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Supporting Information

Assessing the Mechanical Properties of a Molecular Spring

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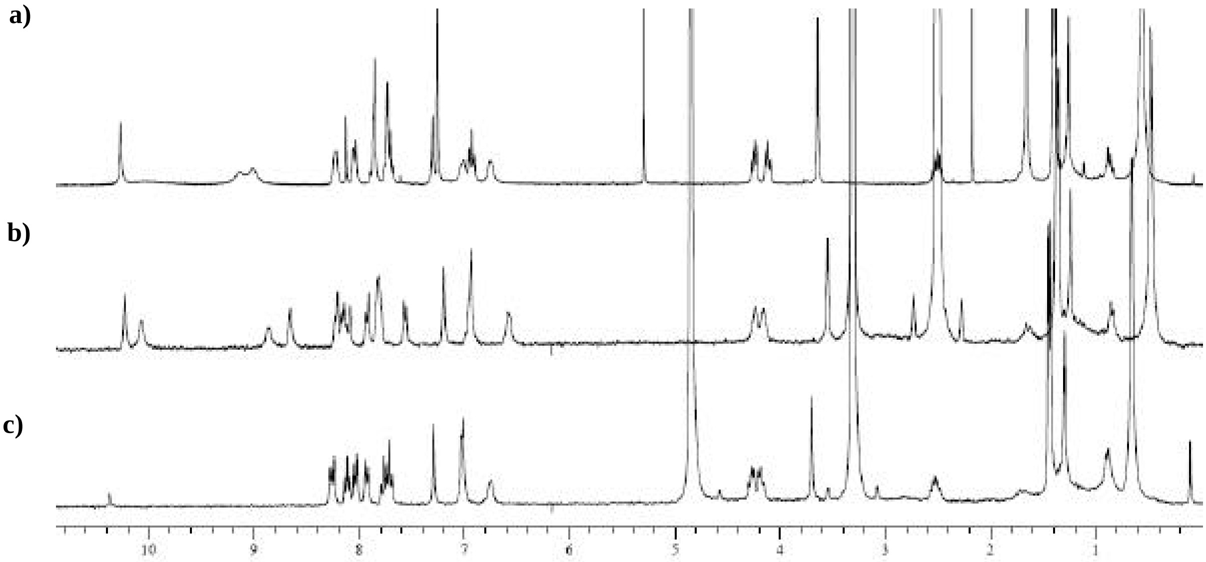


Figure SI-1. 400 MHz ^{1}H NMR spectra of **2** in a) $CDCl_3$, b) DMSO-d6 and c) CD_3OD. All three spectra show that a single species with a symmetrical structure (the signals belonging to one end or the other end of an oligomer are degenerate) prevails. Spectra recorded in solvent mixtures (see Figure SI-2) demonstrate that it is the same species in all three solvents. The signals assigned to amide resonances are not seen in c) because the corresponding protons exchanged for deuterium atoms with the solvent. The solubility of heptamer **2** in a protic solvent is somewhat surprising given that it does not possess any hydrophilic side-chains. Several spectral features are consistent with a double helical dimer in solution: (i) the diastereotopic motifs of the methylene protons belonging to the iBu side chains at 4.2 pmm. Single helical heptameric strands normally undergo fast exchange on the NMR timescale between right- and left-handed conformers, whilst this exchange is slow for double helical dimers; (ii) small chemical shifts variations from solvent to solvent, despite the large solvent polarity changes, suggest that a large portion of the molecule is not exposed to the solvent.

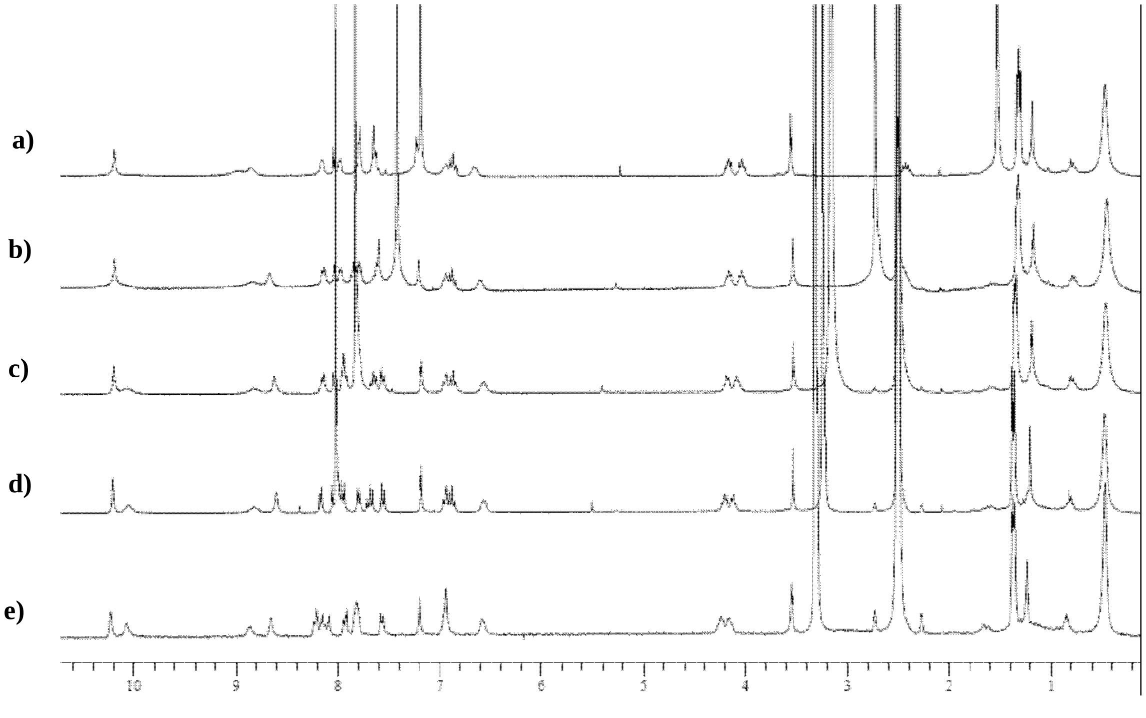


Figure SI-2. 400 MHz ^{1}H NMR spectra of **2** in $CDCl_3$-DMSO-d6 mixtures: a) 0%, b) 11%, c) 33%, d)50%, e) 100% of DMSO- d6. The very small chemical shift variations induced by the solvent change show that the same species is present in CDCl3 and DMSO-d6. Similar results are obtained in $CDCl_3$- CD_3OD mixtures.

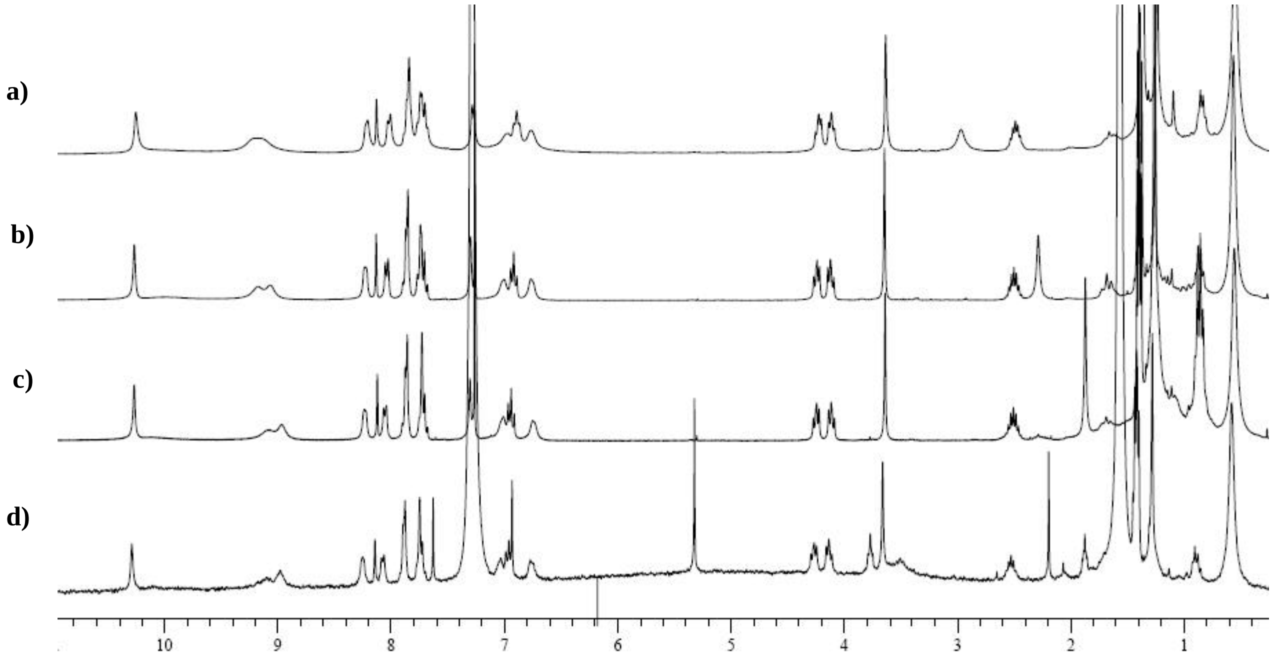


Figure SI-3. 400 MHz ^{1}H NMR spectra of heptamer **2** in CDCl$_3$ at a) 100 mM; b) 39 mM; c)7.5 mM; d) 0.1 mM. The absence of a second set of signals and the absence of significant chemical shift variations indicate that a single species prevail over this wide concentration range, exchange. This species was shown in separate experiments to be a double helical dimer.

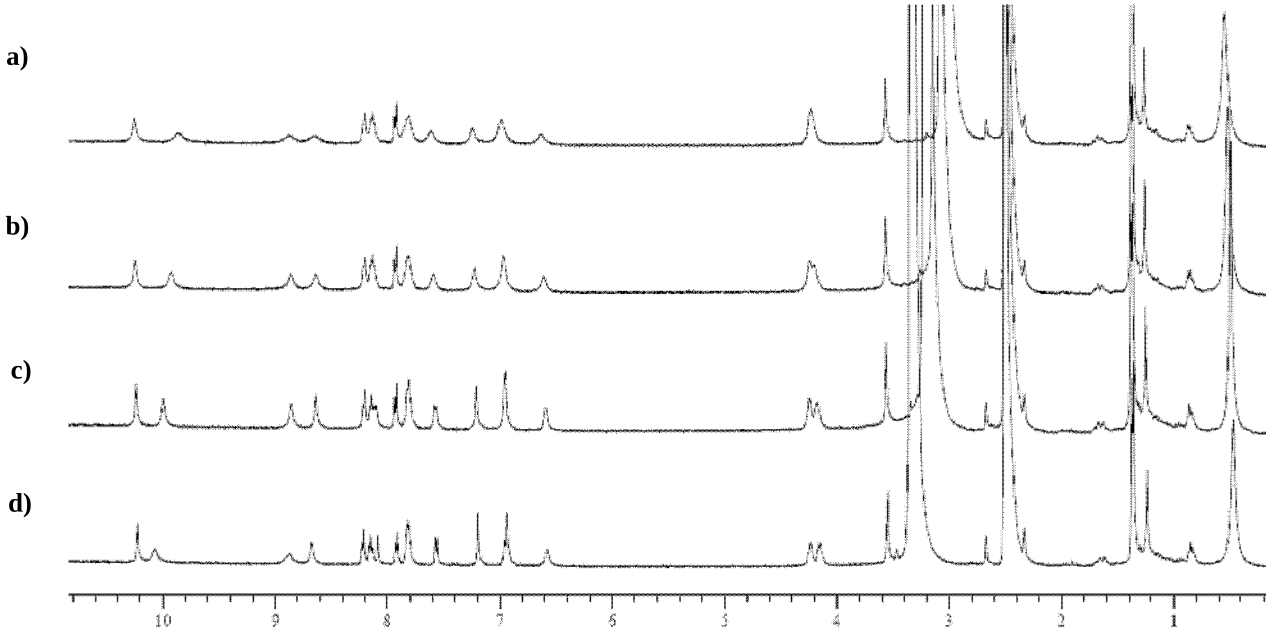
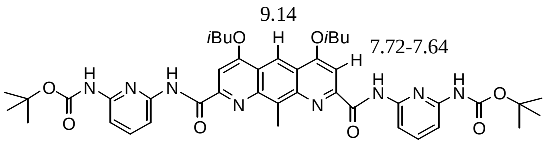


Figure SI-4. 400 MHz ^{1}H NMR spectra of (**2**)$_2$ 2.1 mM in DMSO-d6 at a) 91°C; b) 78°C; c) 58°C; d) 25°C. The main feature of these spectra is the absence of significant chemical shift variations with temperature and the absence of any other signals than those belonging to the main species. They suggest unprecedented double helix stability. It is not clear whether the diastereotopic motifs observed at 4.2 ppm at 25°C undergo a coalescence leading to fast exchange between right- and left-handed conformers at higher temperatures or whether exchange is still slow at high temperature but the chemical shift difference is too small to observe that some protons are not equivalent.



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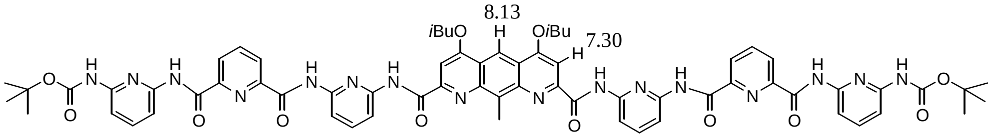

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Figure SI-5. ^{1}H NMR chemical shift values of protons belonging to the anthracene unit of **2** and **9** in $CDCl_3$ at 25°C. These protons can be unambiguously assigned on the basis of their multiplicity – they are singlets – and of their integral values. The upfield shifts of the signals in **2** suggest that the corresponding protons are involved in π–π interactions. Such contacts are incompatible with a single helical conformation because the strand only spans one and a half helical turn, but fully consistent with the double helix observed in the solid state. A chemical shift range is shown for one of the protons of **9** to indicate chemical shift variations with concentration. Slight upfield shifts are observed upon increasing concentration (from 0.5 to 10 mM) arising from non-specific intermolecular π–π interactions. No such variations with concentration are observed with **2** (see Figure SI-3).

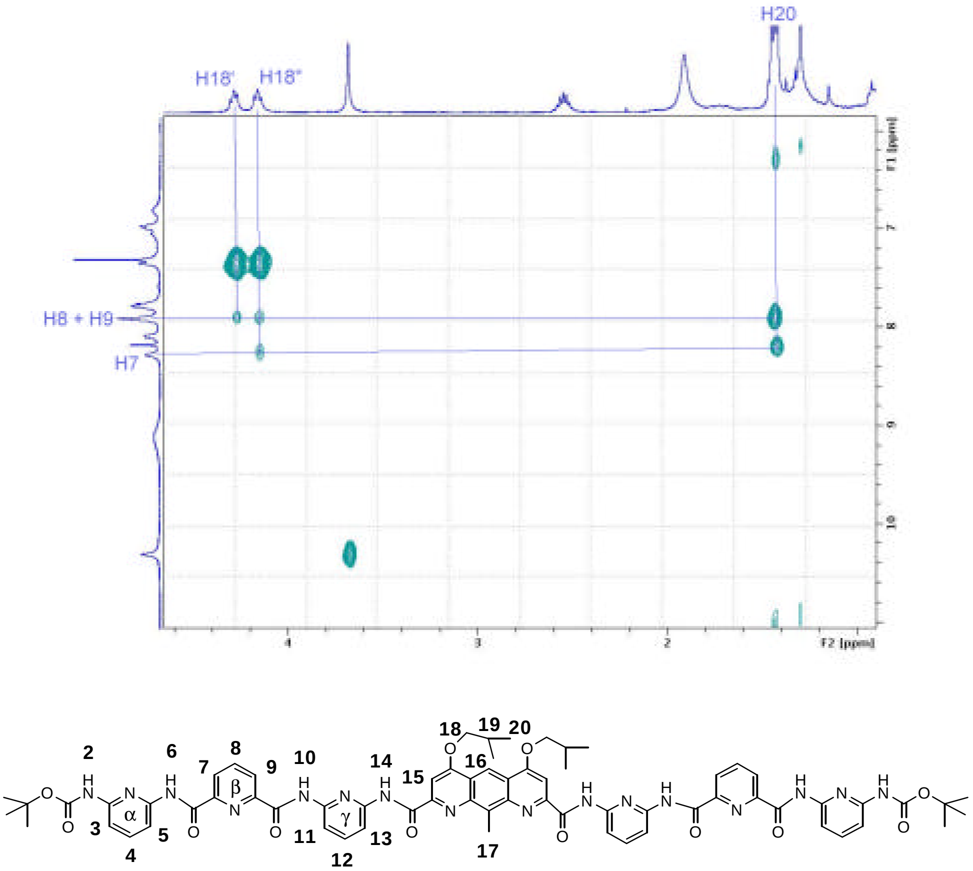

Figure SI-6. Part of the ROESY spectra of heptamer **2** in $CDCl_3$ showing direct evidence of a double helical conformation in solution. Correlations are observed between on the one hand protons 18 and 20 of the isobutyl moiety and, on the other hand, protons of the 2,6-dicarbonylpyridine unit (ring β). Proximity between these protons are impossible within a single helical conformation but fully compatible with the double helical structures observed in the solid state.

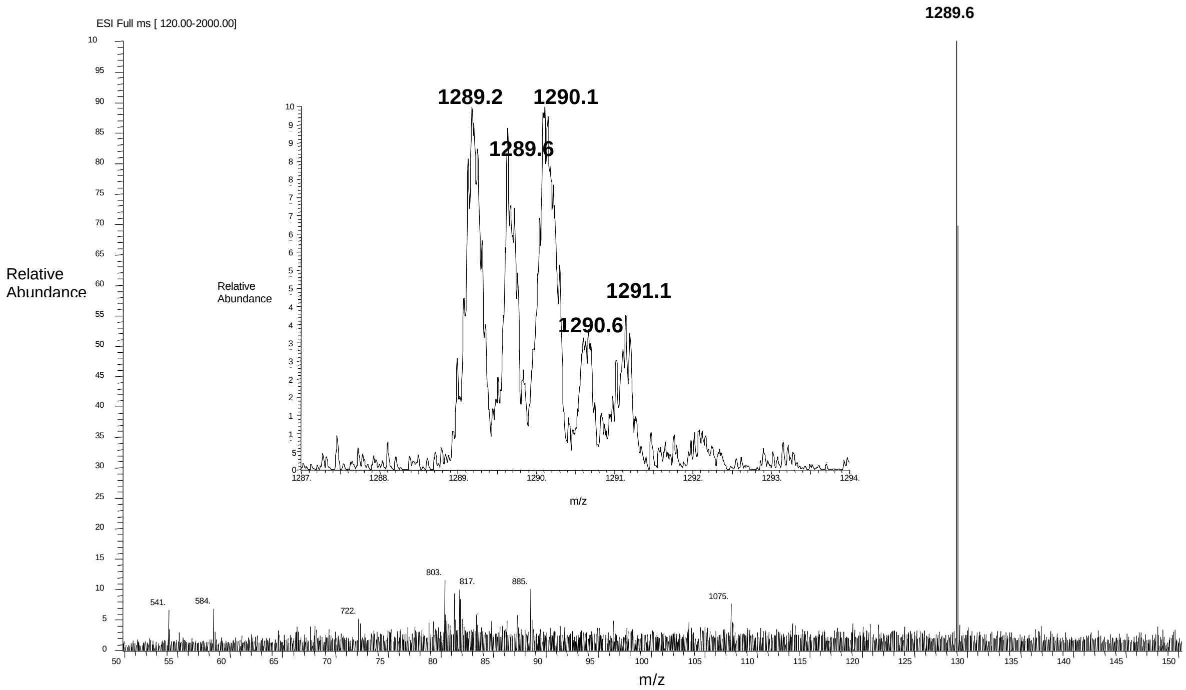

Figure SI-7. ESI Mass spectra of **2**. The inset shows an enlarged view of the major peak which demonstrates the presence of both the monomer as a singly charged species [M+H]+ (peaks at 1289.2, 1290.1, 1291.1) and the dimer as a doubly charged species [M+H]2+ (peaks at 1289.2, 1289.6, 1290.1, 1290.6, 1291.1) in solution

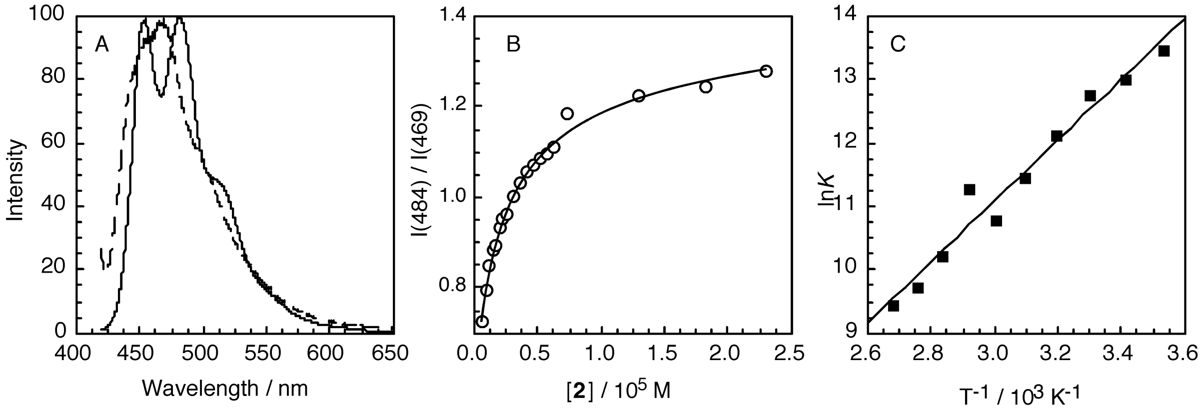

Figure SI-8. a) Normalized fluorescence emission of **2** in aerated pyridine solution (λex = 416 nm) at 2.3 x 10^{-5} M (solid line) and 5.5 x 10^{-7} M (dashed line); b) Binding isotherm obtained from the fluorescence emission of **2** as a function of concentration. Ratiometric analysis (at 484 and 469 nm) was used to circumvent variations in emission intensity due to changes in the absorption spectrum of the sample, see experimental section for details; c) Van't Hoff plot of **2** at 1.4 x 10^{-4} M. The straight line represents the best fit through experimental points (ΔH = - 40.2 kJ.mol^{-1}, ΔS = - 27.6 J.K^{-1}, r =0.986).

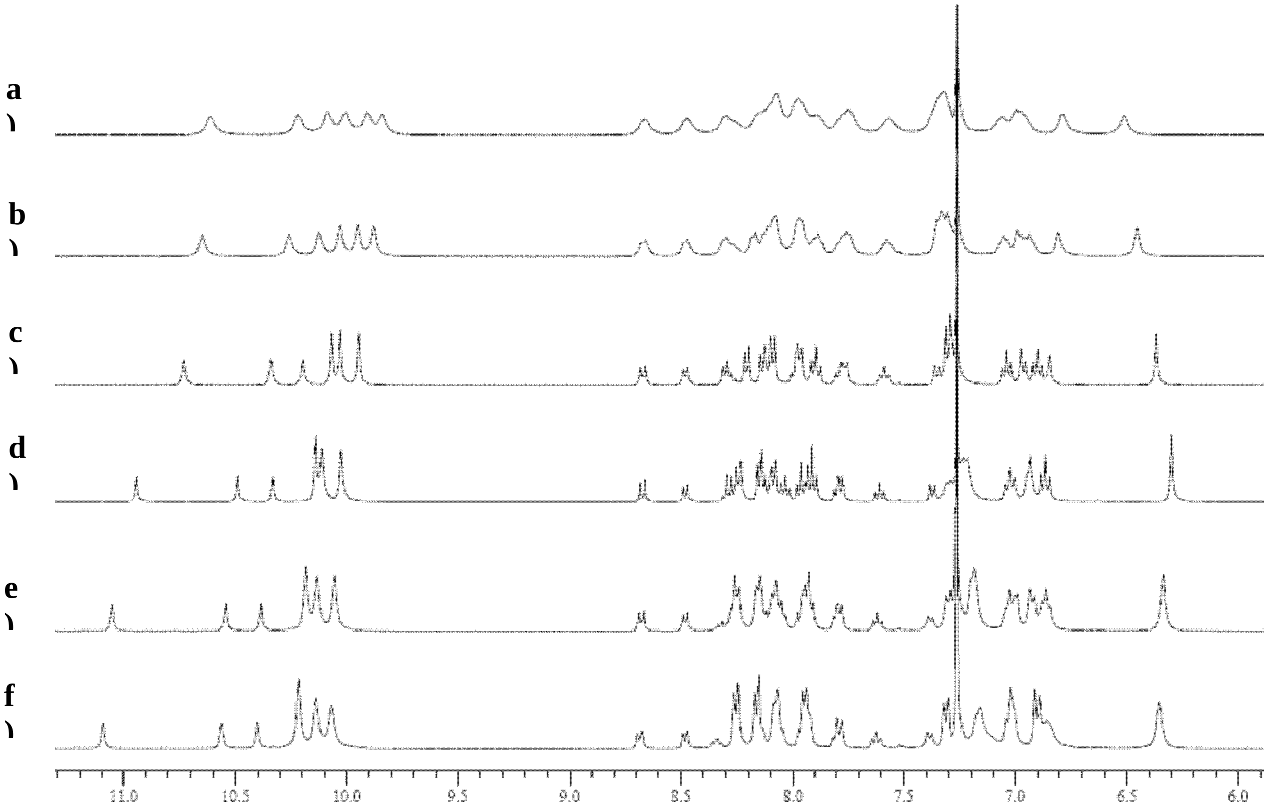

Figure SI-9. 400 MHz ^{1}H NMR spectra of heptamer **1**, 10 mM in $CDCl_3$ at a) 40°C; b) 35°C; c) 25°C; d) 0°C; e) -20°C; f) -40°C. The proportions between the signals of the single helix (major at 40°C) and those of the double helix (major at -40°C) vary little with temperature, which correspond to a small (actually slightly positive) value of ΔS_{dim}.

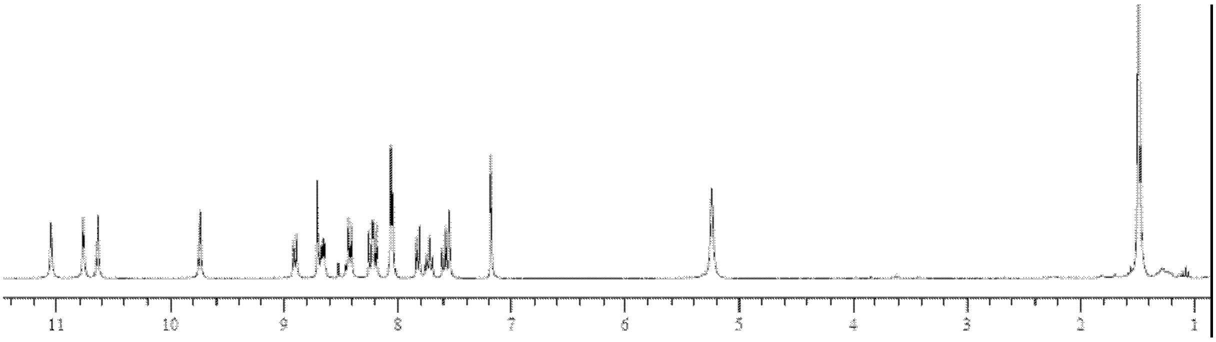

Figure SI-10. 400 MHz ^{1}H NMR spectra of heptamer **1**, 22 mM in pyridine-d5, showing exclusively the single helical conformer.