Electronic Supplementary Information for

Enhanced Chiral Recognition by γ-Cyclodextrin-Cucurbit[6]uril-Cowheeled [4]Pseudorotaxanes

*Ling Dai,[a] Wanhua Wu,[a] Wenting Liang,[b] Wentong Chen,[c] Xinke Yu,[a] Jiecheng Ji,[a] Cao Xiao[a] Cheng Yang[a,]**

[a] Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry and State Key Laboratory of Biotherapy, West China Medical Center, Sichuan University, 29 Wangjiang Road, Chengdu 610064, China;

[b] Institute of Environmental Sciences, Department of Chemistry, Shanxi University, Taiyuan 030006, P. R. China

[c] School of Chemistry and Chemical Engineering, Jinggangshan University, Ji'an, P. R. China

Content

Materials and instruments: γ-Cyclodextrin, 4, 4'-bis(chloromethyl)biphenyl, 1,4-butanediamine and 1, 6-diaminohexane were purchased from Tokyo Chemical Industry and were vacuum-dried before use. CB[6] was prepared according to the literature method.[1] **1a** was synthesized according to the previously reported procedure.[2] ^{1}H and ^{13}C NMR spectra were obtained with a JEOL JNM-EX 400 spectrometer or in D_2O or DMSO-d_6. FAB mass spectra were obtained on a JEOL JMS-DX303 mass spectrometer. UV-vis spectra were recorded using a JASCO V650 spectrometer. Circular dichroism spectra were measured on a JASCO J-1500 spectropolarimeter. Titration calorimetry measurements were performed with a VP-ITC calorimeter. In each microcalorimetric experiment, a constant volume of guest/host solution in 40 mM standard phosphate buffer at pH 4.2 was injected into the reaction cell (1.4 mL) charged with a host/guest solution in the same buffer (5-10 *u*L/injection; 20-30 injections in total).

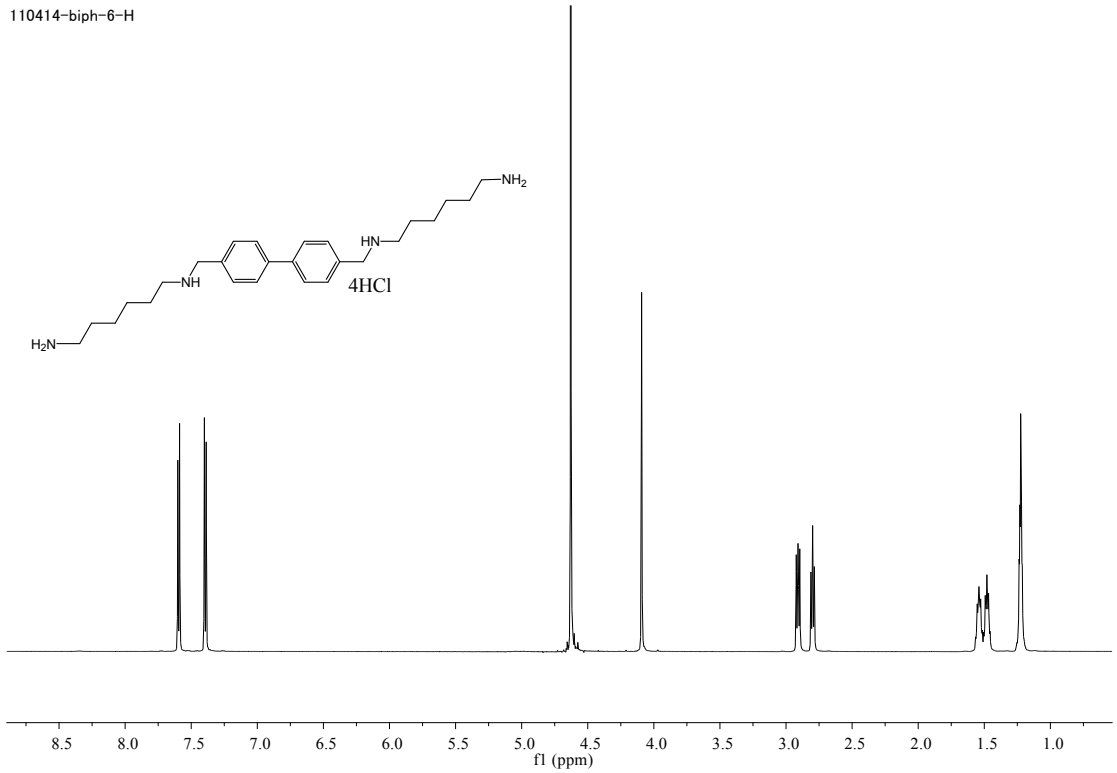
The single crystal structure of the dumbbell structure **1e**@$(CB[6])_2$ can be found at the Cambridge Crystallographic Data Centre, CCDC number: 1821323

Synthesis of axle molecules:

A bis(chloromethyl) aromatic reagent (10 mmol) and an alkyl diamine (80 mmol) were dissolved in anhydrous DMF (100 mL), and the solution was heated under nitrogen at 70 °C for 36h. After the solvent was removed under vacuum, the residue was poured into diethyl ether (300 mL). The resultant precipitate was collected and purified on an ion exchange column (Dowex-50w) to give a pale yellow solid, which is recrystallized from a mixture of acetone and 10% HCl aqueous solution to give white solid.

1b. Yield: 52.1 %, FAB-MS (free amine): 411.3 $[M+1]^+$. ^{1}H NMR (D_2O): δ 7.59 (d, 4H, J=7.2 Hz), 7.39 (d, 4H, J = 7.6 Hz), 4.09 (s, 4H), 2.91 (t, 2H, J = 4.0 Hz, 4.0 Hz), 2.80 (t, 2H, J = 4.0 Hz, 4.0 Hz), 1.56 (m, 2H), 1.48 (m, 2H), 1.22 (m, 2H). ^{13}C NMR (D_2O): δ 140.69, 130.35, 130.25, 127.56, 50.41, 46.84, 39.19, 26.35, 25.15, 24.99.

1c: Yield: 41.2 %, FAB-MS (free amine): 329.2 $[M+1]^+$. ^{1}H NMR (D_2O): δ 7.86 (m, 4H), 7.50 (d, 2H, J=4 Hz), 4.03 (s, 4H), 2.72 (m, 4H), 1.53 (m, 4H), ^{13}C NMR (D_2O): δ 176.40, 133.25, 132.66, 128.66, 128.34, 127.76, 51.33, 46.85, 24.75, 24.10, 23.98.



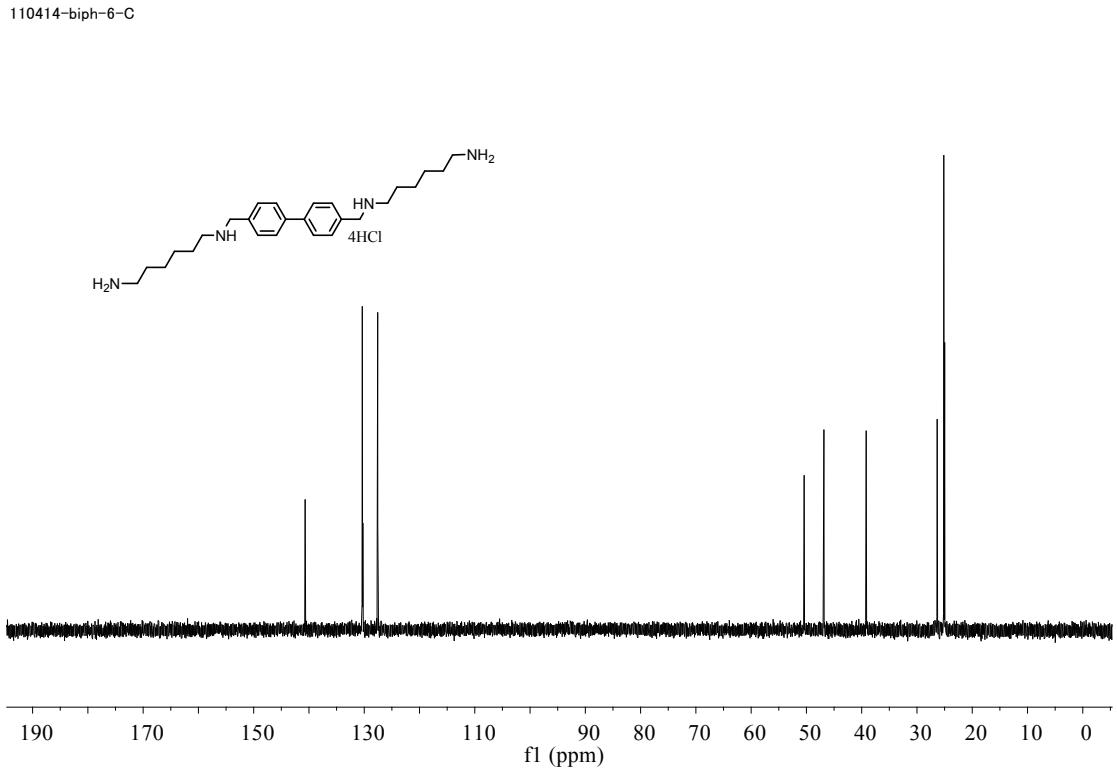


Fig. S1. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **1b** measured in D_2O at 25 °C.

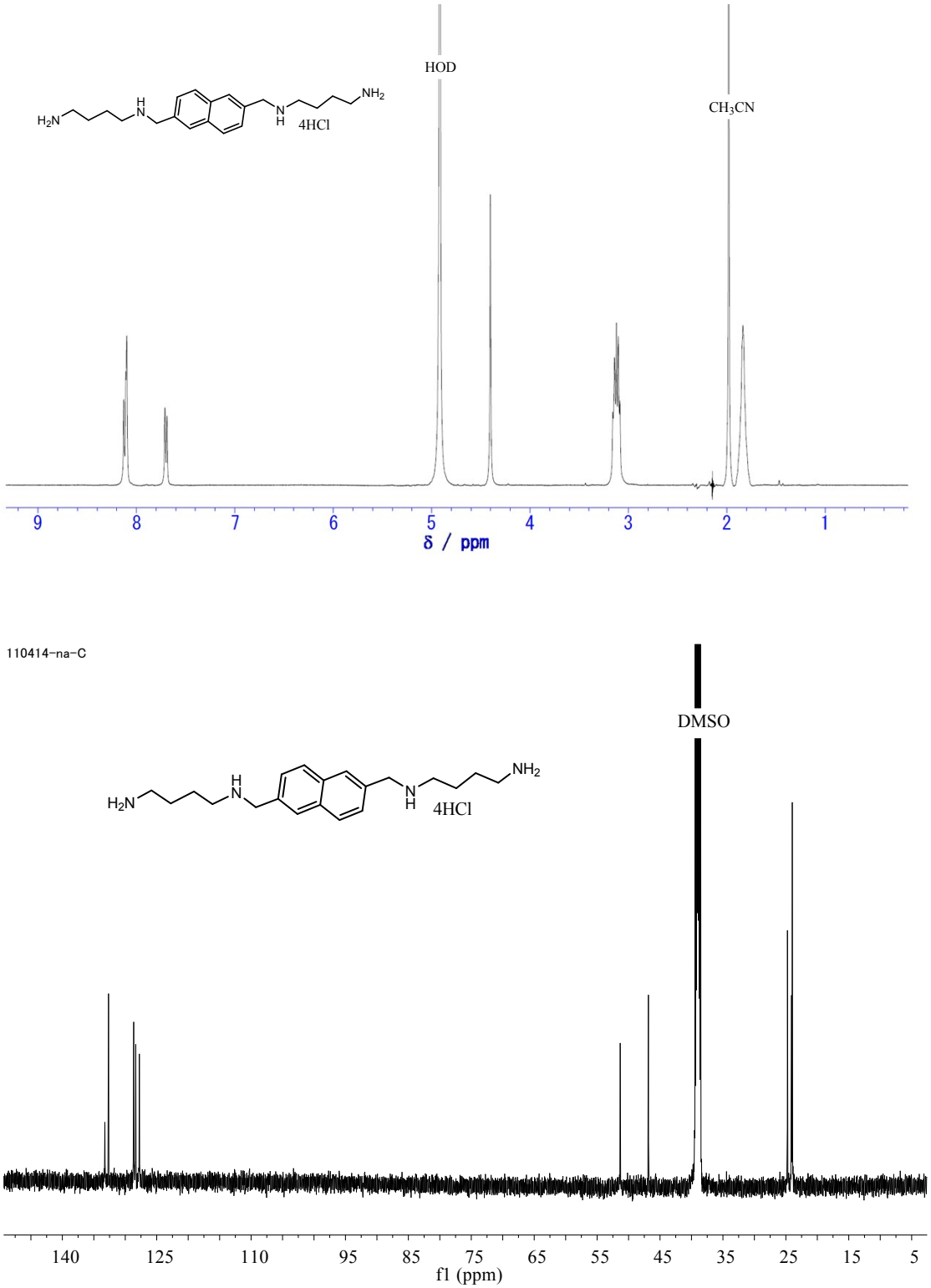


Fig. S2. ^{1}H NMR (upper) and ^{13}C NMR (lower) spectra of **1c** measured in D_2O at 25 °C.

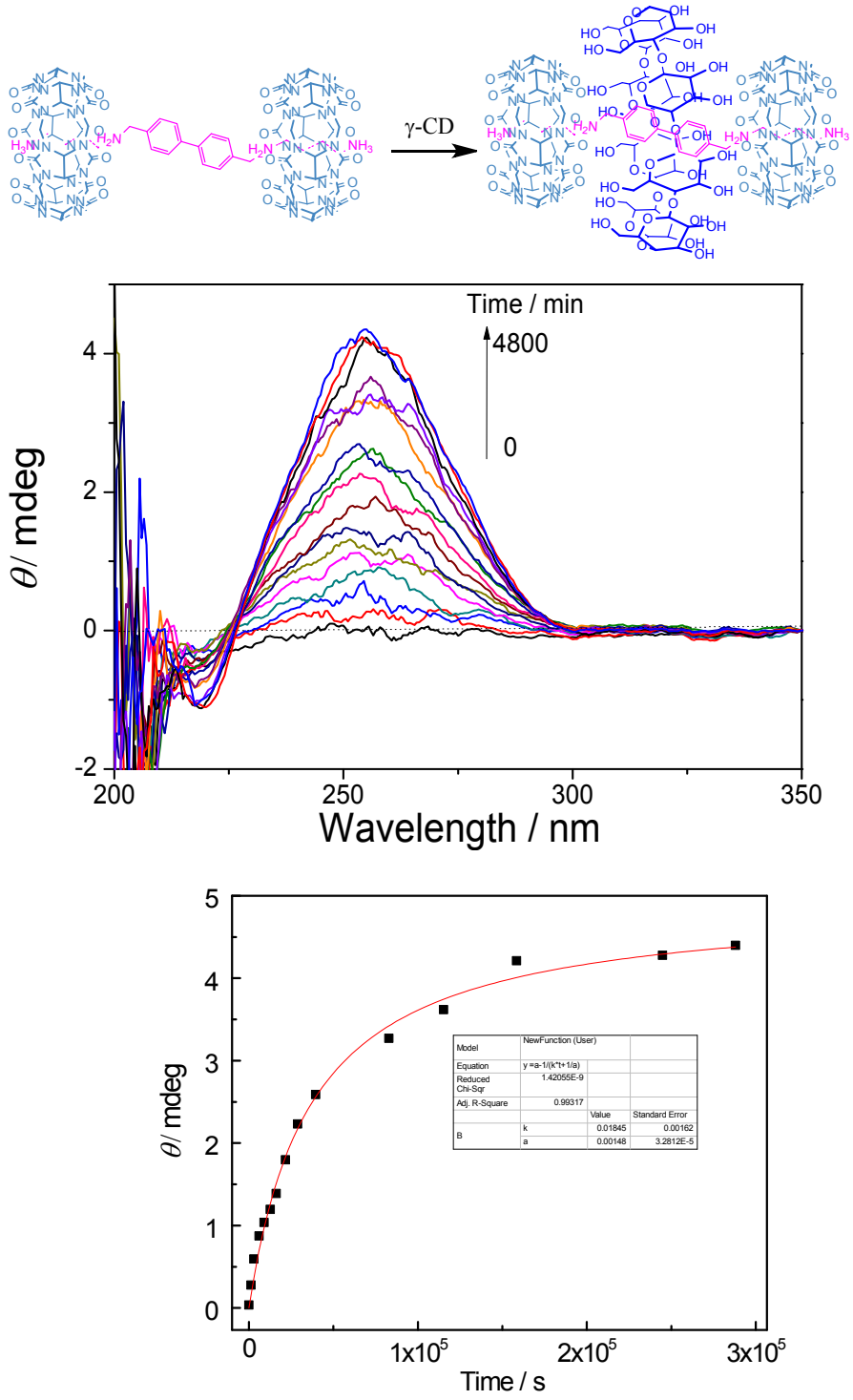


Fig. S3. The time-dependent circular dichroism spectra after adding 5 mM γ-CD into the aqueous solution containing 5 mM **Rot1b**, measured at 25 °C in a 1 mm path length cell (upper) and the curve fitting of the spectral change at λ = 253 nm assuming a second order reaction kinetic (lower). The relatively large deviation at the initial stage of kinetic process should be due to the weak circular dichroism spectral response.

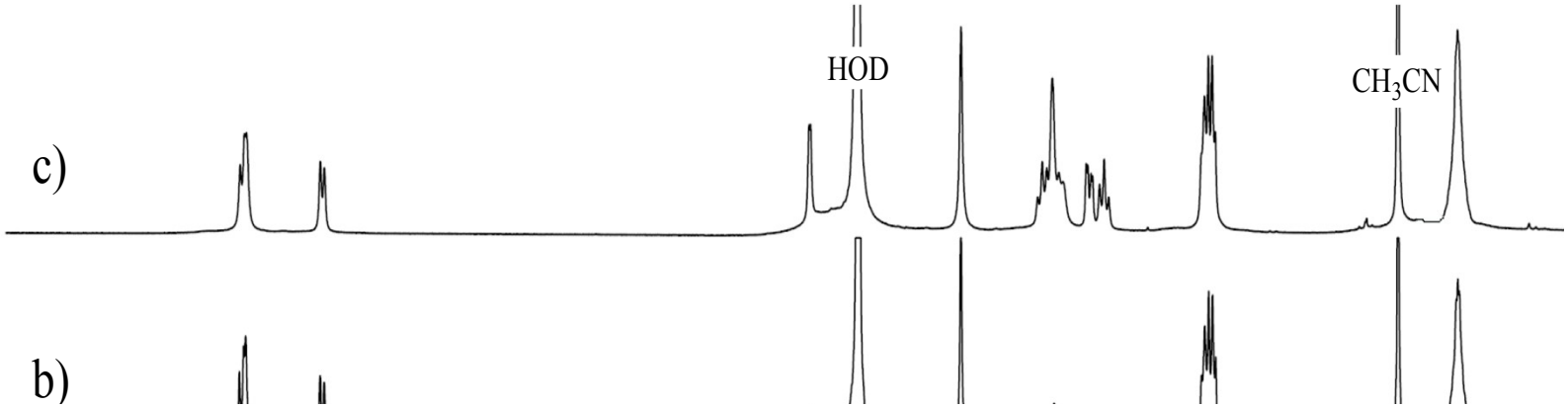


Fig. S4. ^{1}H NMR spectra of 20 mM **1c** in the absence (a) and presence of 3mM (b) and 8 mM (c) γ-CD

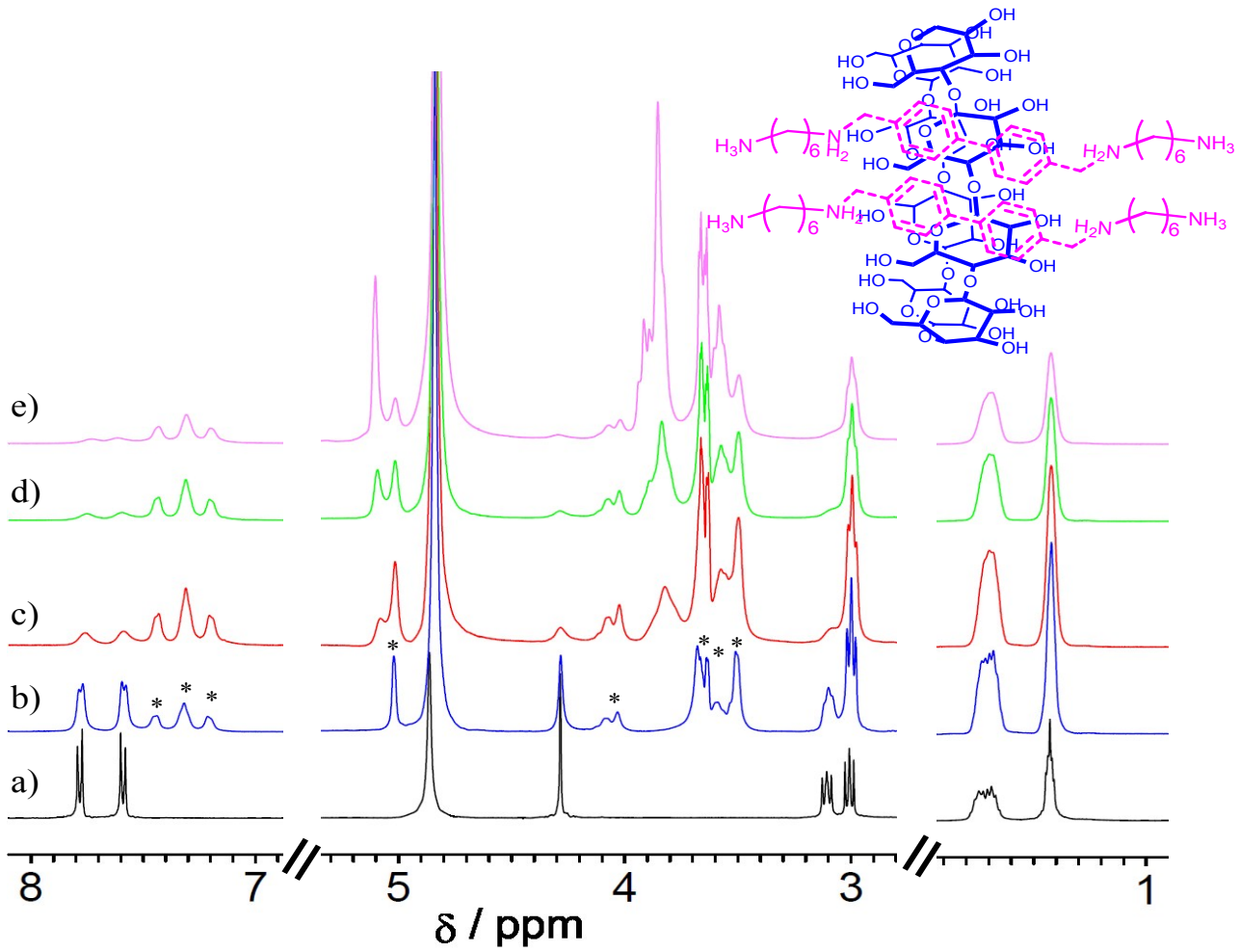


Fig. S5. ^{1}H NMR spectra of 10 mM **1b** in the absence (a) and presence of 2mM (b) 4 mM (c) 6 mM (d) and 8 mM (e) γ-CD, measured in D_2O at 25 °C.

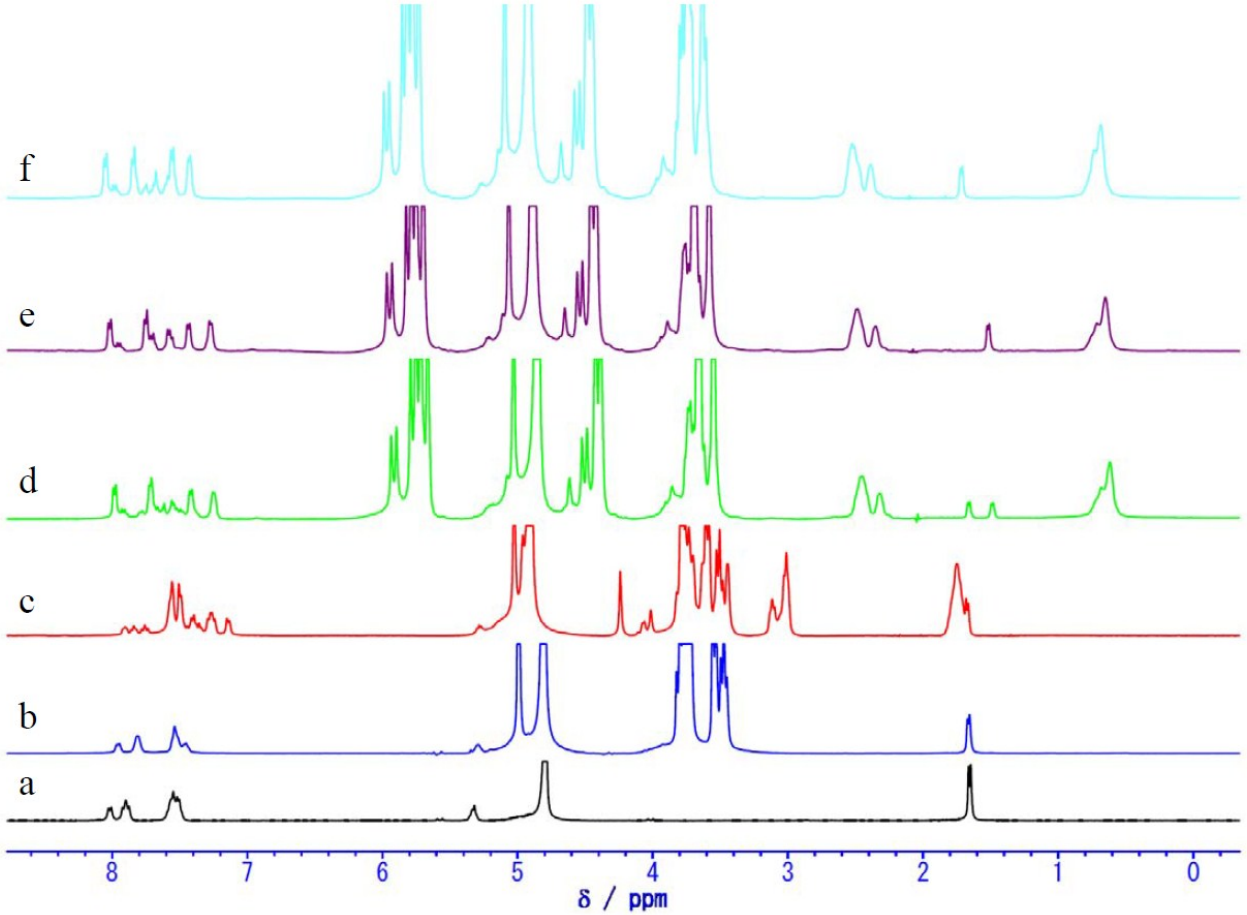


Fig. S6. ^{1}H NMR spectra of (a) 5 mM racemic **2e** (b) 5 mM racemic **2e** and 10 mM γ-CD, (c) 5 mM racemic **2e**, 10 mM **1a** and 10 mM γ-CD (d) 5 mM racemic **2e** and 10 mM **Rot1a**, (e) 5 mM (*R*)-**2e** and 10 mM **Rot1a** and (f) 5 mM (*S*)-**2e** and 10 mM **Rot1a**.

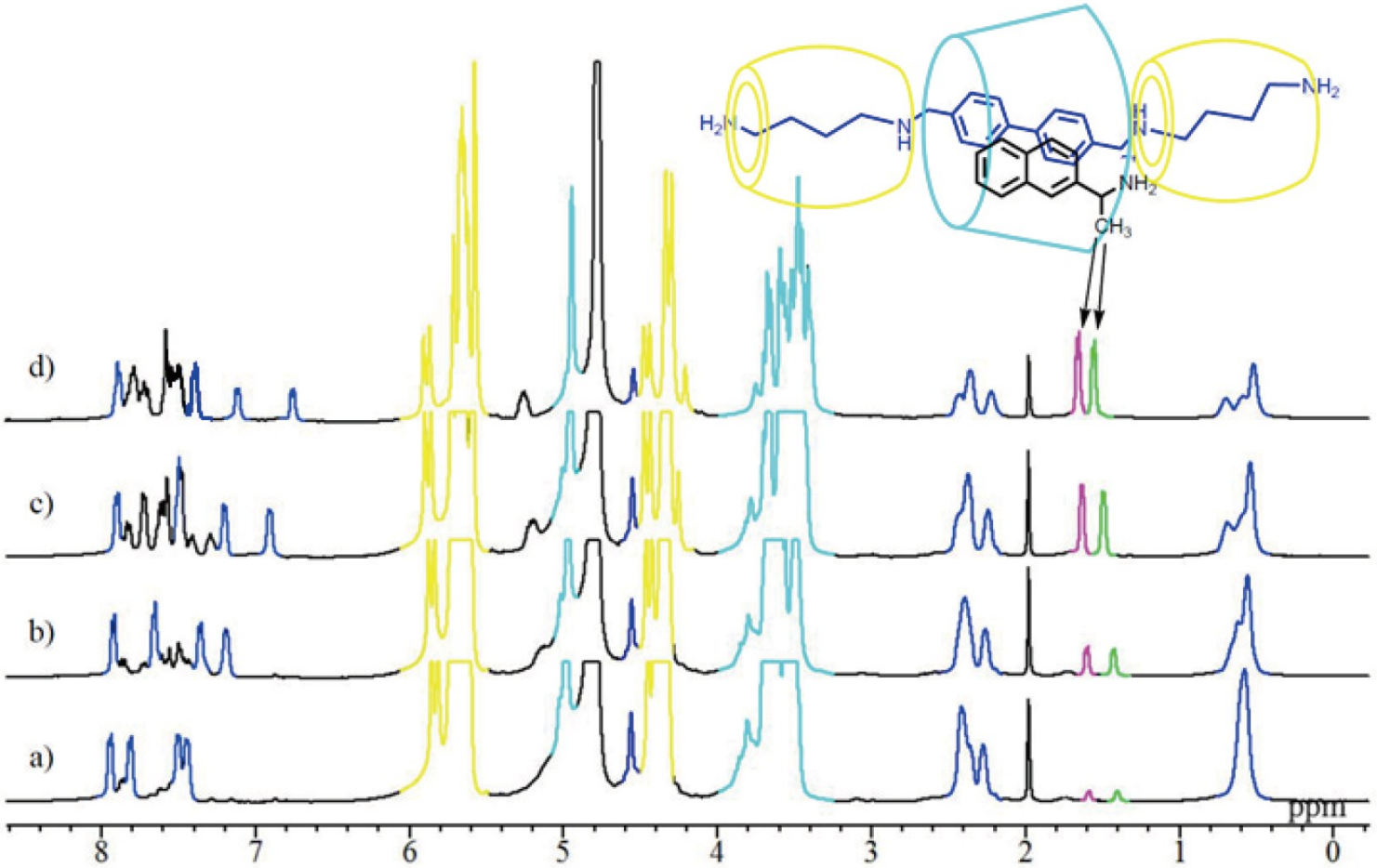


Fig. S7. ^{1}H NMR spectra of 10 mM **Rot1a** in the presence of a) 2 mM, b) 4 mM, c) 6 mM, d) 8 mM and e) 10 mM racemic **2e** in D_2O solution at 25 °C. Signals of **1a**, γ-CD and CB[6] are highlighted in blue, light blue and yellow respectively.

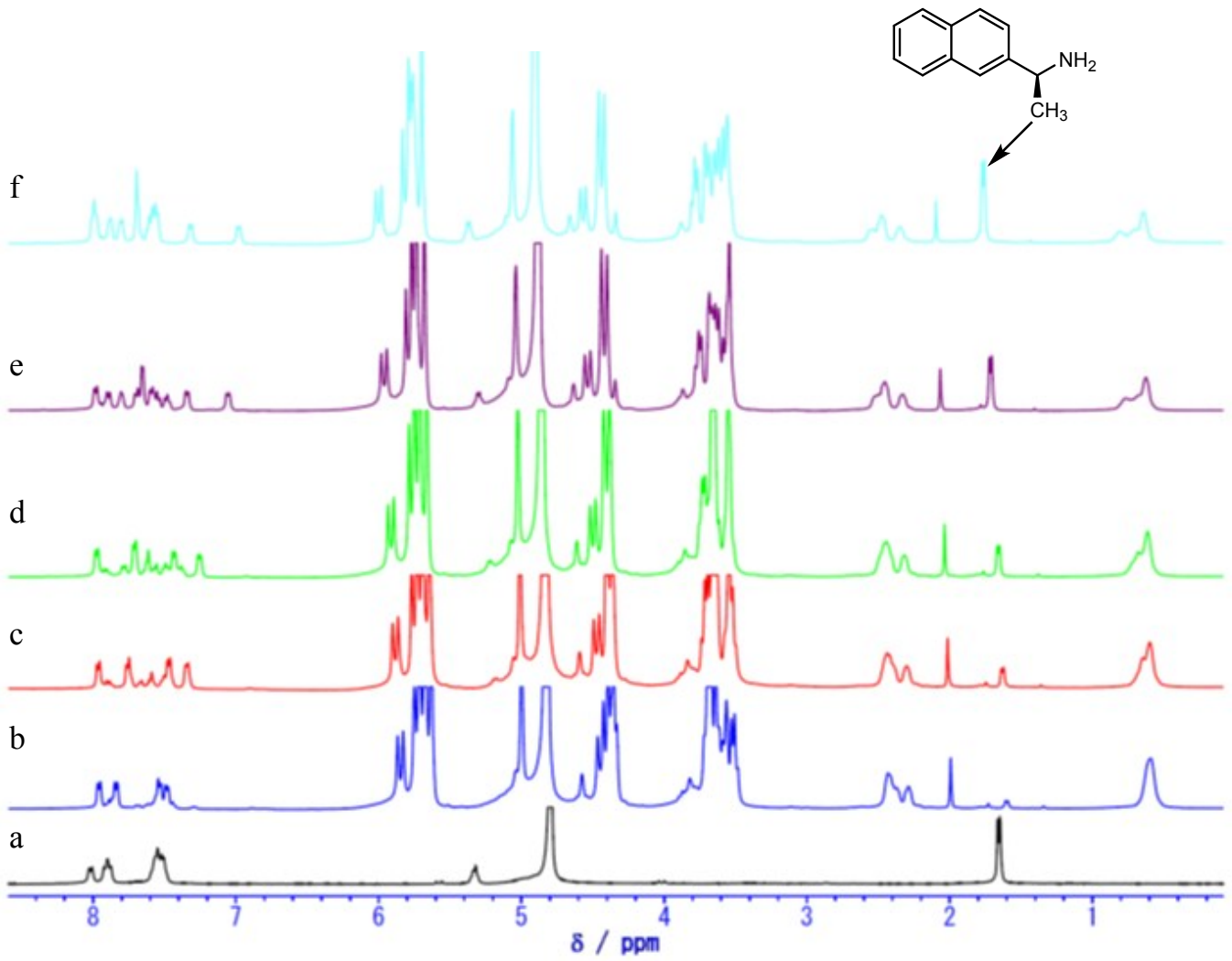


Fig. S8. ^{1}H NMR spectra of (a) 2 mM (*S*)-**2e**, and 10 mM **Rot1a** in presence of (b) 2 mM, (c) 4 mM, (d) 6 mM, (e) 8 mM and (f) 10 mM (*S*)-**2e**.

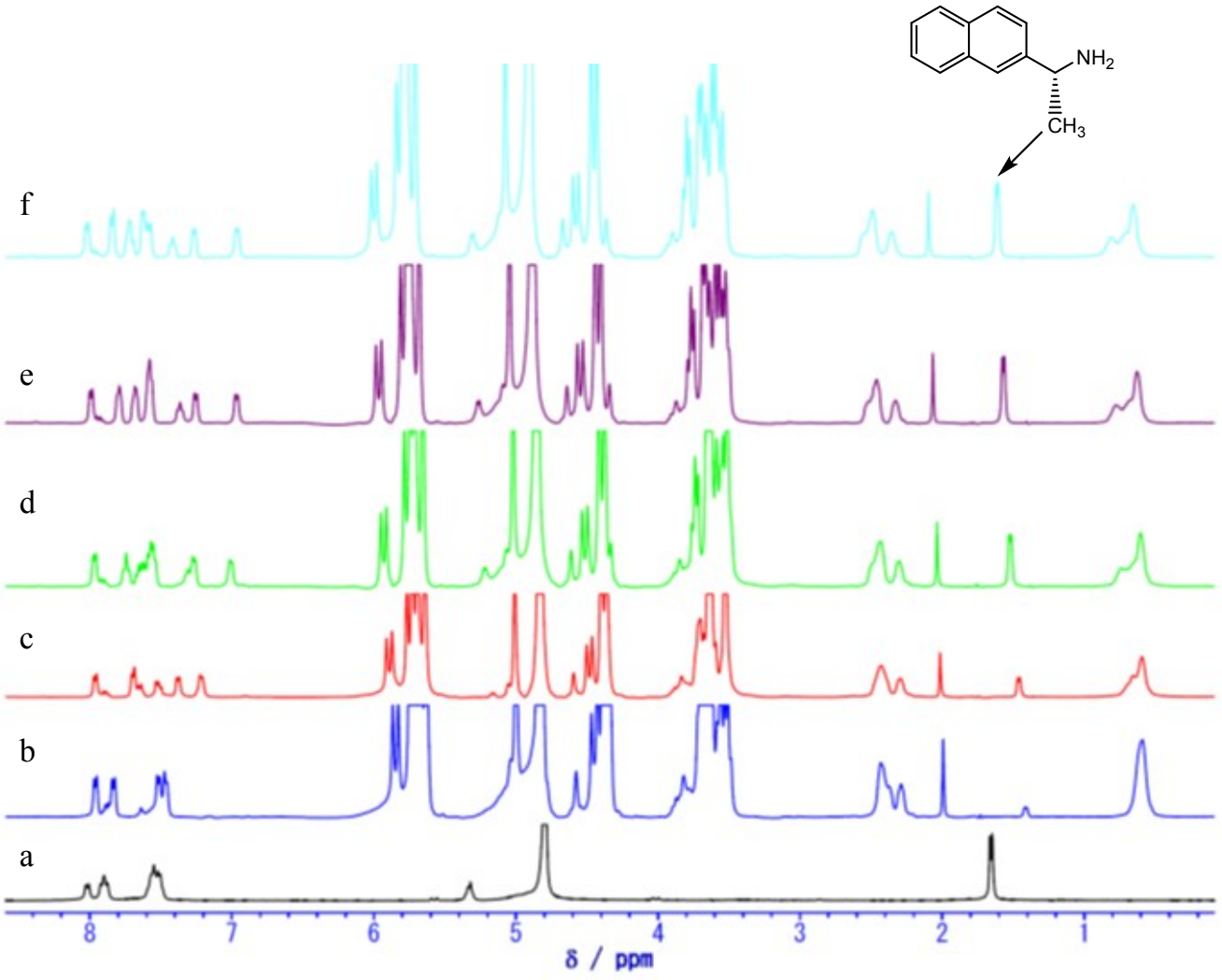


Fig. S9. ^{1}H NMR spectra of (a) 2 mM (*S*)-**2e**, and 10 mM **Rot1a** in the presence of (b) 2 mM, (c) 4 mM, (d) 6 mM, (e) 8 mM and (f) 10 mM (*R*)-**2e**.

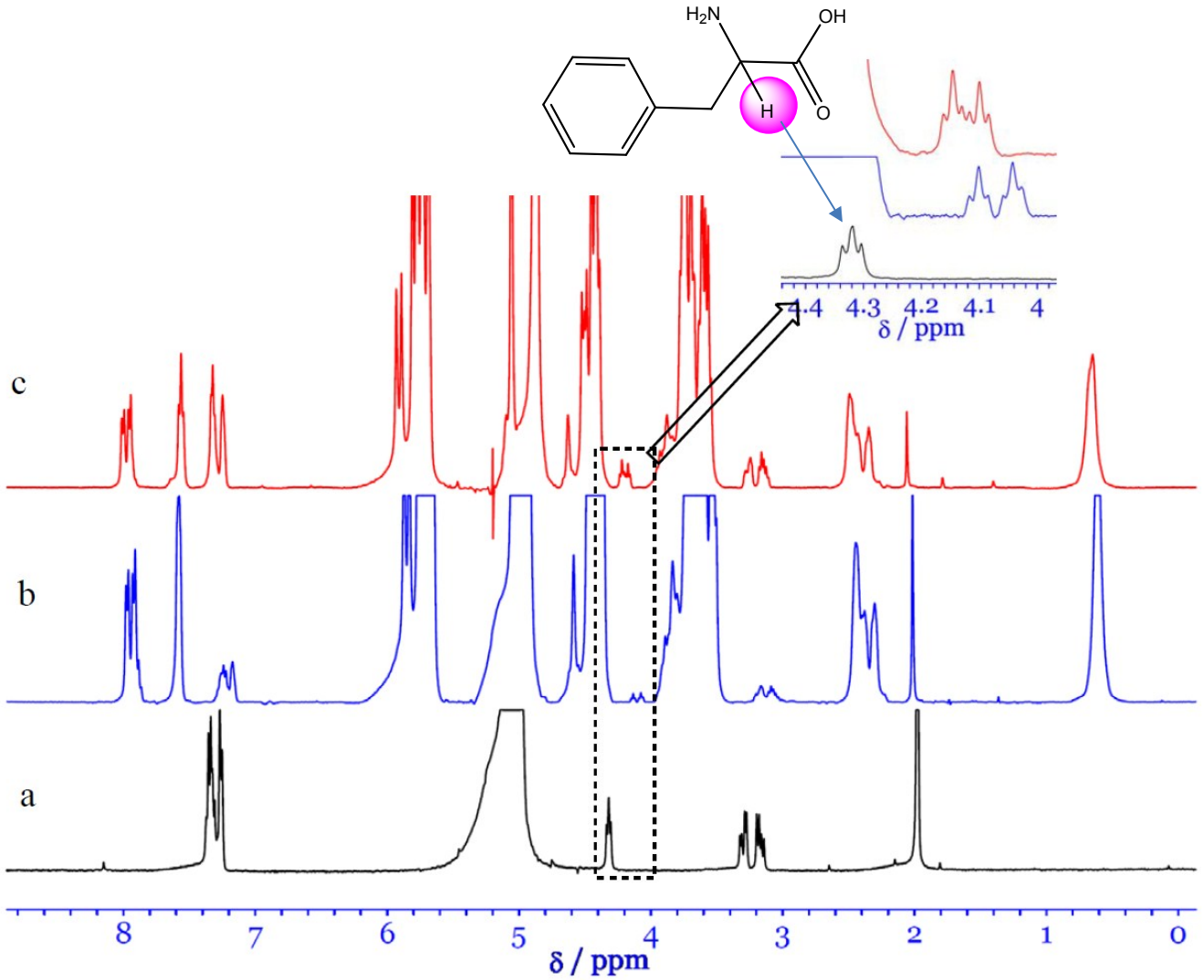


Fig. S10. ^{1}H NMR spectra of (a) 5 mM racemic **2d**, (b) 10 mM **Rot1a** and 5 mM racemic **2d** and (c) 10 mM **Rot1a** and 10 mM racemic **2d** in D_2O at 25 °C.

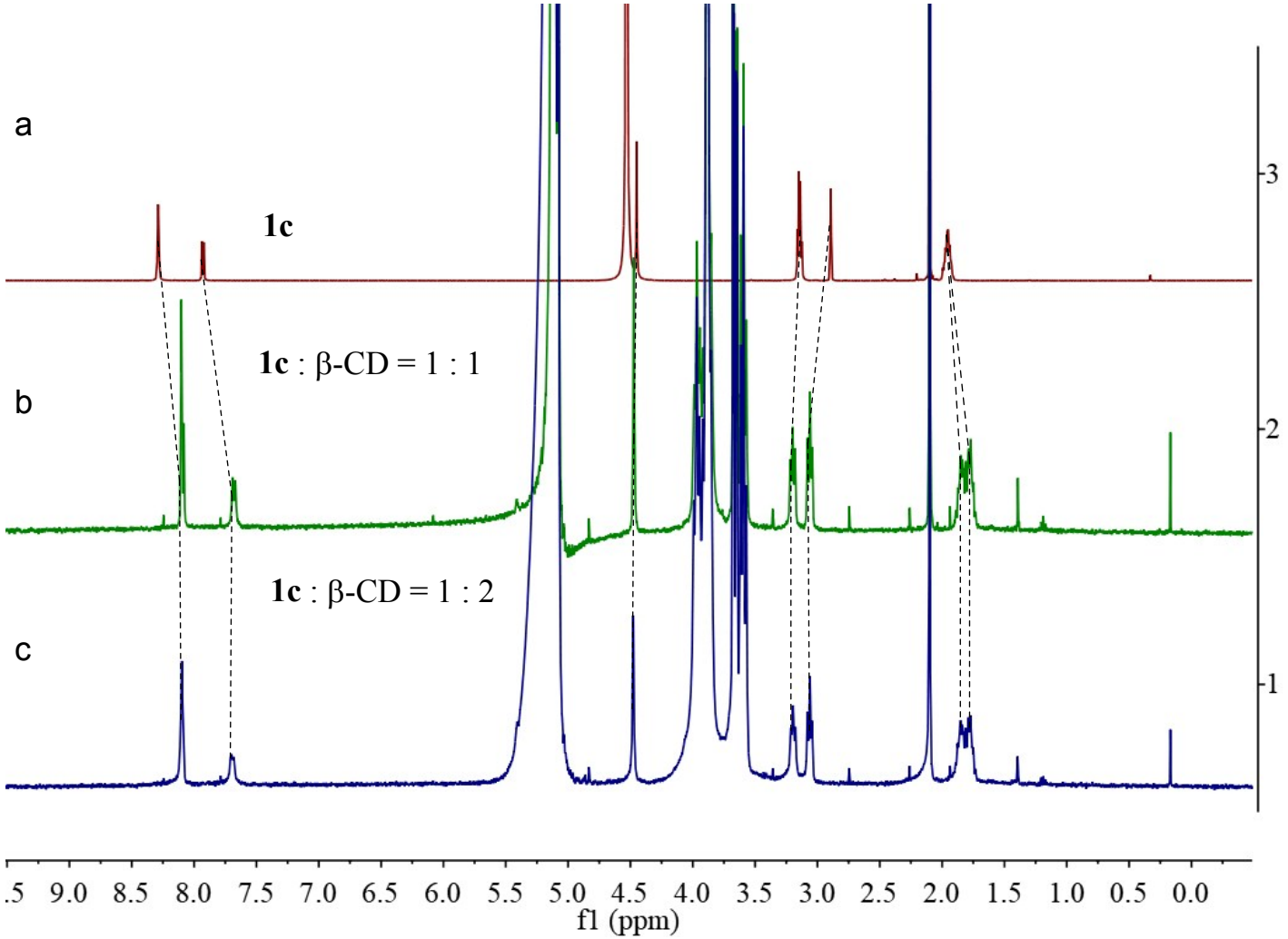


Fig. S11. ^{1}H NMR spectra of (a) 2.0 mM **1c**, (b) 2.0 mM **1c** and 2.0 mM β-CD and (c) 2.0 mM **1c** and 4.0 mM β-CD in D_2O at 25 °C.

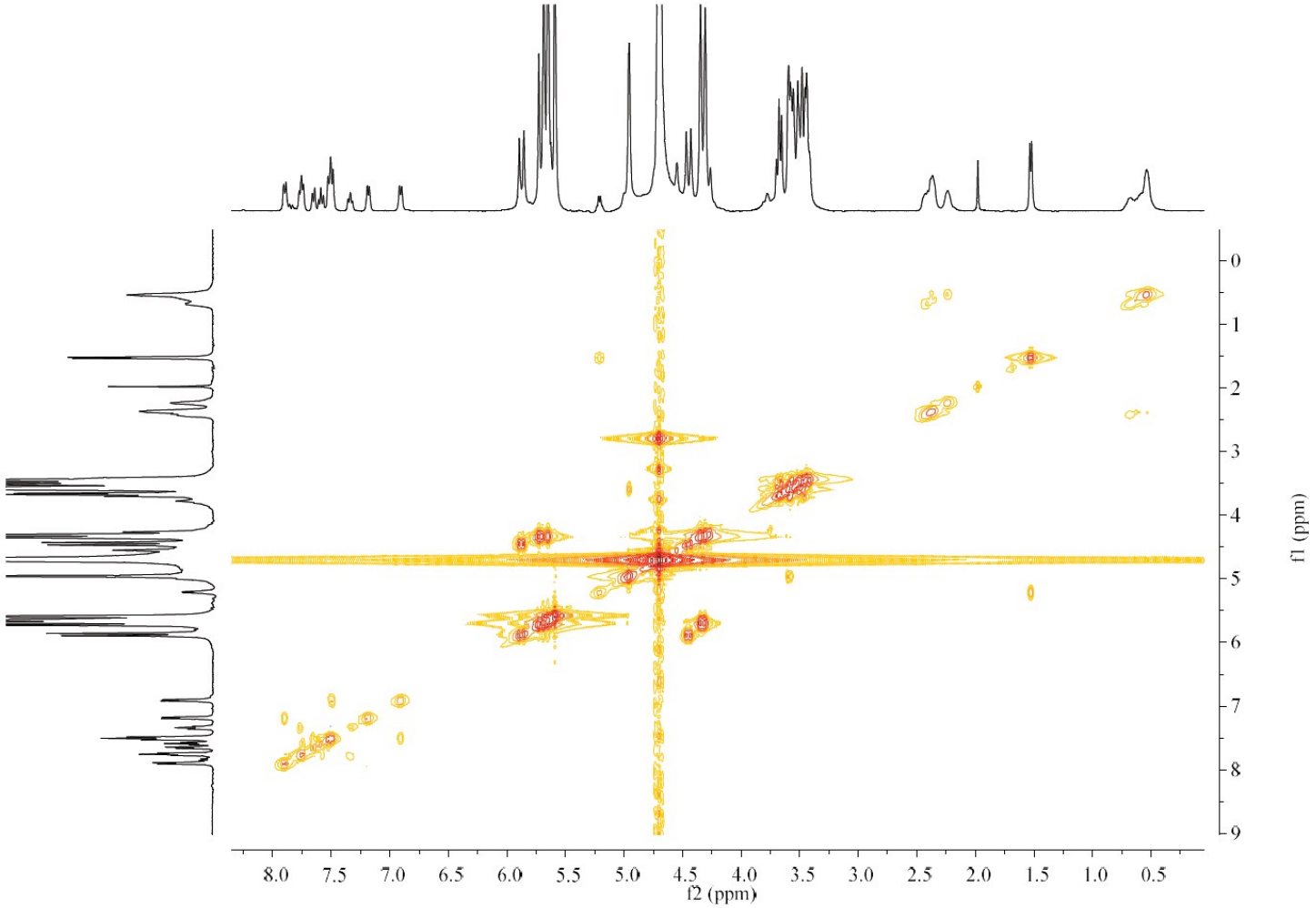


Fig. S12. ^{1}H-^{1}H COSY spectrum of 10 mM **Rot1a** in the absence of 10 mM (*R*)-**2e** measured in D_2O at 25 °C.

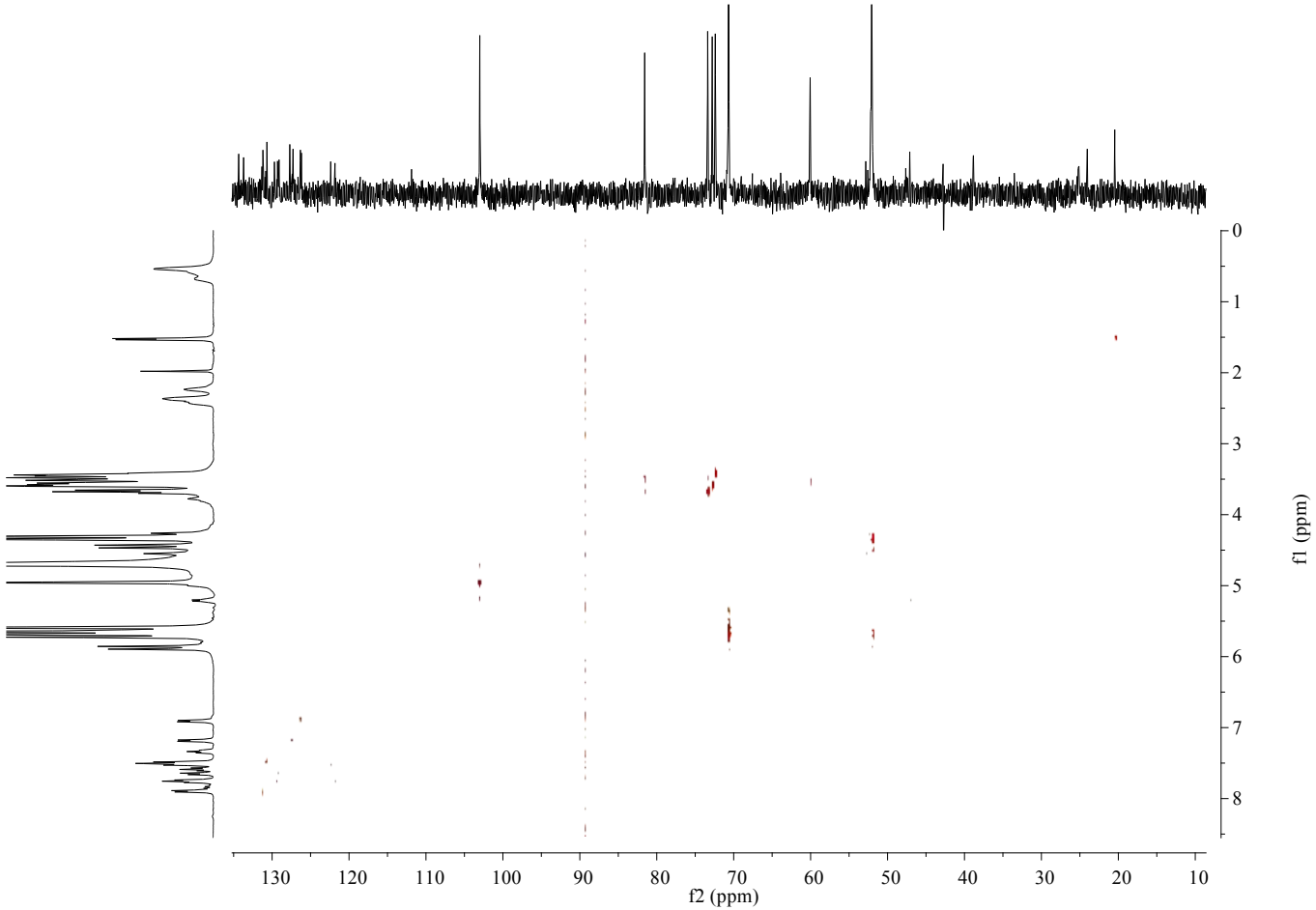


Fig. S13. ^{1}H-^{13}C HMQC spectrum of 10 mM **Rot1a** in the absence of 10 mM (*R*)-**2e** measured in D_2O at 25 °C.

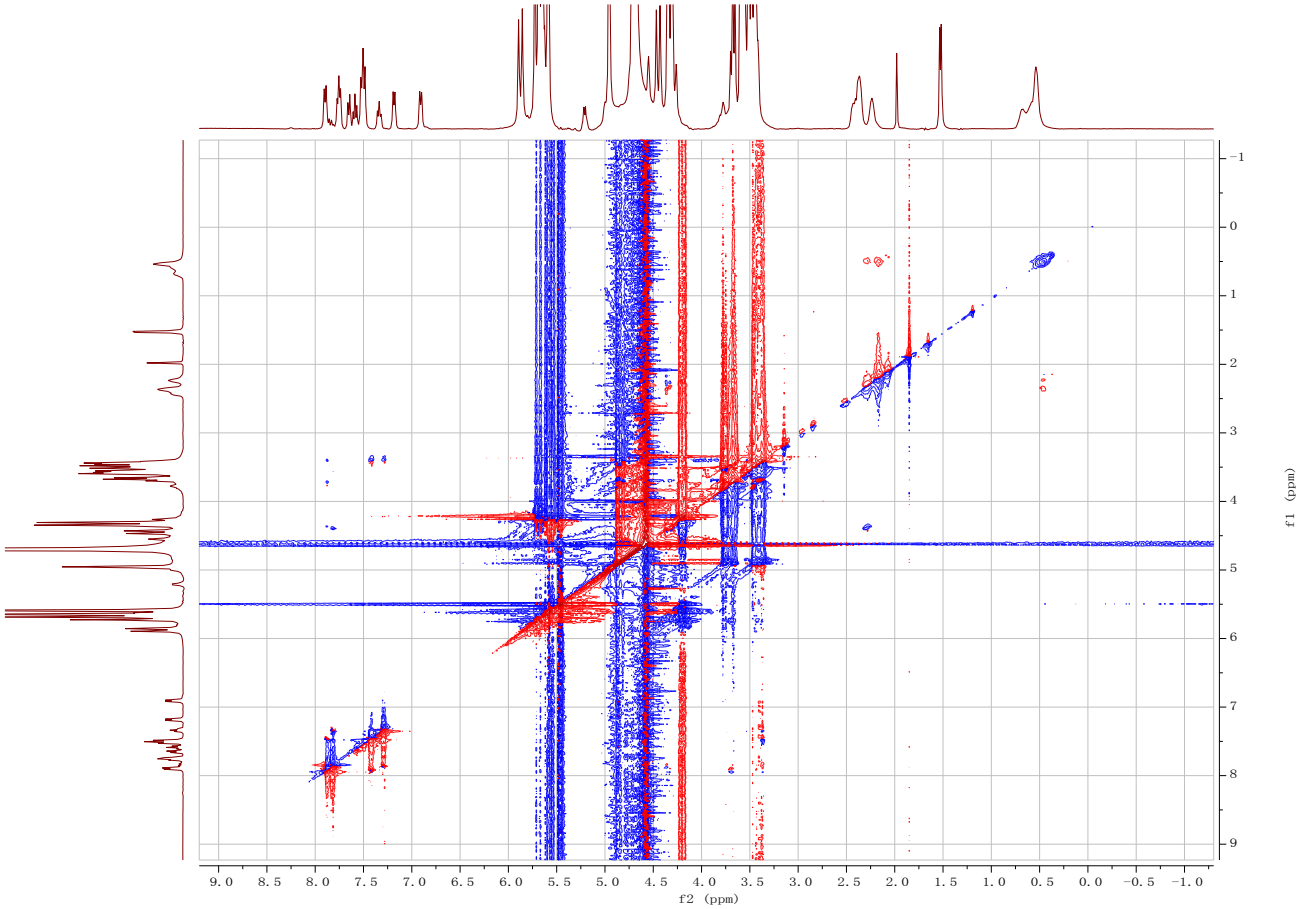


Fig. S14. ROESY spectrum of 10 mM **Rot1a** in the absence of 10 mM (*R*)-**2e** measured in D_2O at 25 °C.

Reference

1. Jon, S. Y.; Selvapalam, N.; Oh, D. H.; Kang, J.-K.; Kim, S.-Y.; Jeon, Y. J.; Lee, J. W.; Kim, K. *J. Am. Chem. Soc.,* **2003**, *125*, 10186.
2. Yang, C.; Ko, Y. H.; Selvapalam, N.; Origane, Y.; Mori, T.; Wada, T.; Kim, K.; Inoue, Y. *Org. Lett.* **2007**, *9*, 4789.