

Supporting Information

Azo-Containing Polymers with Degradation On-Demand Feature

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Fourier transformation infrared (FT-IR) spectra

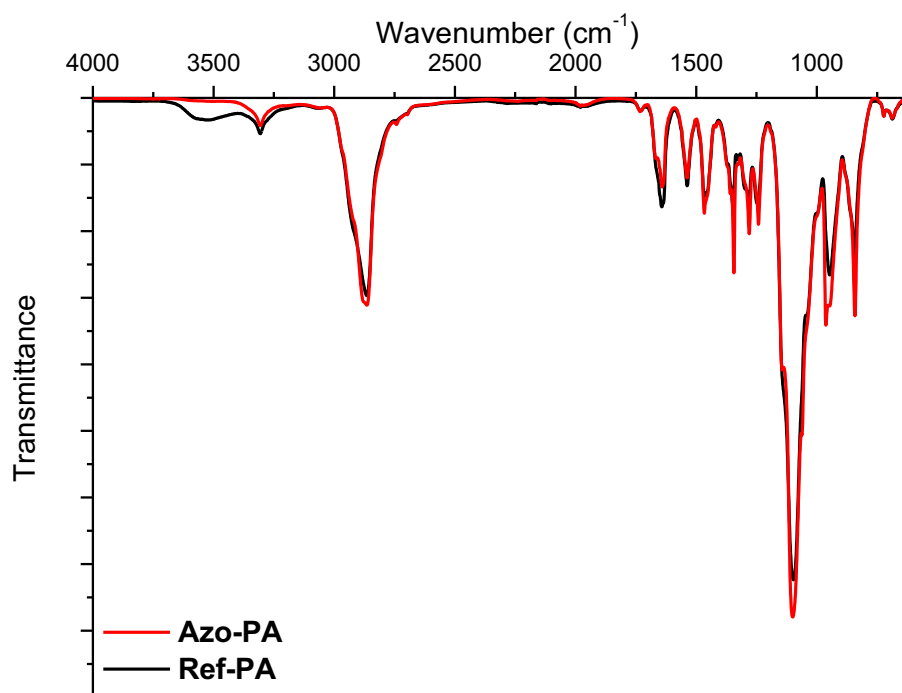


Figure S1. FT-IR spectra of the azo-containing polyamide **azo-PA** (red) and the reference polymer **ref-PA** (black).

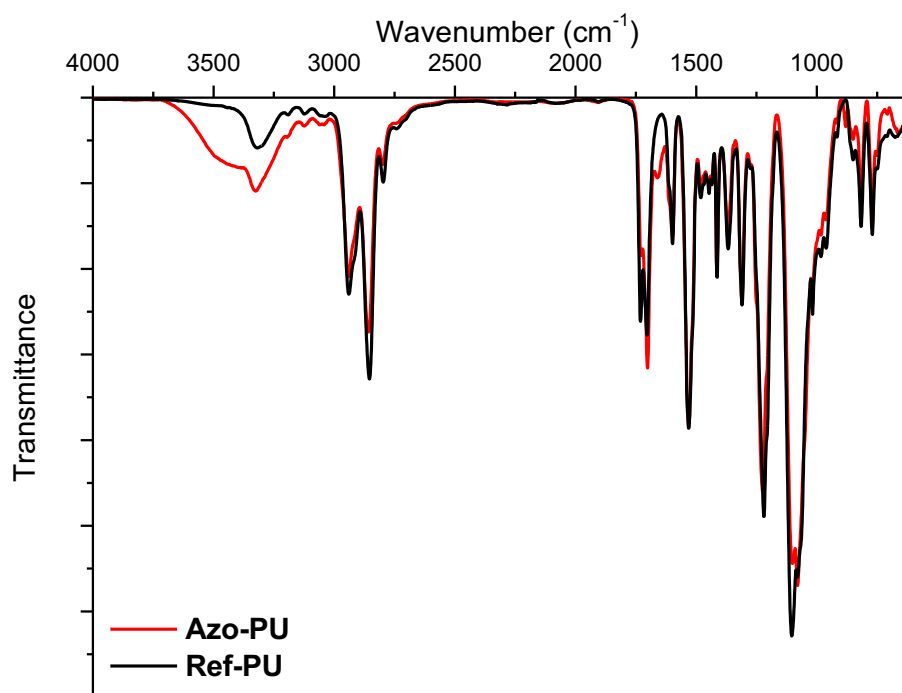
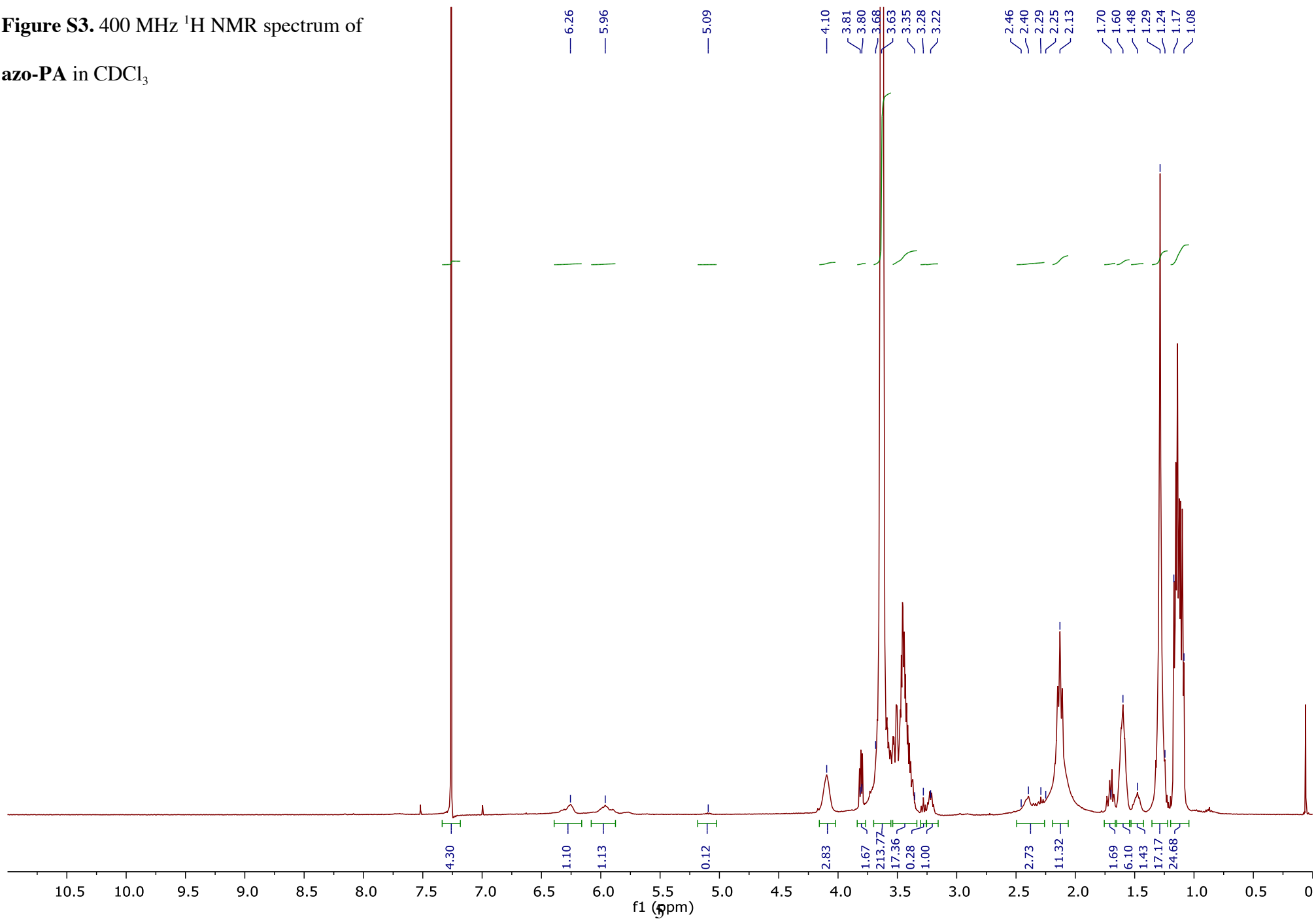


Figure S2. FT-IR spectra of the azo-containing polyurethane **azo-PU** (red) and the reference polymer **ref-PU** (black).

Figure S3. 400 MHz ^1H NMR spectrum of **azo-PA** in CDCl_3



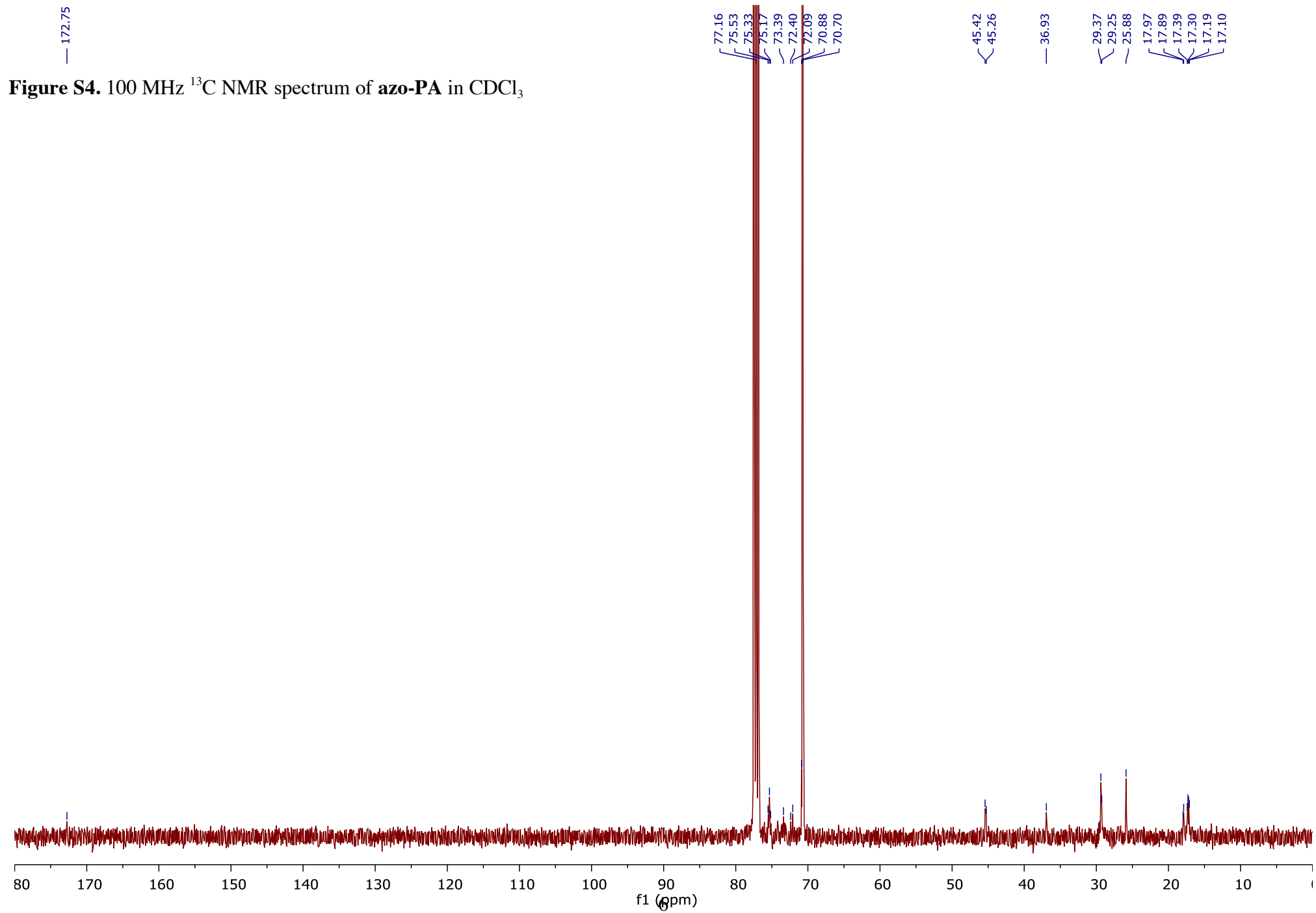


Figure S5a. 400 MHz ^1H NMR spectrum in CDCl_3

of heated (solid state, 140 °C for 5 min) **azo-PA**

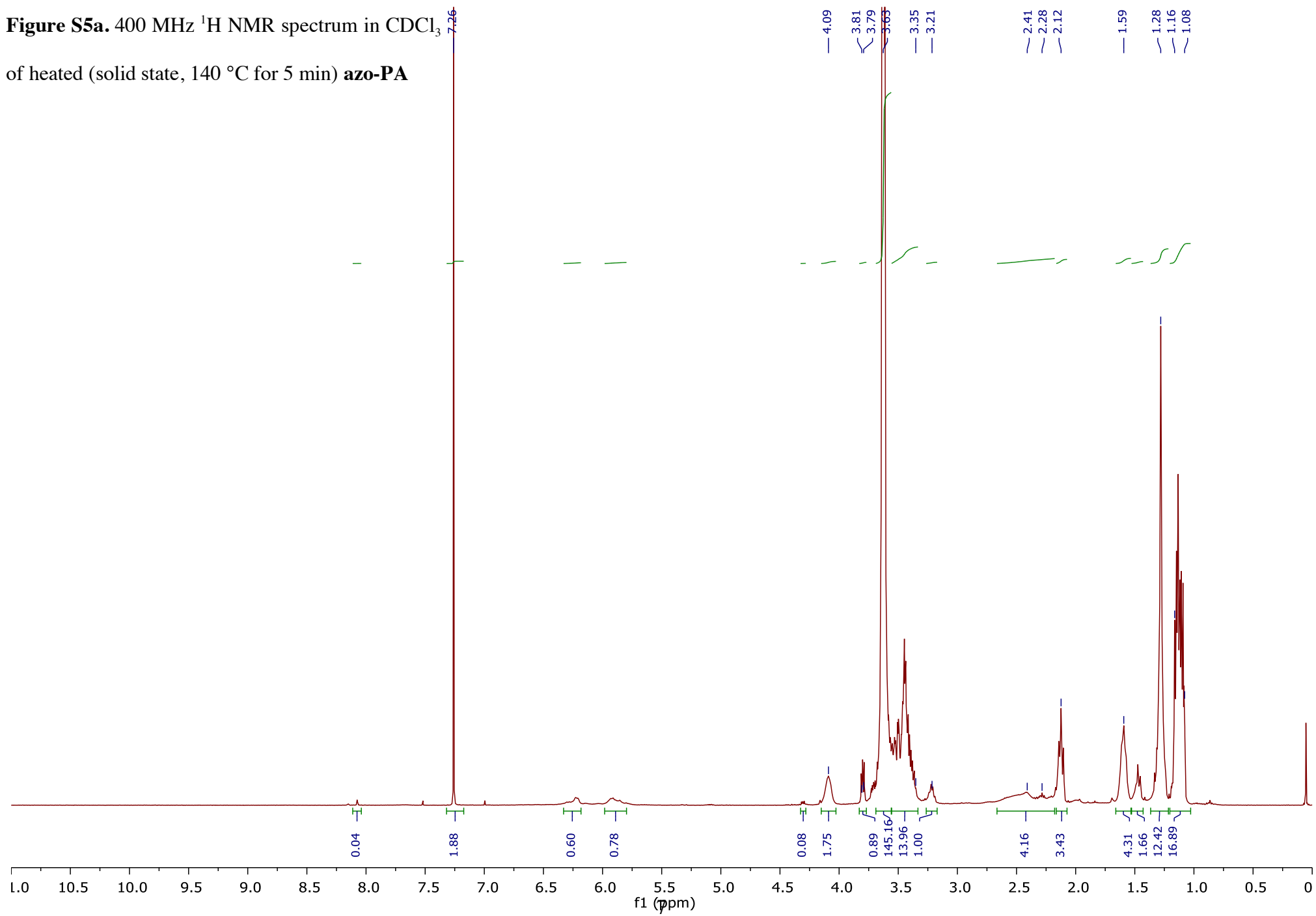
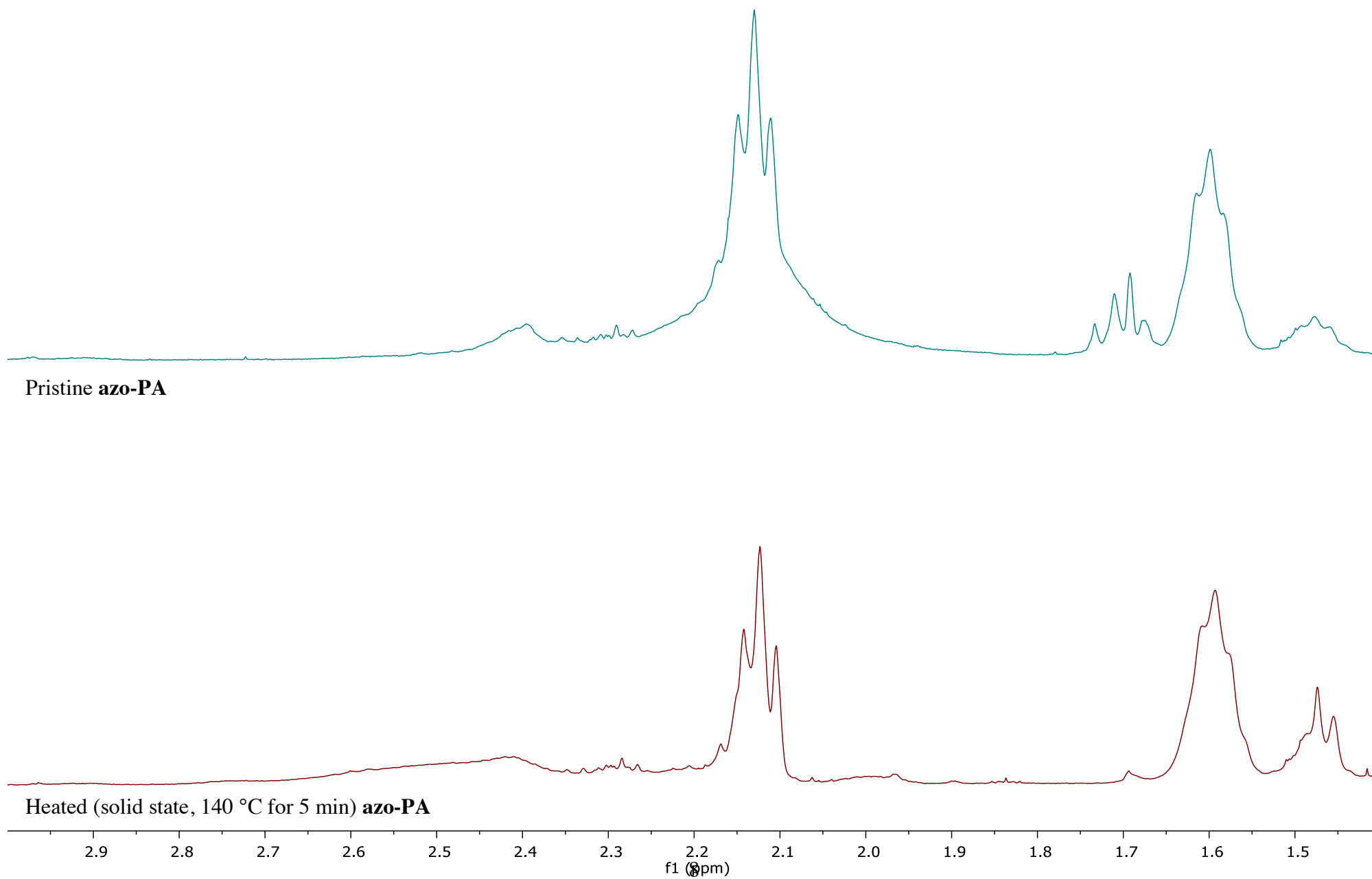


Figure S5b. Magnified 400 MHz ^1H NMR spectra in CDCl_3 of pristine and heated (solid state, 140 $^\circ\text{C}$ for 5 min) **azo-PA**



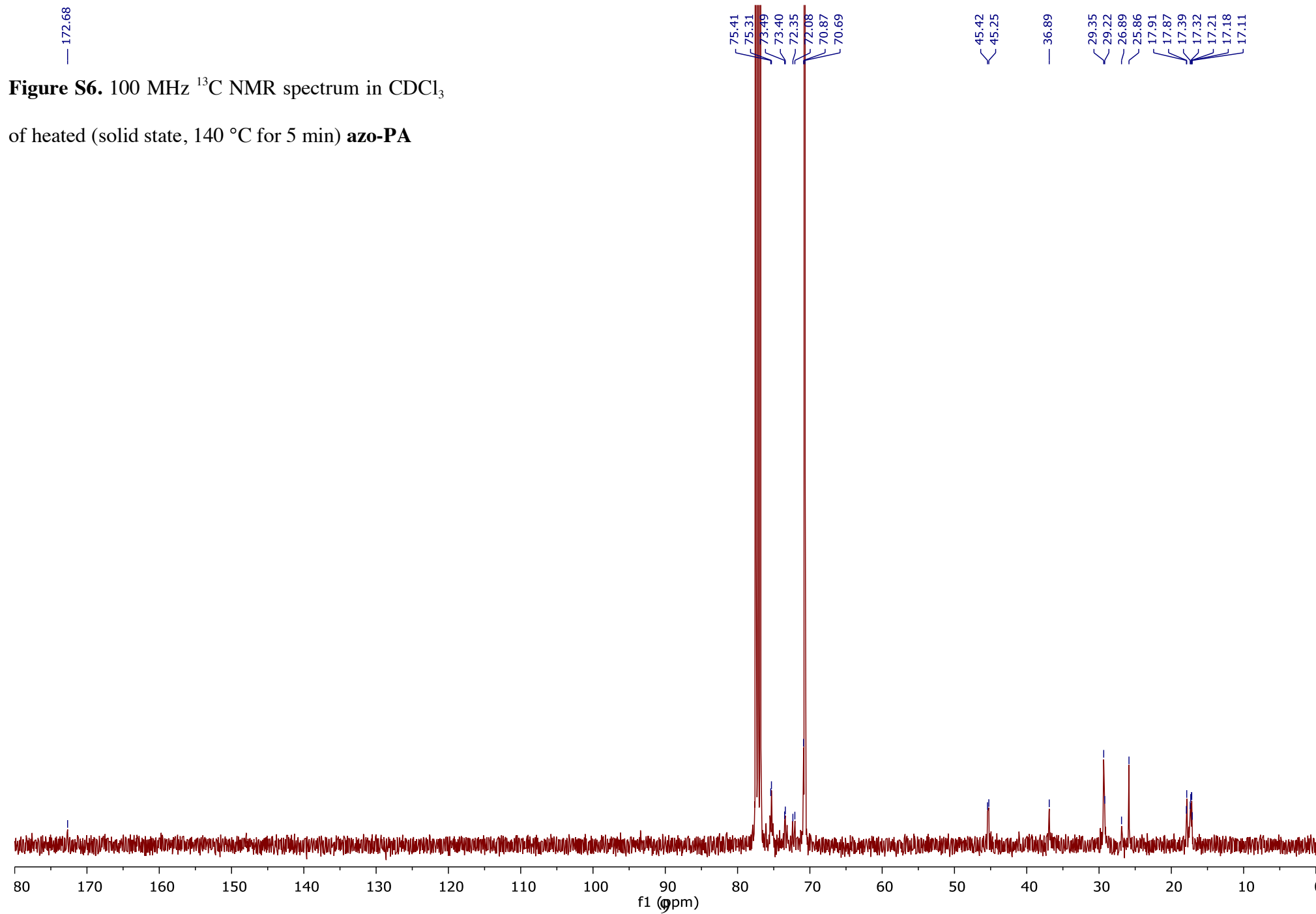
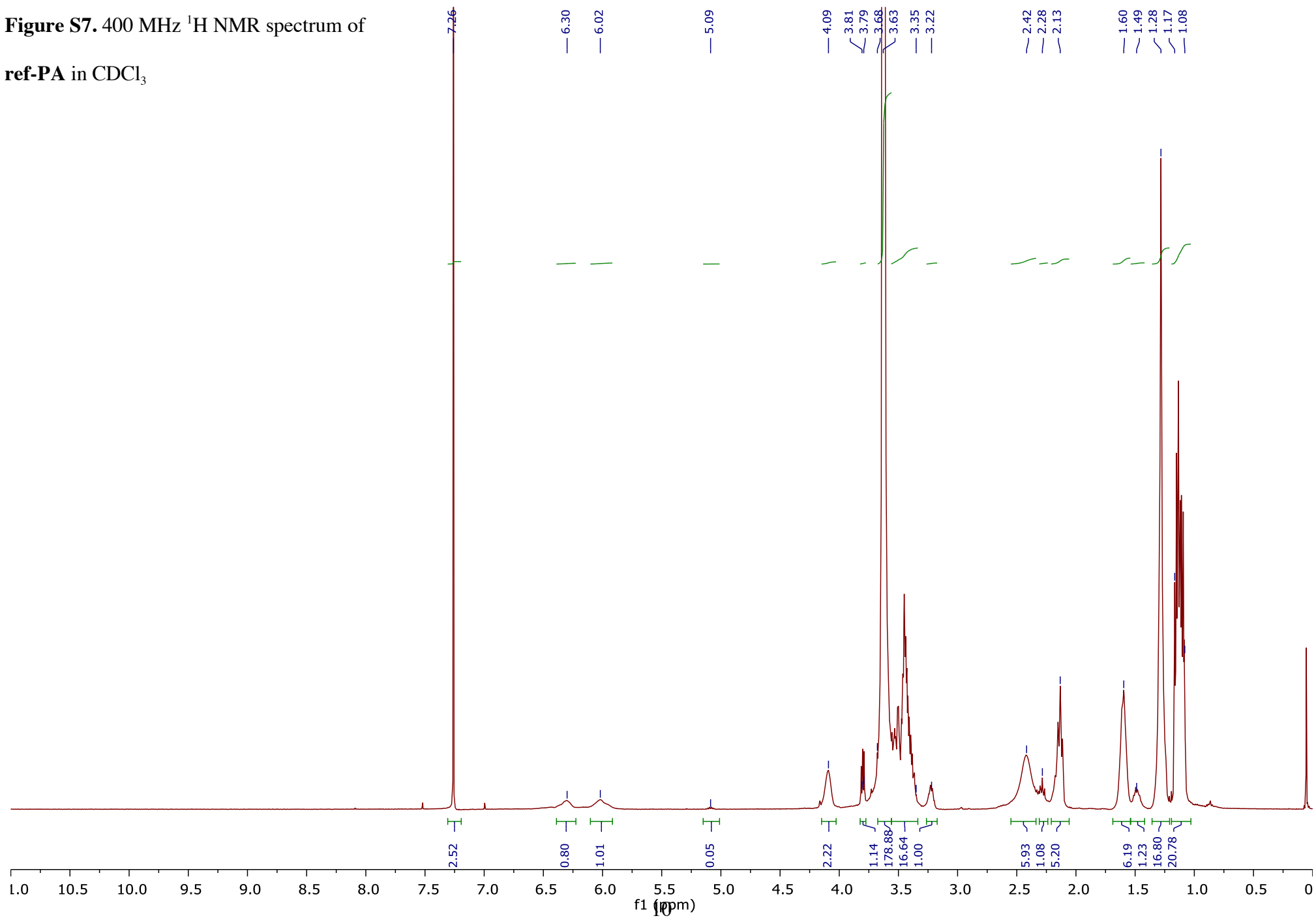


Figure S7. 400 MHz ^1H NMR spectrum of **ref-PA** in CDCl_3



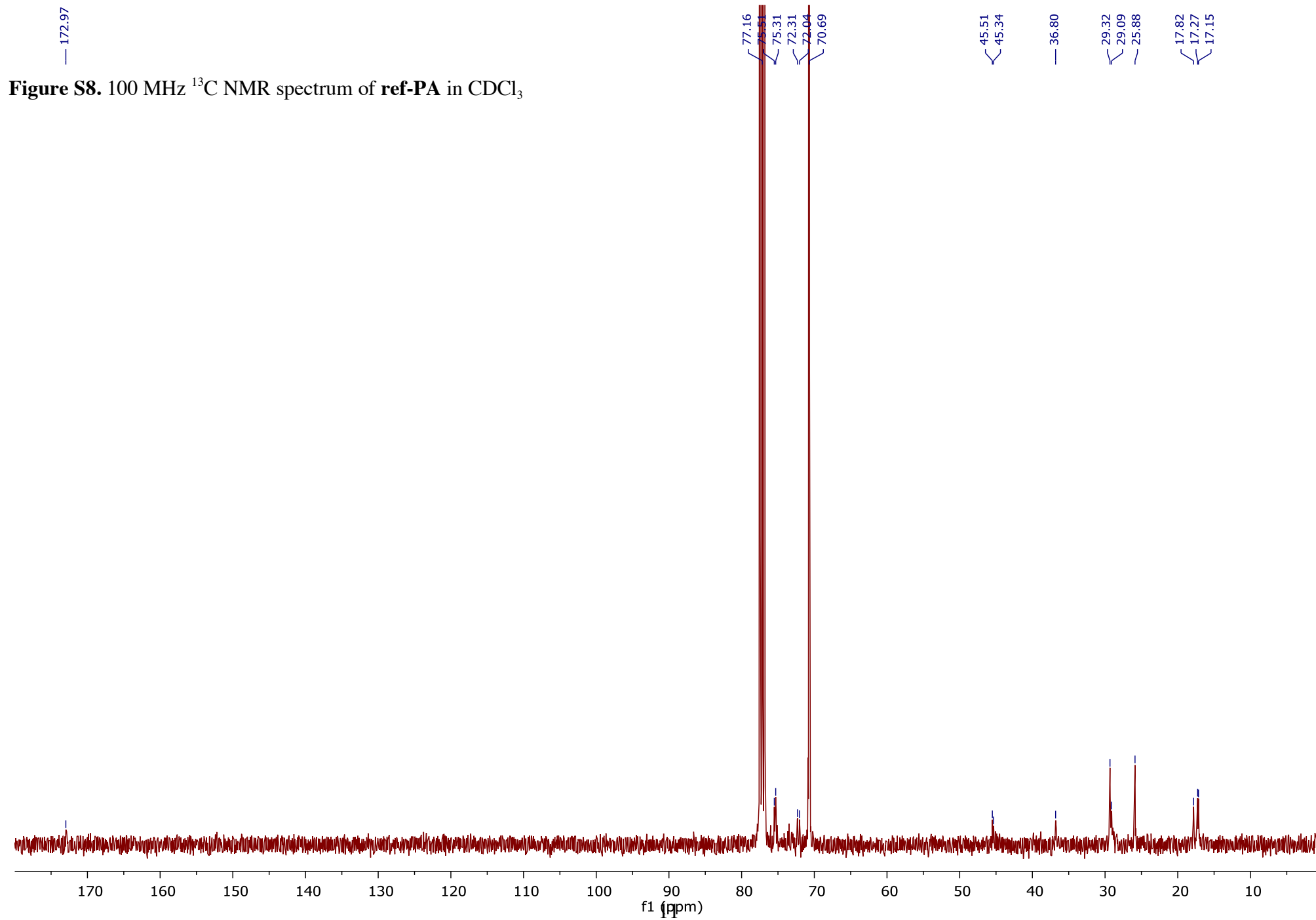


Figure S9. 400 MHz ^1H NMR spectrum in CDCl_3 of heated (solid state, 140 $^\circ\text{C}$ for 5 min) **ref-PA**

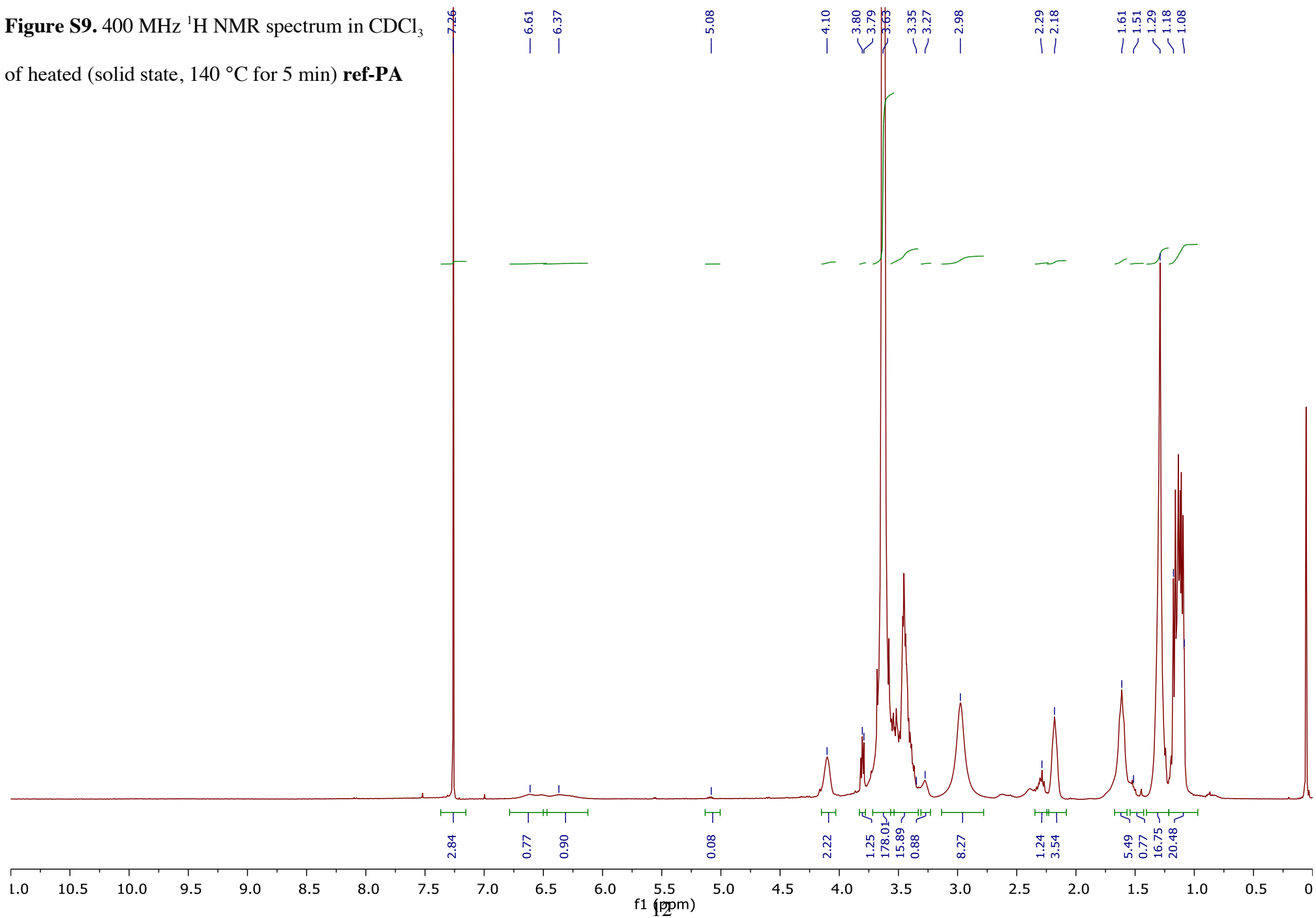


Figure S10. 100 MHz ^{13}C NMR spectrum in CDCl_3

of heated (solid state, 140 °C for 5 min) **ref-PA**

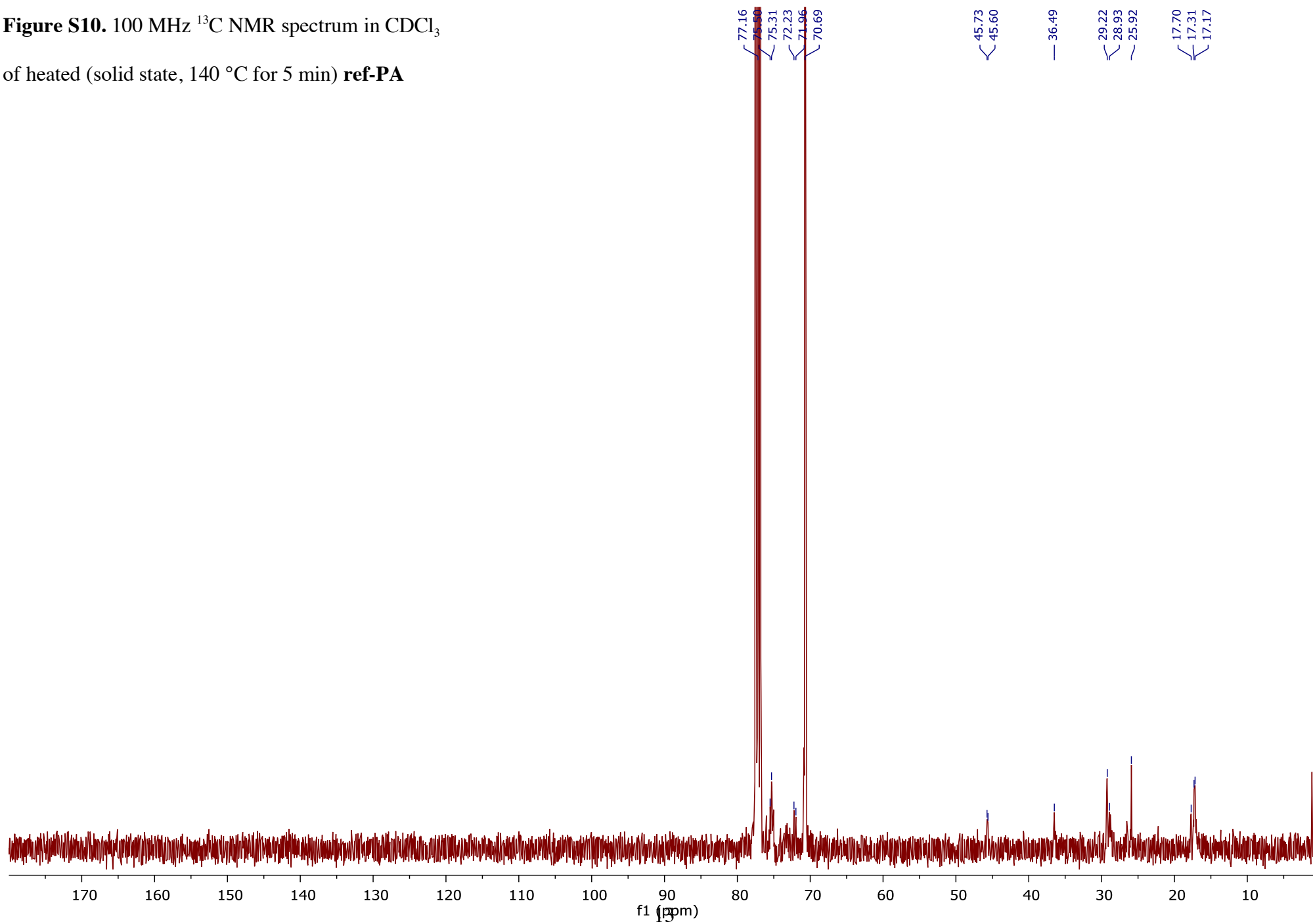
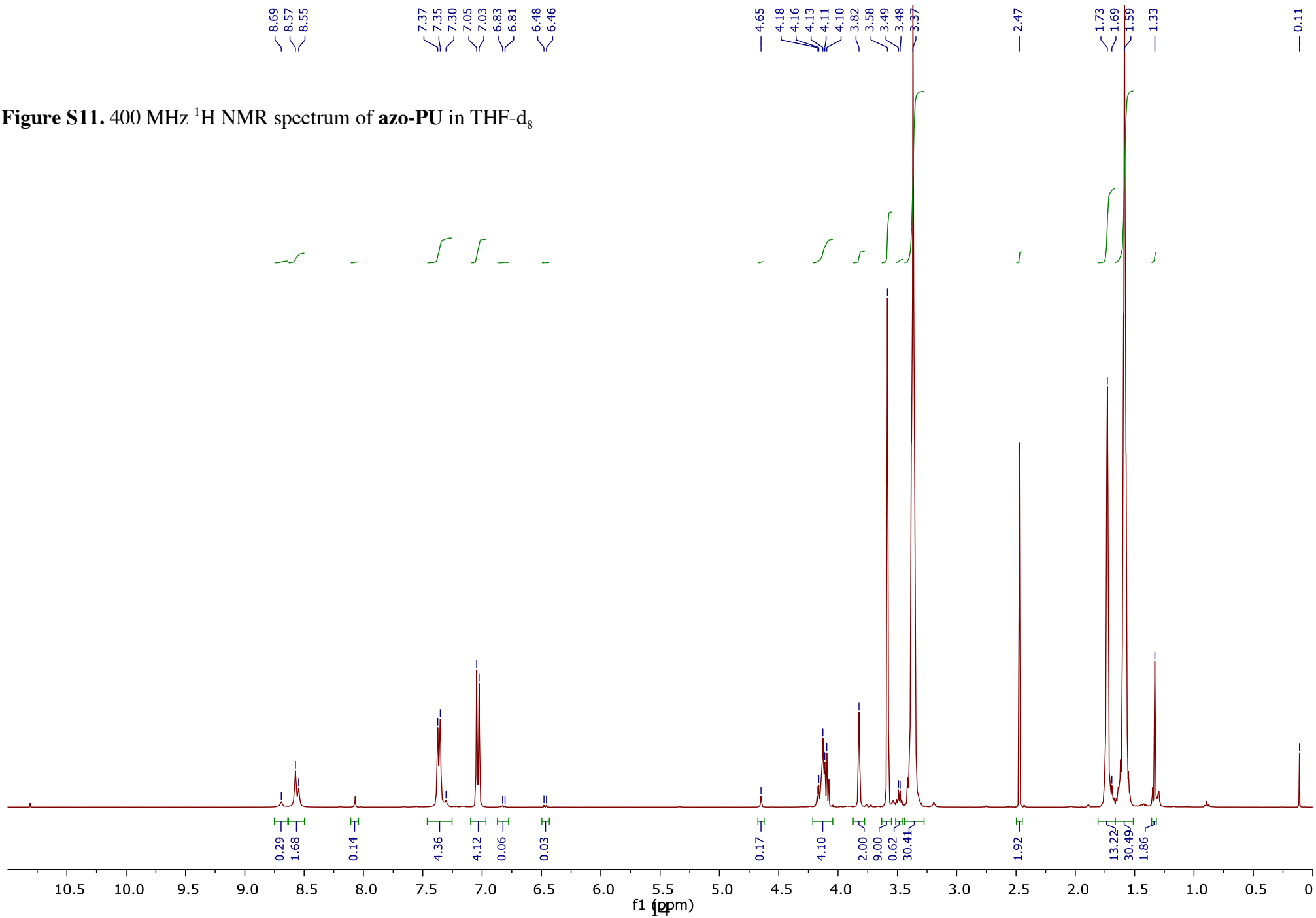
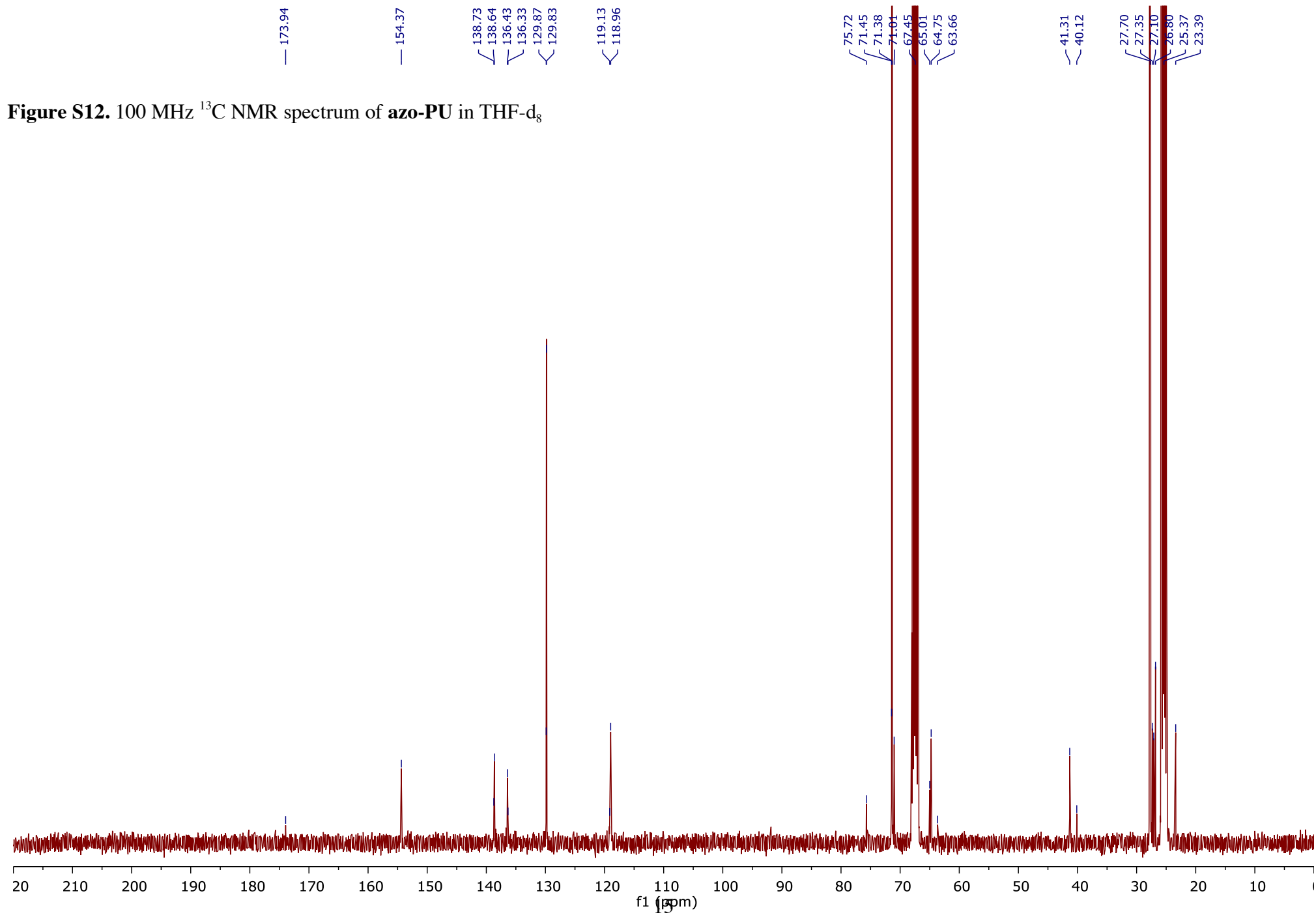
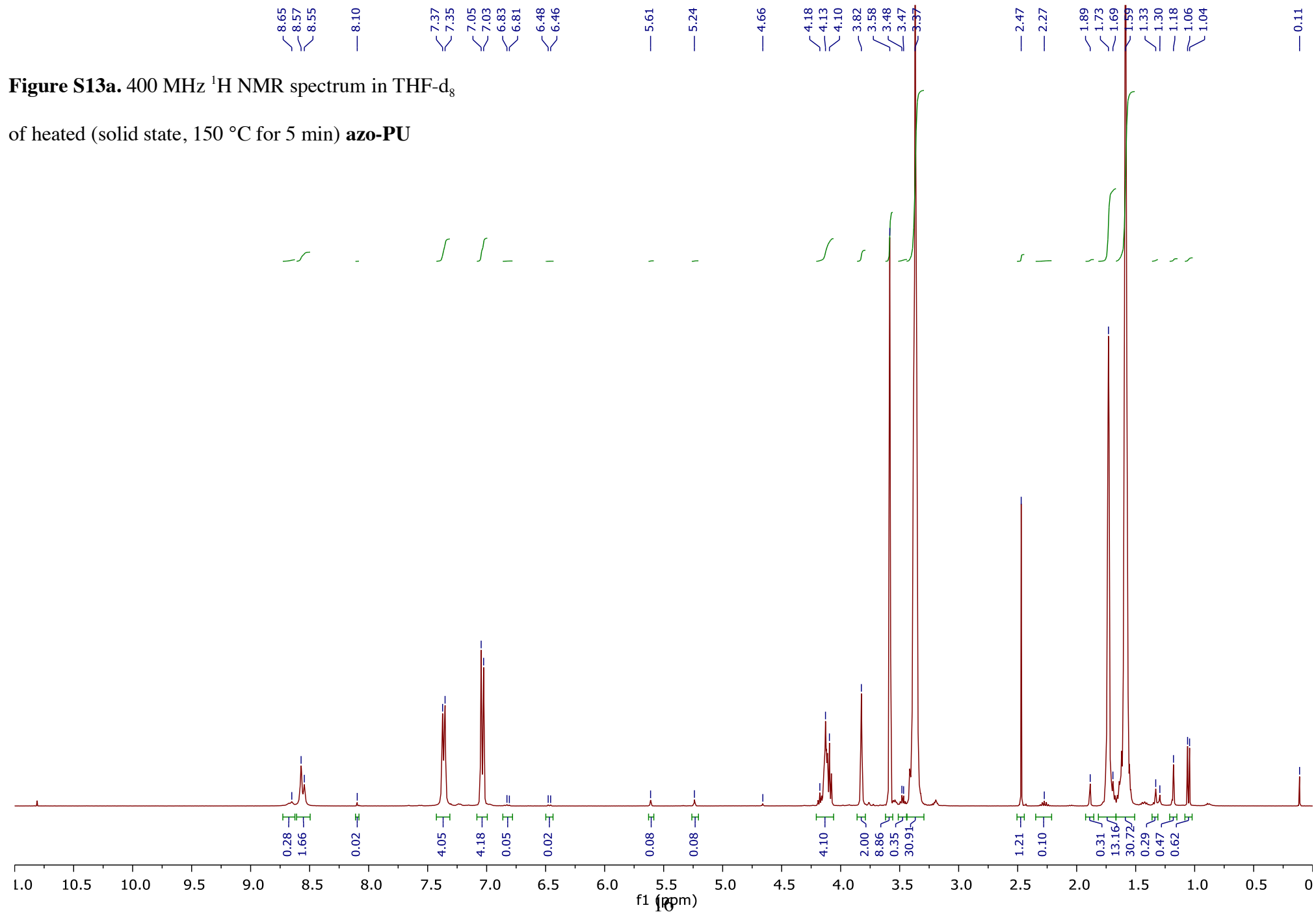


Figure S11. 400 MHz ^1H NMR spectrum of **azo-PU** in THF-d_8







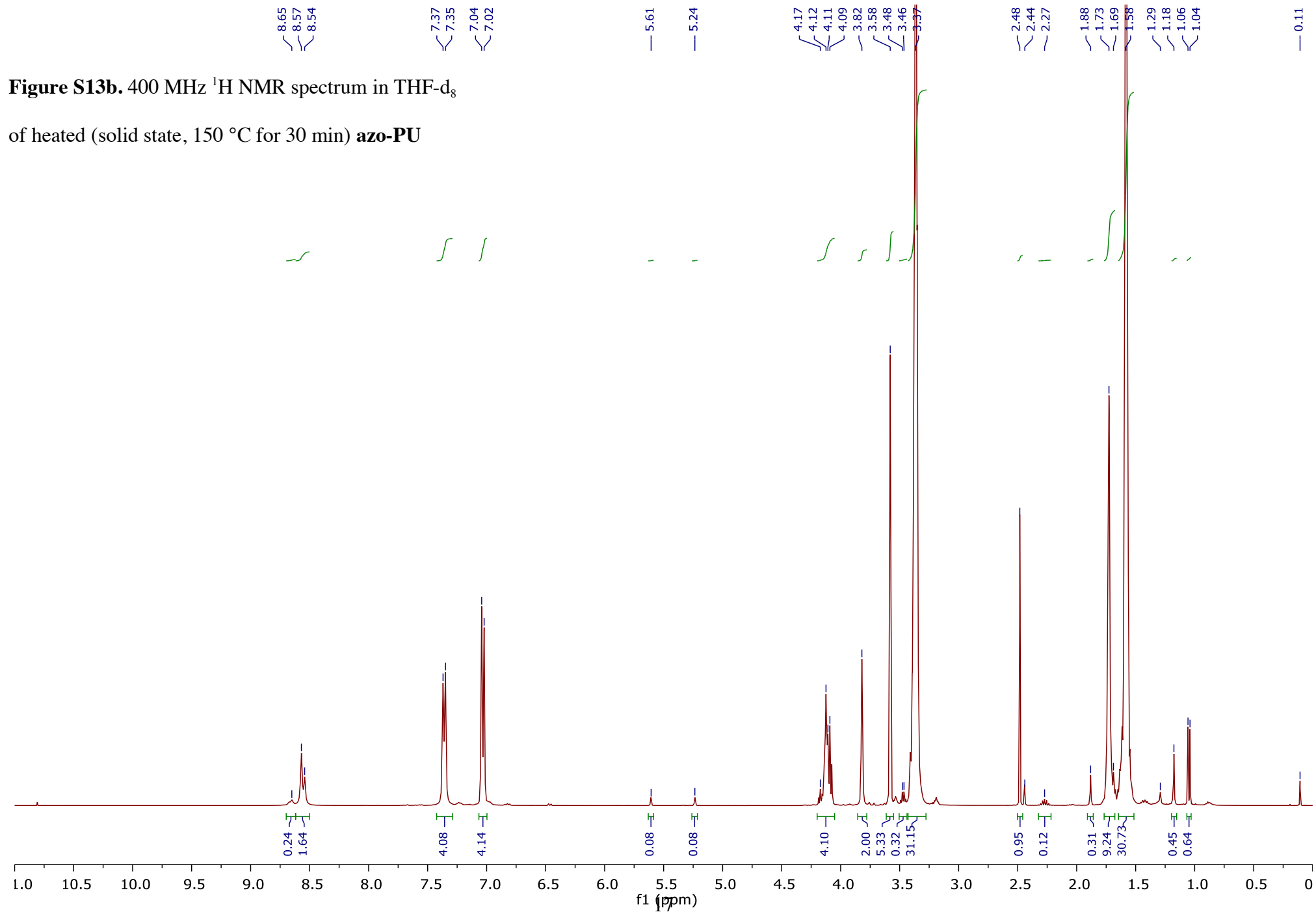
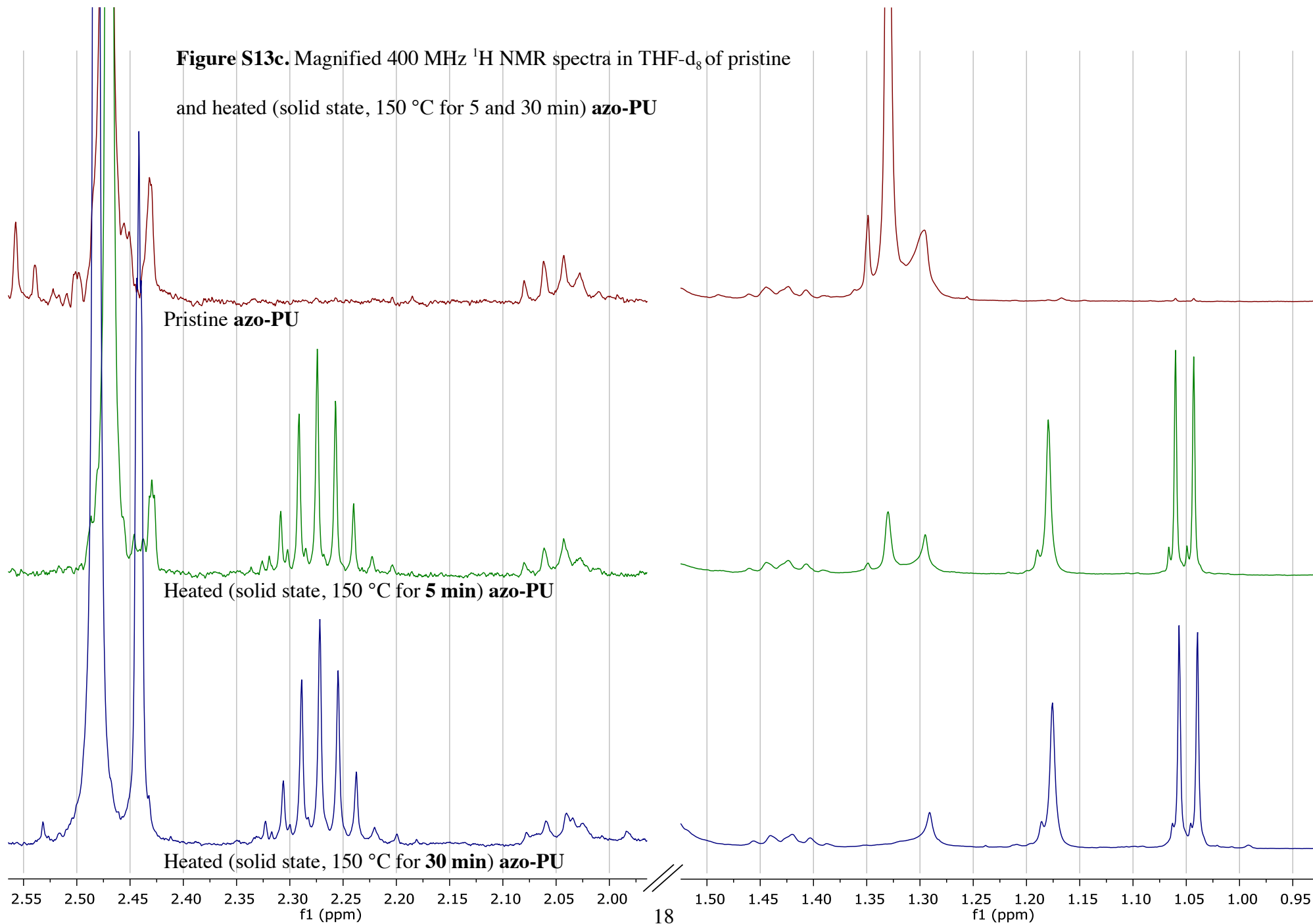
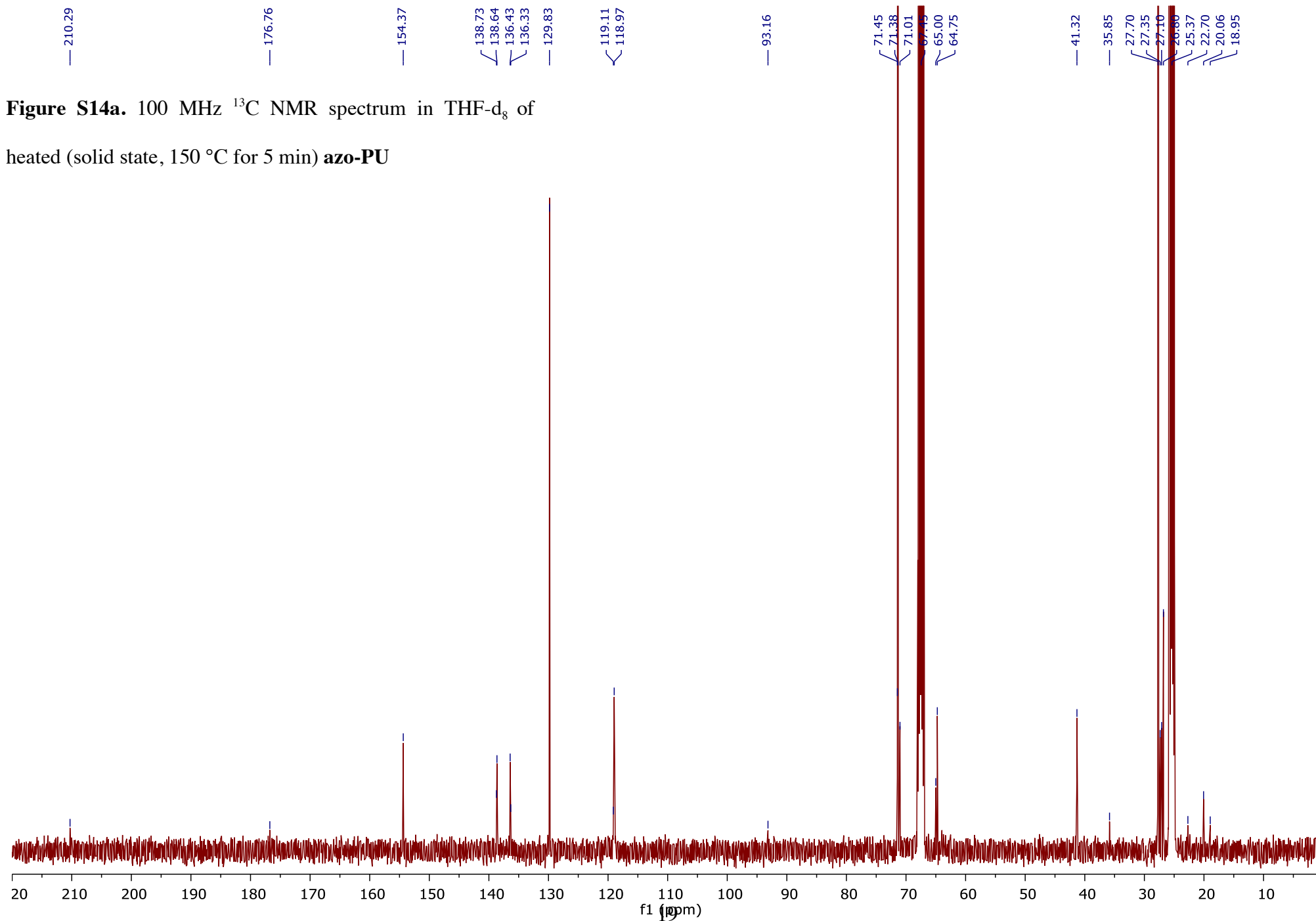
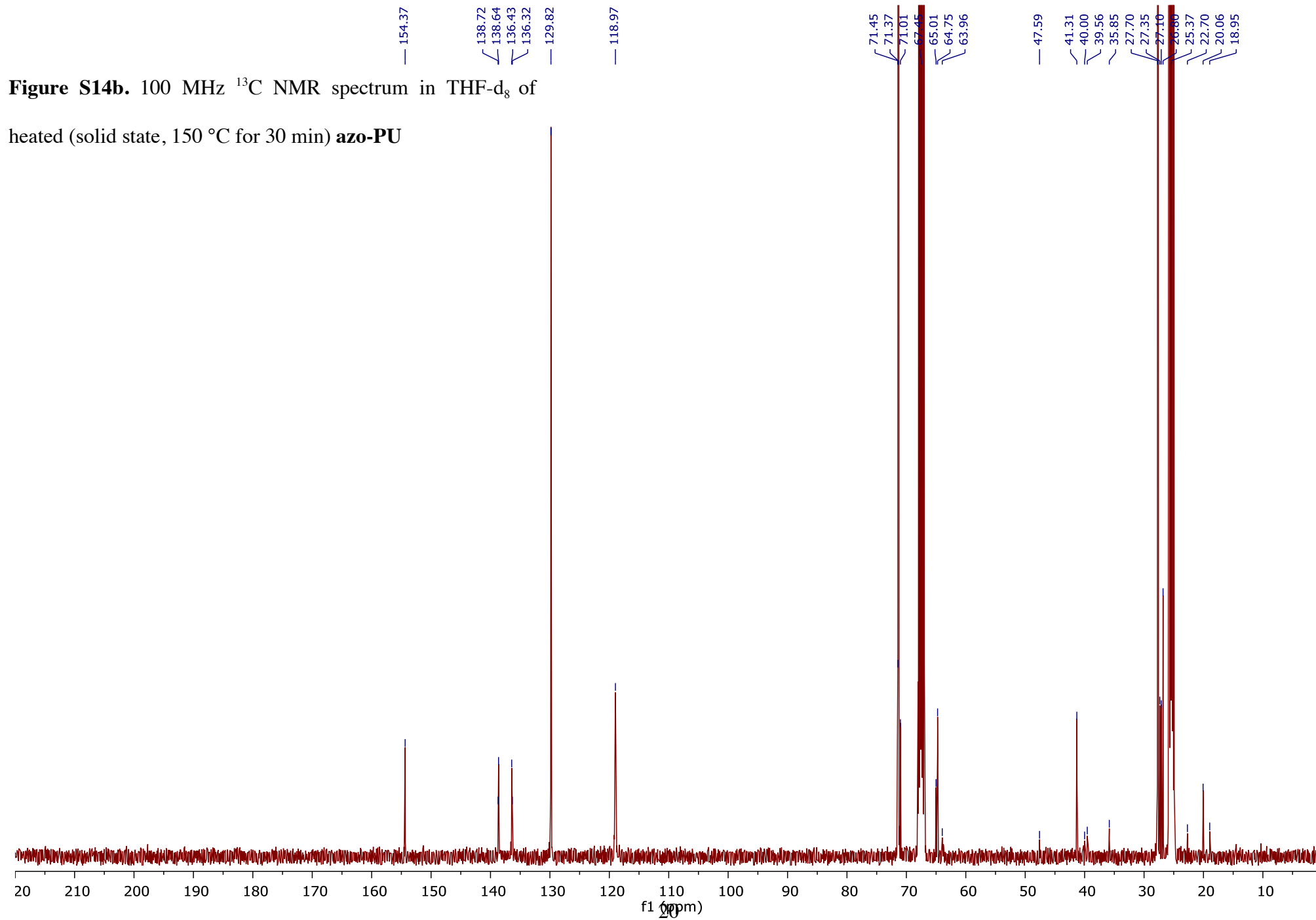
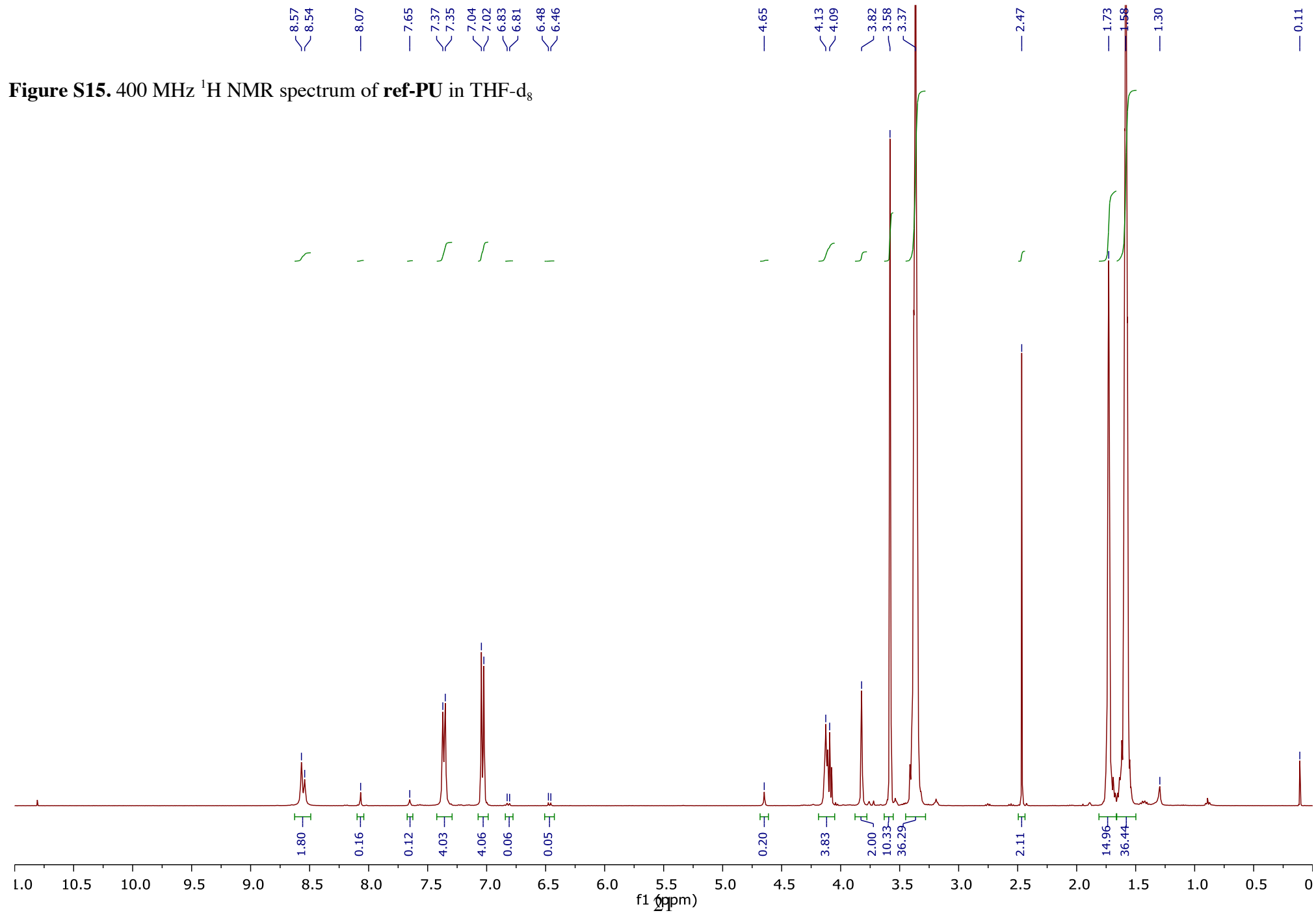


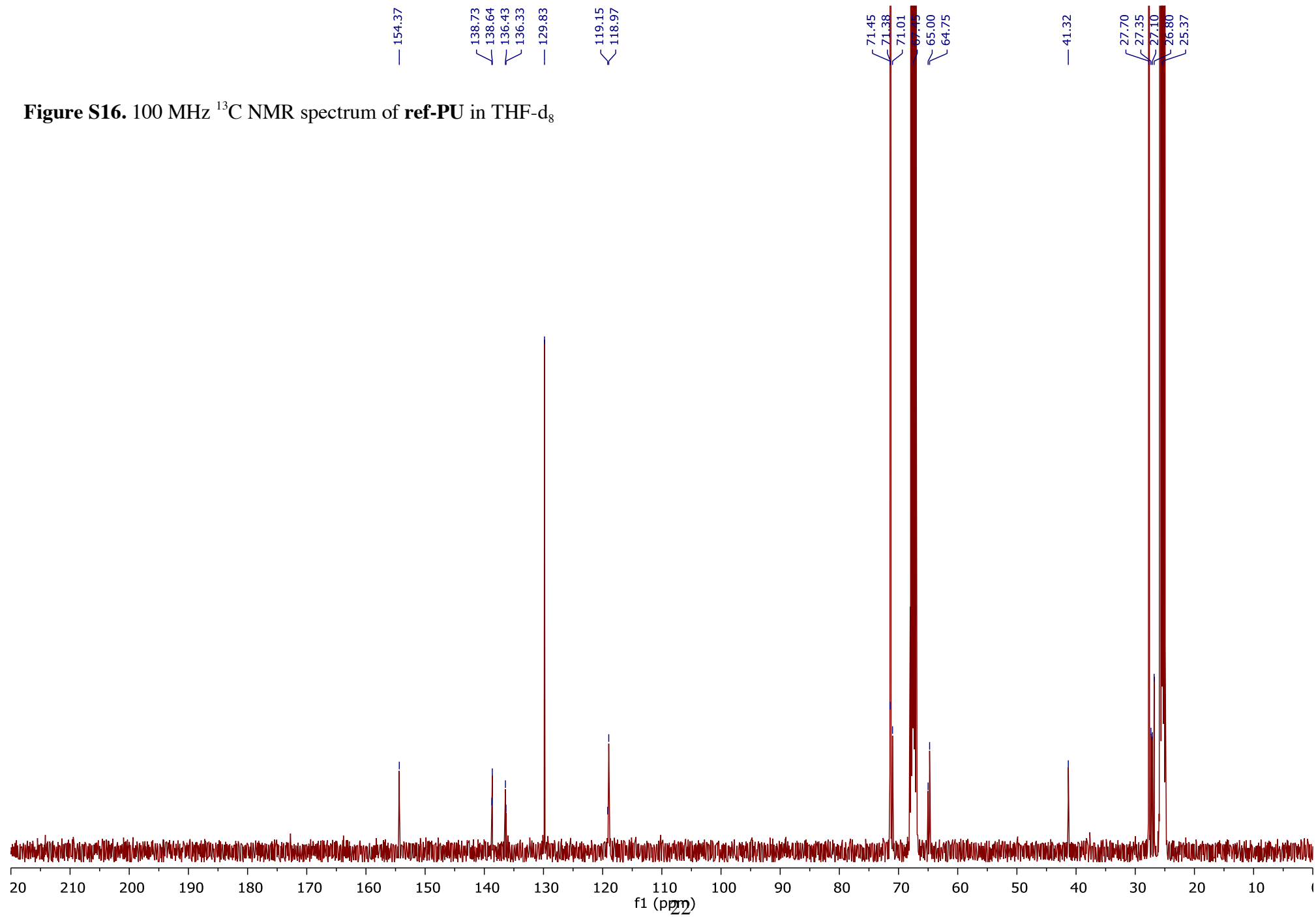
Figure S13c. Magnified 400 MHz ^1H NMR spectra in THF-d_8 of pristine and heated (solid state, 150 °C for 5 and 30 min) **azo-PU**











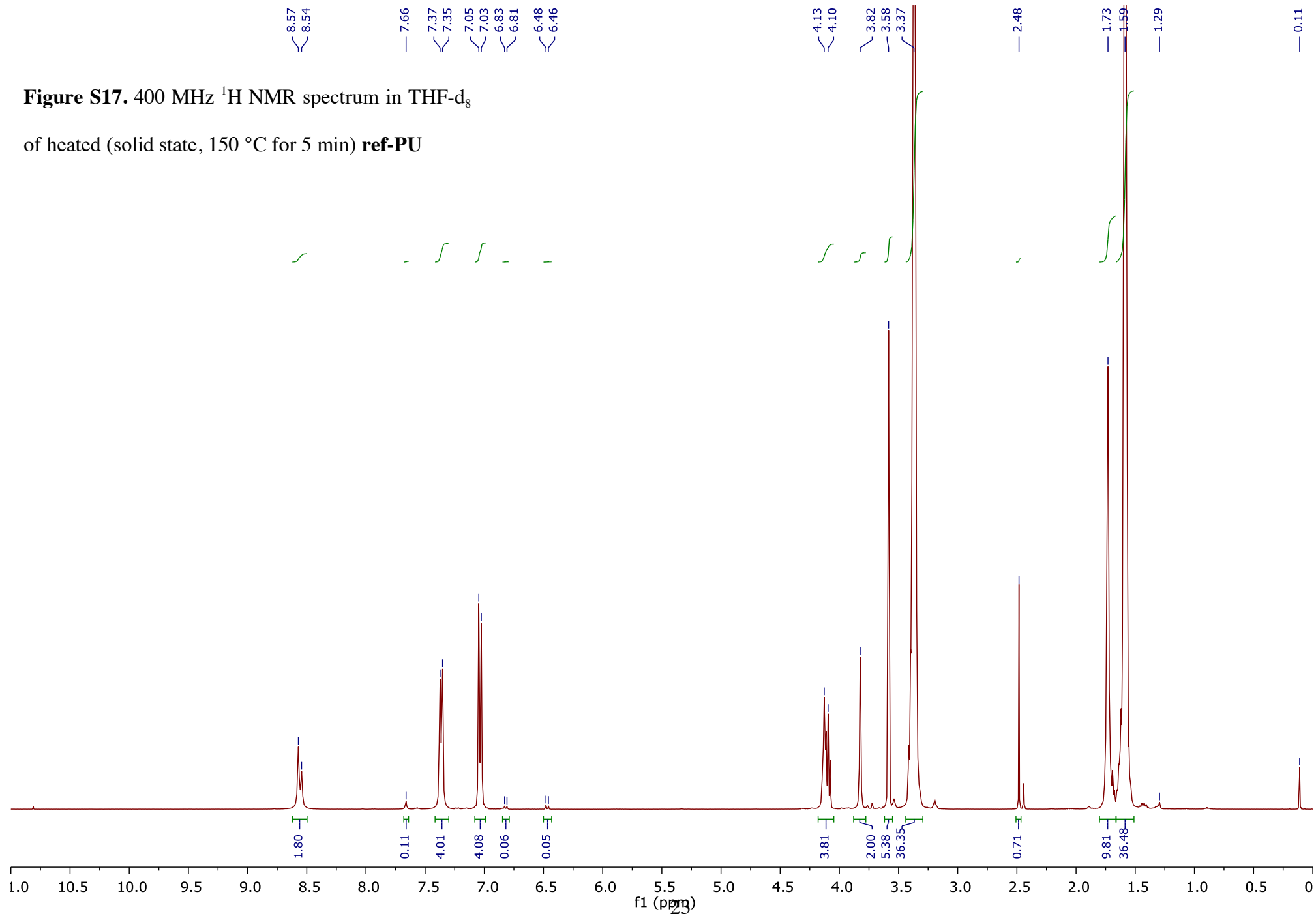
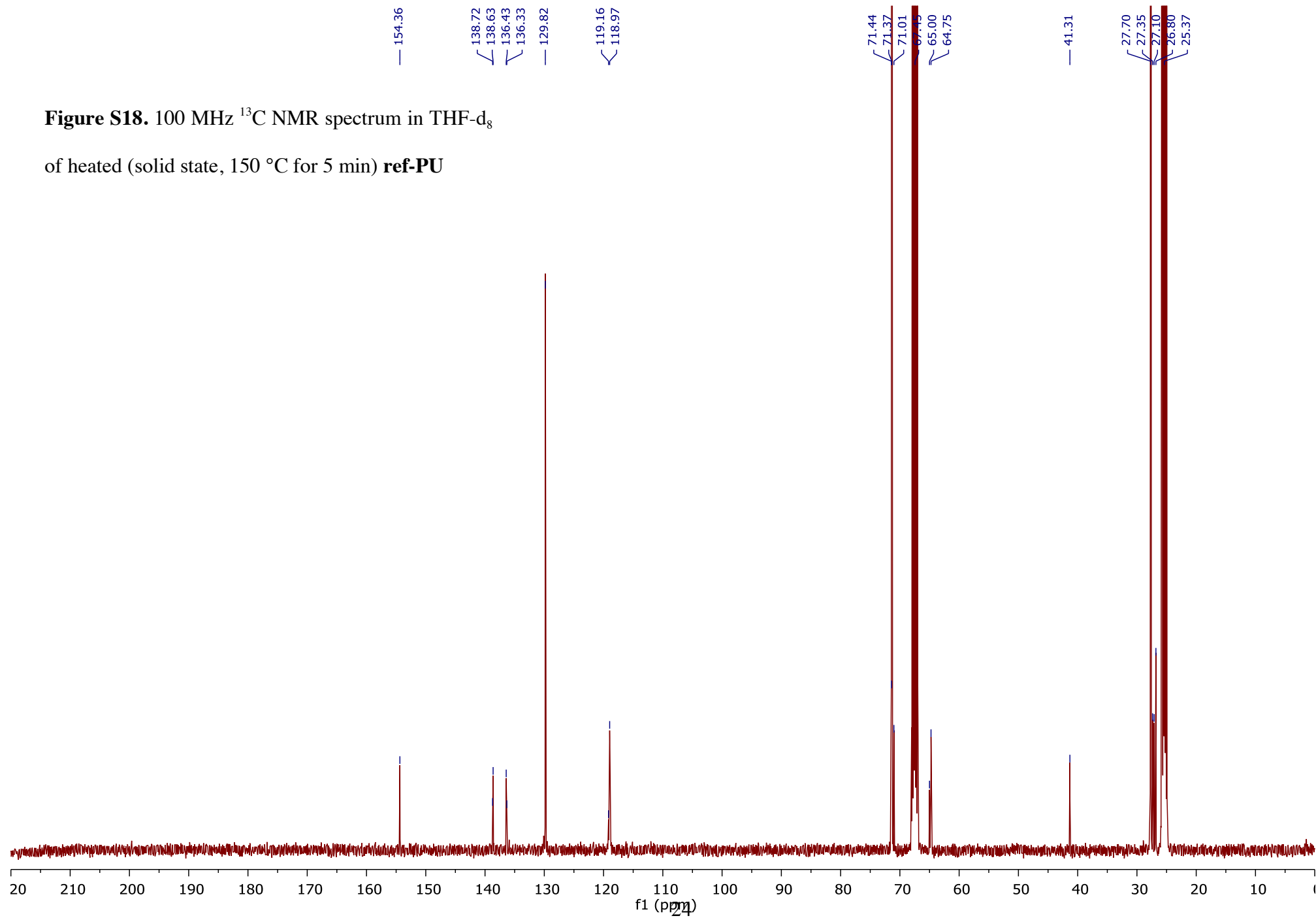


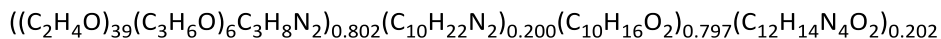
Figure S17. 400 MHz ¹H NMR spectrum in THF-d₈

of heated (solid state, 150 °C for 5 min) **ref-PU**



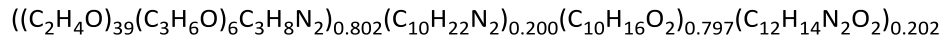
Elemental analyses (EA) of pristine and heated azo-PA, ref-PA, azo-PU, and ref-PU

Pristine azo-PA



Anal. Calcd: C, 57.03; H, 9.41; N, 2.04. Found: C, 56.5; H, 9.8; N, 2.0.

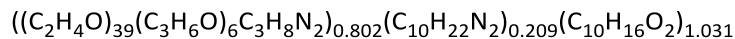
Heated azo-PA (solid state, 140 °C for 5 min)



Anal. Calcd: C, 57.19; H, 9.45; N, 1.75.* Found: C, 56.0; H, 9.7; N, 1.8.

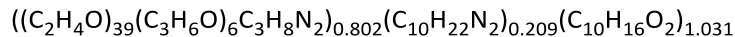
* Assuming dissociation of all azo groups, complete release of N₂, and quantitative recombination of the radicals produced.

Pristine ref-PA



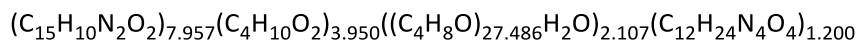
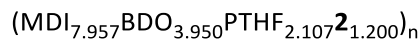
Anal. Calcd: C, 57.30; H, 9.51; N, 1.47. Found: C, 56.2; H, 9.9; N, 1.4.

Heated ref-PA (solid state, 140 °C for 5 min)



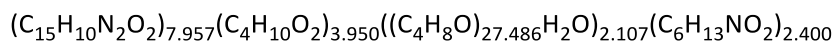
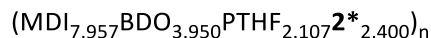
Anal. Calcd: C, 57.30; H, 9.51; N, 1.47. Found: C, 56.7; H, 9.8; N 1.4.

Pristine azo-PU



Anal. Calcd: C, 66.29; H, 8.98; N, 4.20. Found: C, 65.62; 9.25; N, 3.88.

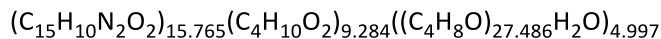
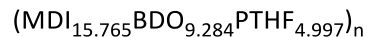
Heated azo-PU (solid state, 150 °C for 5 min)



Anal. Calcd: C, 66.59; H, 9.06; N, 3.73.* Found: C, 65.69; 9.20; N, 3.57.

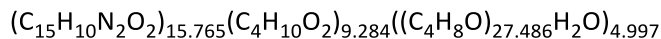
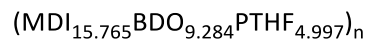
* Assuming dissociation of all azo groups, complete release of N₂, carbon-centered radicals formed and further reaction, i.e. proton abstraction or recombination.

Pristine ref-PU



Anal. Calcd: C, 66.90; H, 9.27; N, 2.99. Found: C, 66.33; H, 9.53; N, 2.87.

Heated ref-PU (solid state, 150 °C for 5 min)



Anal. Calcd: C, 66.90; H, 9.27; N, 2.99. Found: C, 67.1; H, 9.7; N, 2.8.

Thermogravimetric analyses (TGA)

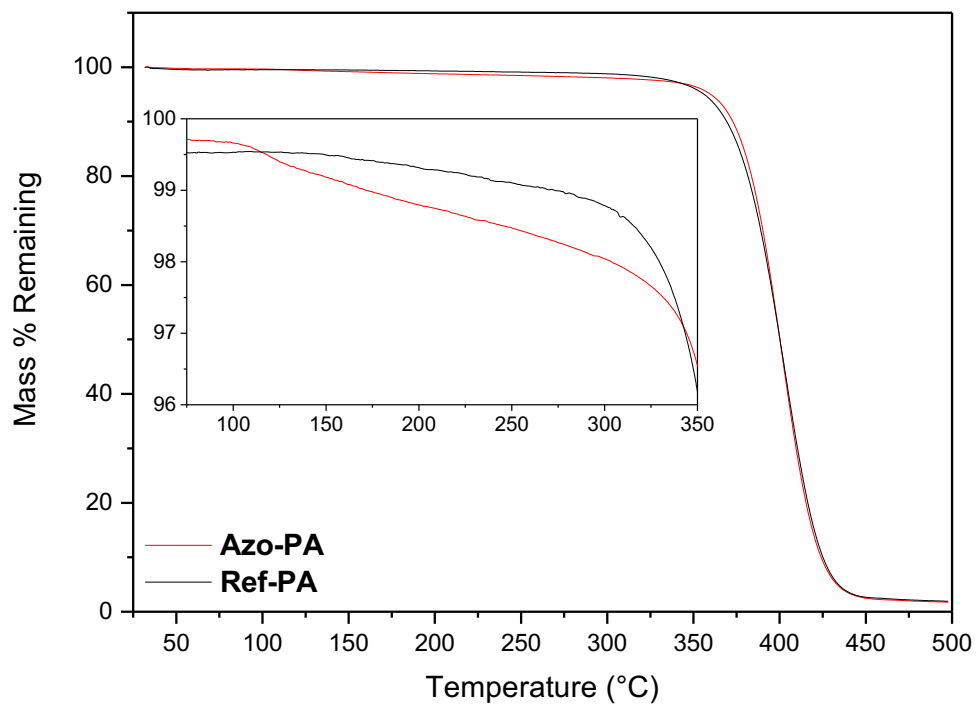


Figure S19. TGA traces of the azo-containing polyamide **azo-PA** (red) and the reference polymer **ref-PA** (black) performed under N_2 at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The samples were dried prior to measurement.

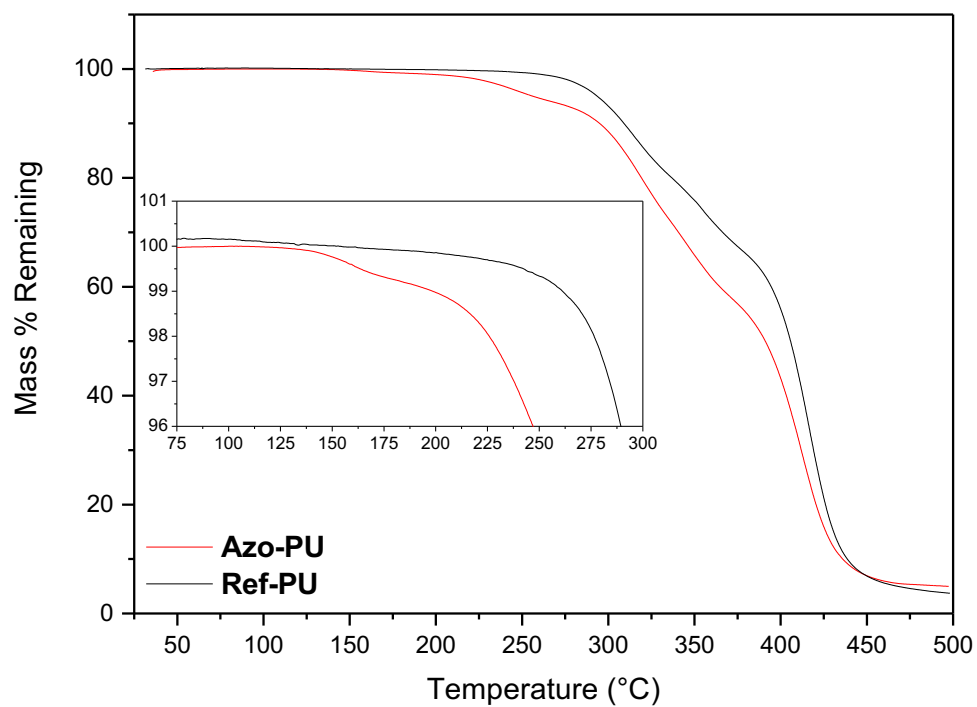


Figure S20. TGA traces of the azo-containing polyamide **azo-PU** (red) and the reference polymer **ref-PU** (black) performed under N₂ at a heating rate of 10 °C/min. The samples were dried prior to measurement.

Differential scanning calorimetry (DSC)

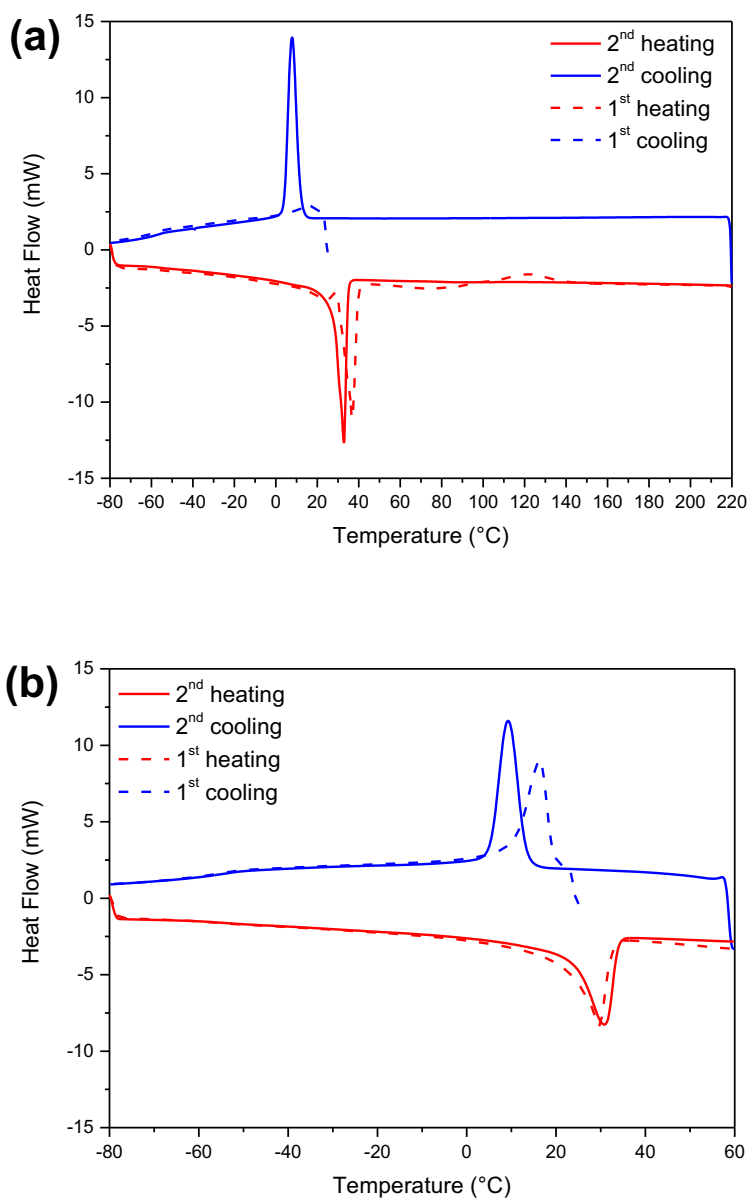


Figure S21. DSC thermograms of the azo-containing polyamide **azo-PA** recorded under N₂ at heating and cooling rates of 10 °C/min in the range from (a) -80 to 220 °C and (b) -80 to 60 °C. The samples (polymer film pieces) were dried prior to the measurements.

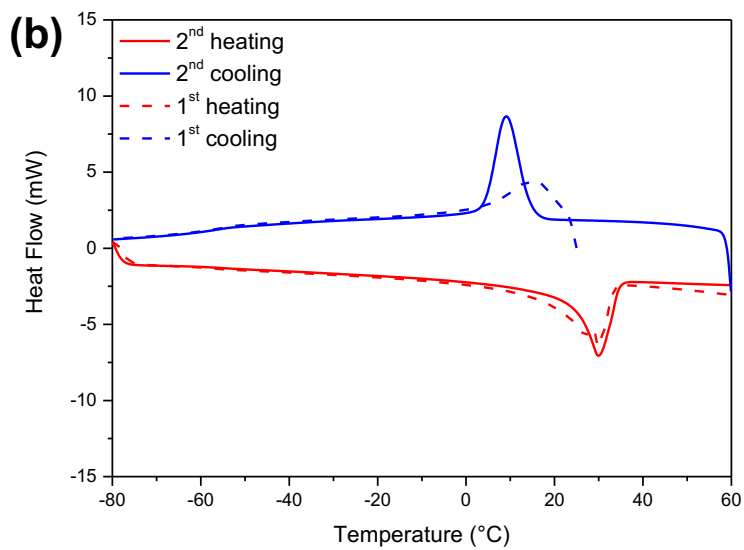
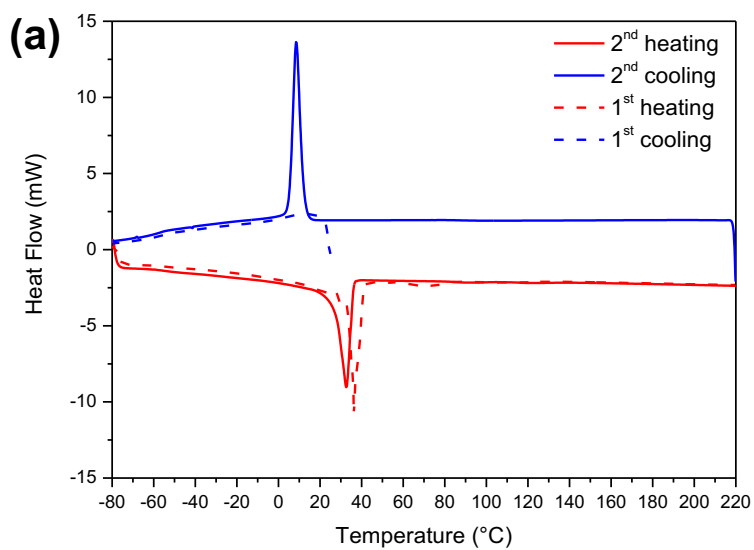


Figure S22. DSC thermograms of the reference polyamide **ref-PA** recorded under N₂ at heating and cooling rates of 10 °C/min in the range from (a) -80 to 220 °C and (b) -80 to 60 °C. The samples (polymer film pieces) were dried prior to measurement.

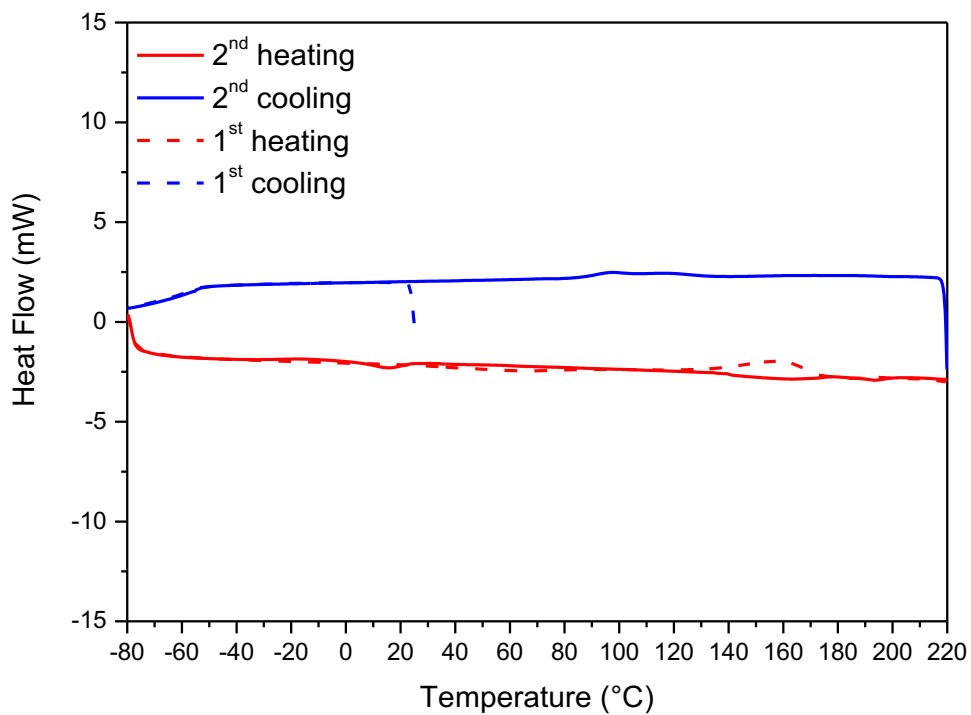


Figure S23. DSC thermograms of the azo-containing polyurethane **azo-PU** recorded under N₂ at heating and cooling rates of 10°C/min. The sample (polymer film piece) was dried prior to measurement.

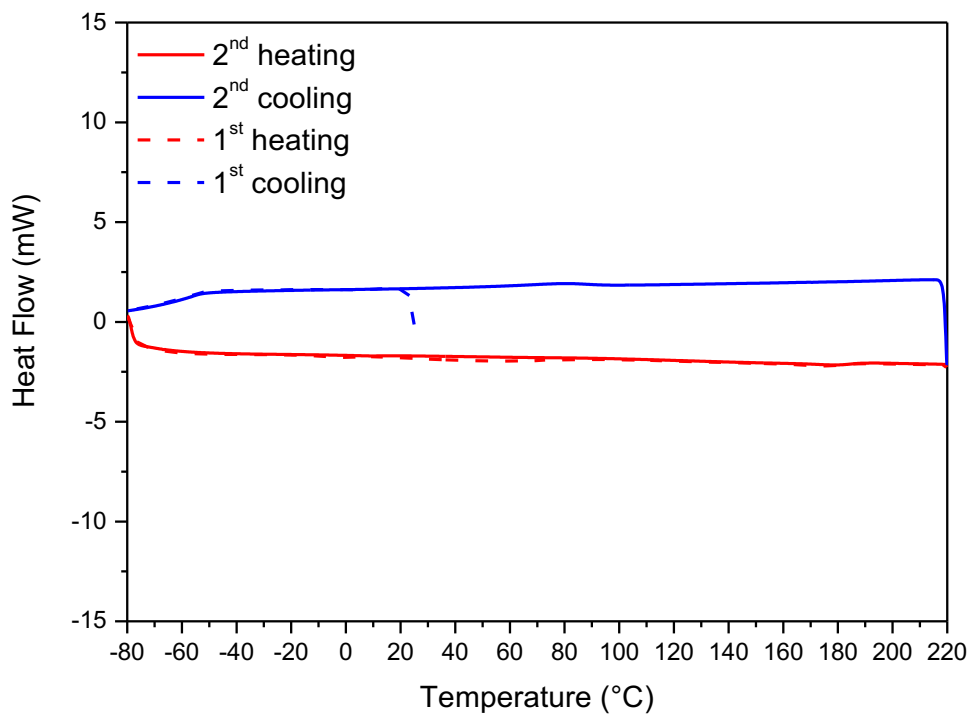
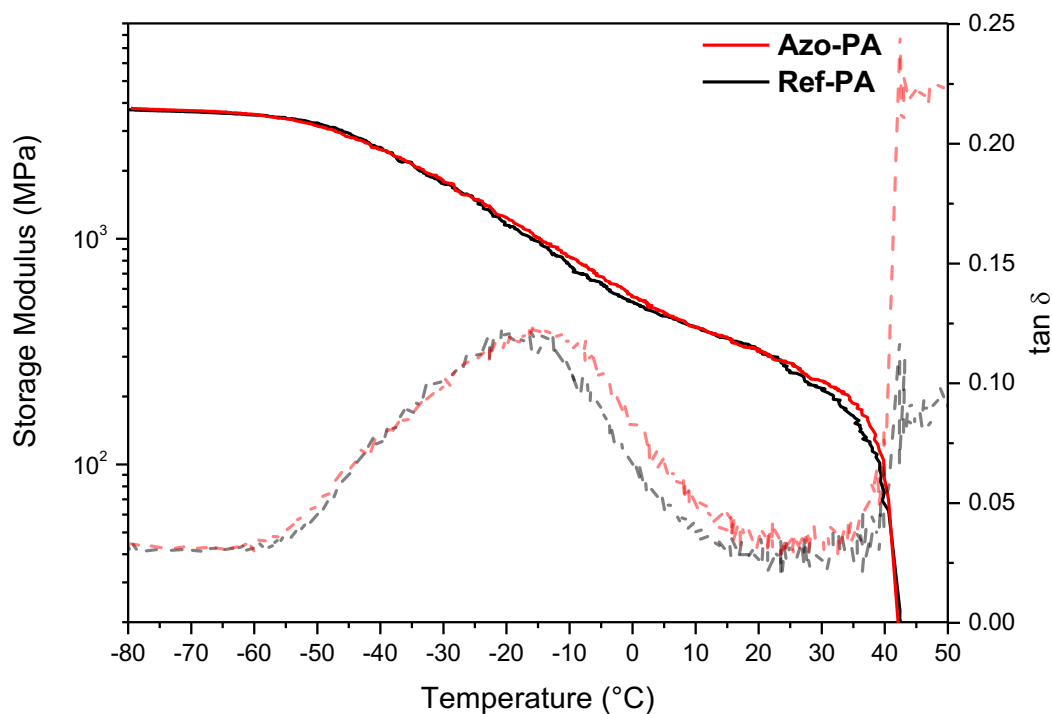


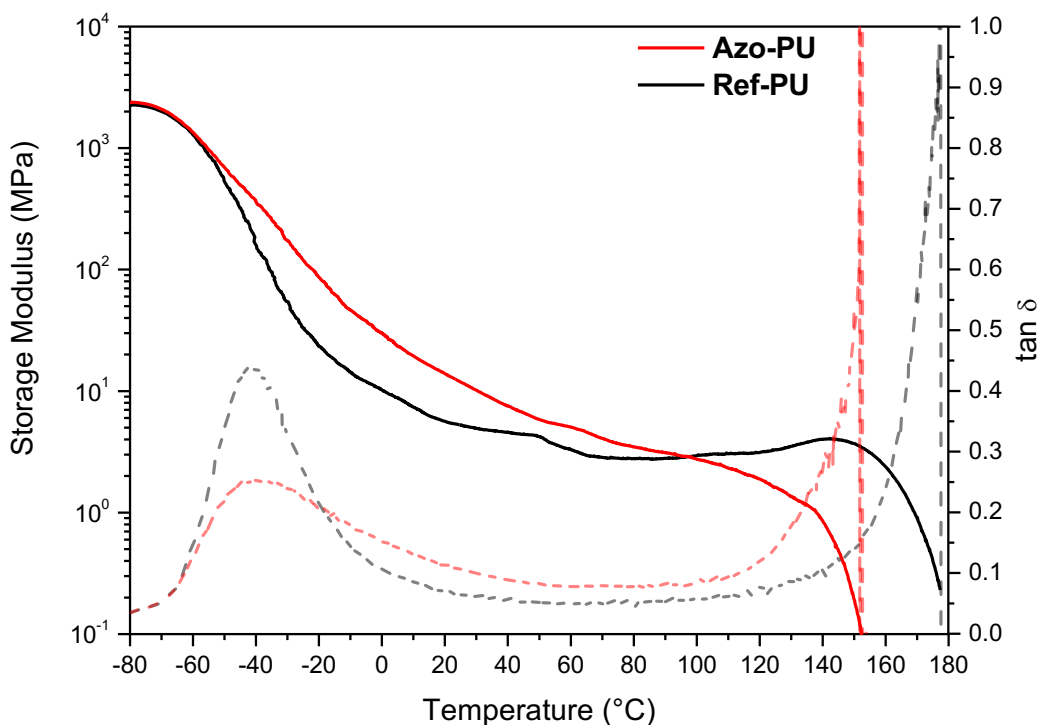
Figure S24. DSC thermogram of the reference polyurethane **ref-PU** recorded under N₂ at heating and cooling rates of 10°C/min. The sample (polymer film piece) was dried prior to measurement.

Dynamic mechanical analyses (DMA)



	E' at -70°C (MPa)	E' at 25°C (MPa)	T_g (°C)
Azo PA	3639 ± 47	234 ± 41	-15 ± 2
Ref- PA	3773 ± 189	264 ± 5	-21 ± 1

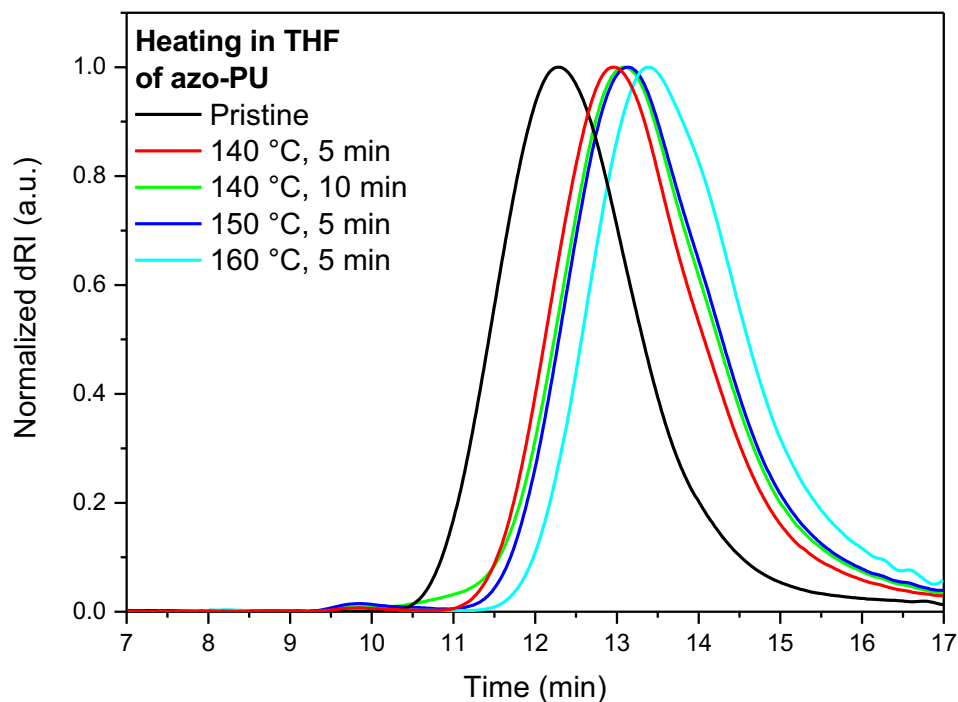
Figure S25. Representative dynamic mechanical analysis (DMA) traces of films of the azo-containing polyamide **azo-PA** (solid red line) and the reference polymer **ref-PA** (black line). The loss tangent ($\tan \delta$) traces of the **azo-PA** (dashed red line) and the reference polymer **ref-PA** (dashed black line) are also shown. The measurements were carried out at a heating rate of 3 °C/min and a frequency of 1 Hz under N₂. The storage moduli (E') at -70 and 25 °C and the glass transition temperatures (T_g , determined from the maxima of the $\tan \delta$ traces) are also reported. Values indicated in the table are averages of 3 samples.



	E' at -70°C (MPa)	E' at 25°C (MPa)	E' at 50°C (MPa)	T_g ($^{\circ}\text{C}$)
Azo-PU	2104 ± 274	18 ± 3	11 ± 3	-38 ± 4
Ref-PU	1993 ± 135	6 ± 3	5 ± 3	-41 ± 2

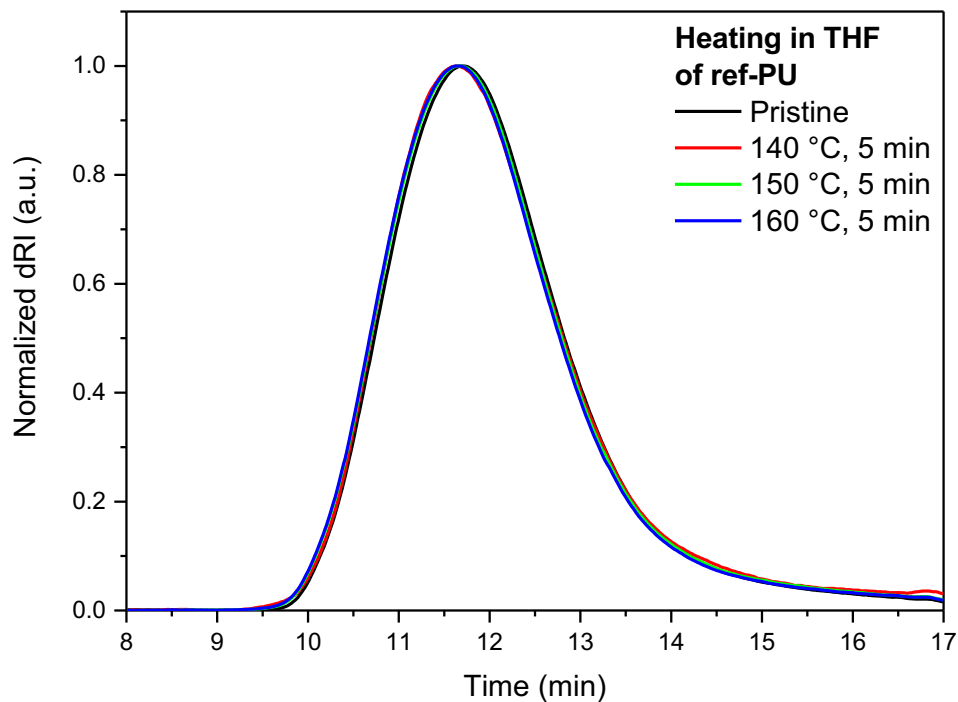
Figure S26. Representative dynamic mechanical analysis (DMA) traces of films of the azo-containing polyurethane **azo-PU** (solid red line) and the reference polymer **ref-PU** (black line). The loss tangent ($\tan \delta$) traces of the **azo-PU** (dashed red line) and the reference polymer **ref-PU** (dashed black line) are also shown. The measurements were carried out at a heating rate of $3^{\circ}\text{C}/\text{min}$ and a frequency of 1 Hz under N_2 . The storage moduli (E') at -70 and 25°C and the glass transition temperatures (T_g , determined from the maxima of the $\tan \delta$ traces) are also reported. Values indicated in the table are averages of 3 samples.

Heating in solution (THF): size exclusion chromatography (SEC) traces of polyurethanes



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	93,700	49,300	1.90
140 °C, 5 min	57,500	27,500	2.09
140 °C, 10 min	56,100	24,600	2.28
150 °C, 5 min	48,900	23,100	2.12
160 °C, 5 min	37,600	18,500	2.03

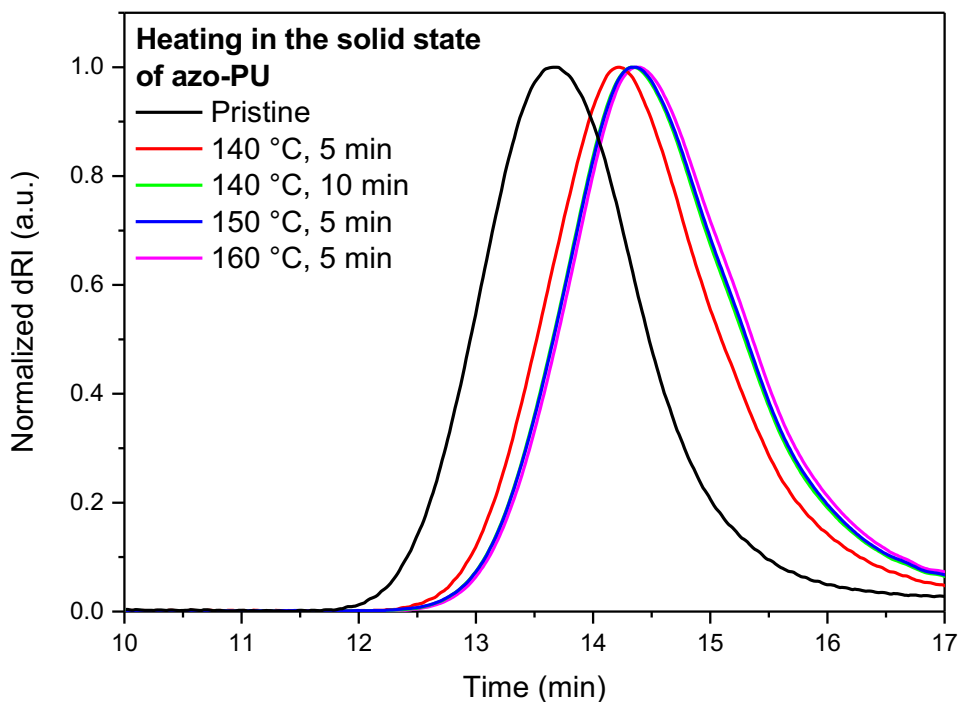
Figure S27. Size exclusion chromatography (SEC) traces of a pristine sample of the azo-containing polyurethane **azo-PU** (black line) and samples of **azo-PU** after heat treatment in solution (THF, microwave synthesizer), at 140 °C for 5 min (red line), 140 °C for 10 min (green line), 150 °C for 5 min (blue line) and 160 °C for 5 min (magenta line). The weight-average (M_w) and number-average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	204,700	93,600	2.19
140 °C, 5 min	196,700	92,500	2.13
150 °C, 5 min	199,600	94,400	2.11
160 °C, 5 min	202,300	96,100	2.11

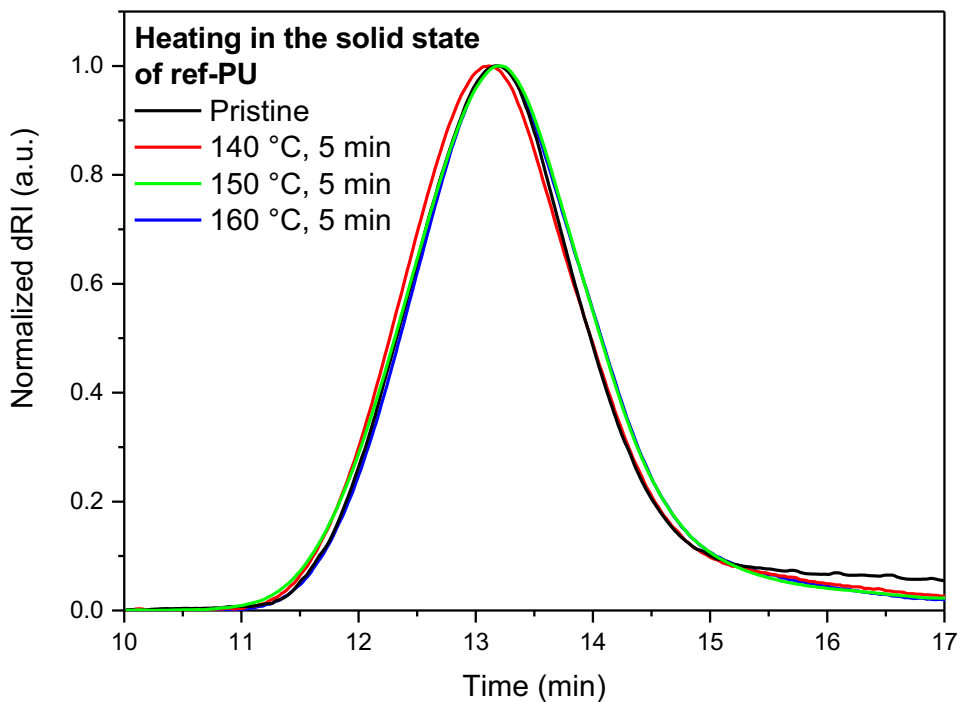
Figure S28. Size exclusion chromatography (SEC) traces of a pristine sample of the reference polyurethane **ref-PU** (black line) and samples of **ref-PU** after heat treatment in solution (THF, microwave synthesizer), at 140 °C for 5 min (red line), 150 °C for 5 min (green line) and 160 °C for 5 min (blue line). The weight-average (M_w) and number-average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).

Heating in the solid state: size exclusion chromatography (SEC) traces of polyurethanes



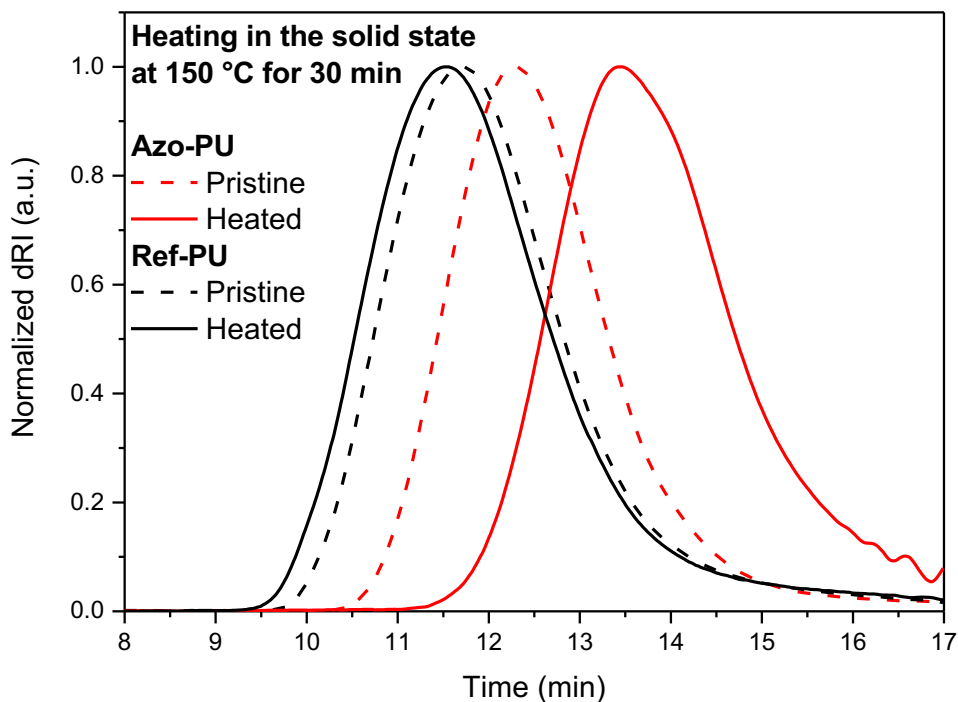
	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	93,700	49,300	1.90
140 °C, 5 min	47,100	22,700	2.07
140 °C, 10 min	39,300	18,500	2.12
150 °C, 5 min	38,400	16,400	2.34
160 °C, 5 min	36,800	15,700	2.34

Figure S29. Size exclusion chromatography (SEC) traces of a pristine sample of the azo-containing polyurethane **azo-PU** (black line) and samples of **azo-PU** after heat treatment in the solid state (pre-heated hot press), 140 °C for 5 min (red line), 140 °C for 10 min (green line), 150 °C for 5 min (blue line) and 160 °C for 5 min (magenta line). The weight-average (M_w) and number-average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	204,700	93,600	2.19
140 °C, 5 min	210,800	93,700	2.25
150 °C, 5 min	208,200	91,800	2.27
160 °C, 5 min	196,400	91,000	2.16

Figure S30. Size exclusion chromatography (SEC) traces of a pristine sample of the reference polyurethane **ref-PU** (black line) and samples of **ref-PU** after heat treatment in the solid state (pre-heated hot press), 140 °C for 5 min (red line), 150 °C for 5 min (green line) and 160 °C for 5 min (blue line). The weight-average (M_w) and number-average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine azo-PU	93,700	49,300	1.90
150 °C, 30 min	36,400	14,100	2.58
Pristine ref-PU	204,700	93,600	2.19
150 °C, 30 min	228,800	98,100	2.33

Figure S31. Size exclusion chromatography (SEC) traces of pristine samples of the azo-containing and reference polyurethanes **azo-PU** and **ref-PU** (red and black dashed lines) and samples of **azo-PU** and **ref-PU** after heat treatment in the solid state (pre-heated hot press) at 150 °C for 30 min (red and black solid lines). The weight-average (M_w) and number-average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).

UV light irradiation in solution (THF): UV-Vis spectrum of the azo compound **2 and size exclusion chromatography (SEC) traces of polyurethanes**

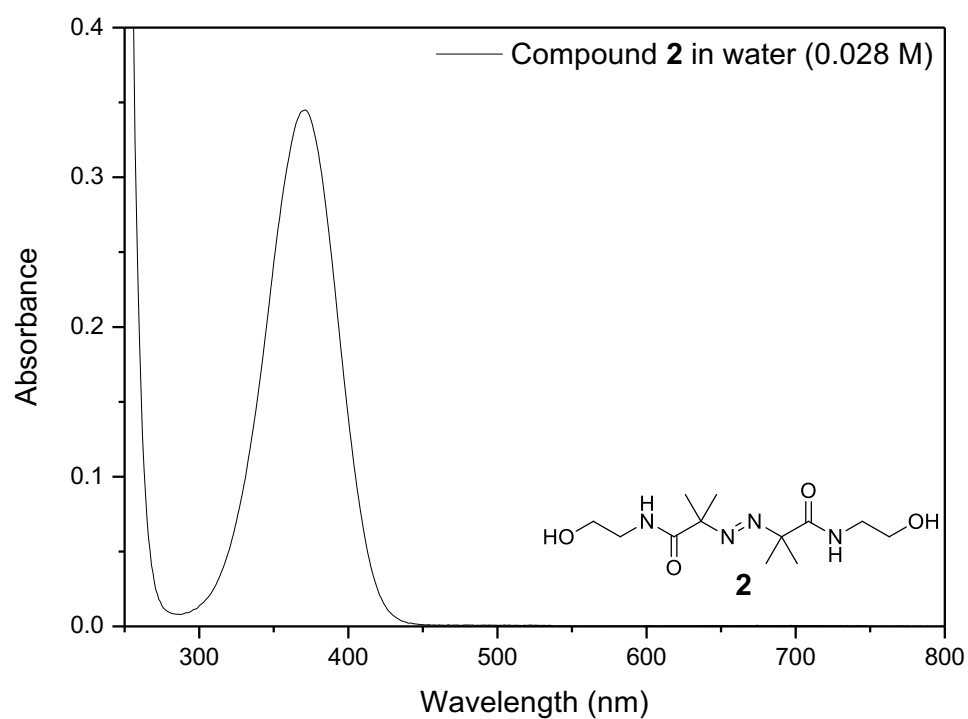
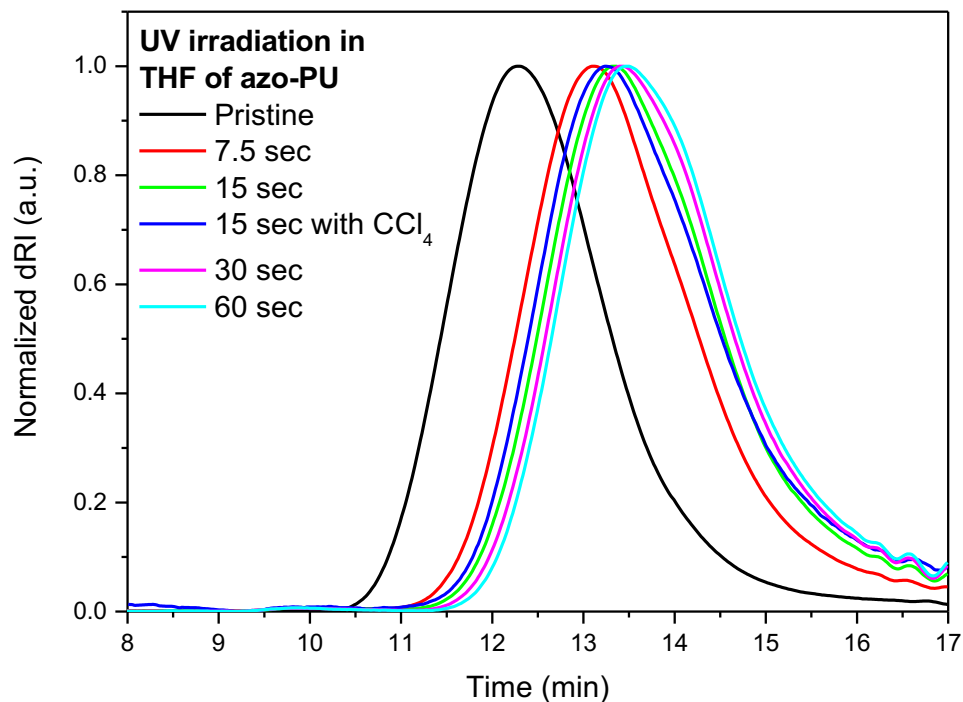
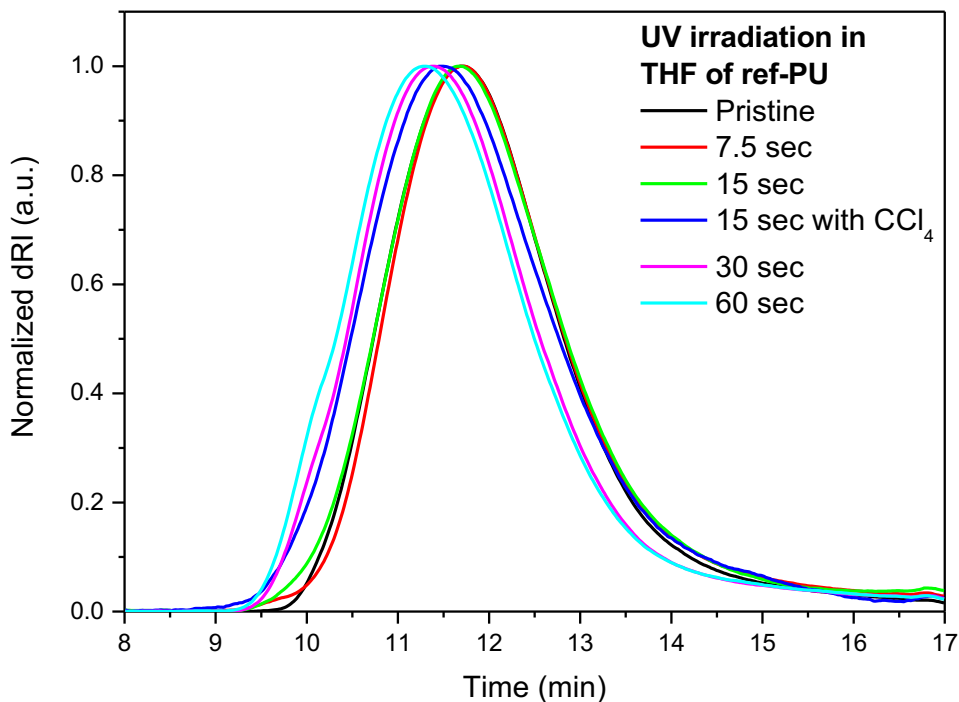


Figure S32. UV-Vis spectrum of the azo compound **2** in water (0.028 M). The extinction coefficient (371 nm) is $12.32 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	93,700	49,300	1.90
7.5 sec	53,100	30,900	1.72
15 sec	41,200	23,700	1.74
15 sec with CCl₄	44,500	24,400	1.82
30 sec	41,200	22,200	1.76
60 sec	36,000	21,000	1.71

Figure S33. Size exclusion chromatography (SEC) traces of a pristine sample of azo-containing polyurethane **azo-PU** (black line) and samples of **azo-PU** after exposure to UV light in solution (THF, 320-390 nm, 600 mW/cm²), for 7.5 sec (red line), for 15 sec (green line), for 15 sec with CCl₄ (blue line), for 30 sec (magenta line) and for 60 sec (cyan line). The weight-average (M_w) and number-average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	204,700	93,600	2.19
7.5 sec	189,700	93,800	2.02
15 sec	200,300	95,400	2.10
15 sec with CCl₄	234,400	97,800	2.40
30 sec	255,900	105,800	2.42
60 sec	277,600	110,600	2.51

Figure S34. Size exclusion chromatography (SEC) traces of a pristine sample of the reference polyurethane **ref-PU** (black line) and samples of **ref-PU** after exposure to UV light in solution (THF, 320-390nm, 600 mW/cm²), for 7.5 sec (red line), for 15 sec (green line), for 15 sec with CCl₄ (blue line), for 30 sec (magenta line) and for 60 sec (cyan line). The weight-average (M_w) and number-average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).

UV light irradiation in the solid state of polyurethanes: UV-Vis spectra, set-up picture, size exclusion chromatography (SEC) traces and temperature vs. time diagrams

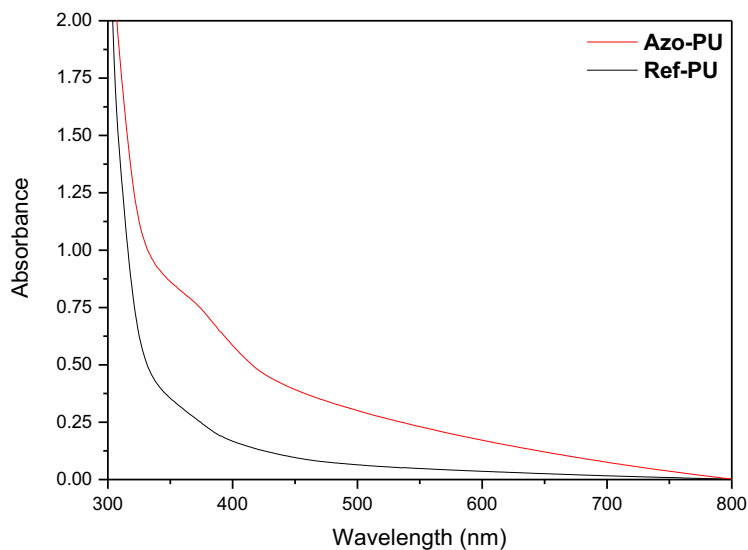


Figure S35. UV-Vis spectra of solid state samples of the azo-containing polyurethane **azo-PU** (red line) and the reference polymer **ref-PU** (black line).

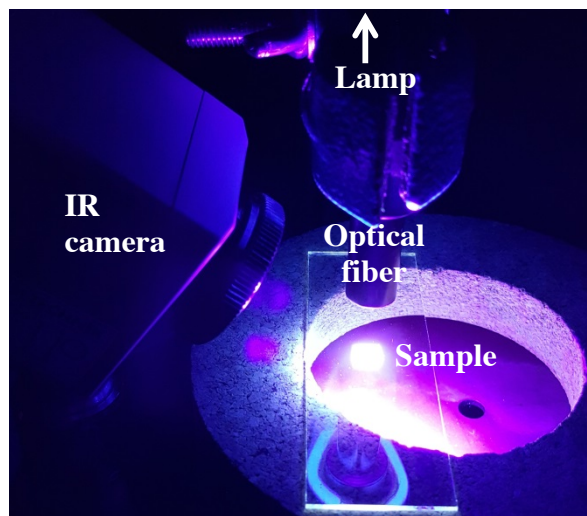
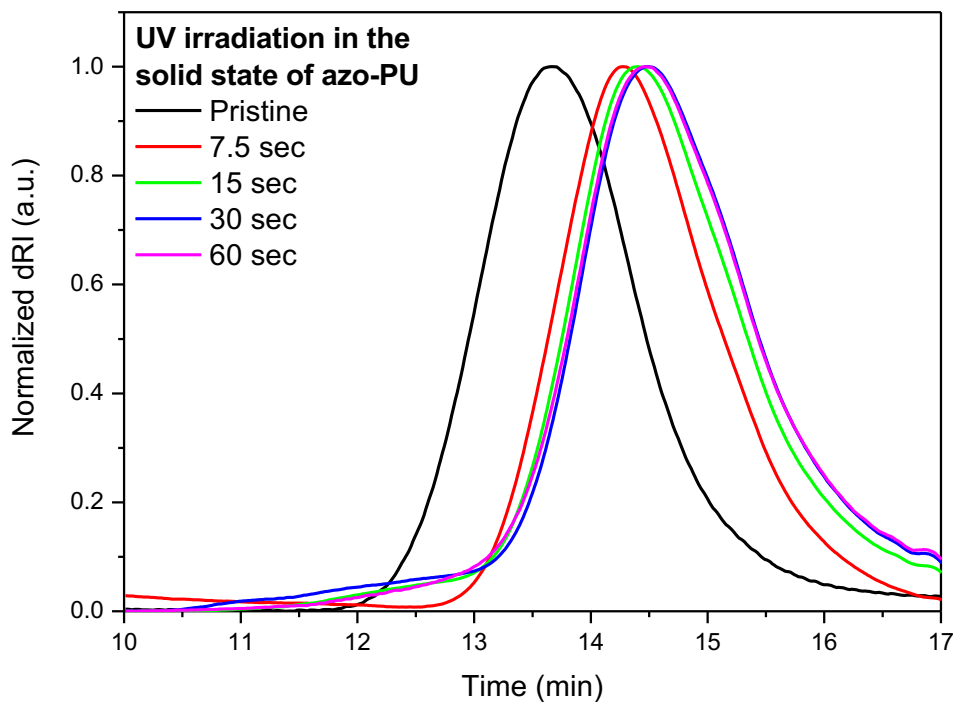


Figure S36. Picture depicting the set-up used for the light irradiation processes. The sample (5x5 mm) deposited on a glass slide was irradiated from the top (15 mm distance) and its temperature was monitored with an IR camera from the left.



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	93,700	49,300	1.90
7.5 sec	40,200	20,000	2.01
15 sec	49,300	15,700	3.14
30 sec	65,500	15,200	4.31
60 sec	47,000	14,900	3.15

Figure S37. Size exclusion chromatography (SEC) traces of a pristine sample of the azo-containing polyurethane **azo-PU** (black line) and samples of **azo-PU** after exposure to UV light in the solid state (320-390 nm, 600 mW/cm²), for 7.5 sec (red line), for 15 sec (green line), for 30 sec (blue line) and for 60 sec (magenta line). The weight average (M_w) and number average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).

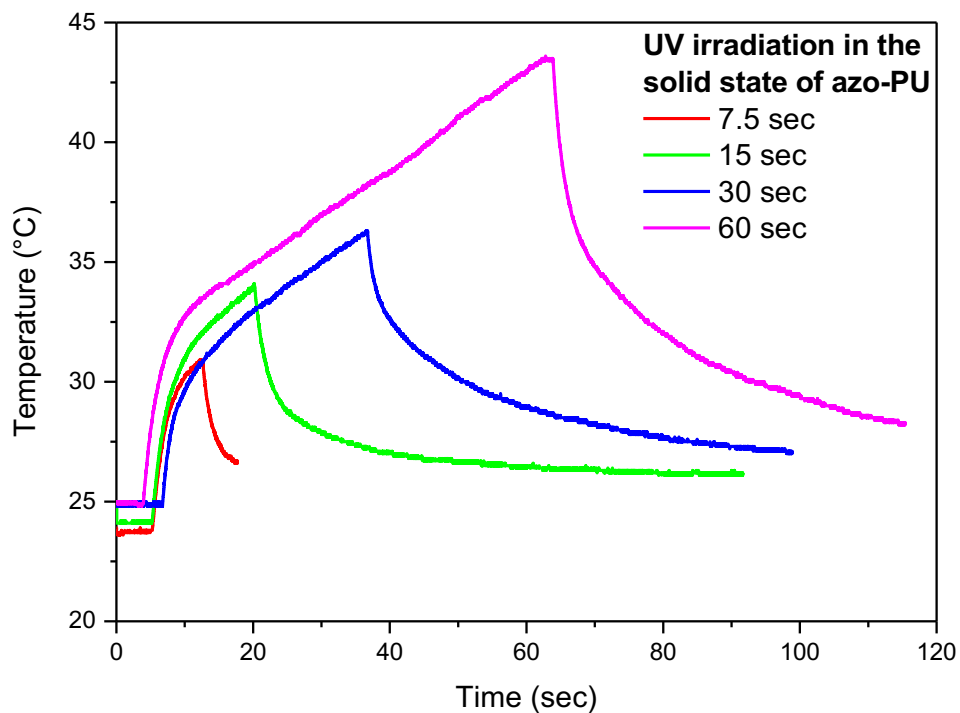
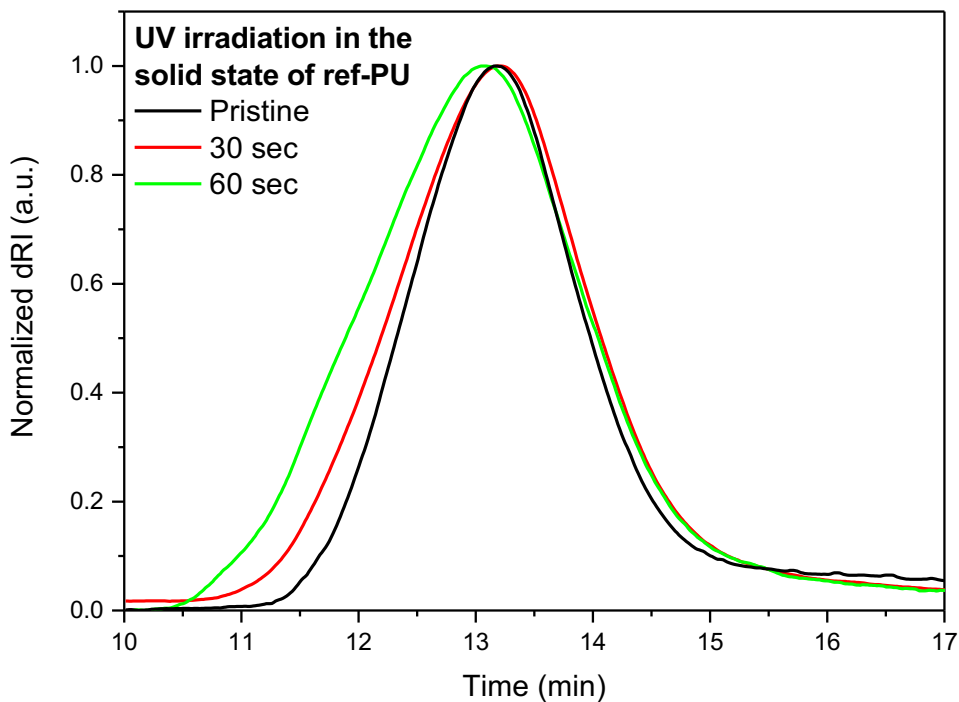


Figure S38. Temperature vs. time curves of azo-containing polyurethane **azo-PU** samples irradiated with UV light in the solid state (320-390 nm, 600 mW/cm²), for 7.5 sec (red line), for 15 sec (green line), for 30 sec (blue line) and for 60 sec (magenta line). The temperature was monitored with an IR camera.



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	204,700	93,600	2.19
30 sec	244,000	93,400	2.61
60 sec	333,500	110,600	3.02

Figure S39. Size exclusion chromatography (SEC) traces of a pristine sample of the reference polyurethane **ref-PU** (black line) and samples of **ref-PU** after exposure to UV light in the solid state (320-390 nm, 600 mW/cm²), for 30 sec (red line) and for 60 sec (green line). The weight-average (M_w) and number-average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).

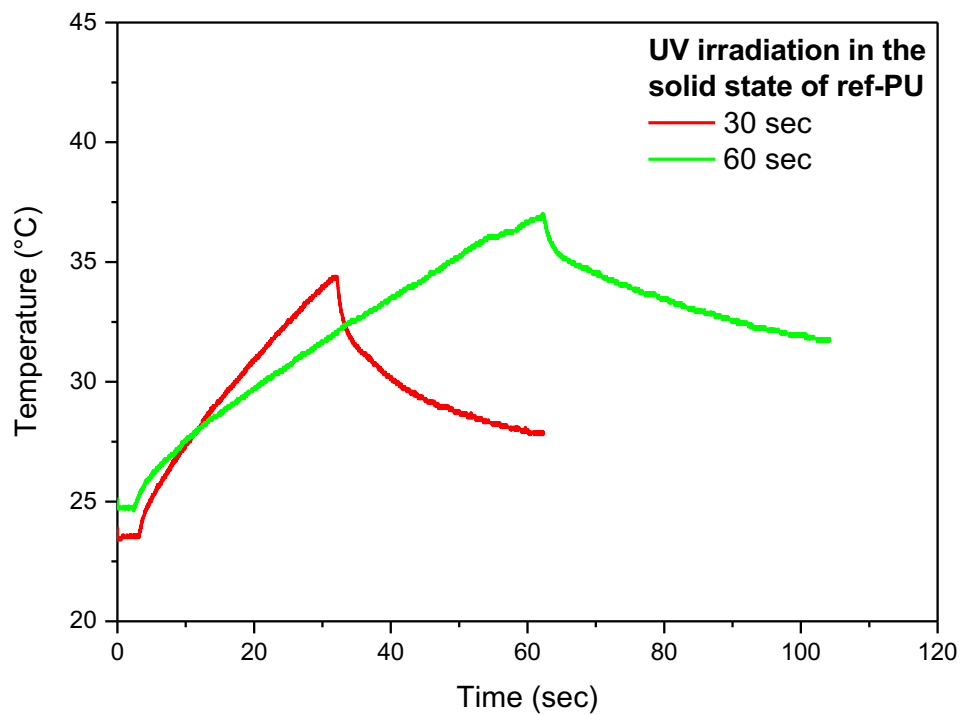
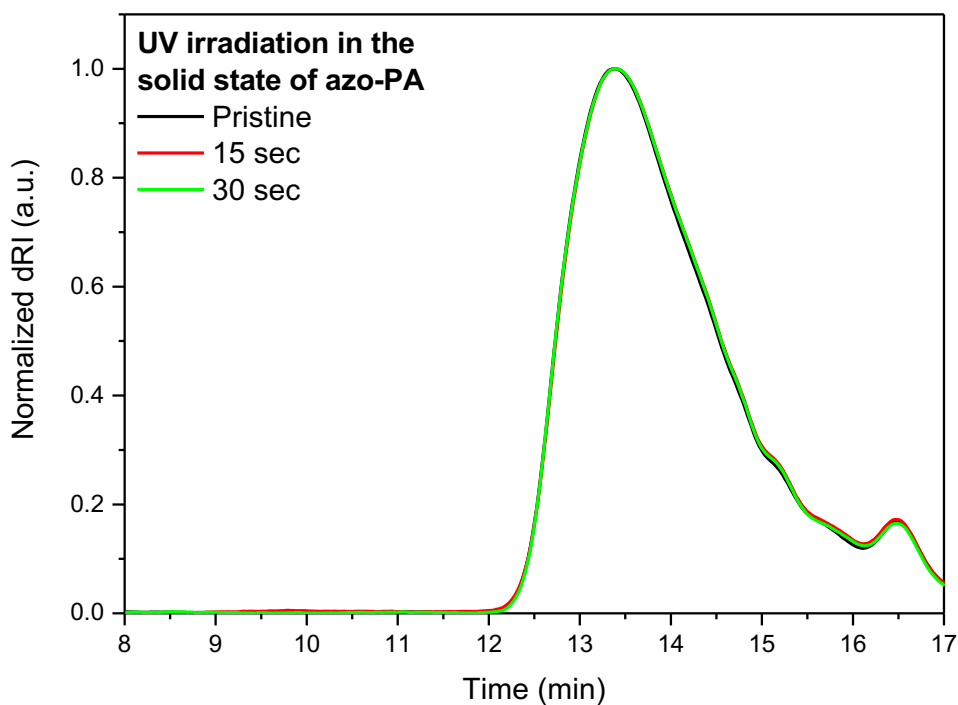


Figure S40. Temperature vs. time curves of reference polyurethane **ref-PU** samples irradiated with UV light in the solid state (320-390 nm, 600 mW/cm²), for 30 sec (red line) and 60 sec (green line). The temperature was monitored with an IR camera.

UV light irradiation in the solid state of polyamides: size exclusion chromatography (SEC) traces and temperature vs. time diagrams



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	33,000	23,400	1.41
15 sec	34,000	23,300	1.46
30 sec	34,100	23,300	1.46

Figure S41. Size exclusion chromatography (SEC) traces of a pristine sample of the azo-containing polyamide **azo-PA** (black line) and samples of **azo-PA** after exposure to UV light in the solid state (320-390 nm, 600 mW/cm²), for 15 sec (red line) and for 30 sec (green line). The weight average (M_w) and number average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).

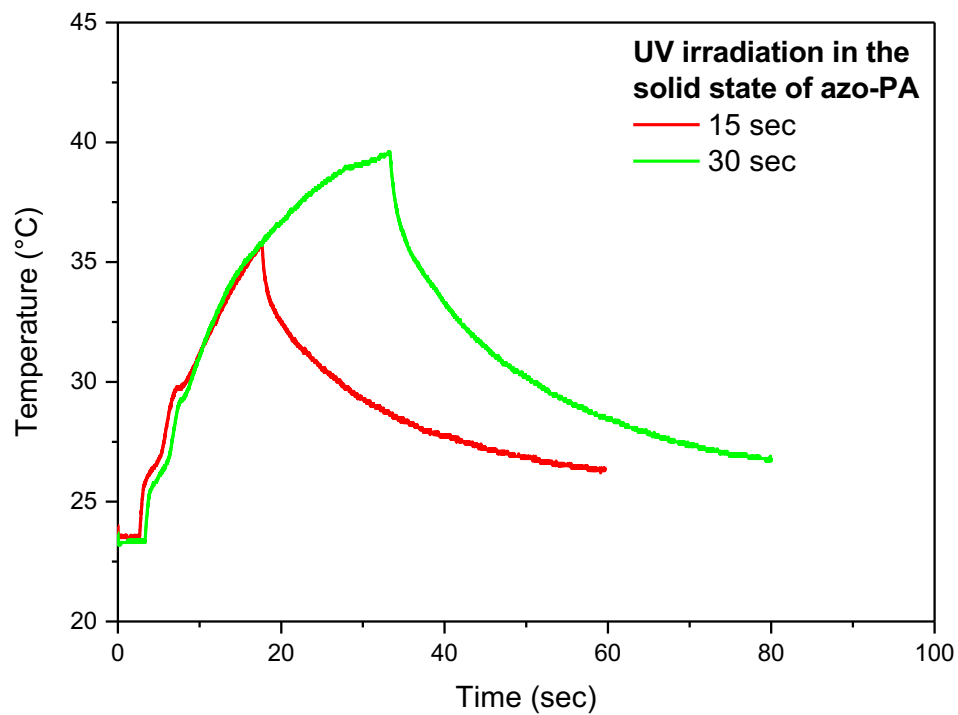


Figure S42. Temperature vs. time curves of azo-containing polyamide **azo-PA** samples irradiated with UV light in the solid state (320-390 nm, 600 mW/cm²), for 15 sec (red line) and for 30 sec (green line). The temperature was monitored with an IR camera.

UV light irradiation in the solid state of dogbone shaped specimens of polyurethanes: set-up pictures and temperature vs. time diagrams

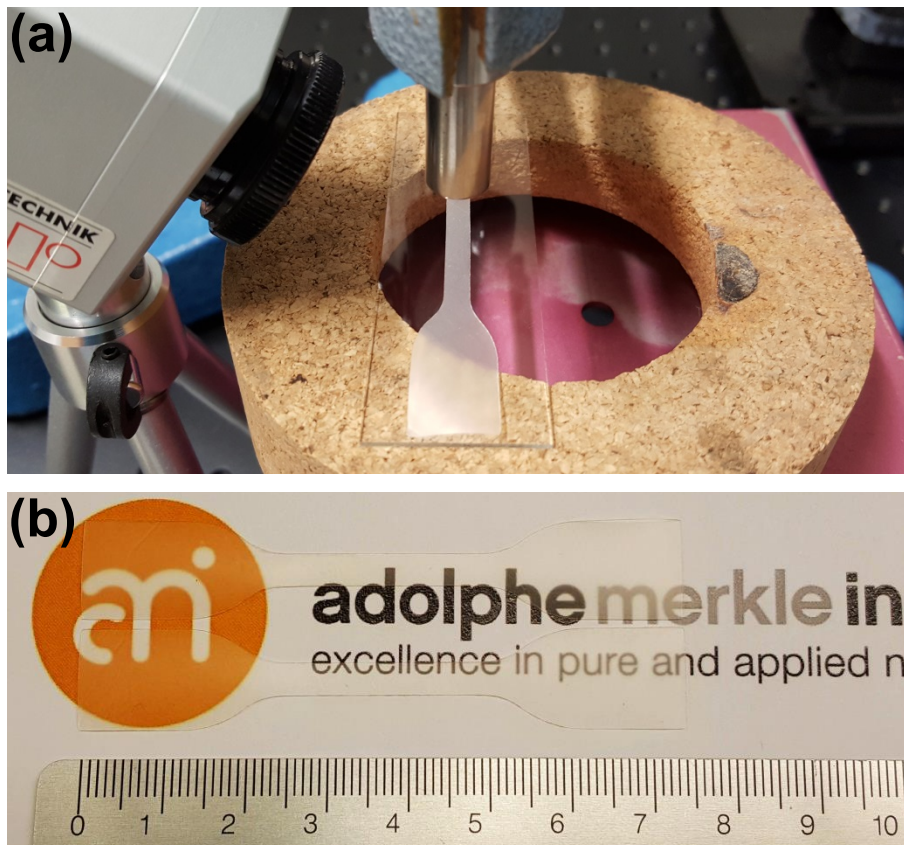
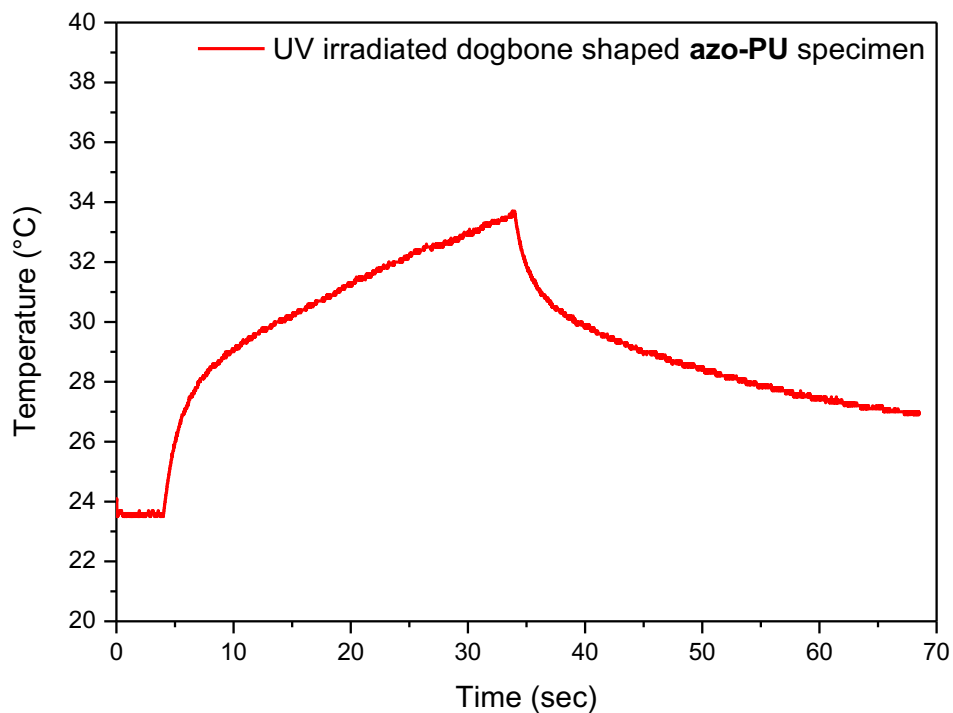
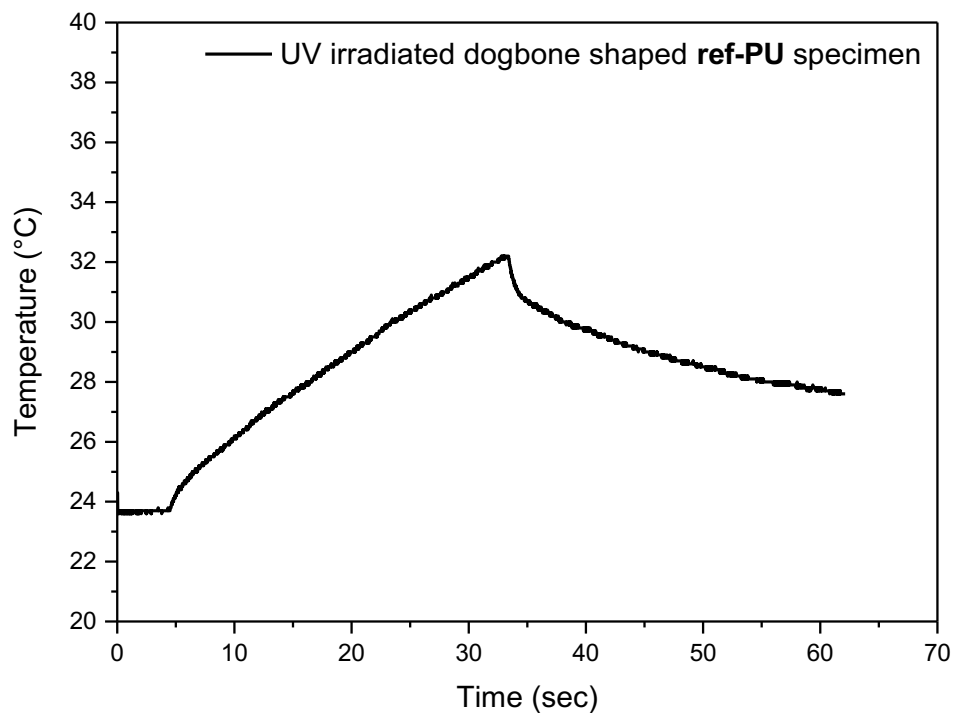


Figure S43. Pictures depicting (a) the set-up used for the UV light irradiation of dogbone shaped specimens of azo-containing and reference polyurethanes **azo-PU** and **ref-PU** prior to the stress-strain measurements and (b) two **azo-PU** dogbone shaped specimens, the top one was irradiated while the bottom one is pristine. The scale is in cm.



	Temperature elevation (°C)
30 sec irradiations	10.7 ± 0.6

Figure S44. Representative temperature vs. time curve of a dogbone shaped specimen of the azo-containing polyurethane **azo-PU** irradiated with UV light (320-390 nm, 600 mW/cm², 30 sec). The temperature was monitored with an IR camera. The temperature elevation value indicated in the table is an average obtained of the 3 samples used for the stress-strain measurements.



	Temperature elevation (°C)
30 sec irradiations	8.0 ± 1.0

Figure S45. Representative temperature vs. time curve of a dogbone shaped specimen of the reference polyurethane **ref-PU** irradiated with UV light (320-390 nm, 600 mW/cm², 30 sec). The temperature was monitored with an IR camera. The temperature elevation value indicated in the table is an average of the 3 samples used for the stress-strain measurements.

Stress-strain data for pristine, heated and irradiated polyurethanes

Table S46. Elongation and stress at break values, and Young's modulus values derived from stress-strain measurements of pristine and samples exposed to heat or UV light.

	Elongation at break^c (%)	Stress at break^c (MPa)	Young's modulus^d (MPa)
Pristine azo-PU	556 ± 25	81 ± 9	41 ± 1
Heated^a	270 ± 35	9 ± 1	24 ± 1
Irradiated^b	333 ± 6	13 ± 1	35 ± 2
Pristine ref-PU	574 ± 14	67 ± 2	19 ± 1
Heated^a	606 ± 70	64 ± 19	22 ± 1
Irradiated^b	563 ± 18	75 ± 5	24 ± 1

^aThe heat treatment (pre-heated hot press, 150 °C for 5 min) undergone by the samples was applied prior to cut them into a dogbone shape. ^bThe UV irradiation (320-390 nm, 600 mW/cm², 30 sec) was performed in the central area of the dogbone shaped specimens after cutting. ^cThe elongation and stress at break values are averages from 3 samples. ^dThe Young's modulus values are averages from the same 3 samples and derived from the slope of the stress-strain curves between 0.5 and 1.0 %.

Visible light irradiation in the solid state: lamp emission spectrum, size exclusion chromatography (SEC) traces of polyurethanes and temperature vs. time diagrams

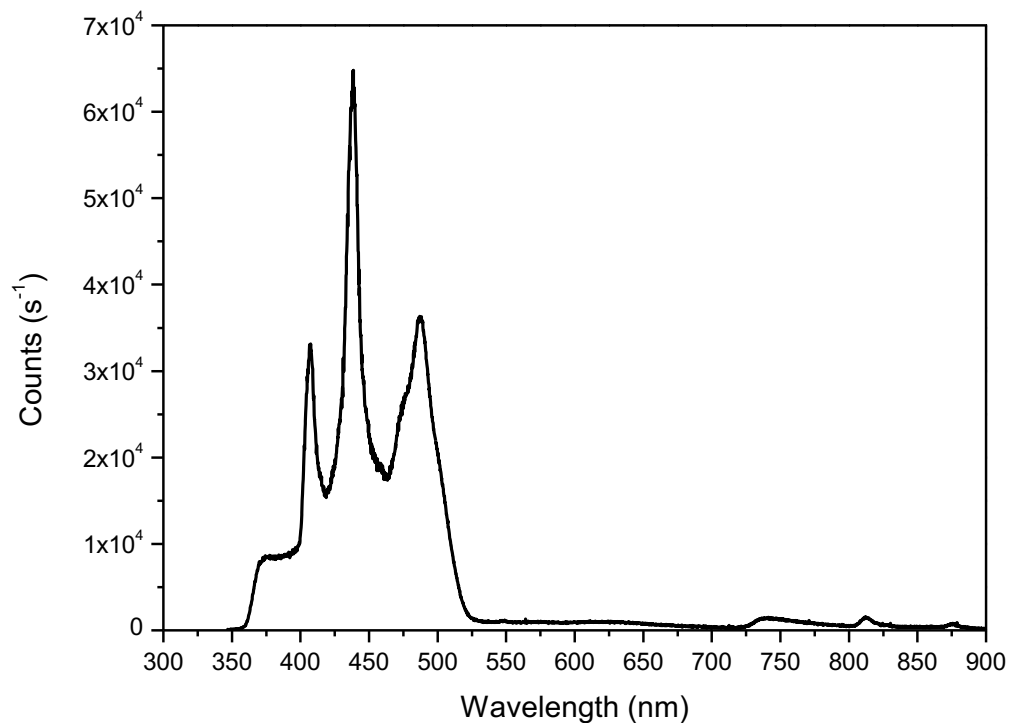
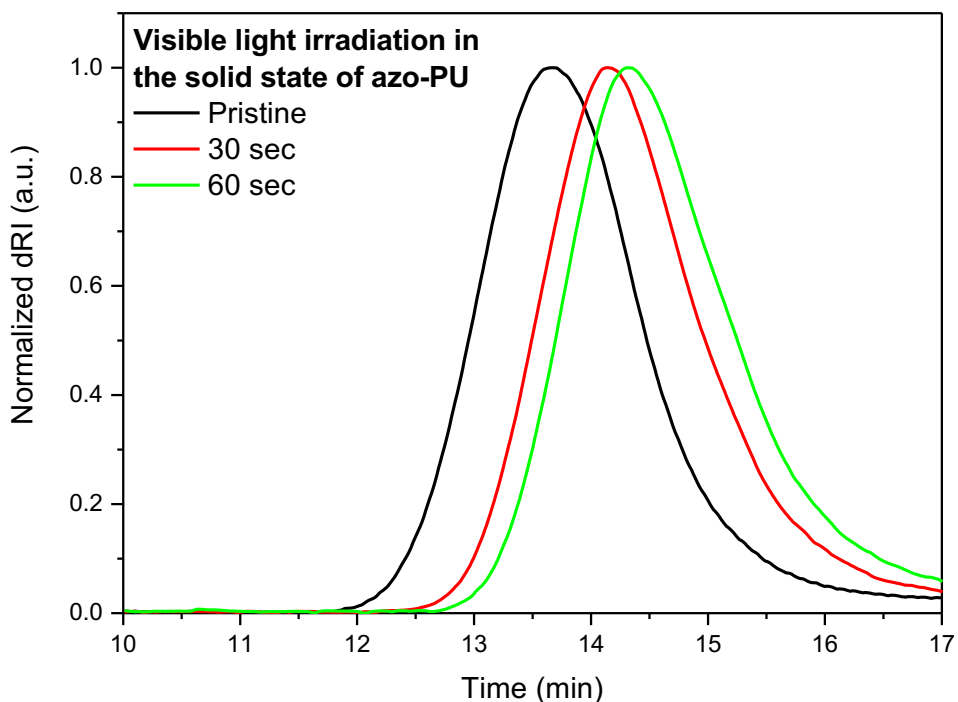


Figure S47. Emission spectrum of the visible light emitting source used (Hönle UV lamp equipped with a 390-500 nm filter).



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	93,700	49,300	1.90
30 sec	48,000	23,000	2.09
60 sec	35,900	15,800	2.27

Figure S48. Size exclusion chromatography (SEC) traces of a pristine sample of the azo-containing polyurethane **azo-PU** (black line) and samples of **azo-PU** after exposure to visible light in the solid state (390-500 nm, 600 mW/cm²), for 30 sec (red line) and for 60 sec (green line). The weight-average (M_w) and number-average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).

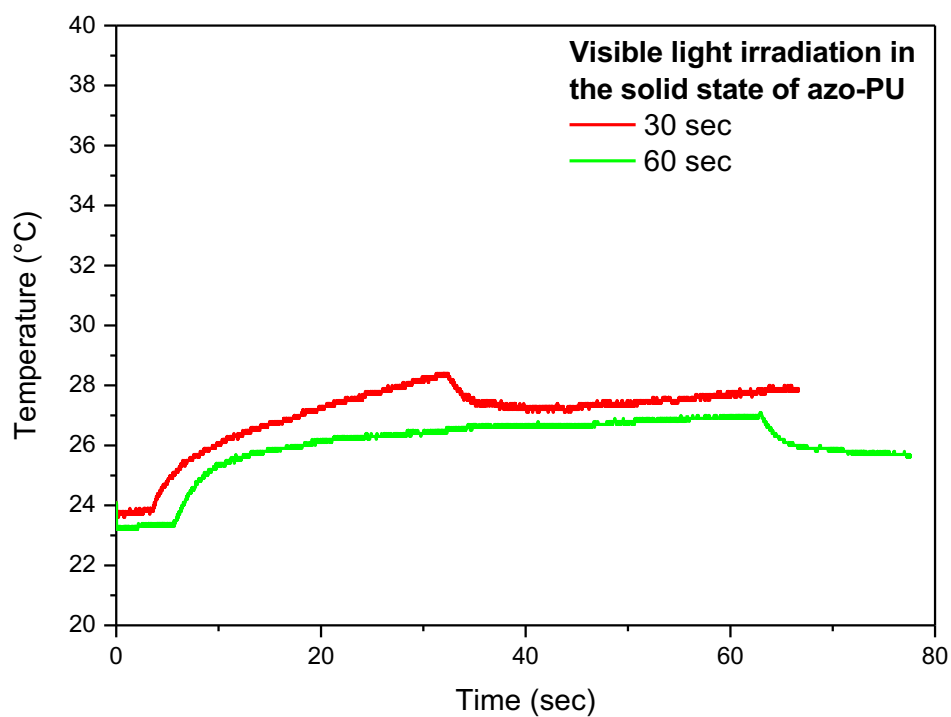
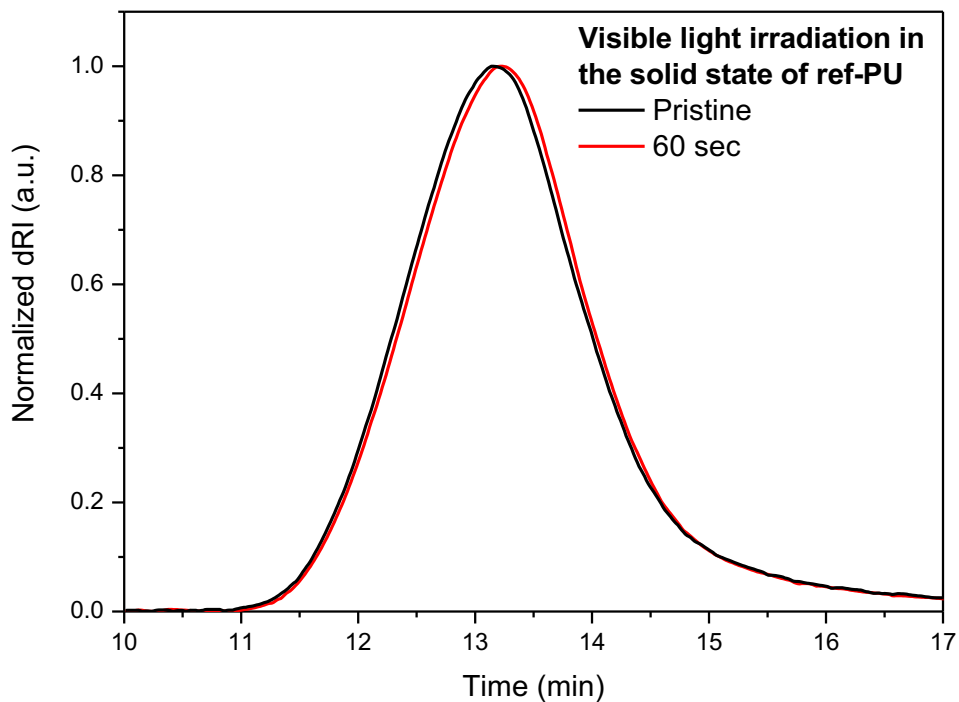


Figure S49. Temperature vs. time curves of azo-containing polyurethane **azo-PU** samples irradiated with visible light in the solid state (390-500 nm, 600 mW/cm²), for 30 sec (red line) and 60 sec (green line). The temperature was monitored with an IR camera.



	M_w (g/mol)	M_n (g/mol)	\mathcal{D}
Pristine	204,700	93,600	2.19
60 sec	199,500	92,500	2.16

Figure S50. Size exclusion chromatography (SEC) traces of a pristine sample of the reference polyurethane **ref-PU** (black line) and samples of **ref-PU** after exposure to visible light in the solid state (390-500 nm, 600 mW/cm²) for 60 sec (red line). The weight-average (M_w) and number-average molecular weight (M_n) values are indicated in the table as well as the dispersity value (\mathcal{D}).

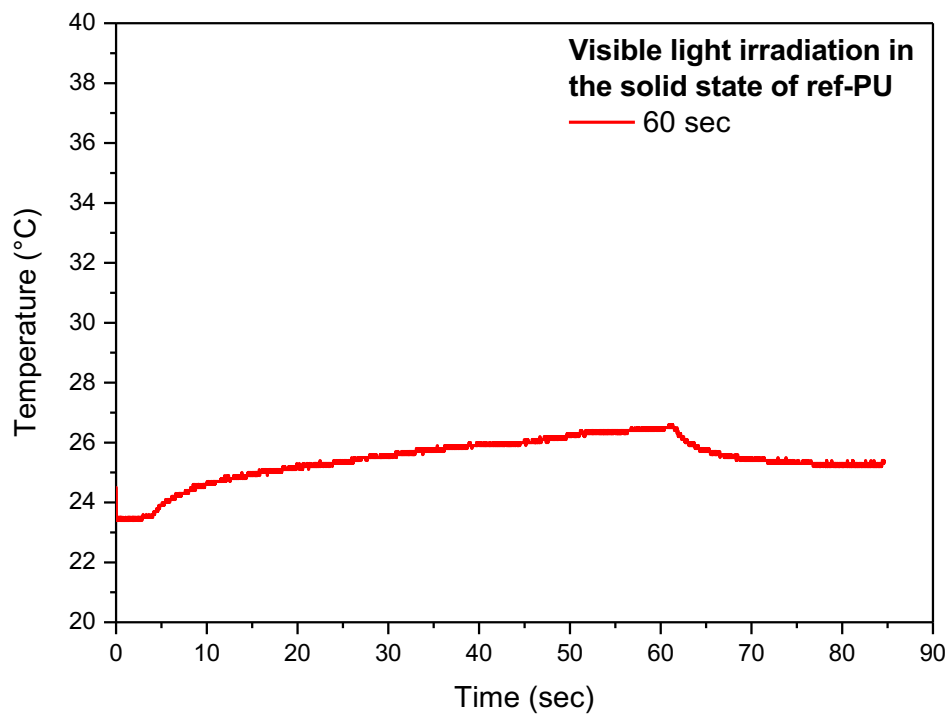


Figure S51. Temperature vs. time curve of a reference polyurethane **ref-PU** sample irradiated with visible light in the solid state (390-500 nm, 600 mW/cm²) for 60 sec. The temperature was monitored with an IR camera.