Electronic Supplementary Information (ESI) for:

Synthesis and Characterization of new Photoswitchable Azobenzene-containing poly(ε-caprolactones).

Appiah Clement[a], Marcel Jorewitz[b], Haitham Barqawi[a], Katrin R. Siefermann[b] and Wolfgang H. Binder *[a]

[a]Institute of Chemistry, Chair of Macromolecular Chemistry, Faculty of Natural Science II (Chemistry, Physics and Mathematics), Martin-Luther University Halle-Wittenberg, Halle (Saale) D-06120, Germany.

[b]Leibniz-Institute of Surface Modification, Permoserstrasse 15, Leipzig, Germany

Corresponding to W. H. Binder (wolfgang.binder@chemie.uni-halle.de).

Synthesis of 4-azidobenzoic acid

The synthesis of 4-azidobenzoic acid was followed as described in the literature[19]. To a suspension of 4-aminobenzoic acid (4.5 g, 33 mmol) in water (25 mL) in a 2 L-round bottom flask was added concentrated HCl (5.6 mL) drop wise while the mixture was vigorously stirred. After the addition has been finished the reaction mixture was cooled down to 0 °C with an ice-salt-mixture. A solution of $NaNO_2$ (2.3 g, 33 mmol) in water (10 mL) was added slowly (about 30 min) via dropping funnel. The colour of the mixture changes to yellow-orange during the addition. Subsequently, a solution of NaN_3 (2.14 g, 33 mmol) in water (25 mL) was added slowly whilst the mixture was vigorously stirred, whereby an enormous foam formation could be observed. The cooling bath was removed and stirring was continued for 90 min and afterwards a 100 mL water and 125 mL ethylacetate were added. The phases were separated via a separating funnel and the water phase was extracted two times with 50 mL ethylacetate. The organic phase was washed with 1 N NaOH (40 mL). The water phase was acidified with 1 N HCl (80 mL), whereby a yellow solid precipitates. During the acidification ethylacetate (150 mL) was added in portions, which solves the yellow solid. The organic phase was separated and the unified organic phases were then dried over Na_2SO_4, filtered and concentrated via vacuum distillation at room temperature to furnish a yellow solid. Yield: 4.98 g (92 %).

^{1}H-NMR (400 MHz, DMSO, δ, ppm): 12.89, (s, 1H), 7.94 (d, 2H, J = 8.63 Hz), 7.19 (d, 2H, J = 8.63 Hz). ^{13}C-NMR (100 MHz, DMSO, δ, ppm): 166.9, 144.4, 131.6, 127.7, 119.6.

IR: 2813, 2541, 2101, 1672, 1600, 1577, 1507, 1424, 1316, 1282, 1177, 1138, 1122, 934, 856, 765

Synthesis of 4-azidobenzoylchloride

4-Azidobenzoic acid (1 g, 6.13 mmol) was added to freshly distilled thionylchloride (22.2 mL, 306 mmol) and refluxed for 4 h at 75 °C. When the reaction has finished the excess thionylchloride was removed under vacuum. The achieved brown solid was dried using high vacuum. Yield: 1.1 g (99 %).

^{1}H-NMR (400 MHz, DMSO, δ, ppm): 8.10 (d, 2H, J = 8.63 Hz), 7.12 (d, 2H, J = 8.63 Hz). ^{13}C-NMR (100 MHz, DMSO, δ, ppm): 167.8, 144.4, 131.6, 127.7, 119.6.

IR: 3098, 2401, 2252, 2119, 1737, 1594, 1498, 1417, 1306, 1282, 1208, 1171, 1121, 876, 837, 815, 804, 726, 696, 642.

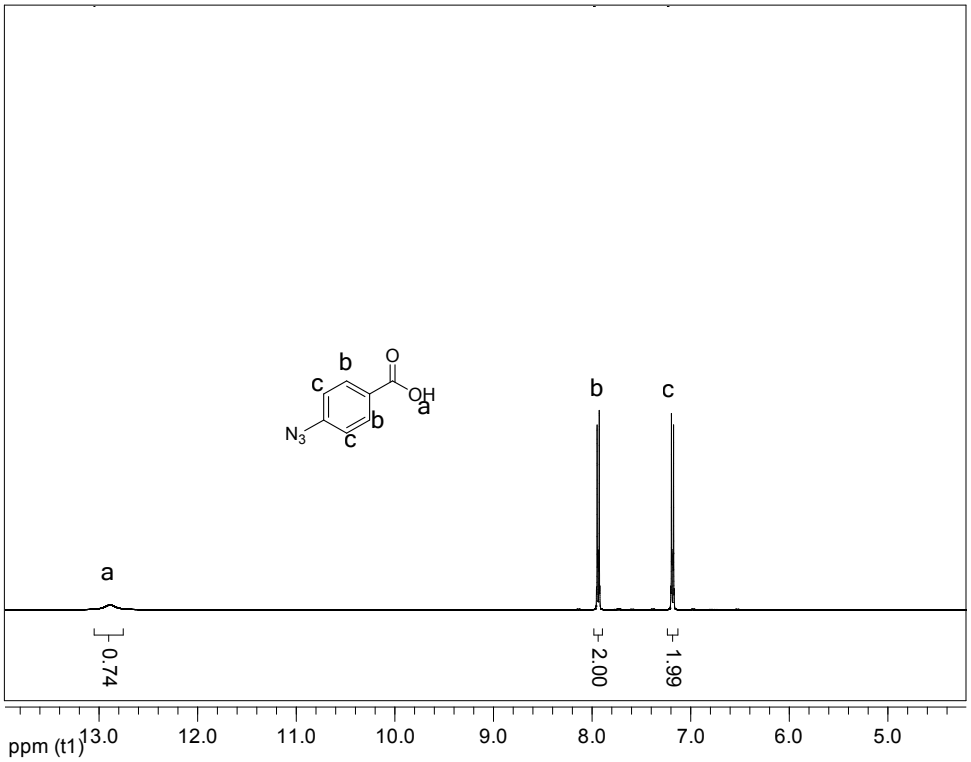

Figure S1: ^{1}H-NMR spectrum of compound 4-azidobenzoic acid

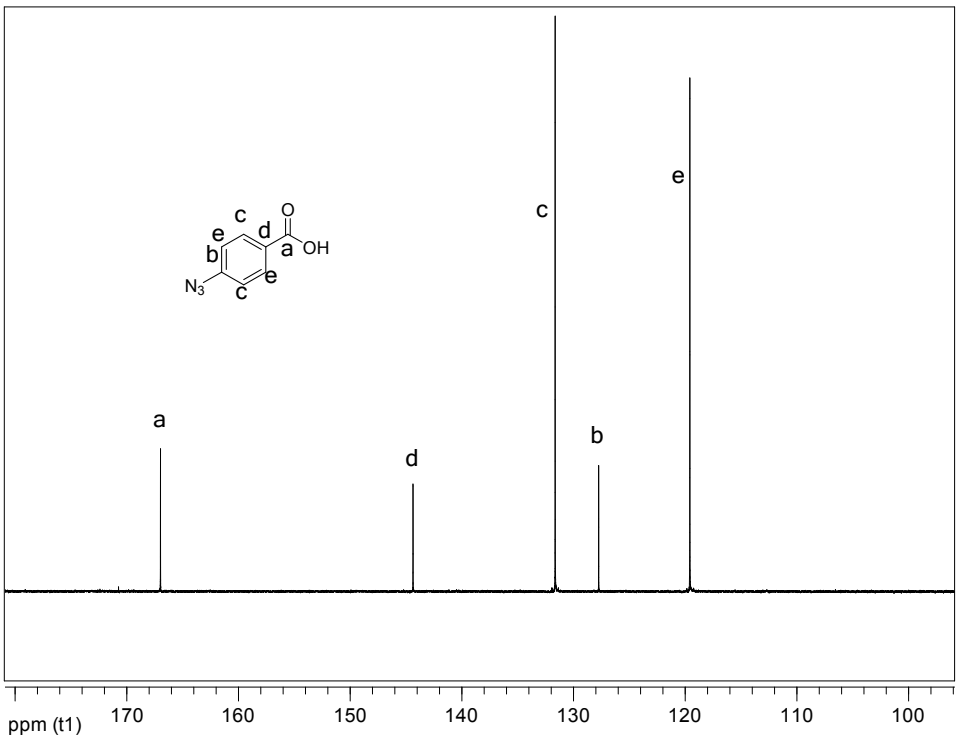

Figure S2: ^{13}C-NMR spectrum of compound 4-azidobenzoic acid

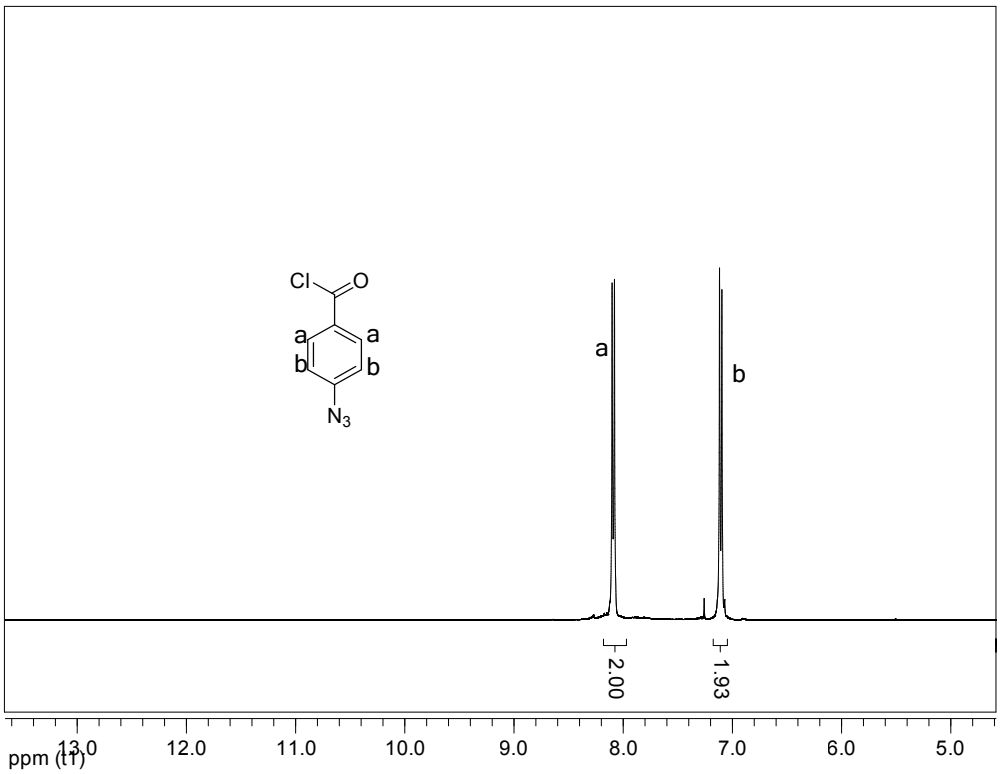

Figure S3: ^{1}H-NMR spectrum of compound 4-azidobezoylchloride

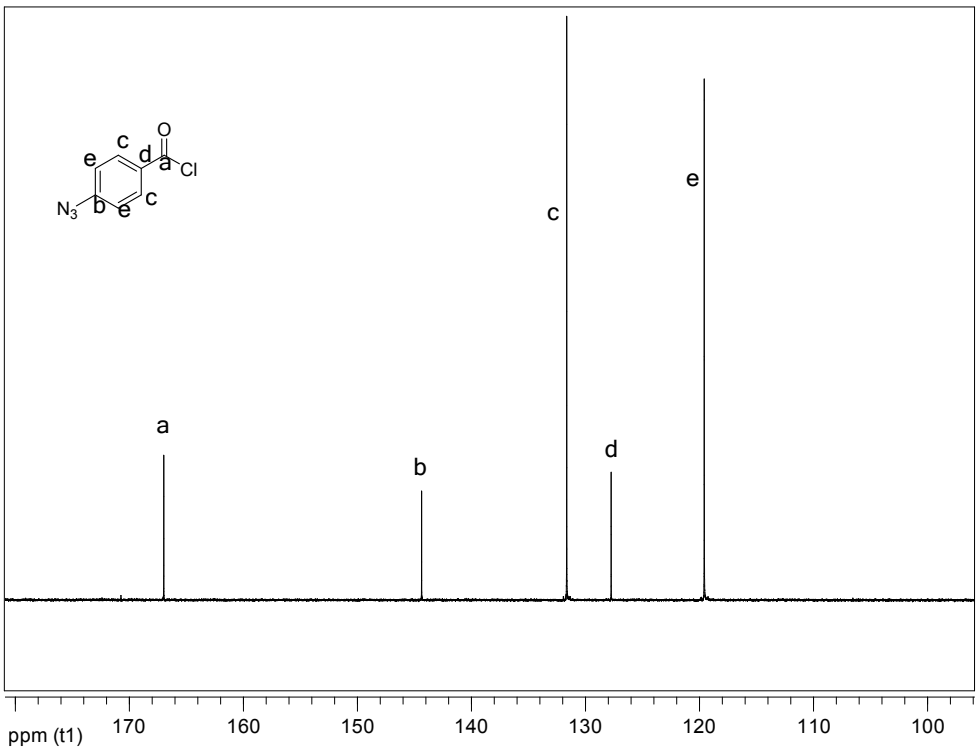

Figure S4: ^{13}C-NMR spectrum of compound 4-azidobezoylchloride

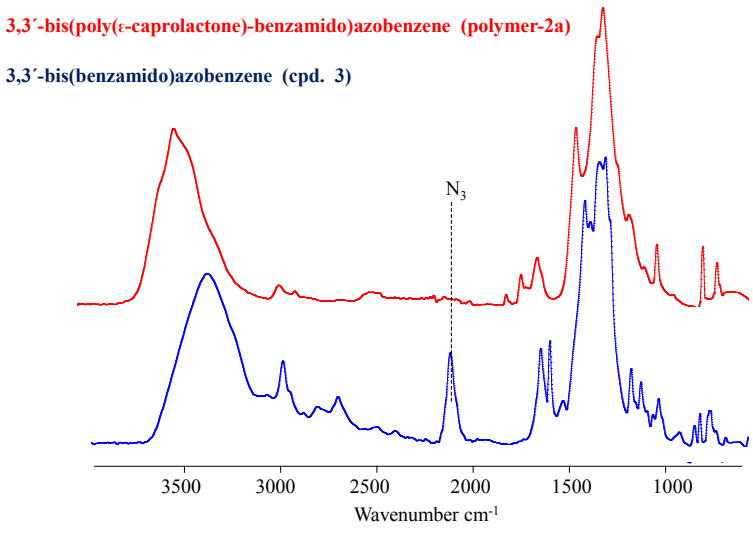

Figure S5a: FTIR spectra of compound **3** and **polymer-2b** showing the disappearance of the azide group after the click chemistry.

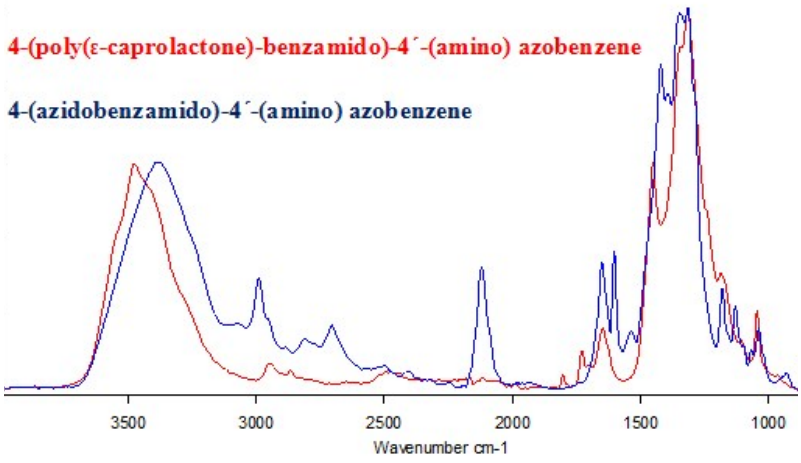

Figure S5b: FTIR spectra of compound **2** and **polymer-1b** showing the disappearance of the azide group after the click chemistry.

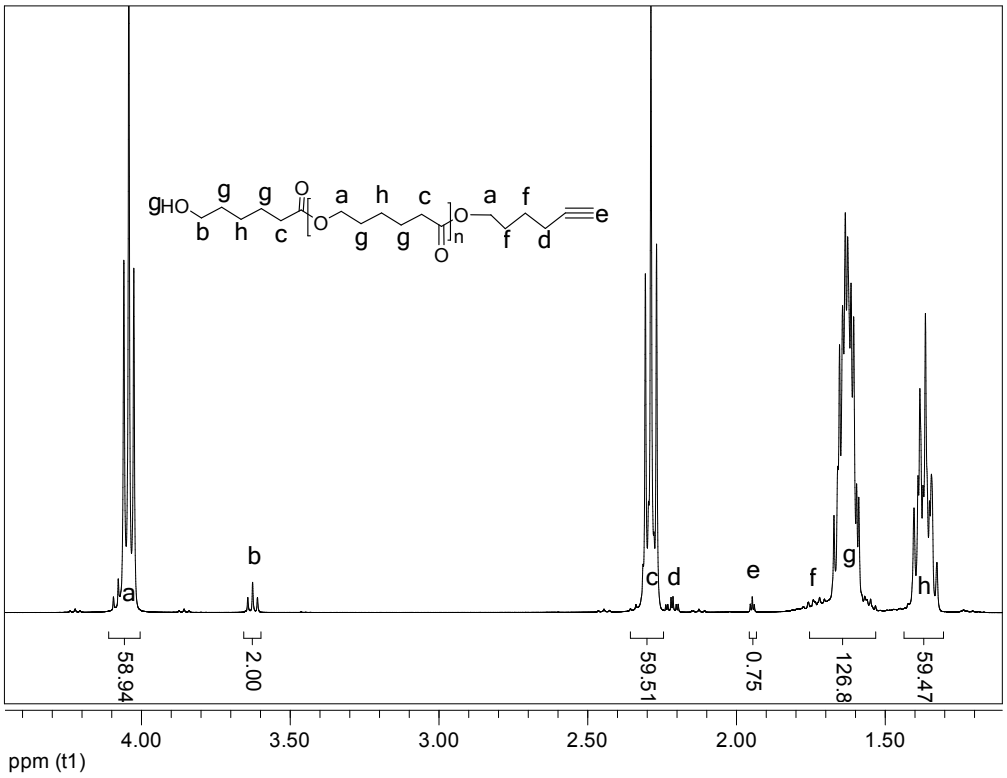

Figure S6: ^{1}H-NMR spectrum of **PCL-alkyne3**

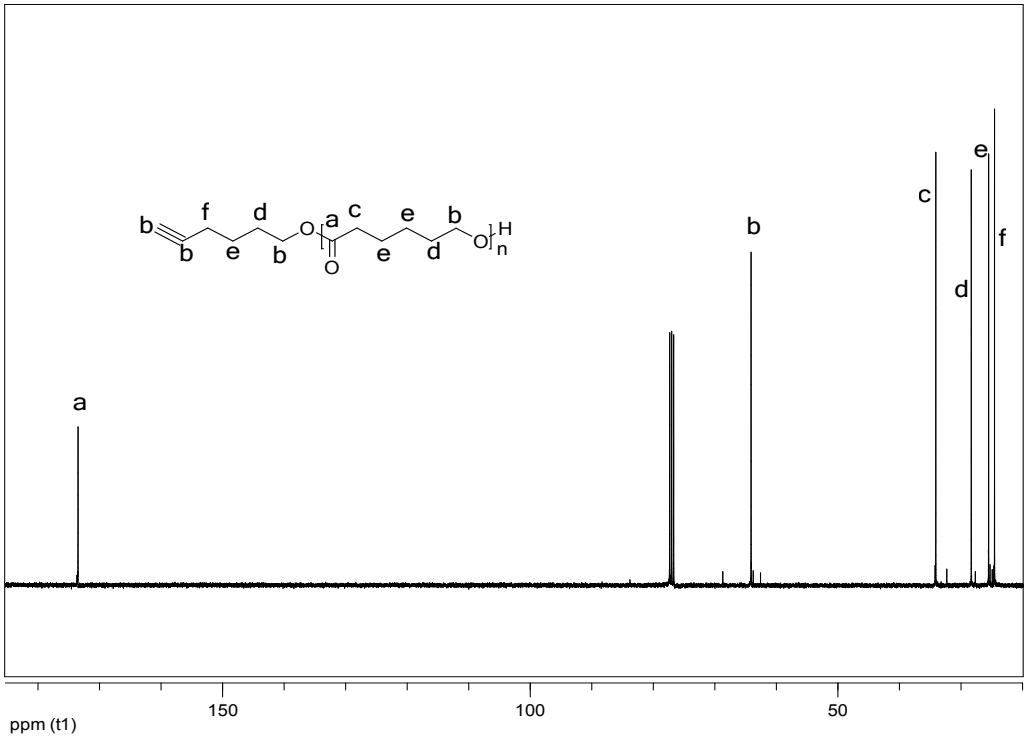

Figure S7: ^{13}C-NMR spectrum of **PCL-alkyne3**

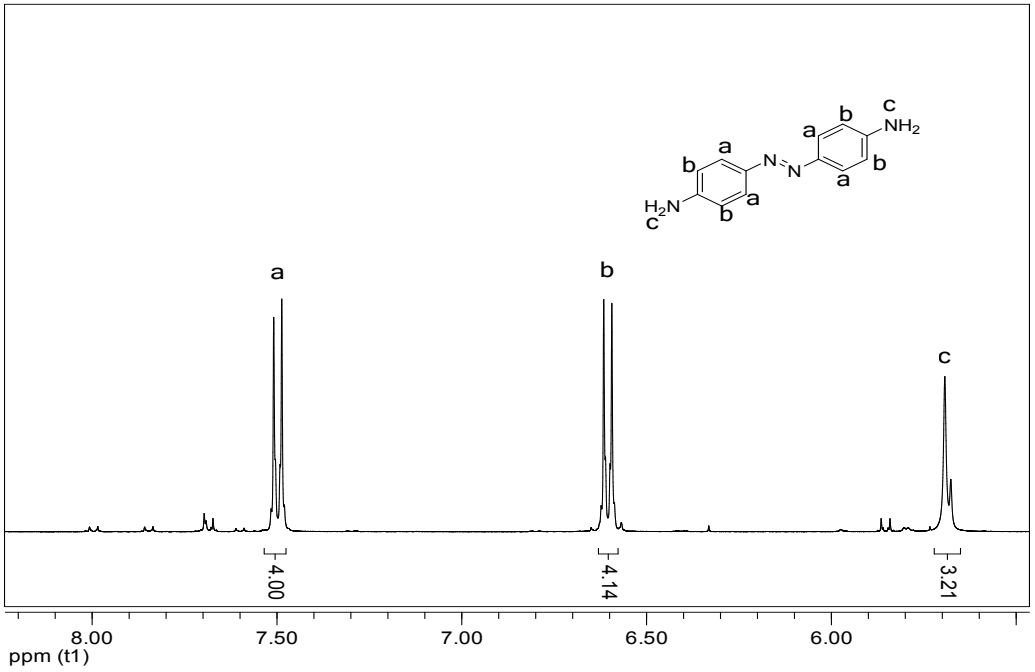

Figure S8: ^{1}H-NMR spectrum of compound **1**

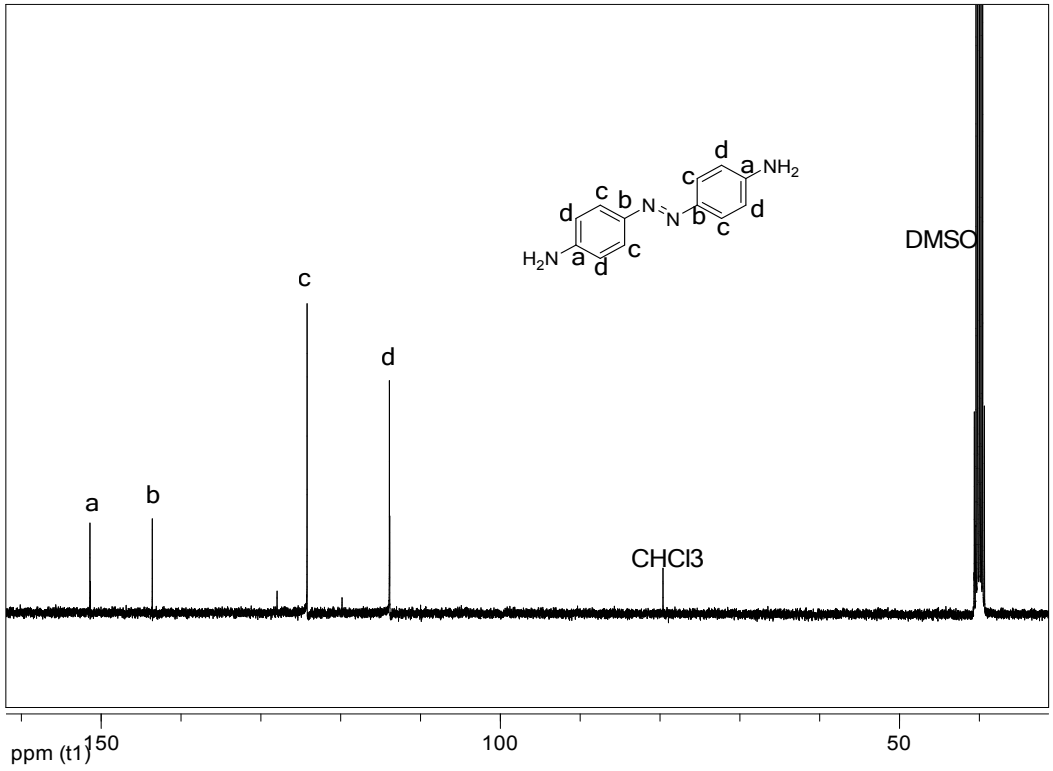

Figure S9: ^{13}C-NMR spectrum of compound **1**

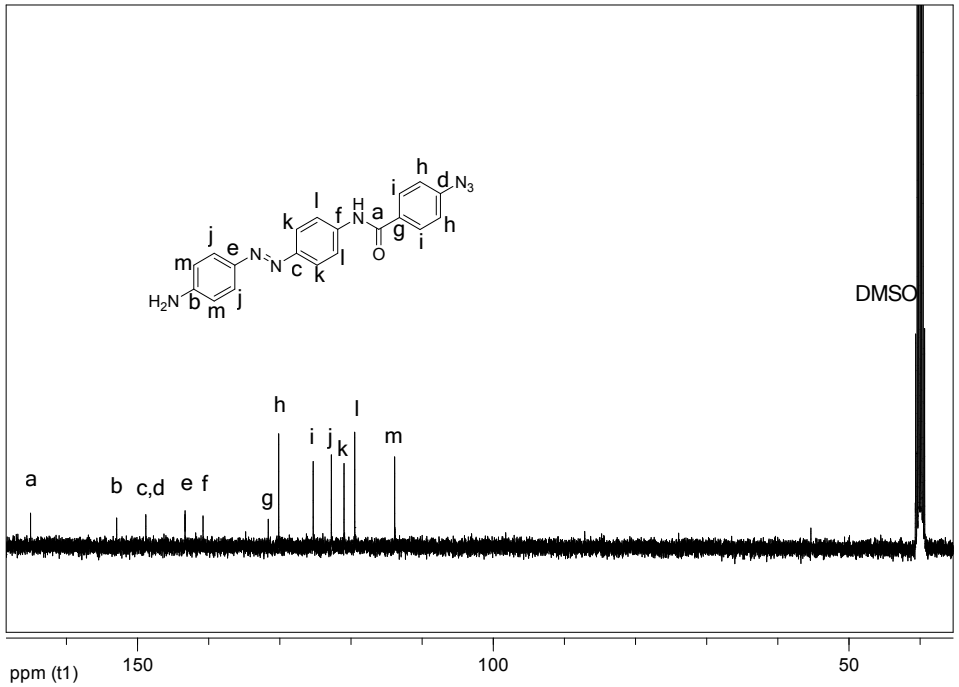

Figure S10: ^{13}C-NMR spectrum of compound **2**

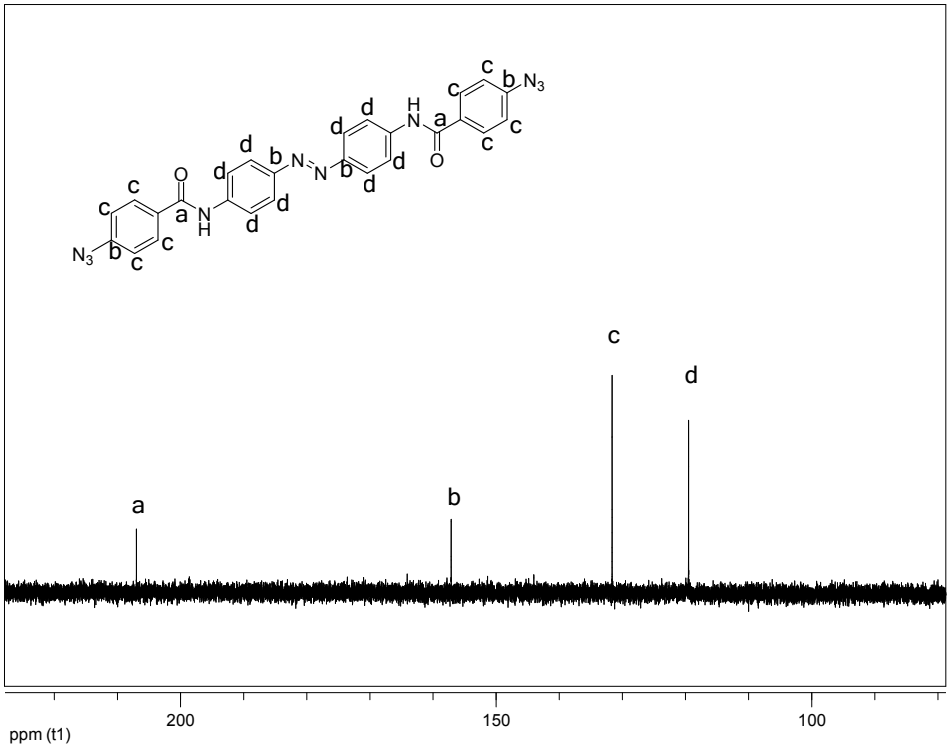

Figure S11: ^{13}C-NMR spectrum of compound **3**

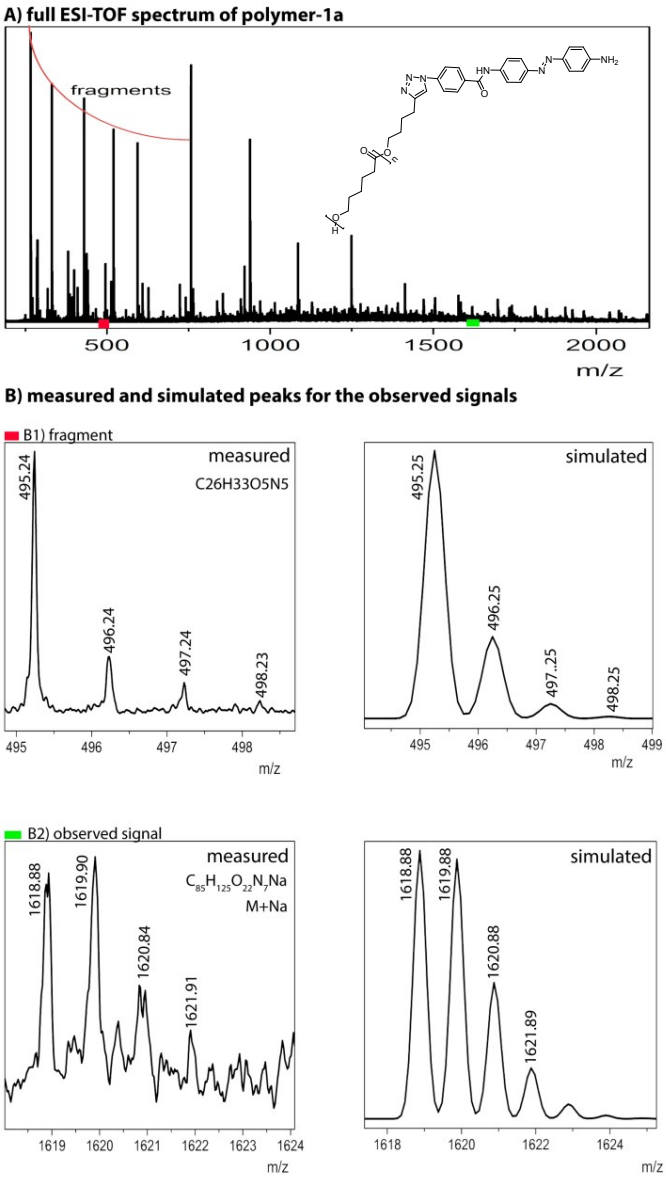

Figure S12. ESI-TOF spectra of the photoswitchable **polymer-1**, showing the observed and simulated signals.

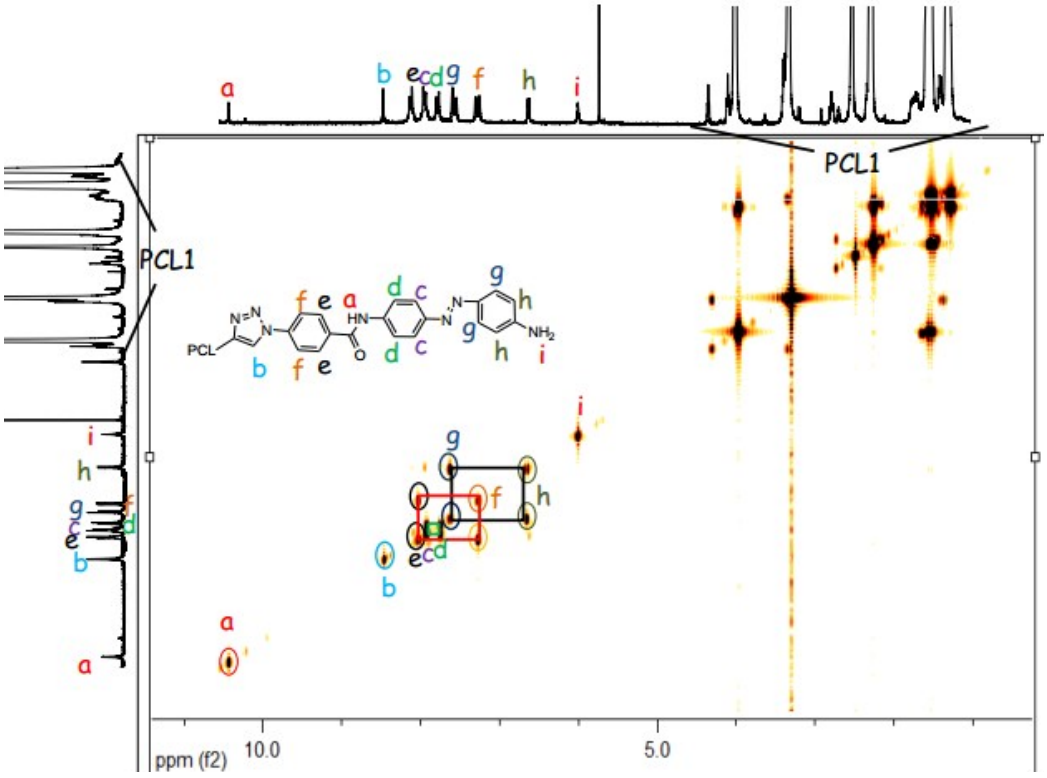

Figure S13. Proton homonuclear correlated 2-dimensional ^{1}H-^{1}H COSY NMR of **polymer-1b**.

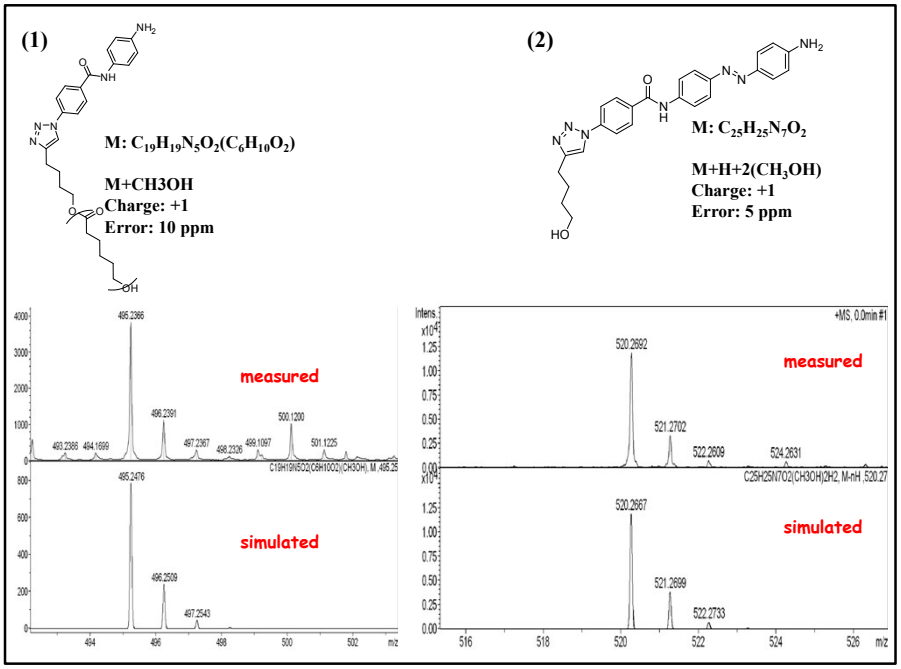

Figure S14: fragmented structures obtained from the ESI-TOF-MS analysis for **polymer-1a**

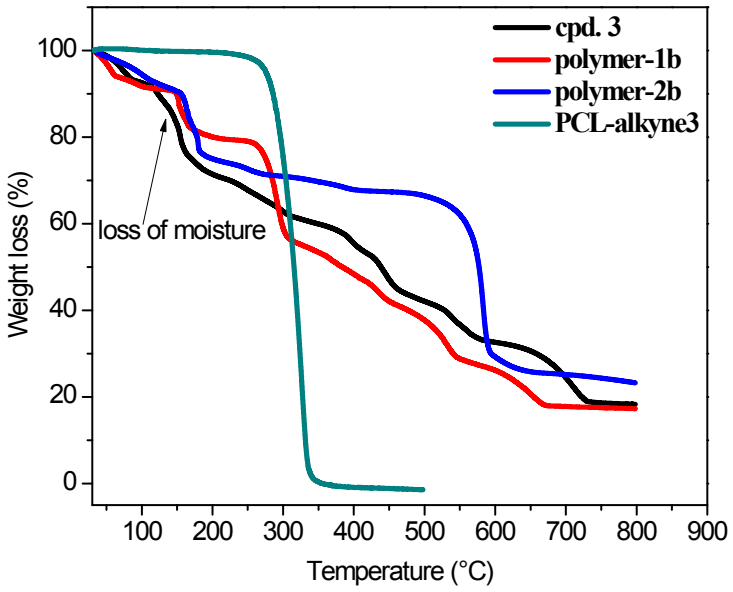

Figure S15: TGA curves of compound **3, polymer-1b**, **polymer-2b** and **PCL-alkyne3.**