Supporting Information

to

N,N'-Substituted Acryloamidines – Novel Comonomers for Melt-Processible Poly(acrylonitrile)-Based Carbon Fiber Precursors

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Table S1: Results for the copolymerization of AN with **1** in DMF at 60 °C using 1 mol-% of AIBN at different molar ratios.

1 [mmol]	AN [mmol]	**1**/AN (feed)	**1**/AN (copolymer)	Yield [%]
0.7	64.2	1/99	1/99	58
6.5	123.2	5/95	5/95	60
6.5	58.4	10/90	10/90	50
28.0	112.0	20/80	18/82	63
45.3	181.5	20/80	19/81	77
4.7	4.7	50/50	45/55	67

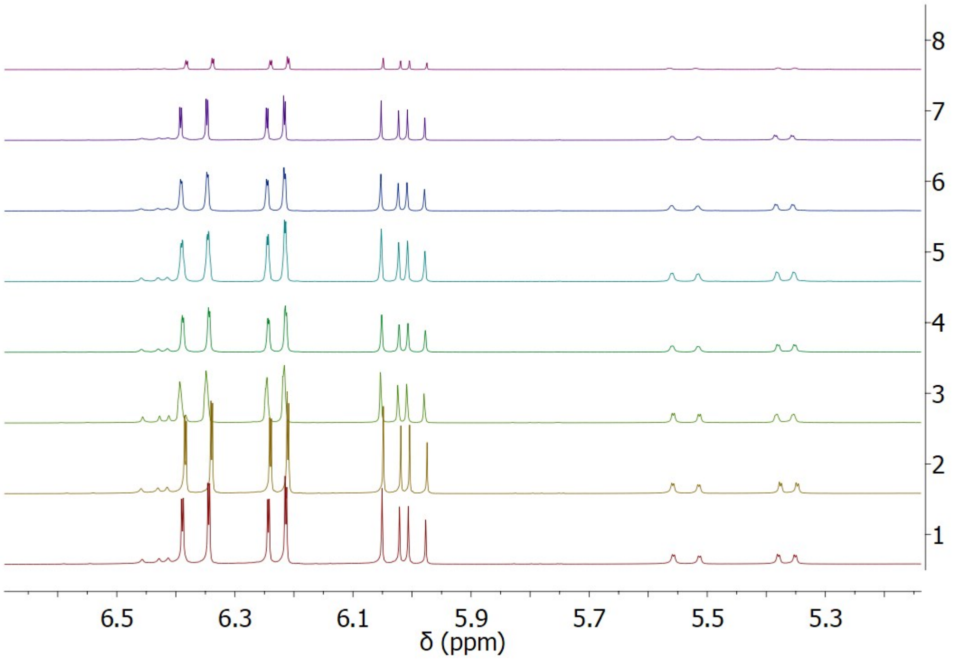

Figure S1: Vinyl region of all stacked ^{1}H NMR spectra (DMSO-d_6) of the copolymerization of **2** and AN. The bottom spectrum shows the starting mixture before copolymerization, the top spectrum was recorded after 24 h.

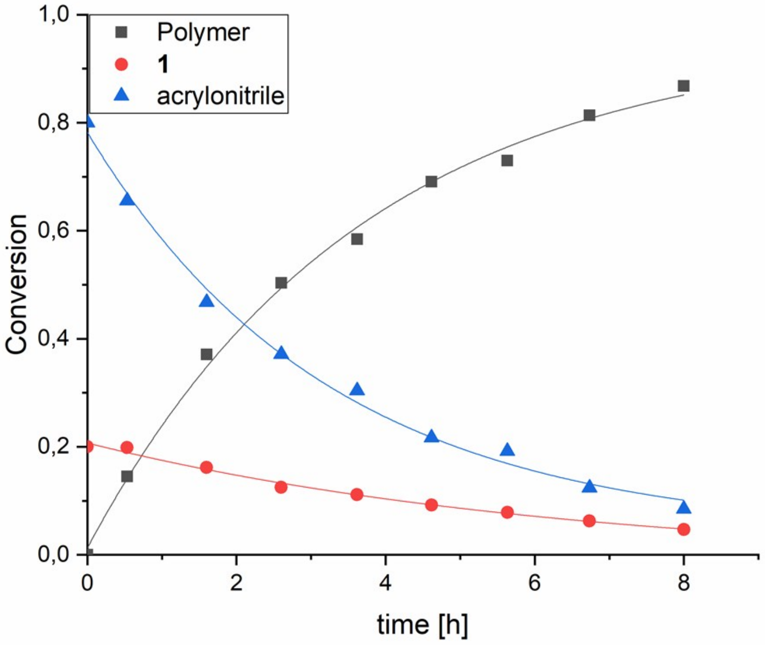

Figure S2: Time-conversion curves of AN with **1** (80 : 20 mol-%) in DMF at 60 °C using 1 mol-% AIBN as initiator.

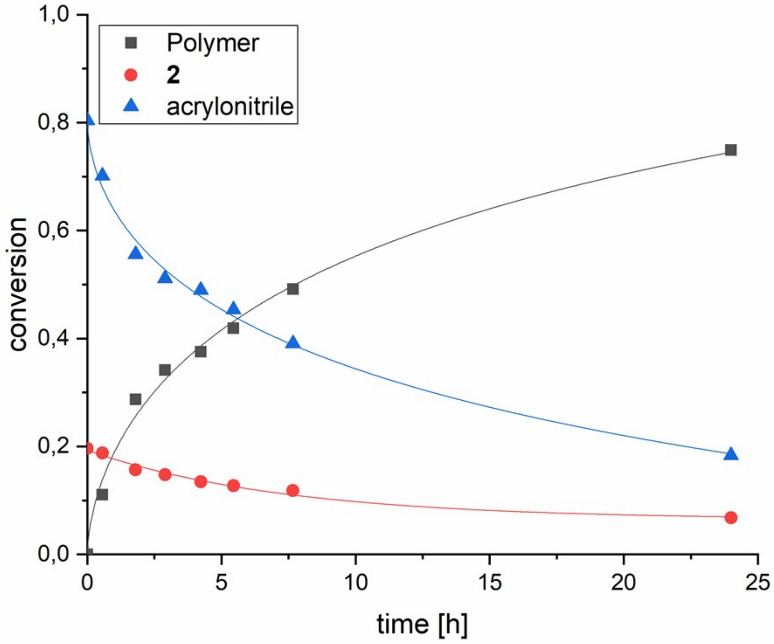

Figure S3: Time-conversion curves of AN with **2** (80 : 20 mol-%) in DMF at 60 °C using 1 mol-% AIBN as initiator.

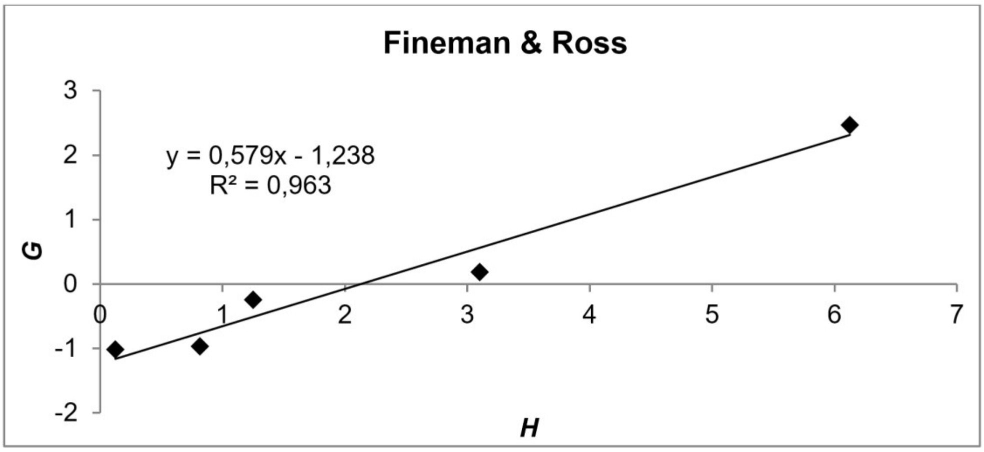

Figure S4: Fineman & Ross plot of the copolymerization system **1**/AN in DMF.

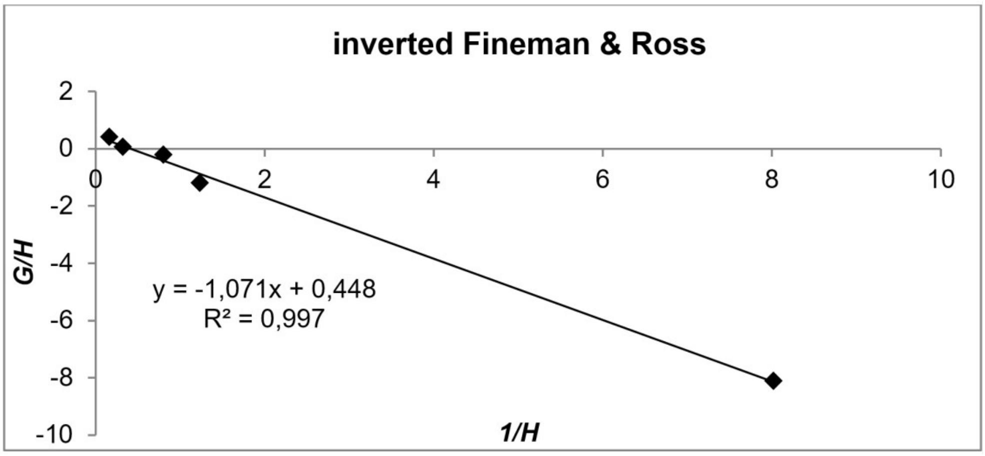

Figure S5: inverted Fineman & Ross plot of the copolymerization system **1**/AN in DMF.

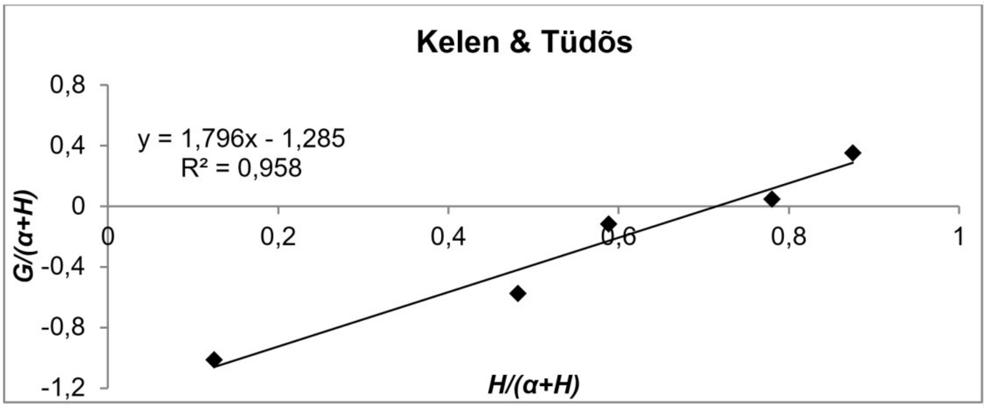

Figure S6: Kelen & Tüdõs plot of the copolymerization system **1**/AN in DMF.

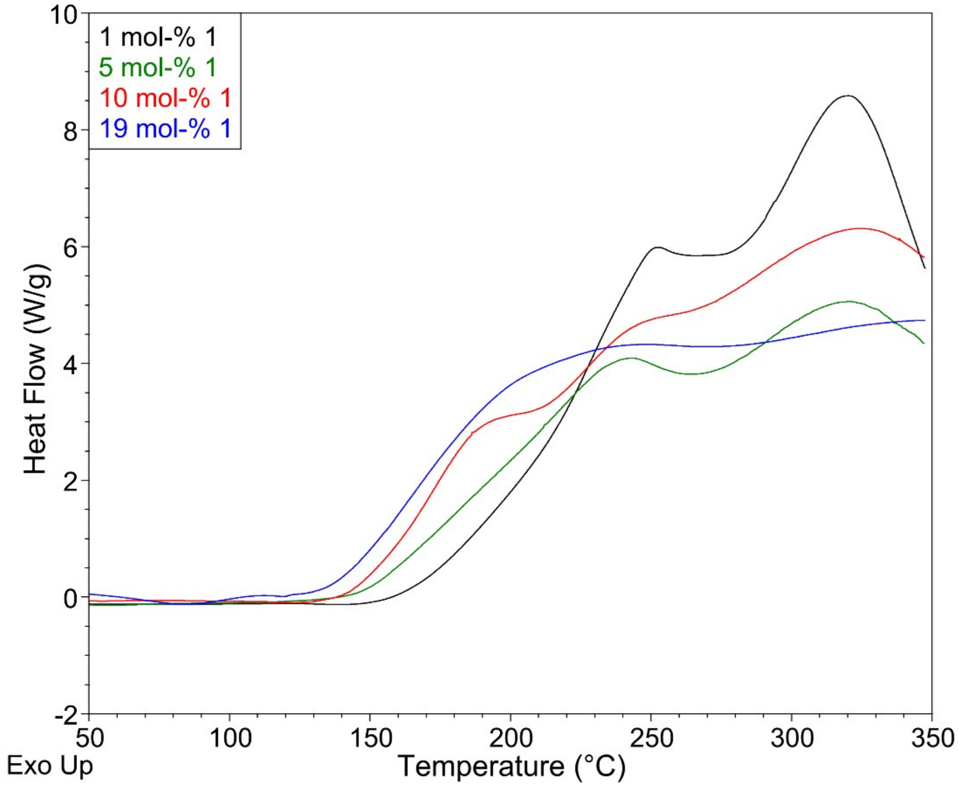

Figure S7: DSC curve in air of a PAN-Copolymer with 1, 5, 10 and 19 mol-% of **1**, heating rate = 10 K/min.

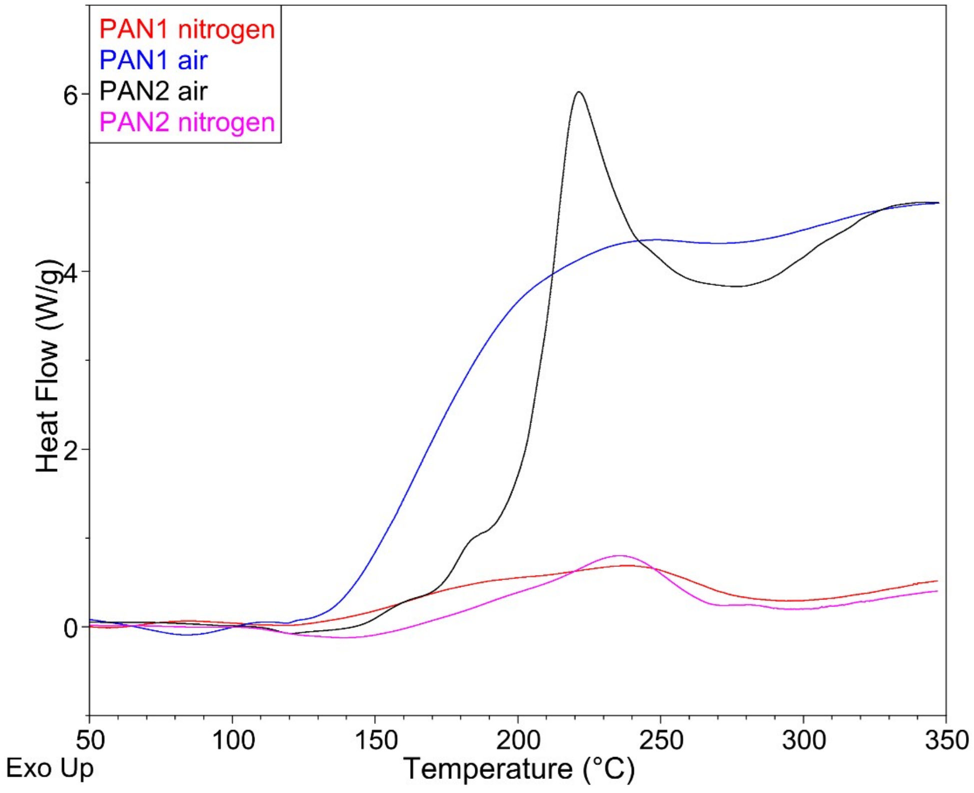

Figure S8: DSC in air and in nitrogen with a heating rate of 10 K/min of PAN**1** and PAN**2.**

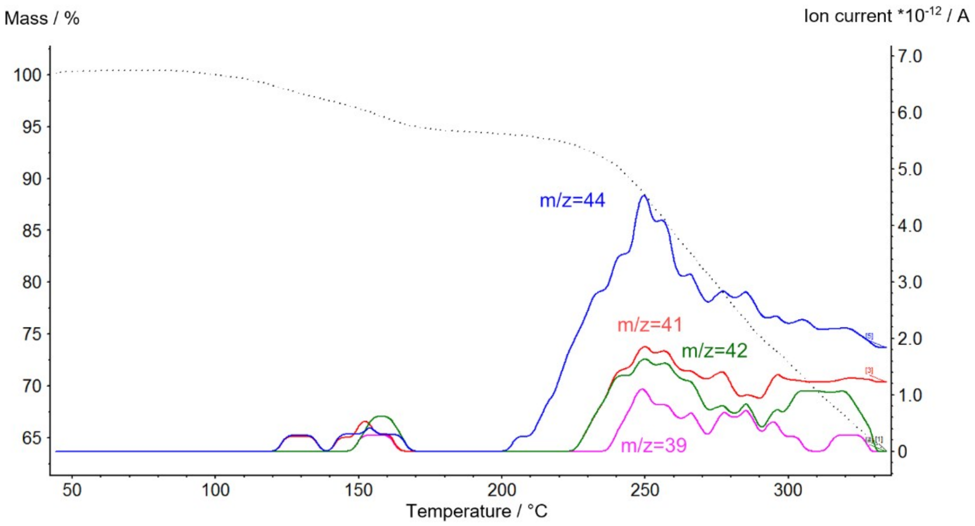

Figure S9: TGA-MS measurement of PAN**1** with a heating rate 10 K/min in Helium. The colored curves correspond to the intensities of the following mass-over-charge ratios *m/z*. purple: *m/z* = 39, red: *m/z* = 41, green: *m/z* = 42, blue: *m/z* = 44. The dotted black line corresponds to the weight loss of PAN**1**.

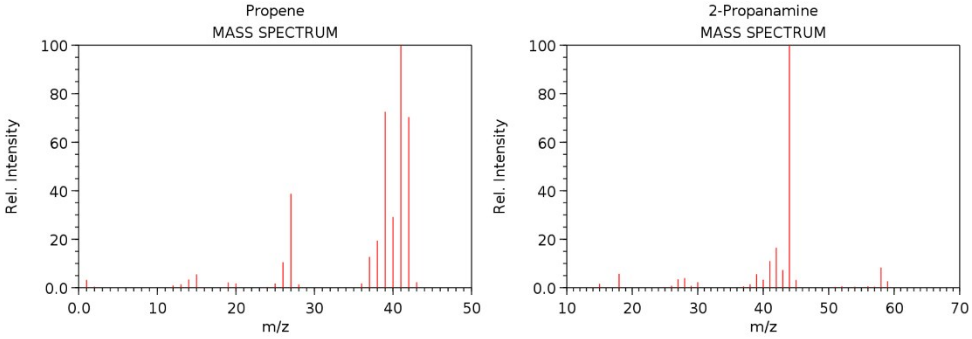

Figure S10: Mass spectra of propene (left) and 2-propylamine (right)[1].

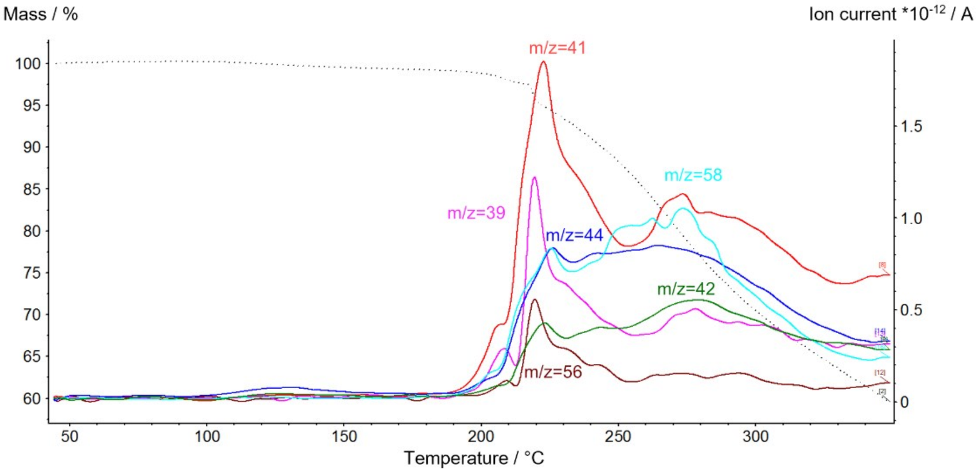

Figure S11: TGA-MS measurement of PAN**2** applying a heating rate 10 K/min under helium. The colored curves correspond to the intensities of the following mass-over-charge ratios *m/z*. purple: *m/z* = 39, red: *m/z* = 41, green: *m/z* = 42, blue: *m/z* = 44, brown: *m/z* = 56, light blue *m/z* = 58.

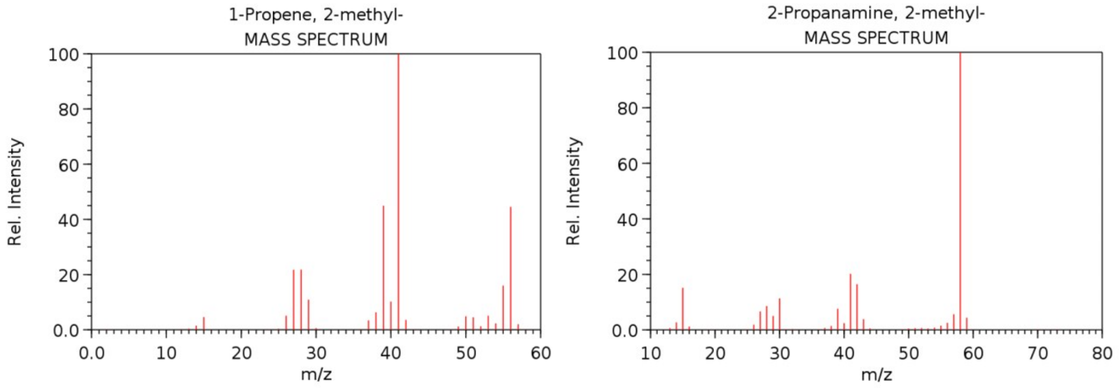

Figure S12: Mass spectra of isobutene (left)and *tert*-butylamine (right)[1].

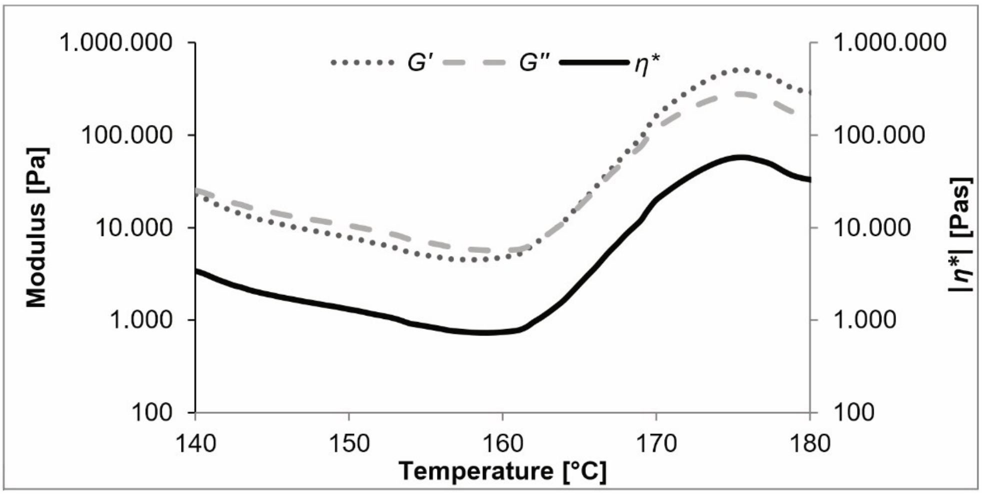

Figure S13: Temperature sweep of PAN**1** (M_n = 24 000 g/mol, *PDI* = 1.8). Shown are the complex viscosity η^*, the storage modulus *G'* and the loss modulus *G''*. Amplitude = 3 %, angular frequency = 10 /s.

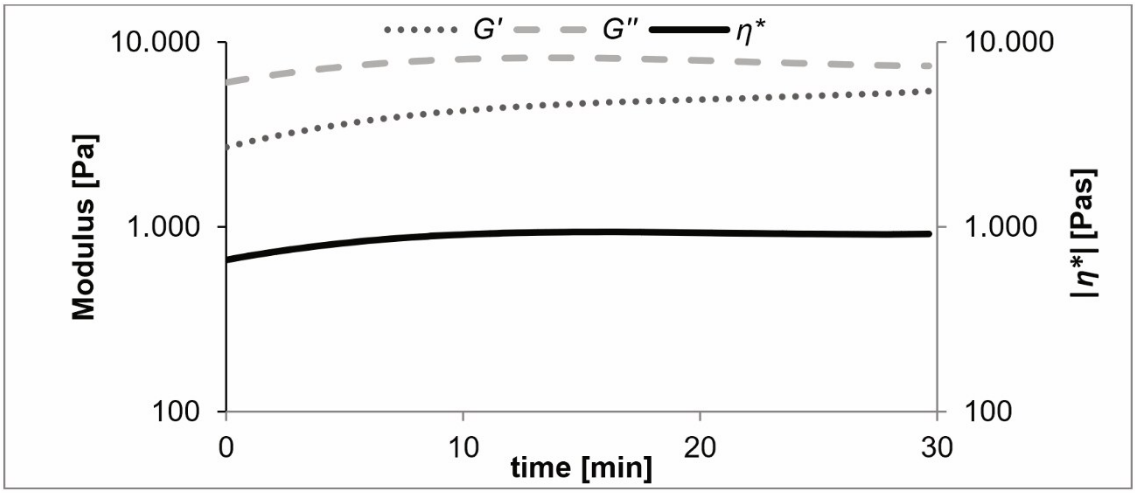

Figure S14: Time sweep measurement of PAN**1** (M_n = 21000 g/mol, *PDI* = 2.0) softened with 10 wt.-% of DMF at 130 °C. Shown are the complex viscosity η^*, the storage modulus *G'* and the loss modulus *G''*. Amplitude = 3 %, angular frequency = 10 1/s.

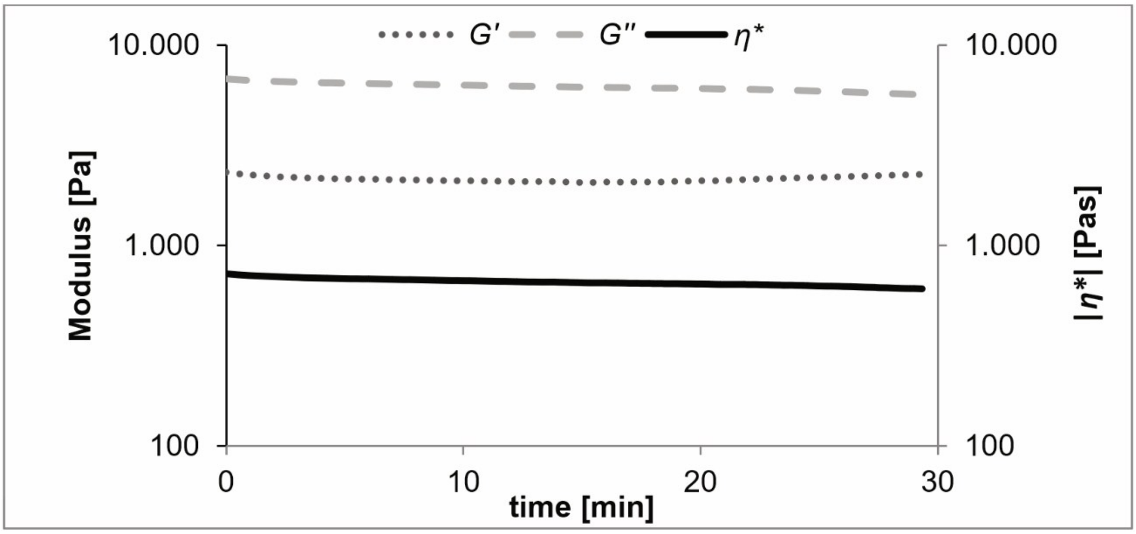

Figure S15: Time sweep measurement of a PAN**2** (M_n = 20,000 g/mol, *PDI* = 1.9) softened with 10 wt.-% of DMSO at 135 °C. Shown are the complex viscosity *η**, the storage modulus *G’* and the loss modulus *G”*. Amplitude = 3 %, angular frequency = 10 /s.

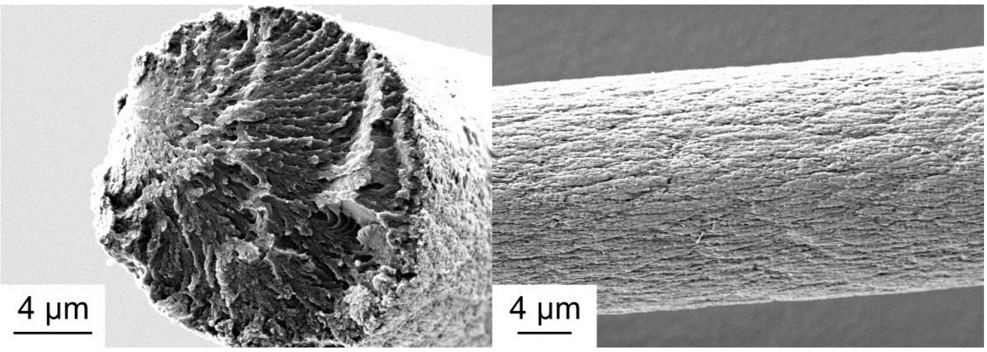

Figure S16: SEM micrographs of the cross-section and surface of fibers of PAN**2** softened with 10 wt.-% DMSO. The shape of the cross section is round, many pores are visible and the surface of the fiber is rough, indicating gas formation during melt spinning

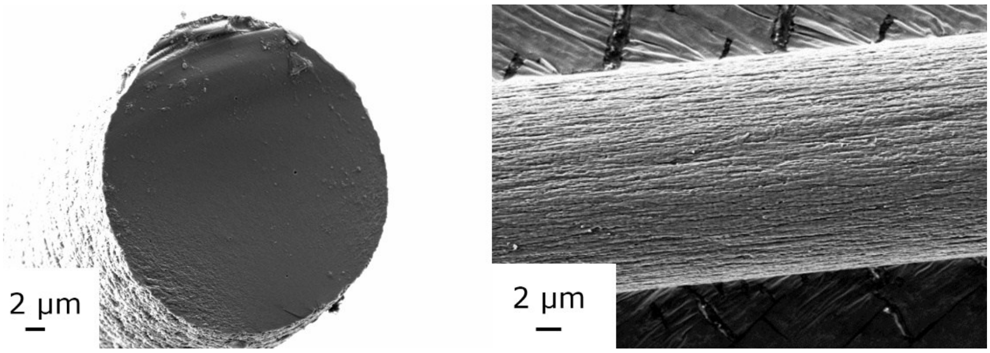

Figure S17: SEM micrographs of the cross-section and surface of stabilized fibers of PAN**1** softened with 10 wt.-% DMF. The shape of the cross section is round, almost no pores are visible. The surface of the fiber is rough and very similar to the non-stabilized fiber, indicating that the fiber was not soft during stabilization.

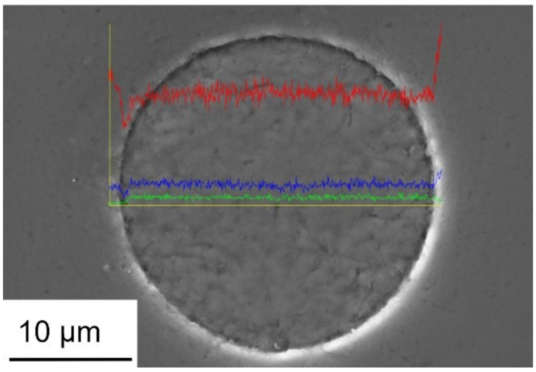

Figure S18: EDX measurement on a cross section of a stabilized PAN**1**-based fiber softened with 10 wt.-% DMF. Red = carbon, blue = oxygen, green = nitrogen.

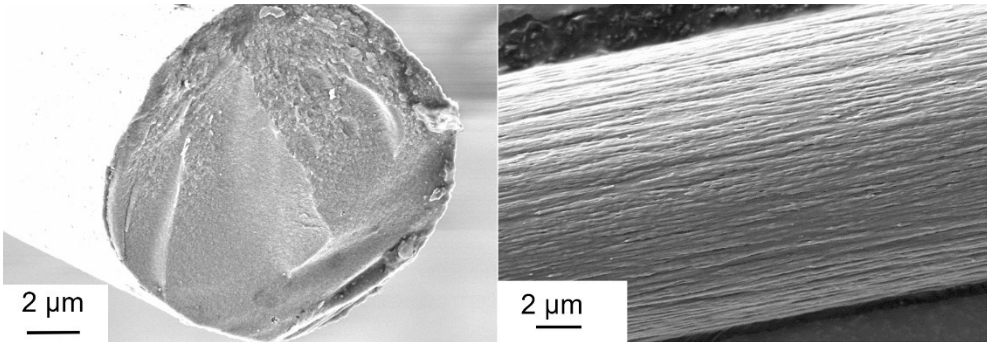

Figure S19: SEM micrographs of the cross section and surface of CFs prepared from PAN**1** softened with 10 wt.-% DMF.

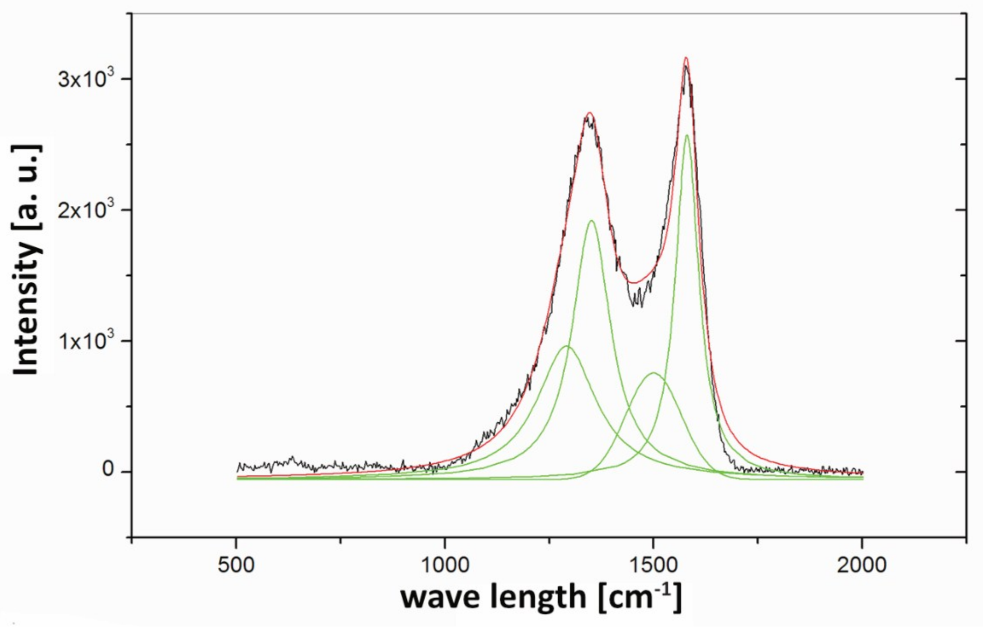

Figure S20: Curve deconvolution of the Raman spectrum of a CF derived from PAN**1** spun with 10 wt.-% DMF, carbonized at 1400 °C. Deconvoluted bands from left to right: D4, Lorentz fit; D1, Lorentz fit; D3, Gauss fit; G, Lorentz fit. The D2 band was not visible.

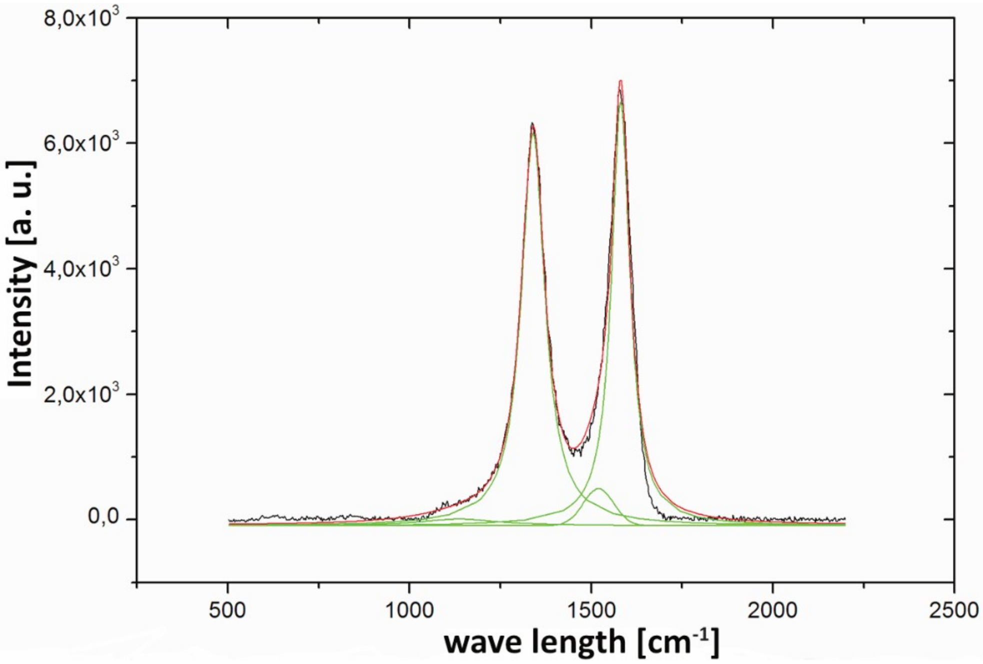

Figure S21: Curve deconvolution of the Raman spectrum of a CF derived from PAN**1** spun with 10 wt.-% DMF, carbonized at 1800 °C. Deconvoluted bands from left to right: D4, Lorentz fit; D1, Lorentz fit; D3, Gauss fit; G, Lorentz fit. The D2 band was not visible.

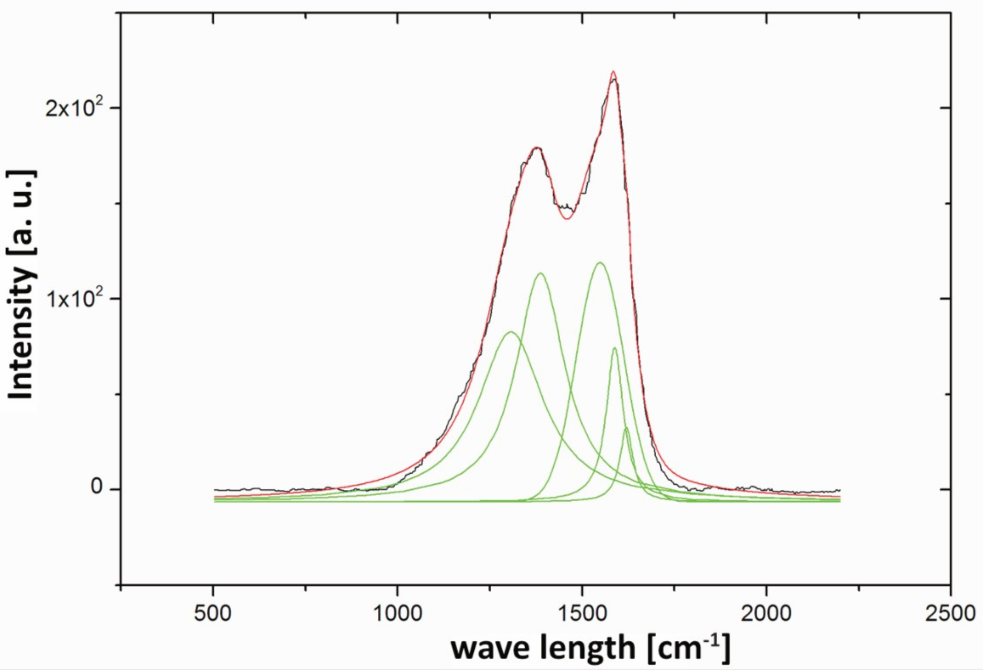

Figure S22: Curve deconvolution of the Raman spectrum of a Toray T300 CF. Deconvoluted bands from left to right: D4, Lorentz fit; D1, Lorentz fit; D3, Gauss fit; G, Lorentz fit, D2, Lorentz fit.

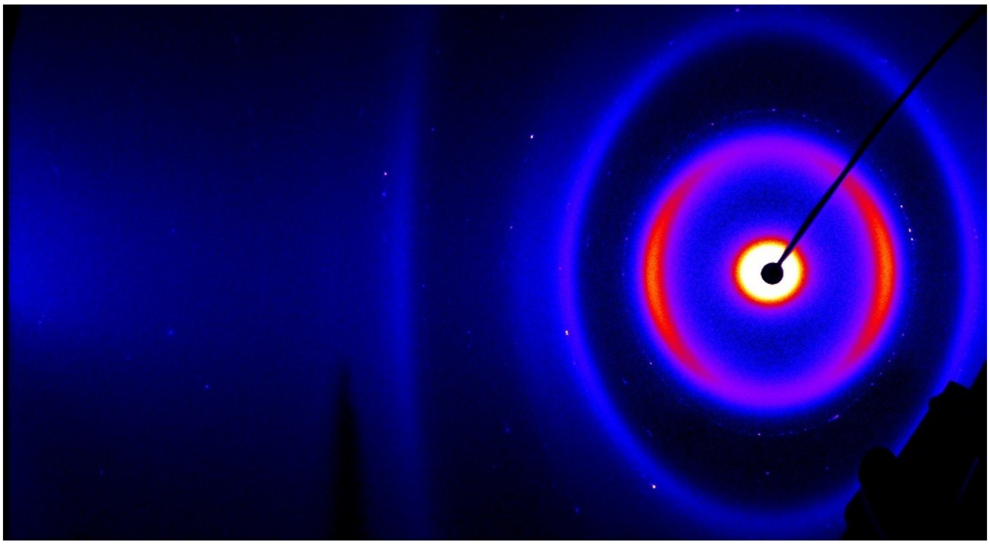

Figure S23: WAXS diffraction pattern of a CF derived of unsoftened PAN**1**.

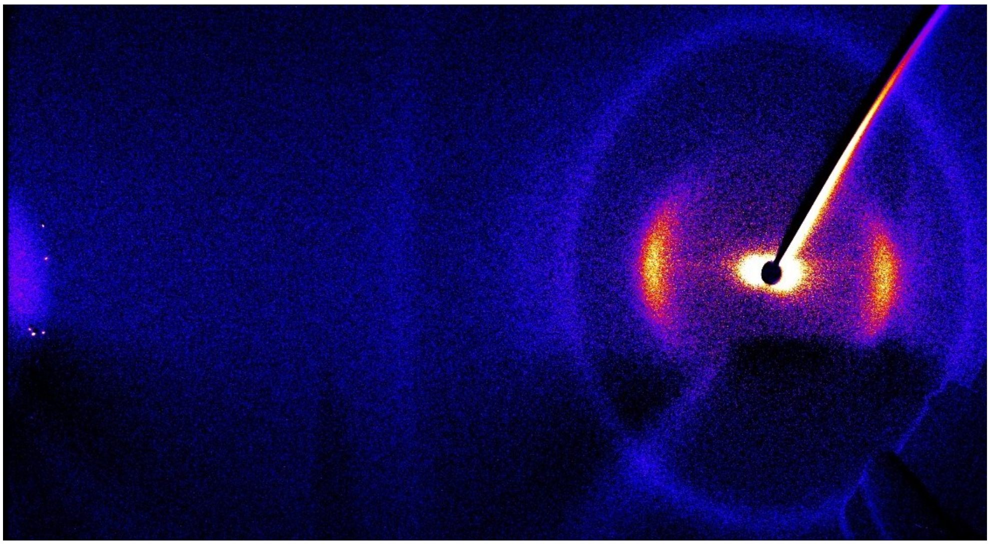

Figure S24: WAXS diffraction pattern of a CF derived of PAN**1** softened with 10 wt.-% DMF.

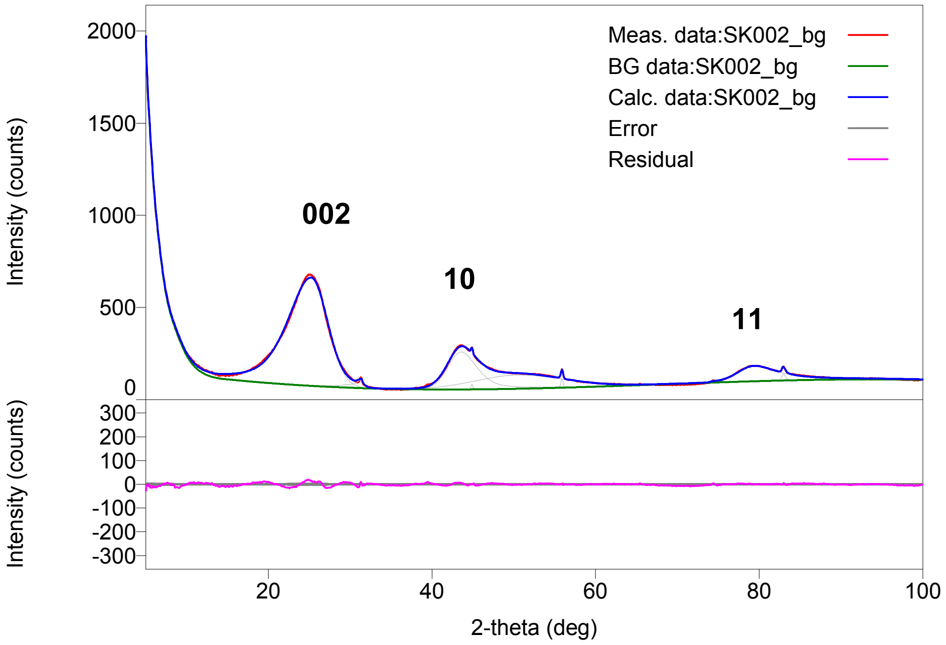

Figure S25: Deconvoluted X-ray diffractograms of PAN**1** spun without softener. The prominent reflections are the (002), (10) and the (11) reflection.

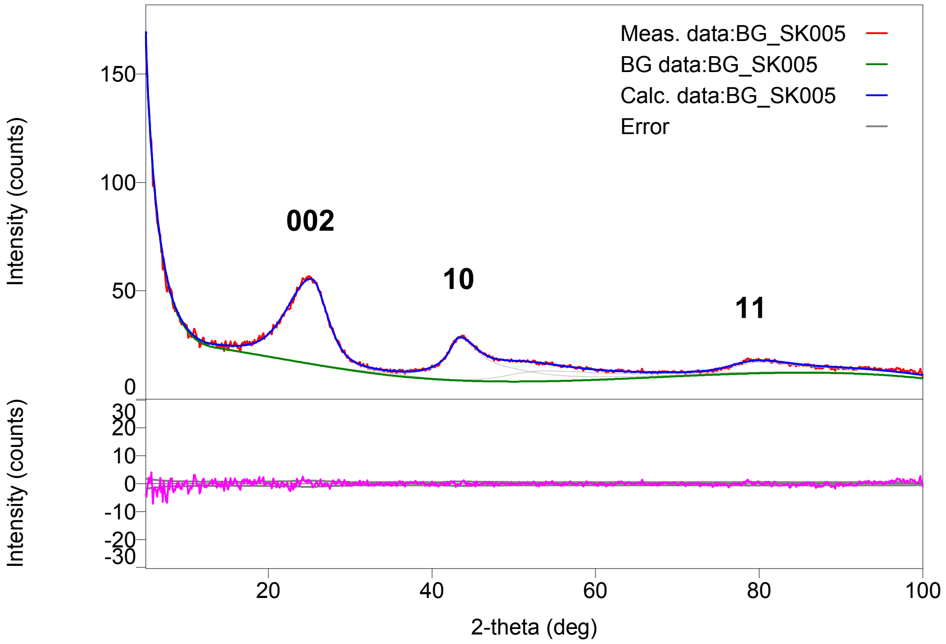

Figure S26: Deconvoluted X-ray diffractograms of PAN**1** spun with 10 wt.-% DMF as softener. The prominent reflections are the (002), (10) and the (11) reflection.

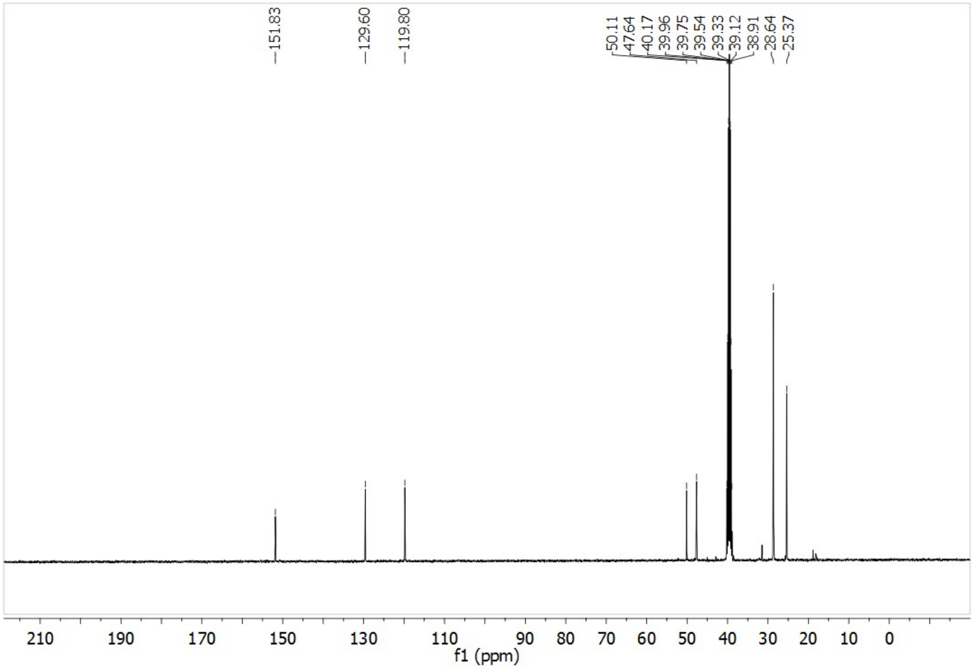

Figure S27: ^{13}C-NMR spectrum of **1** (DMSO-d$_6$), chemical shift in ppm.

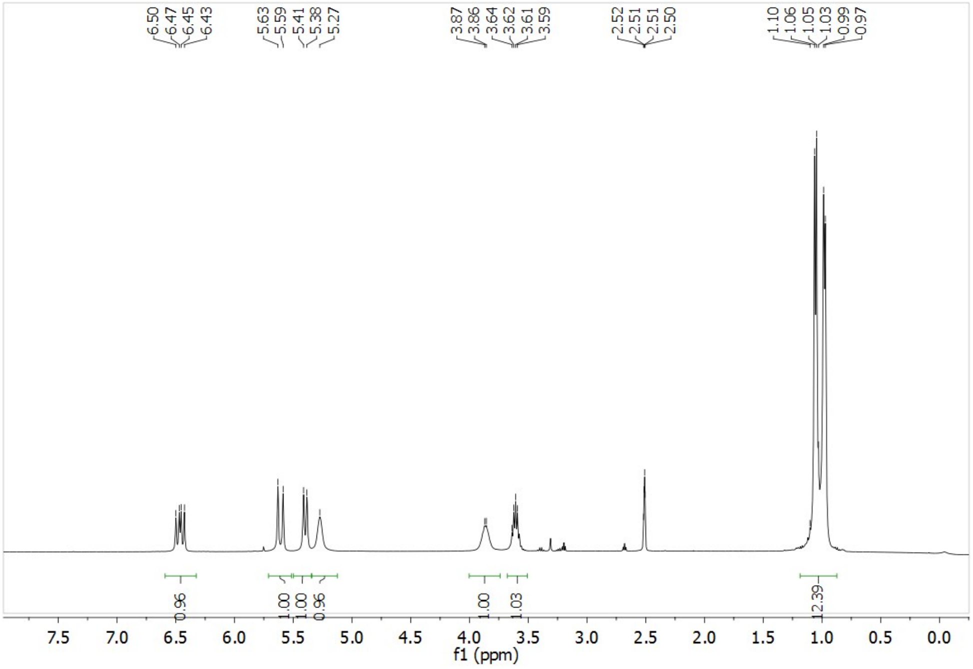

Figure S28: ^{1}H-NMR spectrum of **1** (DMSO-d$_6$), chemical shift in ppm.

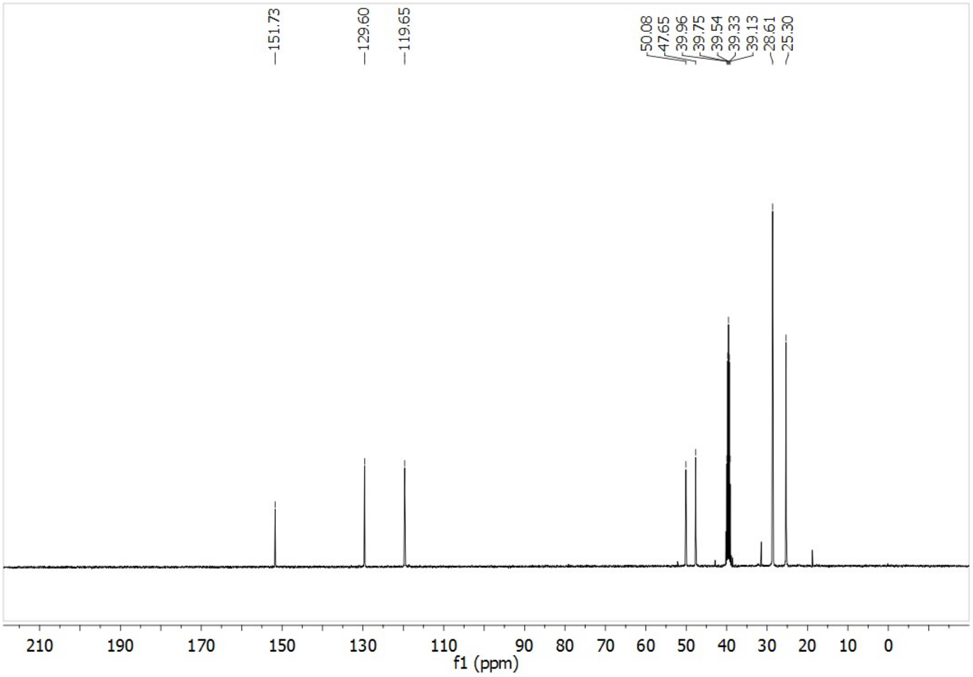

Figure S29: ^{13}C-NMR spectrum of **2** (DMSO-d_6), chemical shift in ppm.

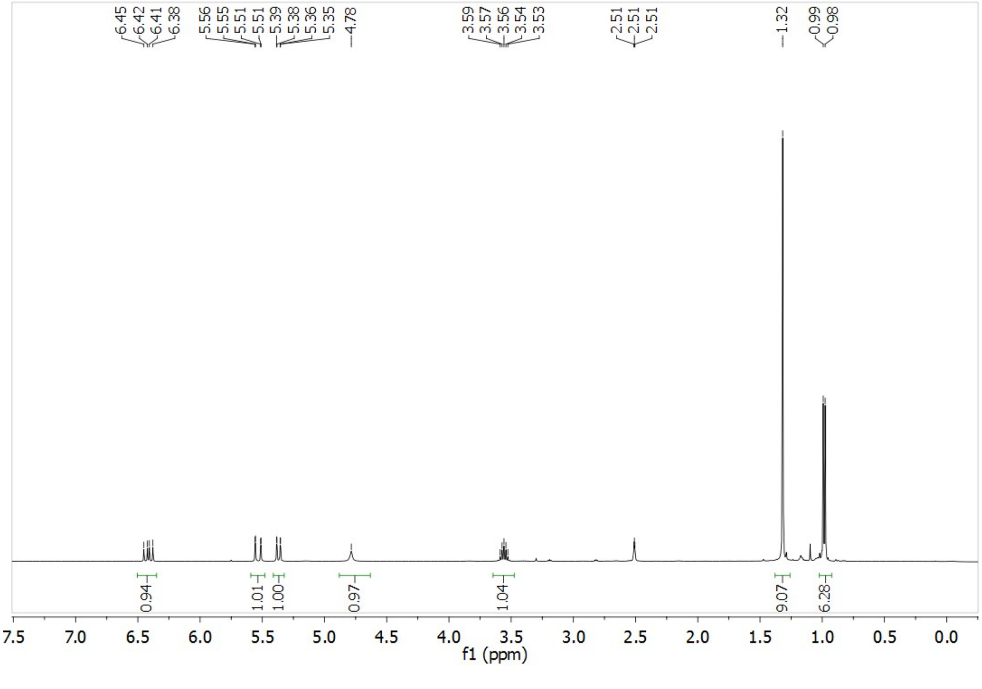

Figure S30: ^{1}H-NMR spectrum of **2** (DMSO-d_6), chemical shift in ppm.

REFERENCES

[1] P. J. Linstrom, W. Mallard, **2001**.