

Nitroarylurea-terminated supramolecular polymers that exhibit facile thermal repair and aqueous swelling-induced sealing of defects

Article

Supplemental Material

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Nitroarylurea-terminated supramolecular polymers that exhibit facile thermal repair and swelling-induced sealing of defects

Supplementary Information

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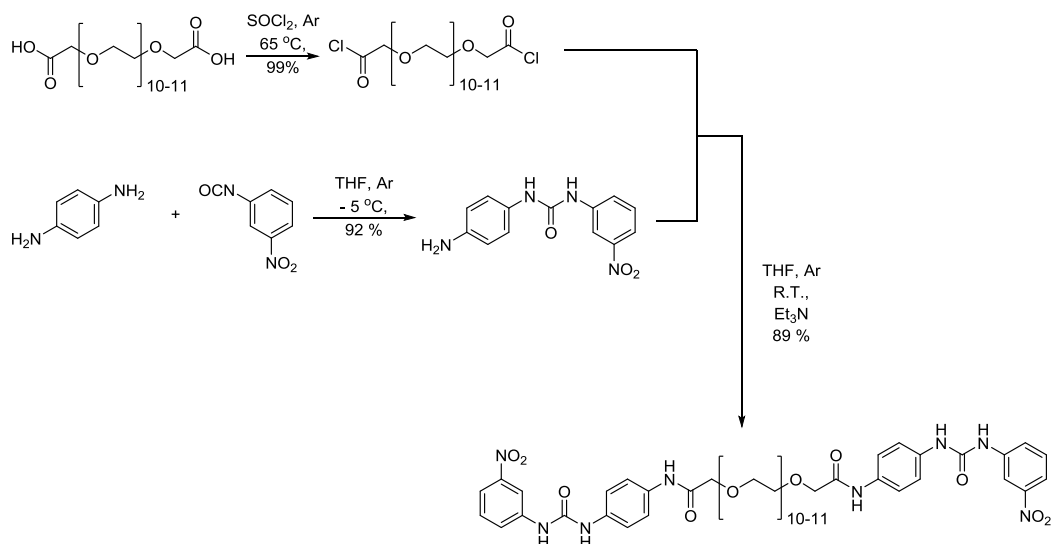
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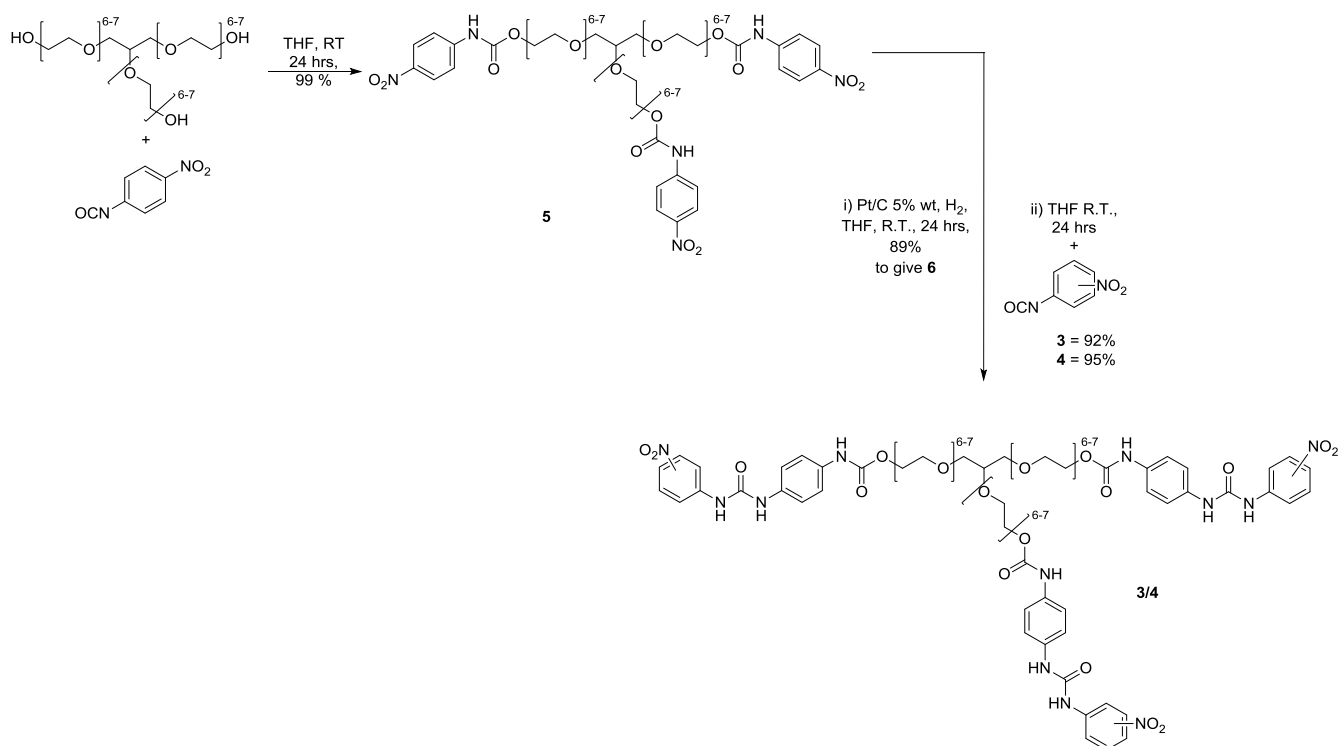
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Scheme S1. Synthetic route to bisfunctionalised PEG **1**.



Scheme S2. Synthetic route to trisfunctionalised PEGS with the terminal nitro moieties in the *meta* (**2**) or *para* (**3**) position.

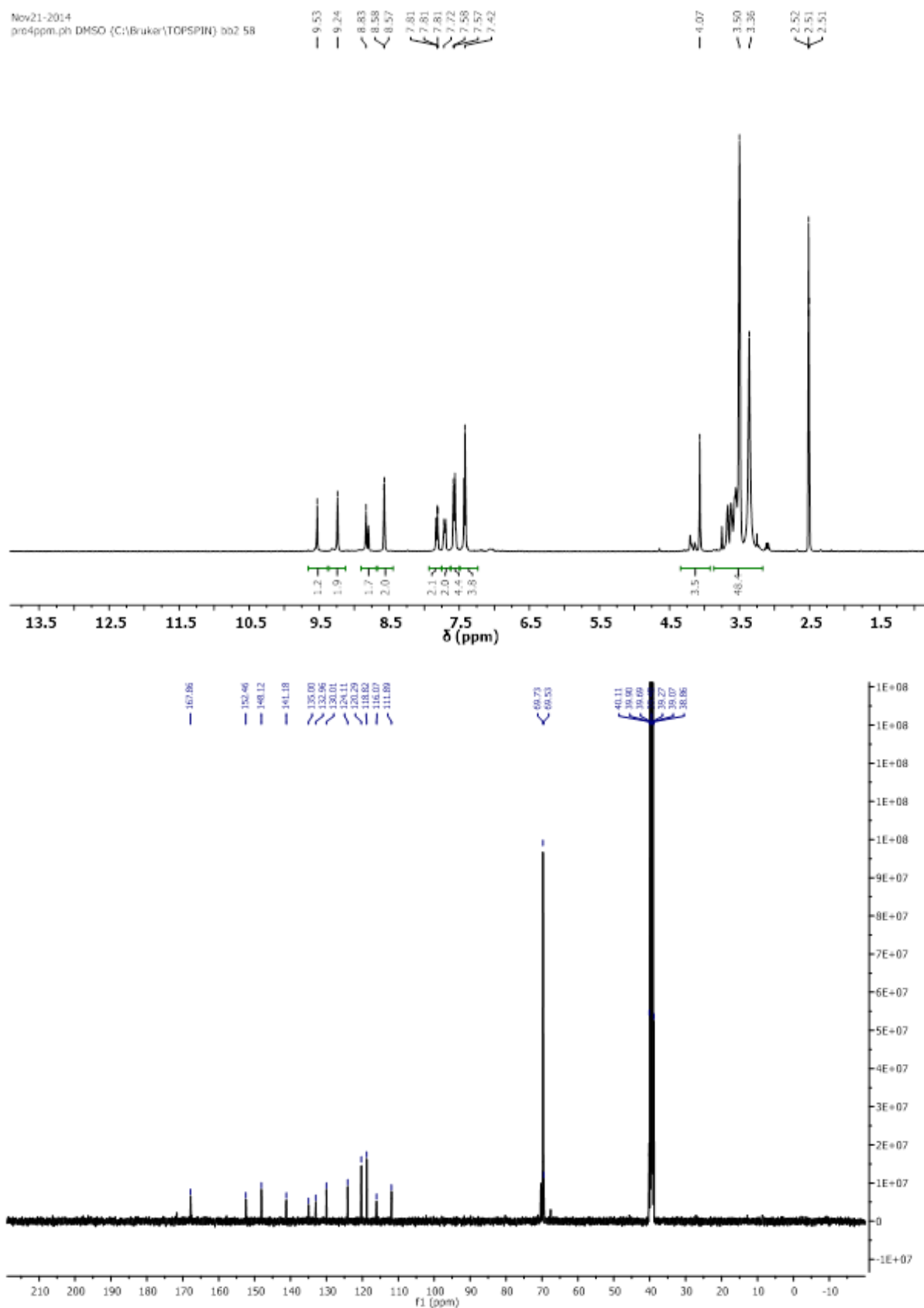


Figure S1. ^1H and ^{13}C NMR spectra of **1** in $\text{DMSO-}d_6$

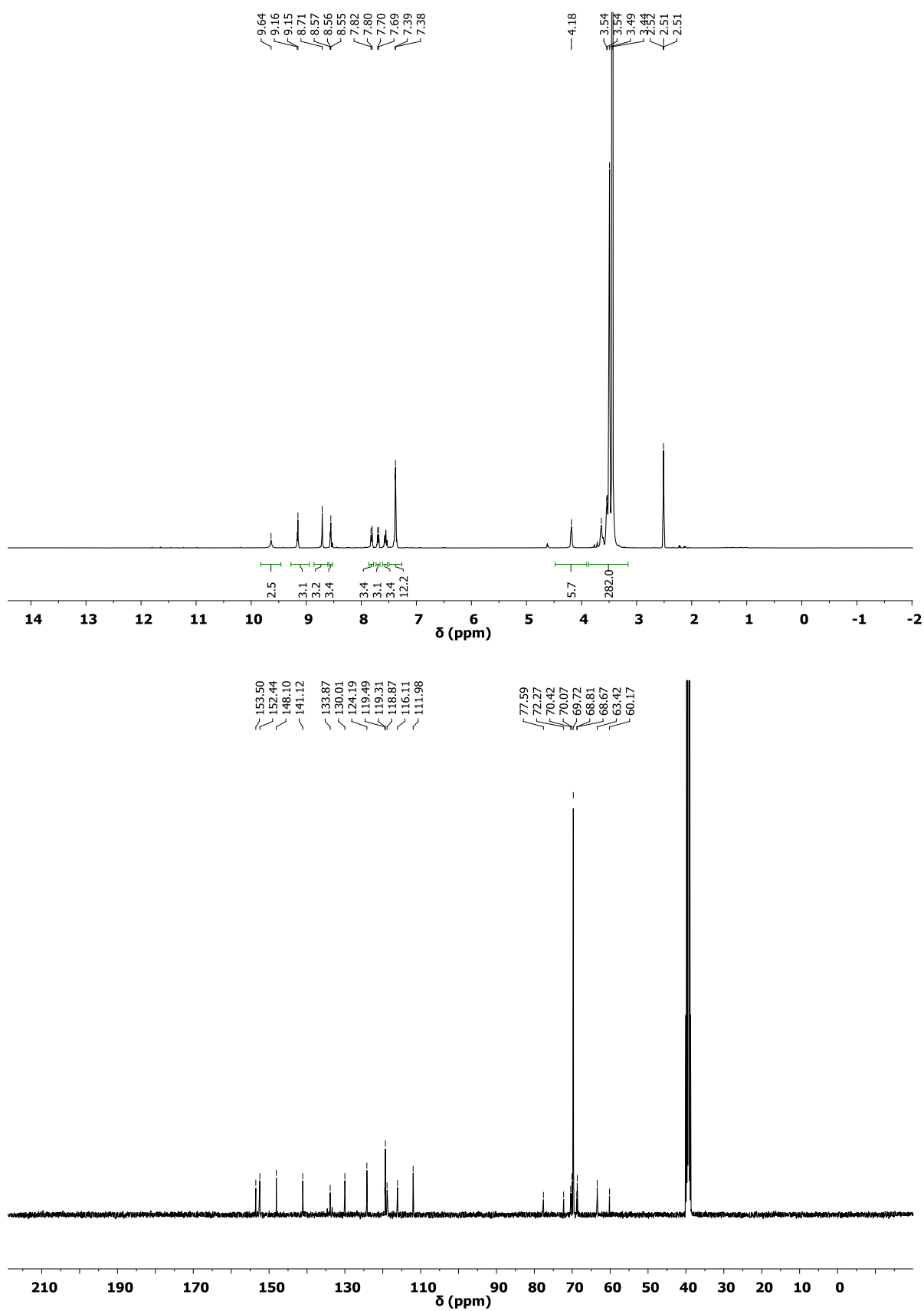


Figure S2. ^1H and ^{13}C NMR spectra of **2** in $\text{DMSO}-d_6$

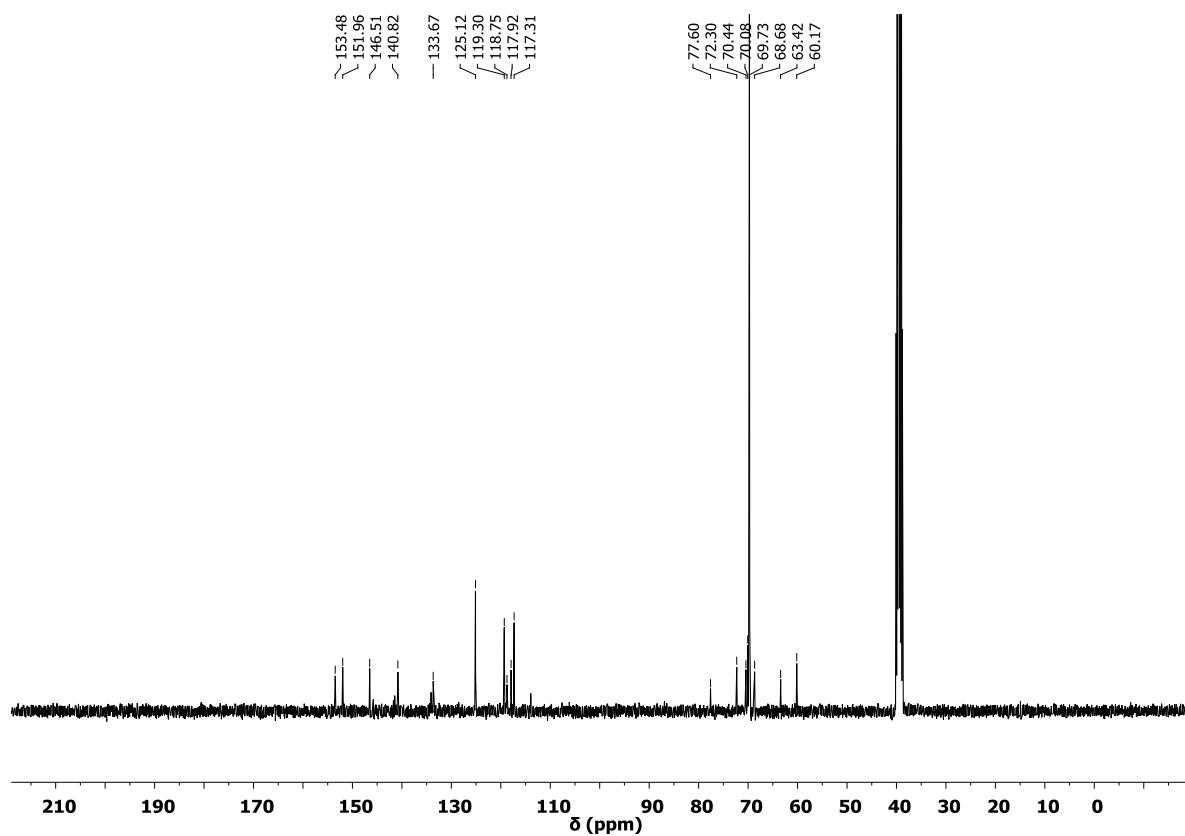
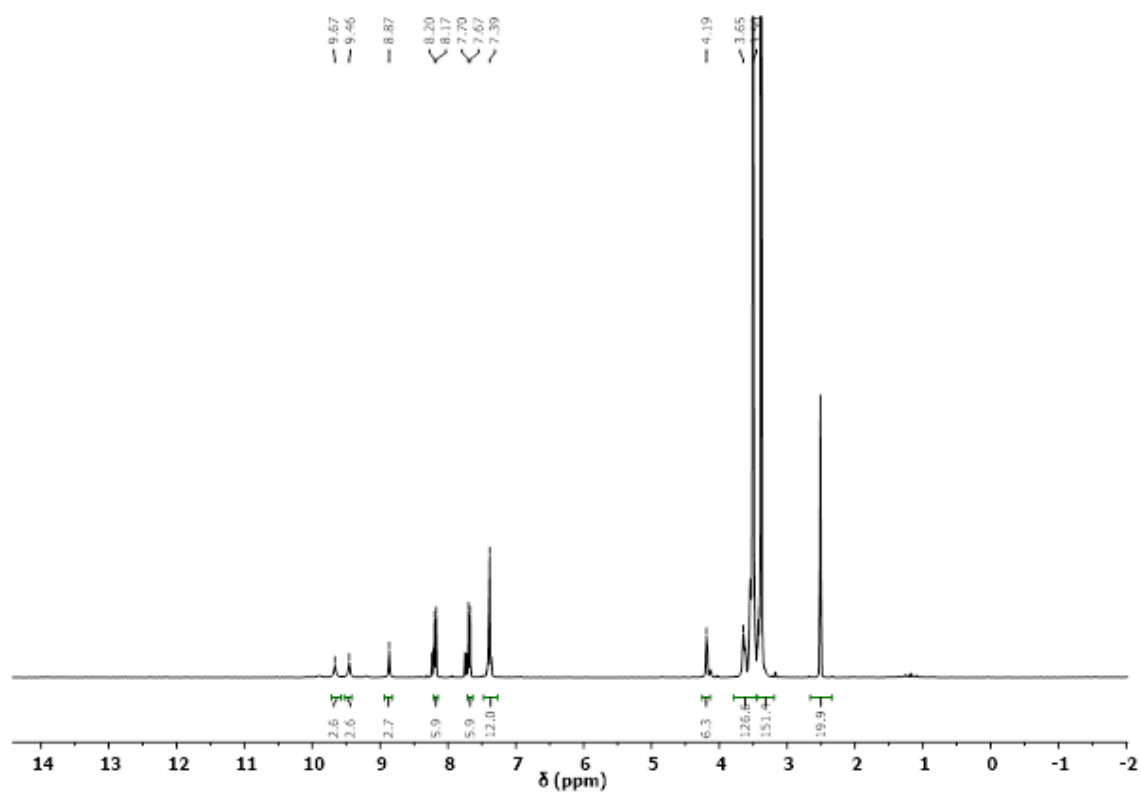


Figure S3. ¹H and ¹³C NMR spectra in 3 DMSO-*d*₆

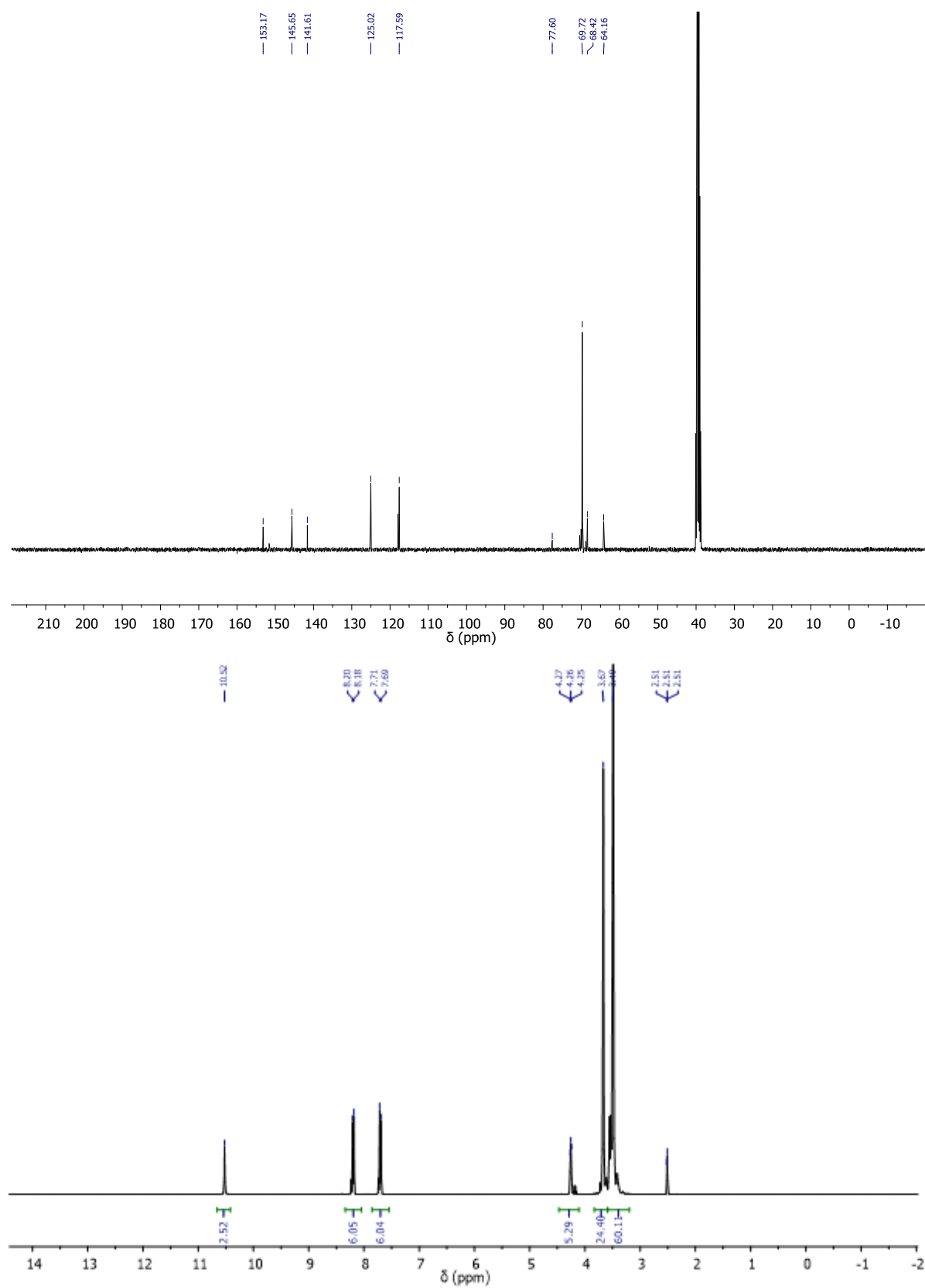


Figure S4. ¹H and ¹³C NMR spectra of tris(4-nitrophenyl carbamato)glycerol ethoxylate (precursor to 2/3) in DMSO-*d*₆

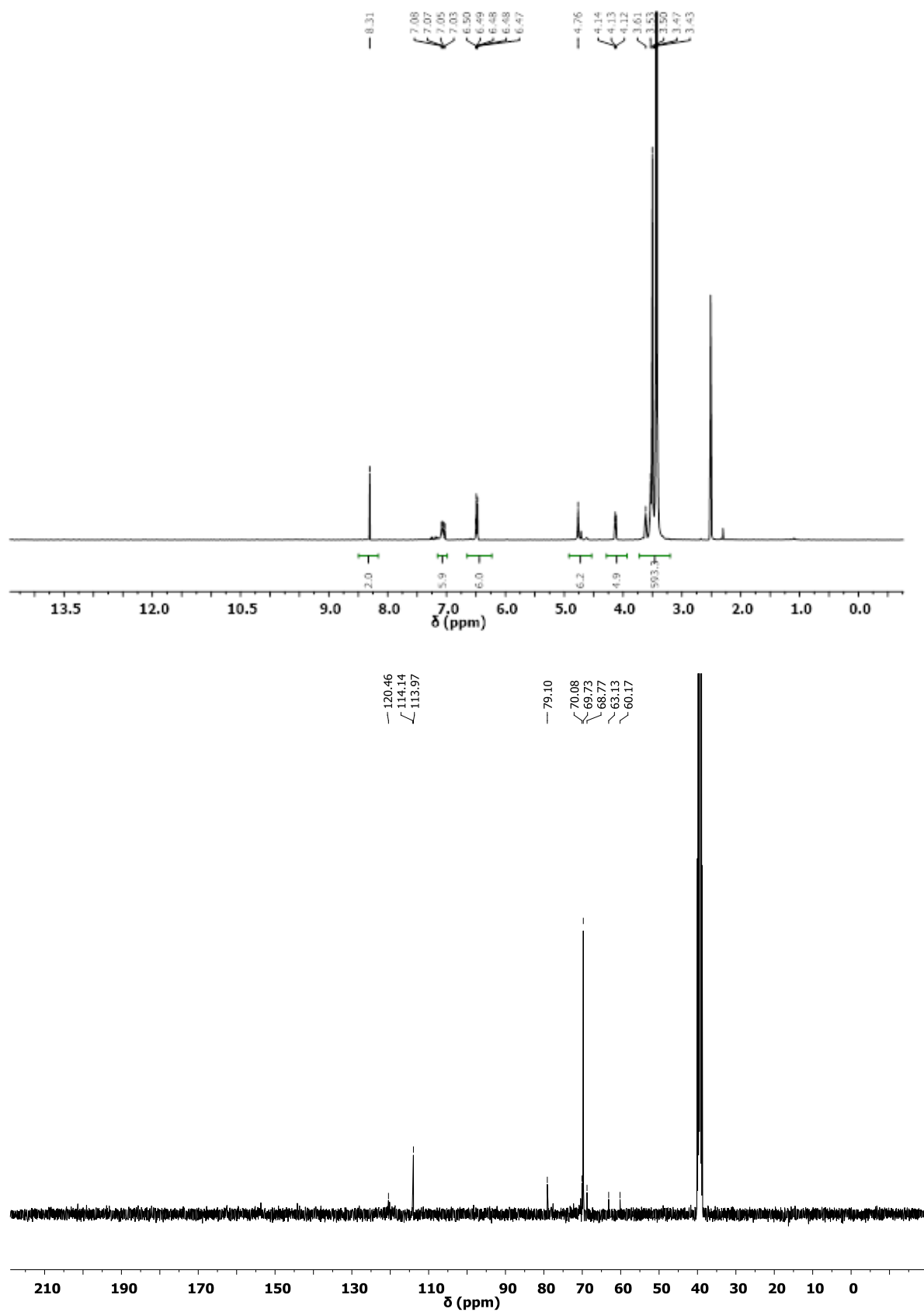


Figure S5. ^1H and ^{13}C NMR spectra of tris[(4-aminophenyl)-3-(3-nitrophenyl)urea]glycerol ethoxylate (precursor to 2/3) in DMSO-*d*₆

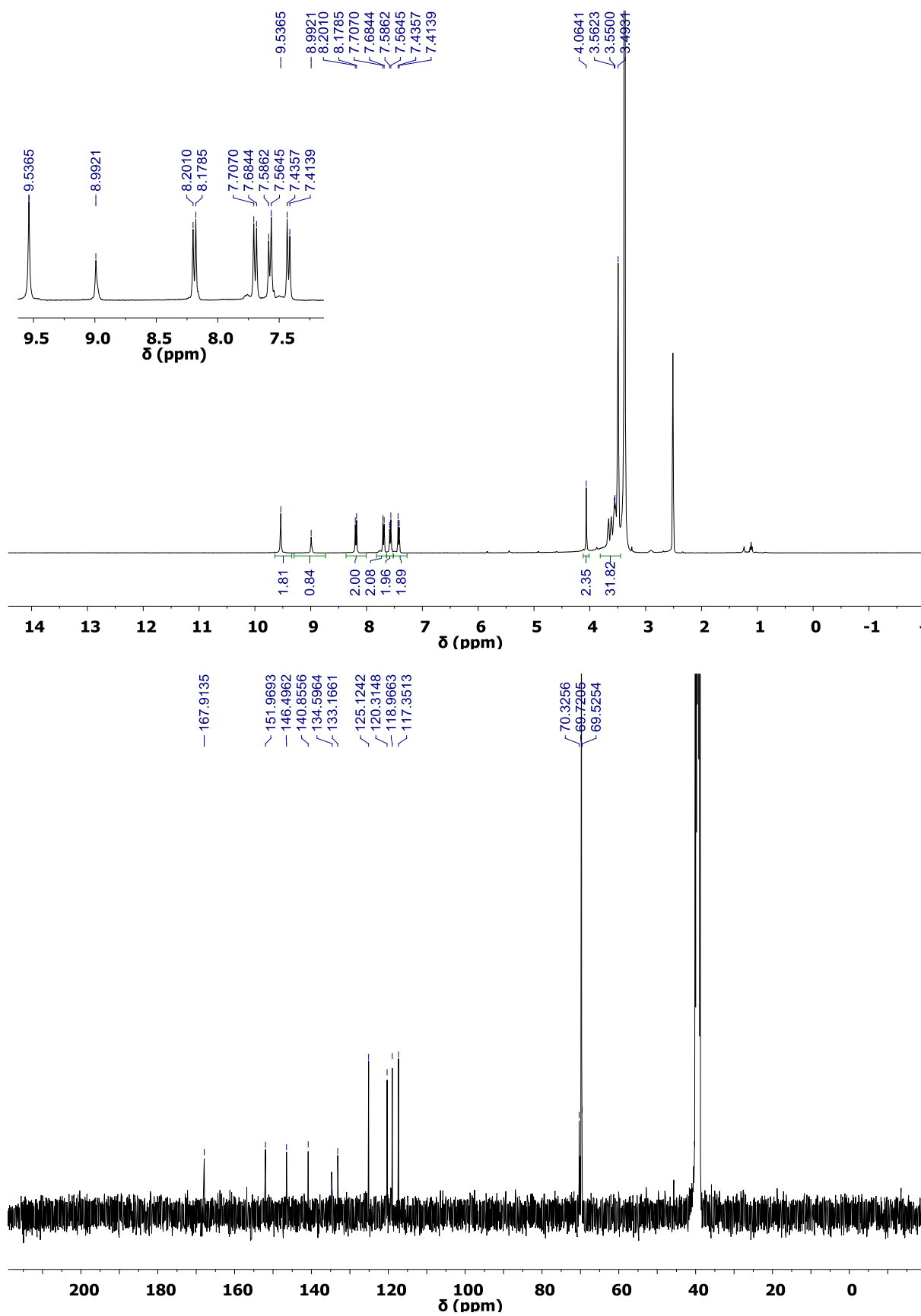


Figure S6. ^1H and ^{13}C NMR spectra of **4** in $\text{DMSO-}d_6$

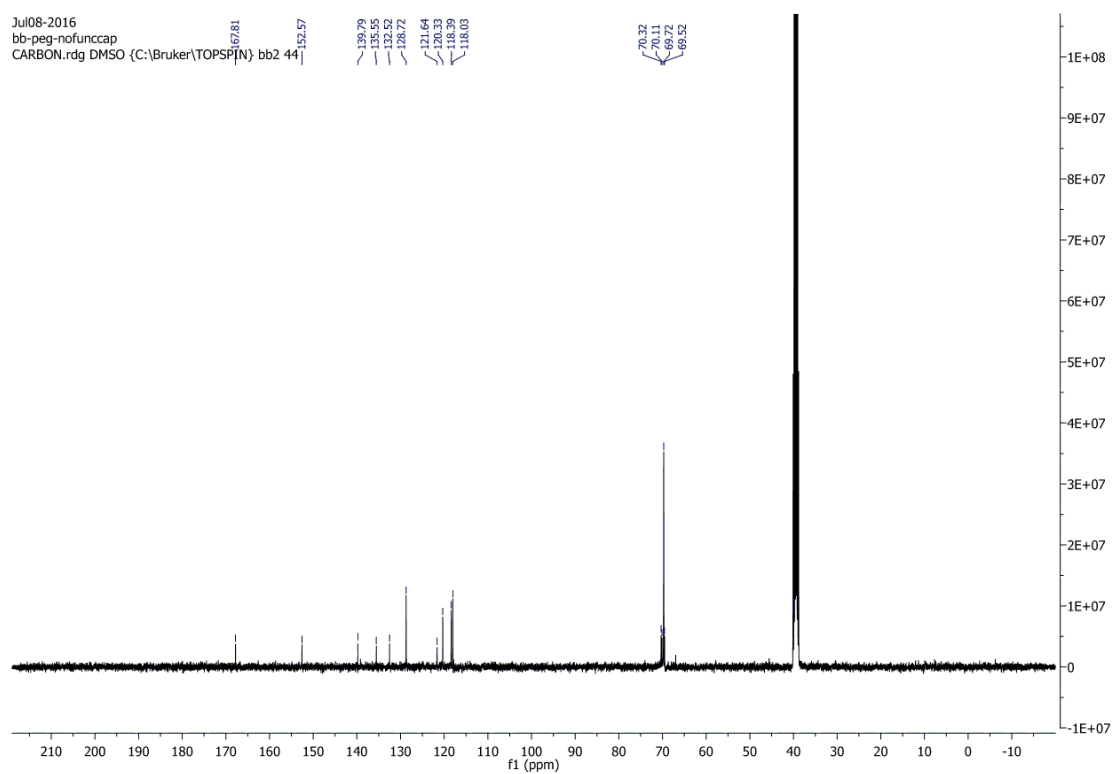
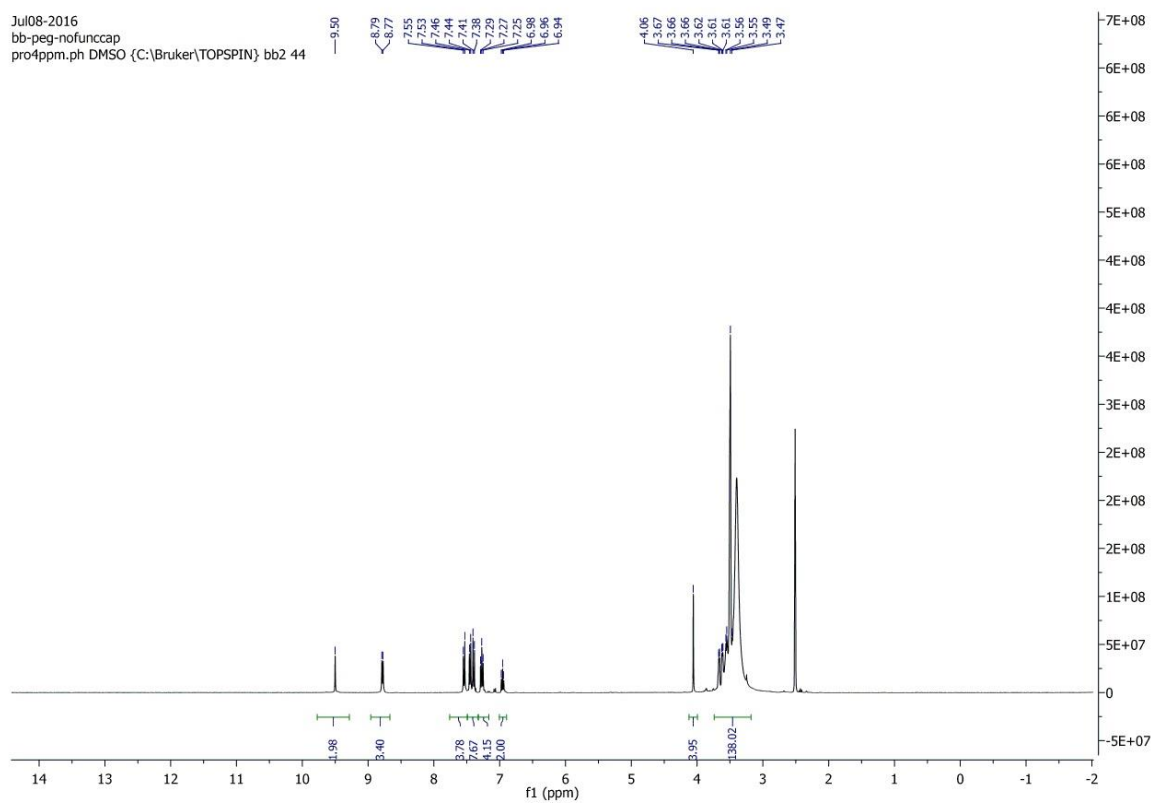


Figure S7. ^1H and ^{13}C NMR spectra of **5** in $\text{DMSO-}d_6$

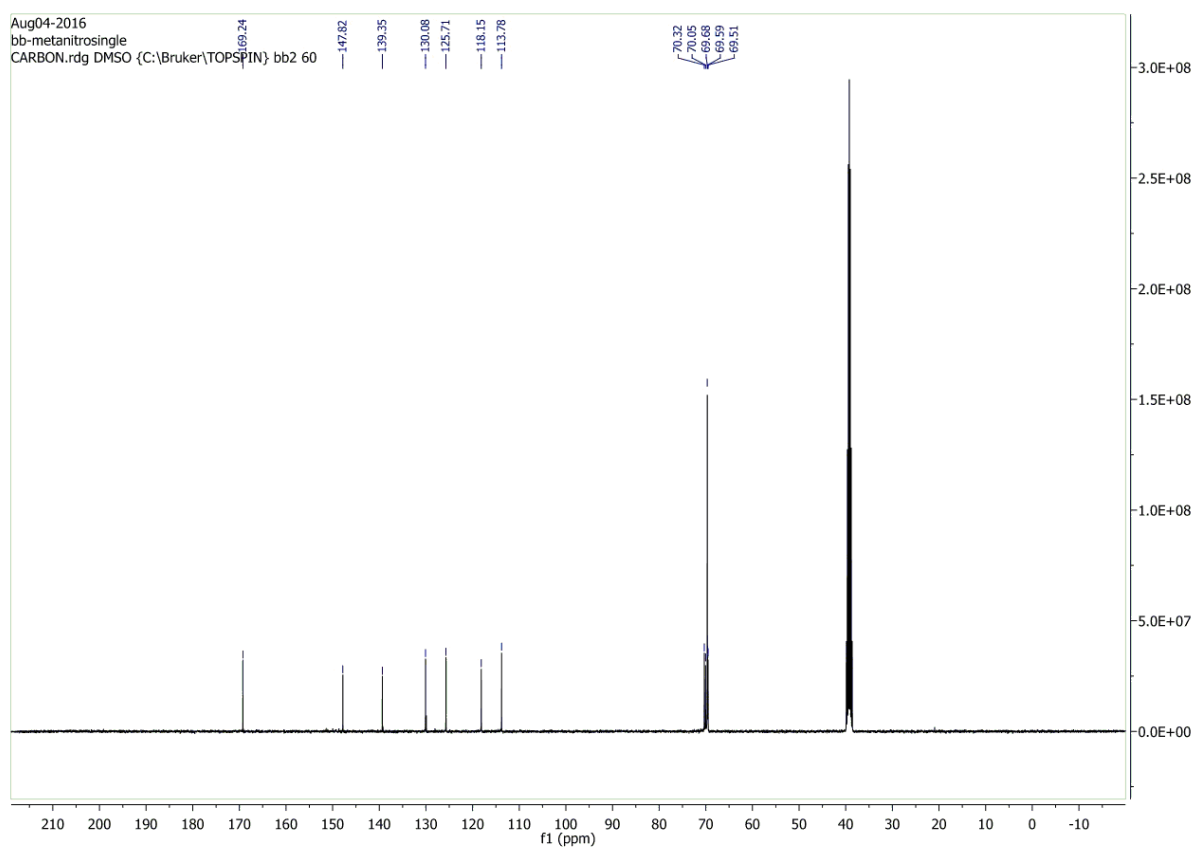
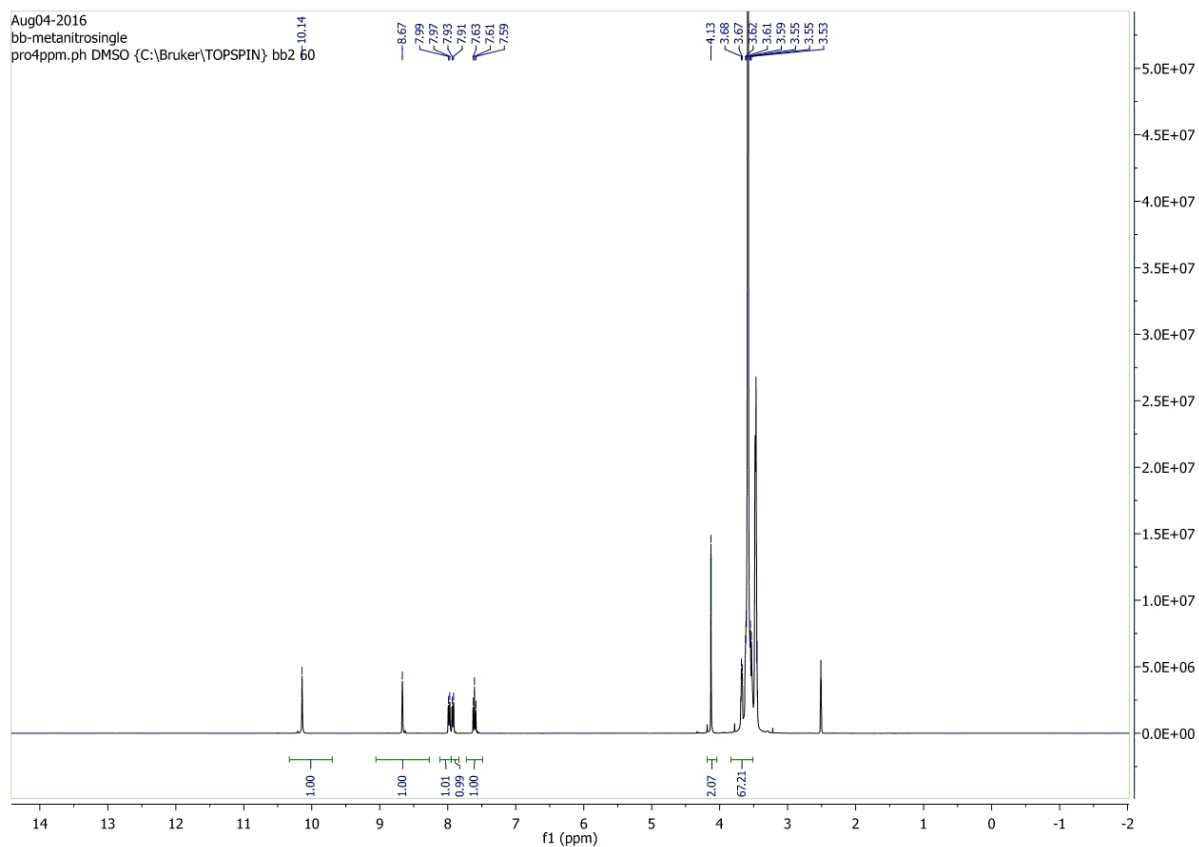


Figure S8. ^1H and ^{13}C NMR spectra of **6** in $\text{DMSO}-d_6$

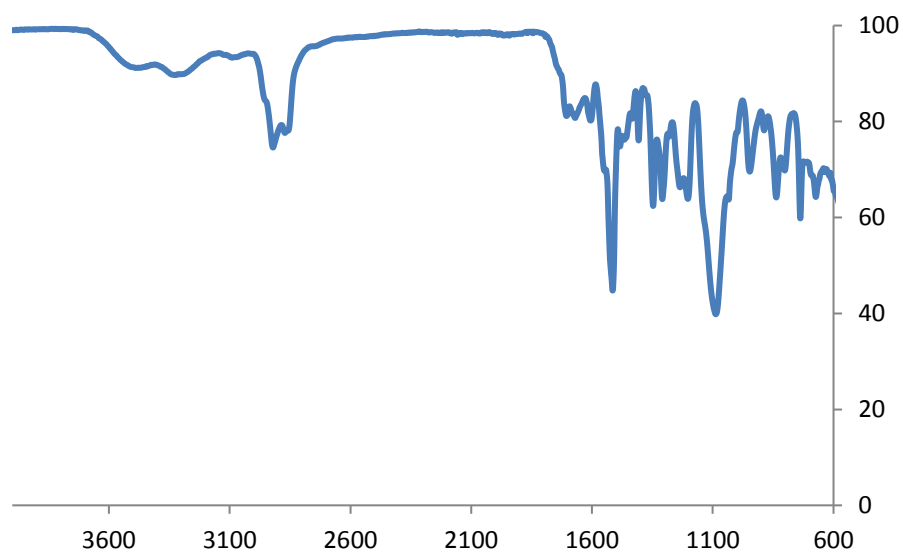


Figure S9. IR spectrum of **1**

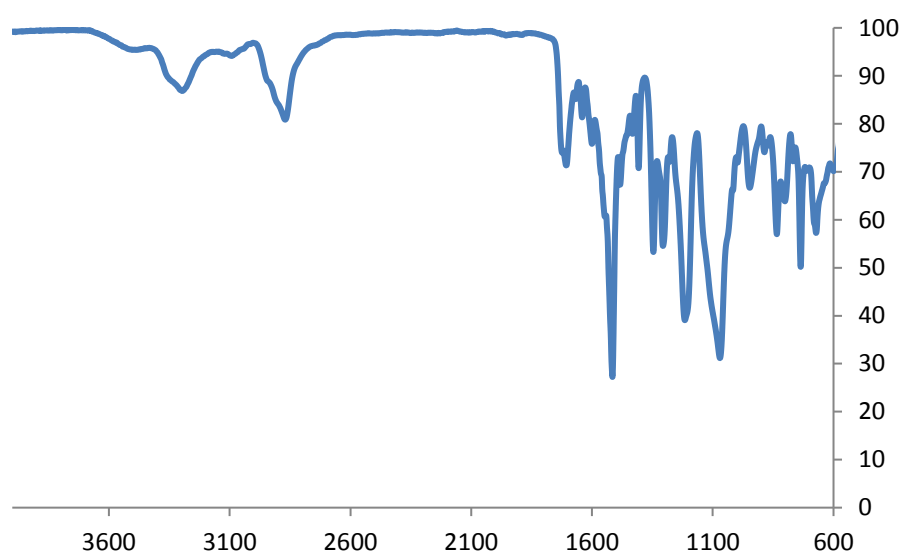


Figure S10. IR spectrum of **2**

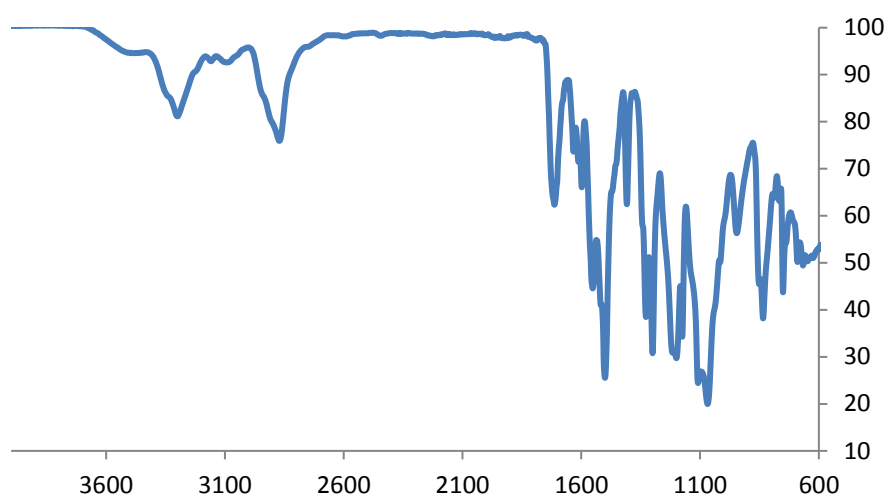


Figure S11. IR spectrum of **3**

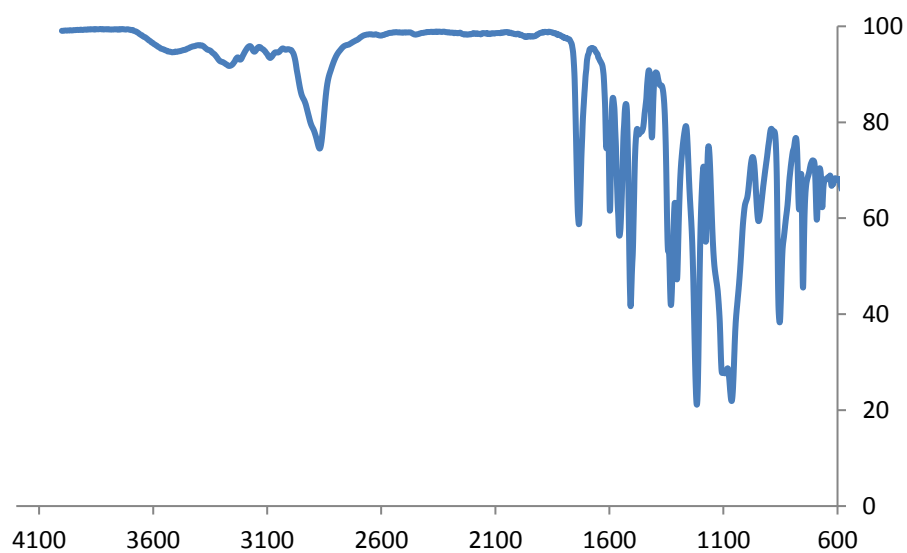


Figure S12. IR spectrum of tris(4-nitro phenyl carbamato)glycerol ethoxylate (precursor to **2/3**)

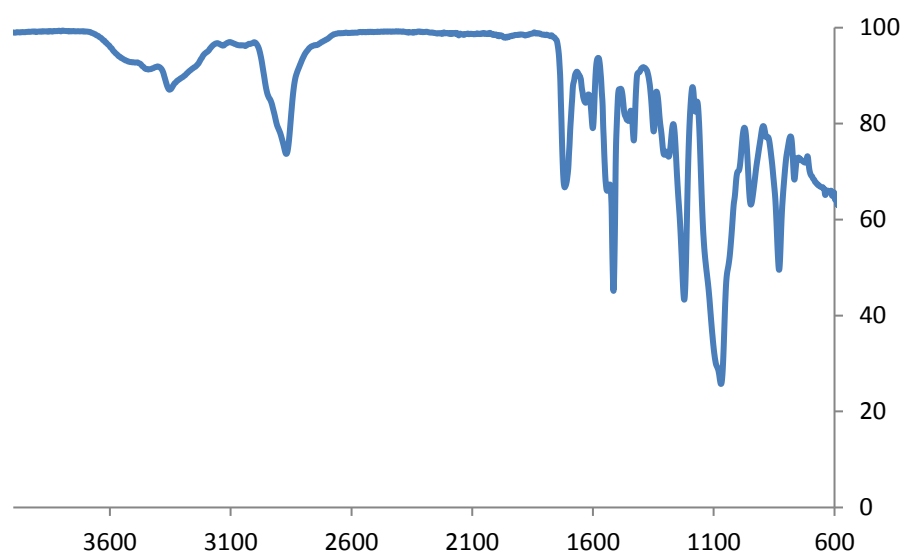


Figure S13. IR spectrum of tris[(4-aminophenyl)-3-(3-nitrophenyl)urea]glycerol ethoxylate (precursor to **2/3**)

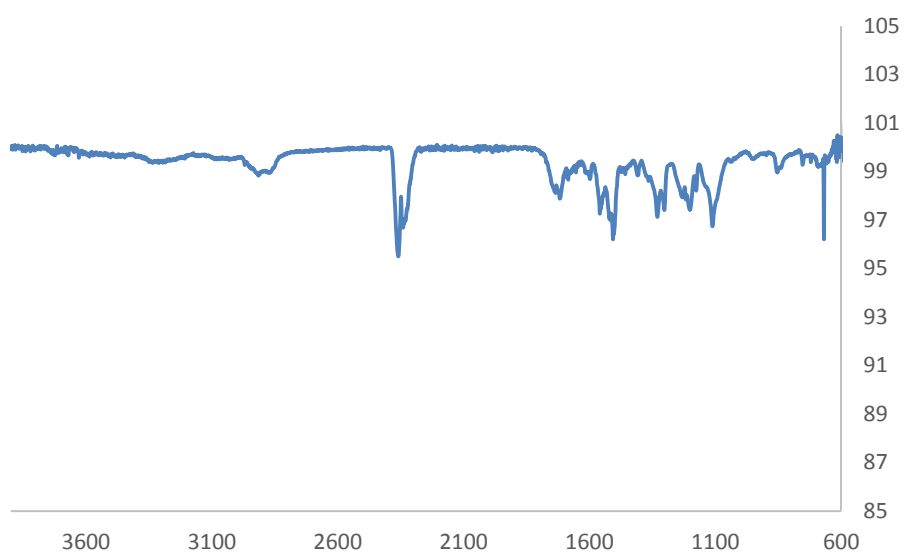


Figure S14. IR spectrum of **4**

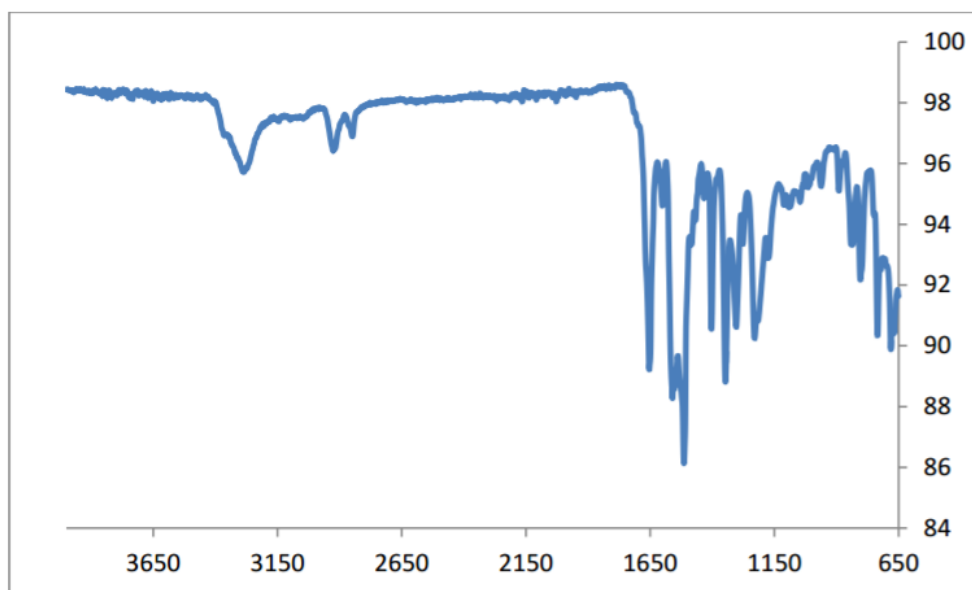


Figure S15. IR spectrum of **5**

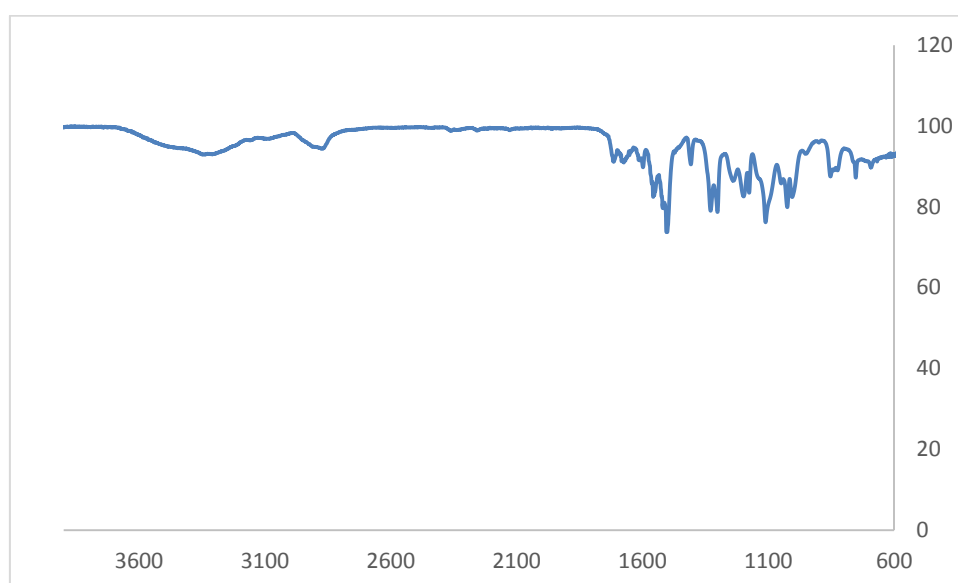
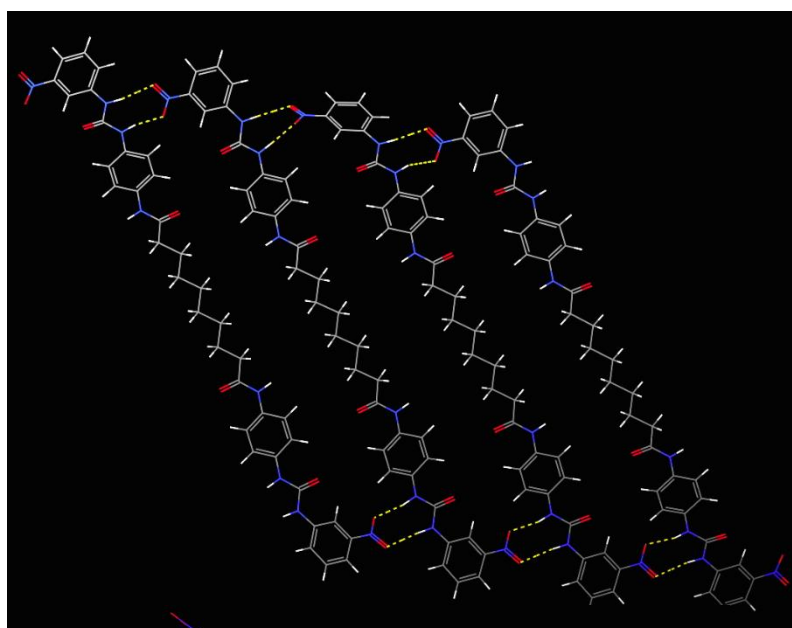


Figure S16. IR spectrum of **6**

A)



B)

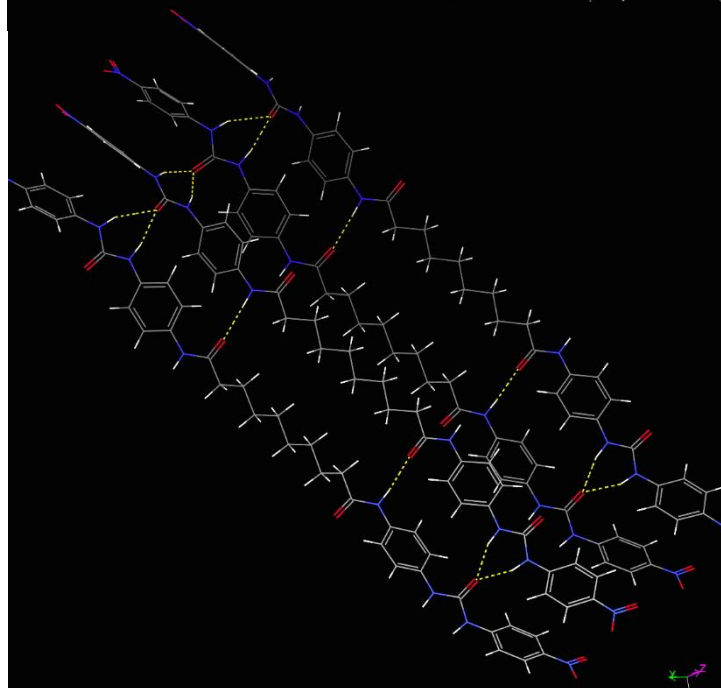


Figure S17. Computational simulation (molecular mechanics) of the interactions between A) bisaromatic nitro gelator, showing the one dimensional growth caused by hydrogen bond formation between the urea groups and the *meta*-nitro groups desirable for gelation, and B) *para*-nitro analogue of the gelator shown in A.

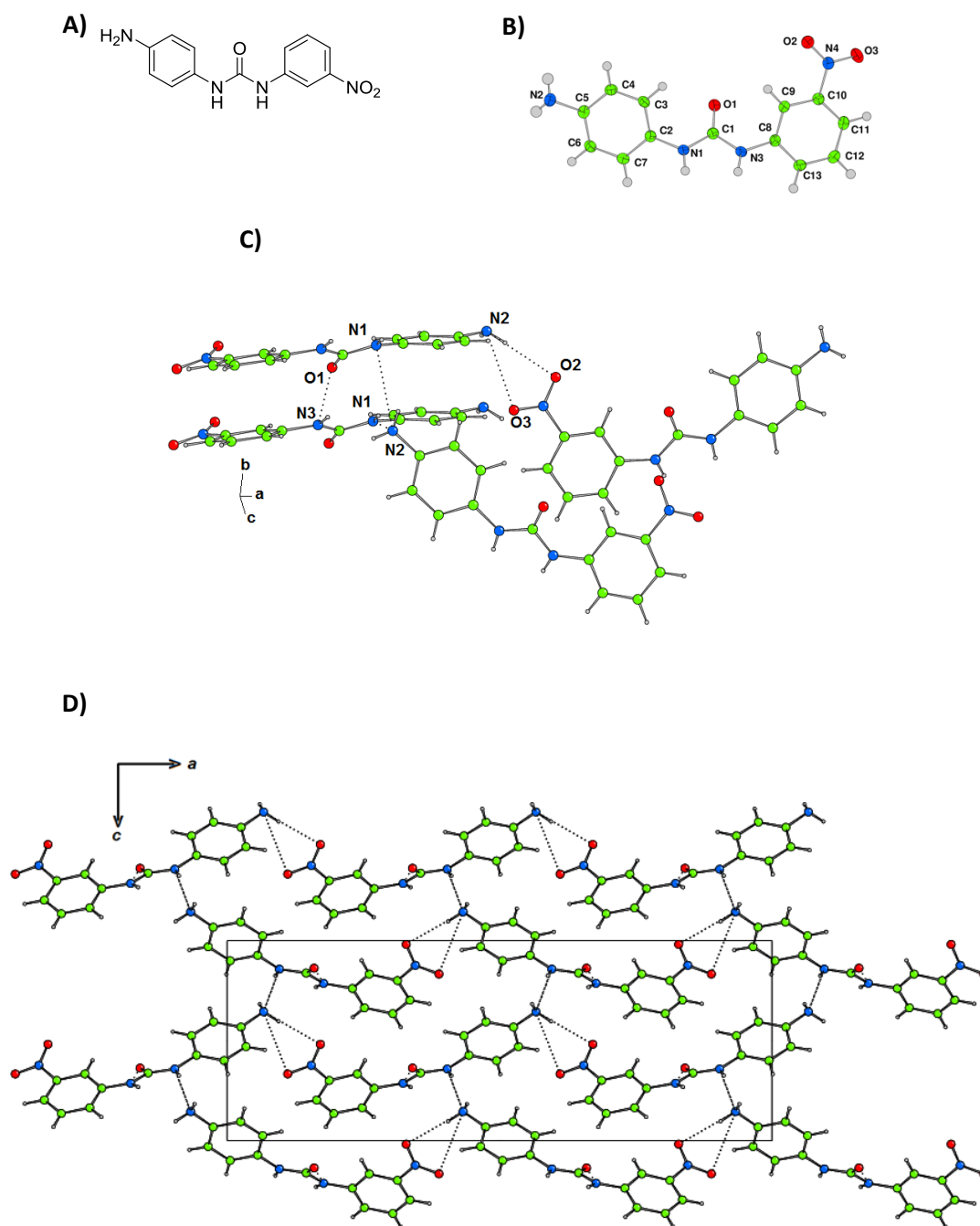


Figure S18. Crystal structure of 1-(4-aminophenyl)-3-(3-nitrophenyl)urea (**7**): a model compound for the end group **A**) molecular formula of (1-(4-aminophenyl)-3-(3-nitrophenyl)urea); **B**) asymmetric unit and numbering scheme; **C**) view showing hydrogen bonds between the meta-nitro groups and the aniline units of **7**; **D**) extended crystal structure of end groups viewed along the *b* axis

Table S1. Crystallographic data for 1-(4-aminophenyl)-3-(3-nitrophenyl)urea (**7**)

Formula	C ₁₃ H ₁₂ N ₄ O ₃
<i>M_r</i>	272.27
Crystal system	orthorhombic
Space group	<i>P c a 2</i> ₁
<i>Z</i>	4
<i>a</i> /Å	26.0654(8)
<i>b</i> /Å	4.86749(15)
<i>c</i> /Å	9.5612(2)
<i>V</i> / Å ³	1213.06(6)
<i>D</i> _{calc} / g cm ⁻³	1.491
Crystal habit	colourless plate
Crystal dimensions /mm	0.01 × 0.04 × 0.07
Radiation	Mo K _α (0.71073 Å)
T /K	150
<i>μ</i> /mm ⁻¹	0.917
<i>R</i> (<i>F</i>), <i>R</i> _w (<i>F</i>)	2.680, 3.096
CCDC cif deposition number	1456760

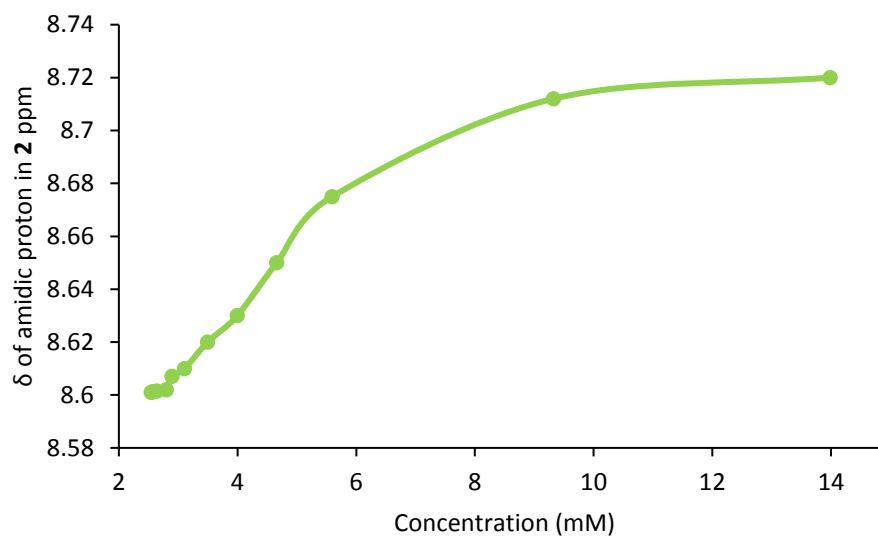


Figure S19. Plot of ^1H NMR chemical shift of amide NH protons vs. concentration of **1** in CDCl_3 .

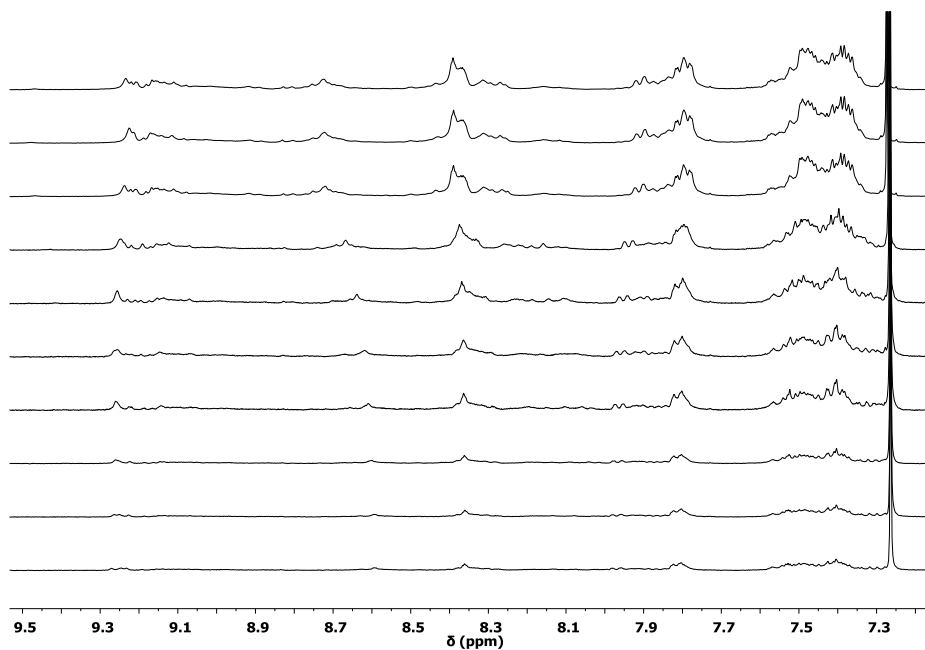


Figure S20. ^1H NMR dilution studies of **1** in CDCl_3 where the concentration ranges from 14.0 mM (top spectrum) to 2.6 mM (bottom spectrum).

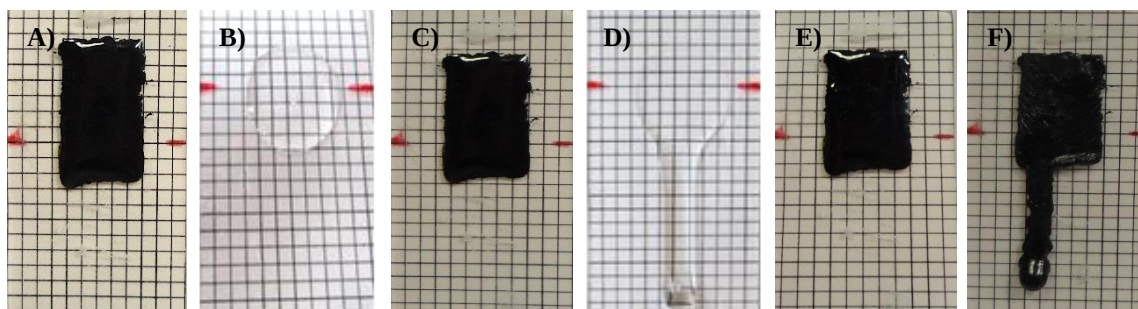


Figure S21. Vertically placed films where; A) **1** at time zero, B) unfunctionalised PEG 600 at time zero, C) **1** at 10 minutes, D) unfunctionalised PEG 600 at 10 minutes, E) **1** at 4 months at 25 °C, F) **1** at 72 hours at 35 °C, on 1 × 1 mm grid backing paper (average film dimensions 5 × 9 × 1 mm)

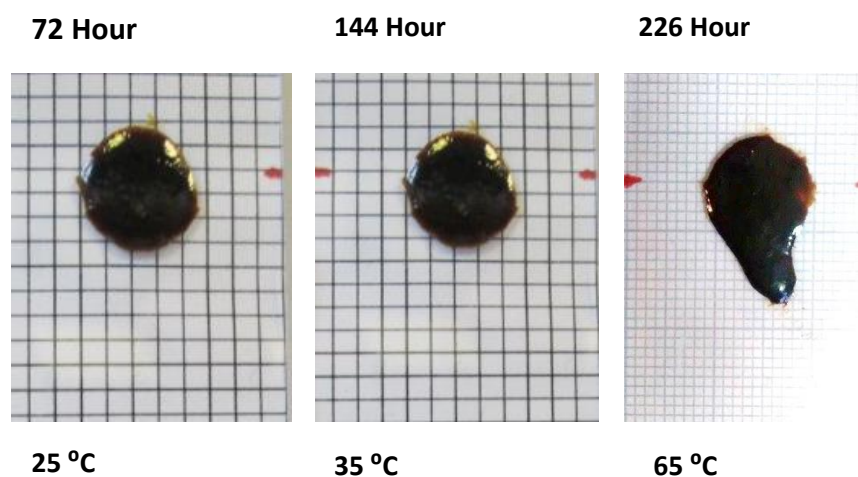


Figure S22. Vertically placed blended film of **1** and **2** (at 1:1 % wt) after 72 hours at 25 °C, 72 hours at 35 °C and 72 hours at 65 °C. The backing paper grid in the two left images is 1 × 1 mm whereas for the right hand image it is 0.5 × 0.5 mm (average film dimensions 5 × 1 mm).

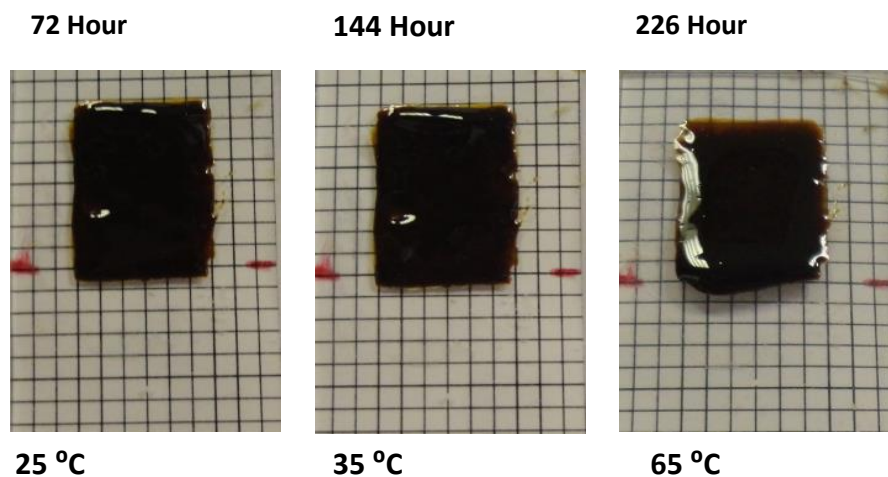


Figure S23. Films of 1/3 (1:1 % wt) after 72 hours at 25 °C, 72 hours at 35 °C and 72 hours at 65 °C. The backing paper grid for these images is 1 × 1 mm.

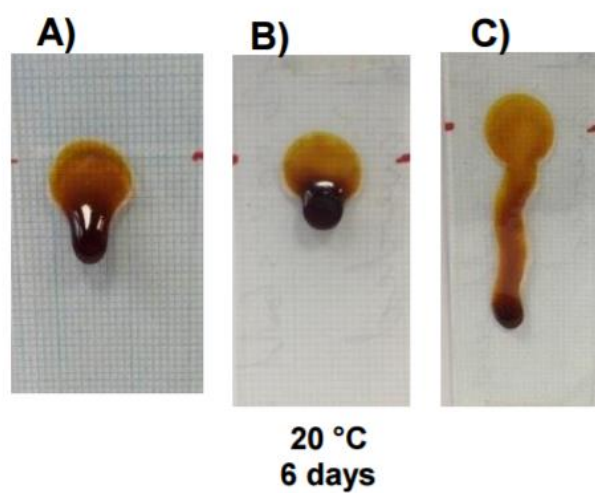


Figure S24. Vertically placed film casts of A) 4, B) 5, C) 6 after 6 days at 20 °C after casting as a circle. The backing paper grid is 0.5 × 0.5 mm (average film dimensions 5 × 1 mm).

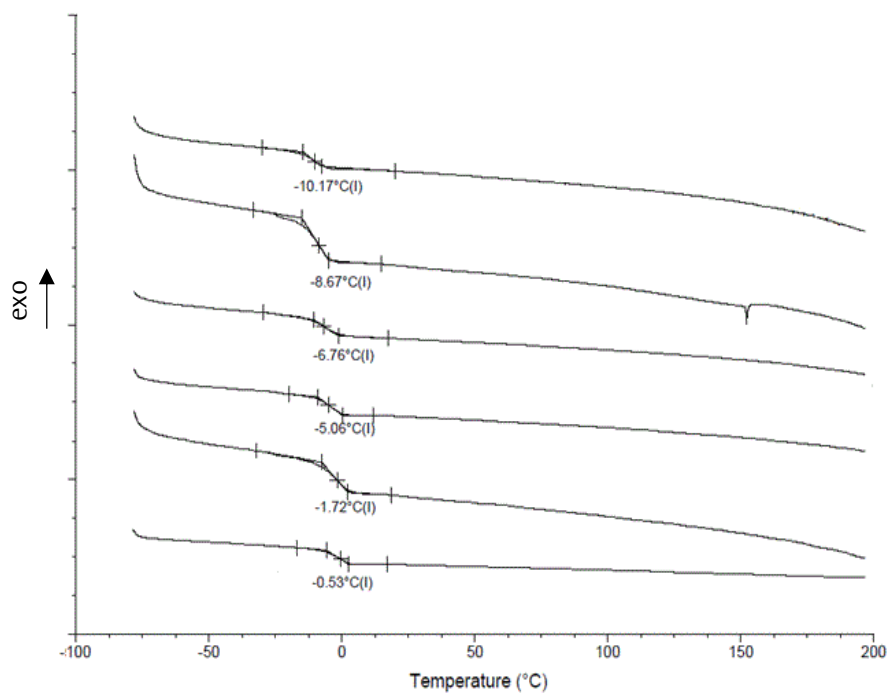


Figure S25. DSC heating curves (second scan) for samples of **1** (top) and blends of **1/2** where the percentage weight of **3** is; 25, 50, 60, 80, 100 (bottom) and heating rate is 10 °C/min. T_g s are shown as midpoints.

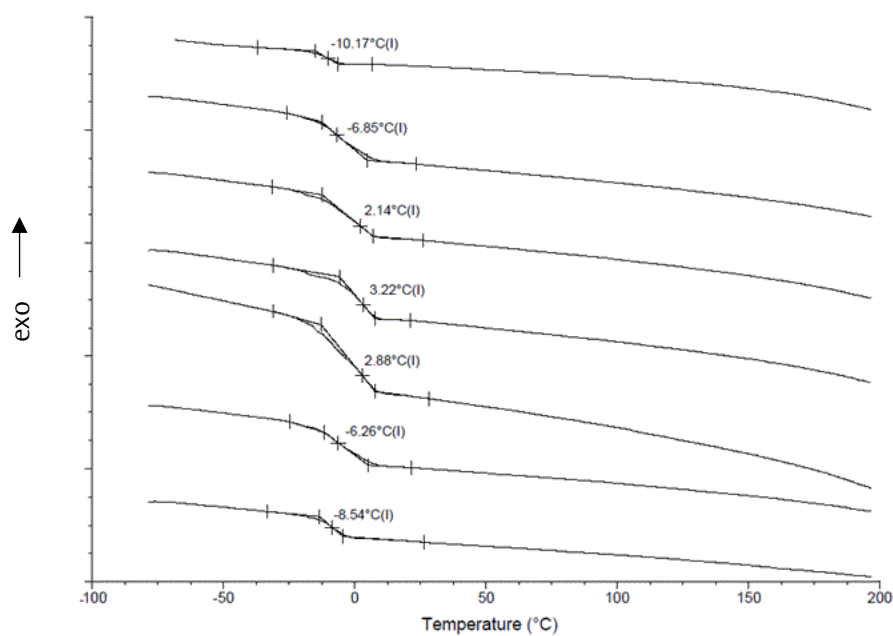


Figure S26. DSC heating curves (second scan) for samples of **1** (top) and blends of **1/3** where the percentage weight of **4** is; 15, 40, 50, 65, 85, 100 (bottom) and heating rate is 10 °C/min. T_g s are shown as midpoints.

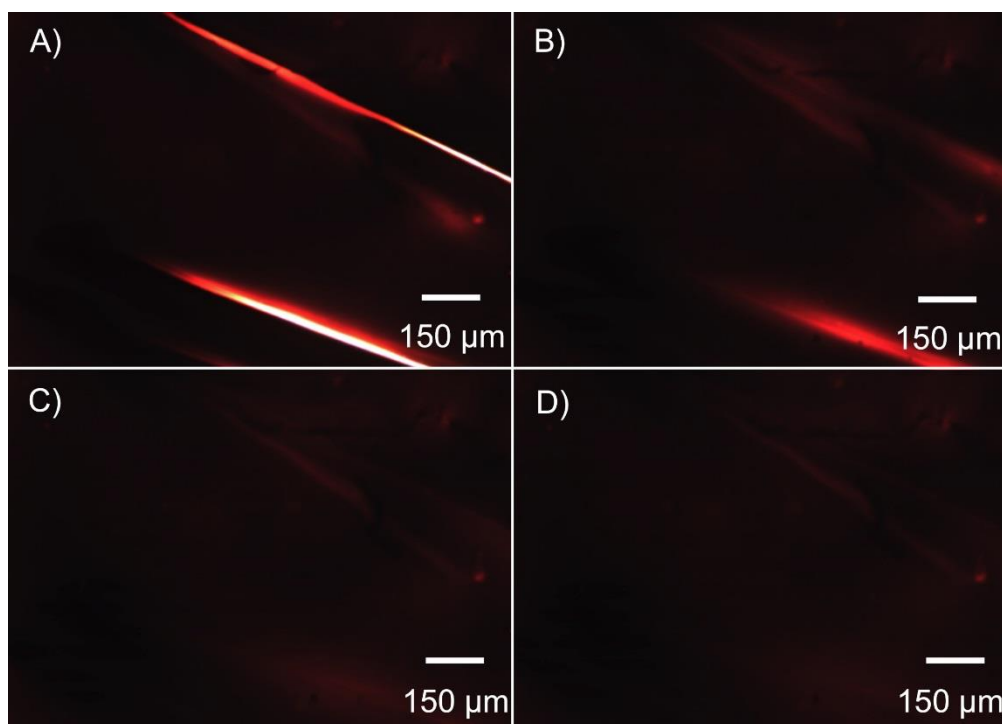


Figure S27. Optical micrographs of film of **1** after defect formation where; A) 0 minutes, B) 10 minutes, C), 20 minutes D) 60 minutes (20 °C) (film thickness = 1 mm).

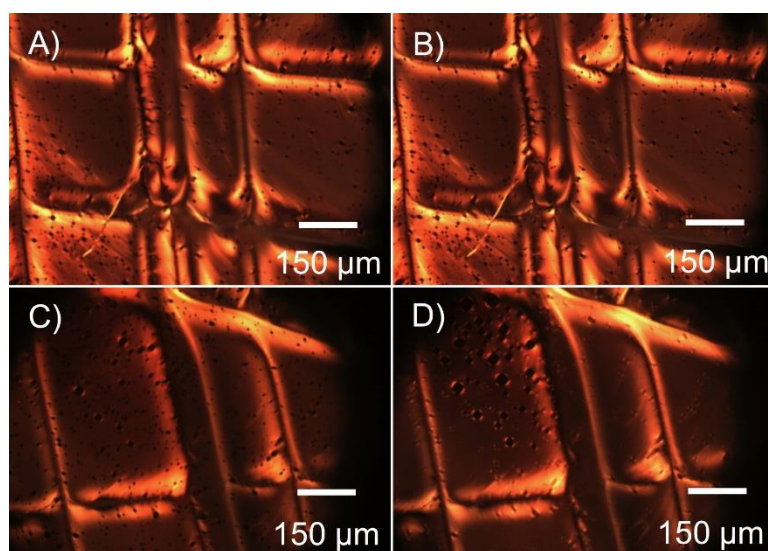


Figure S28. Optical micrographs of film of **2** after defect formation where; A) 0 minutes (20 °C), B) 60 minutes (20 °C), C) heated to 100 °C, D) heated to 200 °C after defect formation, (heating rate 2 °C /min) (film thickness = 1 mm).

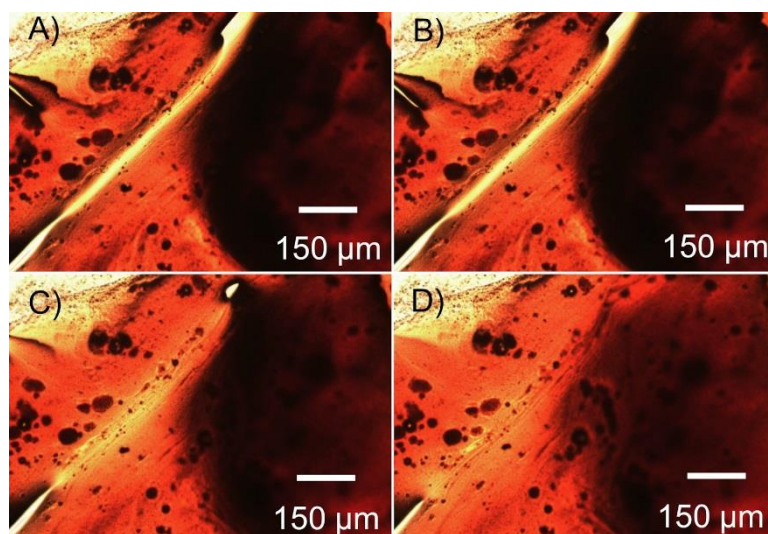


Figure S29. Optical micrographs of film of **3** after defect formation where; A) 0 minutes (20 °C), B) 60 minutes (20 °C), C) heated to 45 °C, D) heated to 50 °C after defect formation (heating rate 2 °C /min) (film thickness = 1 mm).

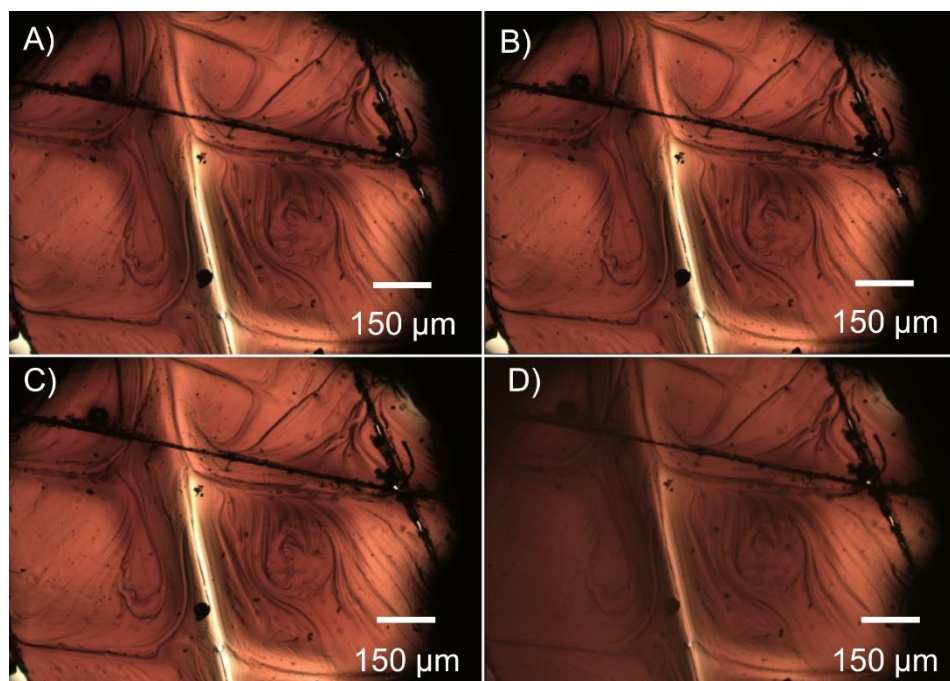


Figure S30. Optical micrographs of film of **1/2** (1:1 % wt) after defect formation where; A) 0 minutes (20 °C), B) 60 minutes (20 °C), C) heated to 100 °C, D) heated to 200 °C after defect formation (heating rate 2 °C /min) (film thickness = 1 mm).

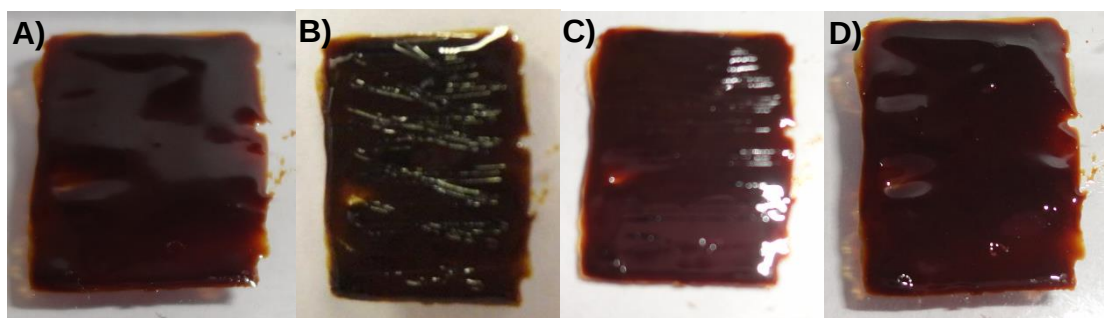


Figure S31. Film of **1**/3 (1:1 by wt.) where; A) pristine cast film, B) damage (scratches) initiated with scalpel, C) slide after 20 minutes, D) healed sample after 40 minutes (average film dimensions $5 \times 9 \times 1$ mm).

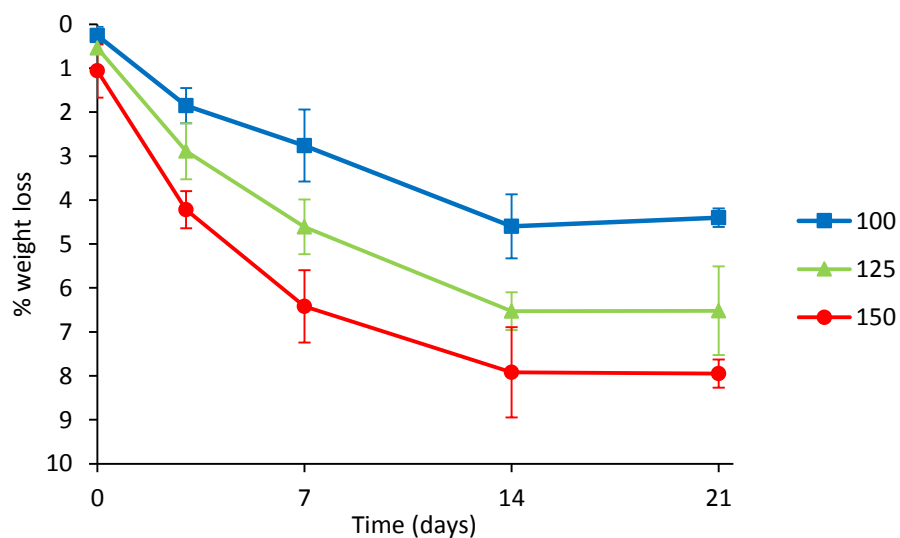


Figure S32. Percentage weight loss (at varying temperatures) from a film of **1** as a function of the time the film had been allowed to equilibrate with atmospheric moisture at ambient temperature, monitored by TGA (heating rate $5\text{ }^{\circ}\text{C}/\text{min}$).

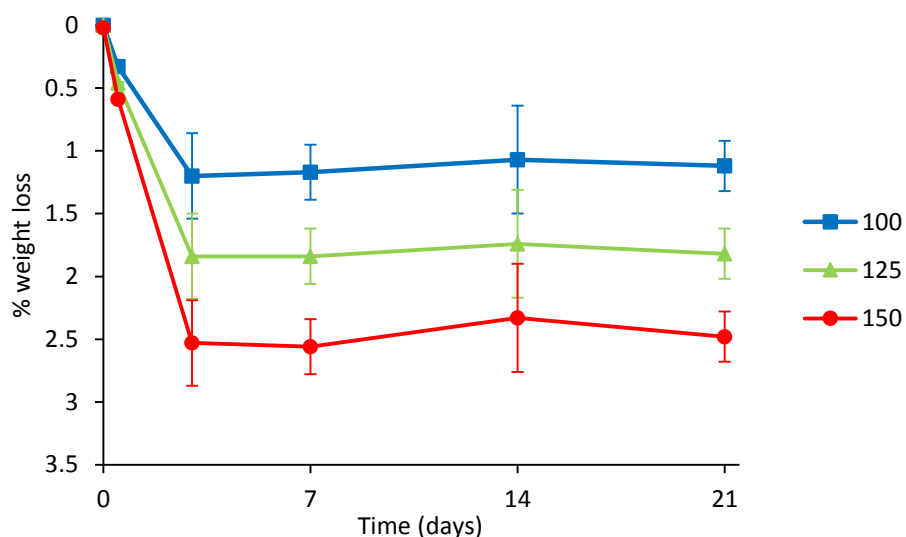


Figure S33. Percentage weight loss (at varying temperatures) from a film of 1/3 (1:1 by wt.) as a function of the time the film had been allowed to equilibrate with atmospheric moisture at ambient temperature, monitored by TGA (heating rate 5 °C/ min).

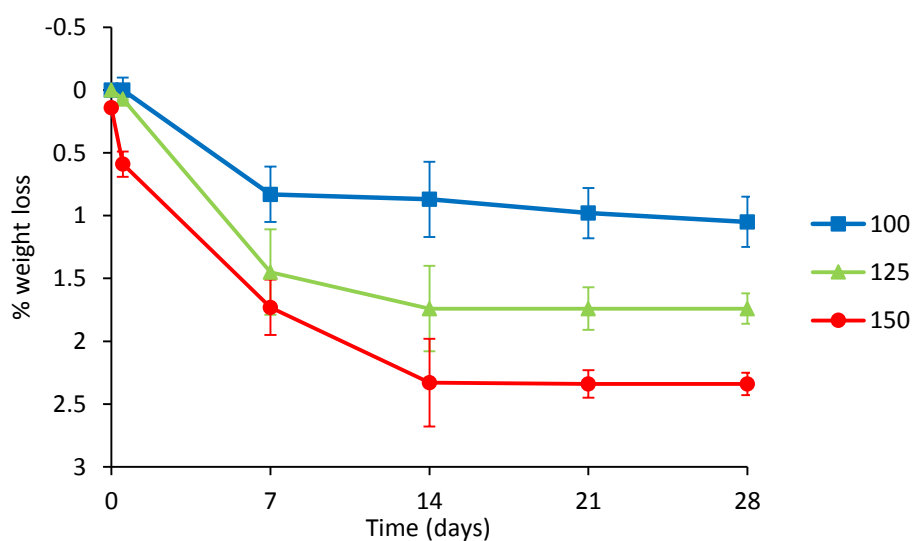


Figure S34. Plot of percentage weight loss (at varying temperatures) from a film of 3 as a function of the time the film had been allowed to equilibrate with atmospheric moisture at ambient temperature, monitored by TGA (heating rate 5 °C/ min).

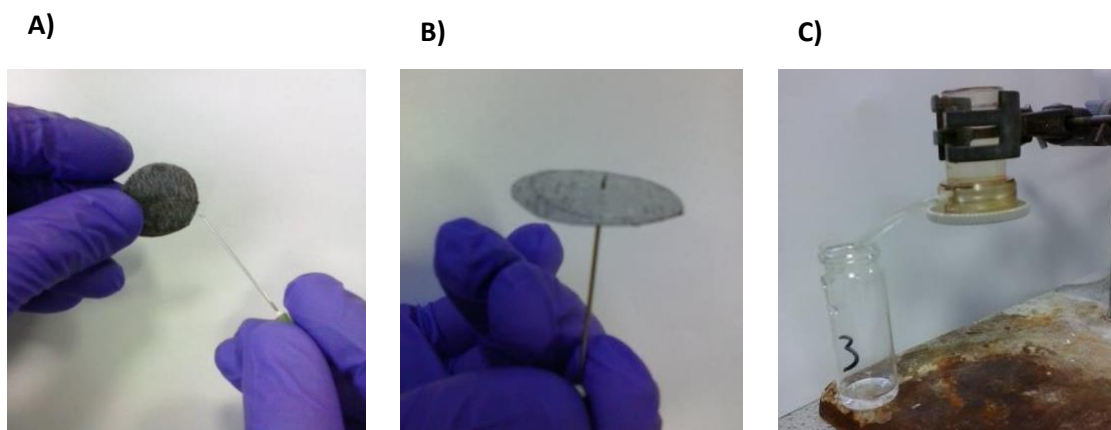


Figure S35. A) Casts of 2/4 (1:1 by wt) between porous paper B) defect formation C) stirred cell system set up for the study of puncture closure via swelling in water.

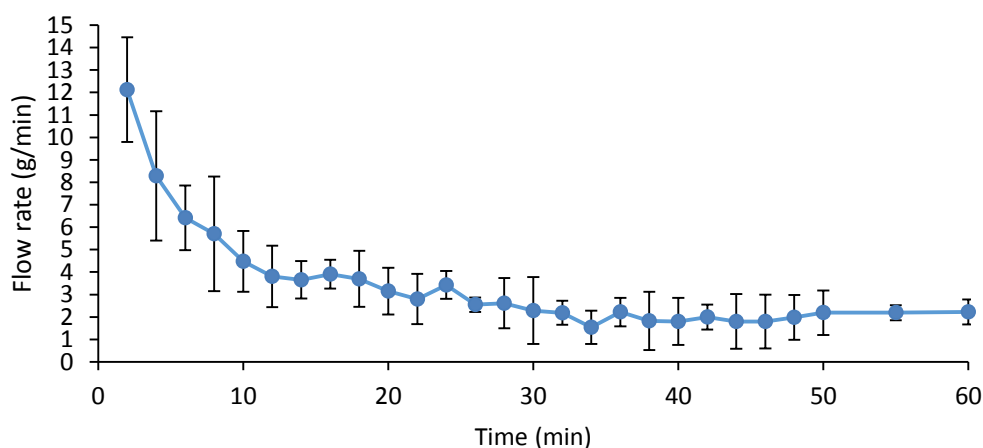


Figure S36. Flow rate of water (under gravity) through a disk of **1** placed between two sheets of porous paper after defects formed via puncture (equivalent to 0.3 % area removal).

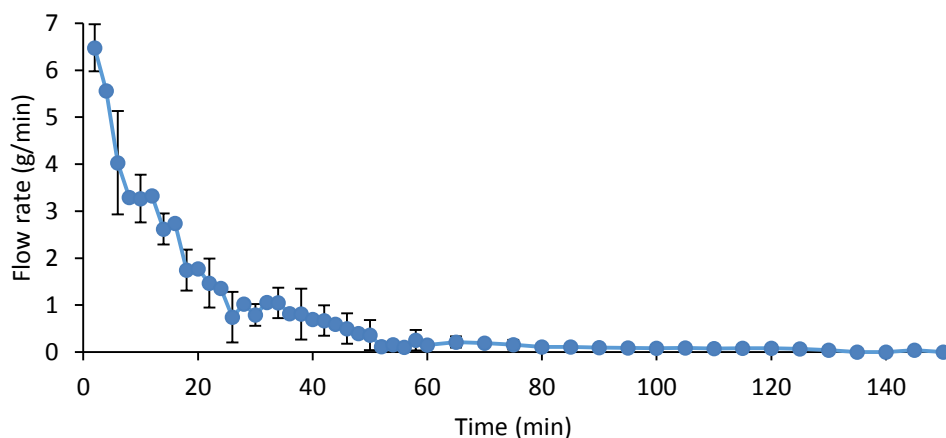


Figure S37. Flow rate of water (under gravity) through a disk **3** placed between two sheets of no-woven PET after defects formed via puncture (equivalent to 0.3 % area removal).

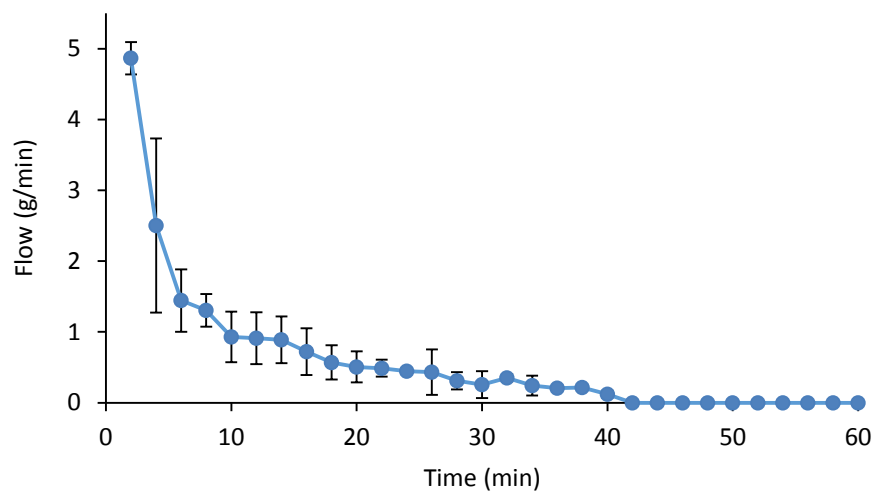


Figure S38. Flow rate of water (under gravity) through a disk of **1/3** (1:1 by wt.) placed between two sheets of non-woven PET after defects formed via puncture (equivalent to 0.3 % area removal).