}, $Đ$ = 2.52.

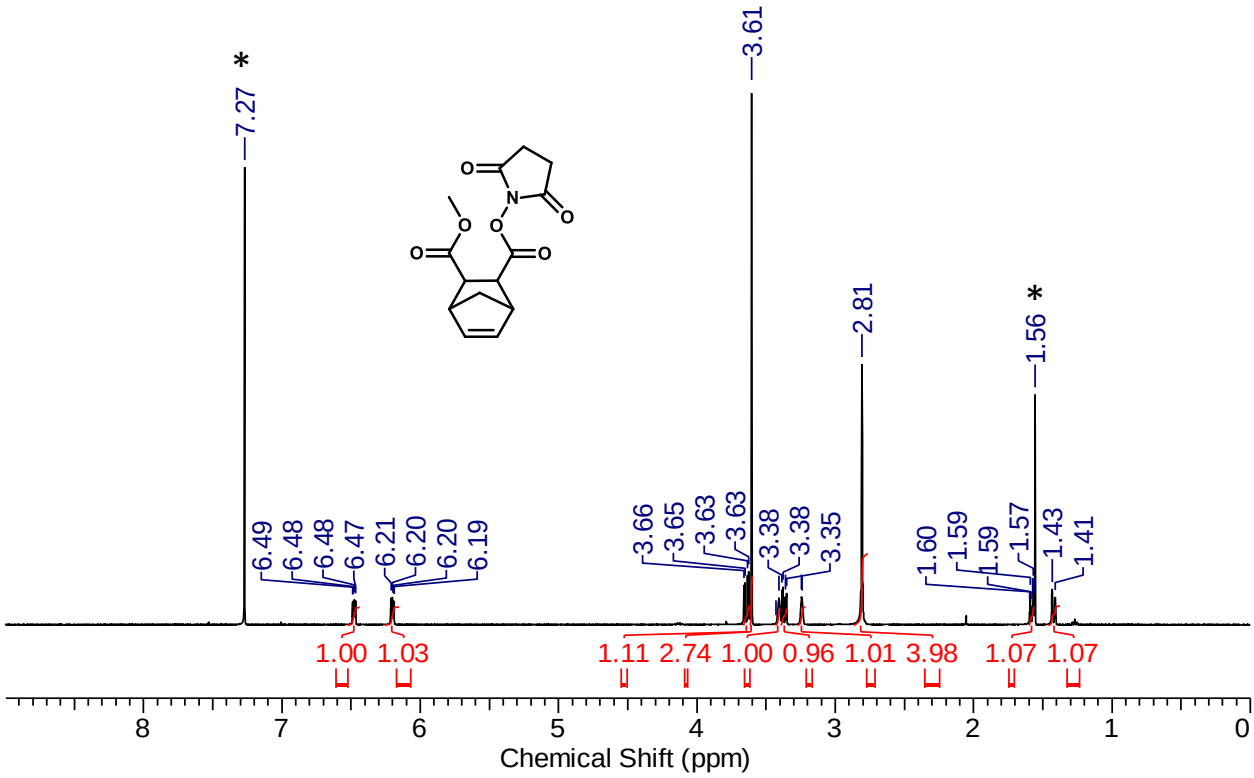


Fig. S1 ^{1}H NMR spectrum of NHS-activated *endo*-monomethyl-5-norbornene-2,3-dicarboxylate in $CDCl_3$. Asterisks denote residual solvent signals.

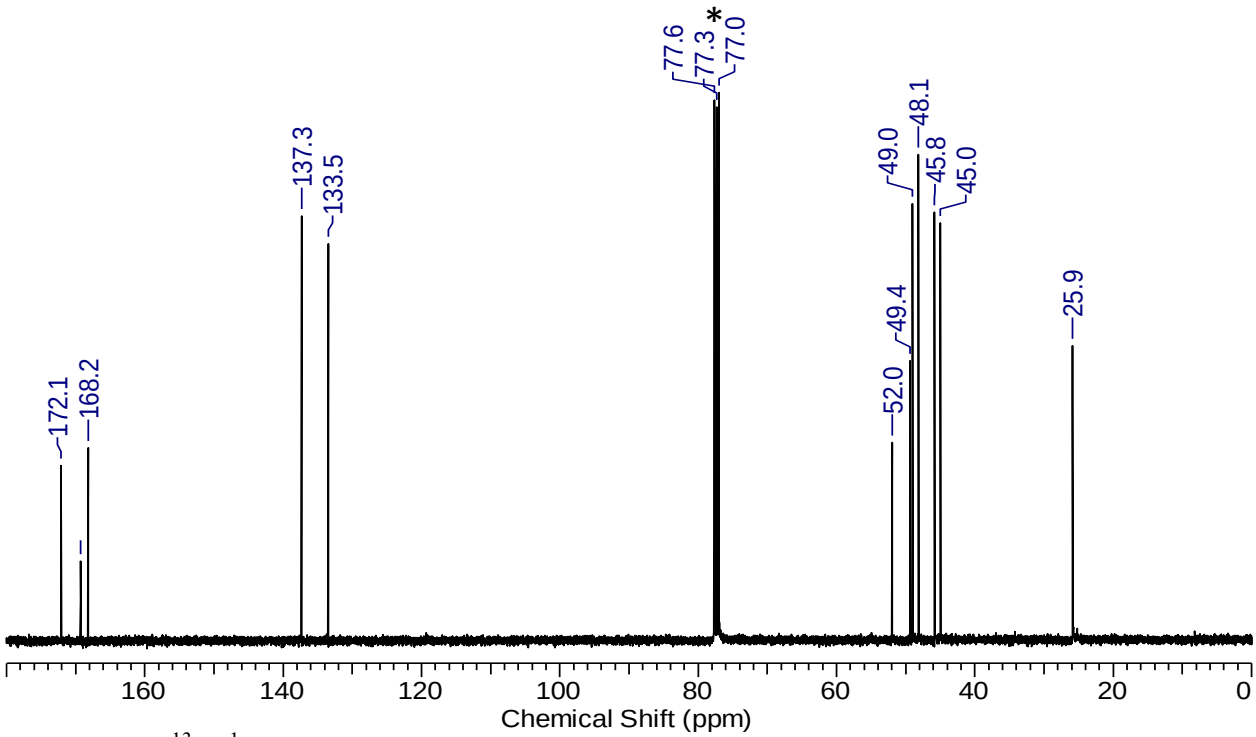


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of NHS-activated *endo*-monomethyl-5-norbornene-2,3-dicarboxylate in $CDCl_3$. Asterisk denotes solvent signal.

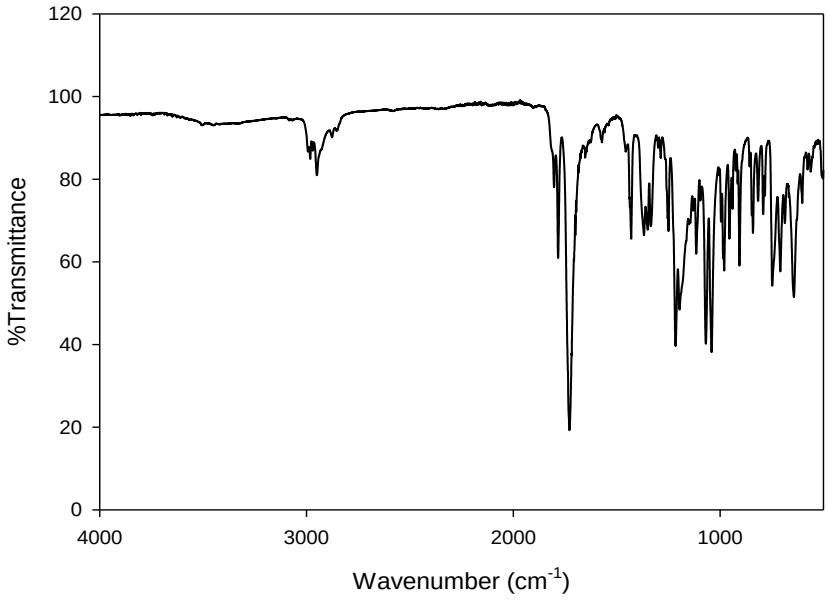


Fig. S3 FT-IR spectrum of NHS-activated *endo*-monomethyl-5-norbornene-2,3-dicarboxylate.

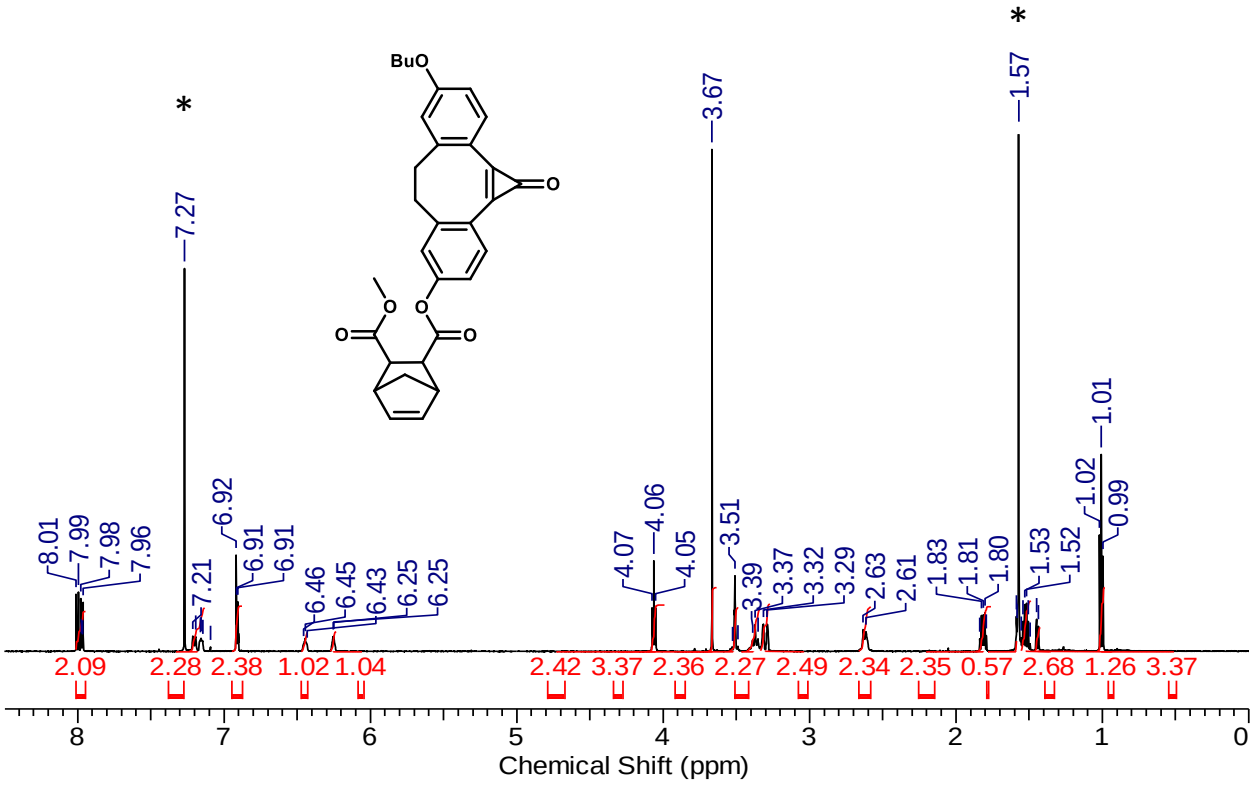


Fig. S4 ^{1}H NMR spectrum of cyclopropenone-masked monomer **1** in $CDCl_3$. Asterisks denote residual solvent signals.

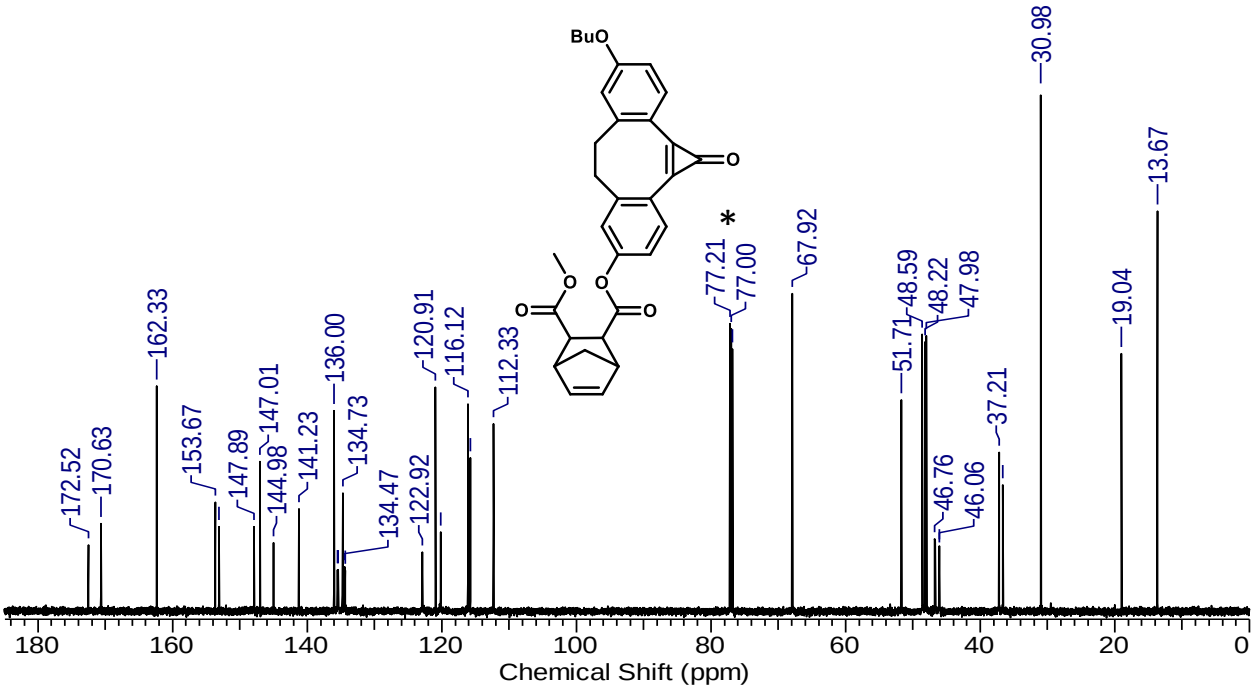


Fig. S5 $^{13}C\{^{1}H\}$ NMR spectrum of cyclopropenone-masked monomer **1** in $CDCl_3$. Asterisk denotes solvent signal.

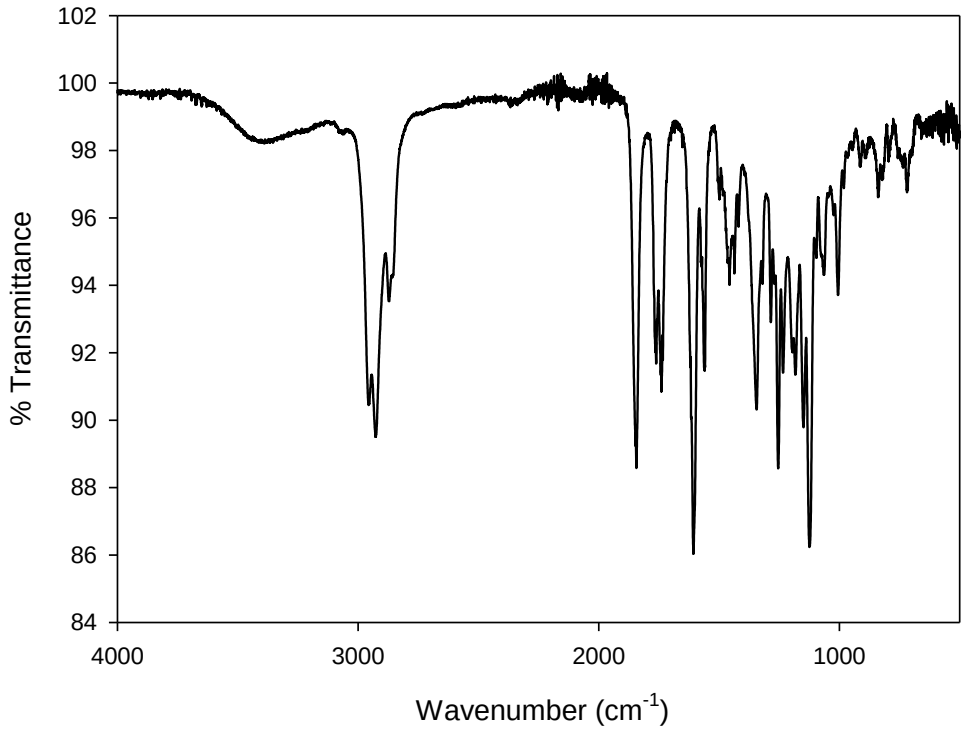


Fig. S6 FT-IR spectrum of cyclopropenone-masked monomer **1**.

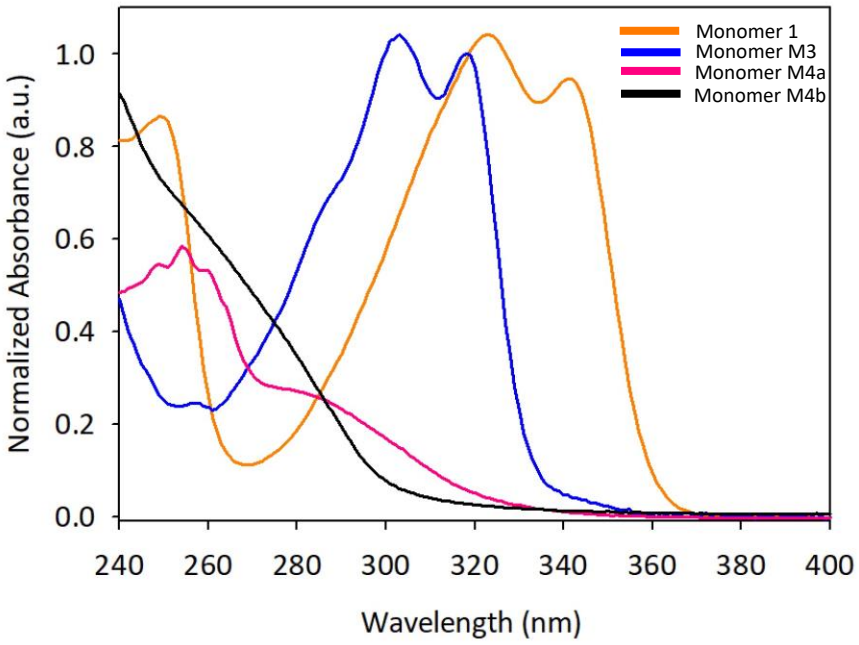


Fig. S7 UV-Vis absorption spectrum of cyclopropenone-masked monomer **1** (orange), strained alkyne monomer **M3** (blue), benzyl-functionalized monomer **M4a** (pink), and ferrocene-functionalized monomer **M4b** (black) in CH_2Cl_2. Spectra were normalised at 220 nm.

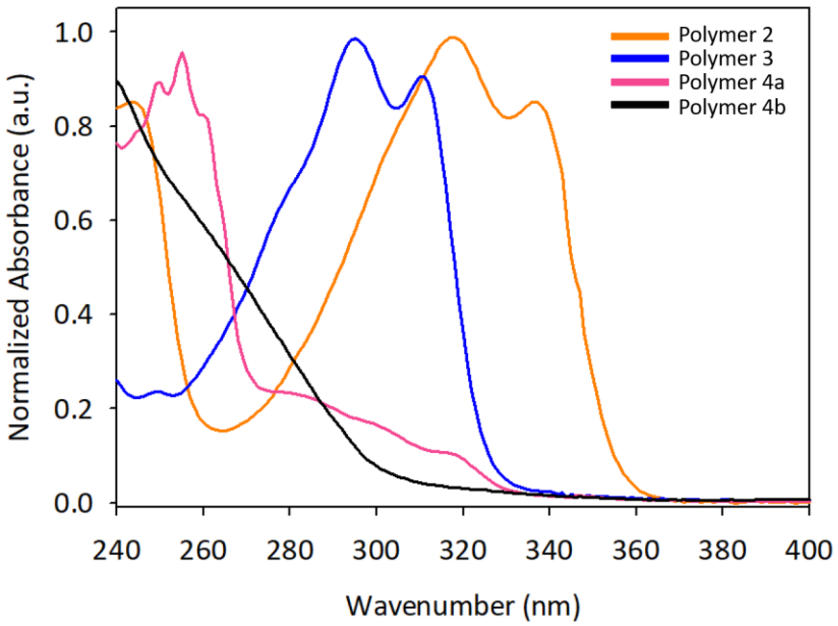


Fig. S8 UV-Vis absorption spectrum of cyclopropenone-masked polymer **2** (orange), strained alkyne polymer **3** (blue), benzyl-functionalized polymer **4a** (pink), and ferrocene-functionalized polymer **4b** (black) in CH_2Cl_2

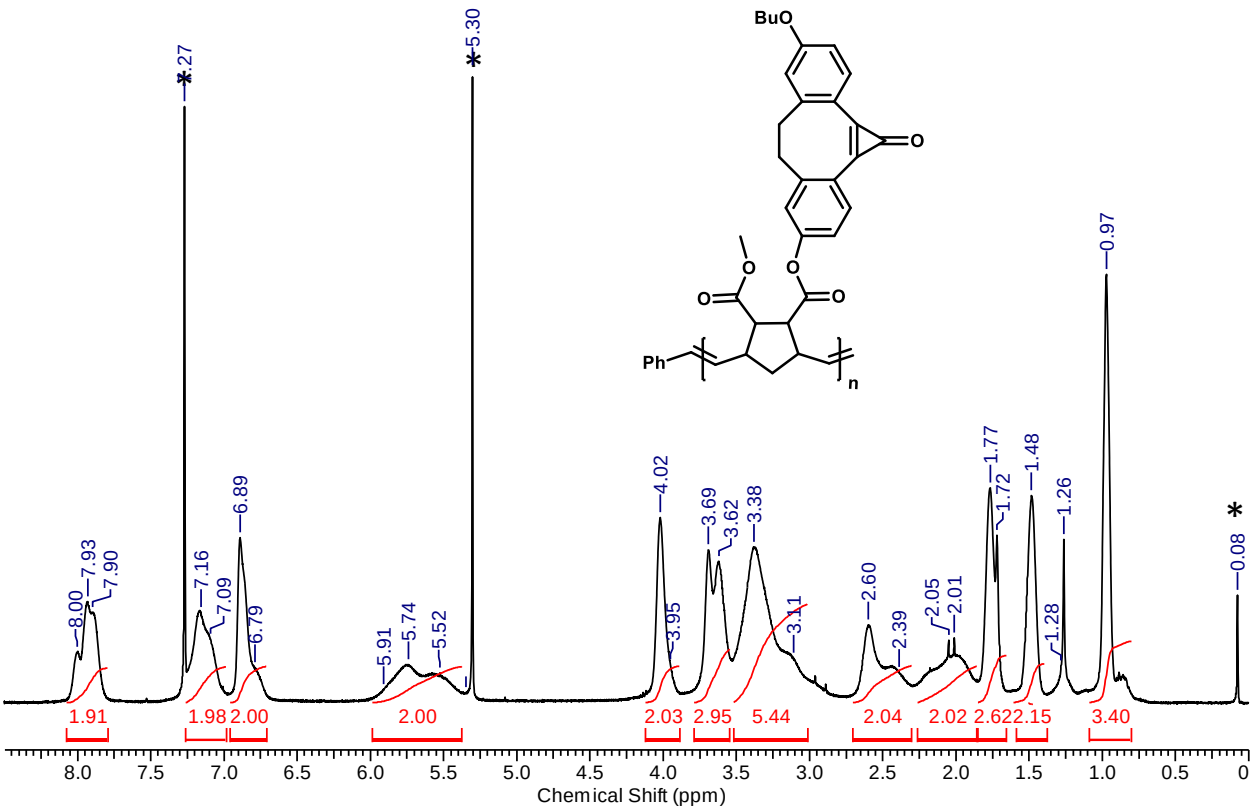


Fig. S9 ^{1}H NMR spectrum of cyclopropenone-masked polymer **2** in $CDCl_3$. Asterisks denote residual solvent and grease signals.

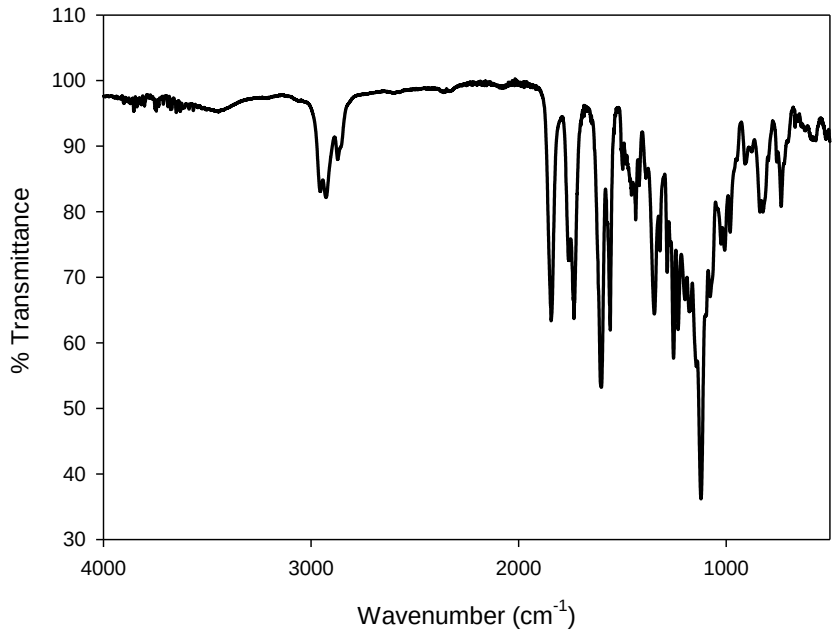


Fig. S10 FT-IR spectrum of cyclopropenone-masked polymer **2**.

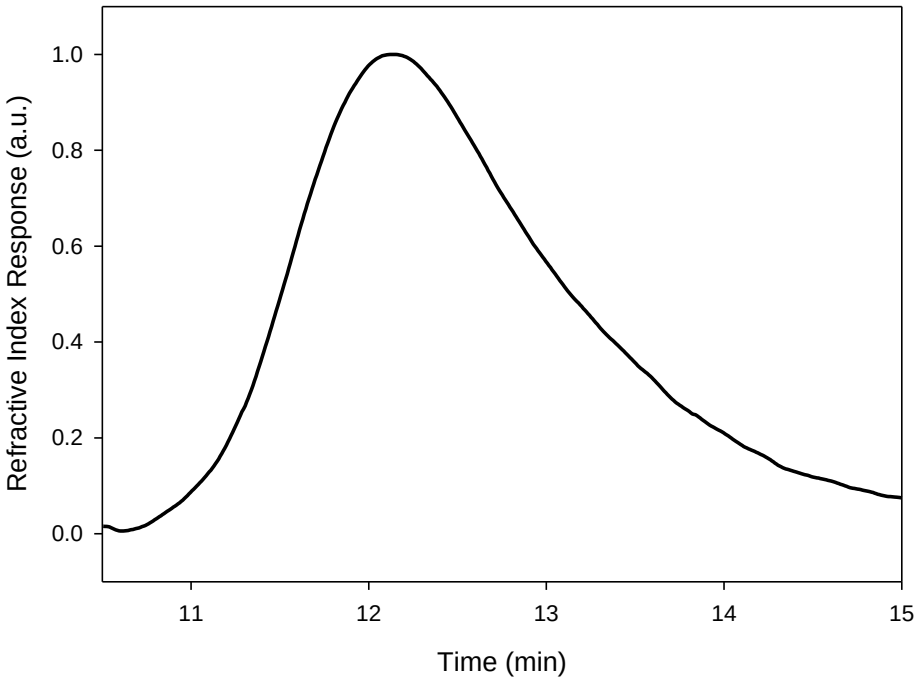


Fig. S11 GPC trace obtained for cyclopropenone-masked polymer **2** in DMF.

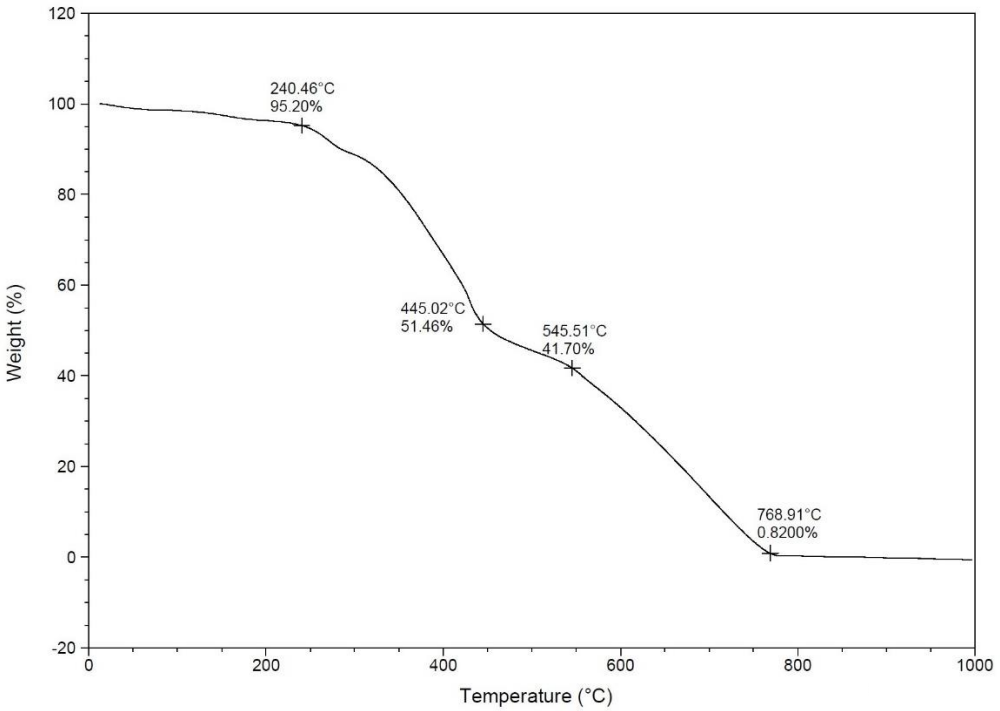


Fig. S12 TGA analysis of cyclopropenone-masked polymer **2**.

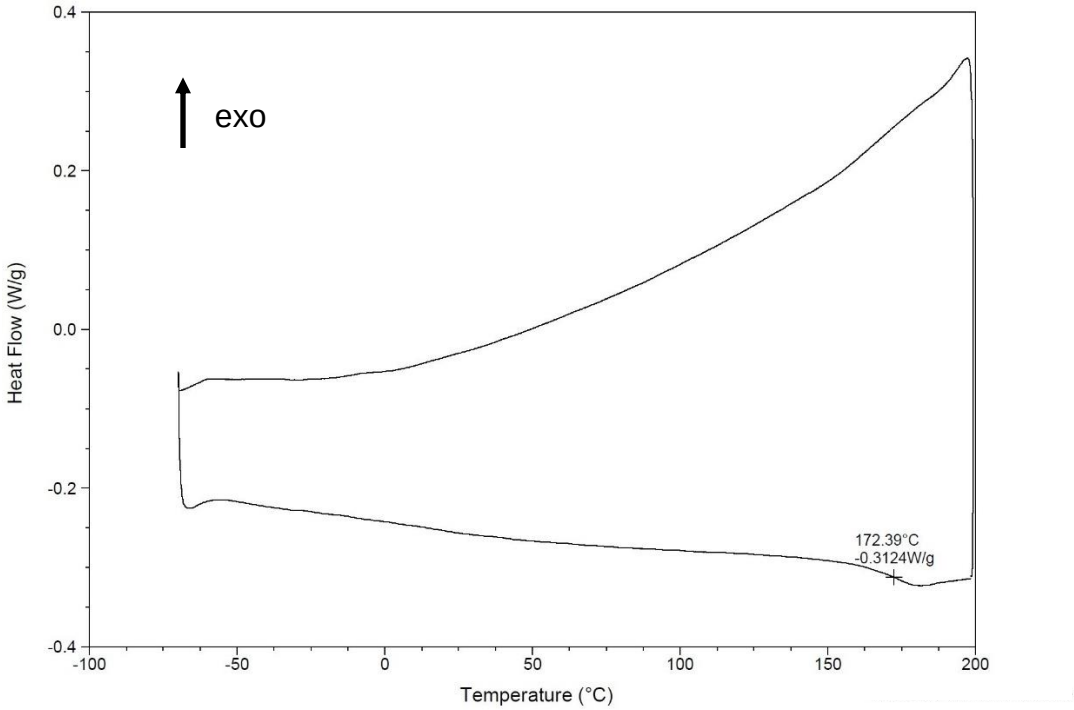


Fig. S13 DSC analysis of cyclopropenone-masked polymer **2**.

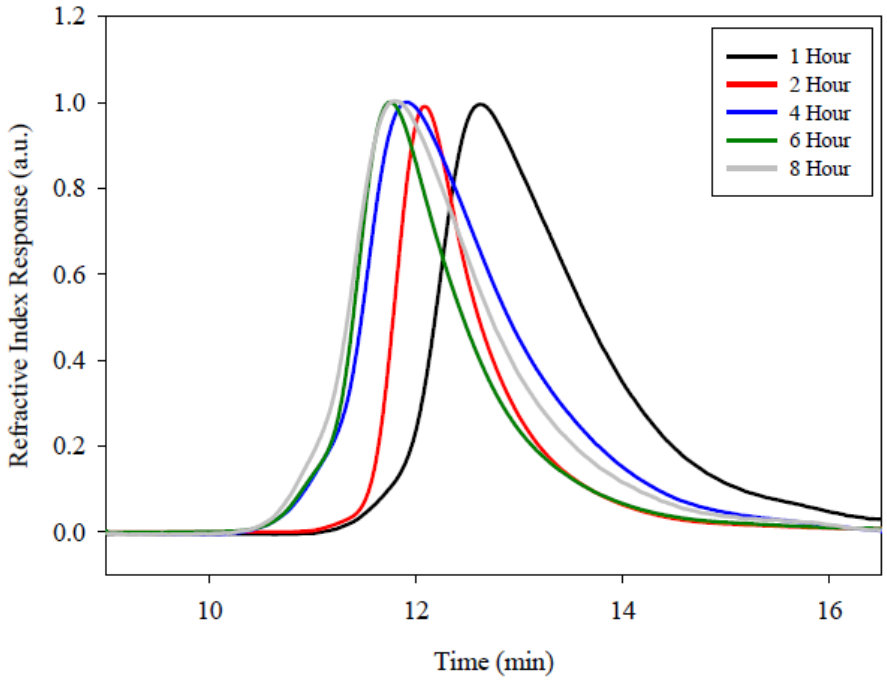


Fig. S14 GPC traces obtained for aliquots taken from the ROMP of cyclopropenone-masked monomer **1** at various times.

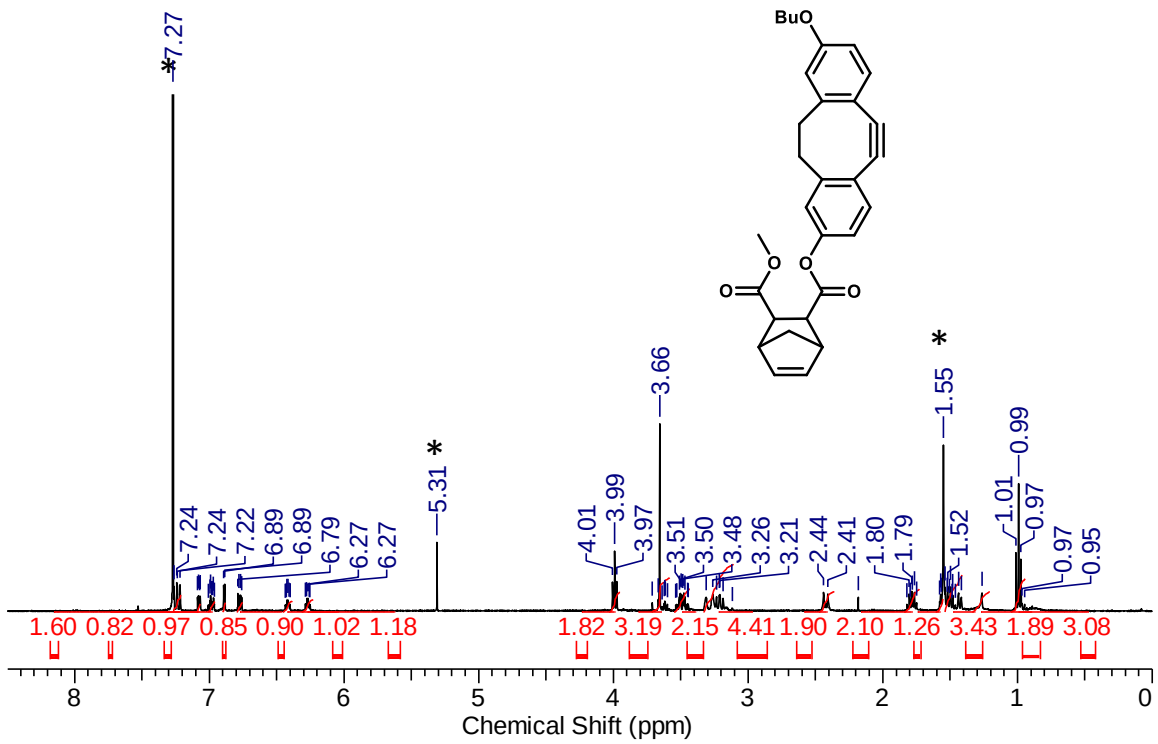


Fig. S15 ^{1}H NMR spectrum of strained alkyne monomer **M3** in $CDCl_3$. Asterisks denote residual solvent signals.

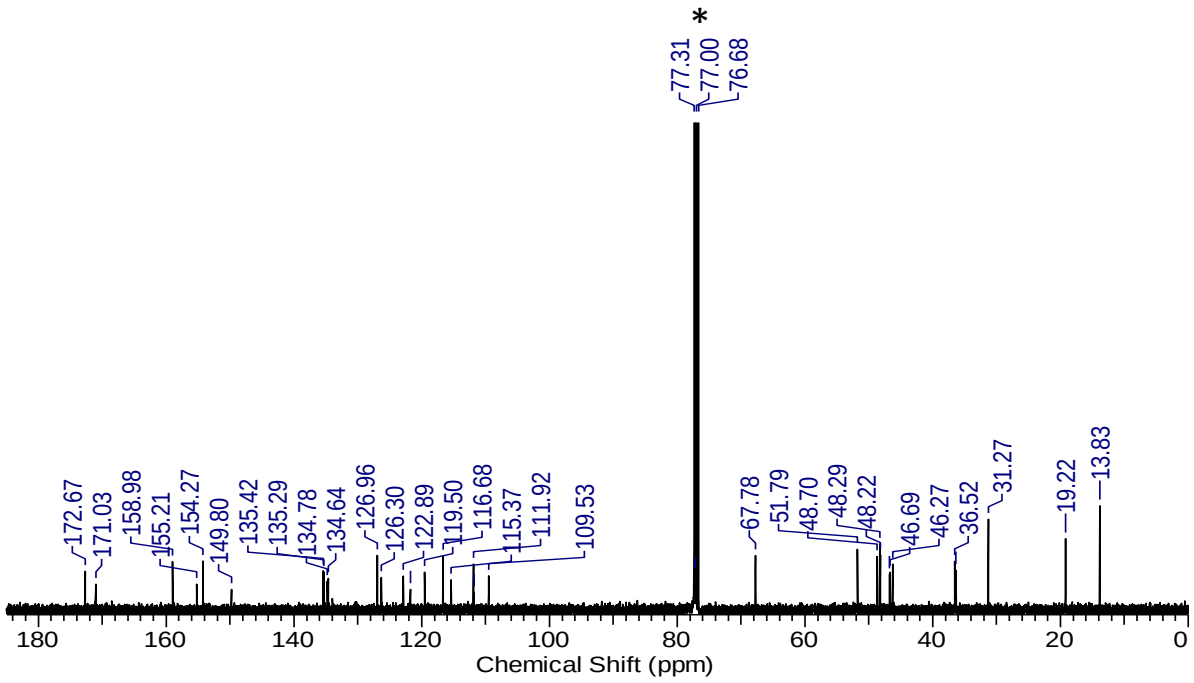


Fig. S16 $^{13}C\{^{1}H\}$ NMR spectrum of strained alkyne monomer **M3** in $CDCl_3$. Asterisk denotes solvent signal.

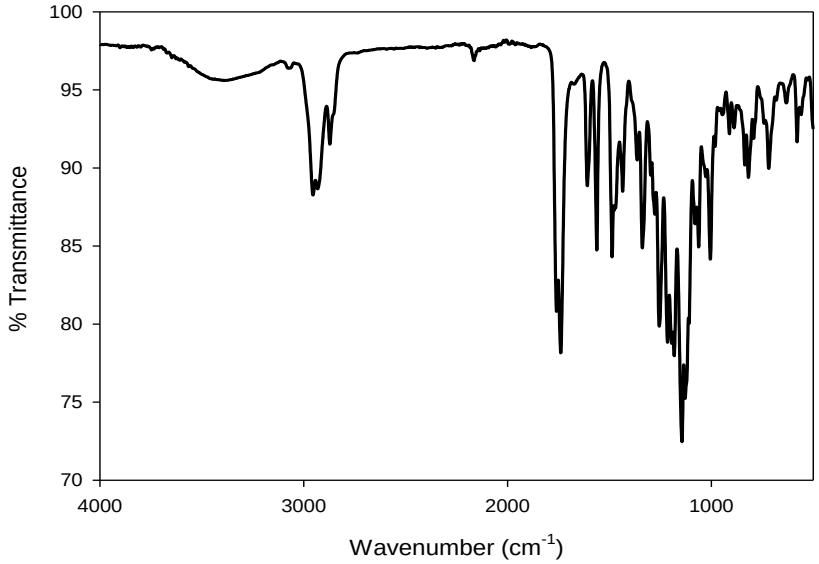


Fig. S17 FT-IR spectrum of strained alkyne monomer **M3**.

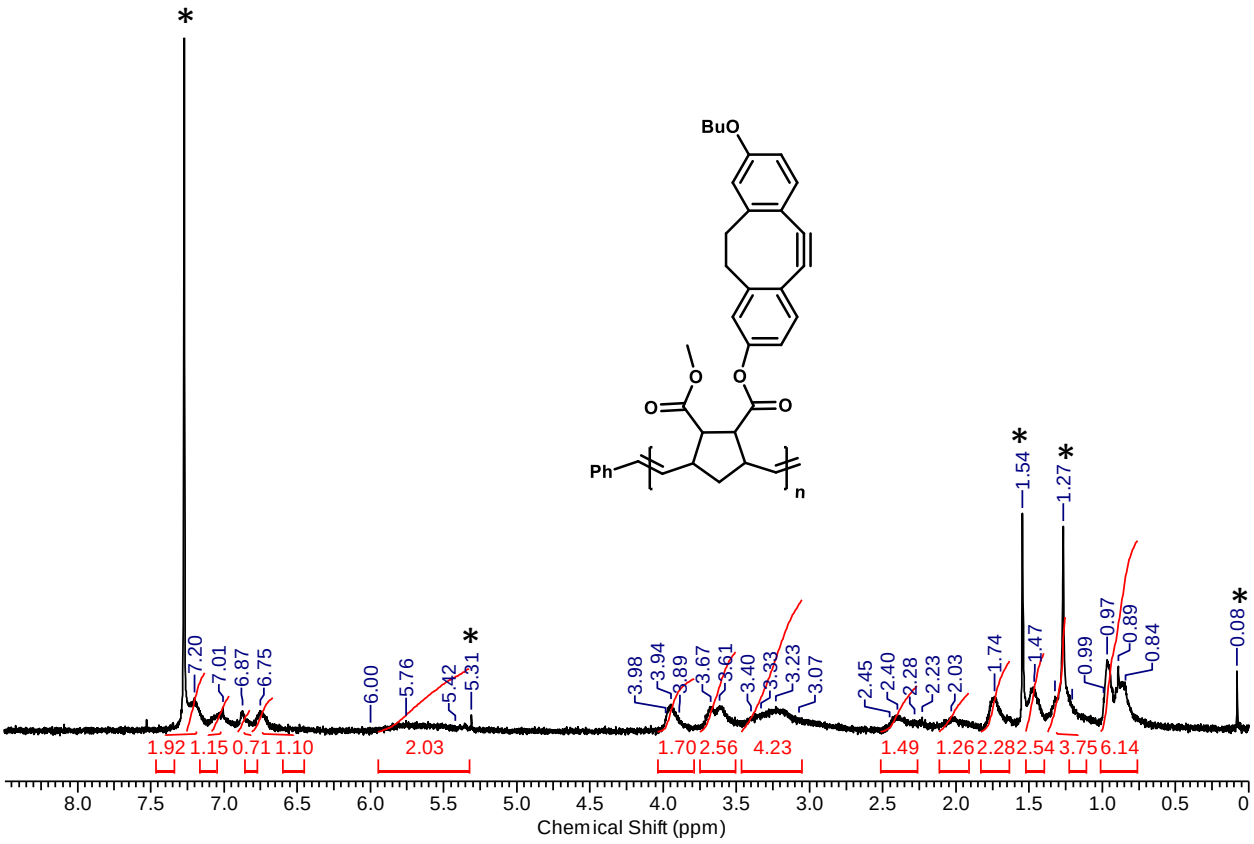


Fig. S18 ^{1}H NMR spectrum of strained alkyne polymer **3** in $CDCl_3$. Asterisks denote residual solvent signals

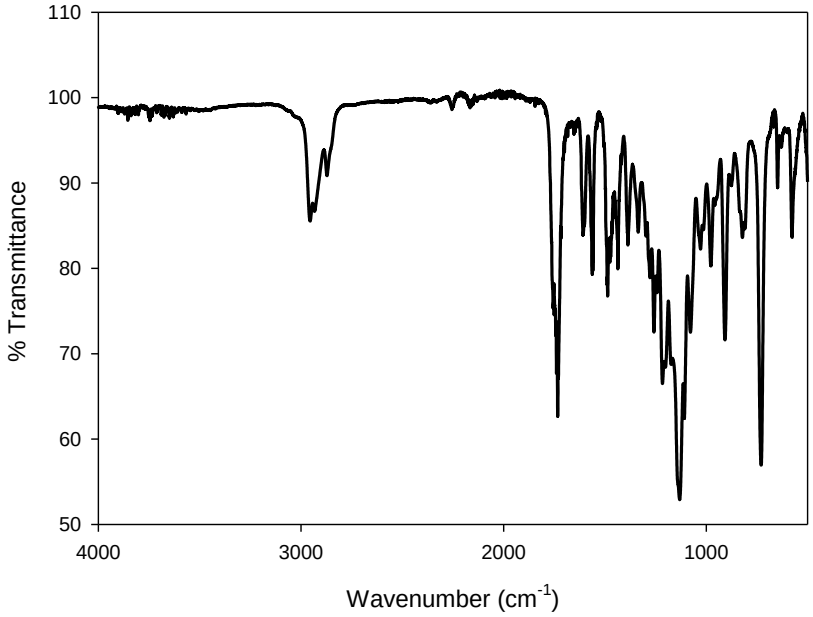


Fig. S19 FT-IR spectrum of strained alkyne polymer **3**.

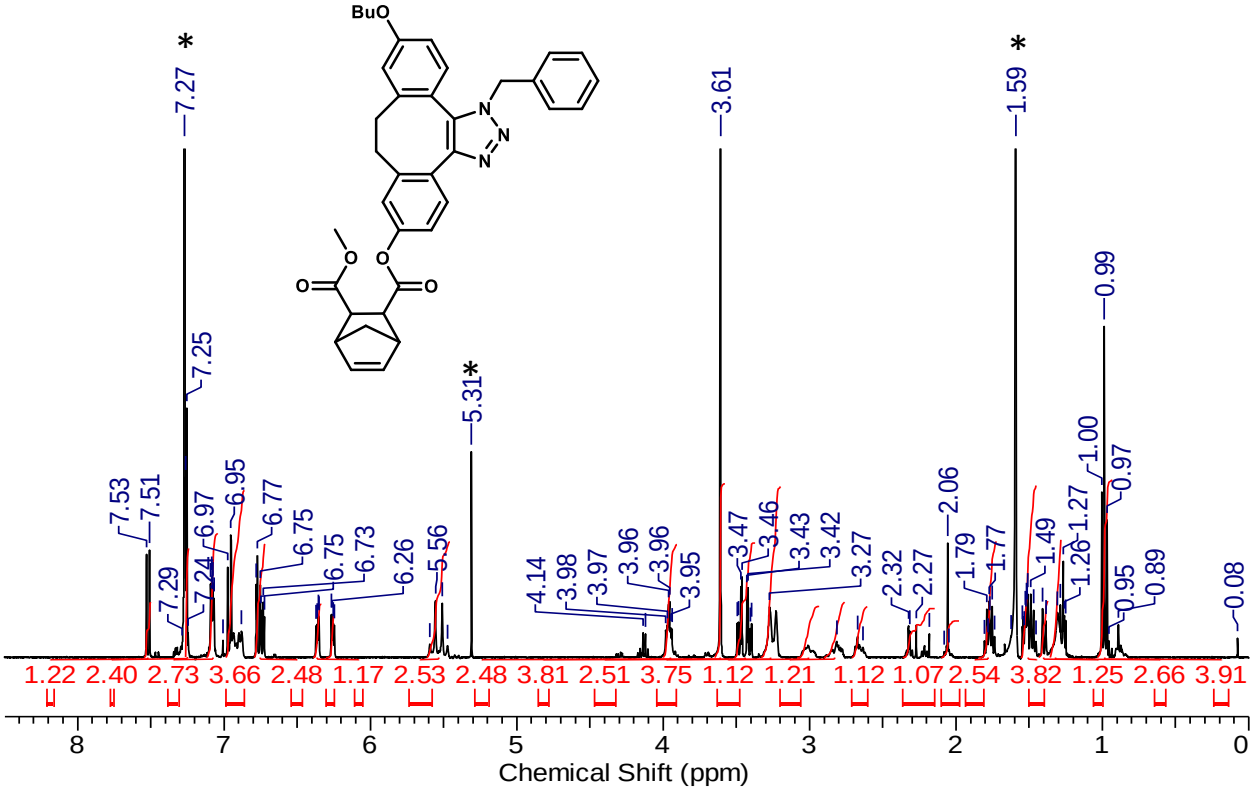


Fig. S20 ^{1}H NMR spectrum of benzyl-functionalized monomer **M4a** in $CDCl_3$. Asterisks denote residual solvent signals.

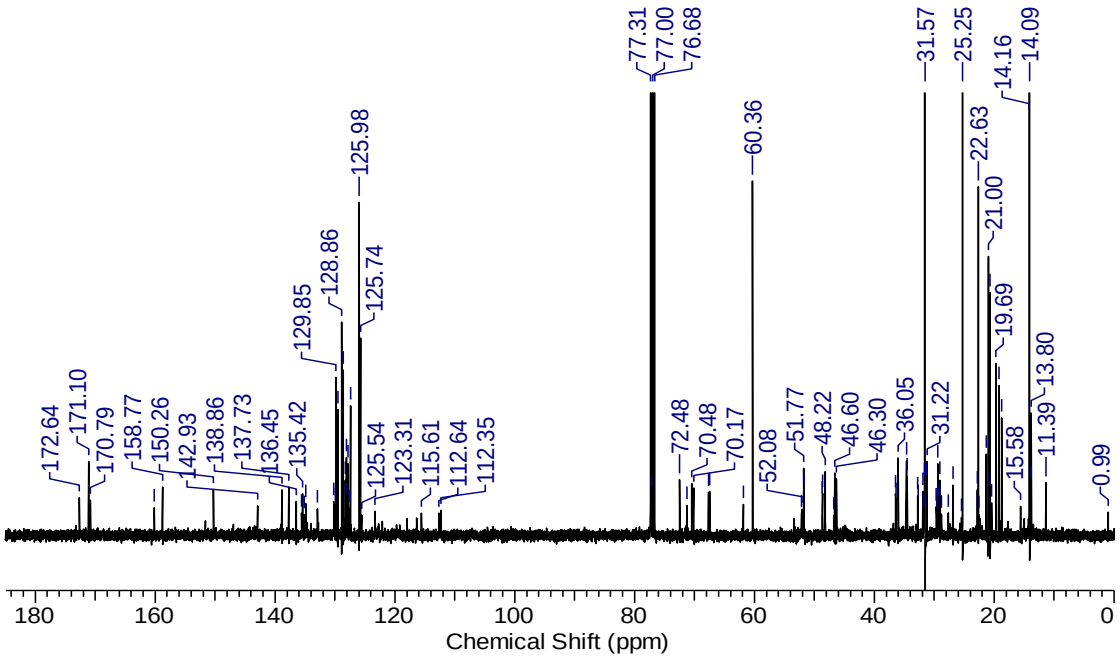


Fig. S21 $^{13}C\{^{1}H\}$ NMR spectrum of benzyl-functionalized monomer **M4a** in $CDCl_3$. Asterisk denotes residual solvent signal.

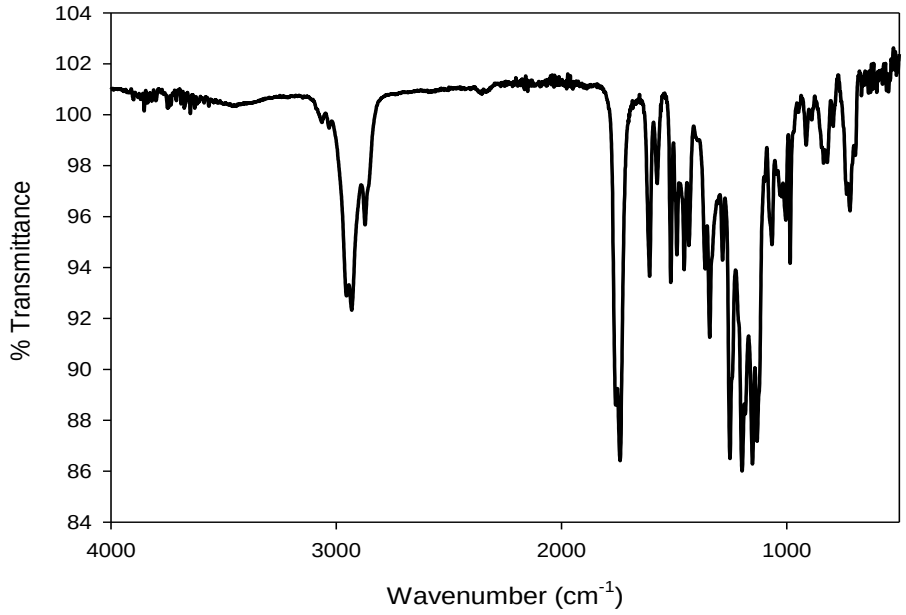


Fig. S22 FT-IR spectrum of benzyl-functionalized monomer **M4a**.

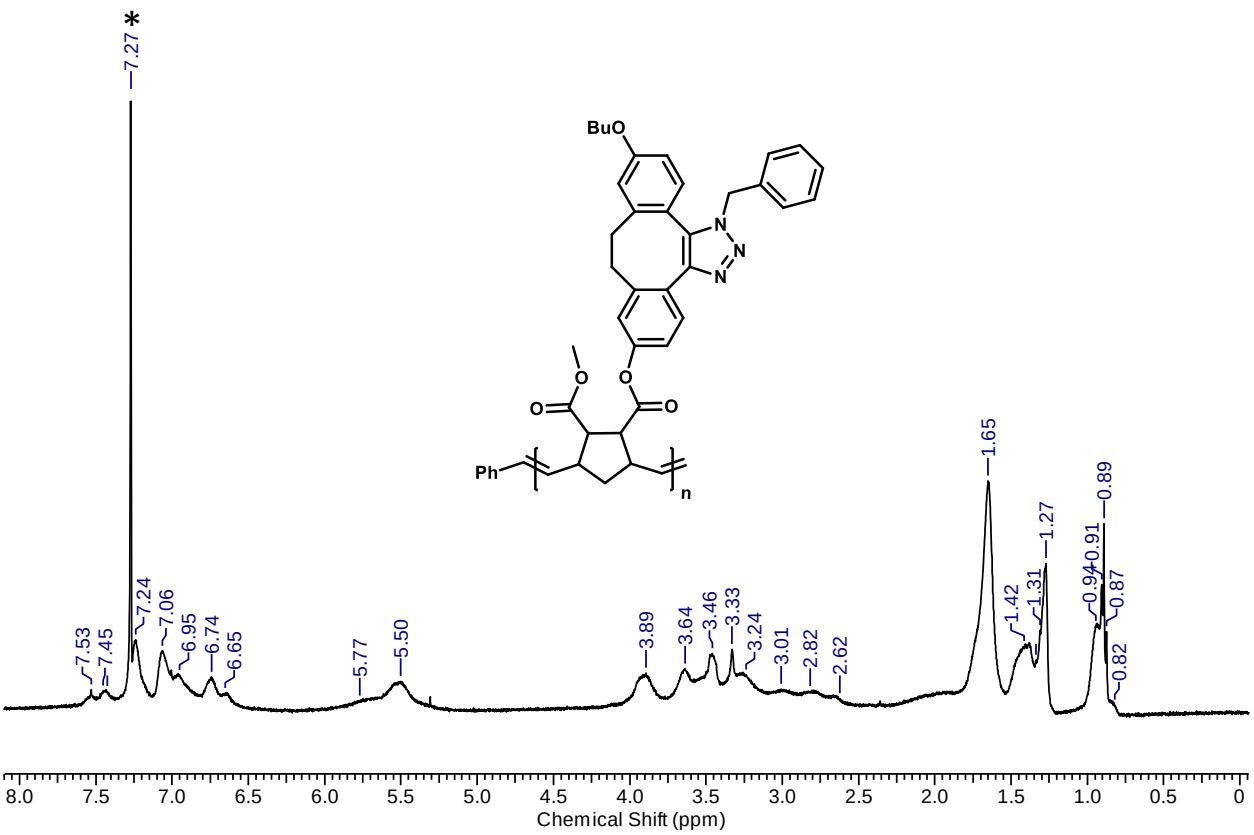


Fig. S23 ^{1}H NMR spectrum of benzyl-functionalized polymer **4a** in $CDCl_3$. Asterisks denote residual solvent signals. Because of the broadness of the spectrum, it was characterized by direct comparison of the chemical shifts and rough integration to the spectrum of the corresponding monomer **M4a**.

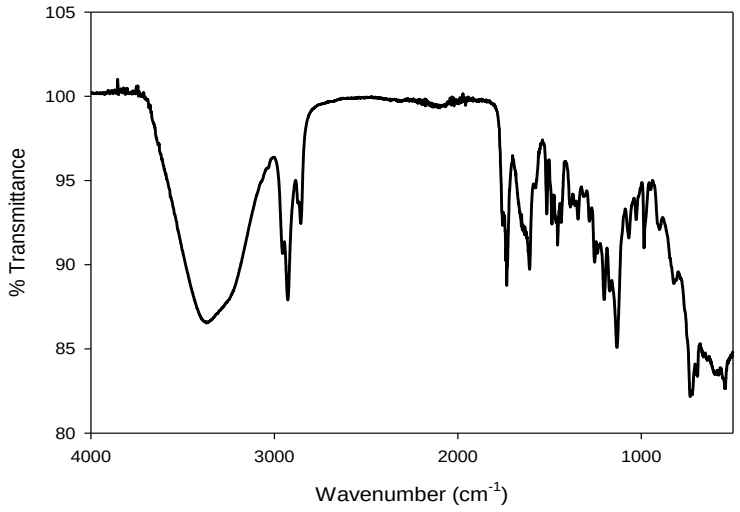


Fig. S24 FT-IR spectrum of benzyl-functionalized polymer **4a**.

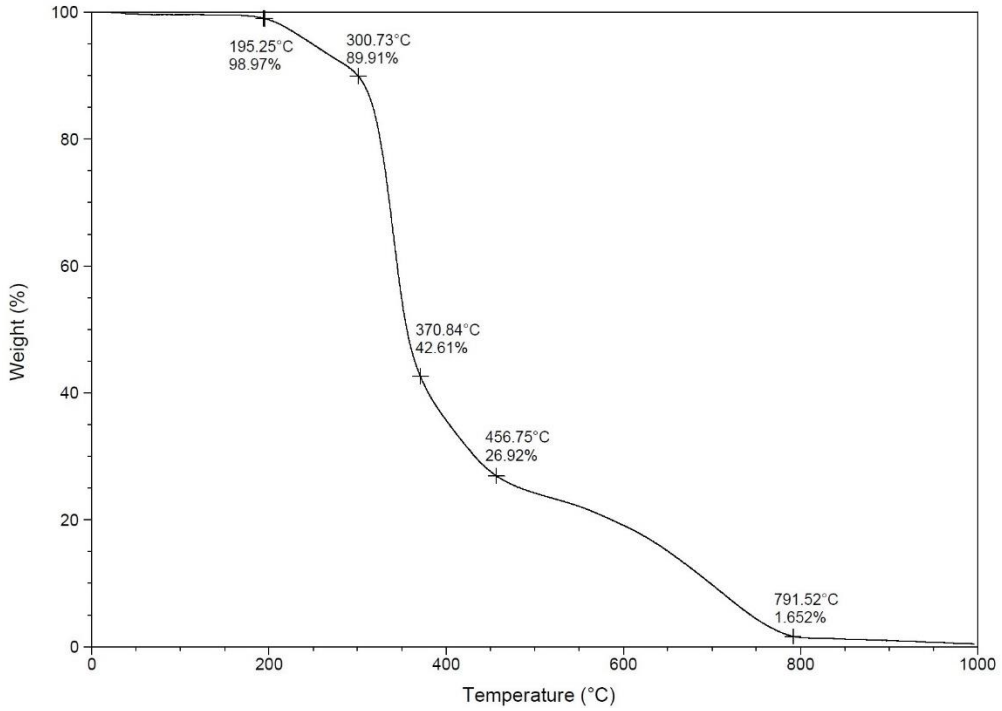


Fig. S25 TGA analysis of benzyl-functionalized polymer **4a**.

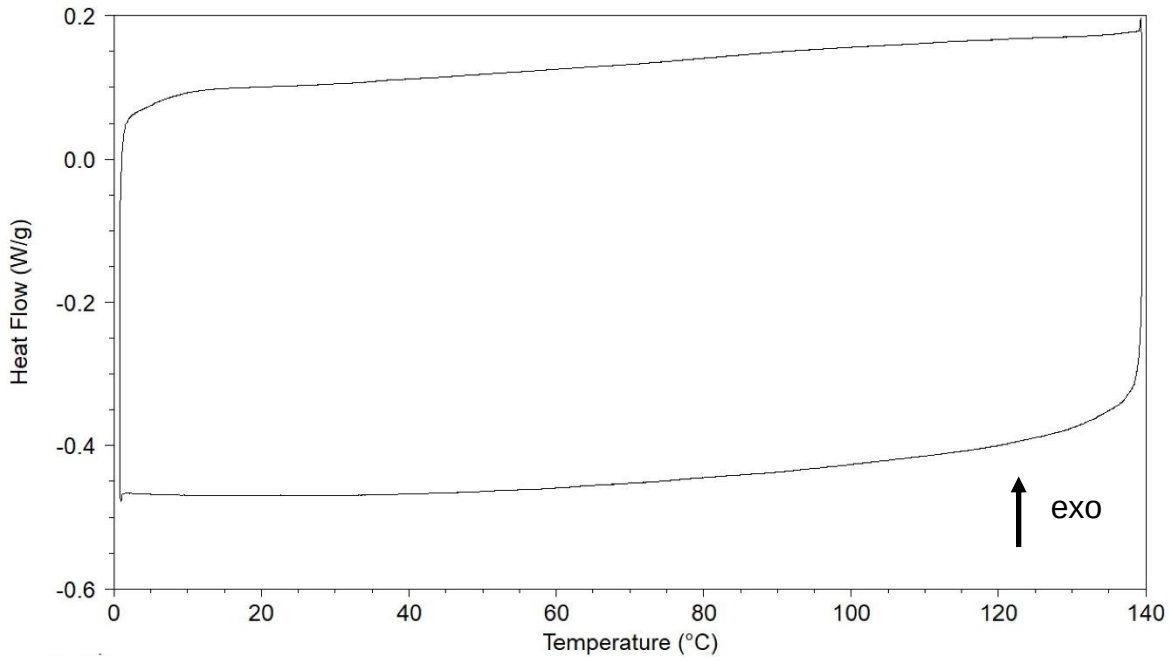


Fig. S26 DSC analysis of benzyl-functionalized polymer **4a**.

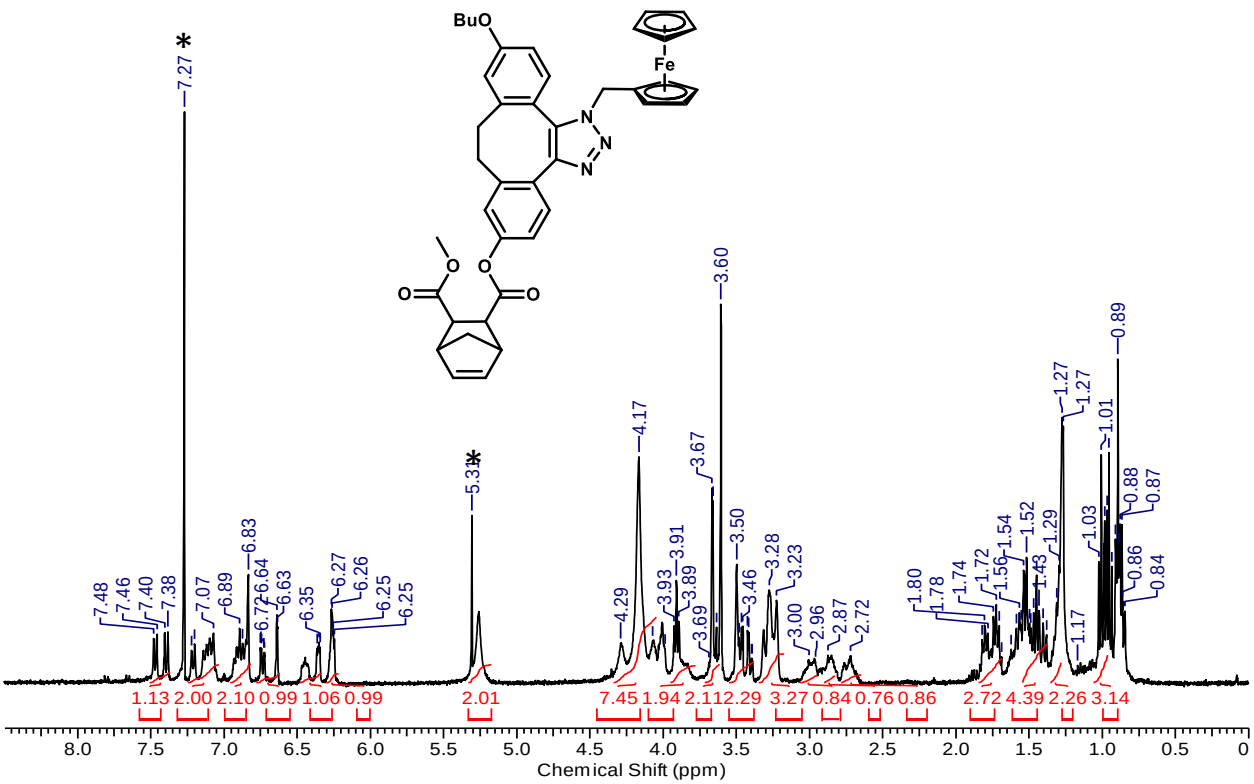


Fig. S27 ^{1}H NMR spectrum of ferrocene-functionalized monomer **M4b** in $CDCl_3$. Asterisks denote residual solvent signals.

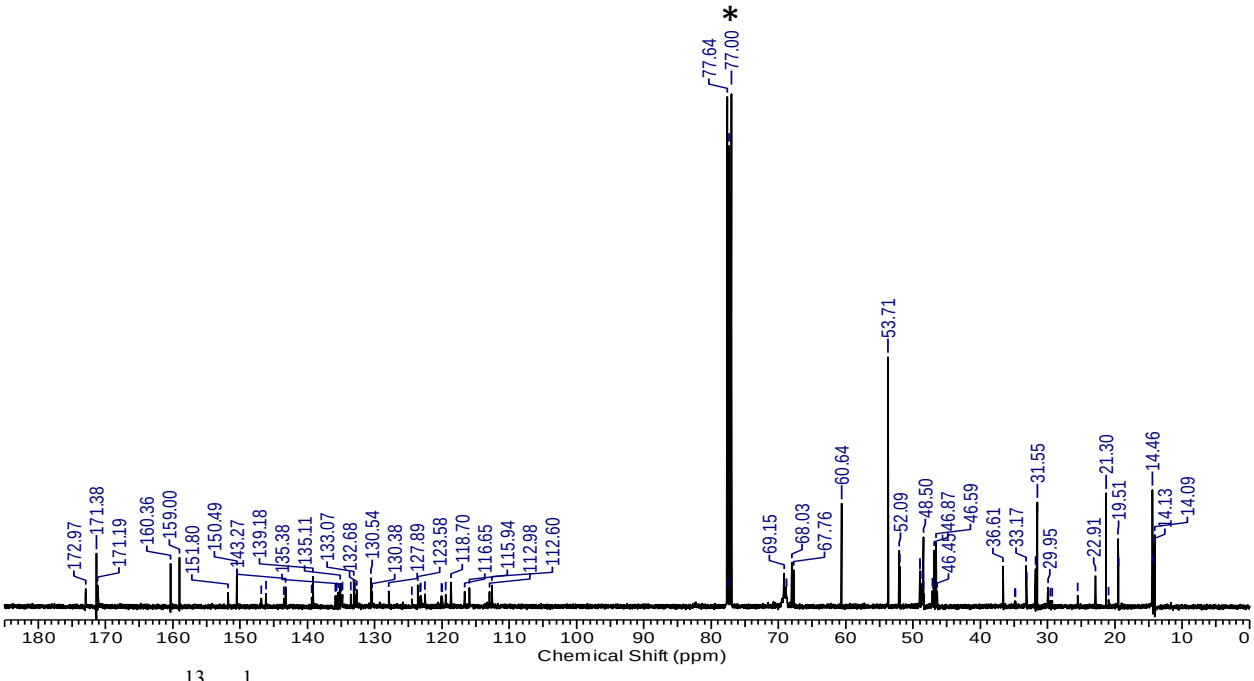


Fig. S28 $^{13}C\{^{1}H\}$ NMR spectrum of ferrocene-functionalized monomer **M4b**. Asterisk denotes residual solvent signal.

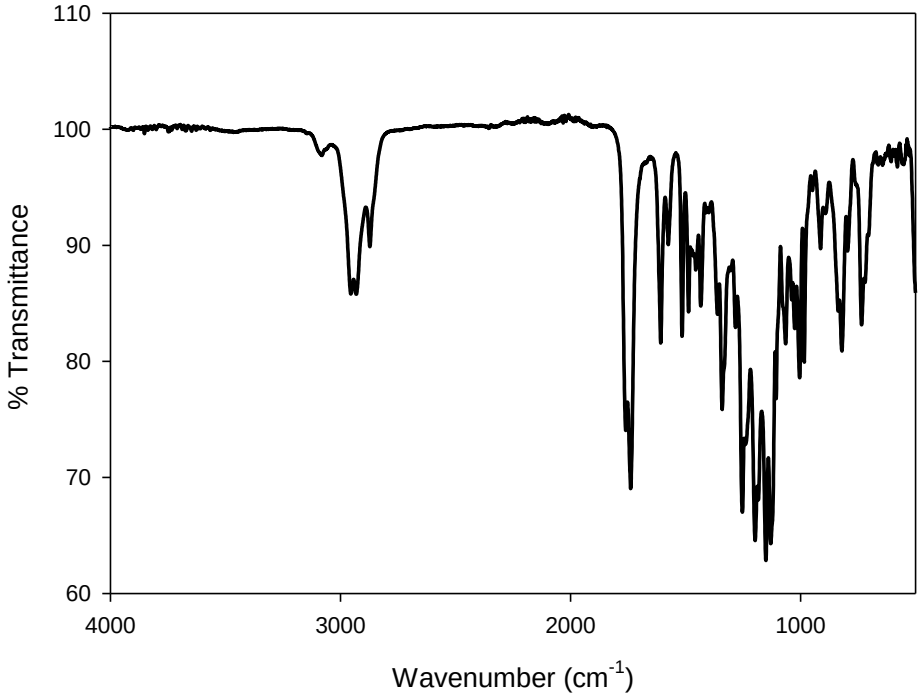


Fig. S29 FT-IR spectrum of ferrocene-functionalized monomer **M4b**.

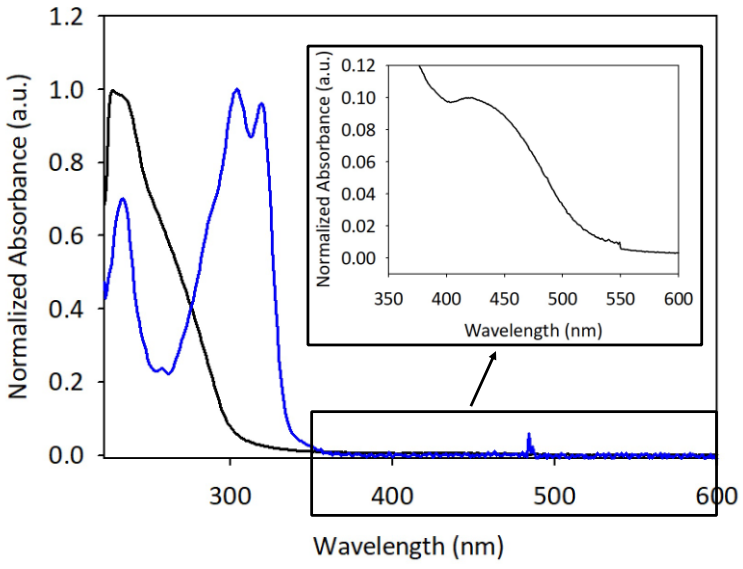


Fig. S30 UV-Vis absorption spectrum of strained alkyne monomer **M3** (blue) and ferrocene-functionalized monomer **M4b** (black) in CH_2Cl_2 with expansion showing the long wavelength absorption of the ferrocene moiety.

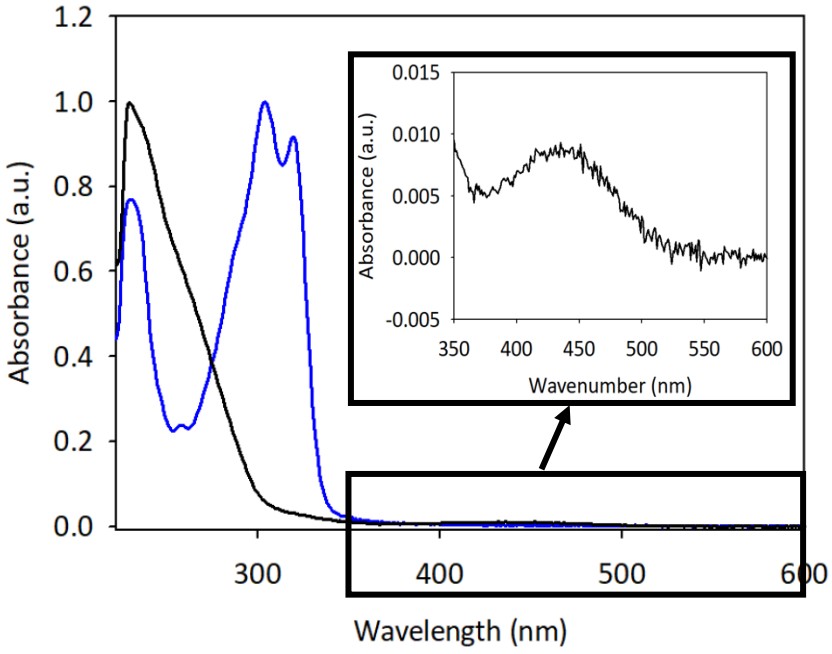


Fig. S31 UV-Vis absorption spectrum of strained alkyne polymer **3** (blue) and ferrocene-functionalized polymer **4b** (black) in CH_2Cl_2 with expansion showing the long wavelength absorption of the ferrocene moiety.

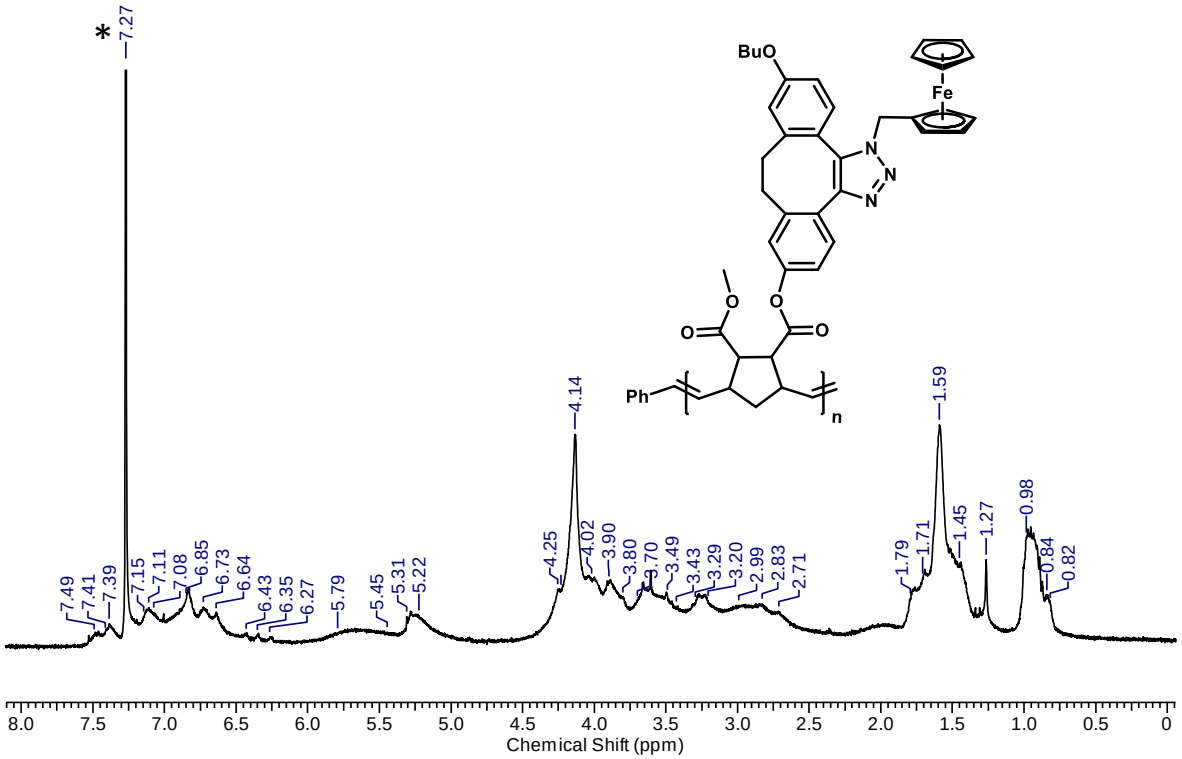


Fig. S32 ^{1}H NMR spectrum of ferrocene-functionalized polymer **4b** in $CDCl_3$. Asterisks denote residual solvent signals. Because of the broadness of the spectrum, it was characterized by direct comparison of the chemical shifts and rough integration to the spectrum of the corresponding monomer **M4b**.

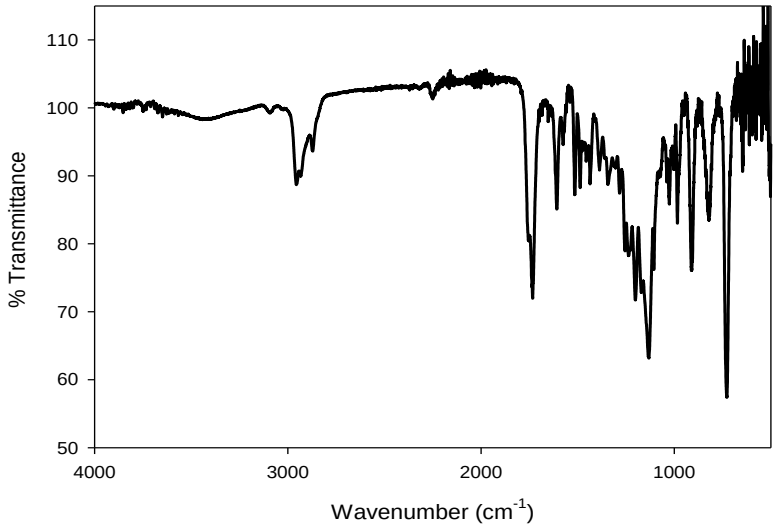


Fig. S33 FT-IR spectrum of ferrocene-functionalized polymer **4b**.

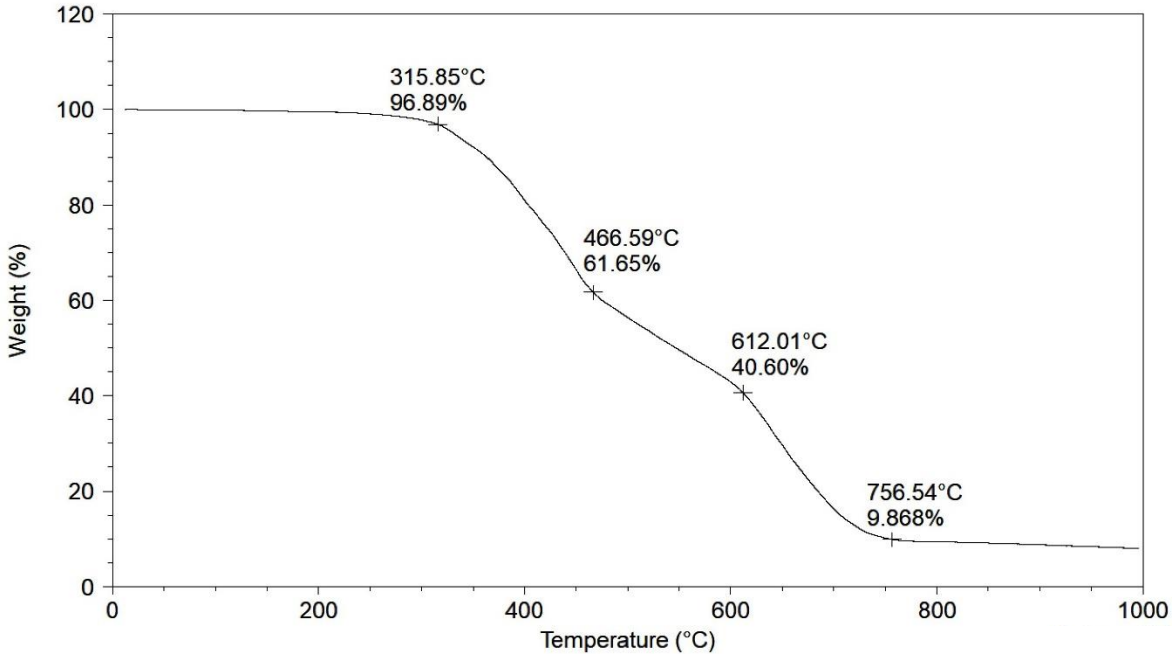


Fig. S34 TGA analysis of ferrocene-functionalized polymer **4b**.

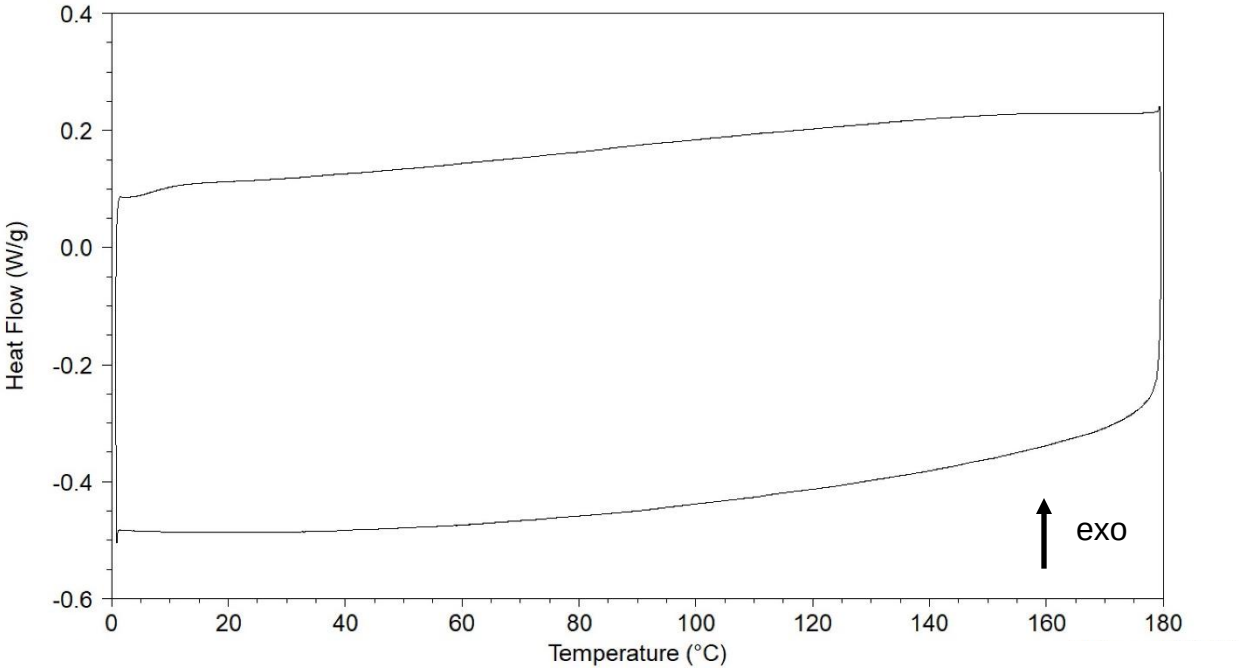


Fig. S35 DSC analysis of ferrocene-functionalized polymer **4b**.

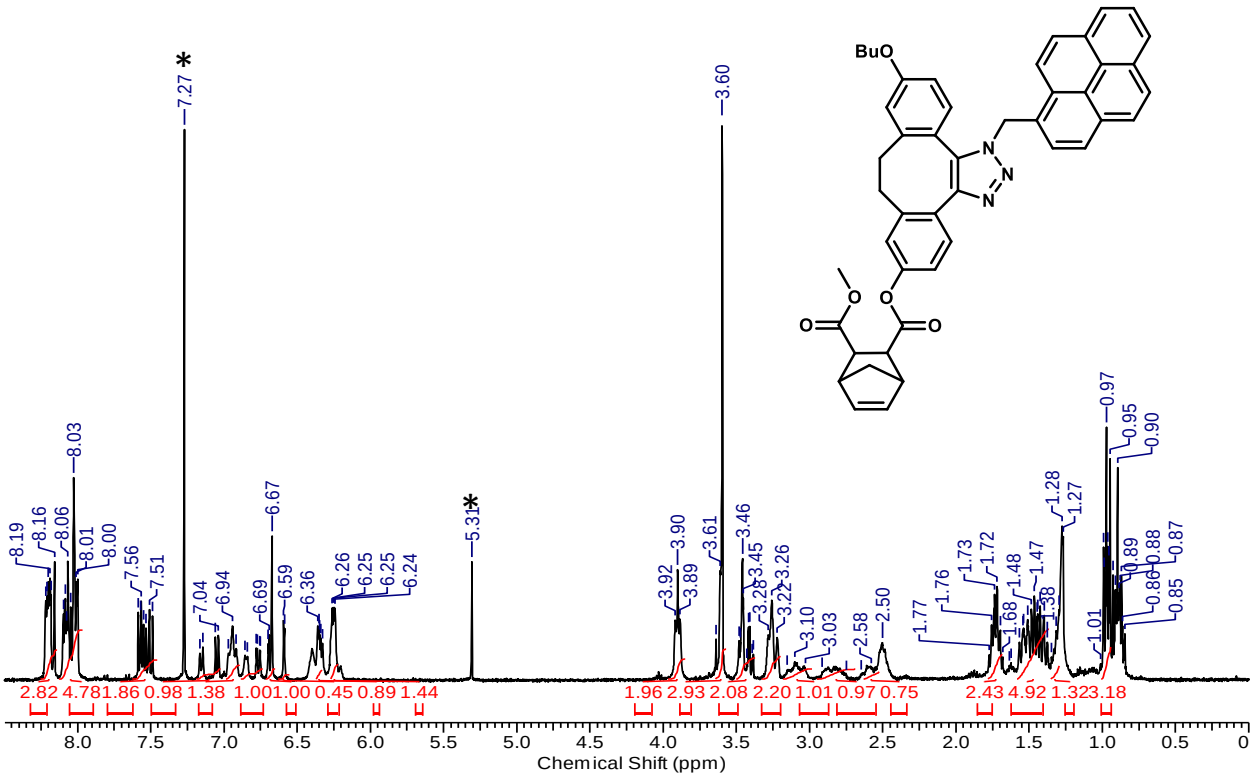


Fig. S36 ^{1}H NMR spectrum of pyrene-functionalized monomer **M4c** in $CDCl_3$. Asterisks denote residual solvent signals.

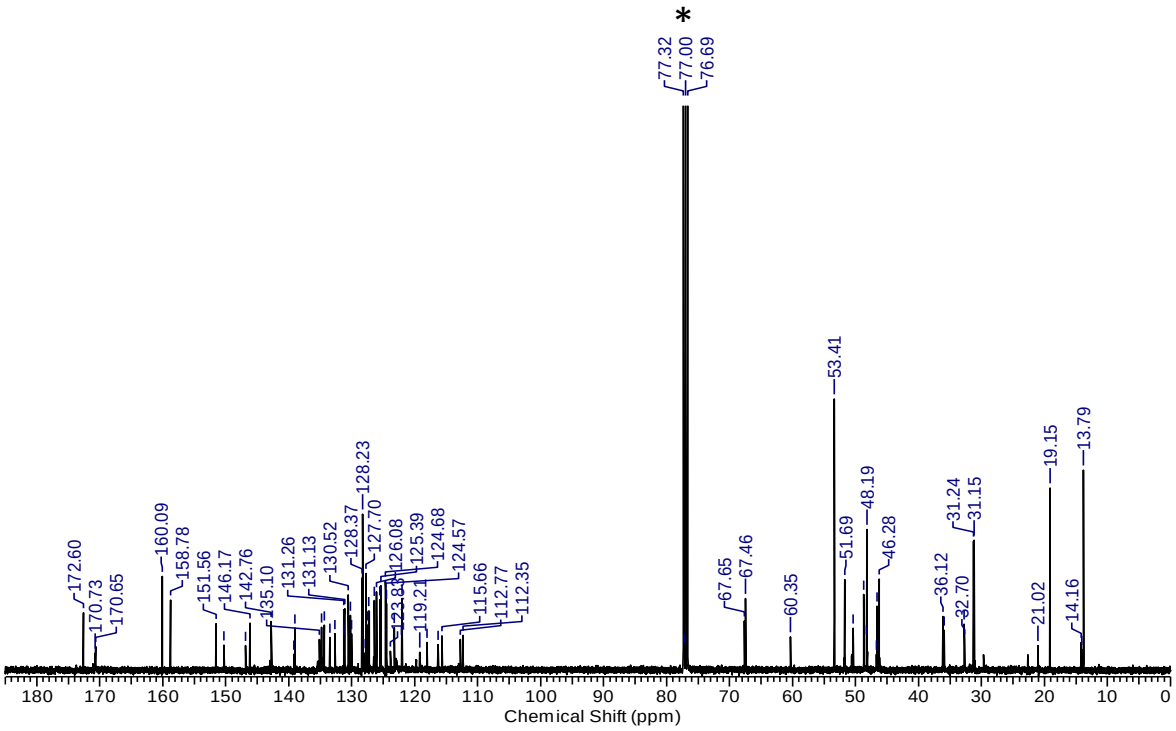


Fig. S37 $^{13}C\{^{1}H\}$ NMR spectrum of pyrene-functionalized monomer **M4c**. Asterisk denotes solvent signal.

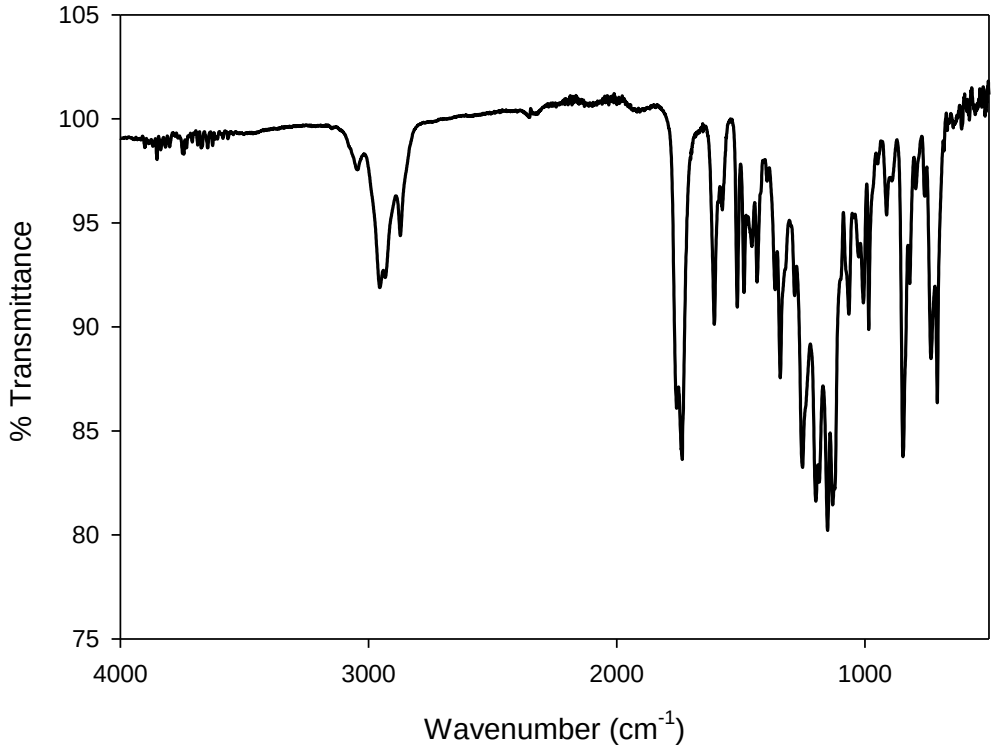


Fig. S38 FT-IR spectrum of pyrene-functionalized monomer **M4c**.

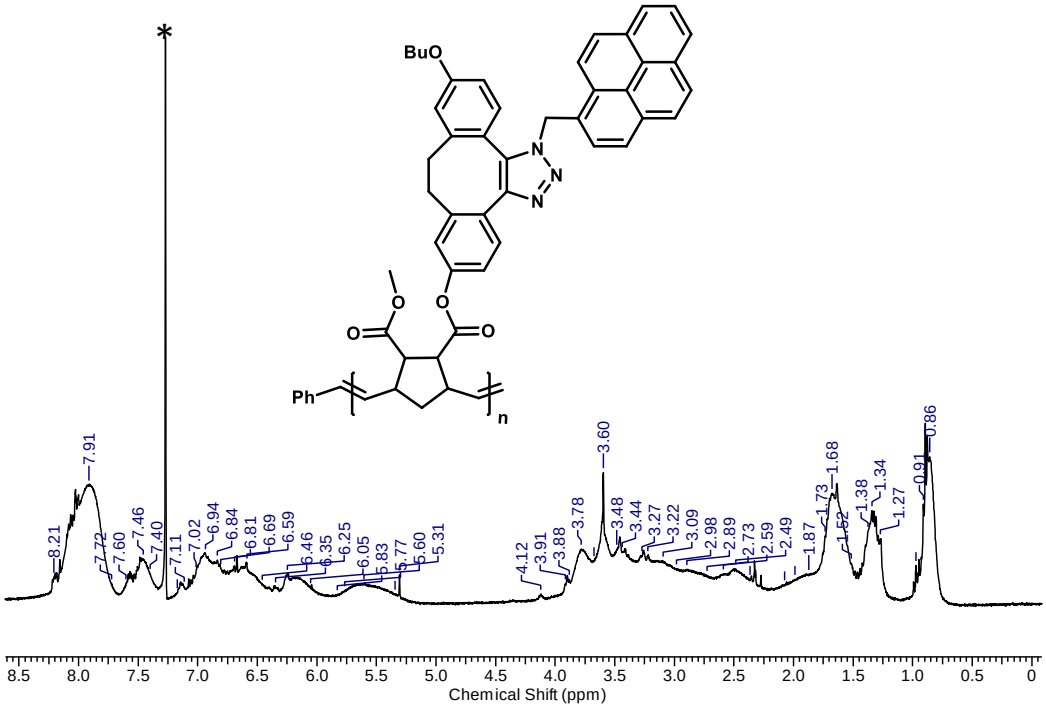


Fig. S39 ^{1}H NMR spectrum of pyrene-functionalized polymer **4c** in $CDCl_3$. Asterisk denotes residual solvent signal. Because of the broadness of the spectrum, it was characterized by direct comparison of the chemical shifts and rough integration to the spectrum of the corresponding monomer **M4c**.

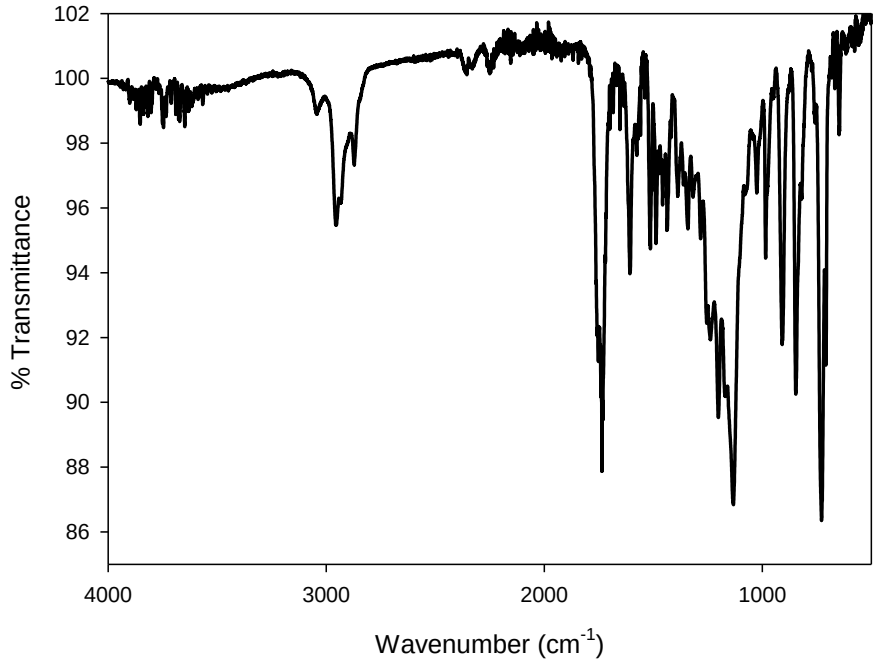


Fig. S40 FT-IR spectrum of pyrene-functionalized polymer **4c**.

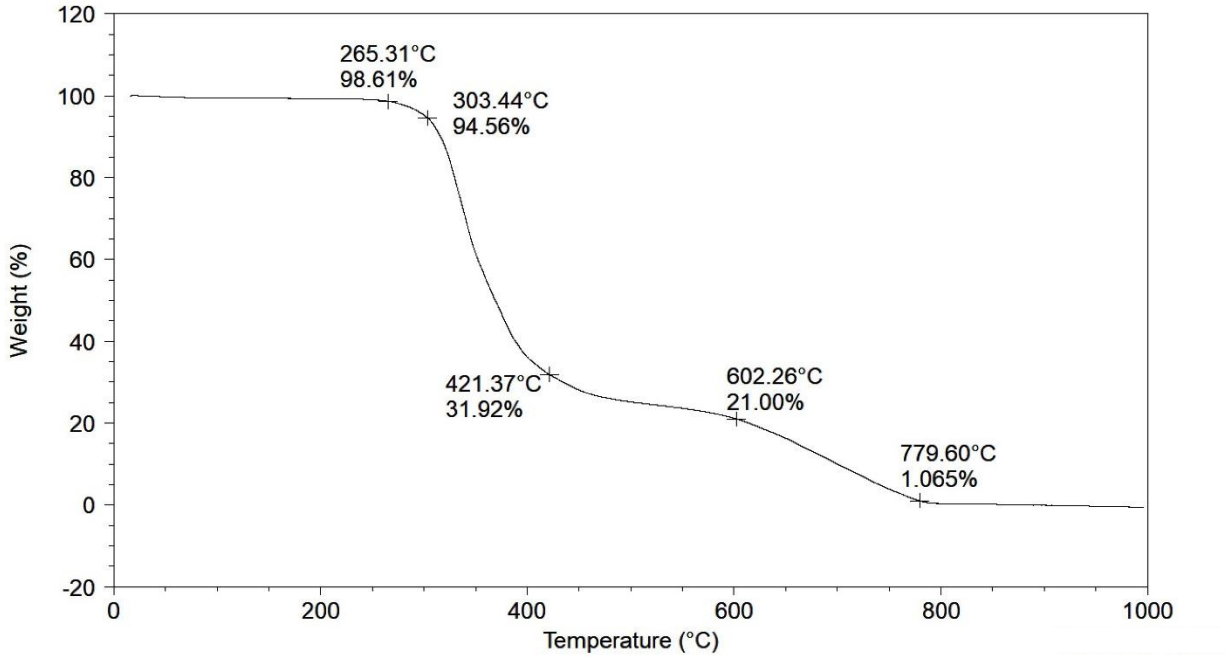


Fig. S41 TGA analysis of pyrene-functionalized polymer **4c**.

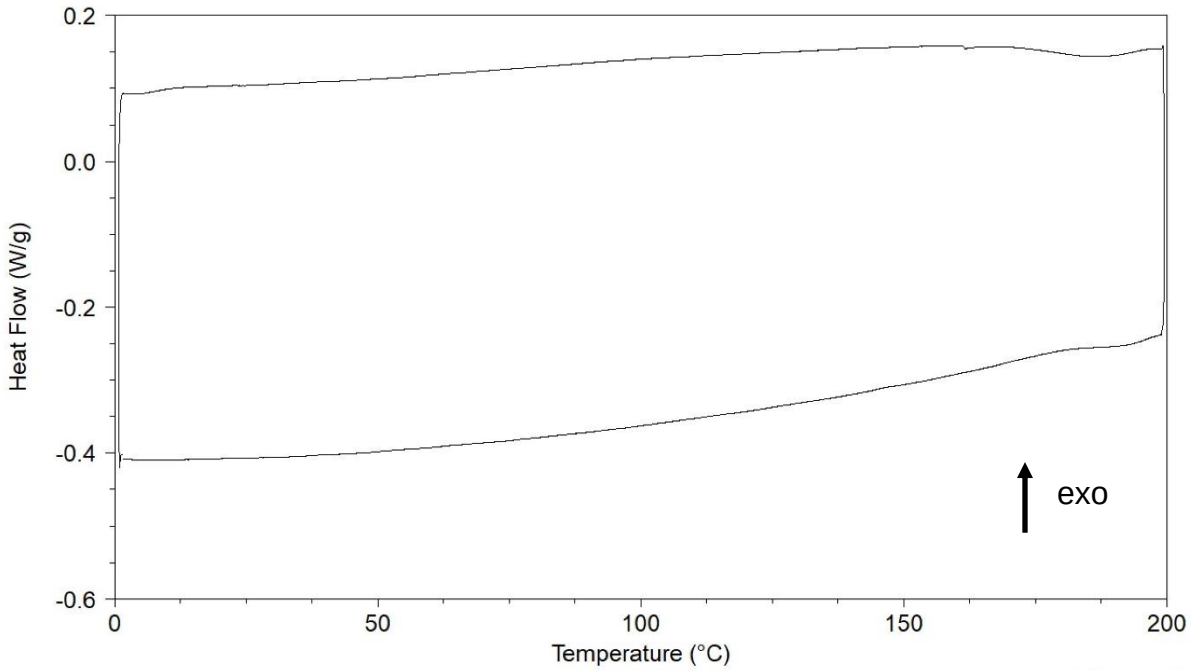


Fig. S42 DSC analysis of pyrene-functionalized polymer **4c**.

Reference

1 R. M. Arnold, C. D. McNitt, V. V. Popik and J. Locklin, *Chem. Commun.*, 2014, **50**, 5307–5309.