Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis and melt-spinning of partly bio-based thermoplastic poly(cycloacetal-urethane)s toward sustainable textiles

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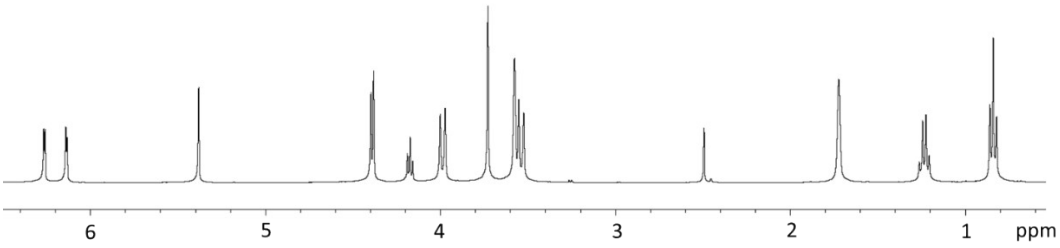

Figure S1. ^{1}H NMR spectrum of Monomer **T**.

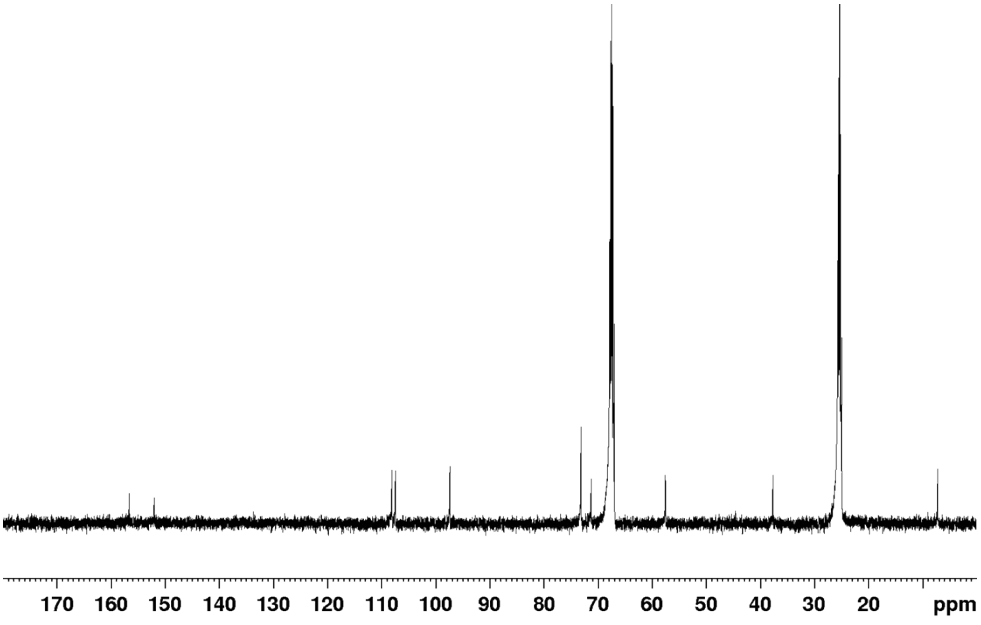

Figure S2. ^{13}C NMR spectrum of Monomer **T**.

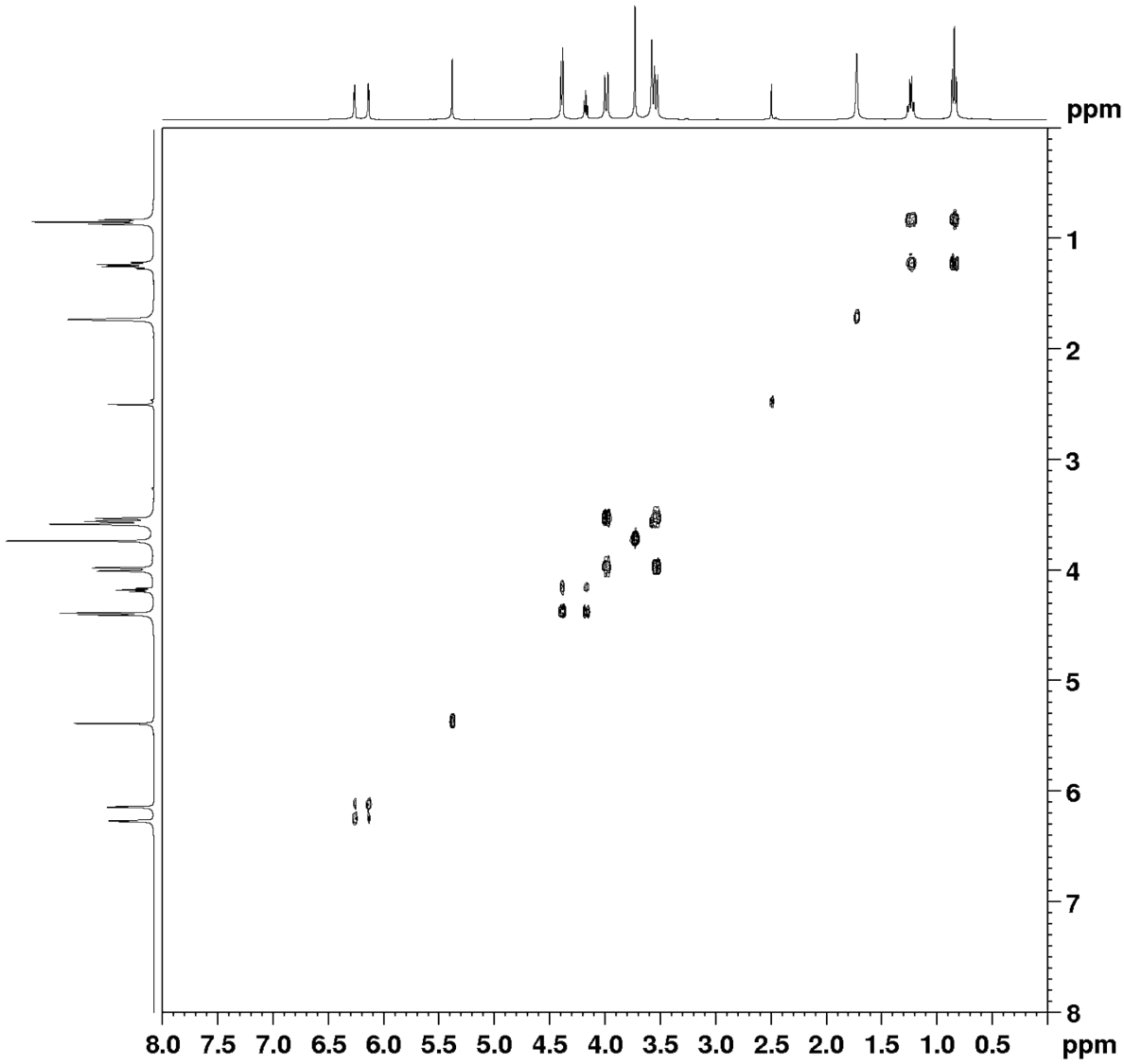

Figure S3. COSY spectrum of Monomer **T**.

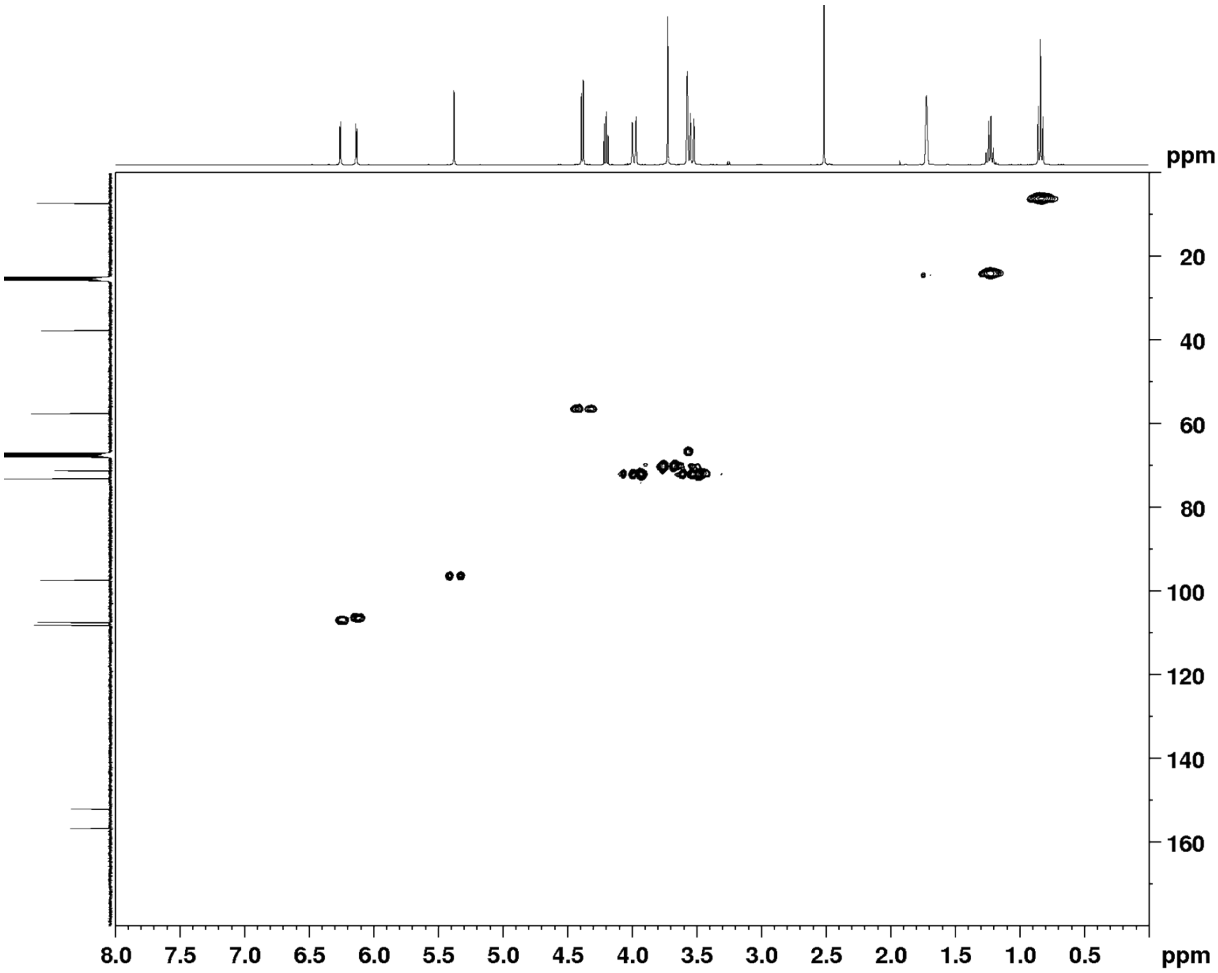

Figure S4. HMQC spectrum of Monomer **T**.

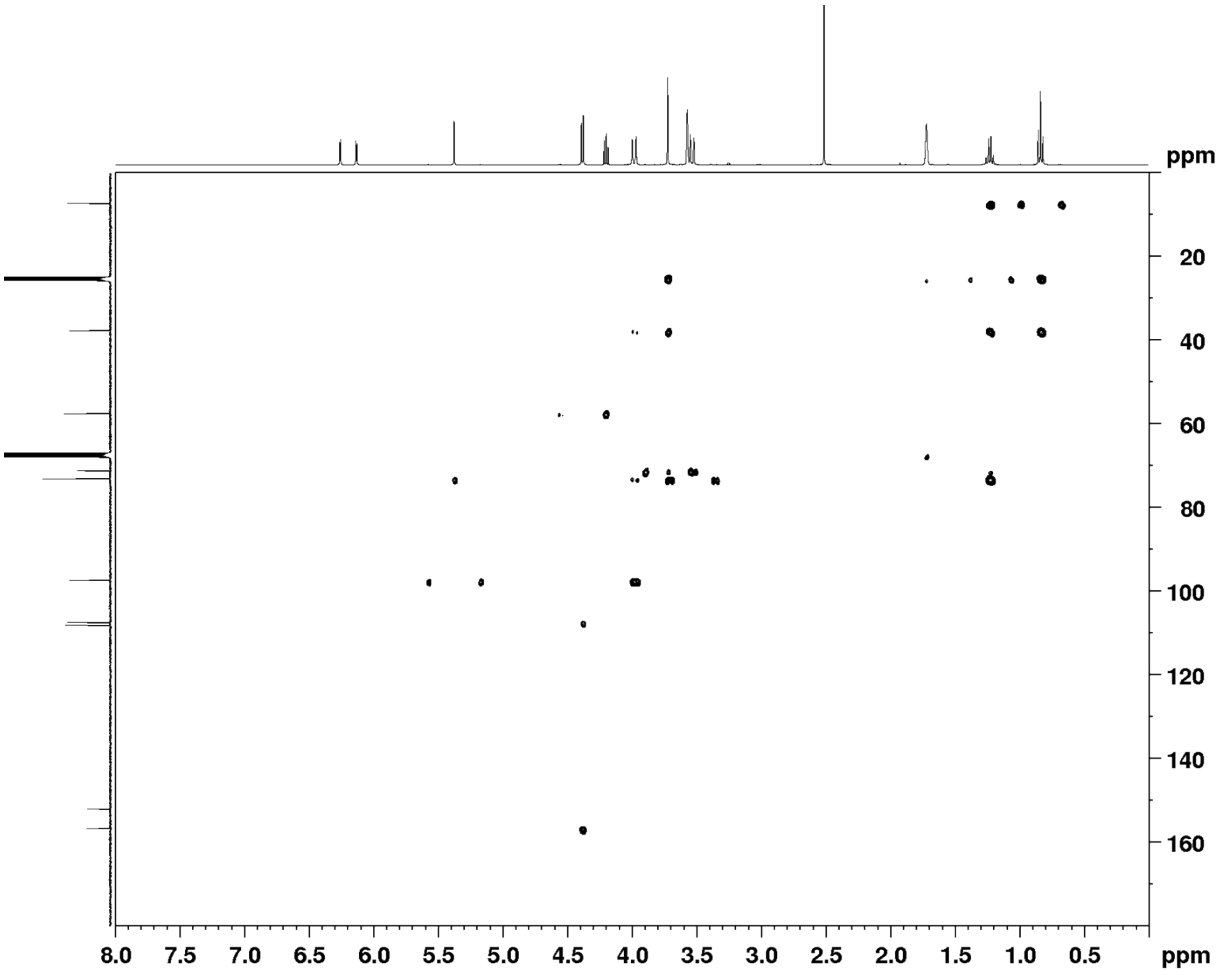

Figure S5. HMBC spectrum of Monomer **T**.

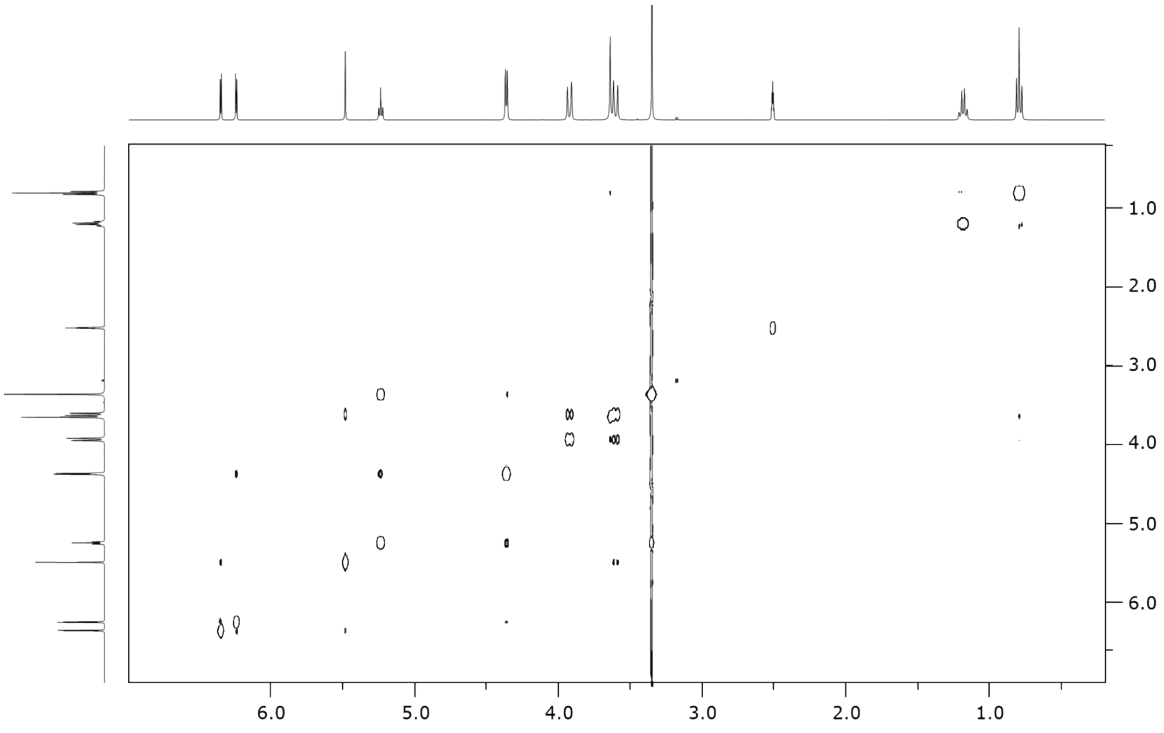

Figure S6. NOESY spectrum of Monomer T.

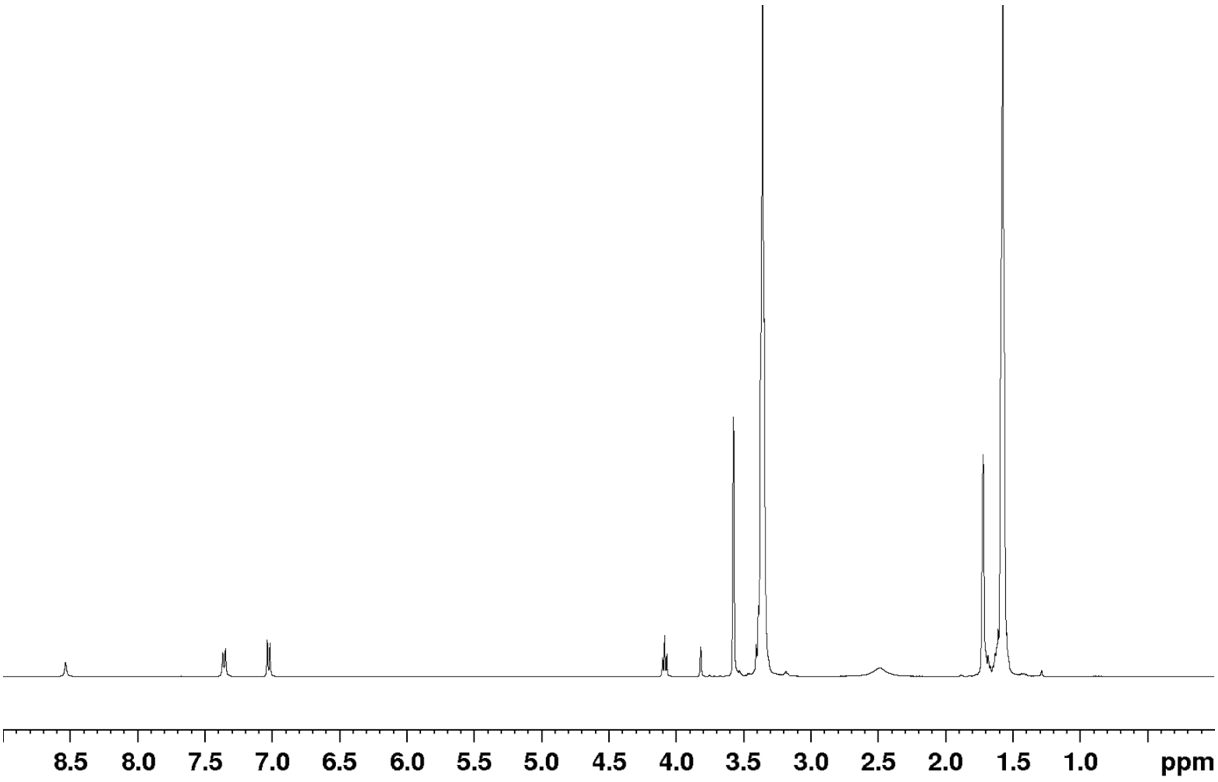

Figure S7. ^{1}H NMR spectrum of PAU-0.

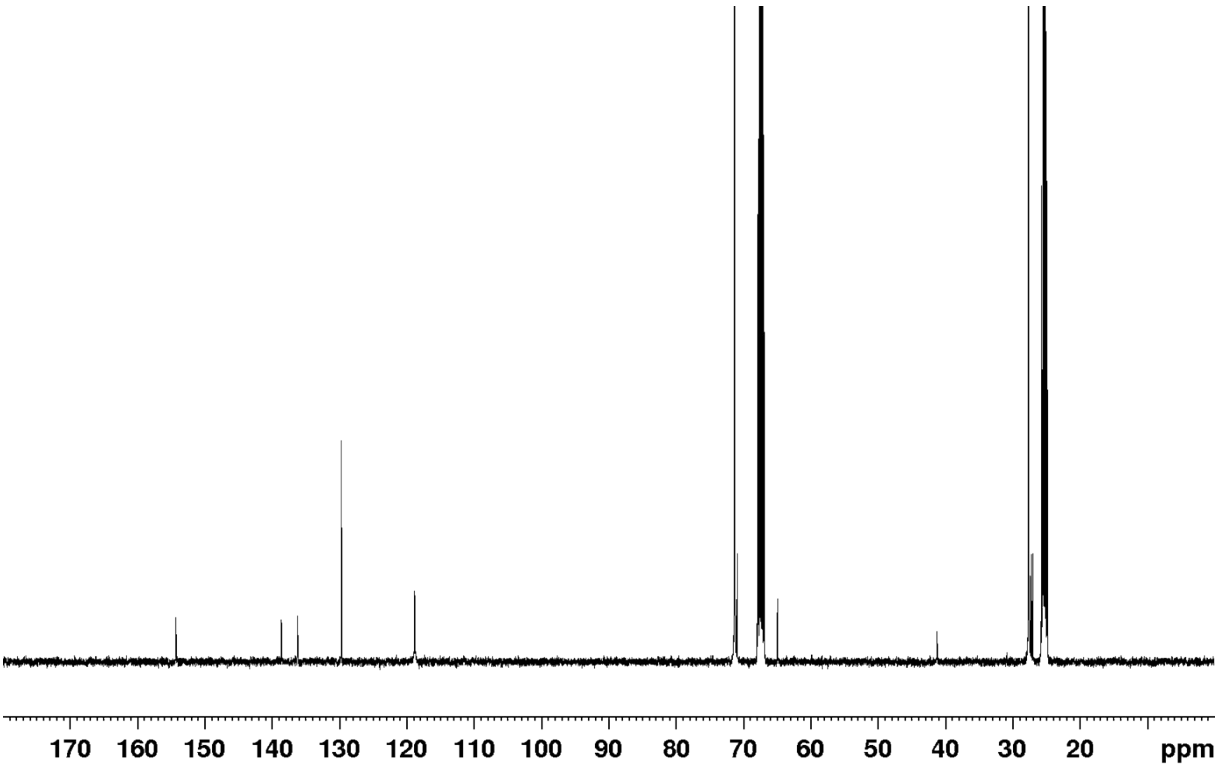

Figure S8. ^{13}C NMR spectrum of PAU-0.

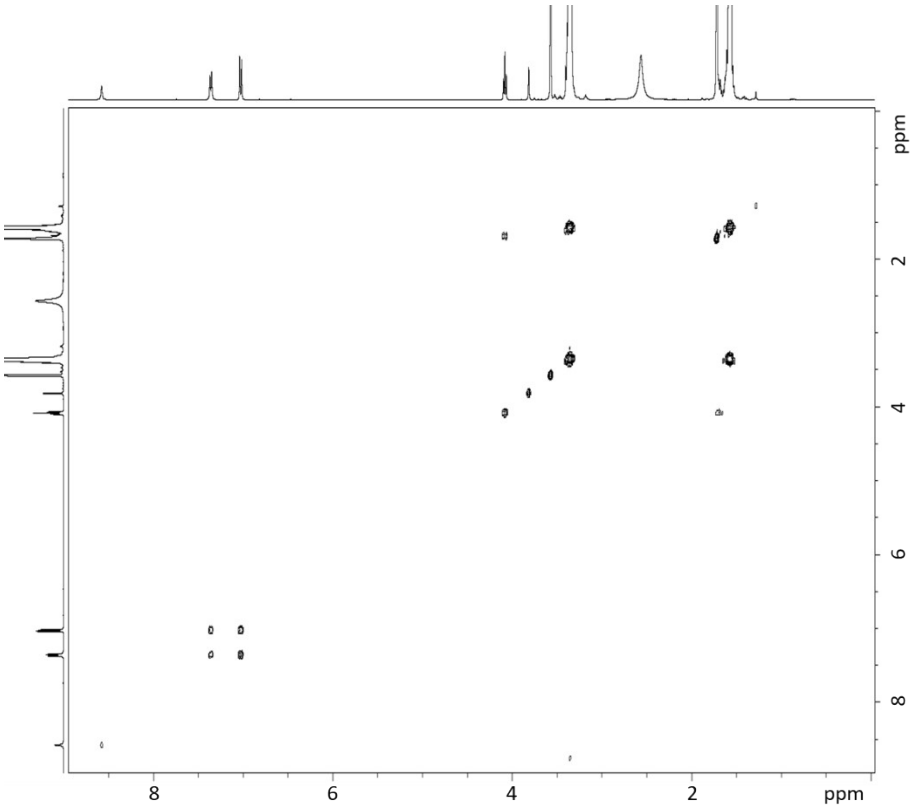

Figure S9. COSY spectrum of PAU-0.

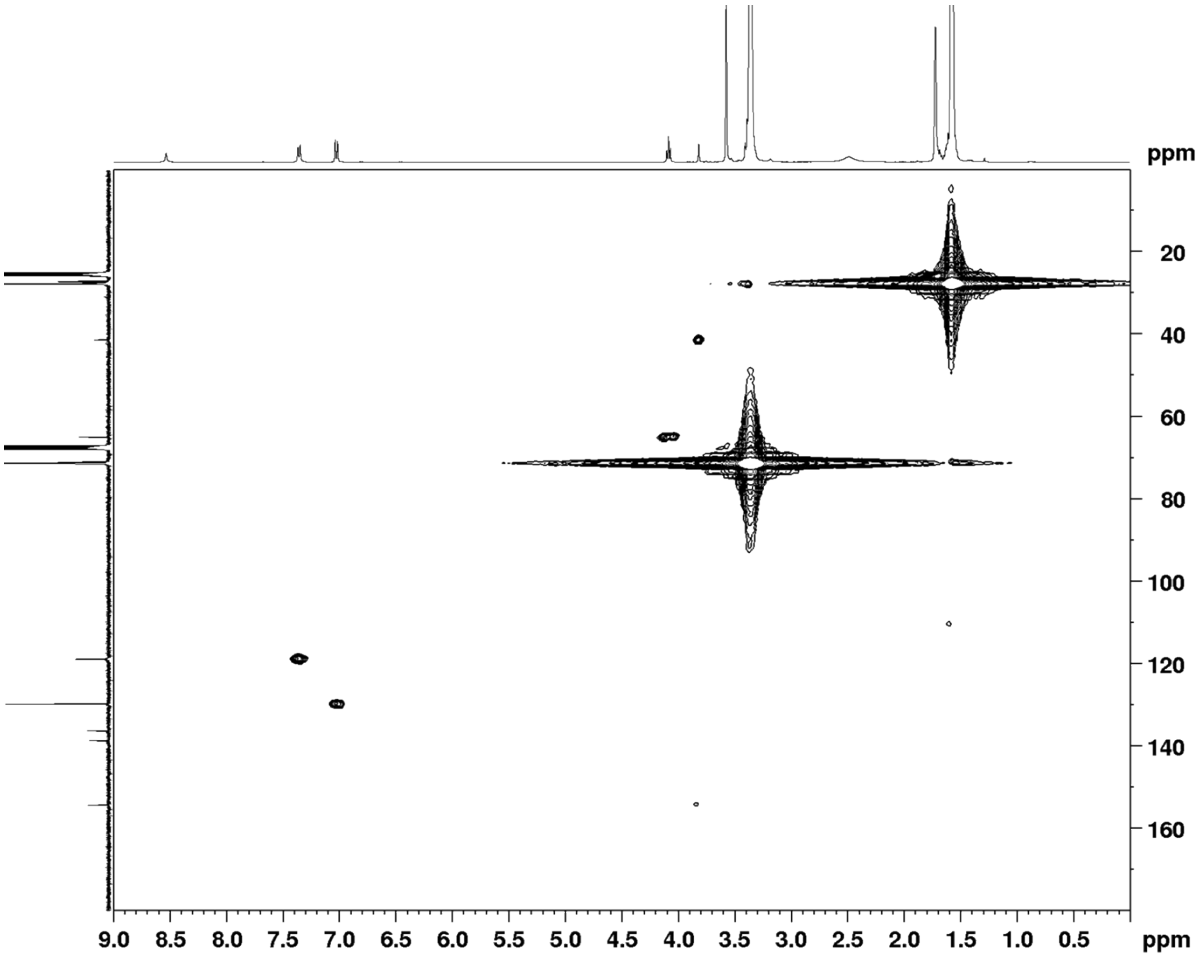

Figure S10. HMQC spectrum of PAU-0.

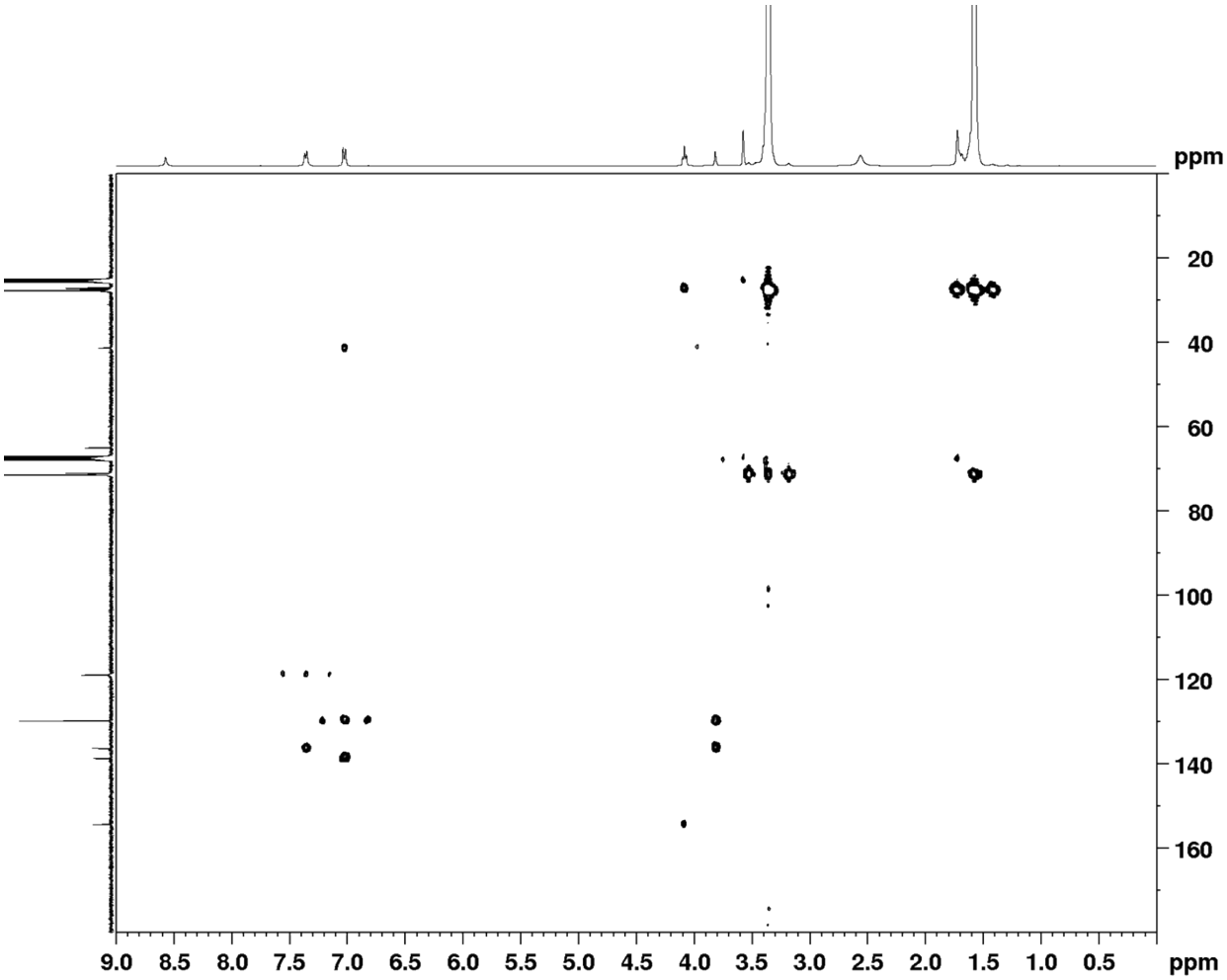

Figure S11. HMBC spectrum of PAU-0.

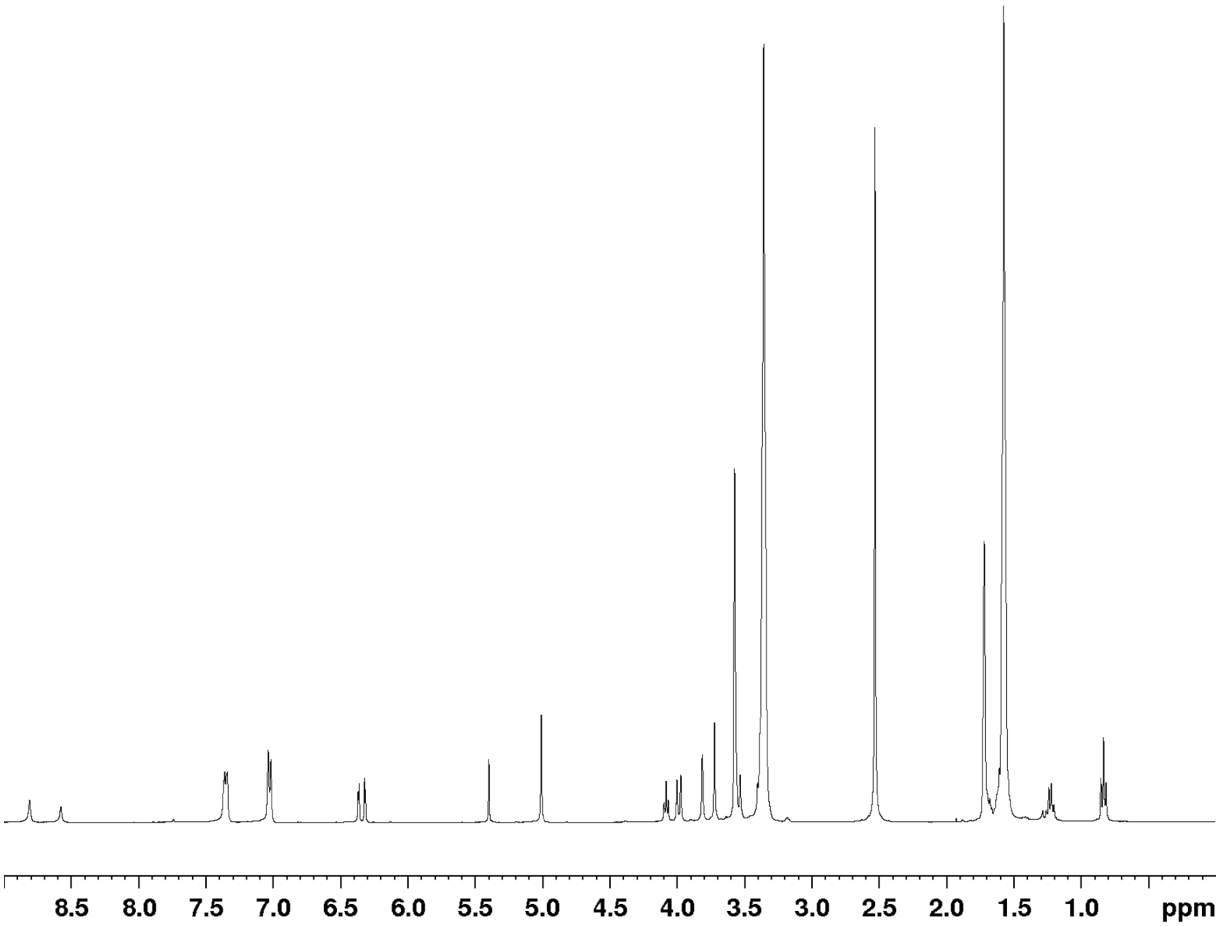

Figure S12. ^{1}H NMR spectrum of PAU-25.

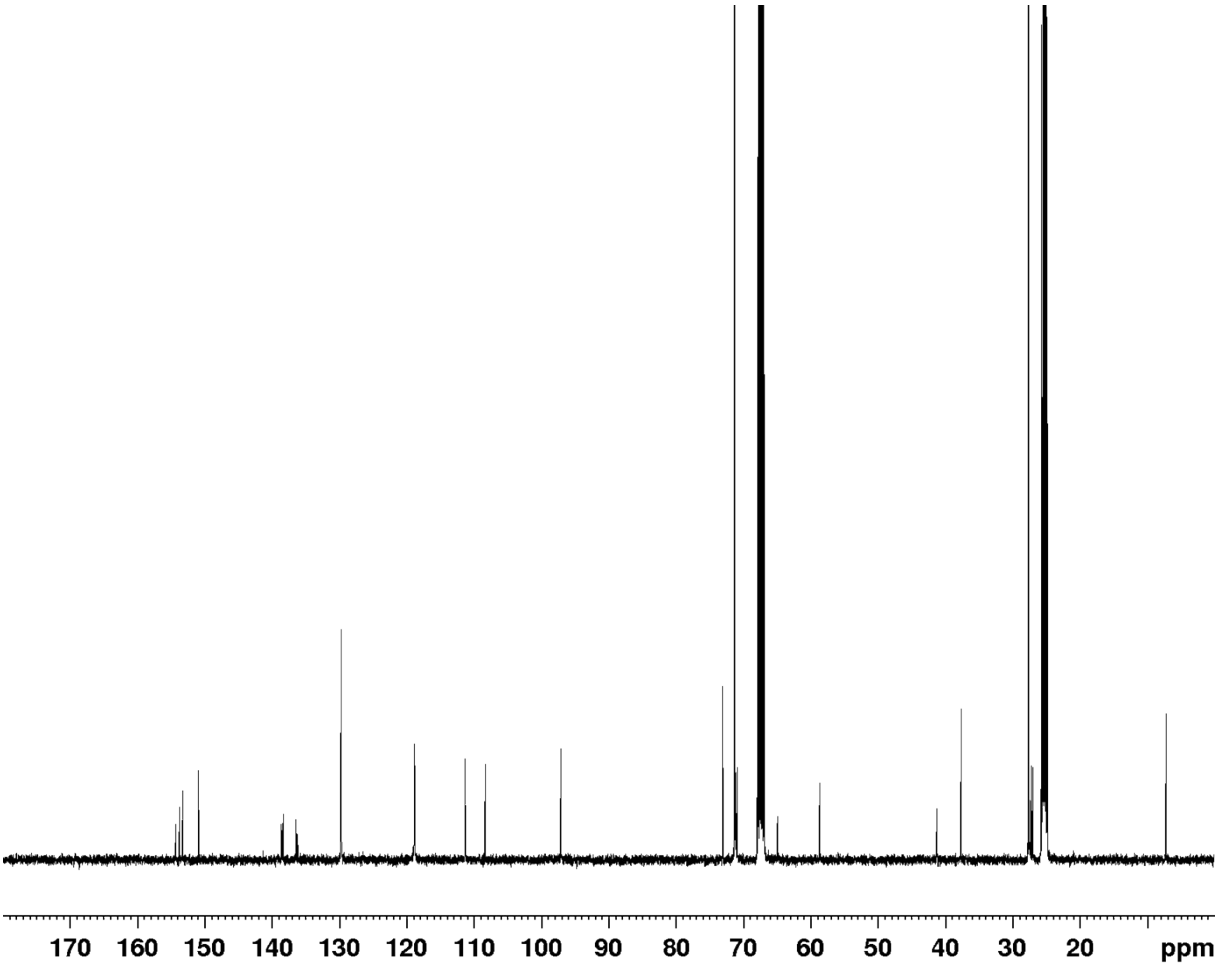

Figure S13. ^{13}C NMR spectrum of PAU-25.

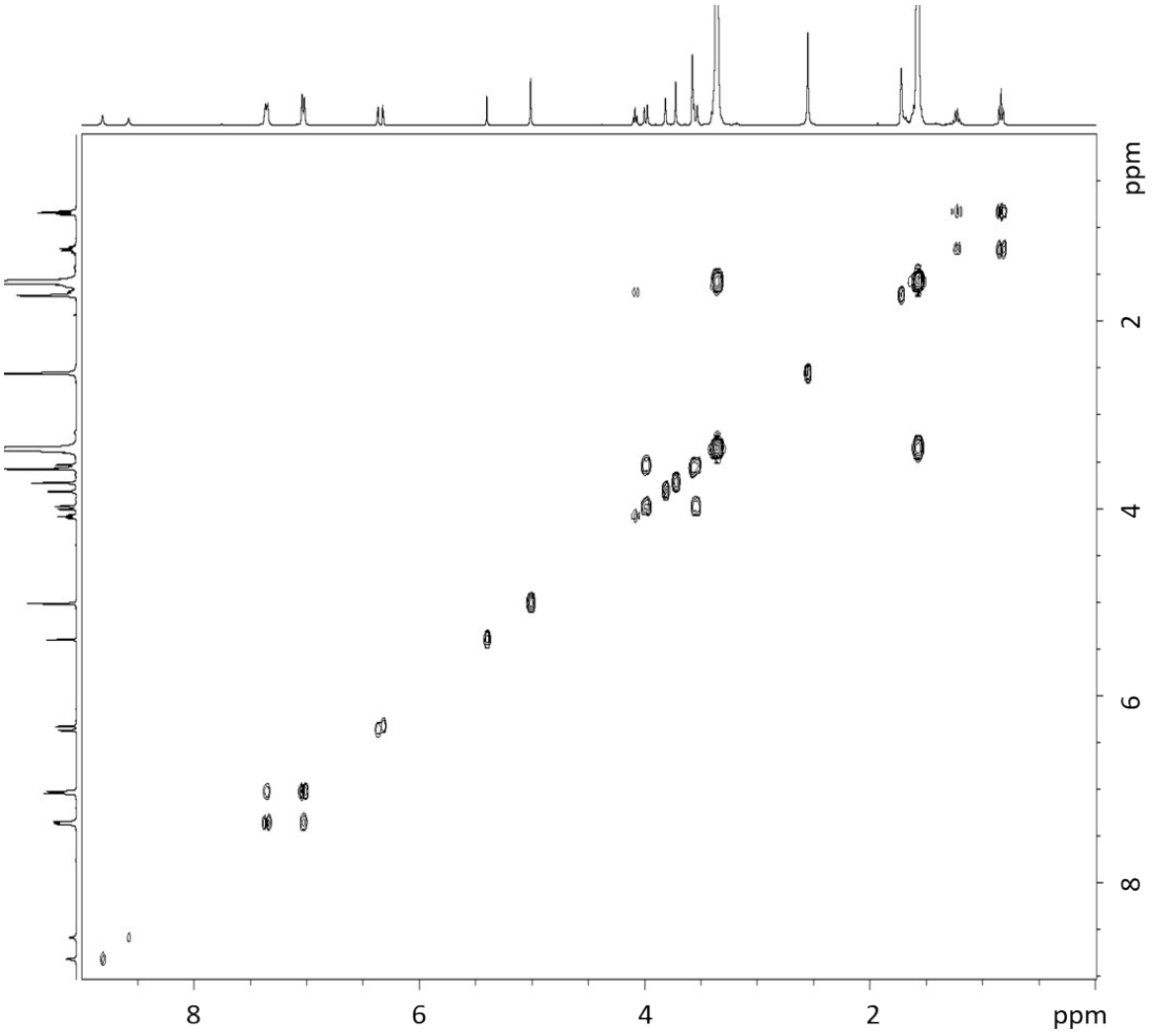

Figure S14. COSY spectrum of PAU-25.

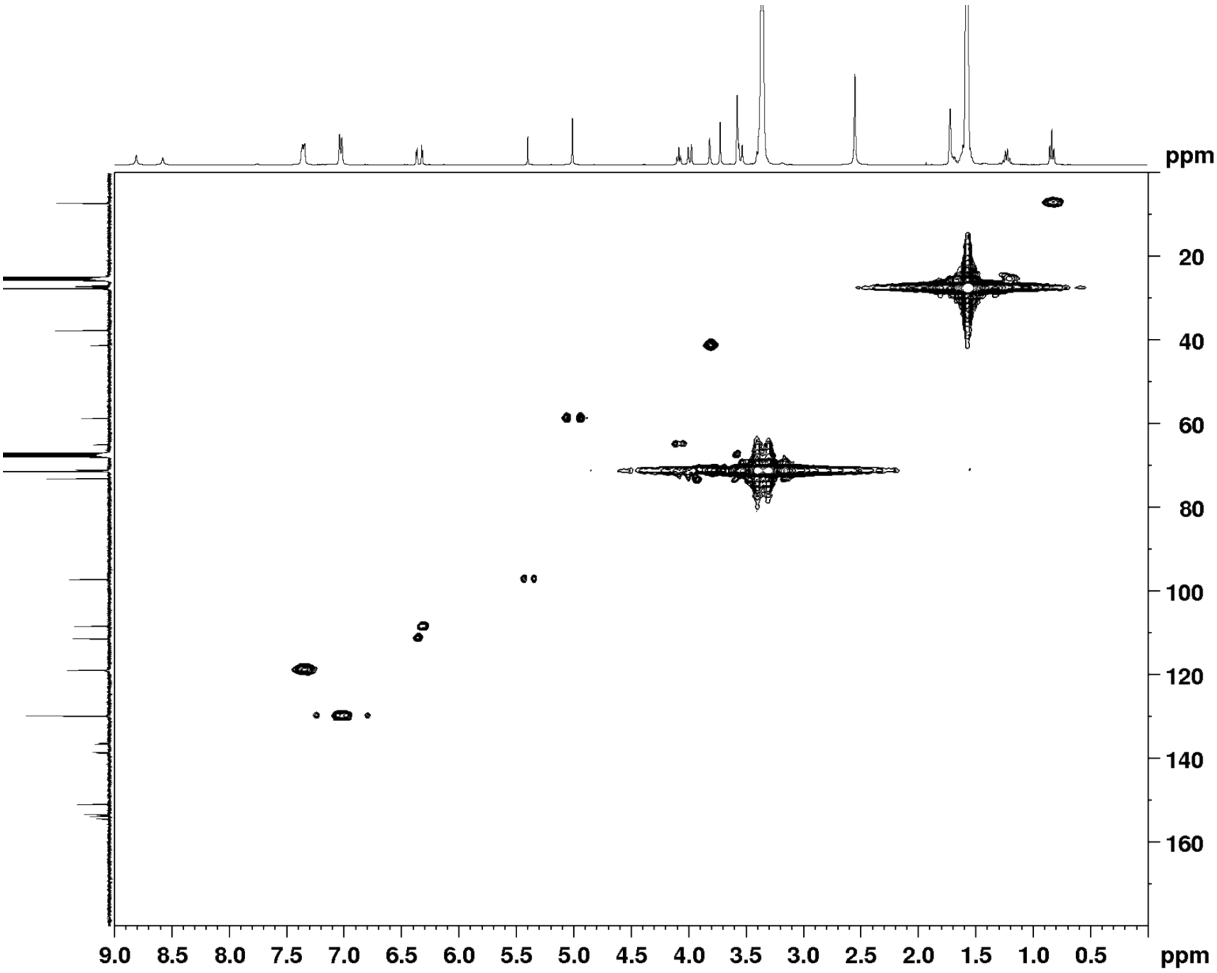

Figure S15. HMQC spectrum of PAU-25.

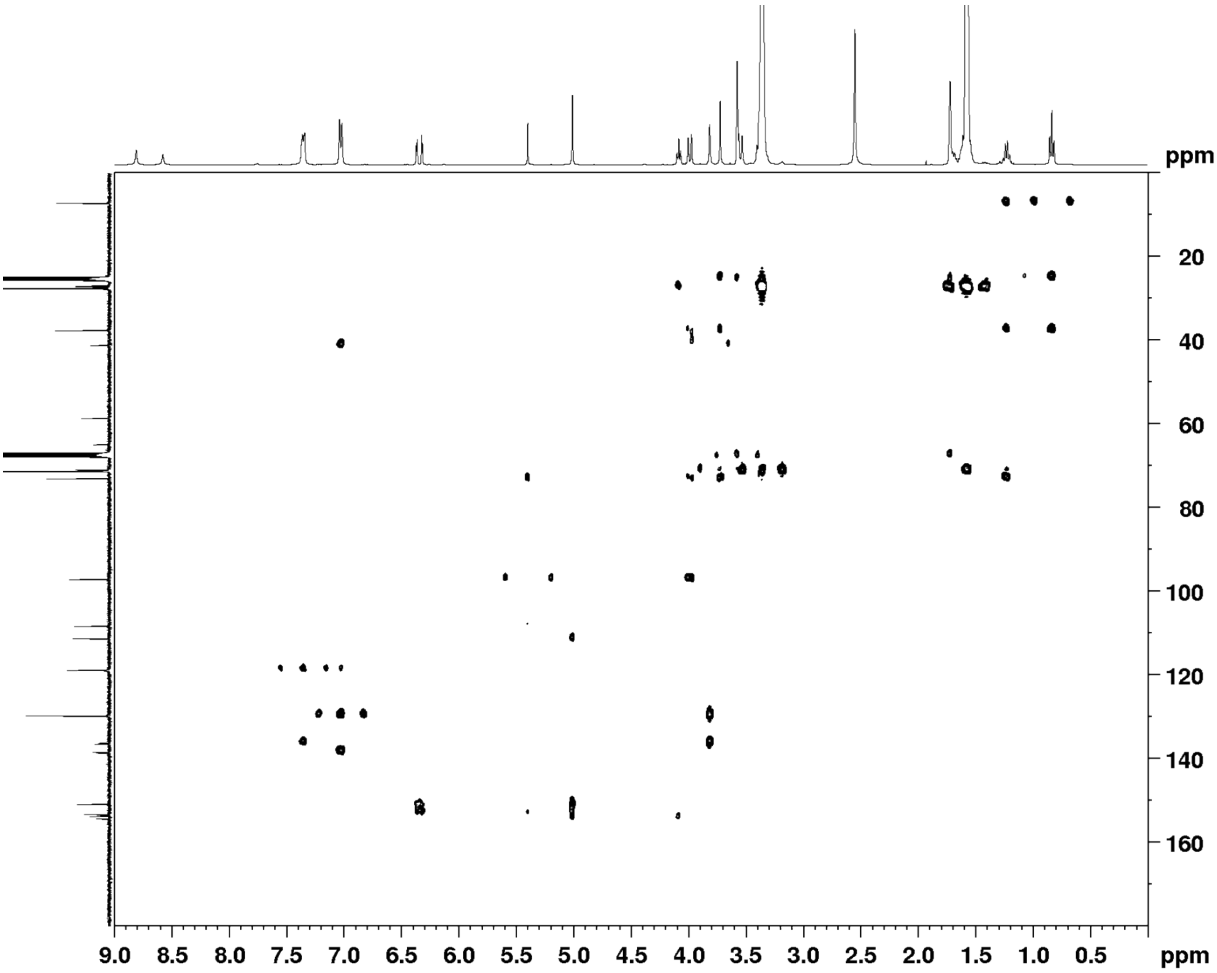

Figure S16. HMBC spectrum of PAU-25.

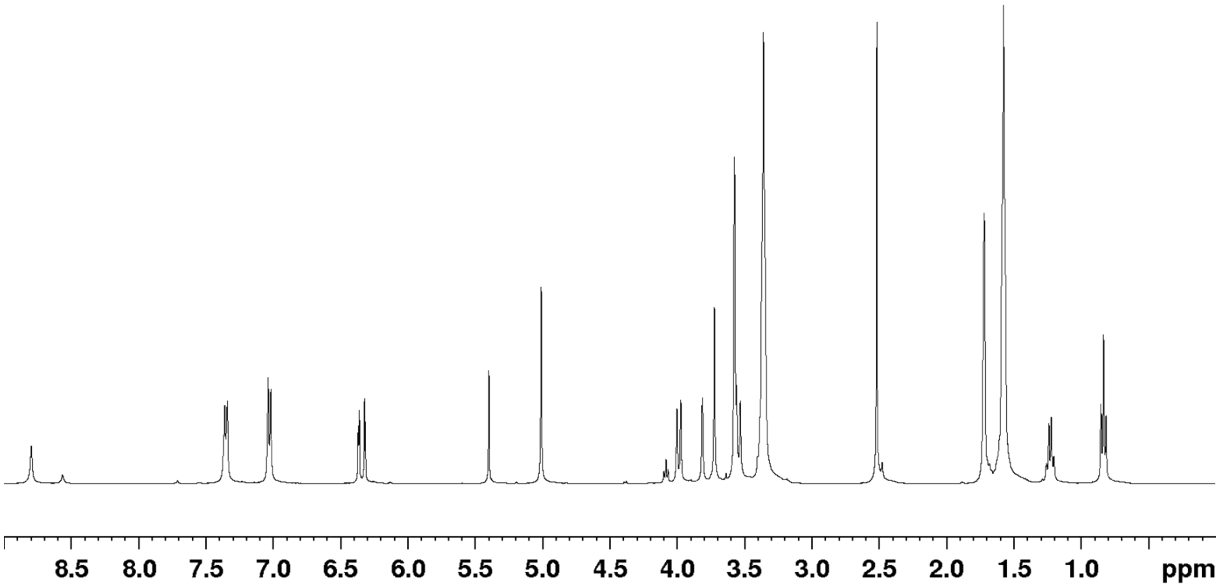

Figure S17. ^{1}H NMR spectrum of PAU-51.

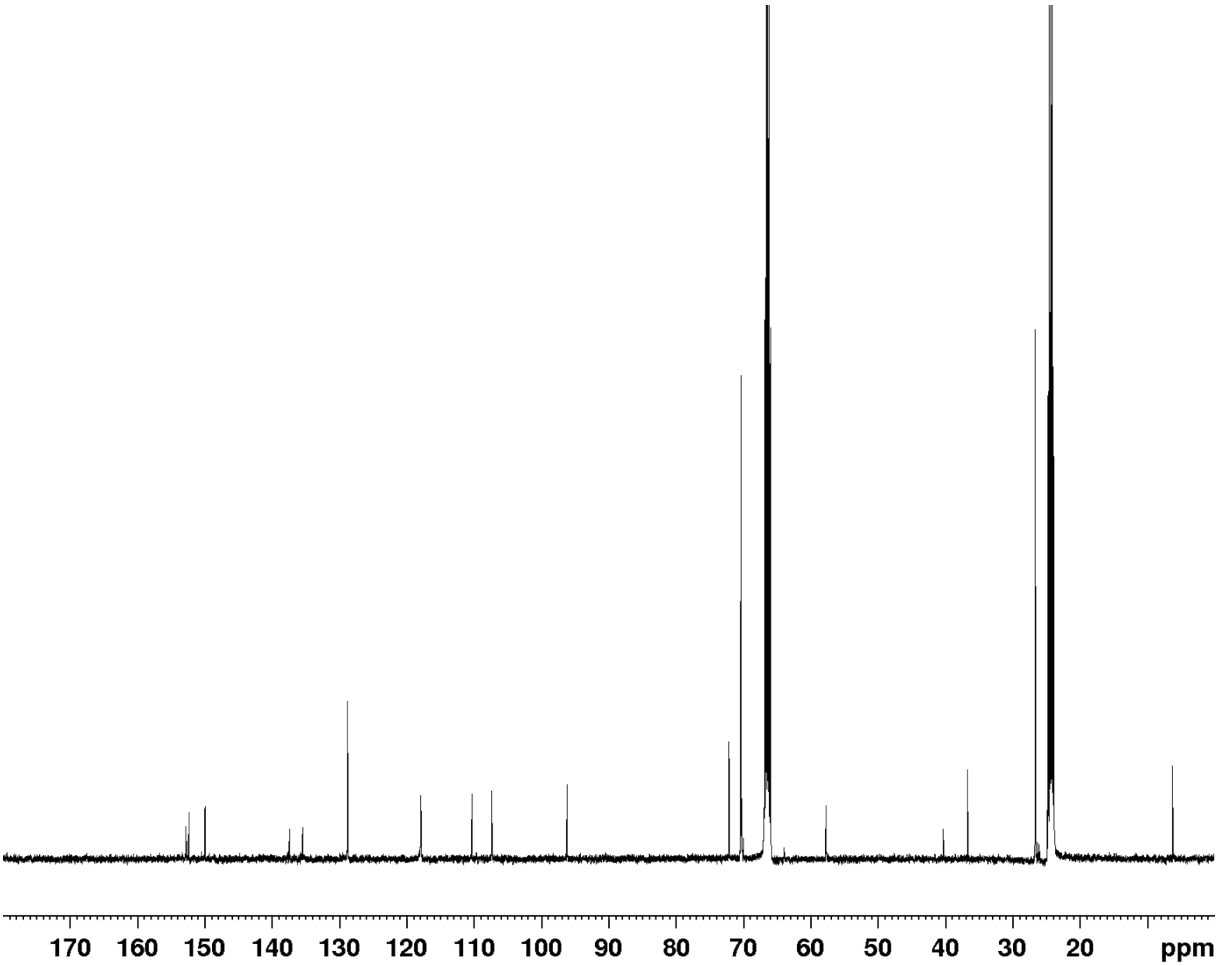

Figure S18. ^{13}C NMR spectrum of PAU-51.

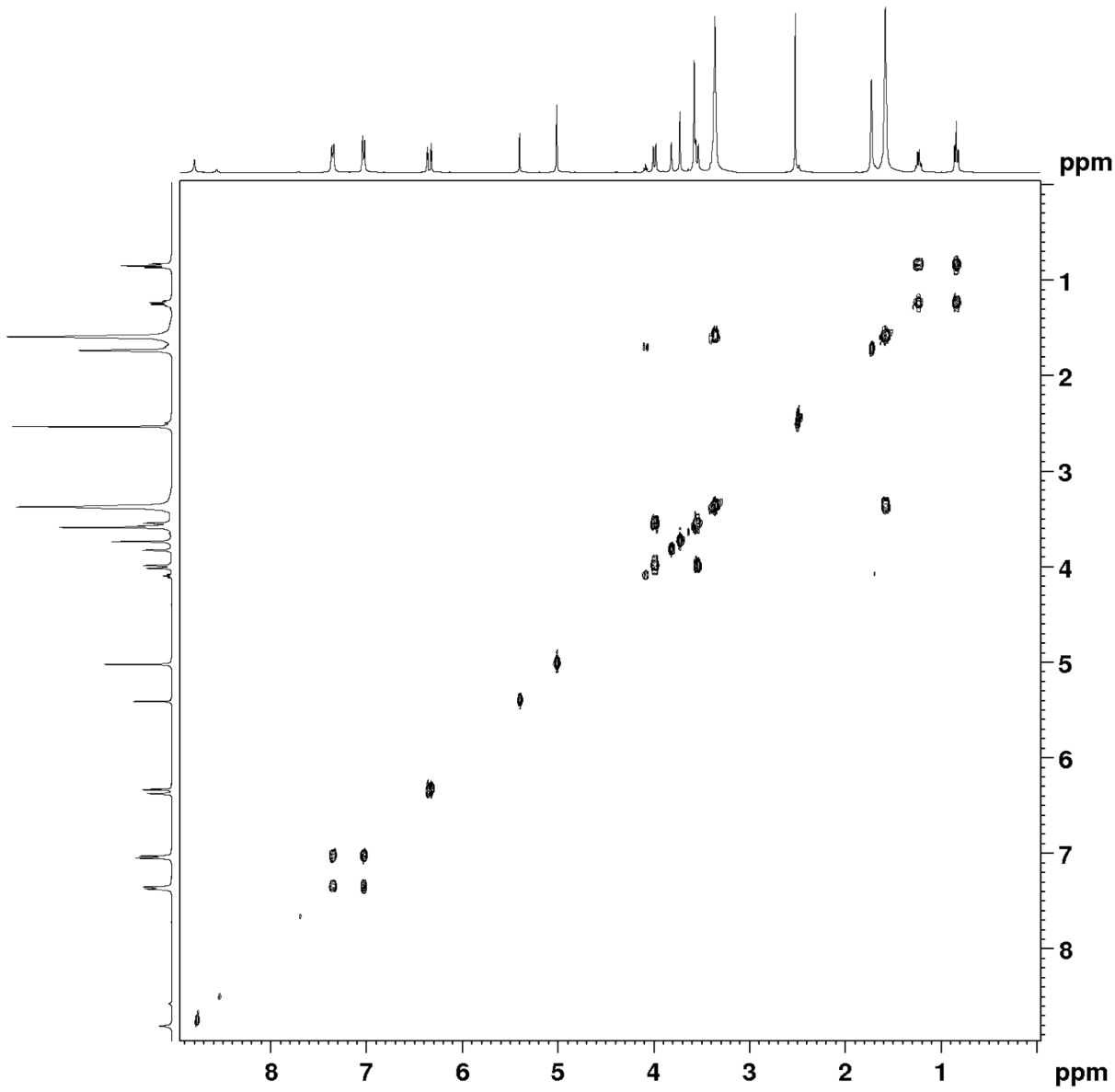

Figure S19. COSY spectrum of PAU-51.

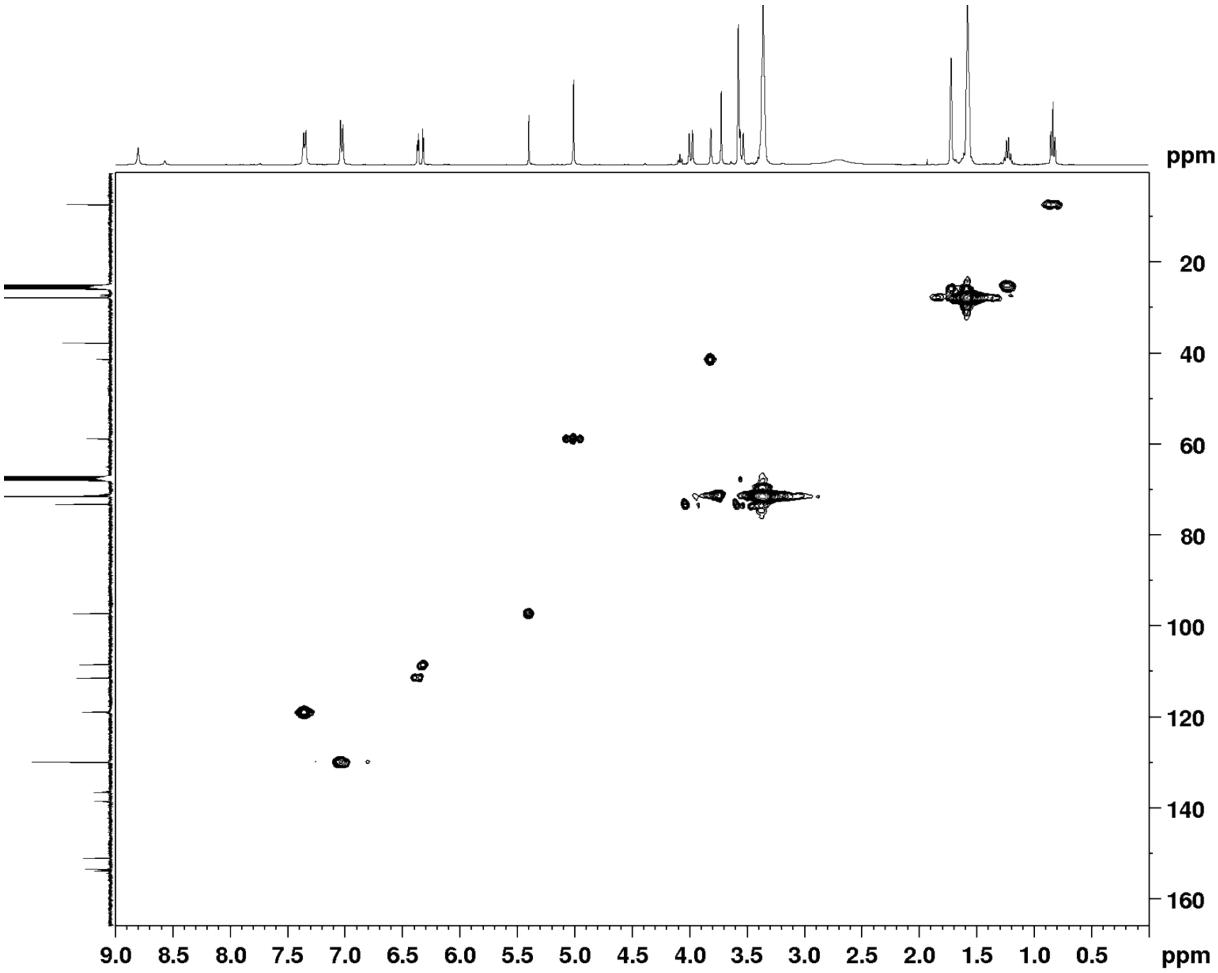

Figure S20. HMQC spectrum of PAU-51.

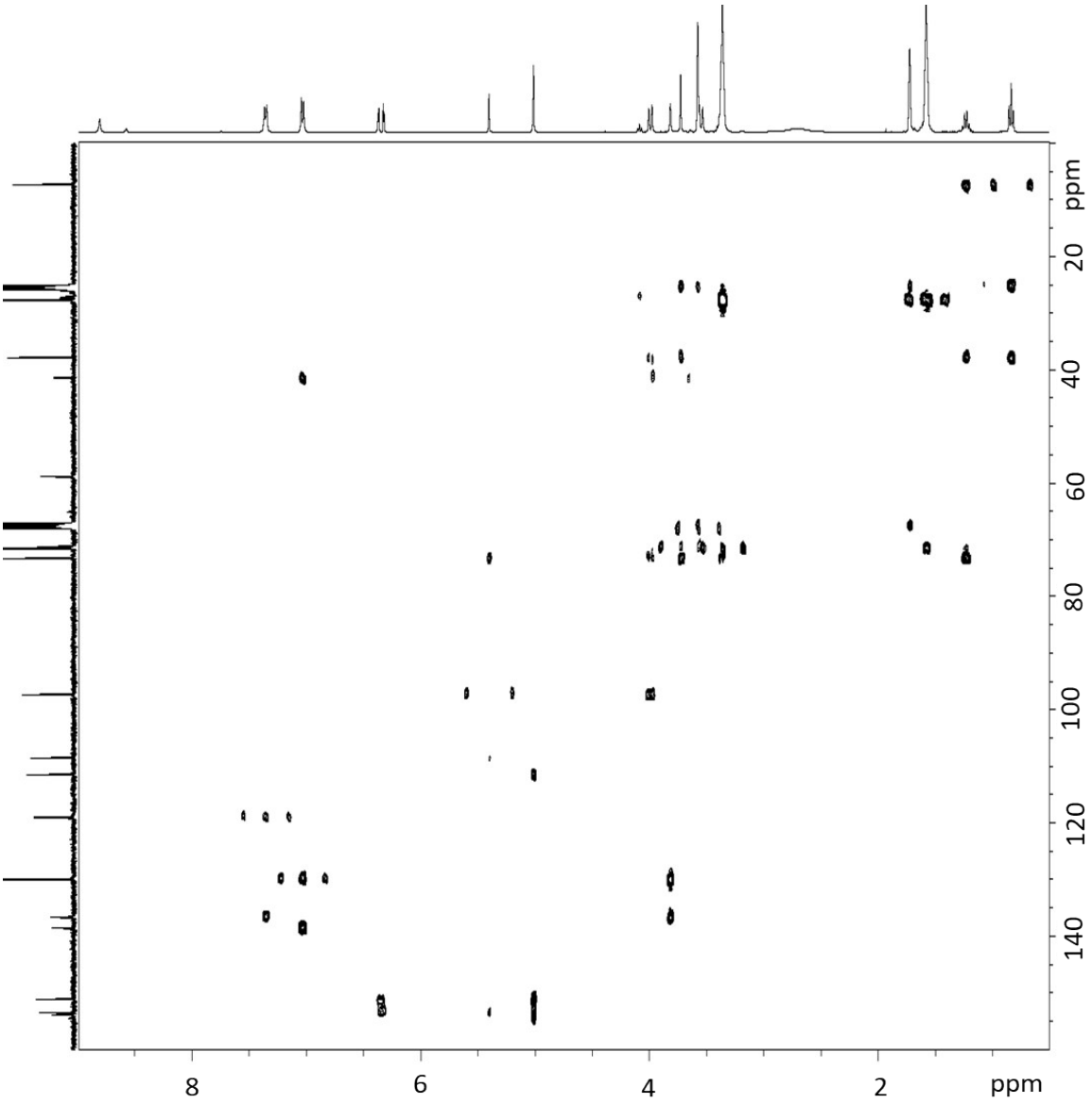

Figure S21. HMBC spectrum of PAU-51.

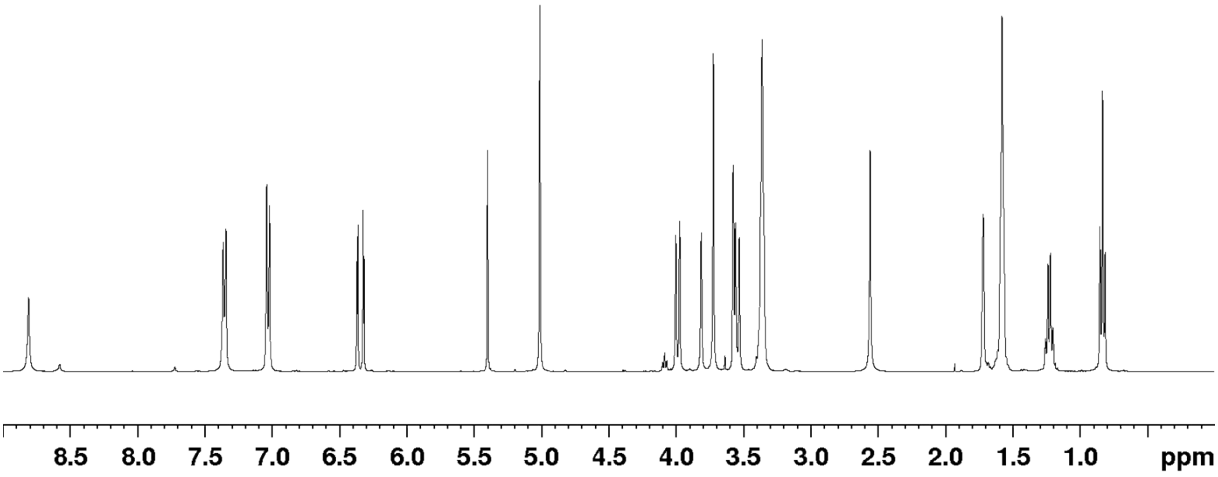

Figure S22. ^{1}H NMR spectrum of PAU-71.

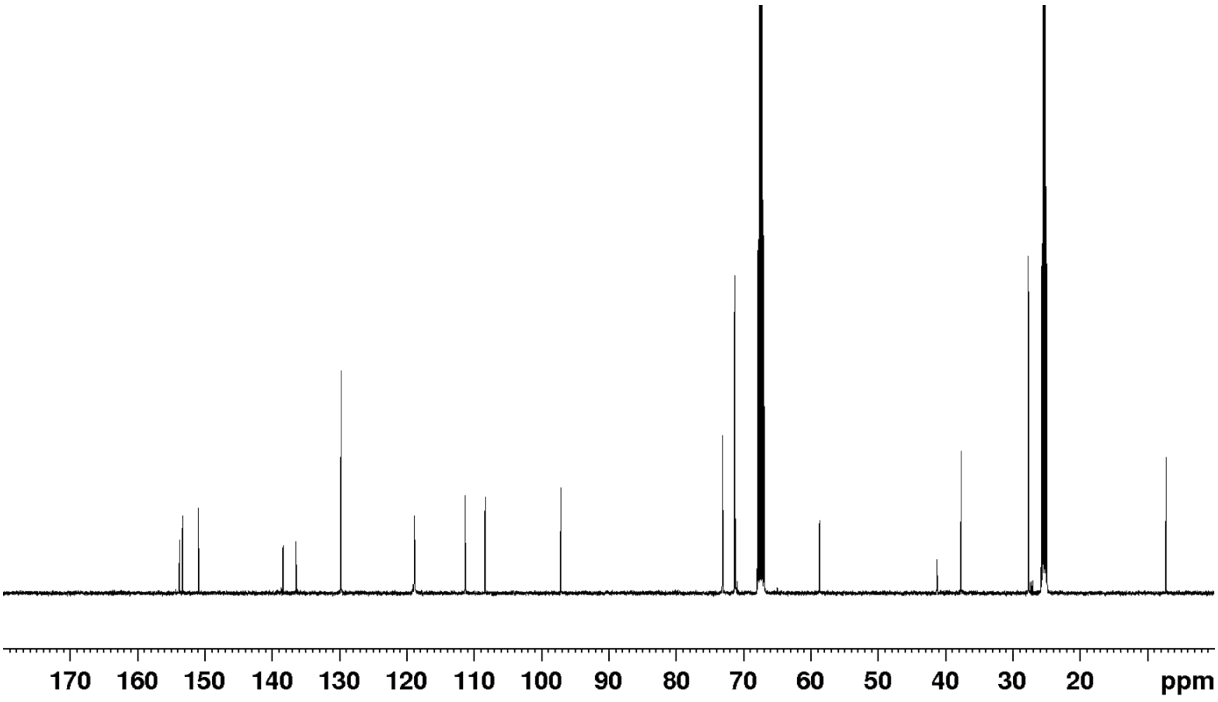

Figure S23. ^{13}C NMR spectrum of PAU-71.

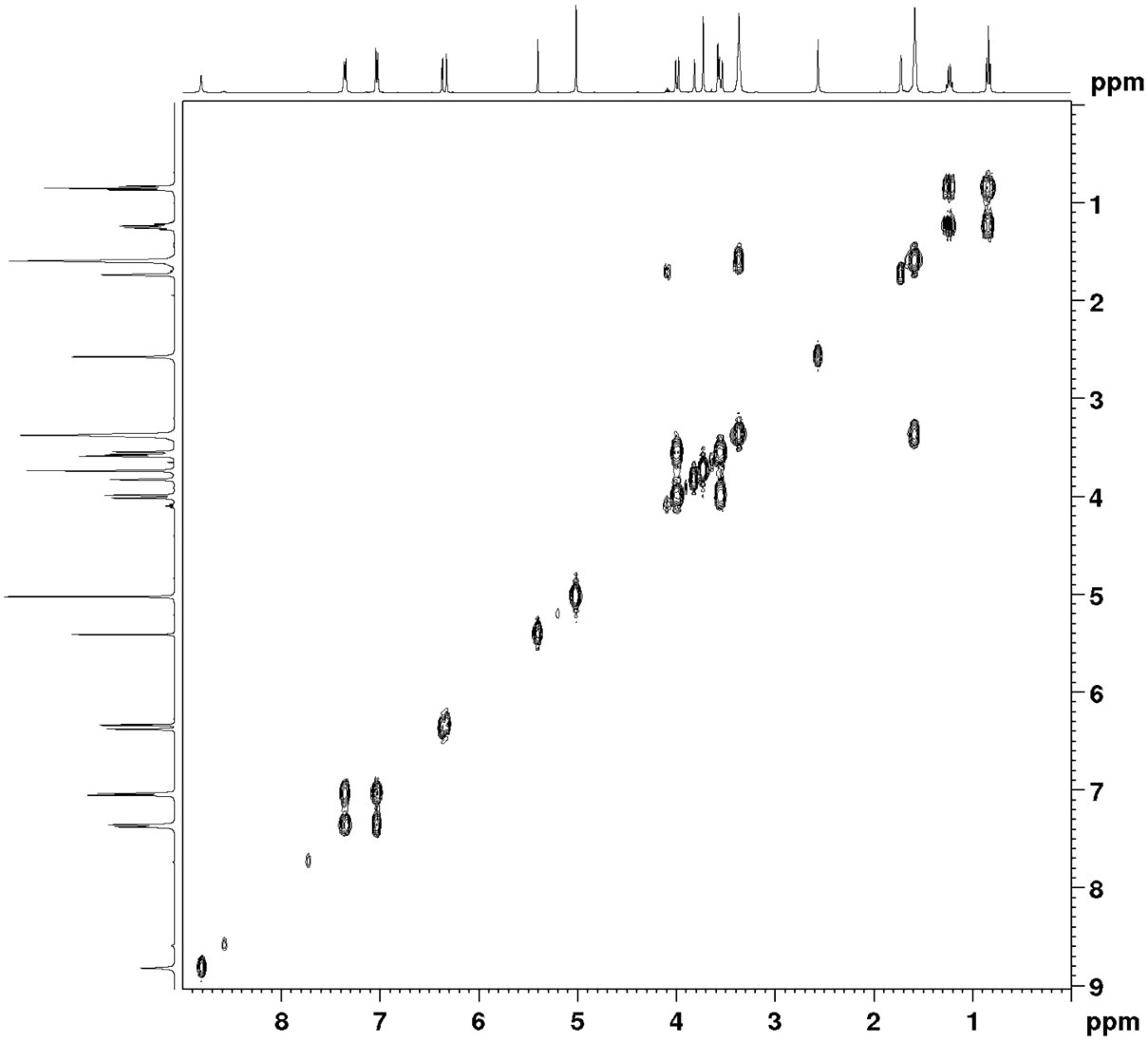

Figure S24. COSY spectrum of PAU-71.

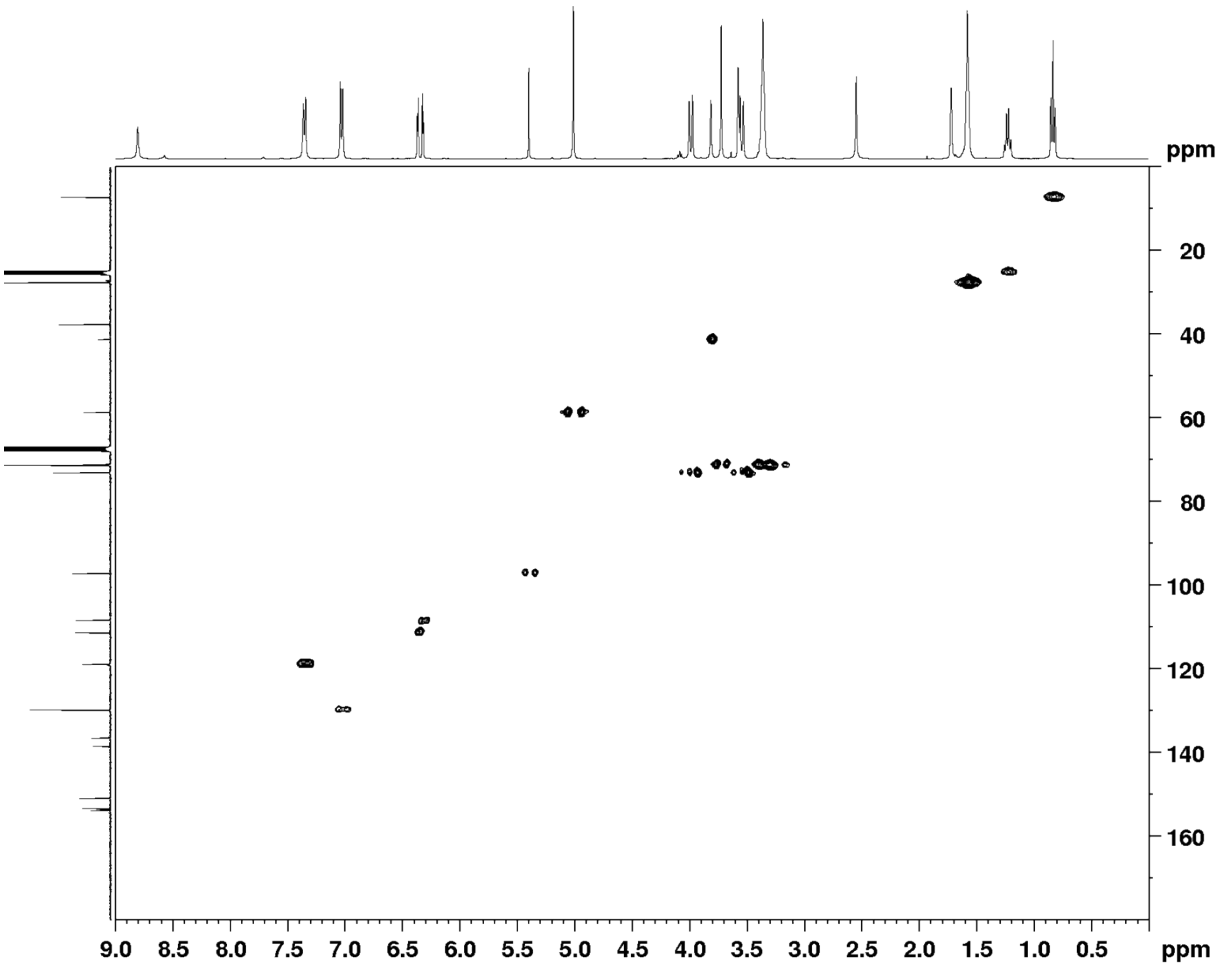

Figure S25. HMQC spectrum of PAU-71.

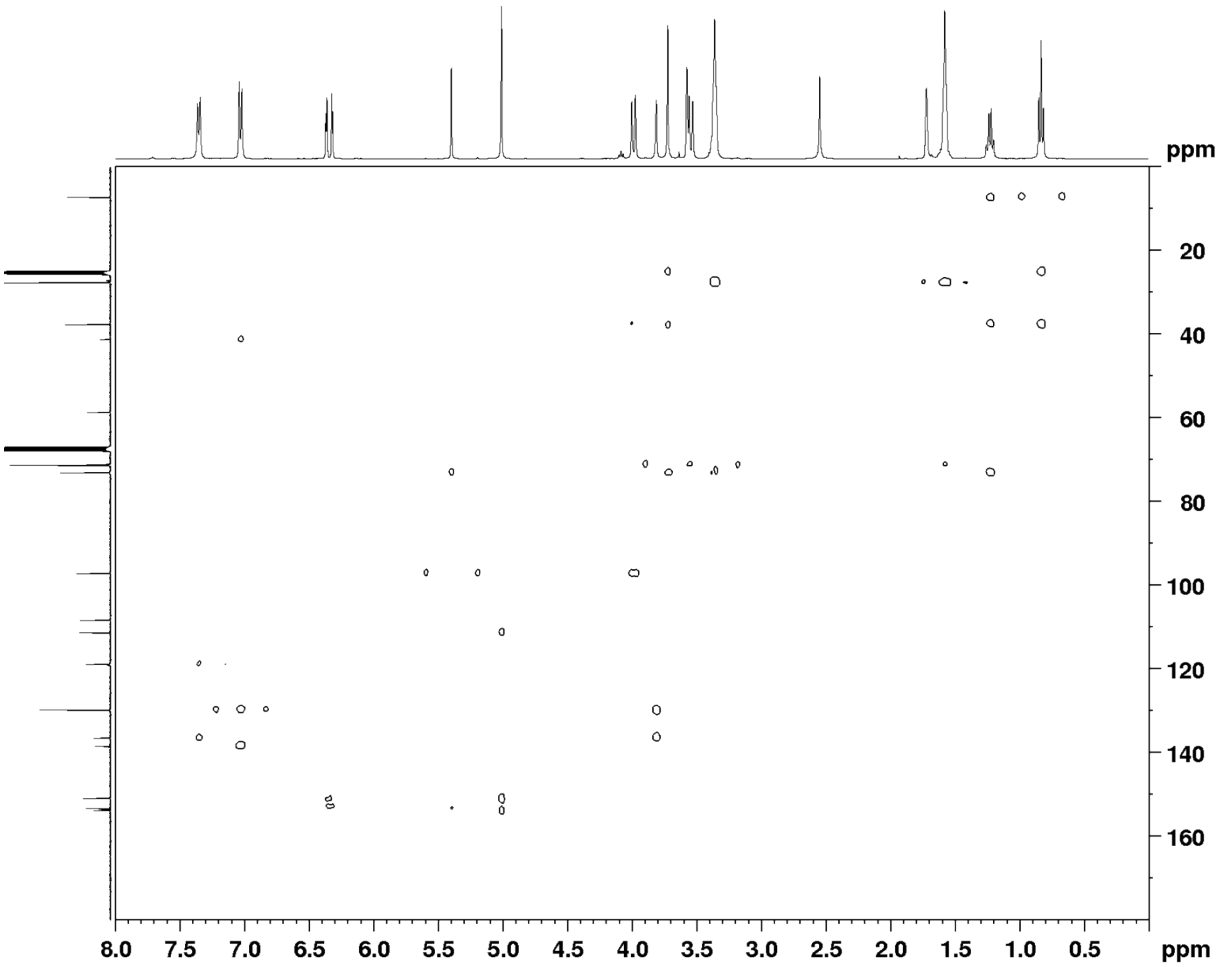

Figure S26. HMBC spectrum of PAU-71.

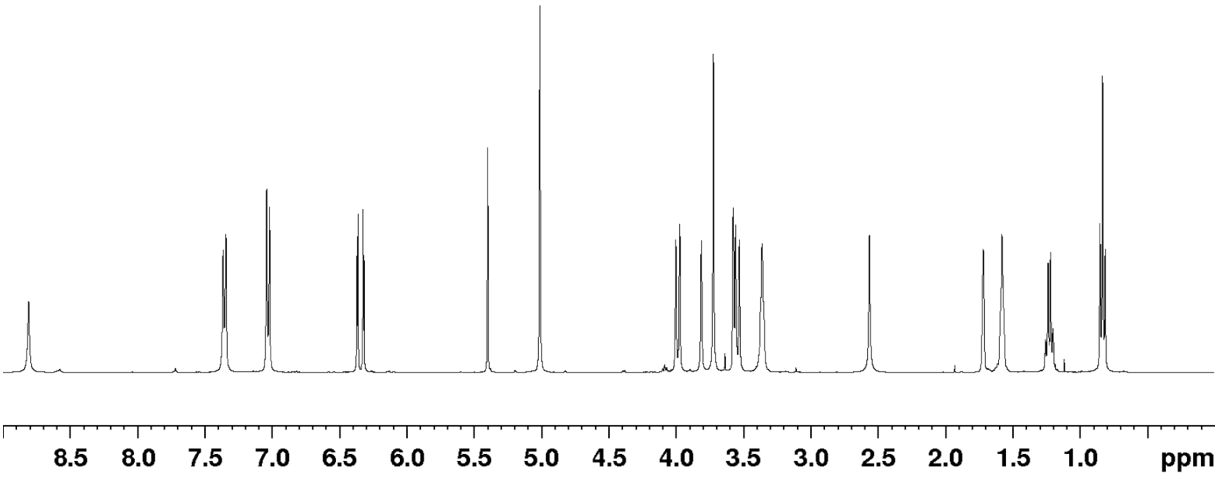

Figure S27. ^{1}H NMR spectrum of PAU-86.

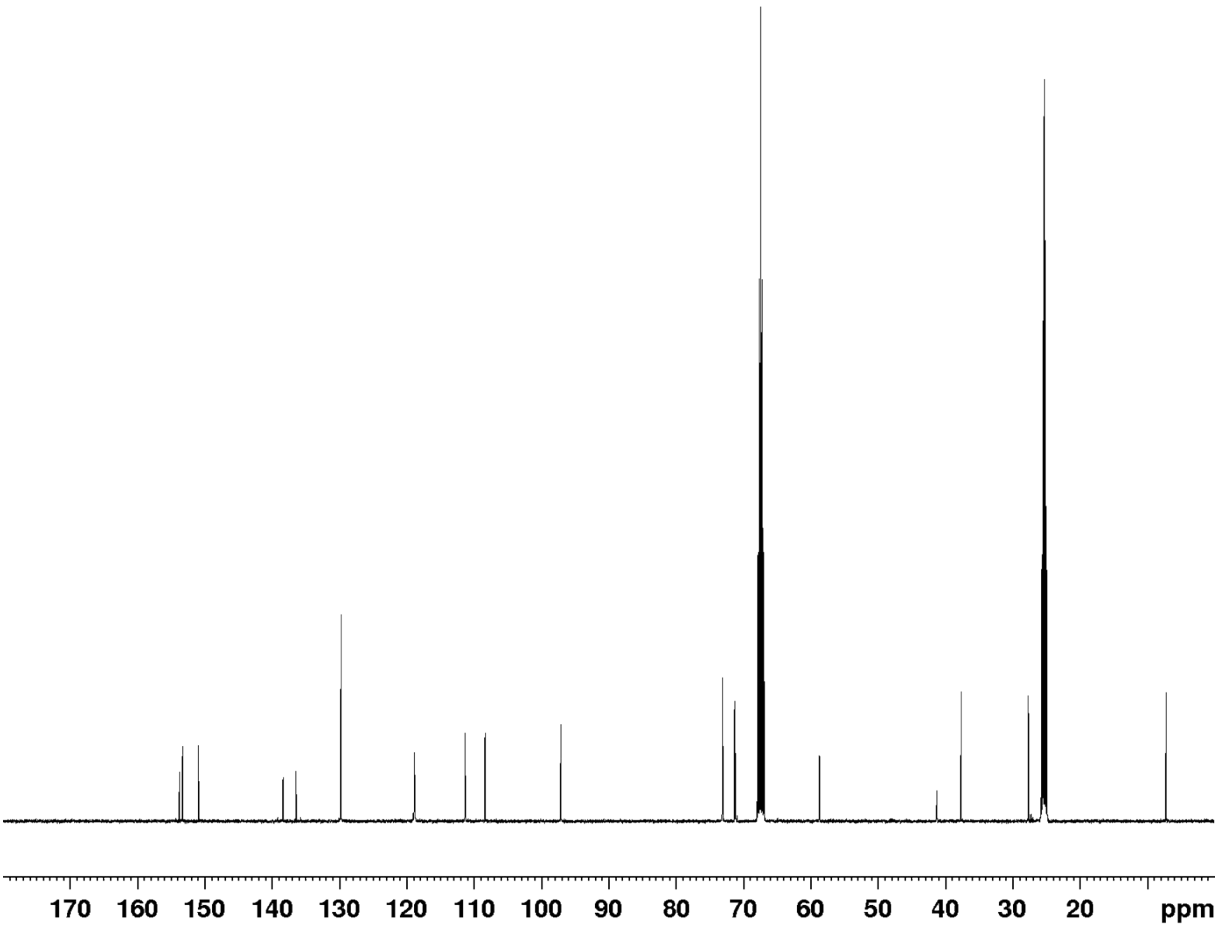

Figure S28. ^{13}C NMR spectrum of PAU-86.

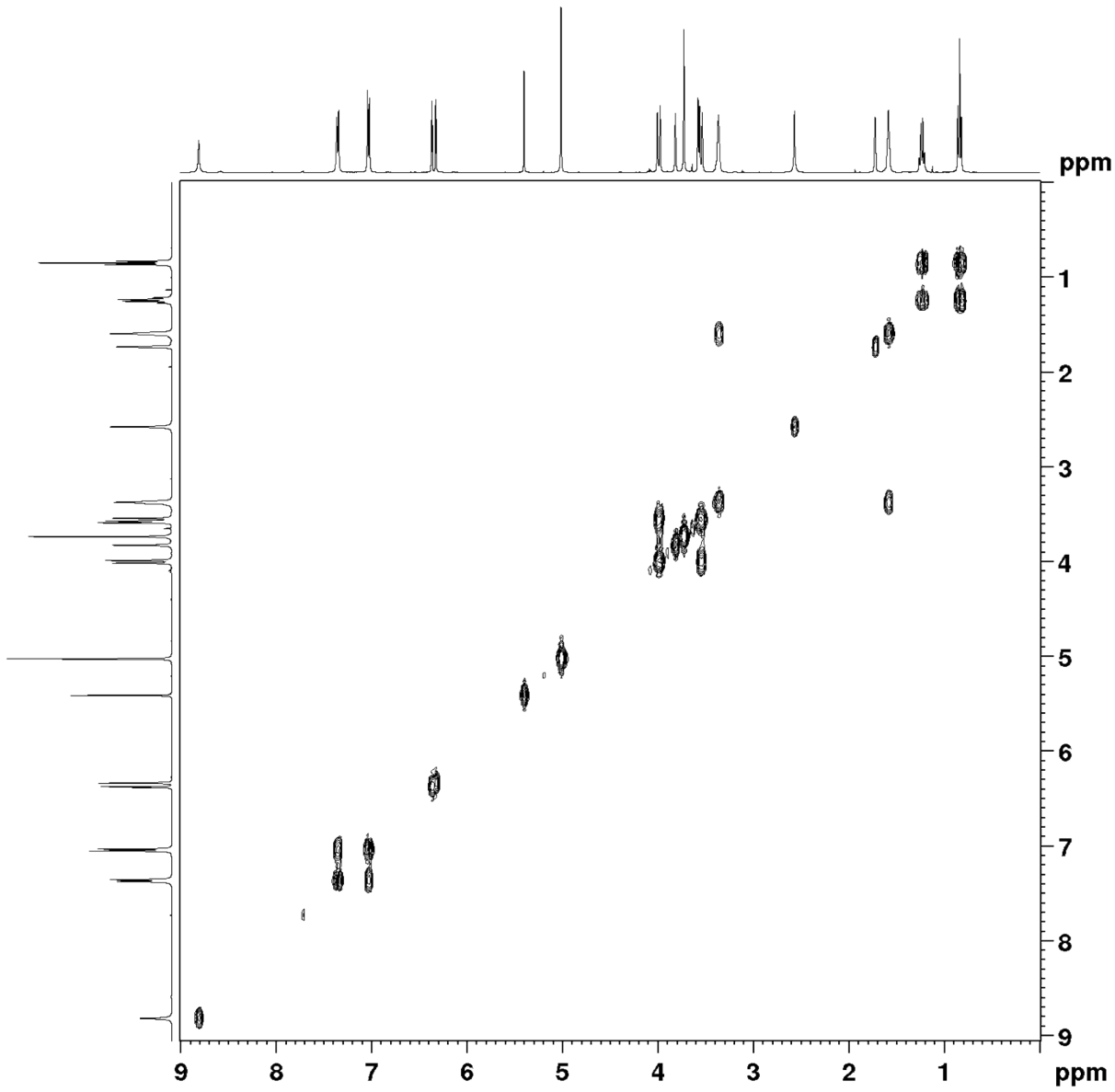

Figure S29. COSY spectrum of PAU-86.

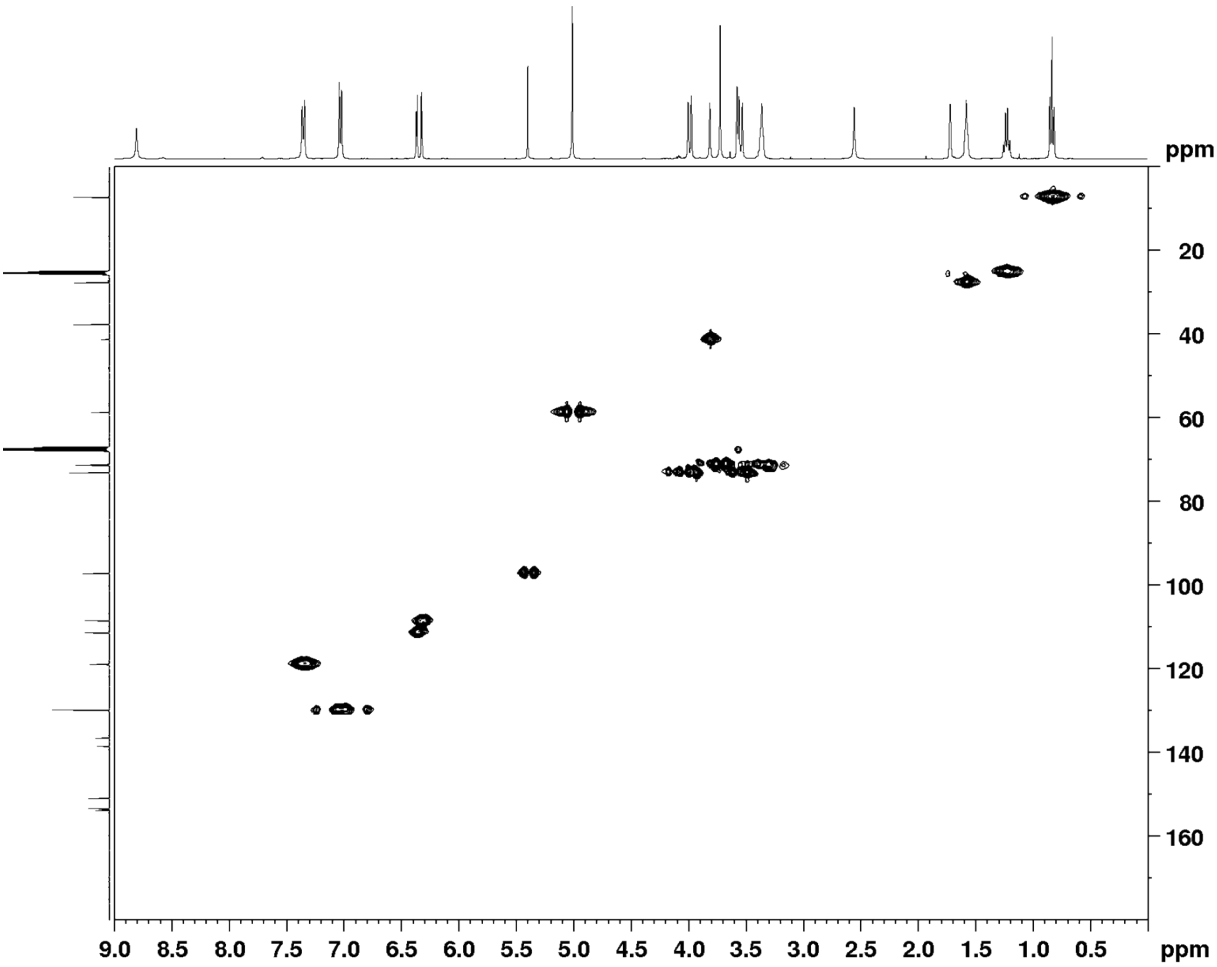

Figure S30. HMQC spectrum of PAU-86.

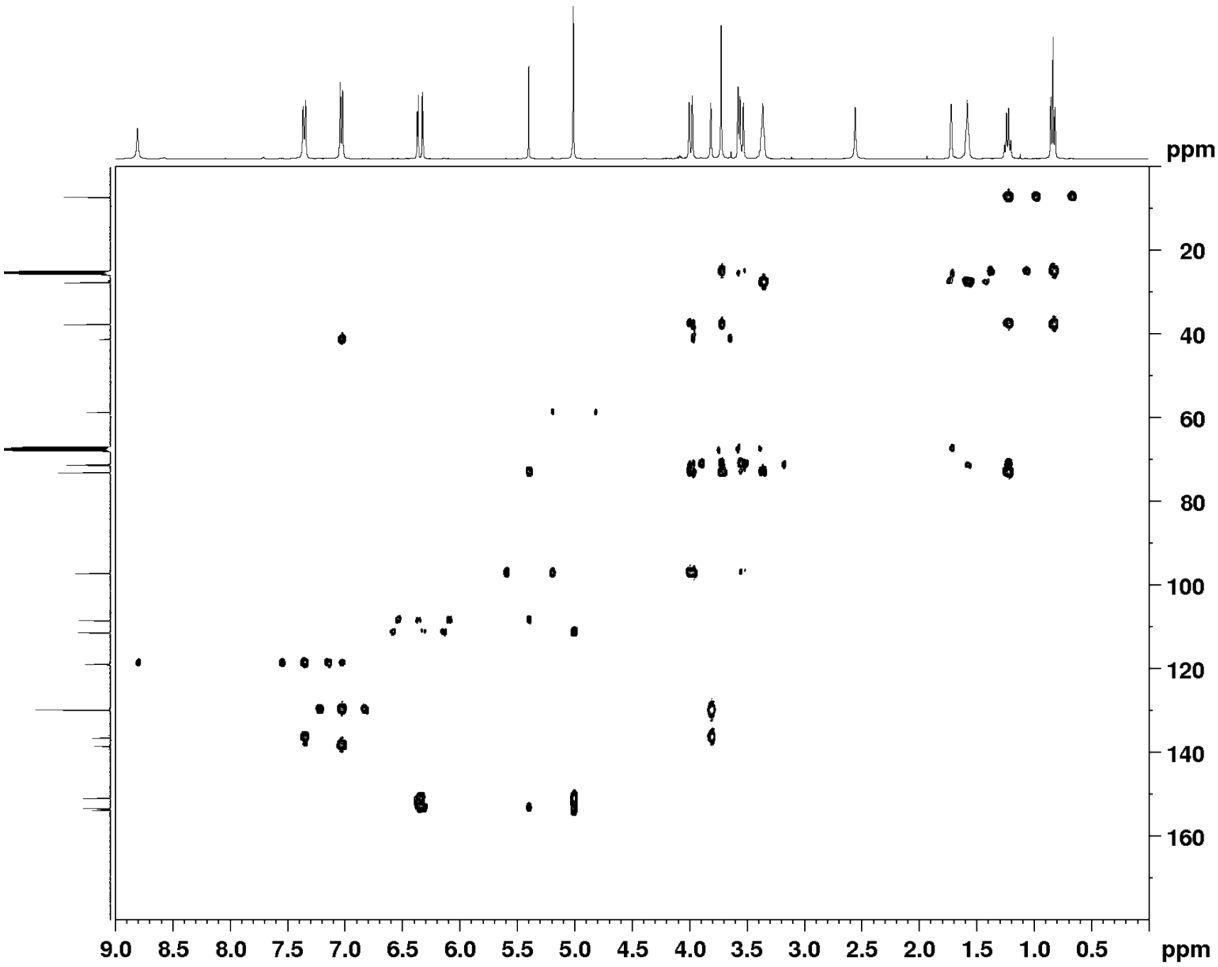

Figure S31. HMBC spectrum of PAU-86.

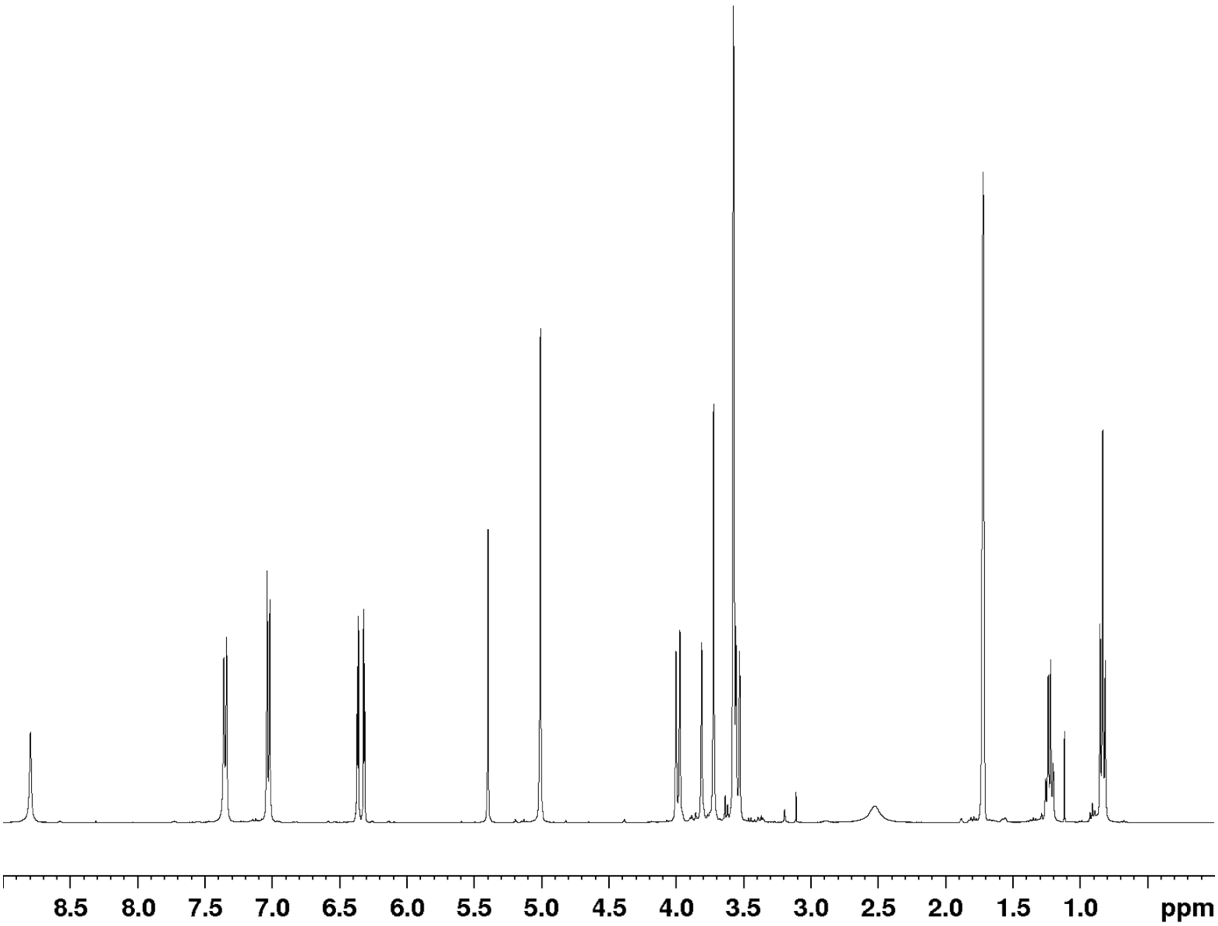

Figure S32. ^{1}H NMR spectrum of PAU-MDI.

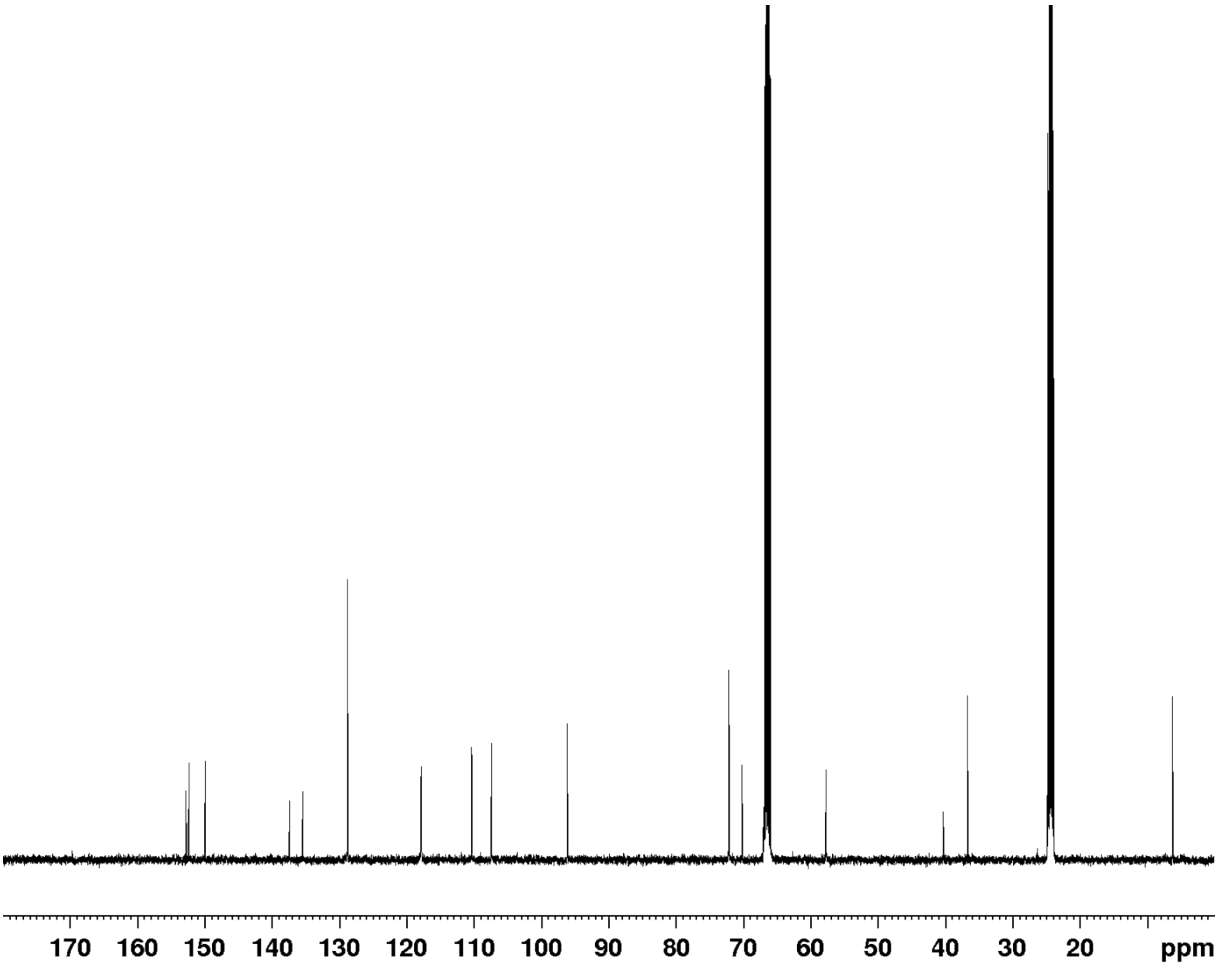

Figure S33. ^{13}C NMR spectrum of PAU-MDI.

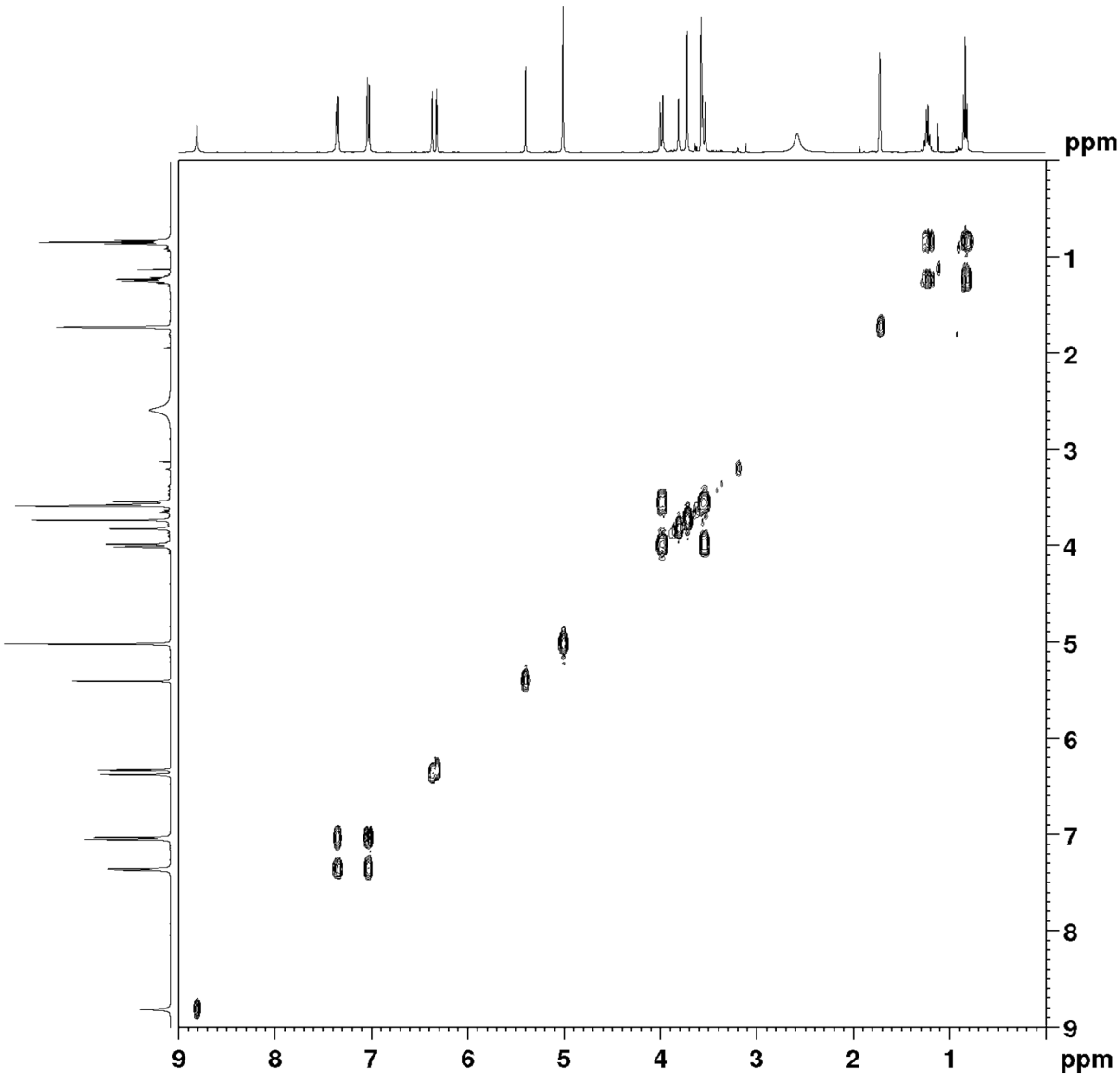

Figure S34. COSY spectrum of PAU-MDI.

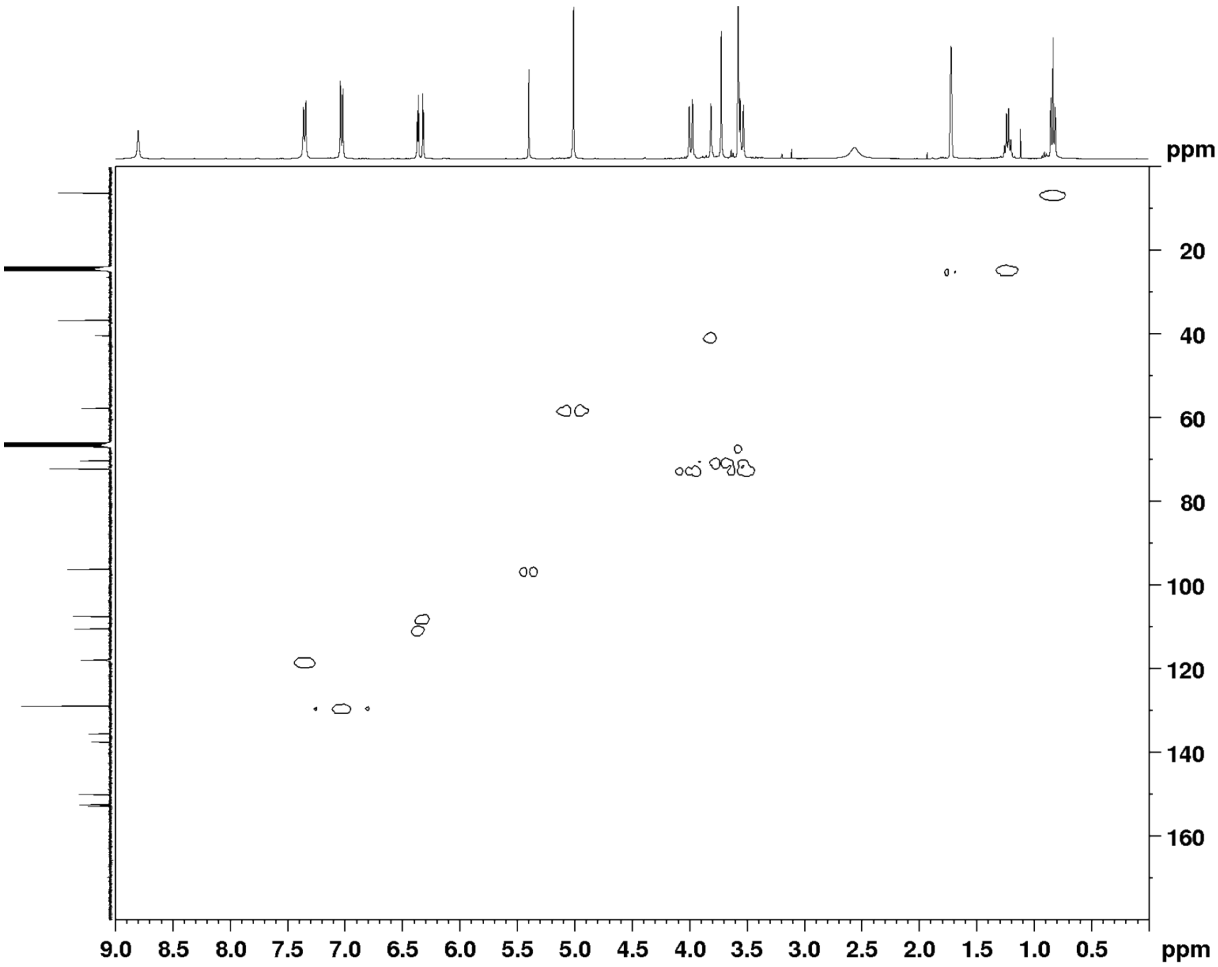

Figure S35. HMQC spectrum of PAU-MDI.

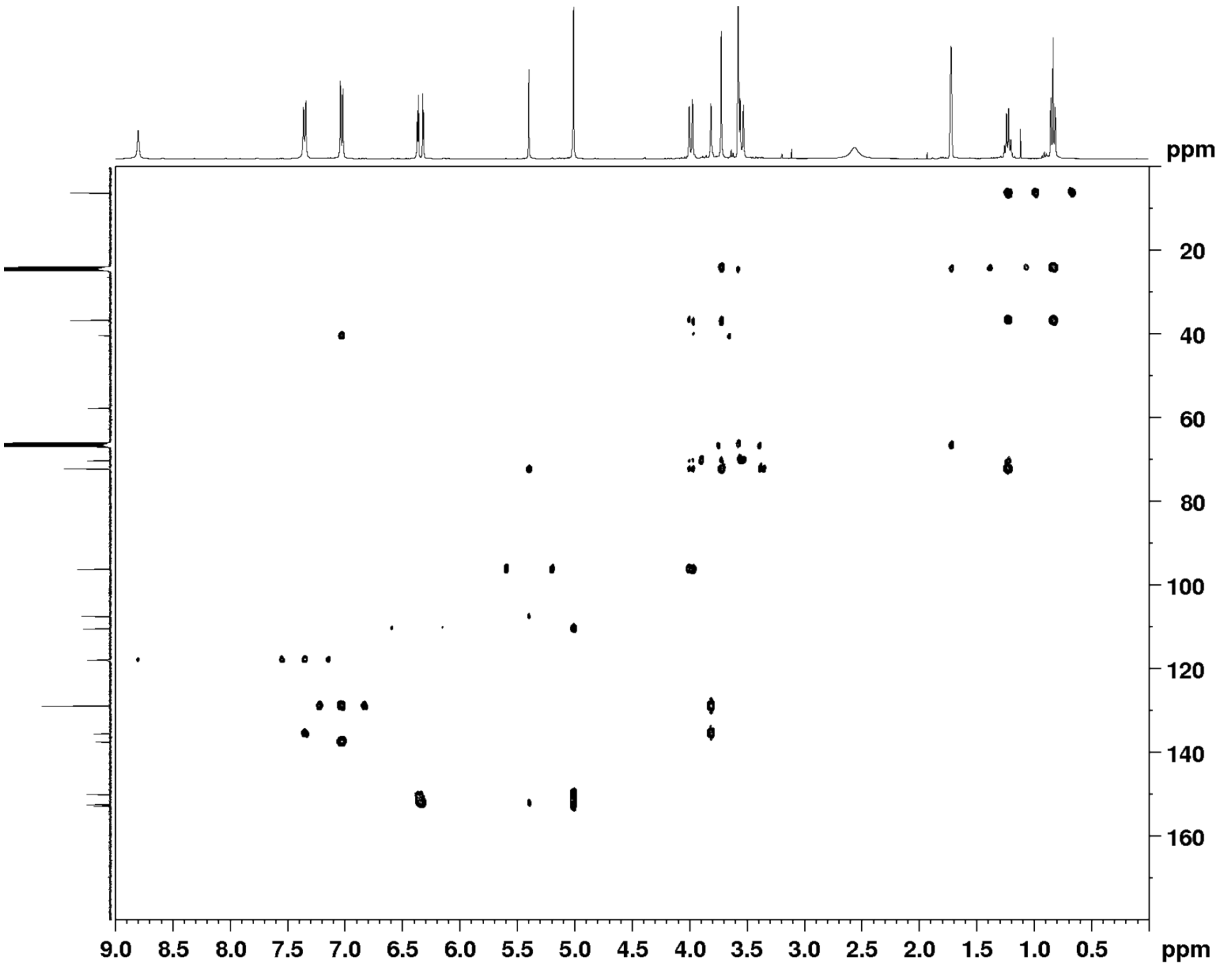

Figure S36. HMBC spectrum of PAU-MDI.

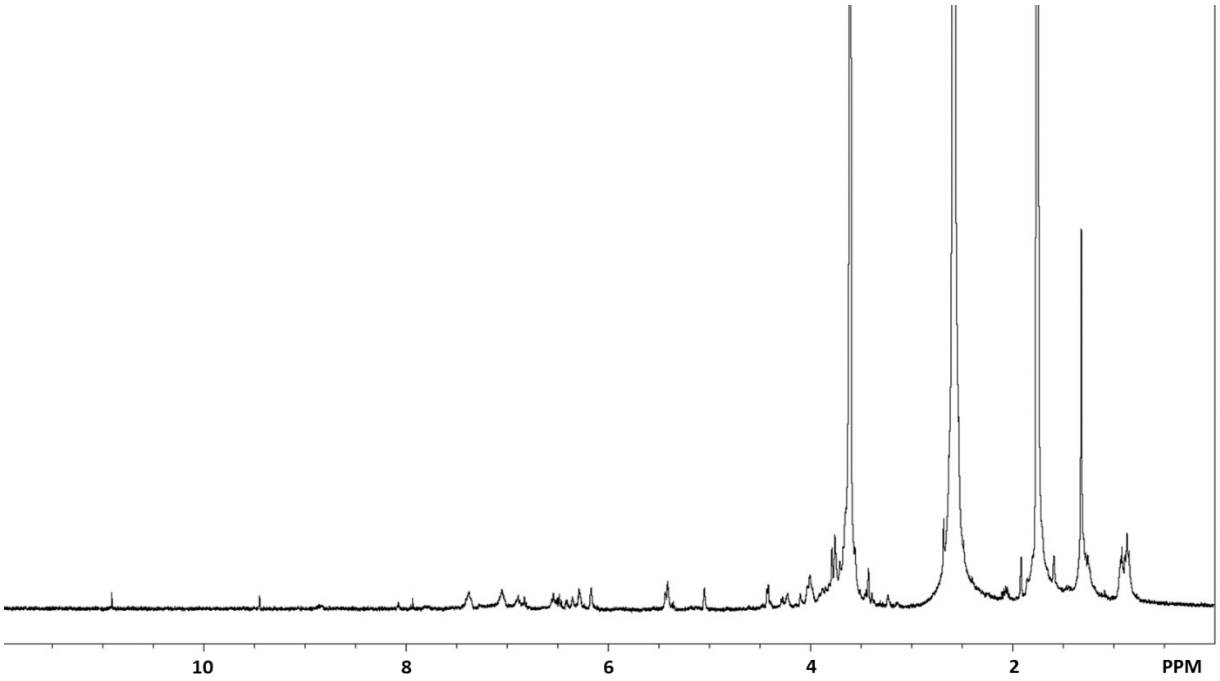

Figure S37. ^{1}H NMR spectrum of the soluble fraction of PU-MDI after TGA measurements.

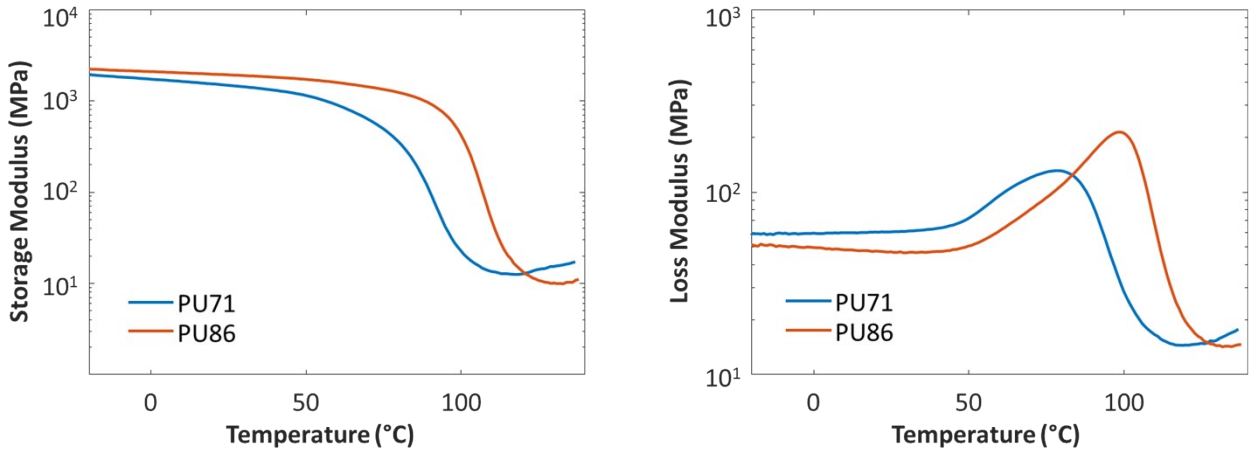

Figure S38. Temperature sweep DMA (left: storage moduli, and right: loss moduli) curves of PAU-71 and PAU-86.

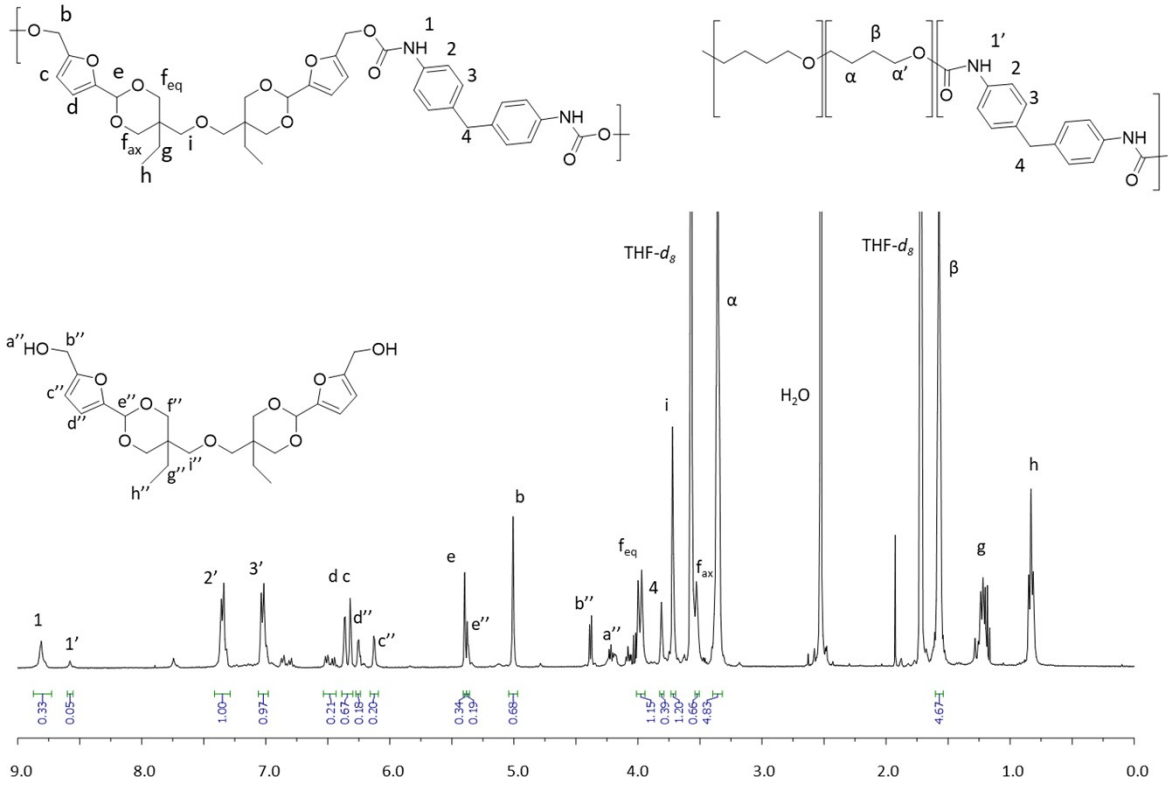

Figure S39. ^{1}H NMR spectrum of PAU-86 after the rheology measurements.

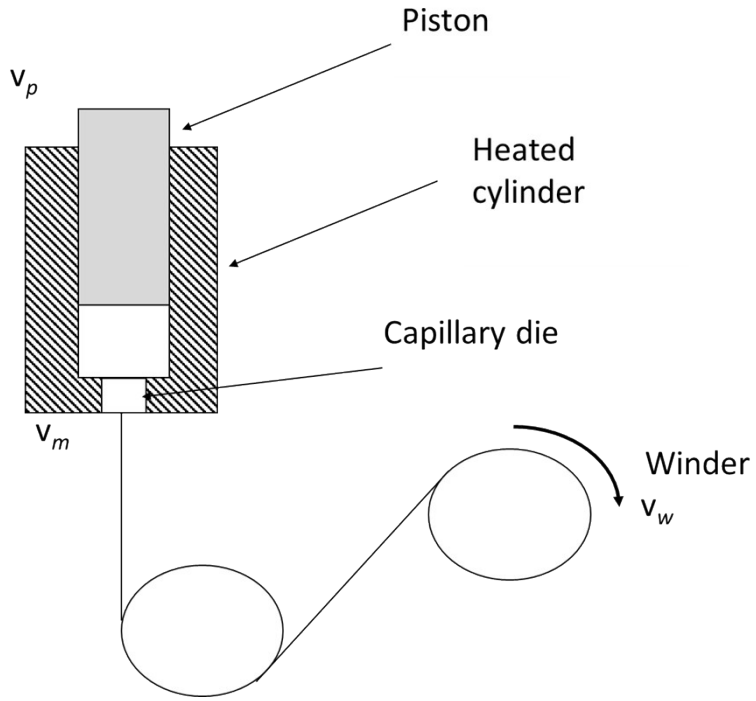

Figure S40. Schematic representation of melt-spinning process.

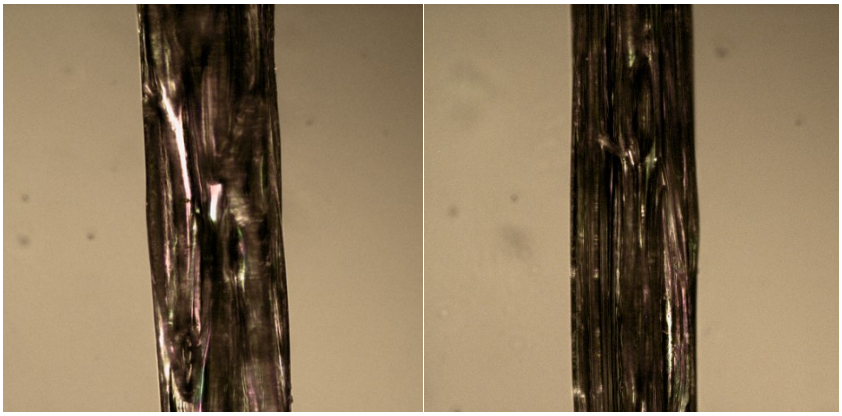

Figure S41. Cross-polarized optical microscopy images of the melt-spun PAU-86 fibre at the beginning of the spinning procedure (left) and at the end of it (right).

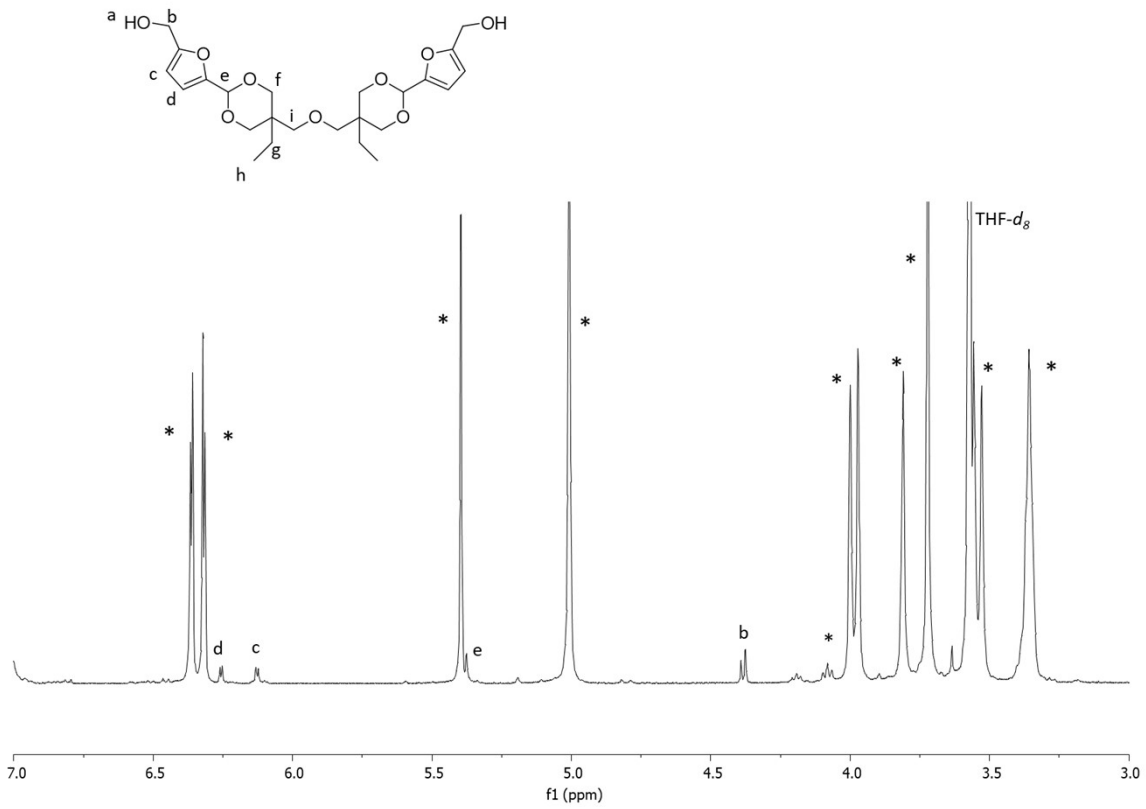

Figure S42. ^{1}H-NMR of PAU-86 fibre. The signals corresponded to Monomer T were indicated. The signals corresponding to PAU-86 were marked by stars (*). For specific assignments, please see Fig. 1.

Figure S43. PAU-85 before fibre spinning.

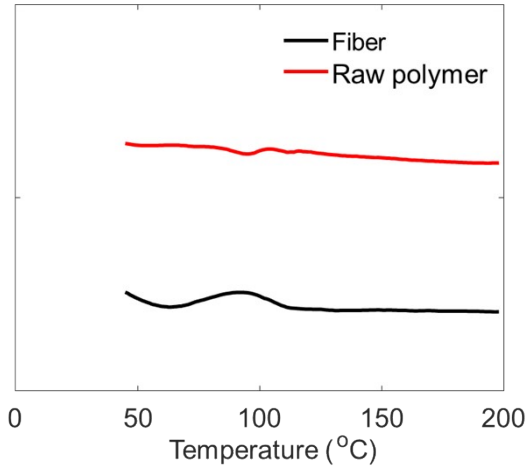

Figure S44. First heating cycle of PAU-86 fibre (black curve) and raw polymer powder before processing (red curve).

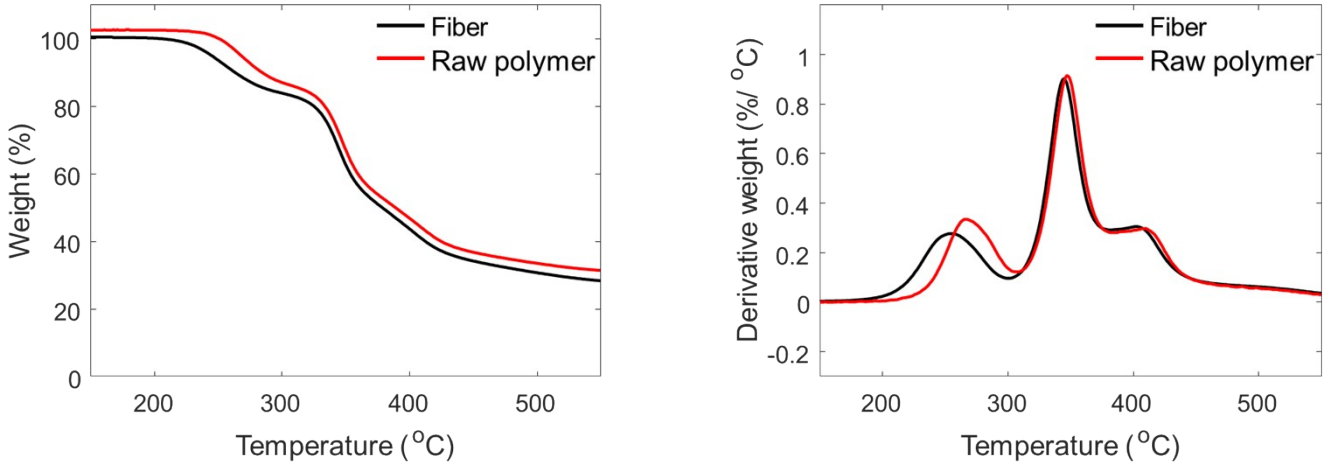

Figure S45. TGA (left) weight loss and (right) derivative weight loss curves of PAU-86 fibre (black curve) and unprocessed polymer powder (red curve).

Table S1. Thermal properties of PU86 before and after fiber spinning. [a] The temperature for maximal degradation rate in TGA. [b] The temperature for 5% weight loss in TGA curves.

	T_d[a] (°C)	T_5[b] (°C)
PU86-fiber	255, 346, 404	244
PU86-raw	266, 349, 411	268

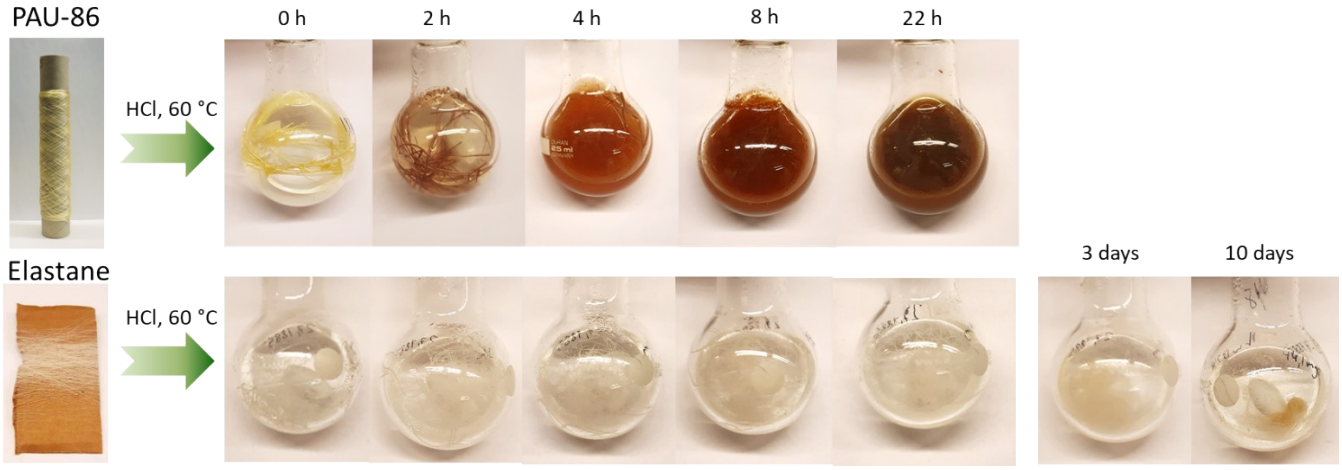

Figure S46. Acid-hydrolysis of the PAU-86 fibre and Elastane. The time above each photo indicates the reaction time when the photo was taken.

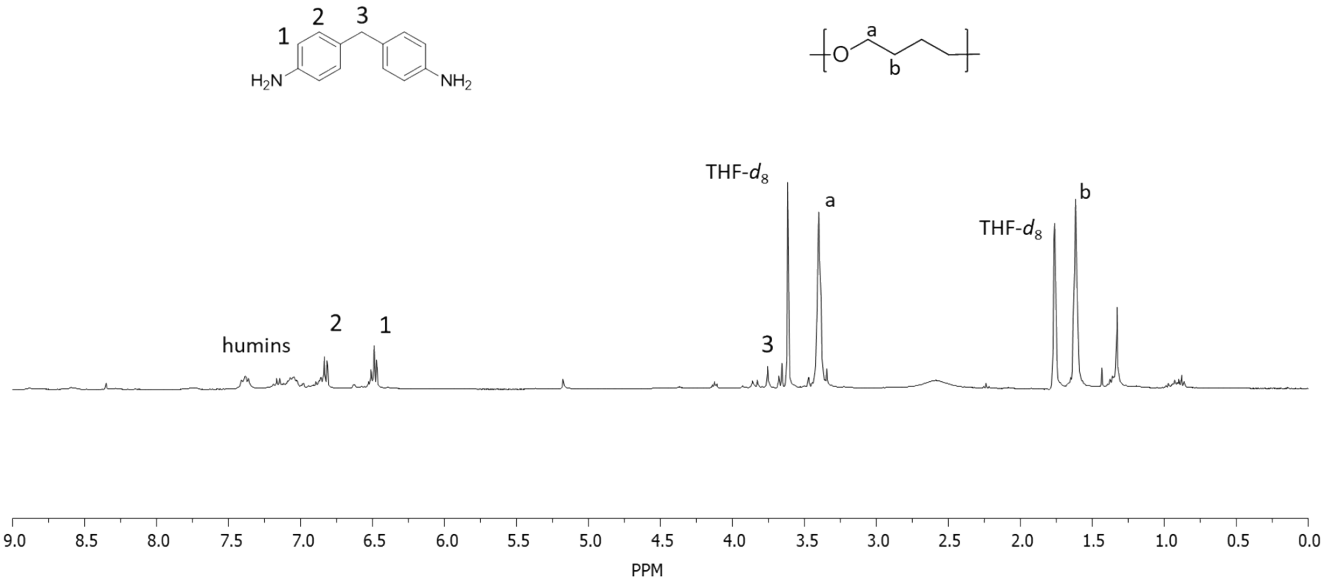

Figure S47. ^{1}H NMR spectrum in THF-d_8 of yielded material extracted by THF from the solid residue remaining of the PAU-86 fibre.

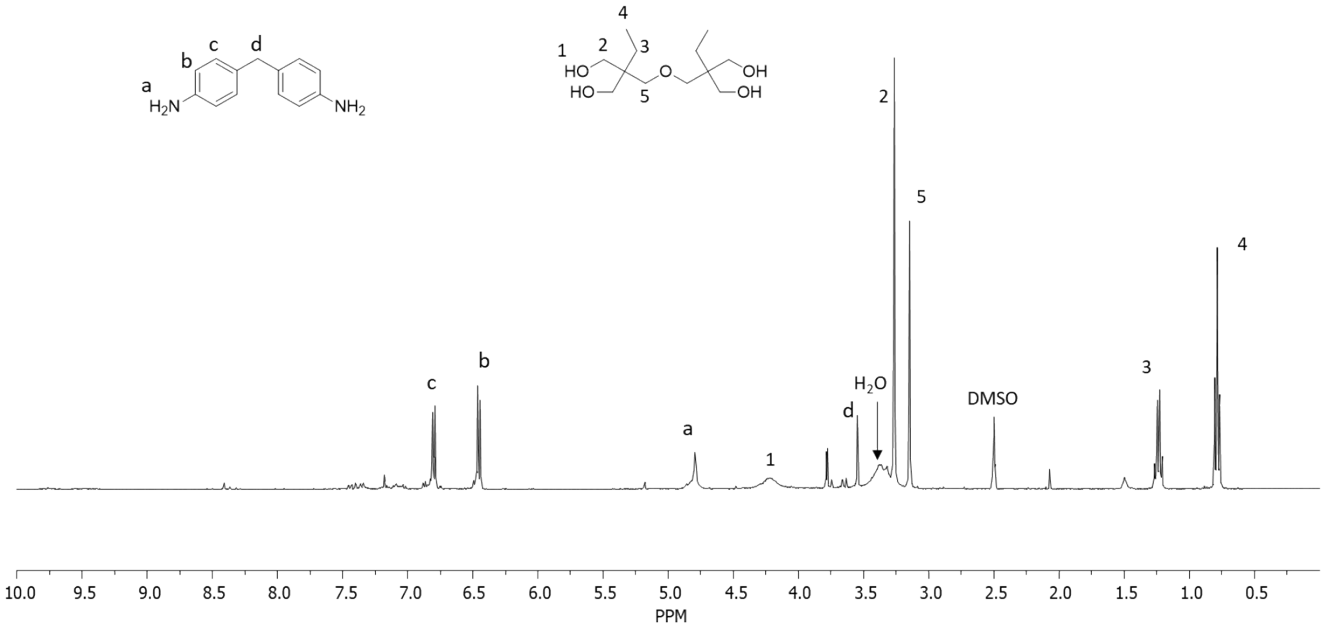

Figure S48. ^{1}H NMR spectrum in DMSO-d_6 of yielded material after hydrolysis of PAU-86 fibre for 24 h. The signals for di-TMP and 4,4-diaminodiphenylmethane were indicated.

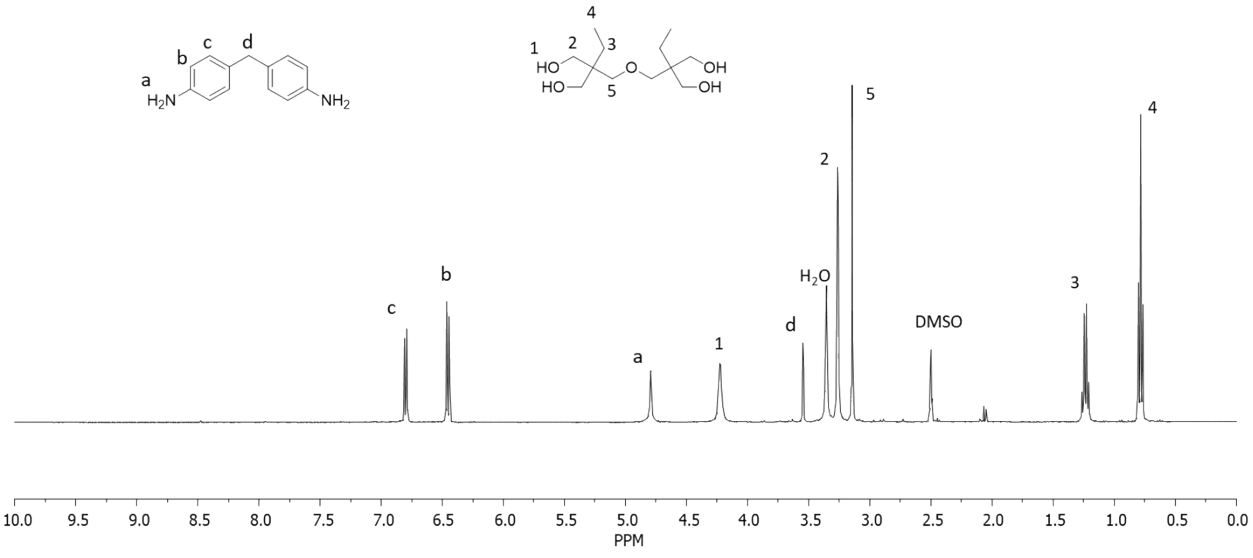

Figure S49. ^{1}H NMR spectrum in DMSO-d_6 of yielded material after hydrolysis of PAU-86 fibre for 48 h. The signals for di-TMP and 4,4-diaminodiphenylmethane were indicated.

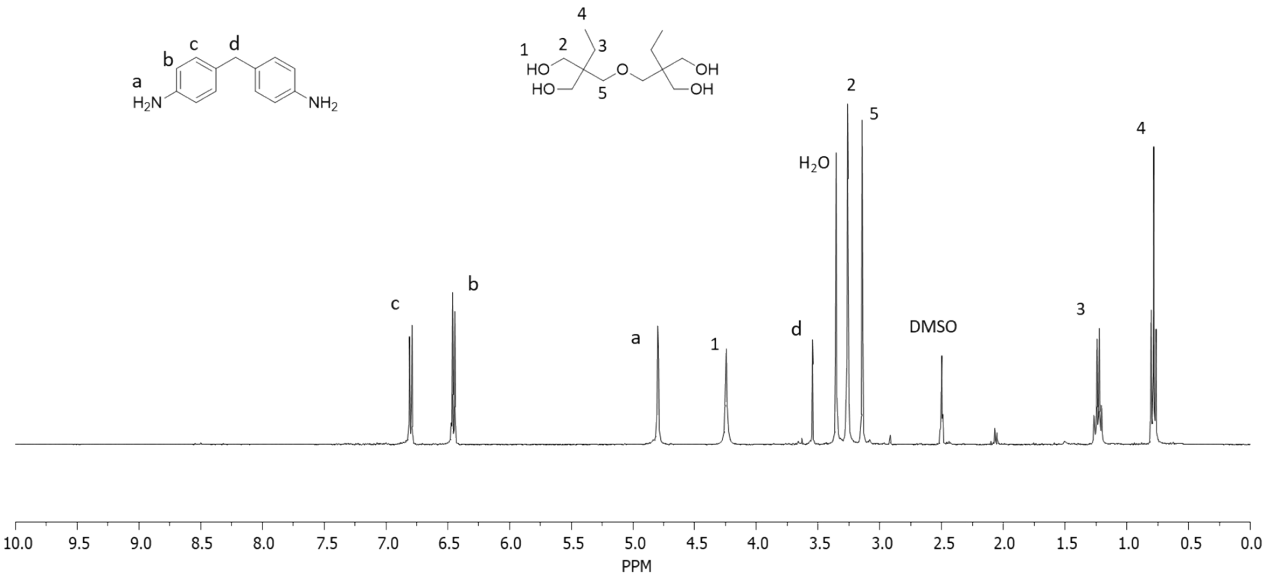

Figure S50. ^{1}H NMR spectrum in DMSO-d_6 of yielded material after hydrolysis of PAU-86 fibre for 52 days. The signals for di-TMP and 4,4-diaminodiphenylmethane were indicated.

Table S2. The yield of the recovered monomers.

Time	yield
24 h	69 % di-TMP 17 % MDA
48 h	77 % di-TMP 18 % MDA
52 days	73% di-TMP 22 % MDA

Table S3. Yield of the recovered monomers when using different solvents for extraction.

Solvent	diTMP	MDA
DCM	15 %	25 %
THF	84 %	20 %
ACN	64 %	20 %
MeOH	-	-

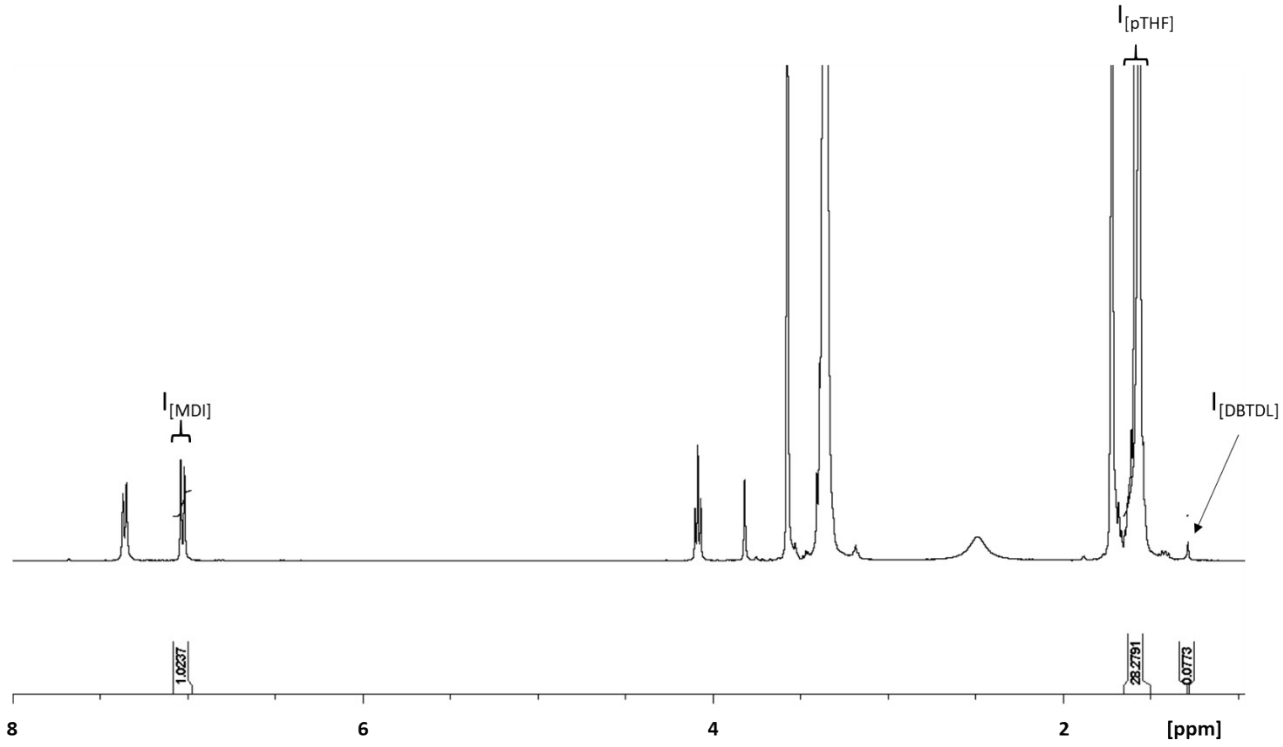

Figure S51. ^{1}H NMR spectrum of PAU-0. The signals necessary for calculating the DBTDL content were indicated. For assignments of all signals see Fig. 1.

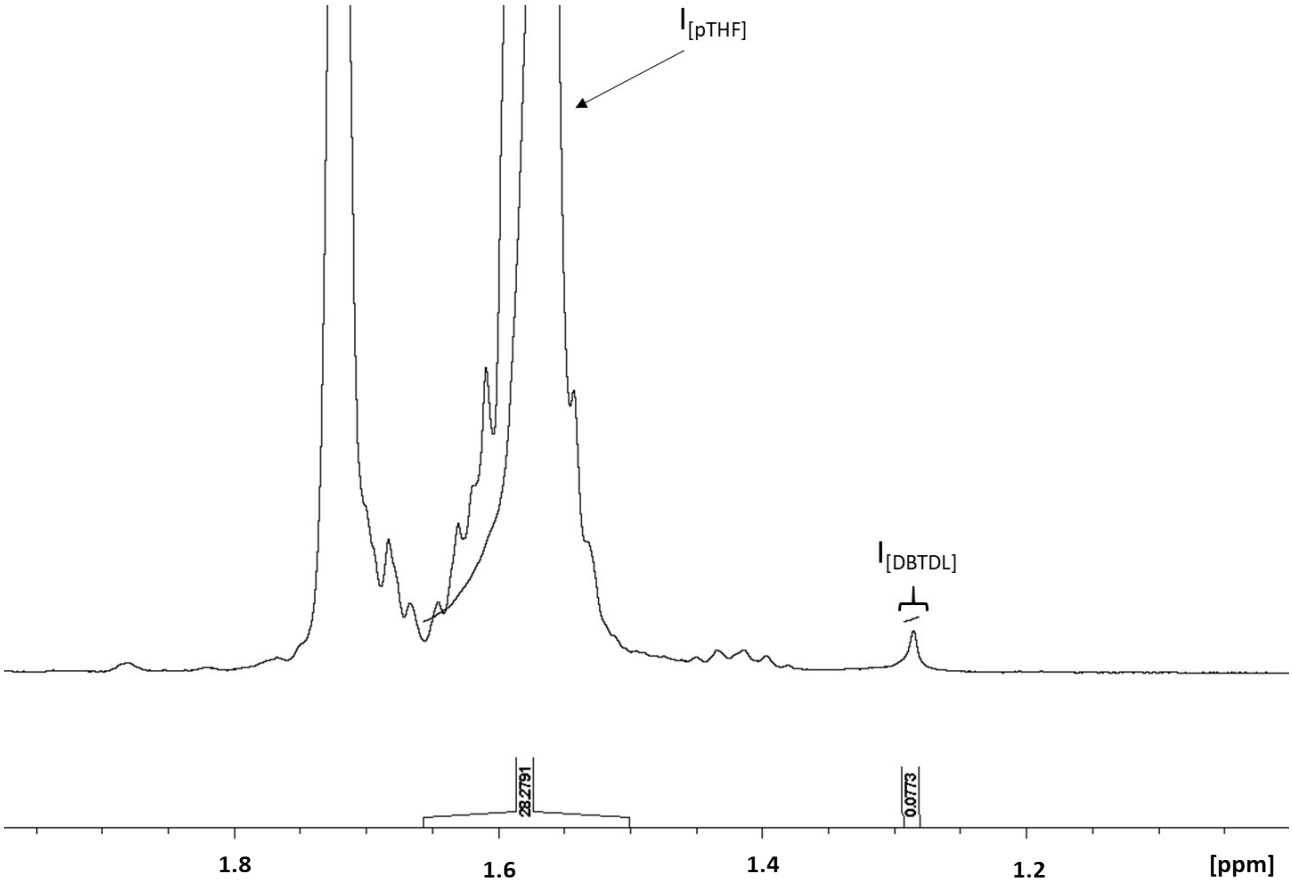

Figure S52. Zoomed-in ^{1}H NMR spectrum of PAU-0. The signals necessary for calculating the DBTDL content were indicated.

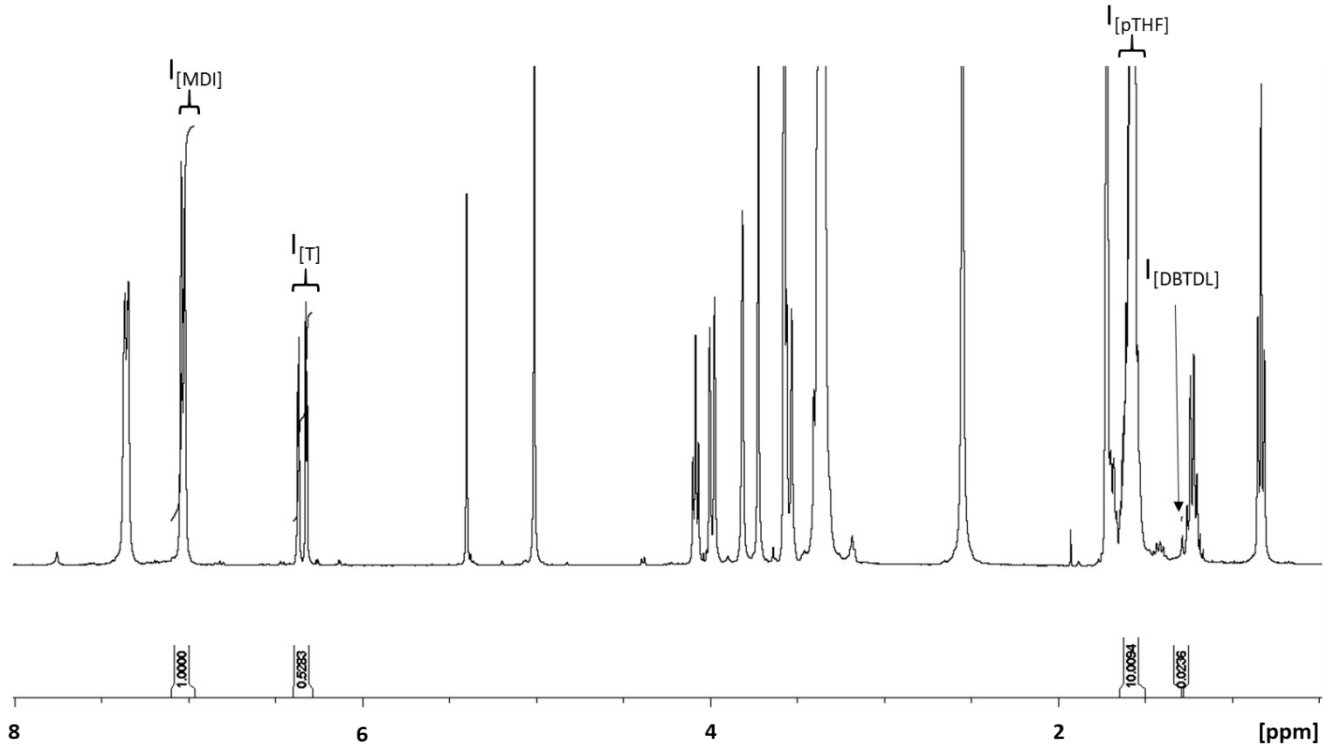

Figure S53. ^{1}H NMR spectrum of PAU-25. The signals necessary for calculating the DBTDL content were indicated. For assignments of all signals see Fig. 1.

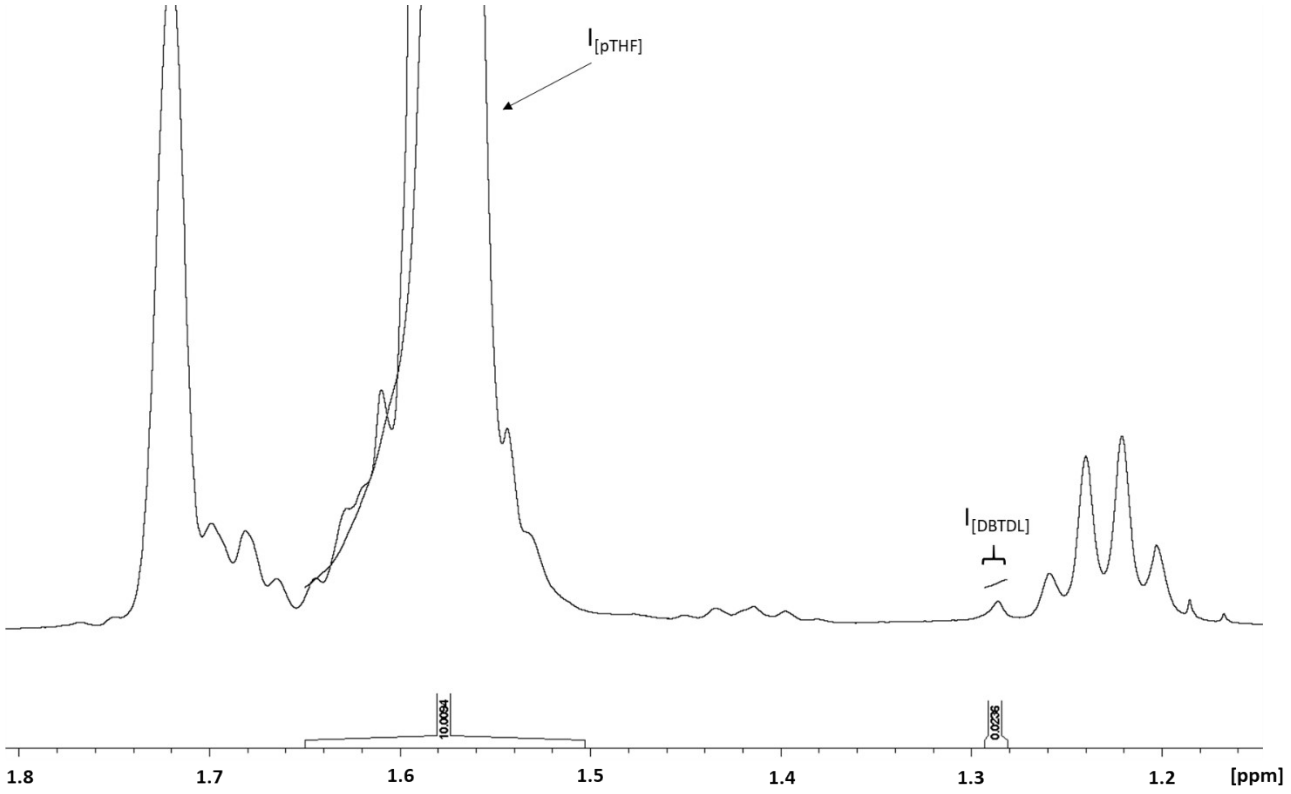

Figure S54. Zoomed-in ^{1}H NMR spectrum of PAU-25. The signals necessary for calculating the DBTDL content were indicated.

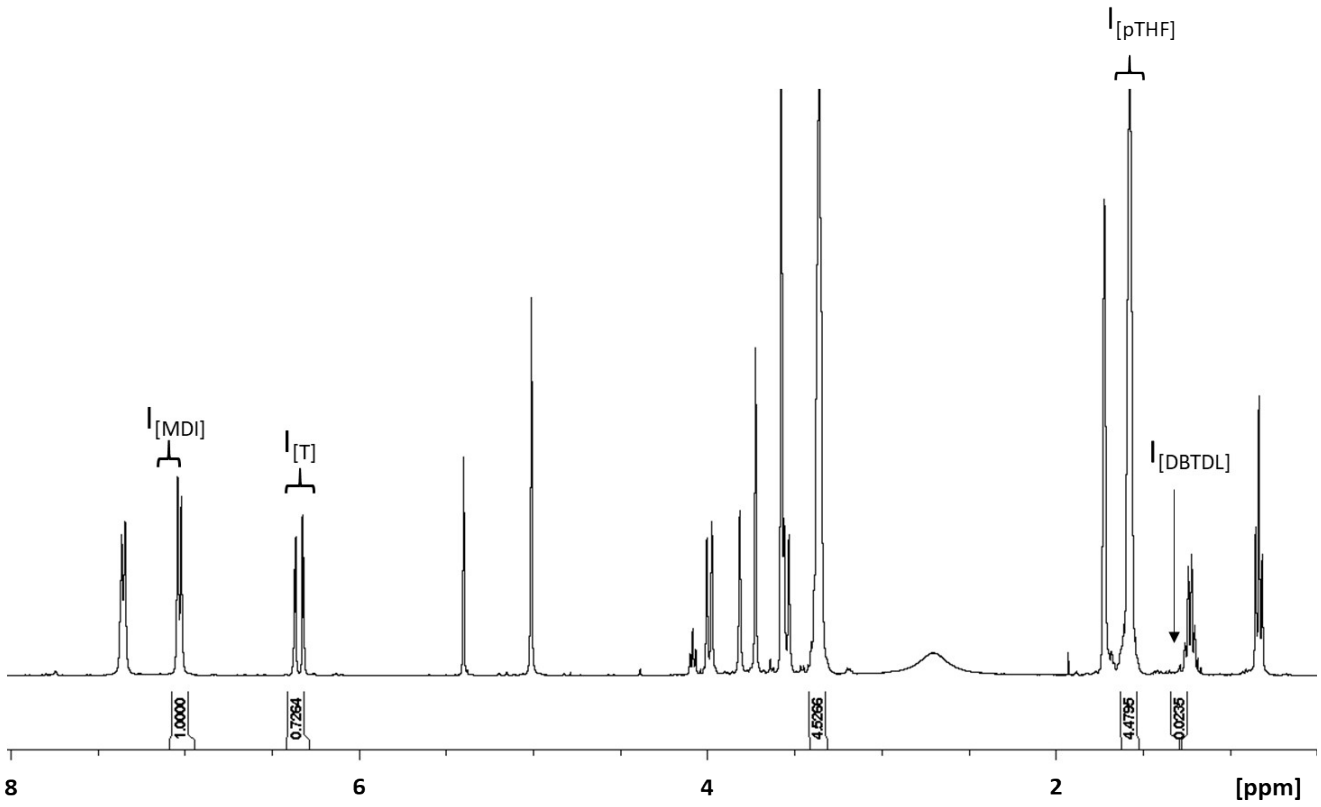

Figure S55. ^{1}H NMR spectrum of PAU-51. The signals necessary for calculating the DBTDL content were indicated. For assignments of all signals see Fig. 1.

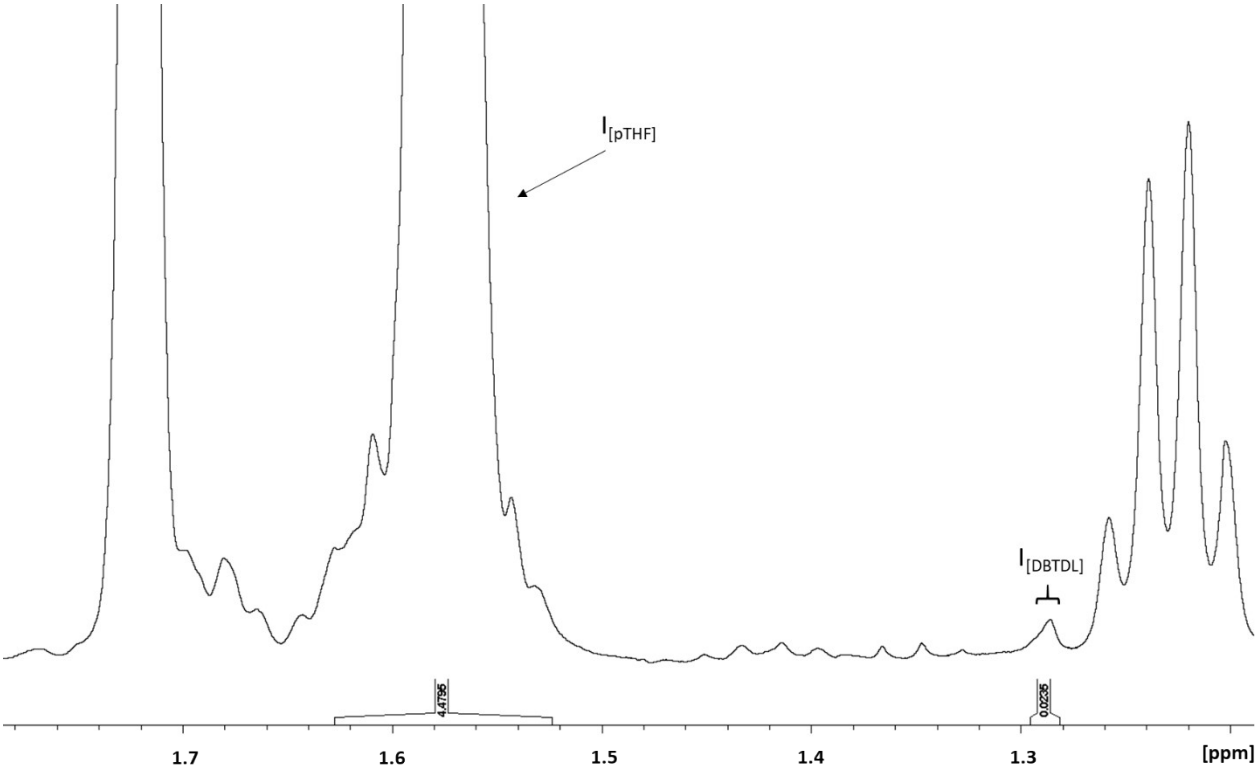

Figure S56. Zoomed-in ^{1}H NMR spectrum of PAU-51. The signals necessary for calculating the DBTDL content were indicated.

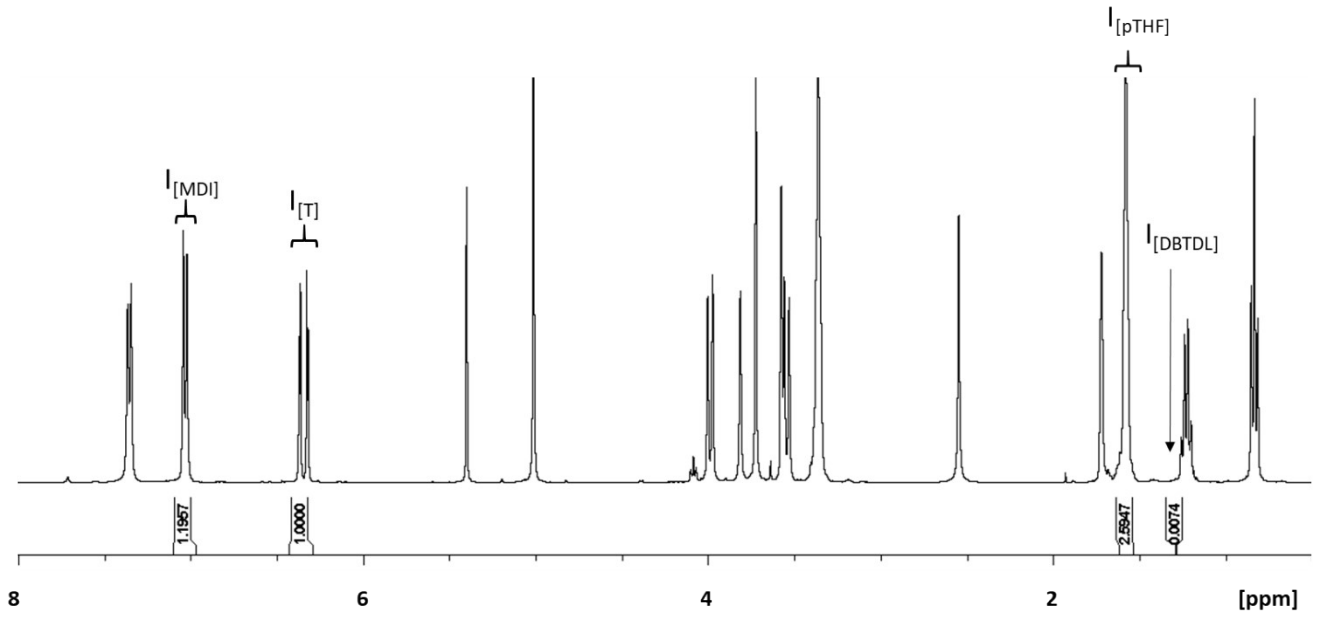

Figure S57. ^{1}H NMR spectrum of PAU-71. The signals necessary for calculating the DBTDL content were indicated. For assignments of all signals see Fig. 1.

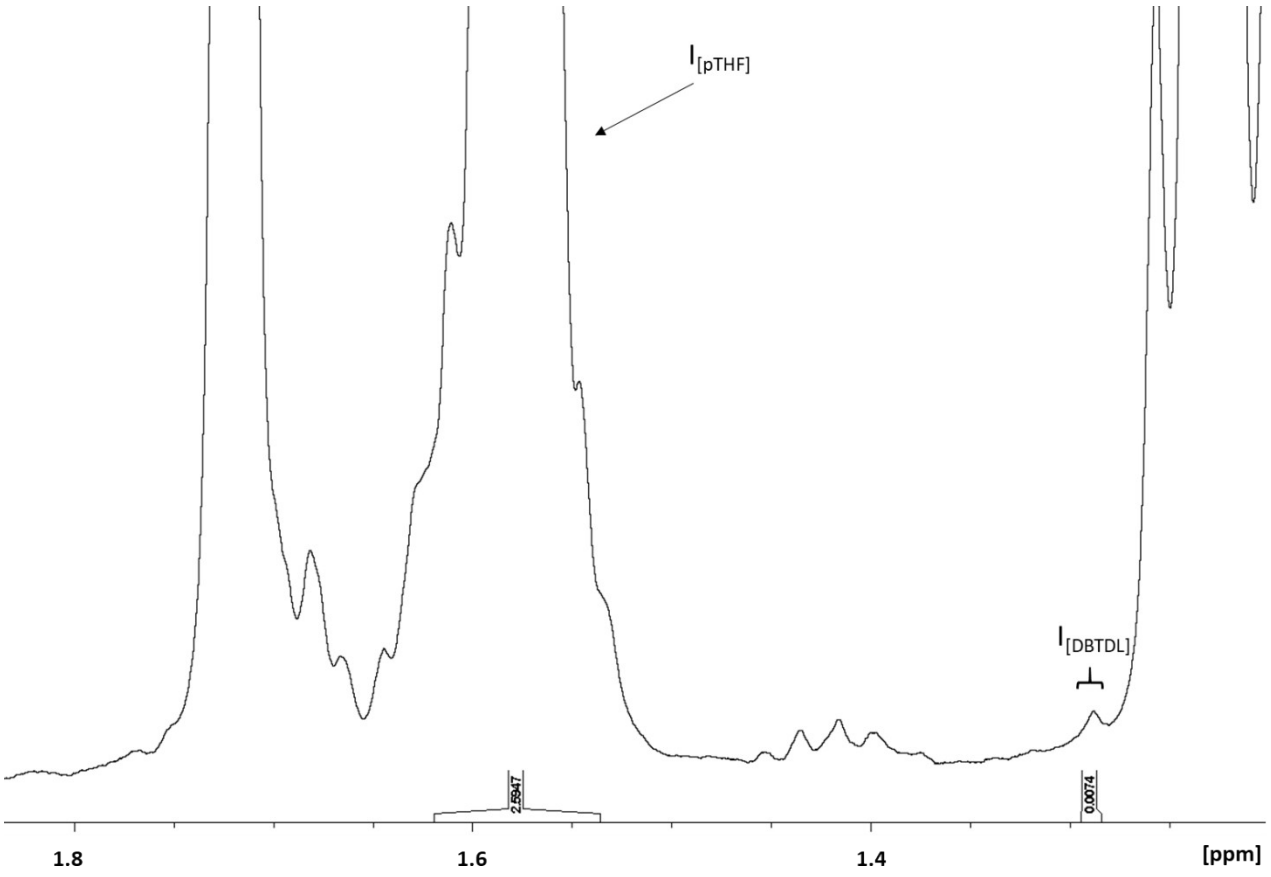

Figure S58. Zoomed-in ^{1}H NMR spectrum of PAU-71. The signals necessary for calculating the DBTDL content were indicated.

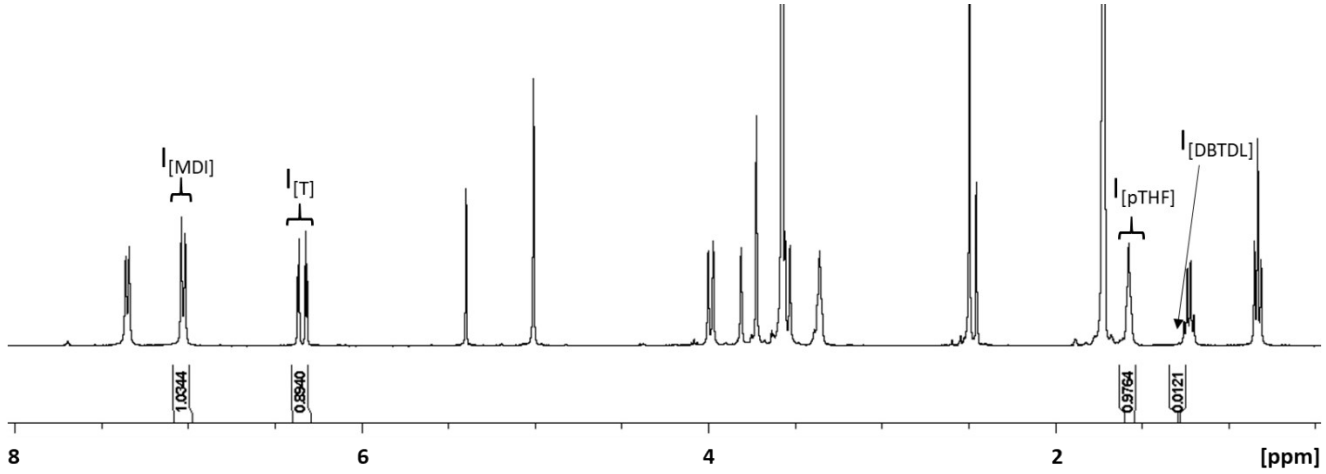

Figure S59. ^{1}H NMR spectrum of PAU-86. The signals necessary for calculating the DBTDL content were indicated. For assignments of all signals see Fig. 1.

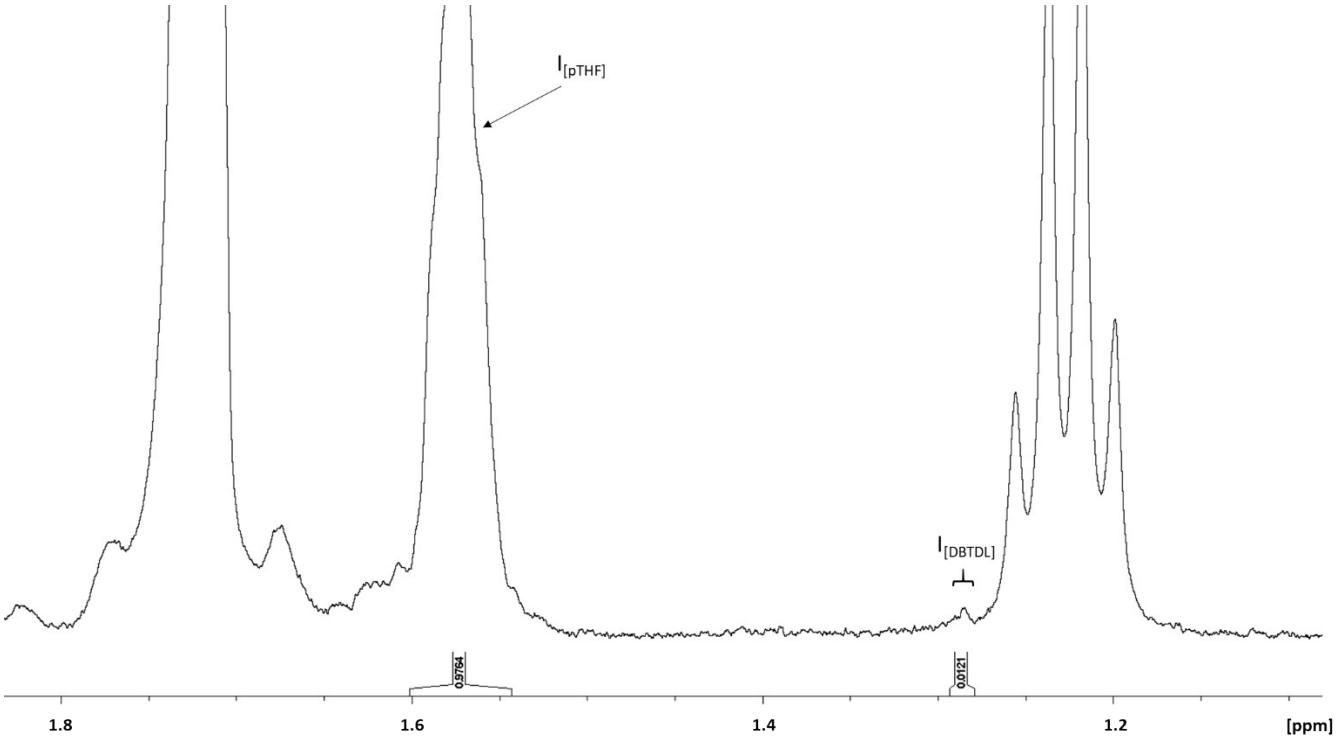

Figure S60. Zoomed-in ^{1}H NMR spectrum of PAU-86. The signals necessary for calculating the DBTDL content were indicated.

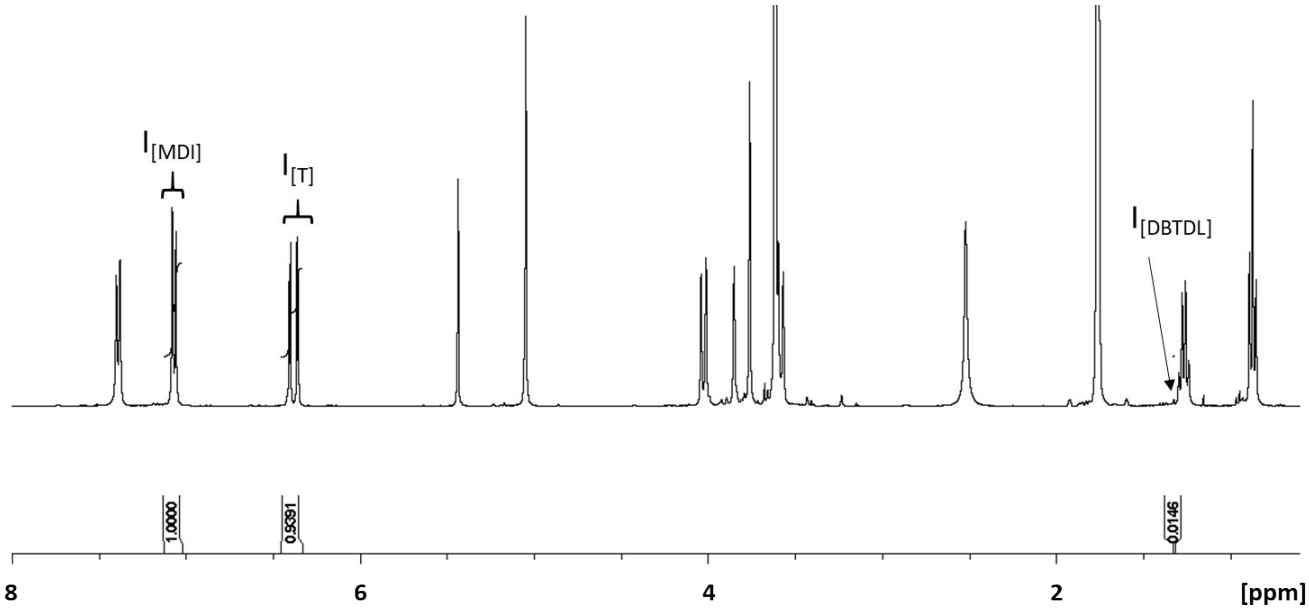

Figure S61. ^{1}H NMR spectrum of PAU-100. The signals necessary for calculating the DBTDL content were indicated. For assignments of all signals see Fig. 1.

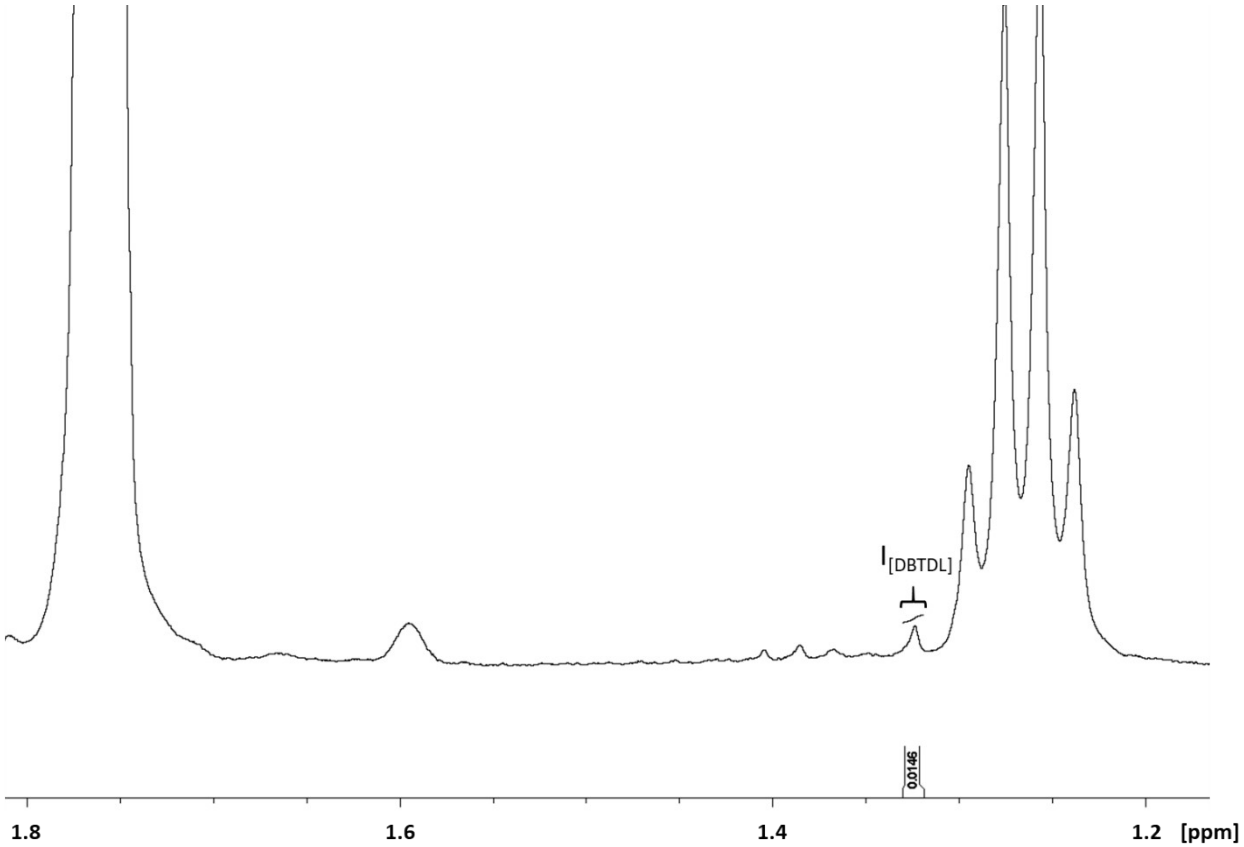

Figure S62. Zoomed-in ^{1}H NMR spectrum of PAU-100. The signals necessary for calculating the DBTDL content were indicated.

The catalyst content of the polymers was estimated using the method below:

M_{MDI} = 250.25 g/mol

M_T = 466.52 g/mol

M_{pTHF} = 2000.00 g/mol

M_{DBTDL} = 631.56 g/mol

The integrals used for each monomer were taken from Fig. S51-62. $I_{[MDI]}$ corresponds to 4 H on the MDI segment, $I_{[T]}$ corresponds to 4 H on the Monomer T segment, $I_{[pTHF]}$ corresponds to 111 H on the pTHF segment and $I_{[DBTDL]}$ corresponds to 44 H on the catalyst DBTDL.

The mass ratio (r_x) between the monomers was then estimated by dividing the integral with the corresponding number of protons ($n_{H\text{-}x}$), and then multiplied with the molecular mass of each monomer (M_x) individually:

Eq. S1
$$\frac{I_{[X]}}{n_{H-X}} * M_x = r_X$$

Where X represents the monomer or the catalyst.

Finally, the wt% DBTDL catalyst was calculated by dividing the mass ratio for DBTDL (r_{DBTDL}) with the total mass:

Eq. S2
$$\frac{r_{DBTDL}}{r_{MDI} + r_T + r_{pTHF} + r_{DBTDL}} * 100 = wt\%\ DBTDL$$

For example, the wt% DBTDL in PAU-86 was calculated below:

$$\frac{I_{[MDI]}}{n_{H-MDI}} * M_{MDI} = r_{MDI} = \frac{1.034}{4} * 250.25 = 64.69$$

$$\frac{I_{[T]}}{n_{H-T}} * M_T = r_T = \frac{0.894}{4} * 466.52 = 104.27$$

$$\frac{I_{[pTHF]}}{n_{H-pTHF}} * M_{pTHF} = r_{pTHF} = \frac{0.9764}{111} * 2000 = 17.59$$

$$\frac{I_{[DBTDL]}}{n_{H-DBTDL}} * M_{DBTDL} = r_{DBTDL} = \frac{0.0121}{44} * 631.56 = 0.1737$$

$$\frac{r_{DBTDL}}{r_{MDI} + r_T + r_{pTHF} + r_{DBTDL}} * 100 = wt\%\ DBTDL$$

$$\frac{0.1737}{64.69 + 104.27 + 17.59 + 0.1737} * 100 = 0.093\ wt\%\ DBTDL$$

Table S4. Catalyst content in the obtained polymers as estimated by the integrals of their corresponding ^{1}H NMR signals.

	wt % DBTDL
PAU-0	0.19
PAU-25	0.11
PAU-51	0.15
PAU-71	0.045
PAU-86	0.093
PAU-100	0.12