

New approaches to the synthesis of strapped porphyrin containing bipyridinium [2]rotaxanes

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Supplementary Information

Variable Temperature Study

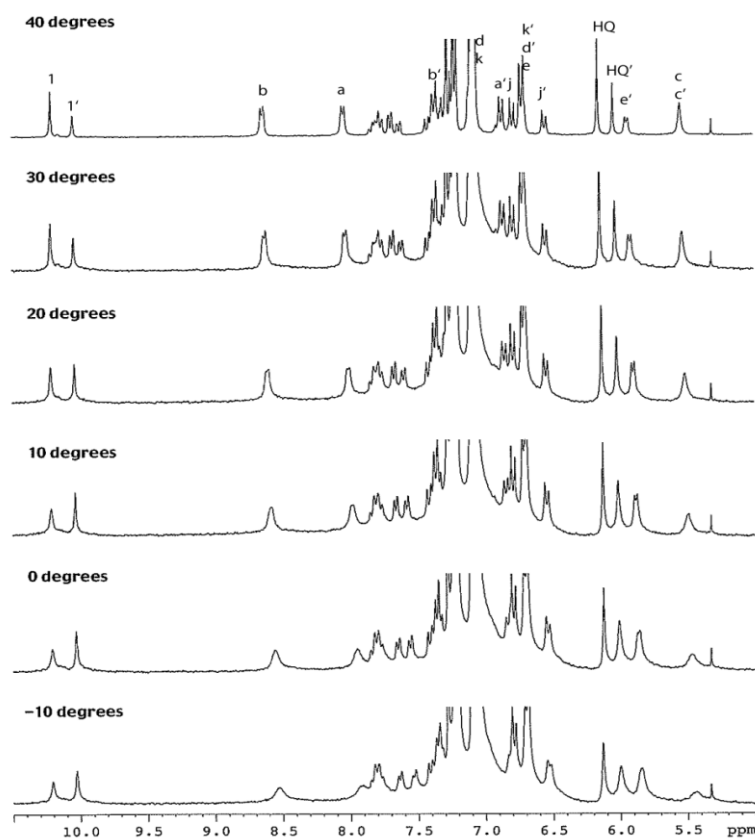


Figure S1: ¹H NMR spectrum acquired at different temperatures for an equimolar mixture of bipyridinium thread **1b** and porphyrin macrocycle **4** in CDCl₃.

Diffusion Ordered Spectroscopy NMR study: The DOSY experiments were conducted on a Bruker 300 MHz spectrometer, at 303 K. Sample volumes were 500 μL and the concentration of the samples was 4 mM in CDCl_3 . Diffusion coefficients and hydrodynamic radii are correlated theoretically by the Stokes-Einstein relation (equation 5).

$$D = \frac{kT}{6\pi\eta r_s} \quad 5$$

where D is the diffusion coefficient, k the Boltzman constant, T the temperature, η the viscosity of the liquid and r_s the (hydrodynamic) radius of the molecule.

Pseudorotaxane Binding Studies

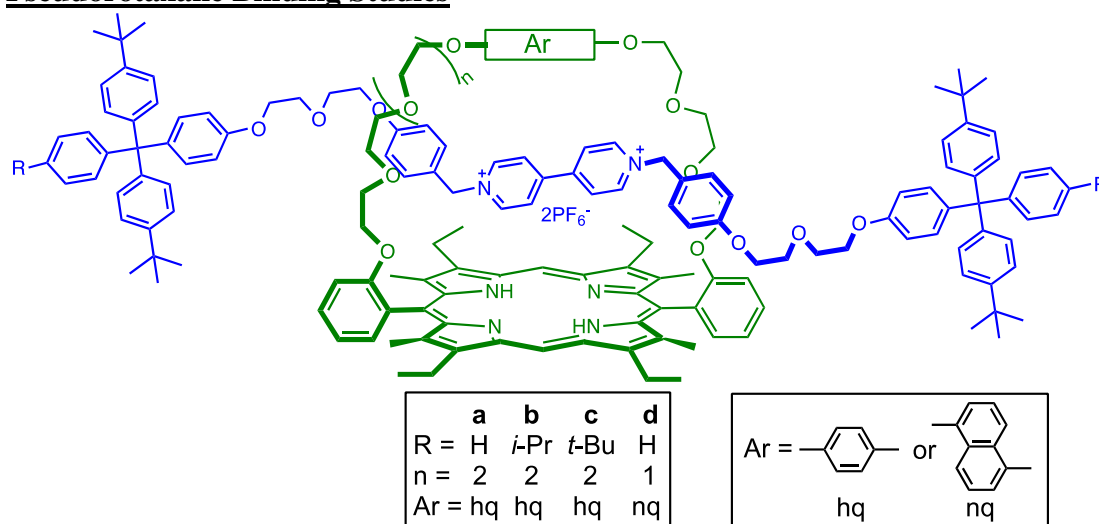


Figure S2: Combinations of bipyrindinium thread and porphyrin macrocycle that showed evidence of pseudorotaxane formation

Table S1: Typical shifts observed upon complexation for an equimolar solution of thread **1b** and macrocycle **4**, in CDCl_3 at 303 K (concentration = 4 mmolL^{-1}).

Position	Uncomplexed	Complexed	$\delta\Delta$ ppm
<i>meso</i>	10.20	10.04	-0.16
b	8.81	7.38	-1.43
a	8.18	6.86	-1.32
k	7.08	6.79	-0.29
d	7.07	6.76	-0.31
j	6.81	6.55	-0.26

e	6.70	5.93	-0.77
HQ	6.17	6.04	-0.13
Ethyl CH3	2.49	1.80	-0.69
NH porphyrin	-2.35	-2.98	-0.63

Calculation of binding constants: Equimolar (4 mmolL⁻¹) solutions of bipyridinium thread **1a-c** and strapped porphyrins **2-4** were made up in CDCl₃ (500 uL). ¹H NMR spectra were recorded periodically to monitor the relative intensities of the complexed and uncomplexed *meso* porphyrin peaks in order to ascertain when equilibrium had been reached. Once equilibrium was established, integration of each of the bound versus unbound peaks was used to calculate binding constants for the pseudorotaxane systems using eqn 1. All measurements were carried out at 303 K.

$$K = \frac{[C]e}{[G]e[H]e} \quad \mathbf{1}$$

where the concentration of thread (G), the porphyrin macrocycle (H) and the pseudorotaxane (C) can be calculated using equations 2-4 with int meaning the integration of the ¹H NMR peaks, i meaning the initial peaks, and e referring to the peaks once equilibrium had been reached.

$$\frac{[C]e}{[H]e} = \frac{int(C)e}{int(C)e + int(H)e} \quad \mathbf{2}$$

$$[G]e = [G]i - [C]e \quad \mathbf{3}$$

$$[H]e = [H]i - [C]e \quad \mathbf{4}$$

Crystal Structure Data

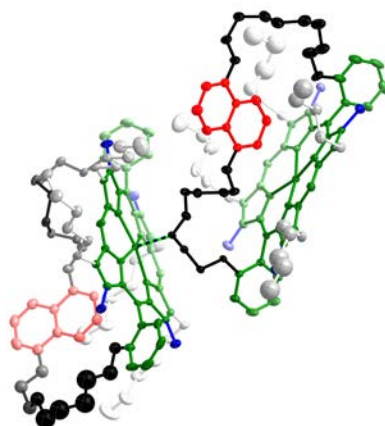


Figure S3: Crystal structure of **5** with 50 % thermal ellipsoids. The colour scheme is similar to Scheme 1 (green = porphyrin ring, black = strap ethoxy bridges, red = naphthoquinone aromatic, blue = methyl side chains and grey = hexyl side chains. Protons have been omitted for clarity.

Selected NMR spectra

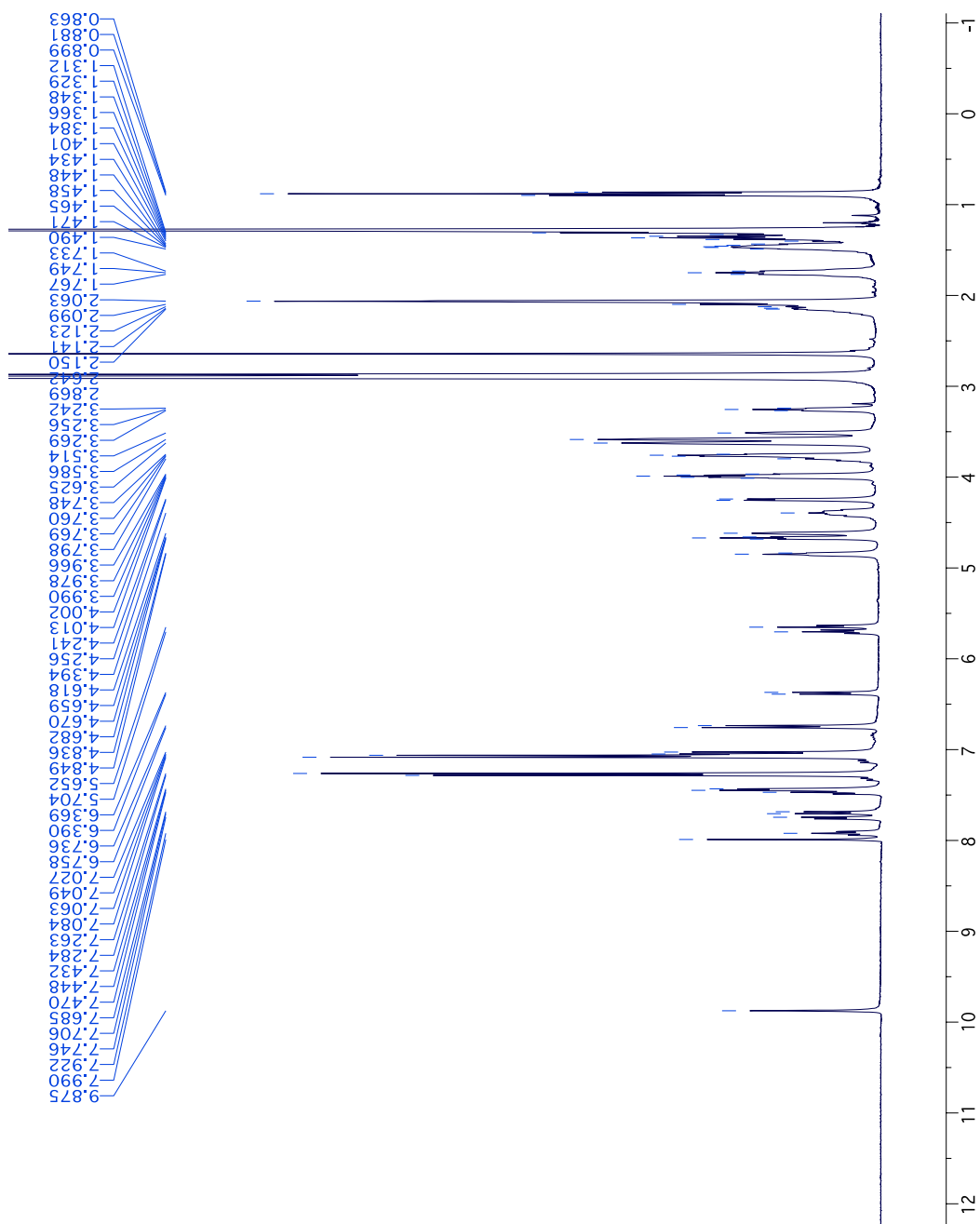


Figure S4: ¹H NMR spectrum of rotaxane **8** in acetone-*d*₆.

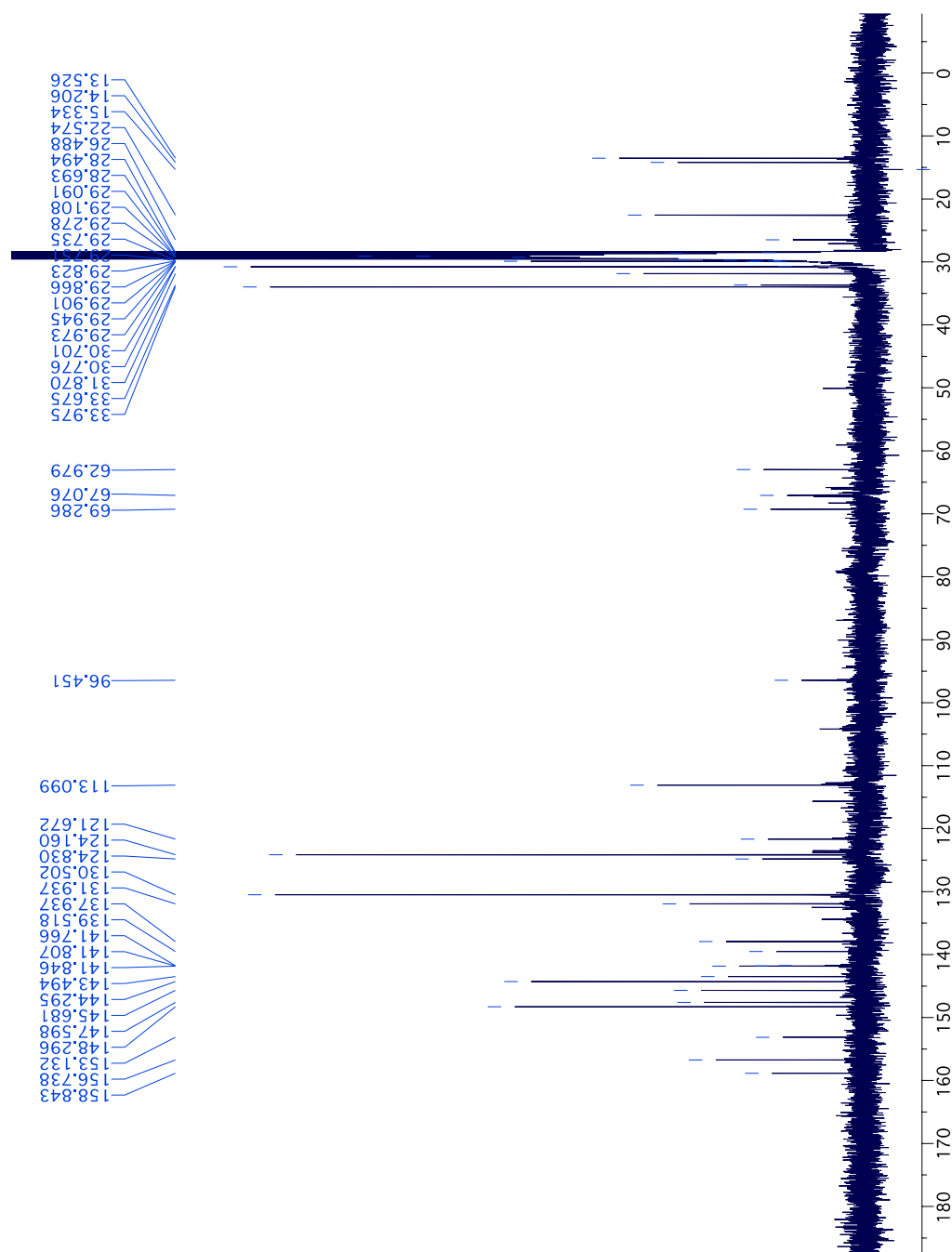


Figure S5: ¹³C NMR spectrum of rotaxane **8** in acetone-*d*₆.

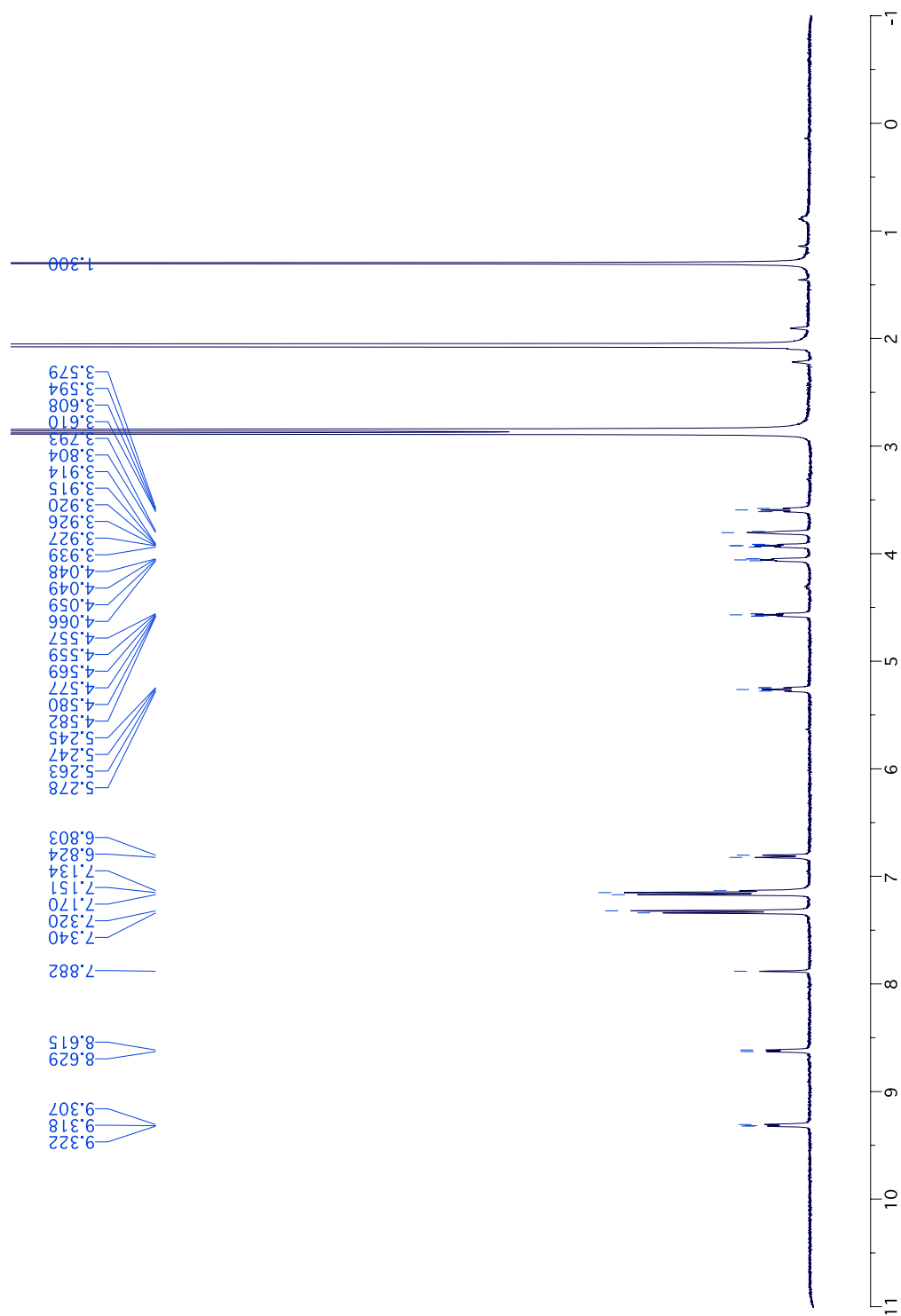


Figure S6: ¹H NMR spectrum of bipyridinium stoppered thread **9** in acetone-*d*₆.

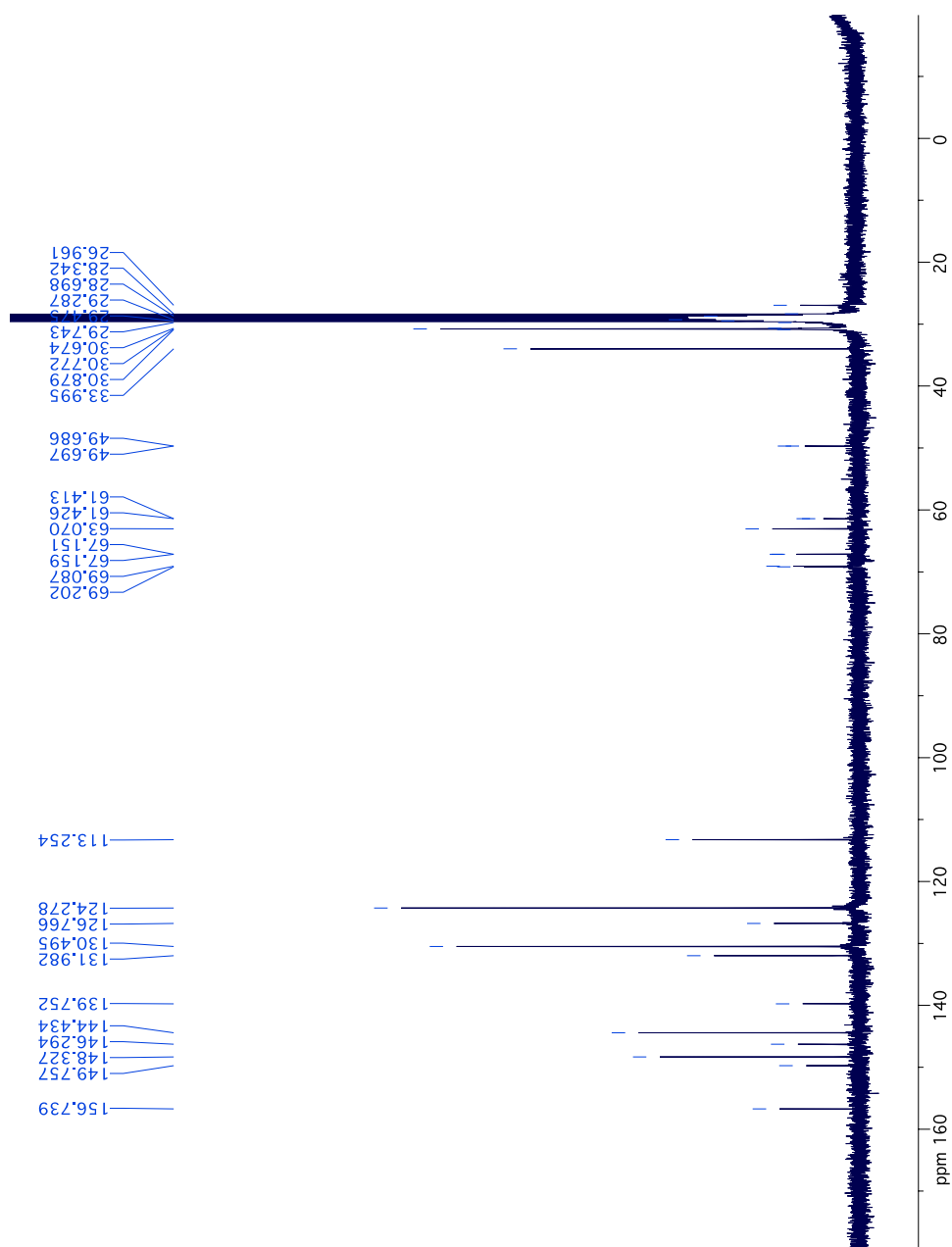


Figure S7: ¹³C NMR spectrum of bipyridinium stoppered thread **9** in acetone-*d*₆.