

Electronic Supporting Information

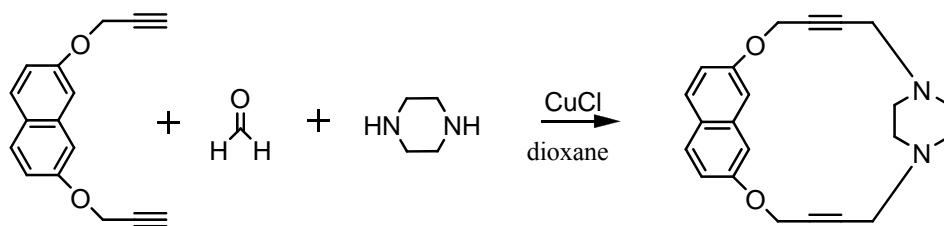
An Unprecedented Triple Helix: Based on A Tetrameric Assembly of Macrocycle driven by weak C–H \cdots π and C–H \cdots O Interaction†

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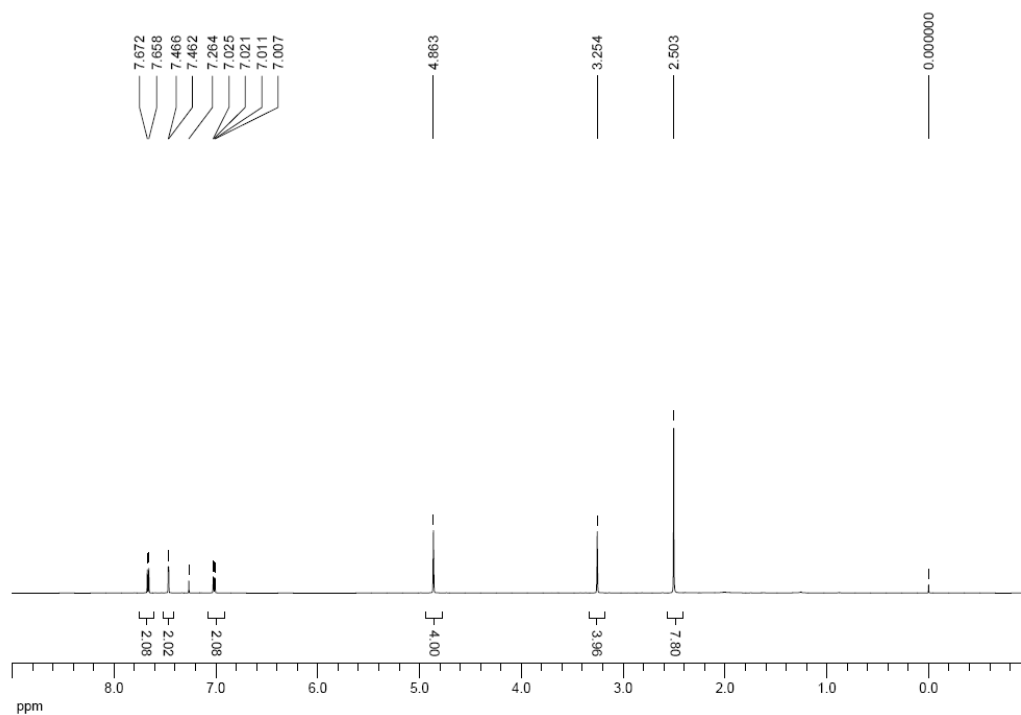
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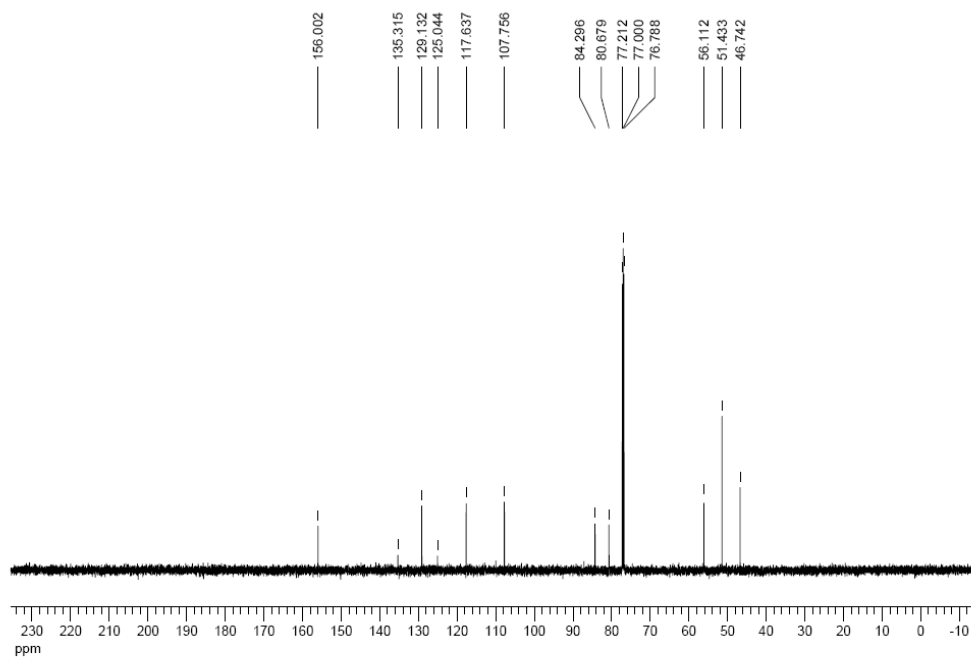
General experimental procedure for compound 1:¹ Preparation of products: 1.0 mmol of terminal diyne, 1.0 mmol of secondary diamine and 2.0 mmol of formaldehyde in the presence of 1.0 mmol CuCl in 30 mL of dioxane were heated at 90°C. After workup (monitored by TLC), the solvent was removed under reduced pressure. The solid residue was purified by flash chromatography (SiO₂, CHCl₃/CH₃OH) to give the products **1** (46%) as a white solid. IR (KBr, cm⁻¹): 3422, 2944, 2901, 2808, 1625, 1512, 1453, 1203, 1103, 770 cm⁻¹. ¹H NMR (600 MHz, CDCl₃): 7.67(d, J=8.4, 2H), 7.46(d, J=2.4, 2H), 7.02(q, J=2.4, 2H), 4.86(s, 4H), 3.25(s, 4H), 2.50(s, 8H) ¹³C NMR (150 MHz, CDCl₃): 156.0, 135.3, 129.1, 125.0, 117.6, 107.8, 84.3, 80.7, 56.1, 51.4, 46.7. HRMS (ESI): m/z [M + H]⁺calcd for C₂₂H₂₂N₂O₂: 346.17; found:347.1744.

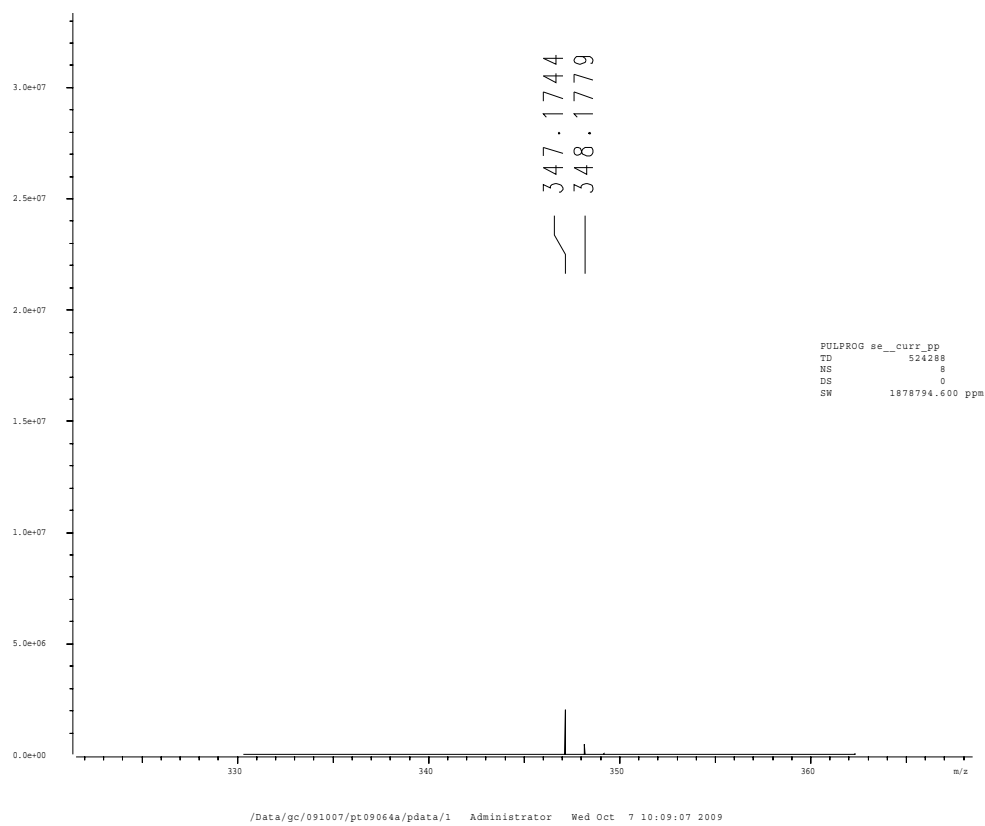
1 A. H. Sharba and K. Charry, *Abhath Al-Yarmouk, Basic Sciences and Engineering*, **2002**, 11(2A), 655.

^1H NMR of Compound 1



^{13}C NMR of Compound 1





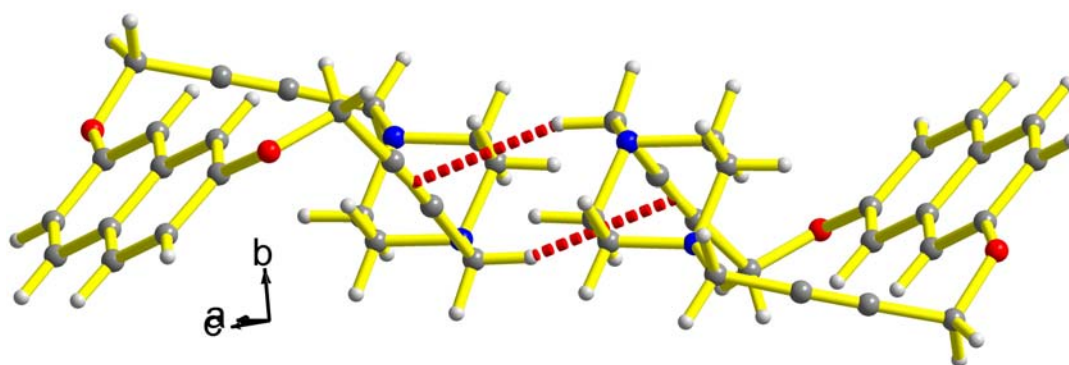


Figure S1. Expanded view of Figure 1b. The zigzag motif observed in the x-ray structure of **1**. Color code: C, gray; H, white; N, blue; O, red; C–H... π interactions, red striped.

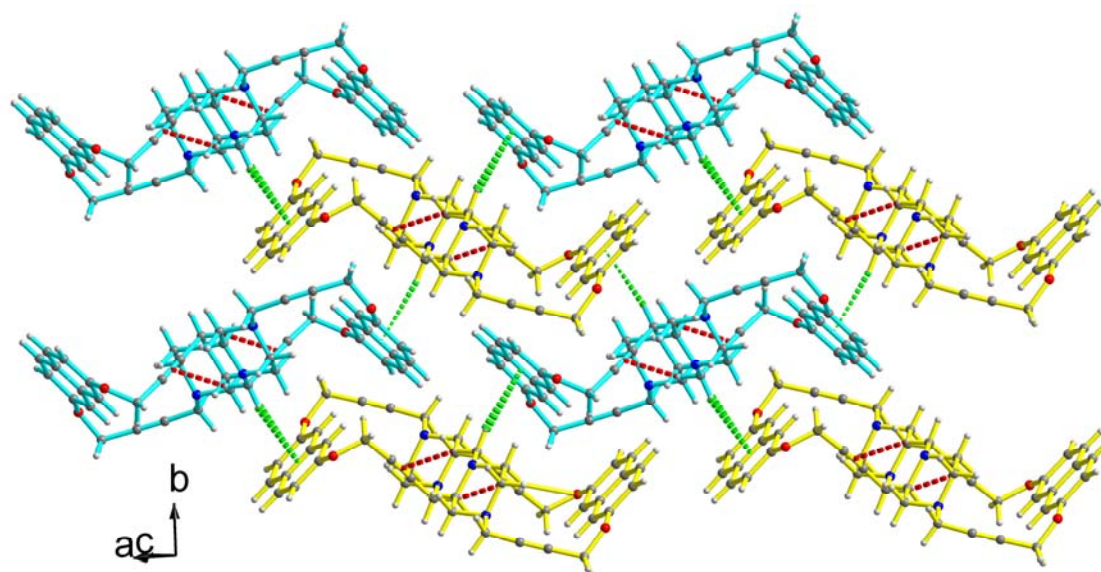


Figure S2. Expanded view of Figure 2b.

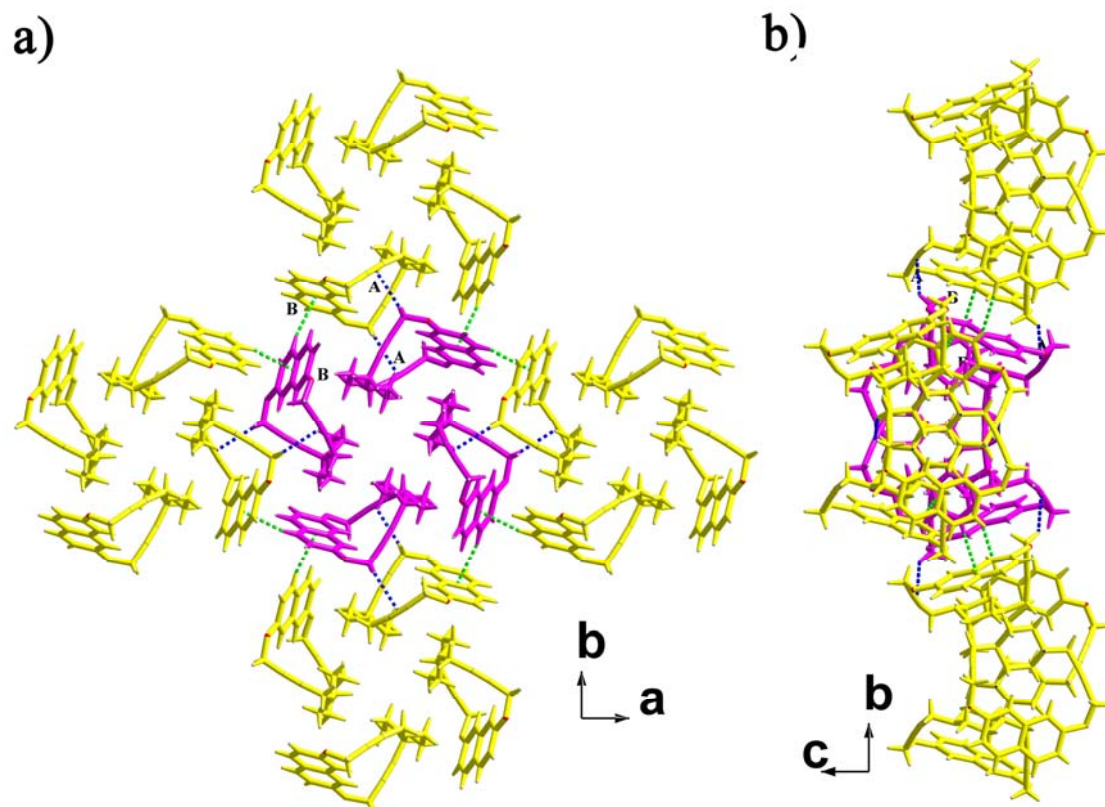


Figure S3. Expanded view of Figure 3. (a) Space filling model of the packing of (1)₄ in the crystal of form II. Stacking of (1)₄ viewed down the c-axis. (b) Stacking of (1)₄ viewed down the a-axis.

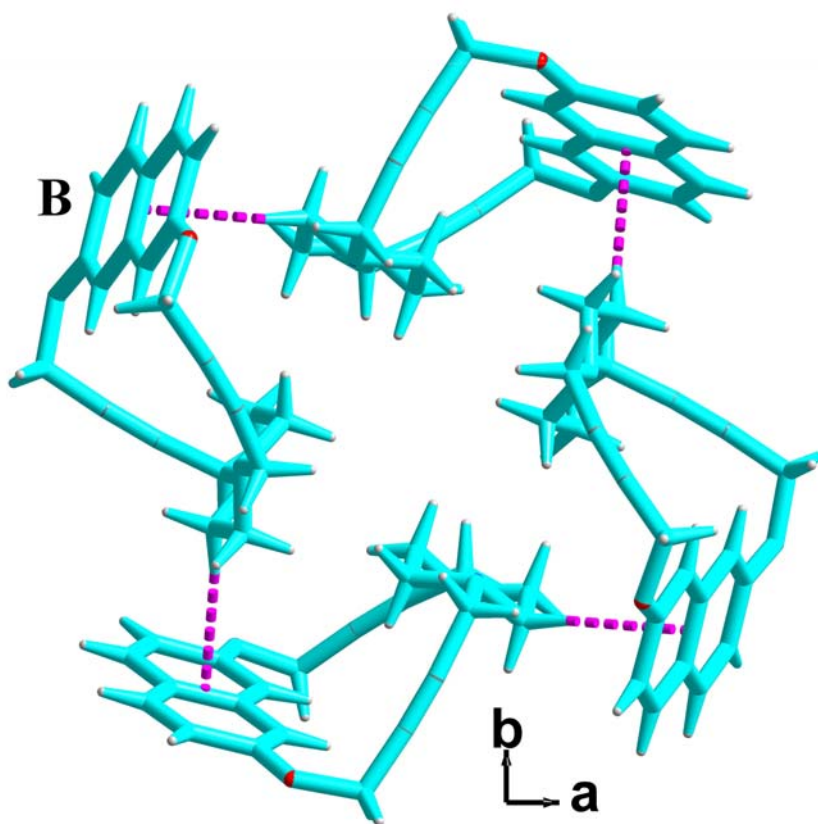


Figure S4. Expanded view of Figure 4a. Details of the C–H... π interactions in the windmill-shaped structural unit of **1** in form **II** viewed down the c-axis.

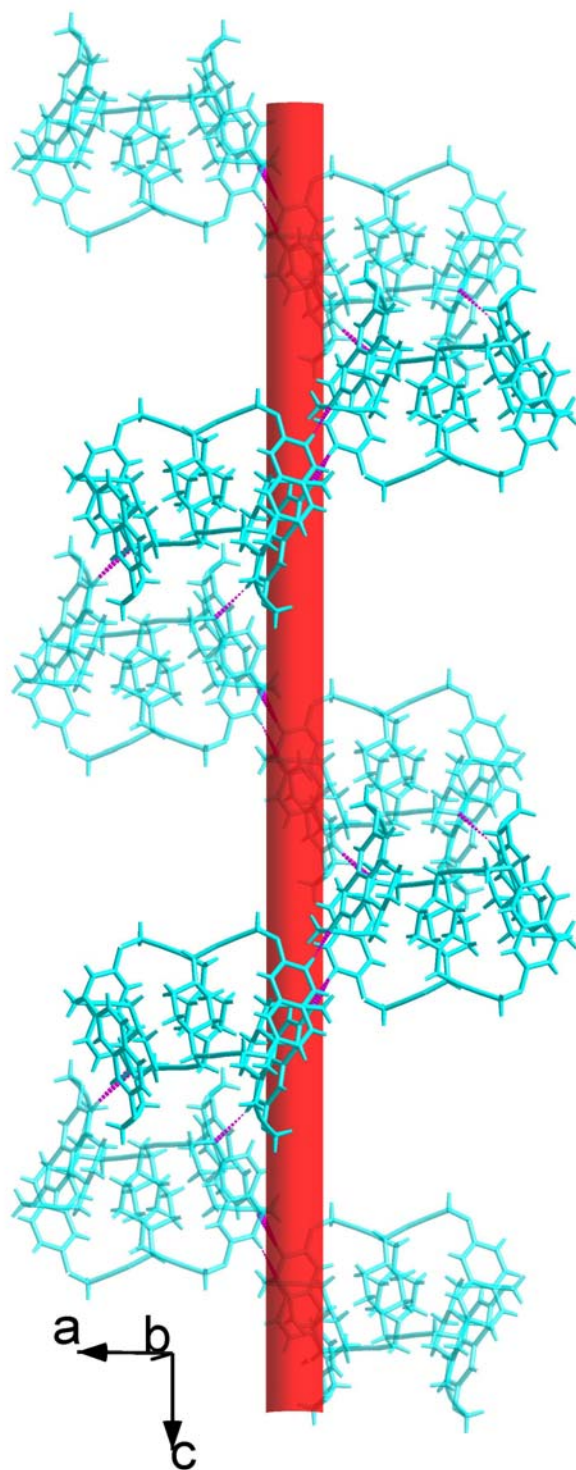


Figure S5. Expanded view of Figure 4c. Perspective and space-filling views of the 1D helical structure in form II.

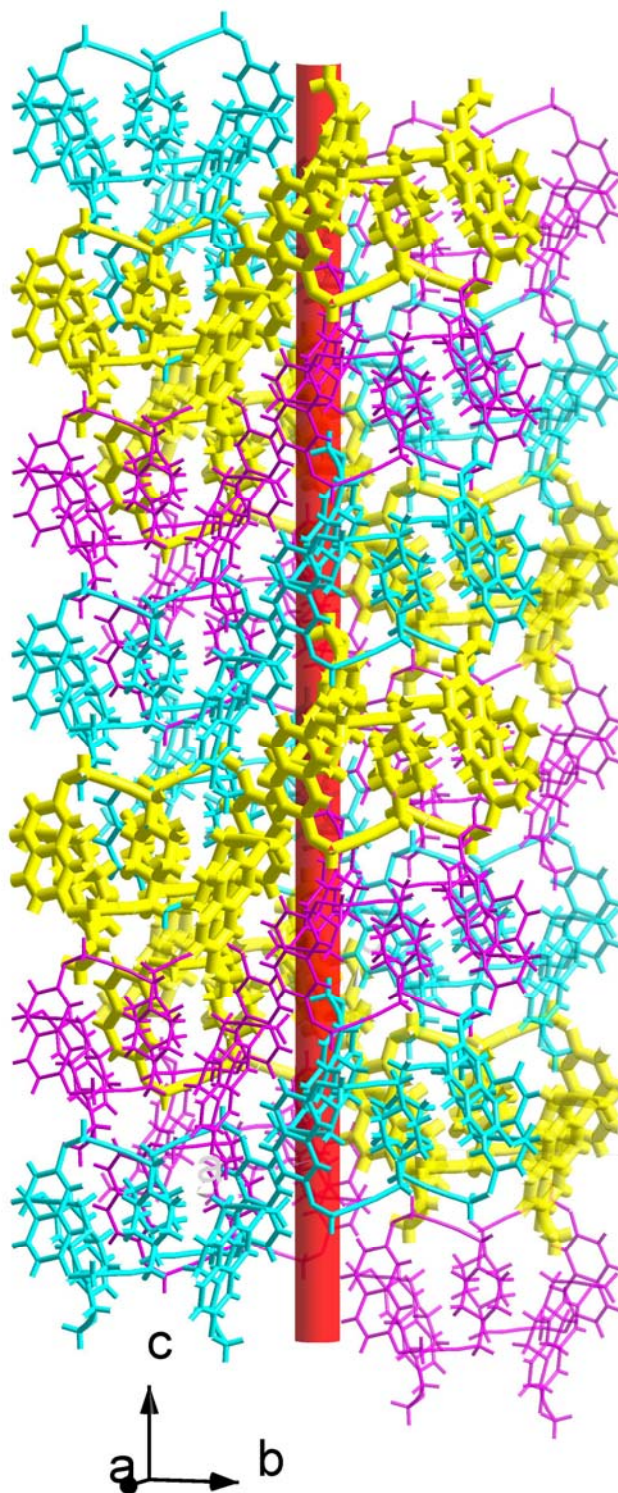


Figure S6. Expanded view of Figure 4c. Views of the triple helical 1D braid; each strand of the triple helix is colour coded in yellow, red, and blue.

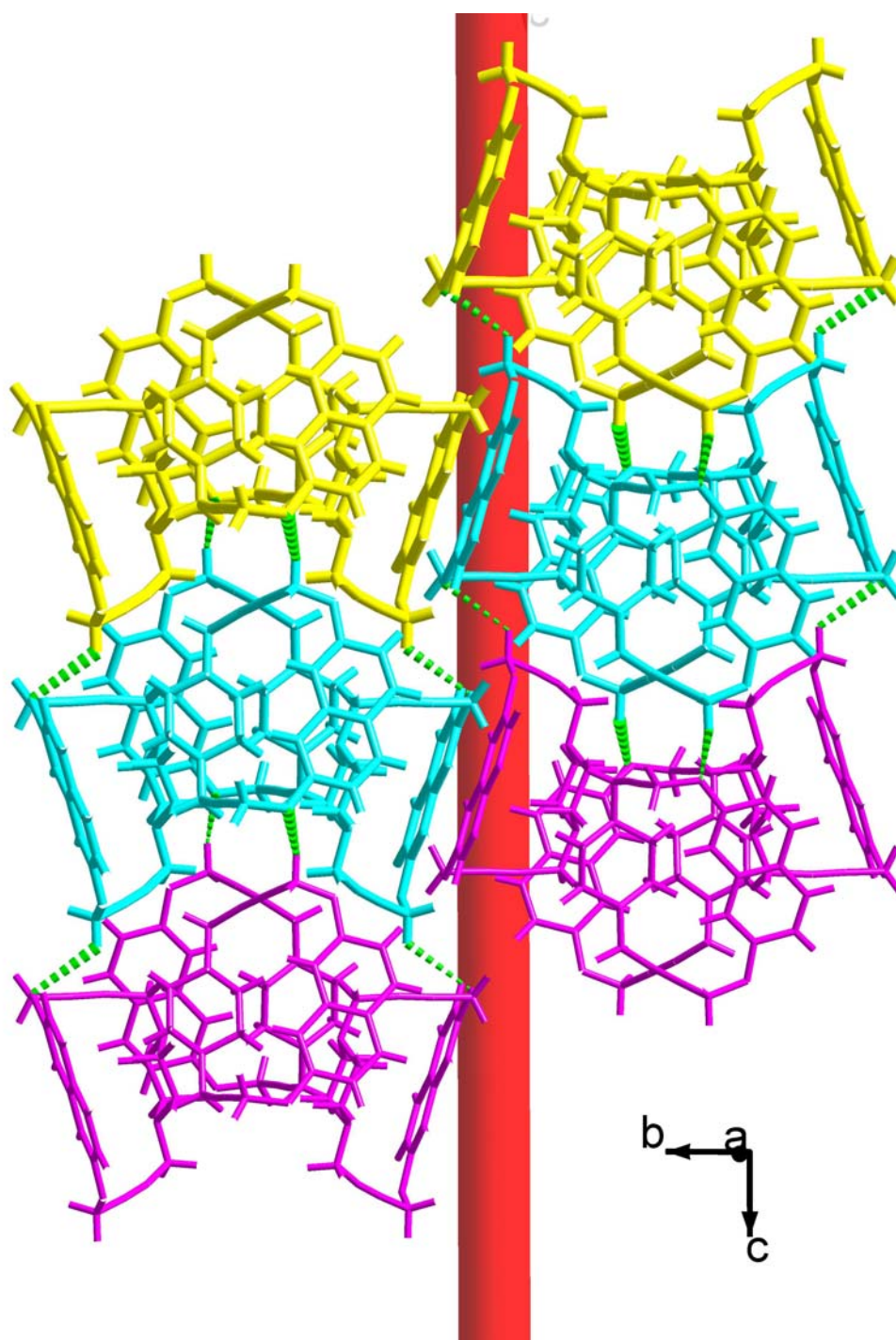


Figure S7. Views of the triple helical 1D braid constructed of single helix through strong hydrogen-bonding interactions.

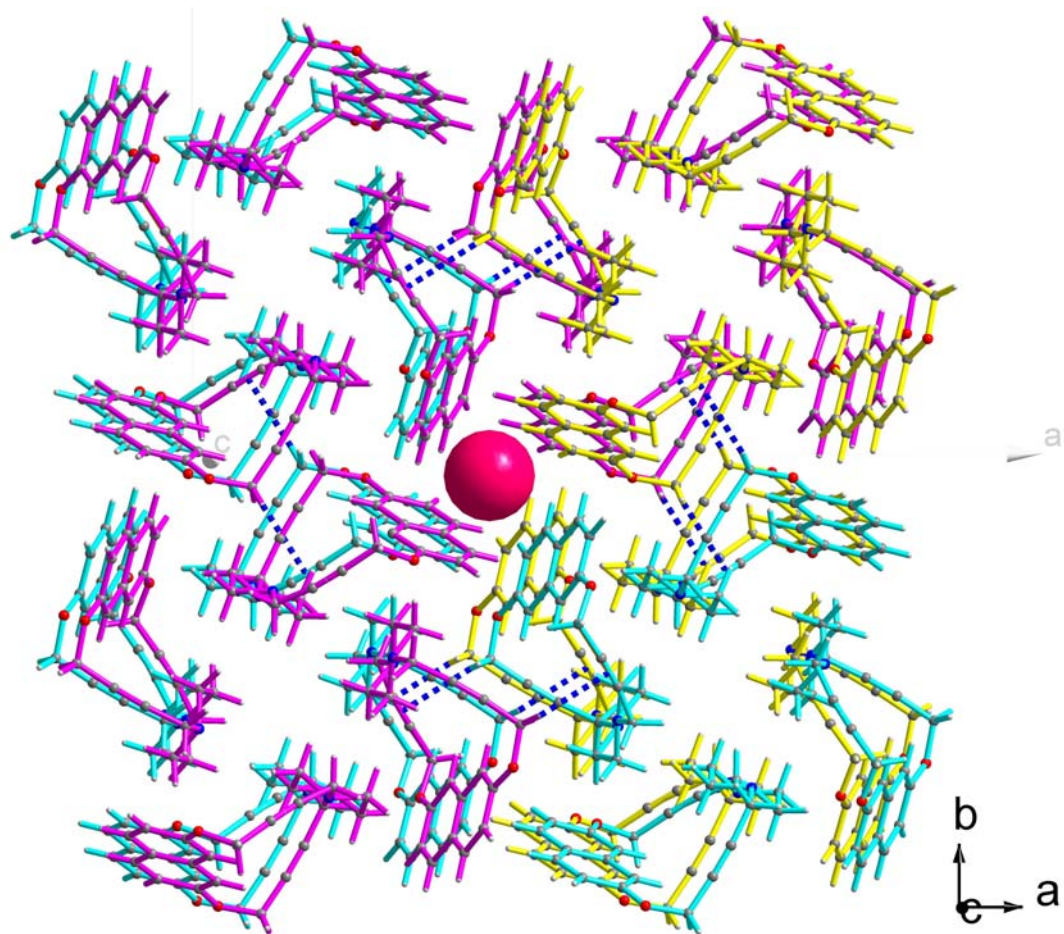


Figure S8. Views of the triple helical 1D braid constructed of single helix through complementary C–H \cdots π interactions.

^1H NMR Binding Experiments with **1**

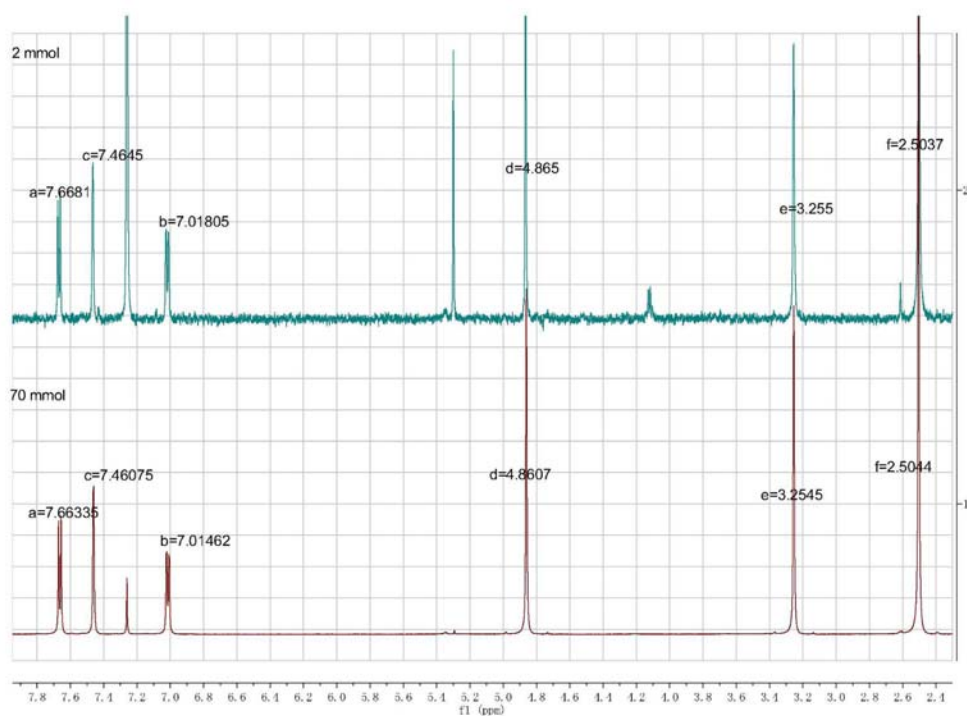


Figure S9. ^1H NMR spectra changes of **1** (600 MHz, CDCl_3 , 298 K) by variable concentration.

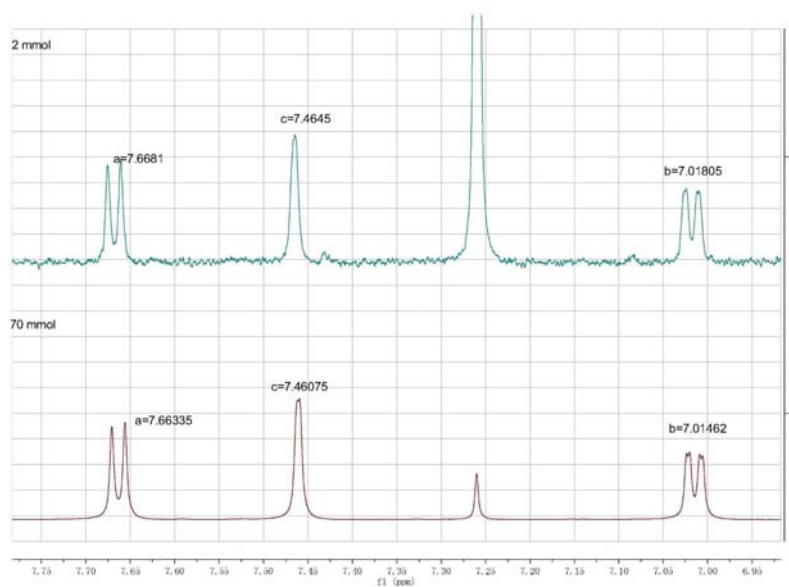


Figure S10. Partial ^1H NMR spectra changes of **1** (600MHz, CDCl_3 , 298K) in variable concentration.

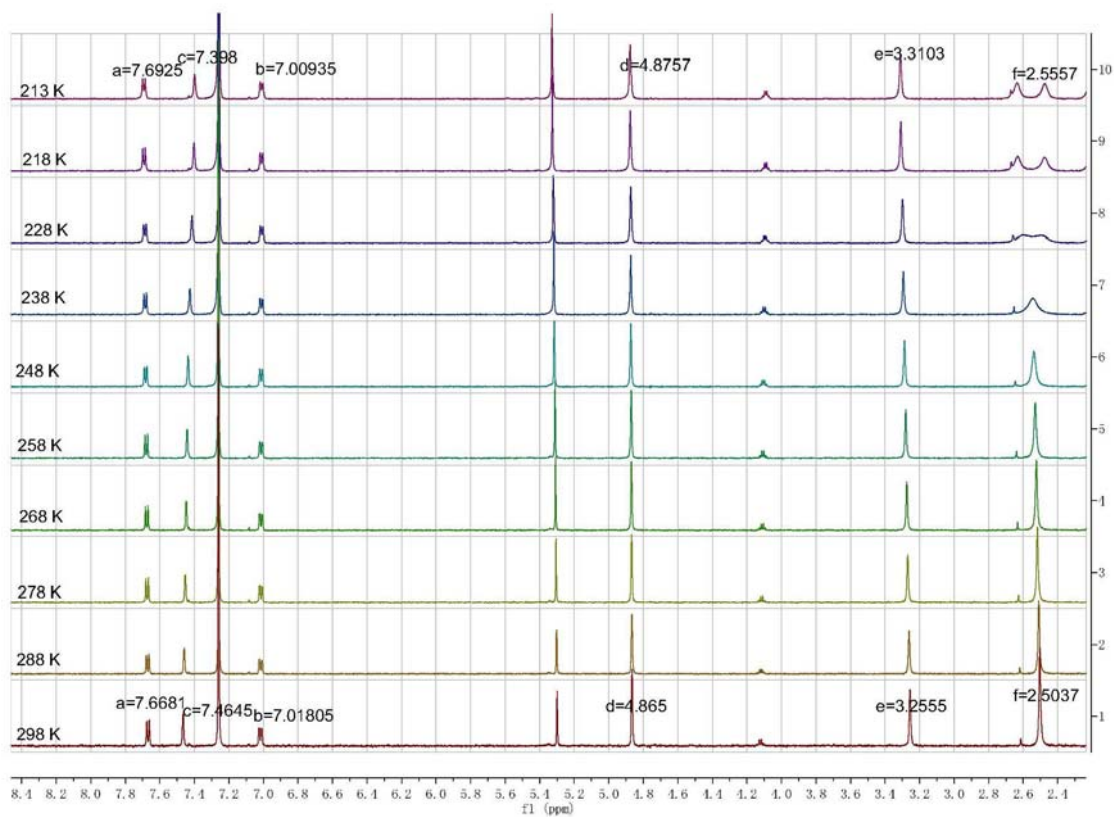


Figure S11. ^1H NMR spectra changes of (600MHz , CDCl_3 , 298K) in variable temperature. [**1**] = 2mM.

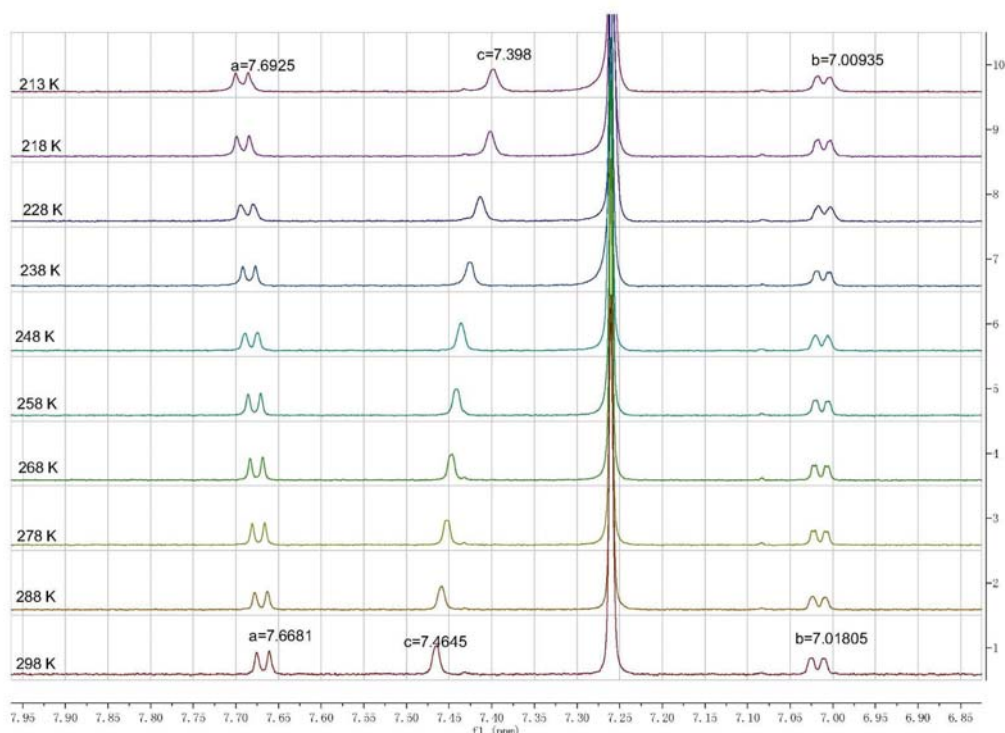


Figure S12. Partial ^1H NMR spectra changes of (600MHz, CDCl_3 , 298 K) in variable temperature. [**1**] = 2mM.

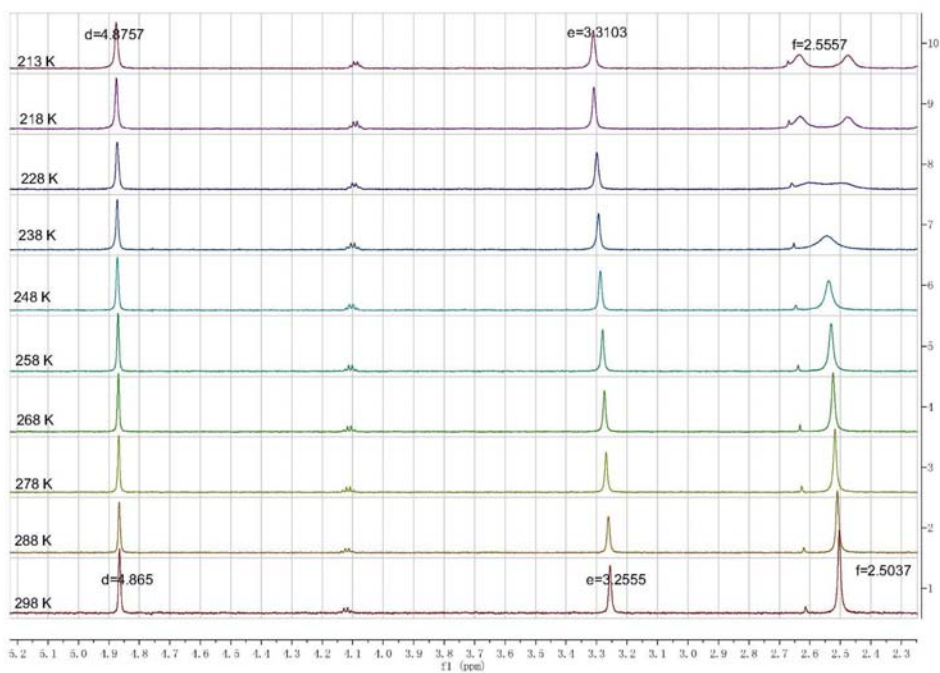


Figure S13. Partial ^1H NMR spectra (600MHz, CDCl_3 , 298 K) in variable temperature.

[1] = 2mM.

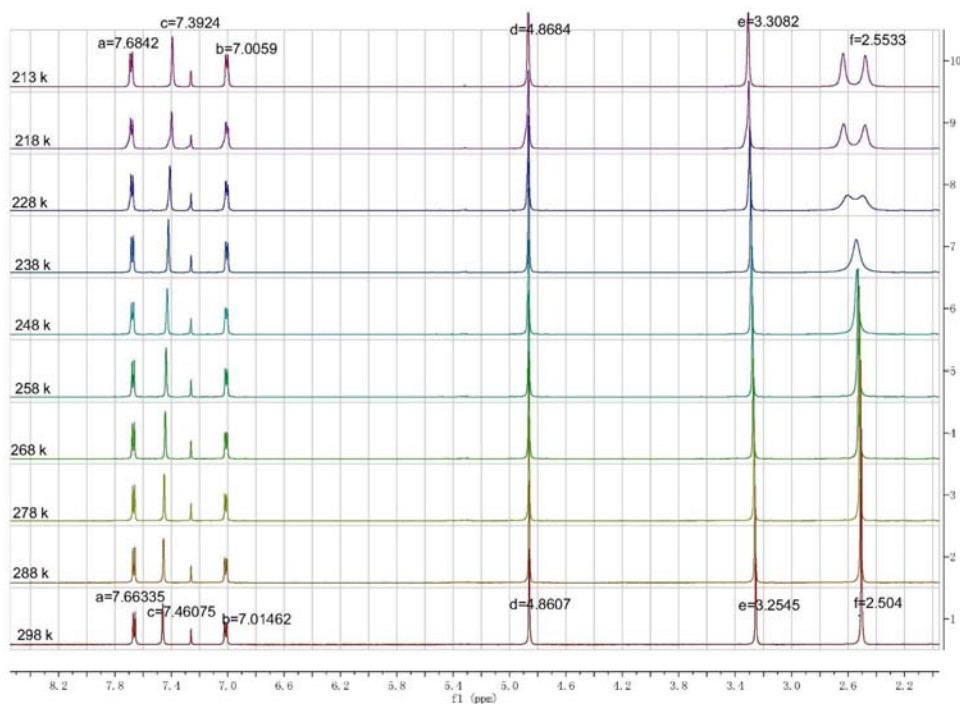


Figure S14. ^1H NMR spectra (600MHz, CDCl_3 , 298 K) in variable temperature. [1] = 70mM.

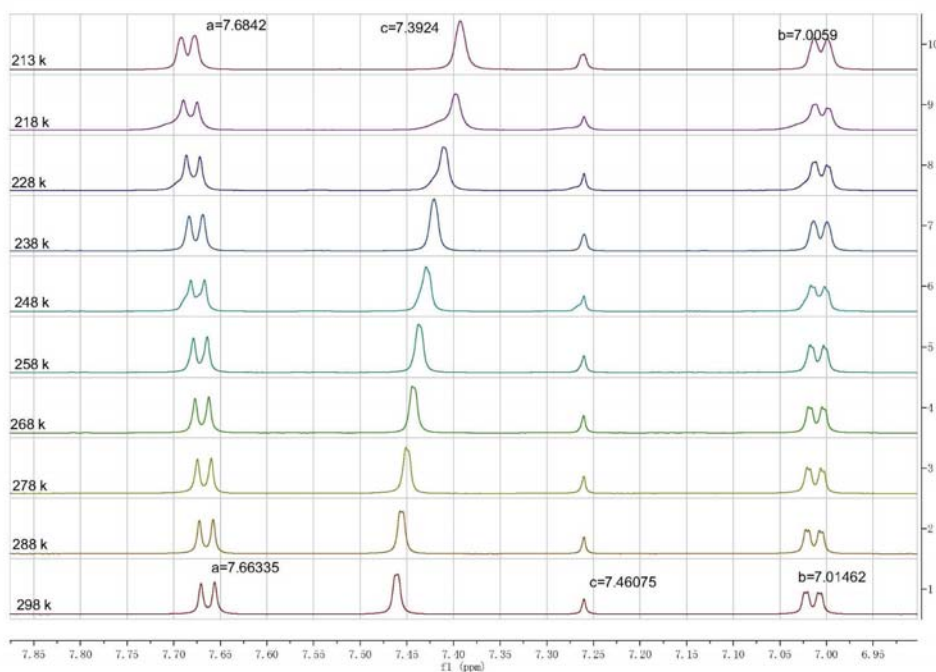


Figure S15. Partial ^1H NMR spectra (600MHz, CDCl_3 , 298 K) in variable temperature. [1] = 70mM.

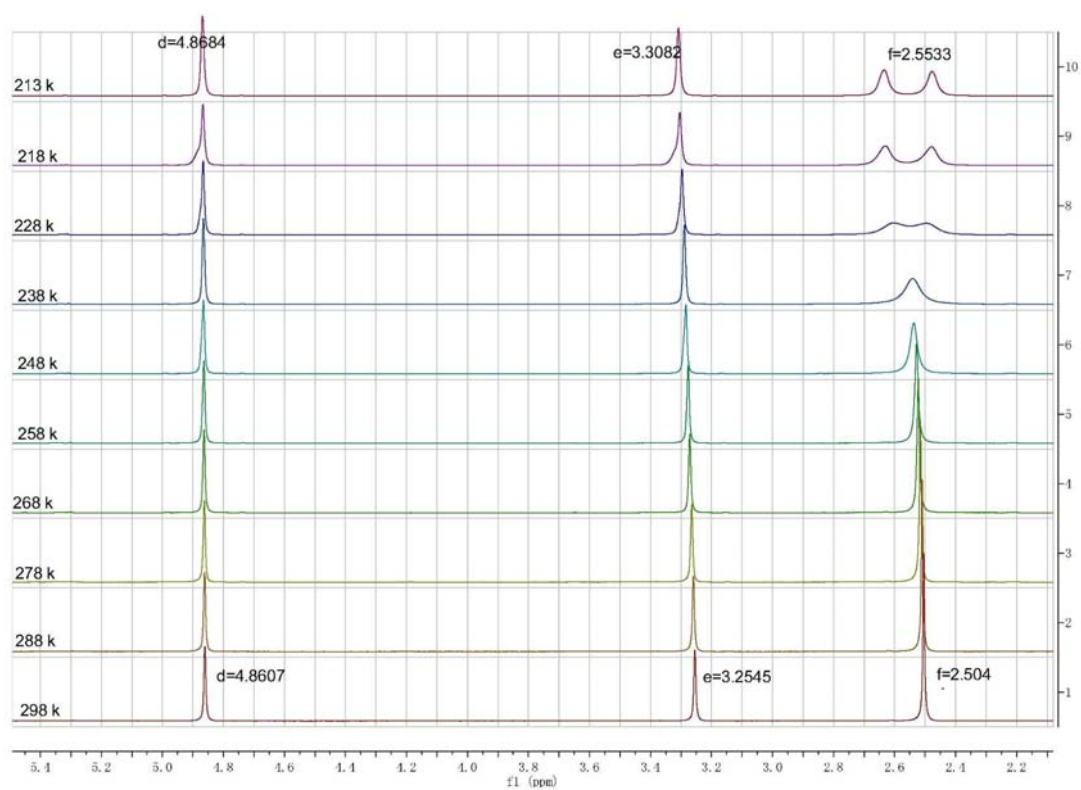


Figure S16. Partial ^1H NMR spectra (600MHz, CDCl_3 , 298 K) in variable temperature. $[\mathbf{1}] = 70\text{mM}$.

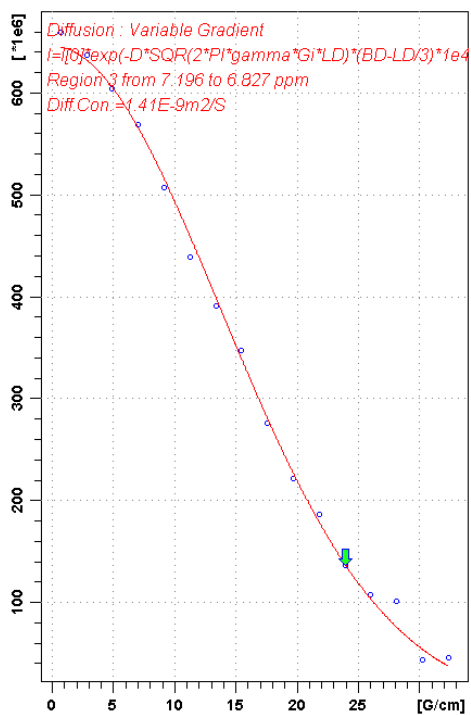


Figure S17. DOSY-2mmol-1-plot, $D = 14.1 \times 10^{-10} \text{ m}^2/\text{s}$

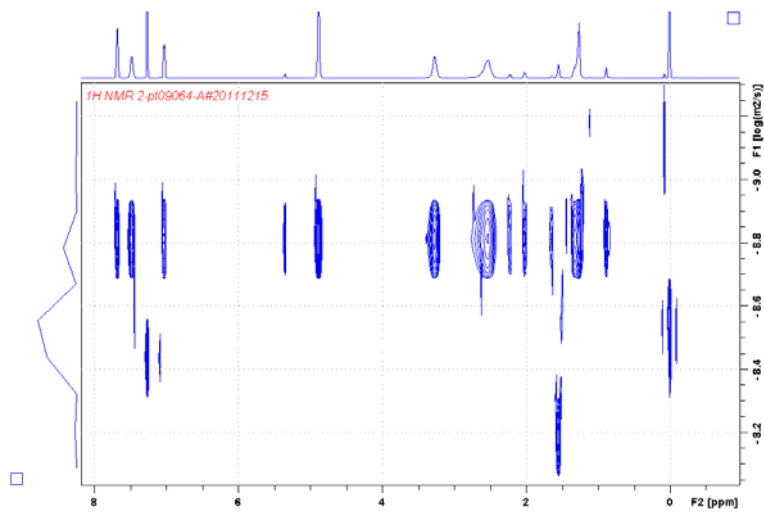


Figure S18. 2DDOSY spectrum (600MHz, CDCl₃, 298 K) of **1**. [1] = 2 mM

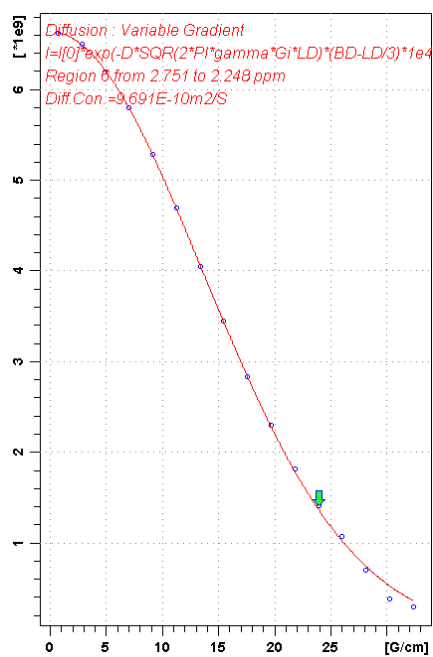


Figure S19. DOSY-70mmol-1-plot, $D=9.69 \times 10^{-10} \text{ m}^2/\text{s}$

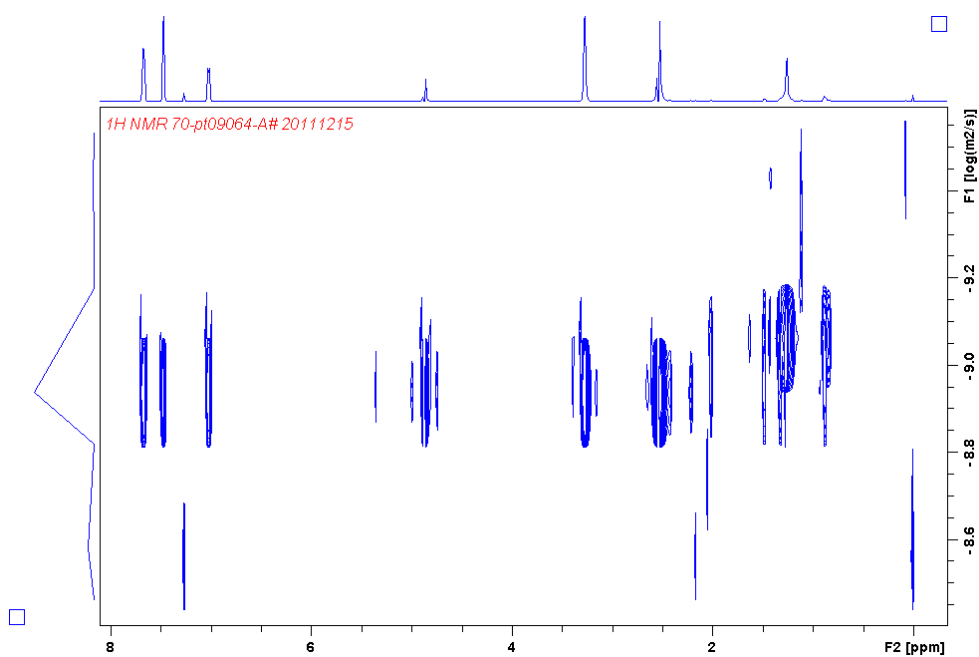


Figure S20. 2DDOSY spectrum (600MHz, CDCl₃, 298 K) of 1. [1] = 70 mM.