

Cucurbit[10]uril – Supporting Information

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Experimental Section.

General. The guests used in this study were purchased from commercial suppliers and were used without further purification. Compound **1** and CB[10]•CB[5] were prepared by the literature procedures.¹ Melting points were measured on a Meltemp apparatus in open capillary tubes and are uncorrected. IR spectra were recorded on a commercial spectrophotometers as KBr pellets and are reported in cm^{-1} . NMR spectra were measured on spectrometers operating at 400 or 500 MHz for ^1H and 100 or 125 MHz for ^{13}C . Mass spectrometry was performed using a VG 7070E magnetic sector instrument by fast atom bombardment (FAB) using the indicated matrix or on a JEOL AccuTOF electrospray instrument. Computational results were obtained using Spartan 02 running on a Macintosh personal computer.

Preparation, Purification and Characterization of CB[10]. A mixture of CB[10]•CB[5] (2.10 g, 0.78 mmol) and **1** (2.20 g, 3.89 mmol) in water (500 mL) was heated at 90 °C for 30 min. The solution was allowed to cool and the solid (935 mg, contains CB[5]•**1**, CB[10]•CB[5], and CB[10]•**1**.) removed by filtration. The solution was concentrated to 120 mL and allowed to stand in the refrigerator for 2 h and filtered to give CB[5]•**1** (40 mg). The solution was then concentrated to dryness. The resulting solid was repeatedly washed with MeOH (150 mL portions) which gave CB[10]•**1** as a white solid (1.18 g, 0.53 mmol, 68%). A suspension of CB[10]•**1** (1.12 g, 0.50 mmol) in acetic anhydride (30 mL) was heated at 100 °C for 16 h. The precipitate was removed by centrifugation and washed repeatedly with small portions of MeOH (20 mL portions), DMSO (20 mL portions), and H₂O (20 mL portions). Drying at high vacuum gave CB[10] (610 mg, 0.367 mmol, 73%).

CB[10]. White solid. M.p. > 300 °C. IR (KBr, cm^{-1}): 3445s, 2998w, 2924w, 2850w, 1724s, 1636m, 1468m, 1374m, 1313m, 1226s, 1189m, 1160w, 974m, 810s. ^1H NMR (400 MHz, 20% DCl / D₂O): 5.50 (d, $J = 15.1$, 20H), 5.44 (s, 20H), 4.10 (d, $J = 15.1$, 20H). ^{13}C NMR (125 MHz, 20% DCl / D₂O): 159.2, 74.6, 56.9. MS (ES): m/z 831 (100, $[\text{M} + 2\text{H}]^{2+}$, m/z spacing = 0.5 confirmed for molecular ion). HR-MS (ES): m/z 831.2504 ($[\text{M} + 2\text{H}]^{2+}$, $(\text{C}_{60}\text{H}_{62}\text{N}_{40}\text{O}_{20})/2$, calcd 831.2532).

References:

(1) (a) Liu, S.-M.; Ruspic, C.; Mukhopadhyay, P.; Chakrabarti, S.; Zavalij, P.; Isaacs, L. *J. Am. Chem. Soc.* **2005**, *127*, ASAP. (b) Day, A. I.; Arnold, A. P.; Blanch, R. J.; Snushall, B. *J. Org. Chem.* **2001**, *66*, 8094-8100. (c) Day, A. I.; Blanch, R. J.; Arnold, A. P.; Lorenzo, S.; Lewis, G. R.; Dance, I. *Angew. Chem. Int. Ed.* **2002**, *41*, 275-277.

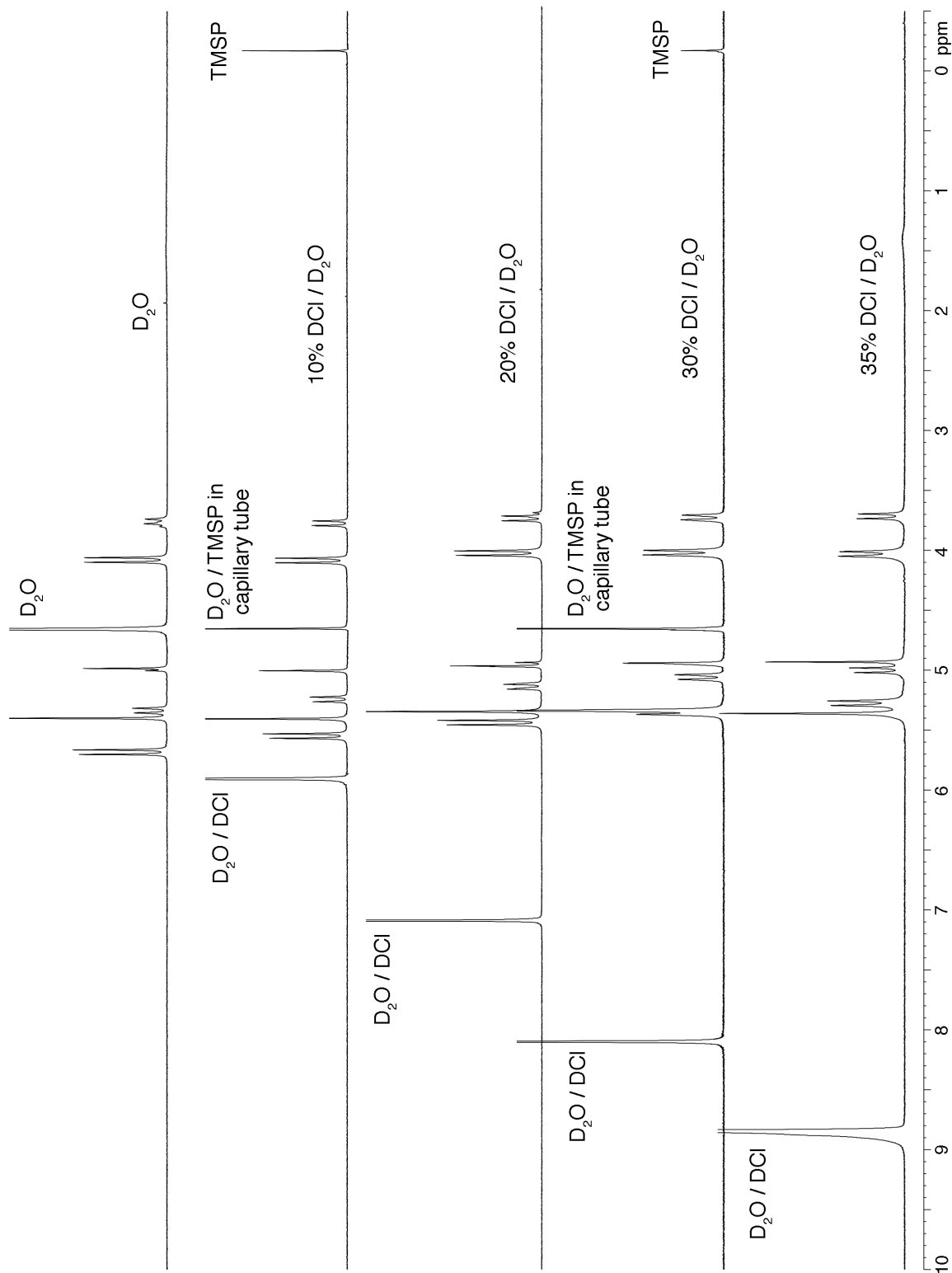


Figure S1. ^1H NMR spectrum recorded CB[10]•CB[5] (400 MHz, RT) in DCI / D_2O (0 – 35%). We attribute the small additional set of peaks to the ability of CB[5] to bind chloride ion as demonstrated by Day and co-workers. TMSP = $\text{Me}_3\text{SiCD}_2\text{CD}_2\text{CO}_2\text{H}$.

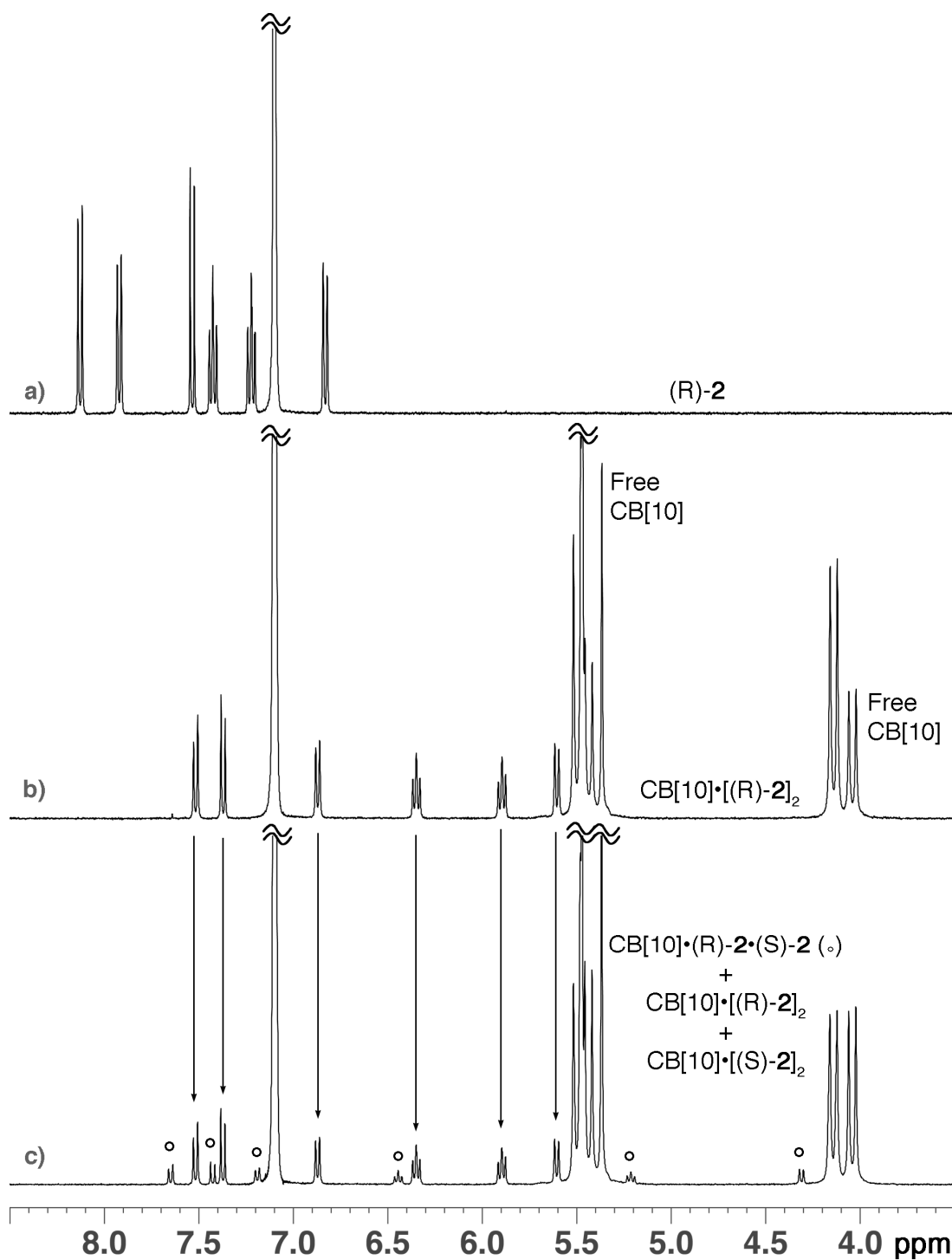


Figure S2. ¹H NMR spectra recorded (400 MHz, 20 % DCl / D₂O, RT) for: a) (*R*)-**2** alone, b) a mixture of free CB[10] and CB[10]•[(*R*)-**2**]₂ prepared from CB[10] and (*R*)-**2**, and c) a mixture of the racemate (CB[10]•[(*R*)-**2**]₂ and CB[10]•[(*S*)-**2**]₂) and the *meso*-complex CB[10]•(*R*)-**2**•(*S*)-**2** (resonances indicated with “o”) prepared from CB[10] and (±)-**2**. Integration indicates the racemate to *meso*-complex ratio is 3:1.

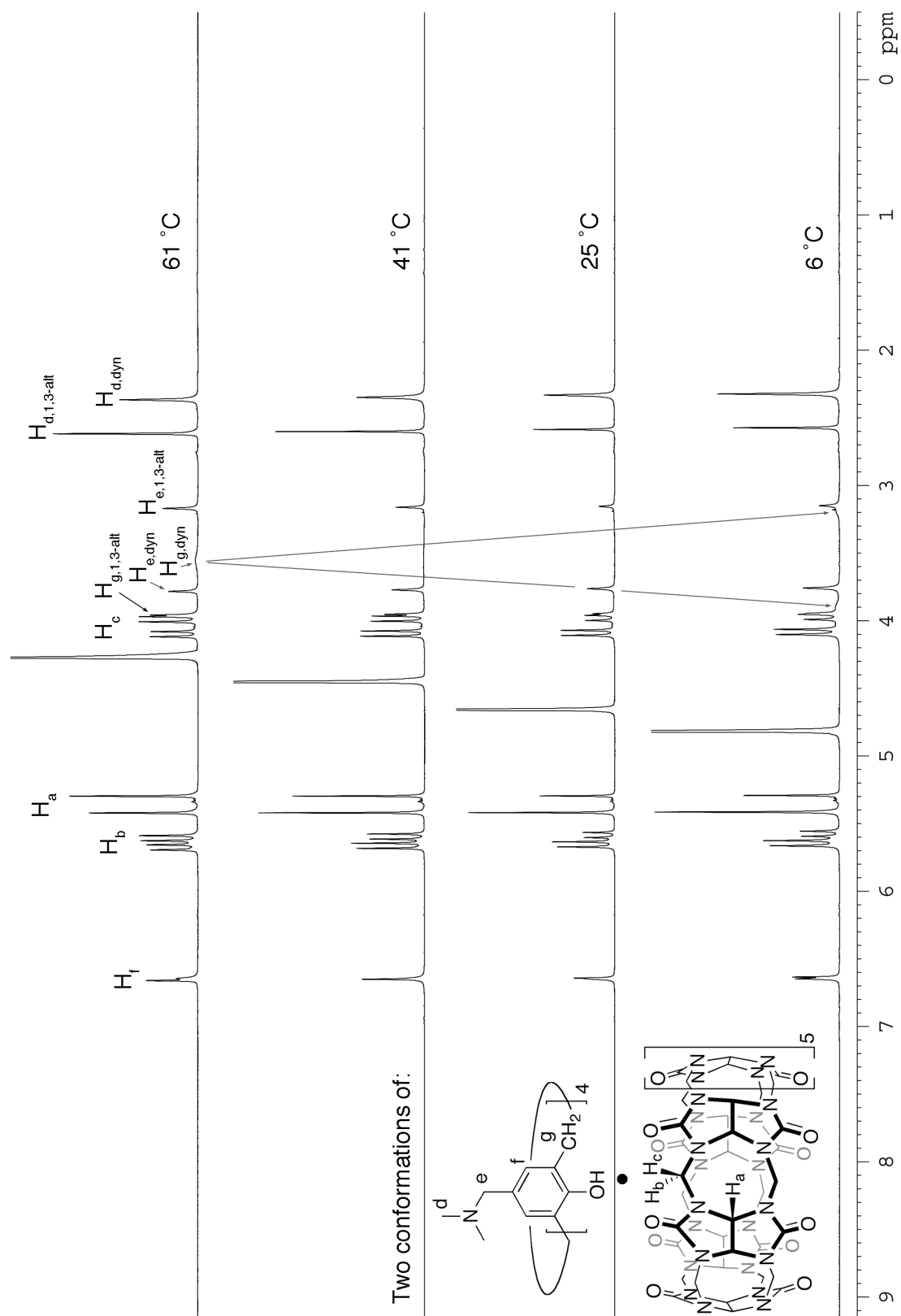
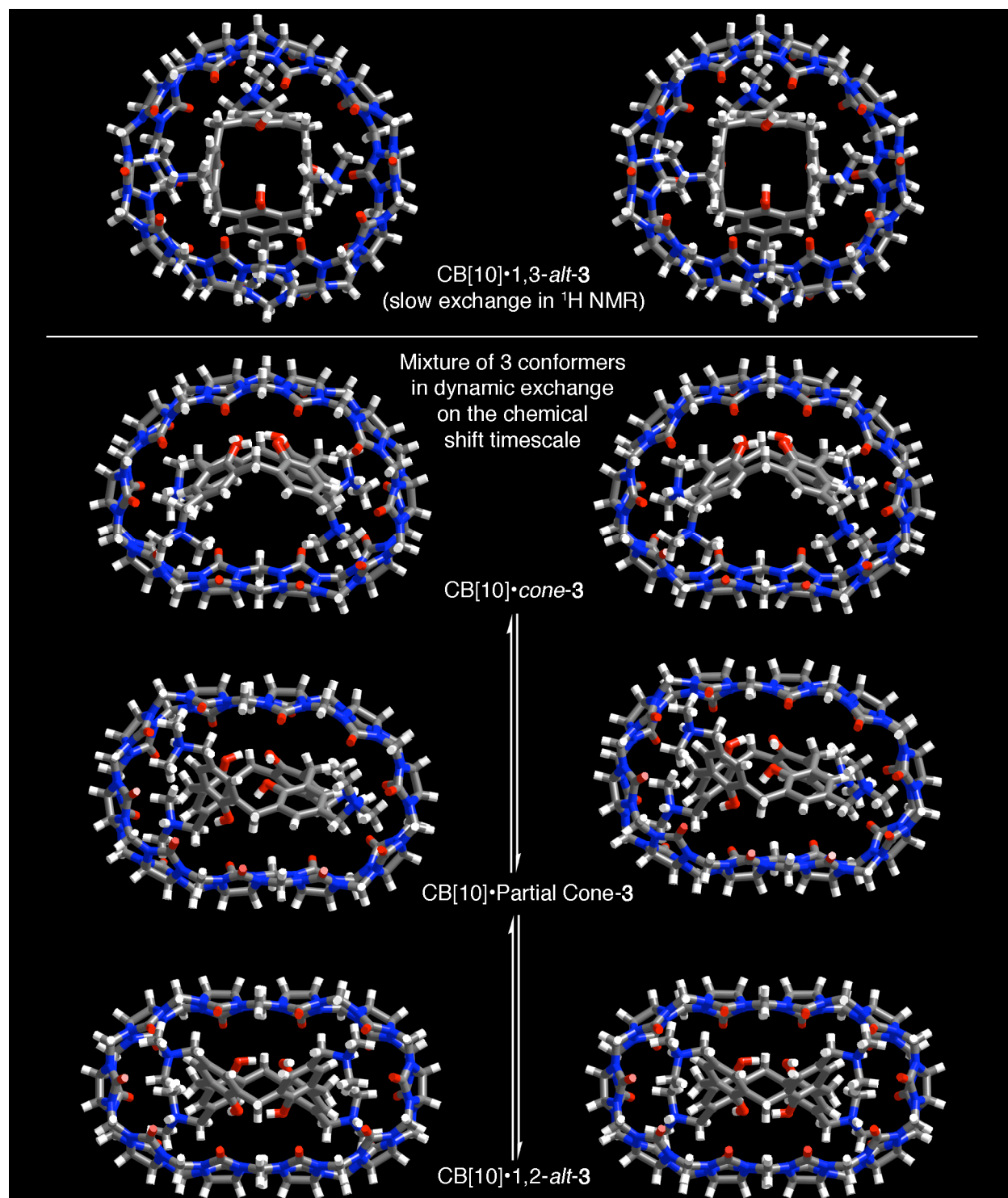


Figure S3. Variable temperature ¹H NMR spectra recorded CB[10]•3 (400 MHz, D₂O / DCl). The subscript “dyn” refers to the dynamic mixture of cone, 1,2-alternate, and partial cone conformations.



Scheme S1. Cross-eyed stereoviews of the MMFF minimized structures of CB[10]•1,3-*alt*-3, CB[10]•*cone*-3, CB[10]•1,2-*alt*-3, and CB[10]•*partial cone*-3 rendered with CrystalMaker.

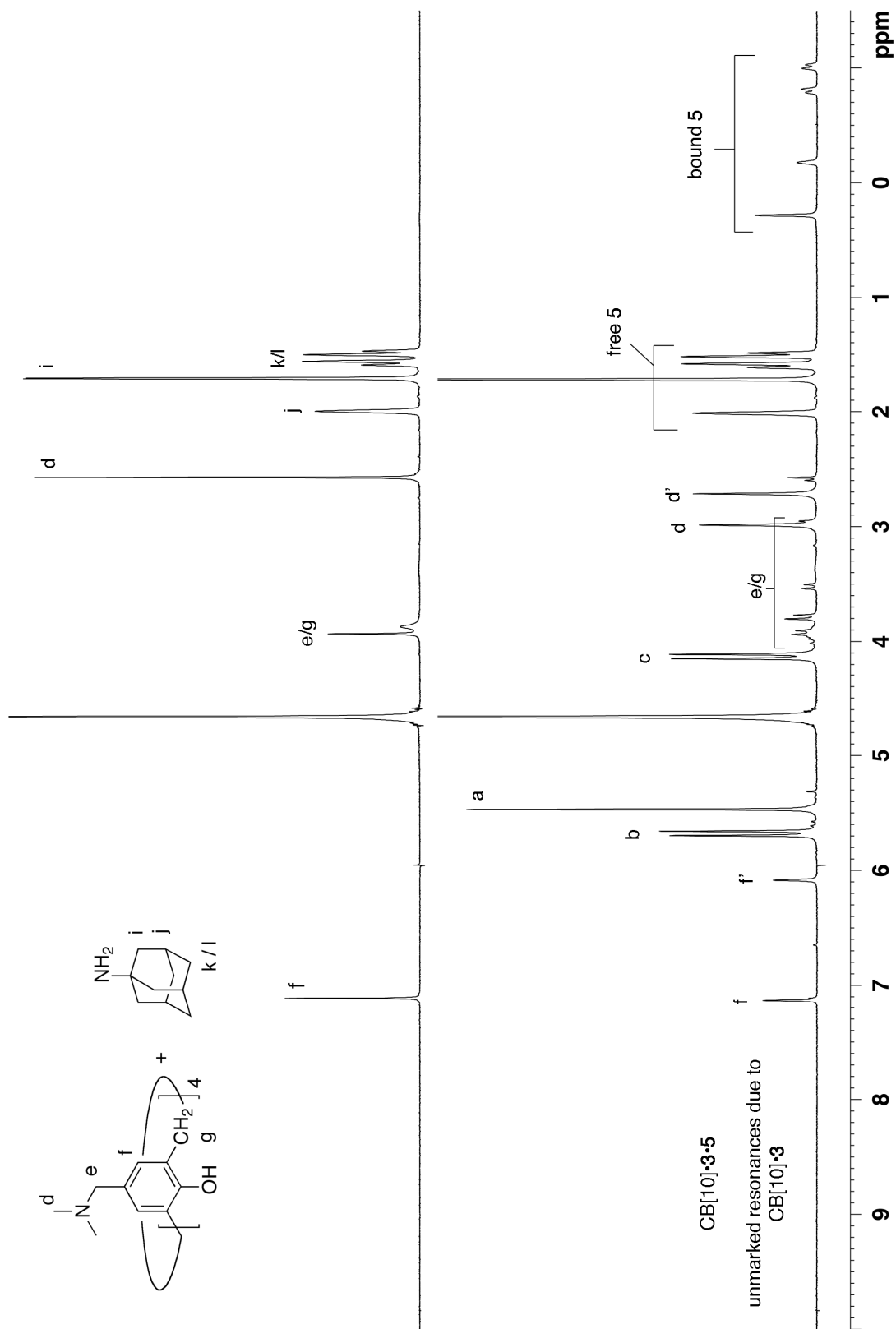


Figure S4. ^1H NMR spectra recorded (400 MHz, RT, D_2O) for: (left) a mixture of **3** and **5**, and (right) $\text{CB}[10]\cdot\mathbf{3}\cdot\mathbf{5}$ with excess **5**.

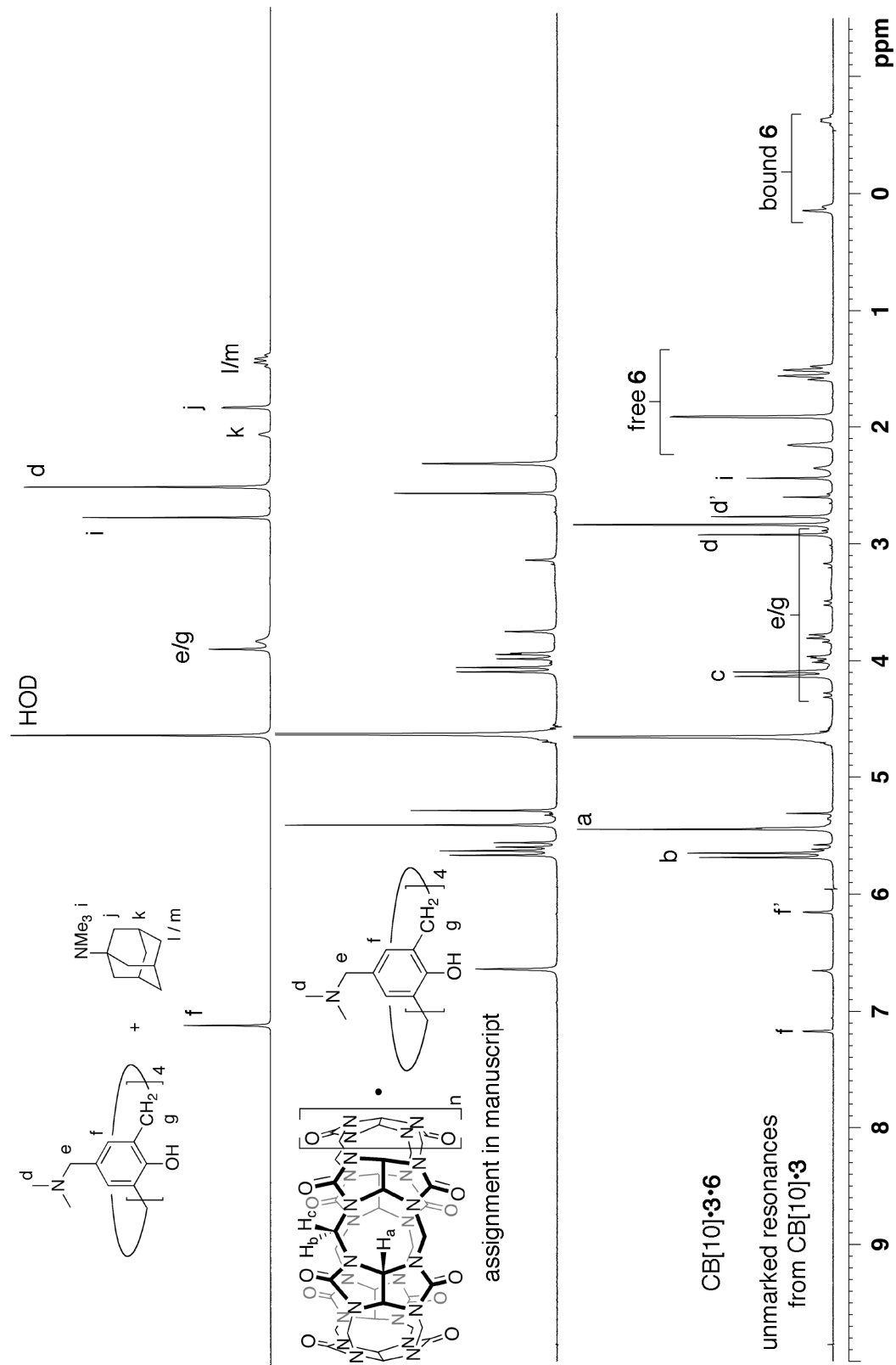


Figure S5. ^1H NMR spectra recorded (400 MHz, RT, D_2O) for: (left) a mixture of **3** and **6**, (middle) $\text{CB}[10]\cdot\mathbf{3}$, and (right) $\text{CB}[10]\cdot\mathbf{3}\cdot\mathbf{6}$ with excess **6**.

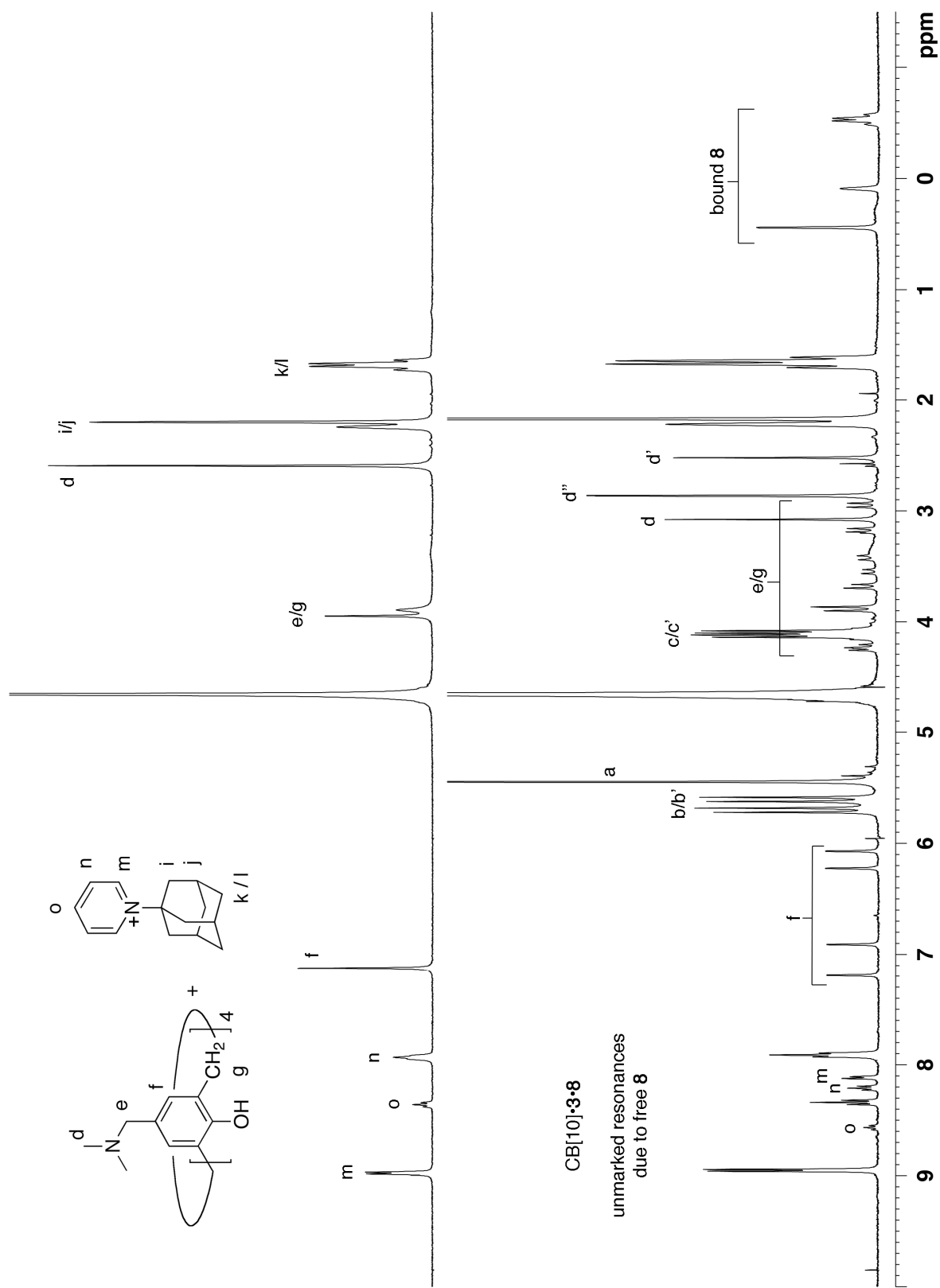


Figure S7. ^1H NMR spectra recorded (400 MHz, RT, D_2O) for: (left) a mixture of **3** and **8** and (right) $\text{CB}[10]\cdot\mathbf{3}\cdot\mathbf{8}$ with excess **8**.

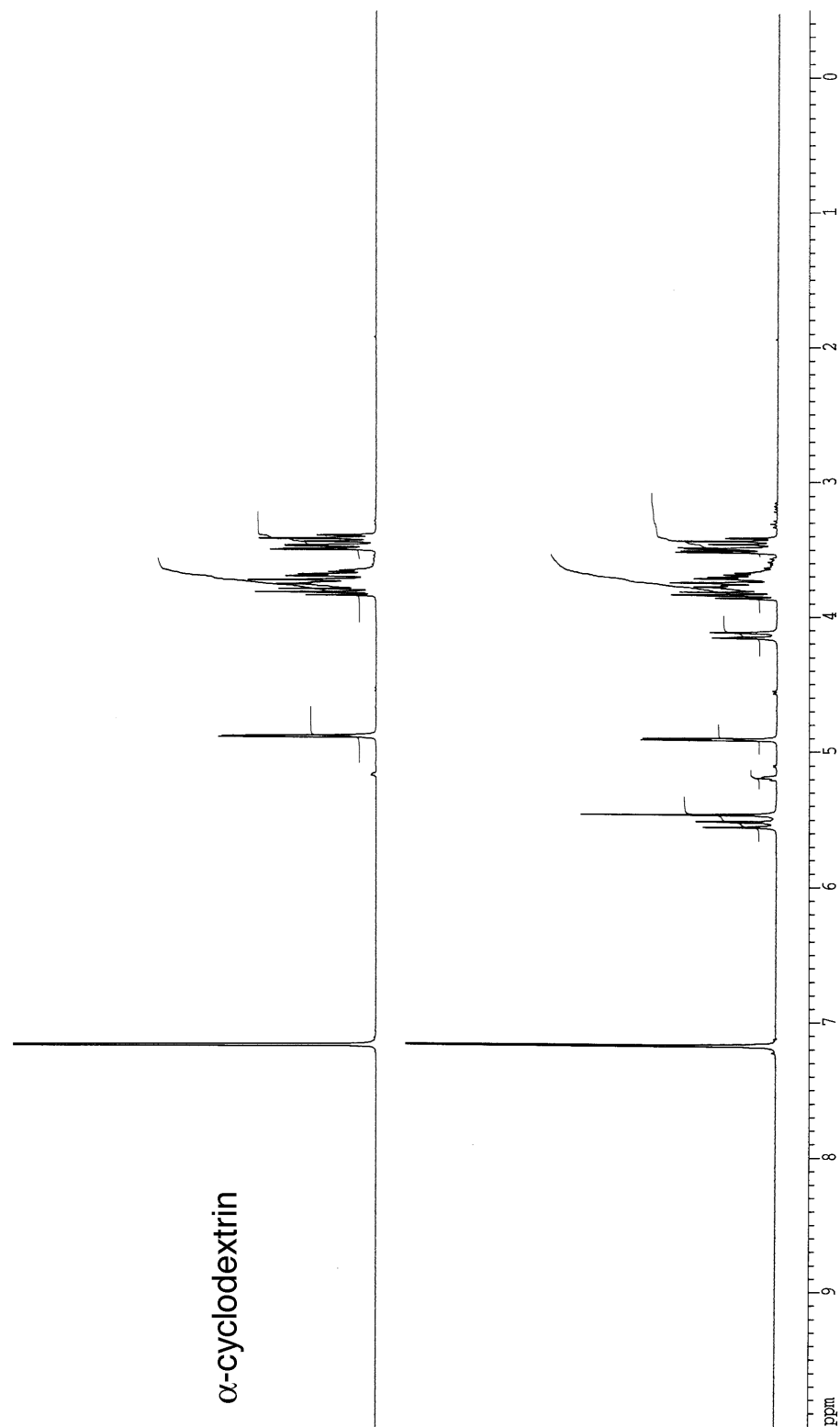


Figure S8. ¹H NMR spectrum recorded (400 MHz, RT, 20% DCl / D₂O) for α-cyclodextrin and a mixture of α-cyclodextrin and CB[10]. The small resonances at ≈ 3.2–3.3 and 4.6 ppm are impurities in the commercially available α-cyclodextrin. α-Cyclodextrin and CB[10] remain in their free states and do not form a complex.

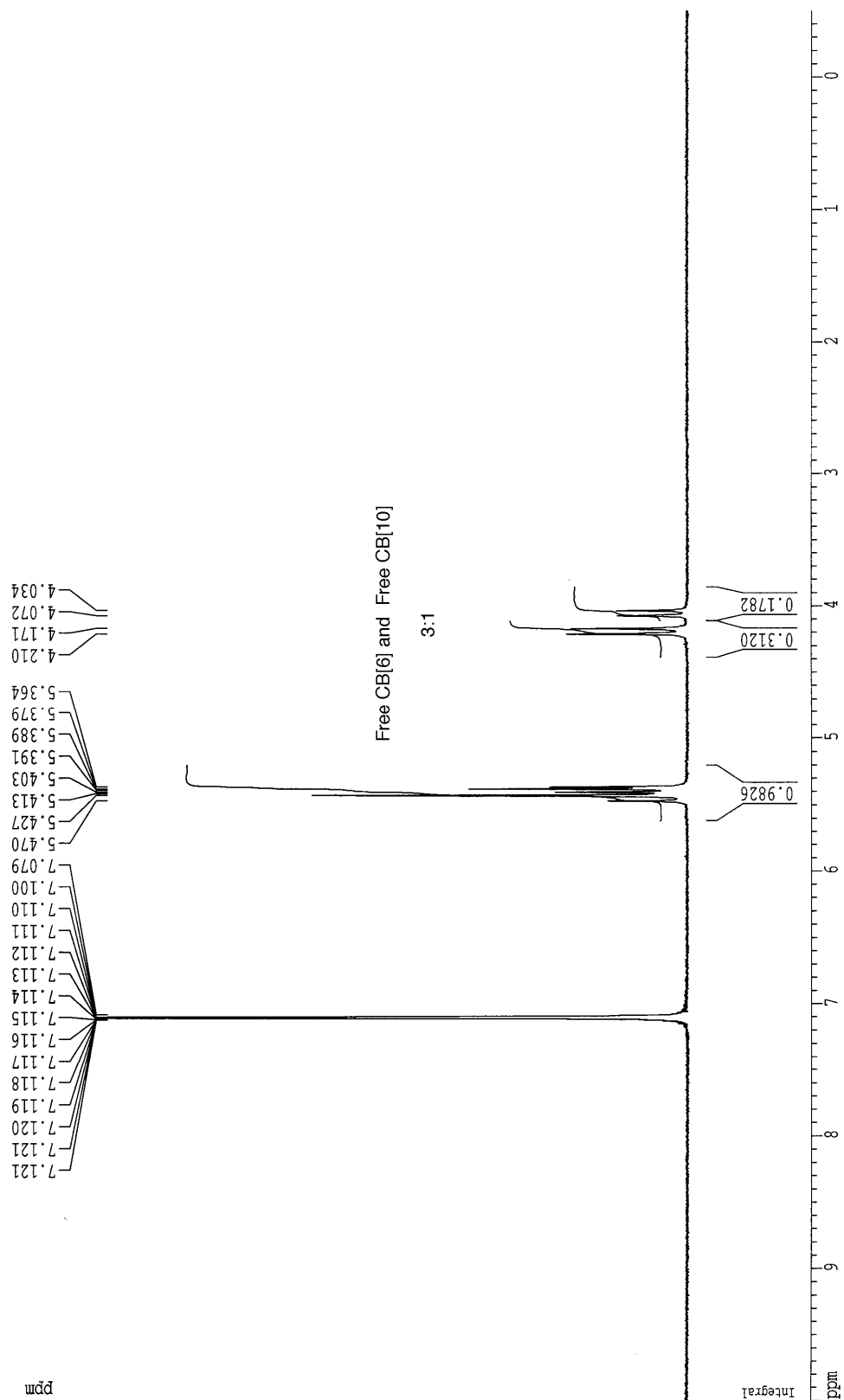


Figure S9. ^1H NMR spectrum recorded (400 MHz, RT, 20% DCl / D_2O) for a 3:1 mixture of CB[6] and CB[10]. CB[6] and CB[10] remain in their free states and do not form a complex.

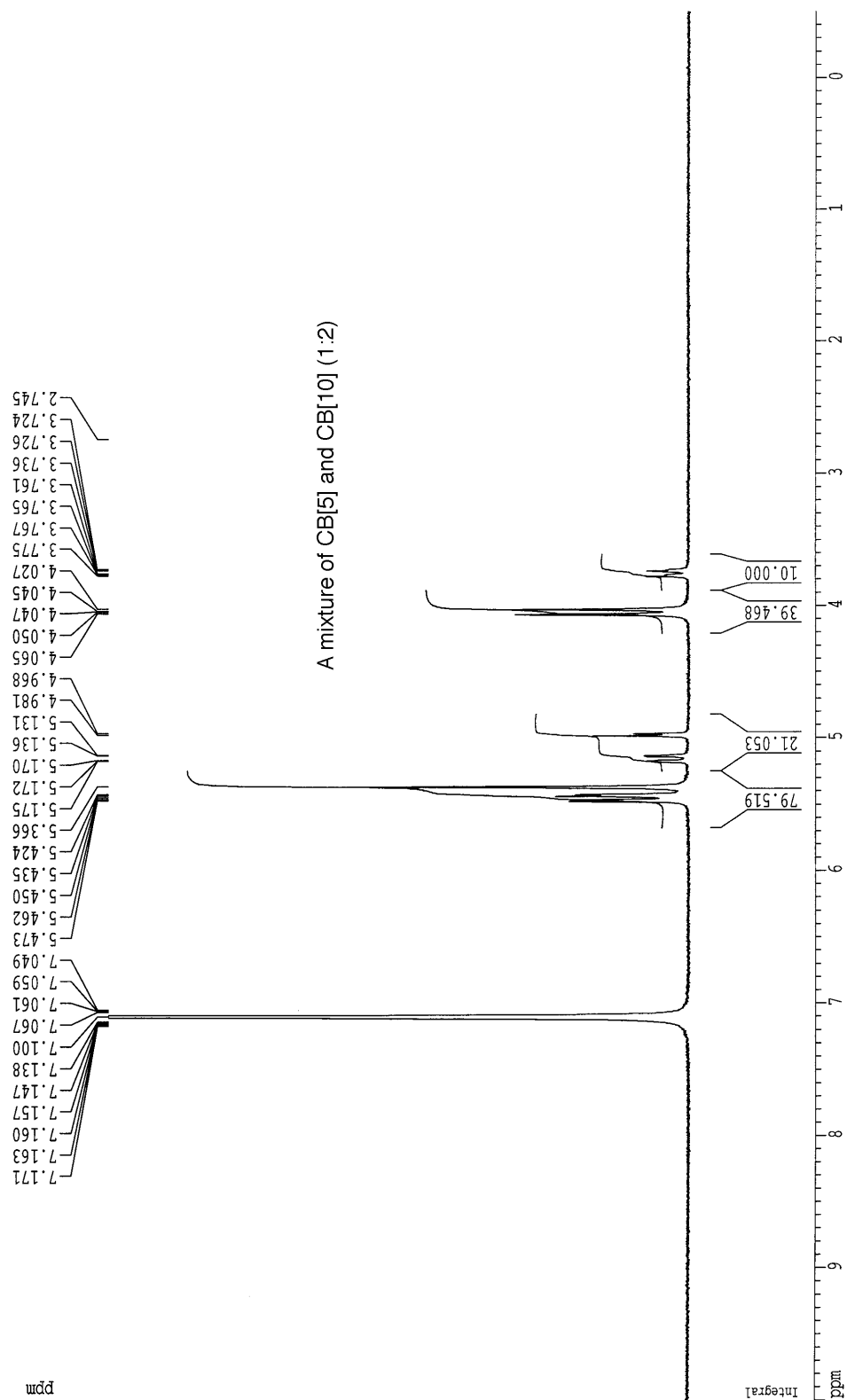


Figure S10. ^1H NMR spectrum recorded (400 MHz, RT, 20% $\text{DCI} / \text{D}_2\text{O}$) for a 1:2 mixture of purified CB[5] and CB[10]. Purified CB[10] retains the ability to bind CB[5]. Excess CB[10] is present as its free form.

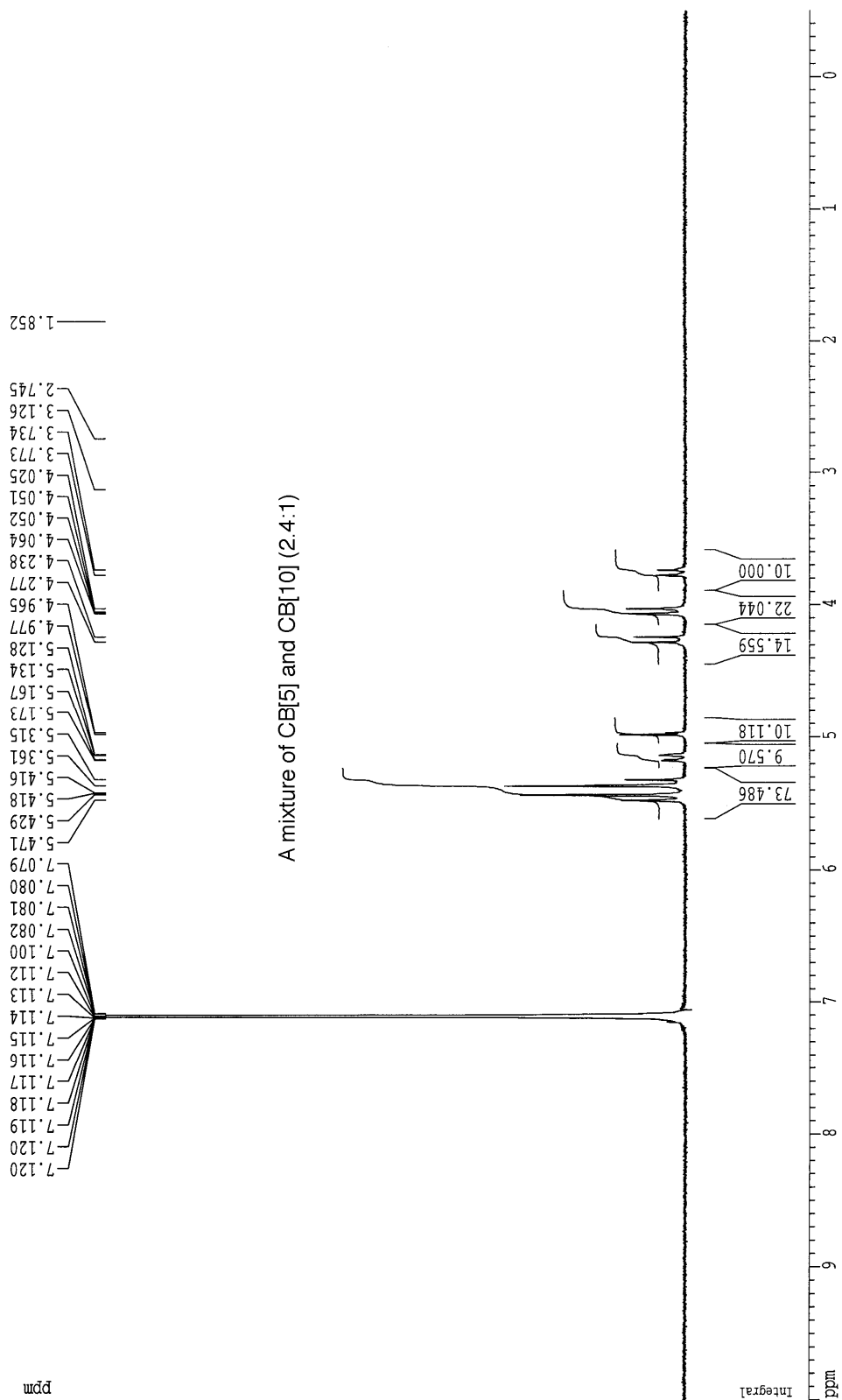


Figure S11. ^1H NMR spectrum recorded (400 MHz, RT, 20% DCl / D_2O) for a 2.4:1 mixture of purified CB[5] and CB[10]. Purified CB[10] retains the ability to bind CB[5]. Excess CB[5] is present as its free form.

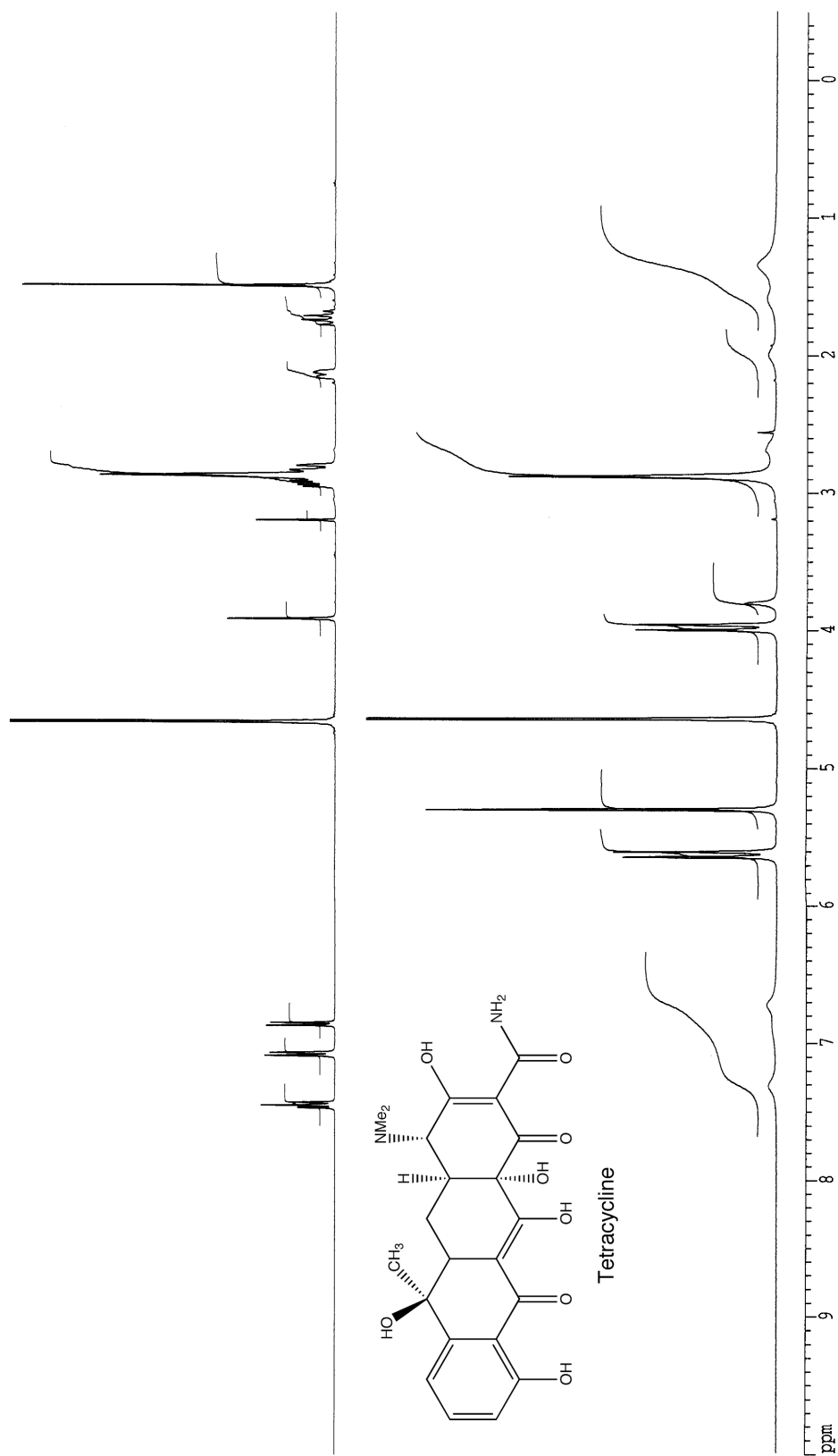


Figure S12. ¹H NMR spectrum recorded (400 MHz, RT, D₂O) for tetracycline and a mixture of tetracycline and CB[10].

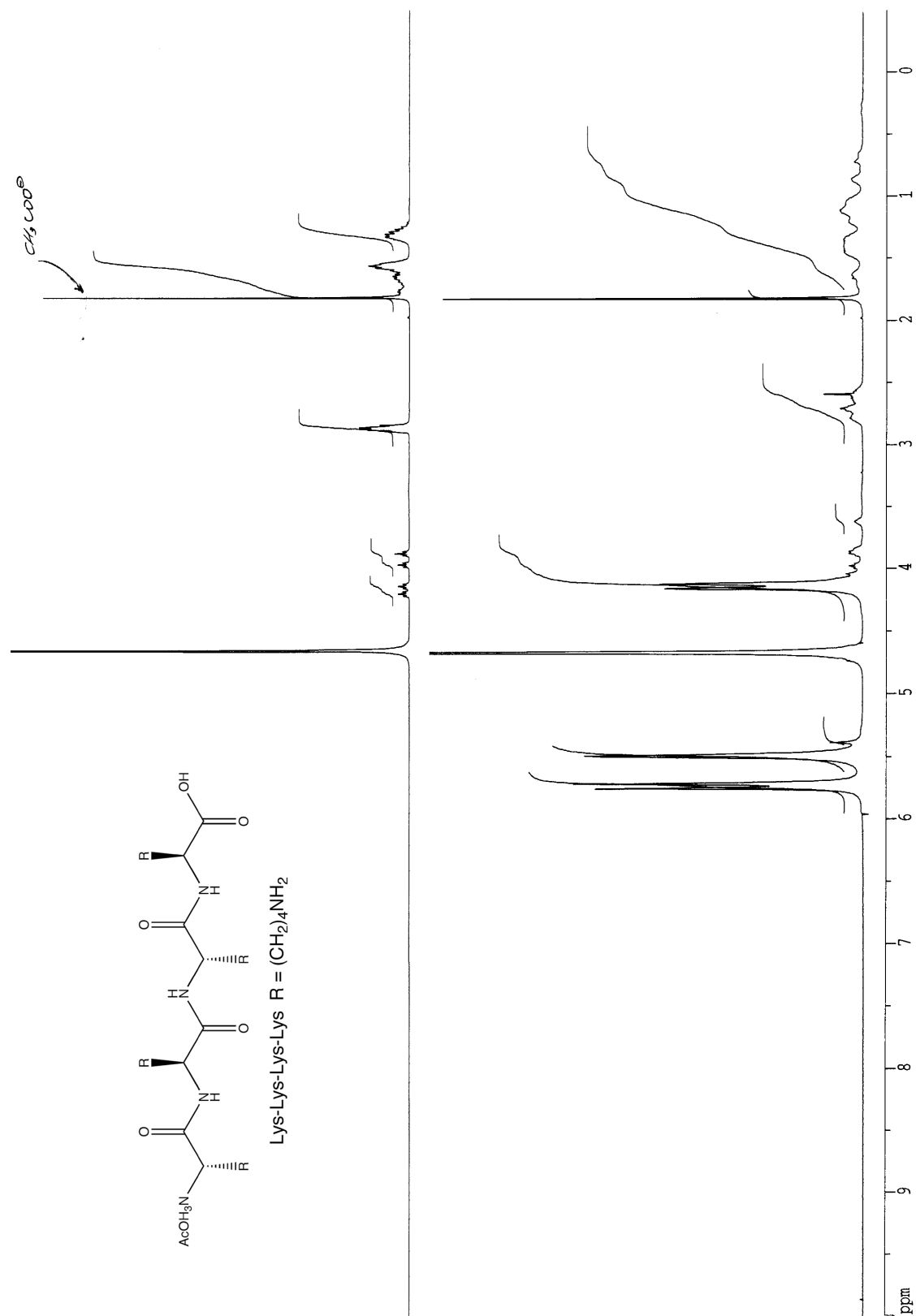


Figure S13. ^1H NMR spectrum recorded (400 MHz, RT, D_2O) for tetralysine and a mixture of tetralysine and CB[10].

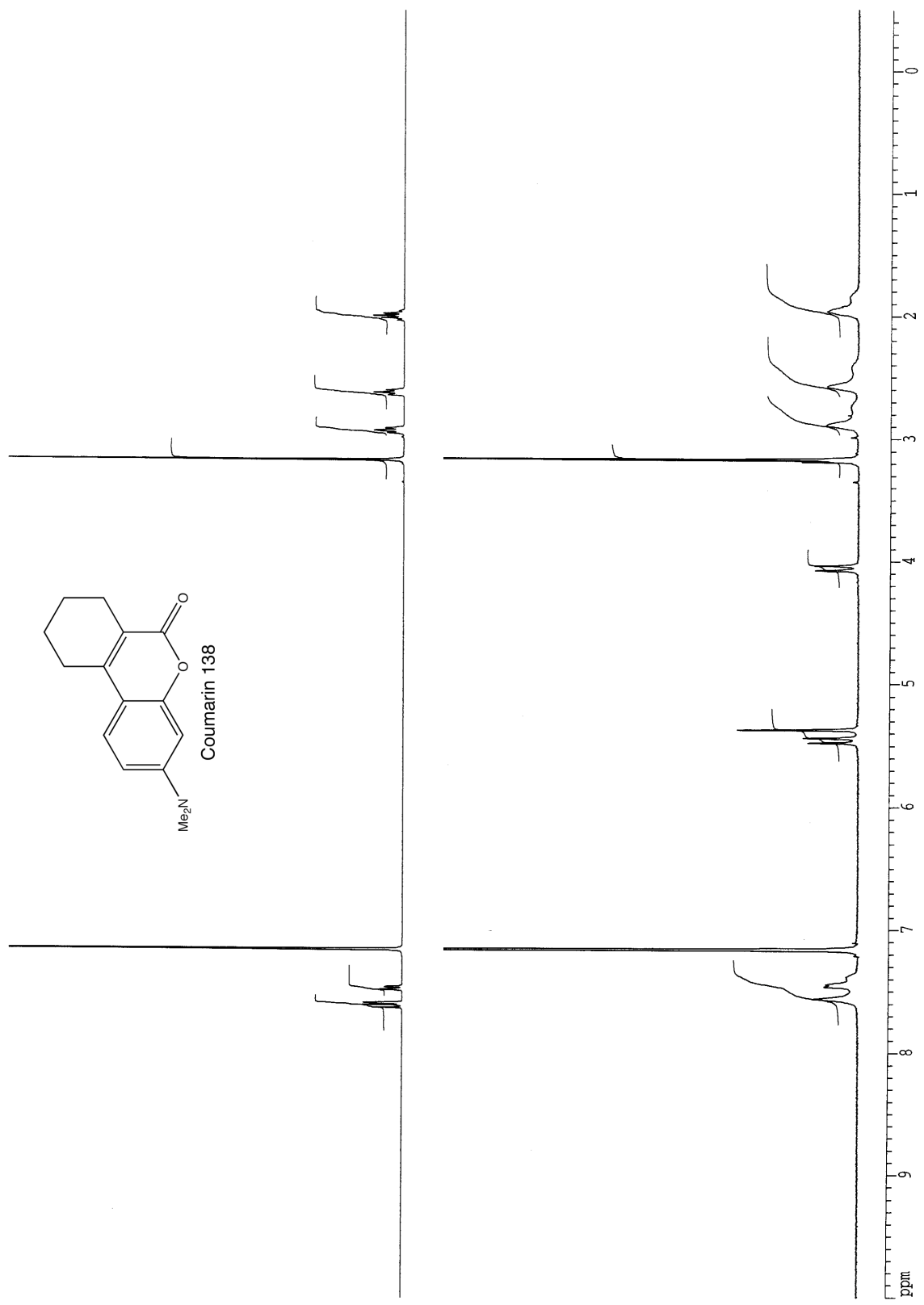


Figure S14. ^1H NMR spectrum recorded (400 MHz, RT, 20% DCl / D_2O) for coumarin 138 and a mixture of coumarin 138 and CB[10].

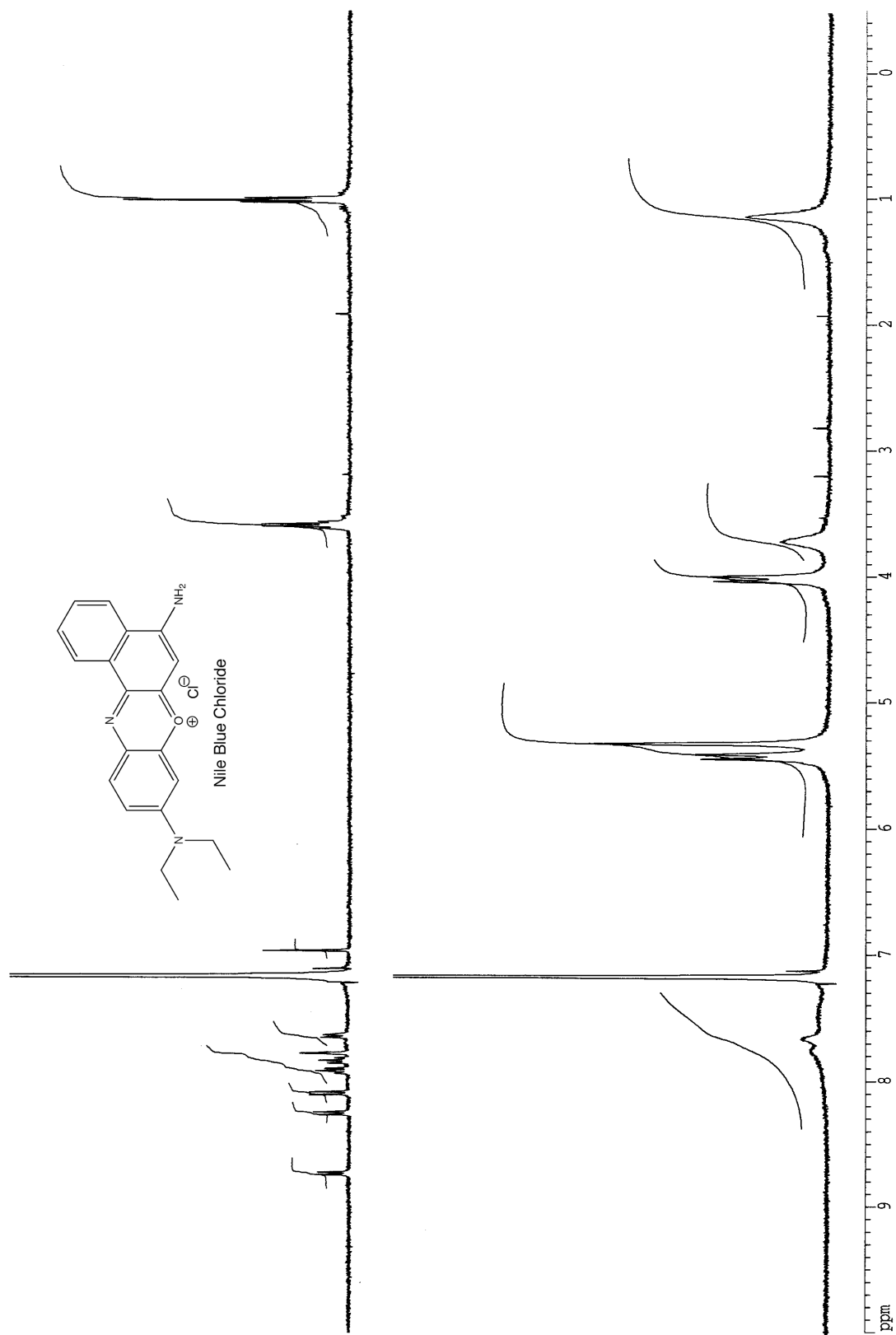


Figure S15. ^1H NMR spectrum recorded (400 MHz, RT, 20% DCl / D_2O) for Nile Blue and a mixture of Nile Blue and CB[10].

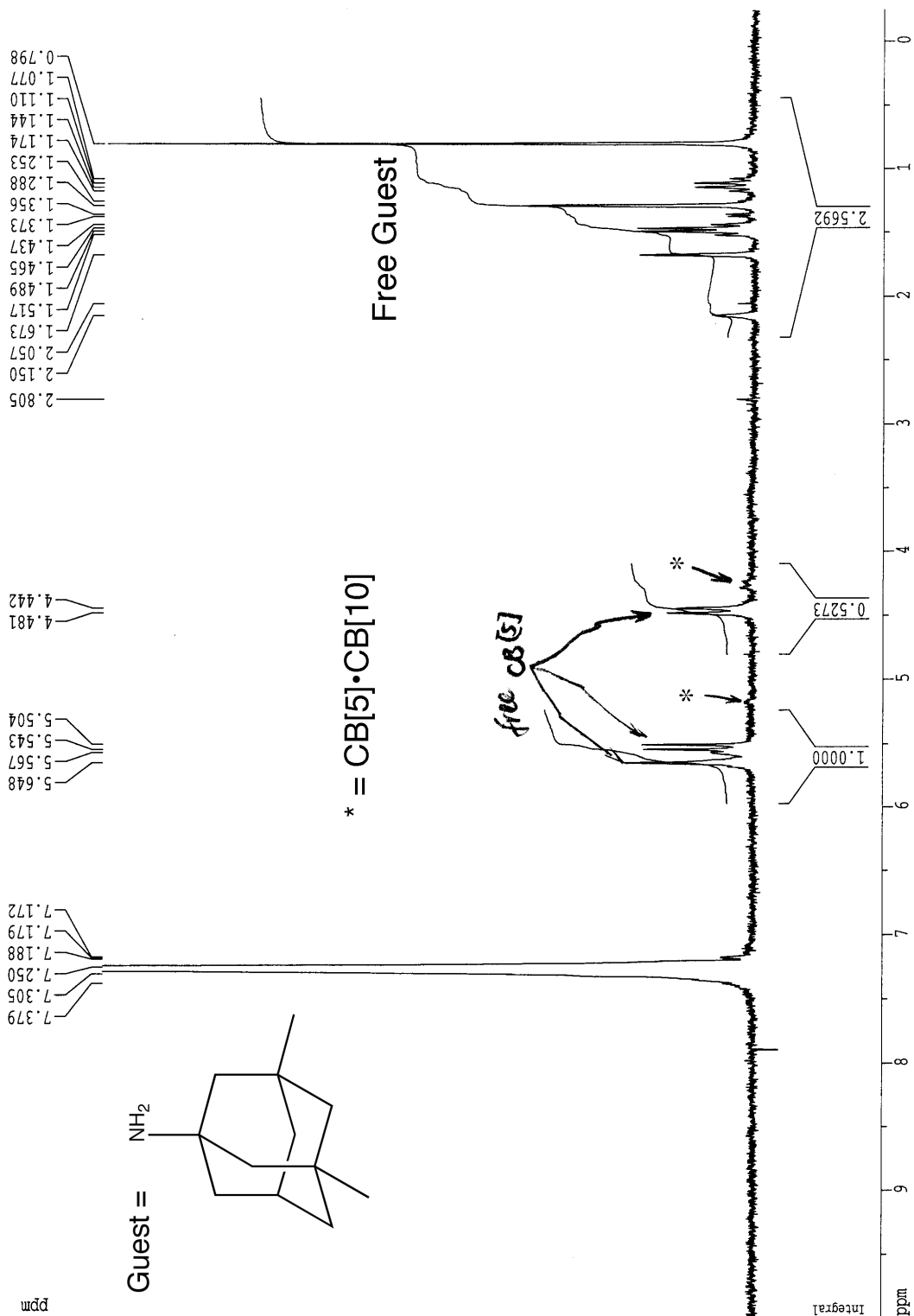


Figure S16. ^1H NMR spectrum recorded (400 MHz, RT, 20% $\text{DCI} / \text{D}_2\text{O}$) for a mixture of $\text{CB}[10]\cdot\text{CB}[5]$ and 3,5-dimethyl-1-aminoadamantane. The guest displaces $\text{CB}[5]$ from the $\text{CB}[10]\cdot\text{CB}[5]$ complex. The $\text{CB}[10]\cdot\text{CB}[5]$ complex is insoluble, precipitates from solution, and is not seen in the ^1H NMR spectrum. Excess free guest and $\text{CB}[5]$ remain in solution. * = small amount of $\text{CB}[10]\cdot\text{CB}[5]$

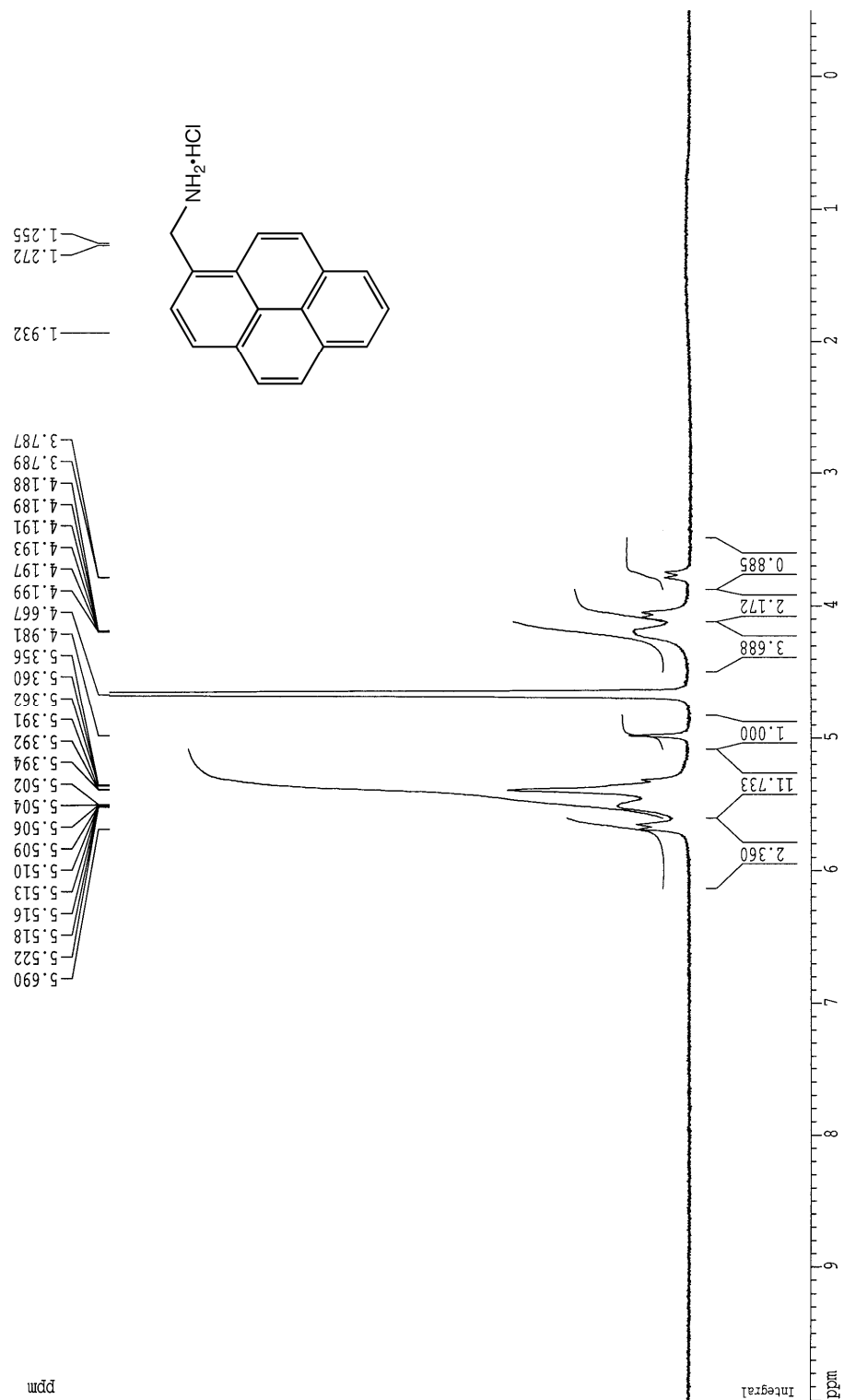


Figure S17. ^1H NMR spectrum recorded (400 MHz, RT, D_2O) for CB[10]•CB[5] after addition of ≈ 0.8 eq. pyrenemethylamine hydrochloride. The guest displaces CB[5] from the CB[10]•CB[5] complex. The CB[10]•pyrenemethylamine complex is insoluble, precipitates from solution, and is not seen in the ^1H NMR spectrum. Displaced CB[5] and residual remain in solution. The broadness reflects chemical exchange between free and bound CB[5].

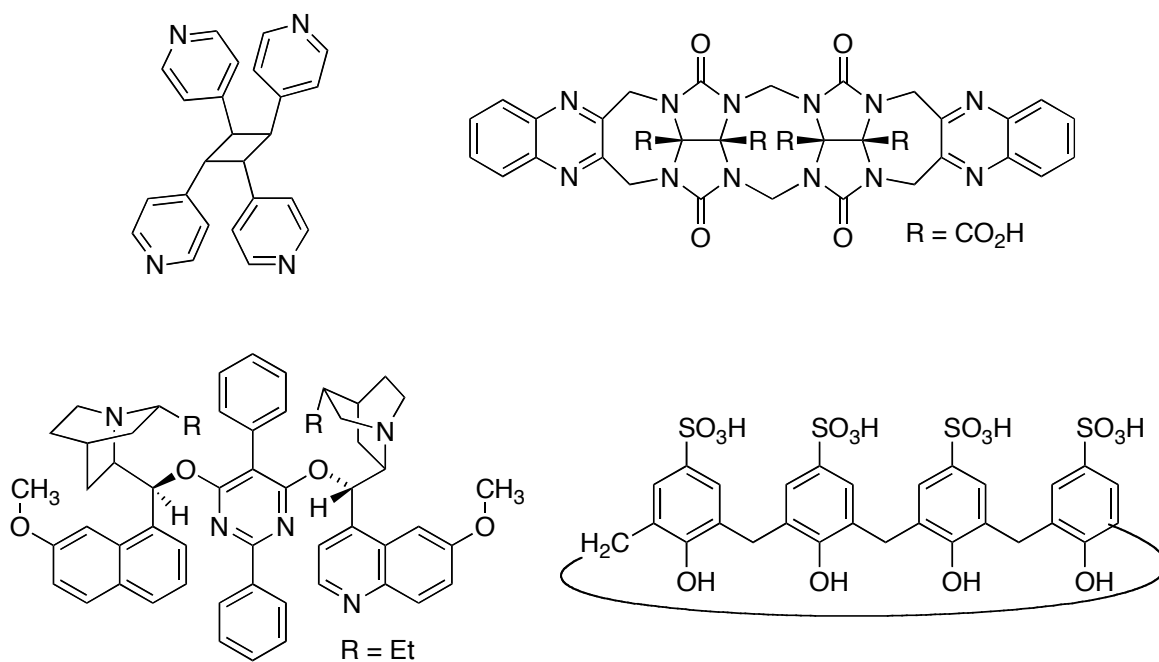


Figure S18. Chemical structures of some additional guests that do not form complexes with CB[10] in DCl / D₂O solution.

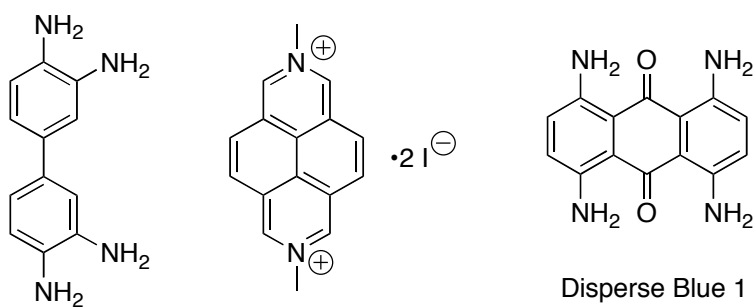


Figure S19. Chemical structures of some additional guests that form insoluble precipitates when mixed with CB[10] in DCl / D₂O solution.

Crystal Structure Information for UM # 1234

Issued by: Peter Y. Zavalij

Crystal No. & ID : 1234: Isaacs/Liu 1050B+KI #2 @ -40C redo from non-split crystal
Compound name : CB10 @ bis-diammonium tetraiodide hydrate
Chemical formula : (C₆₀ H₆₀ N₄₀ O₂₀), (C₁₇ H₂₁ N₇ O)₄, I₈, (H₂ O)_{65.87}
Final R₁ [I>2σ(I)] : 8.74 %

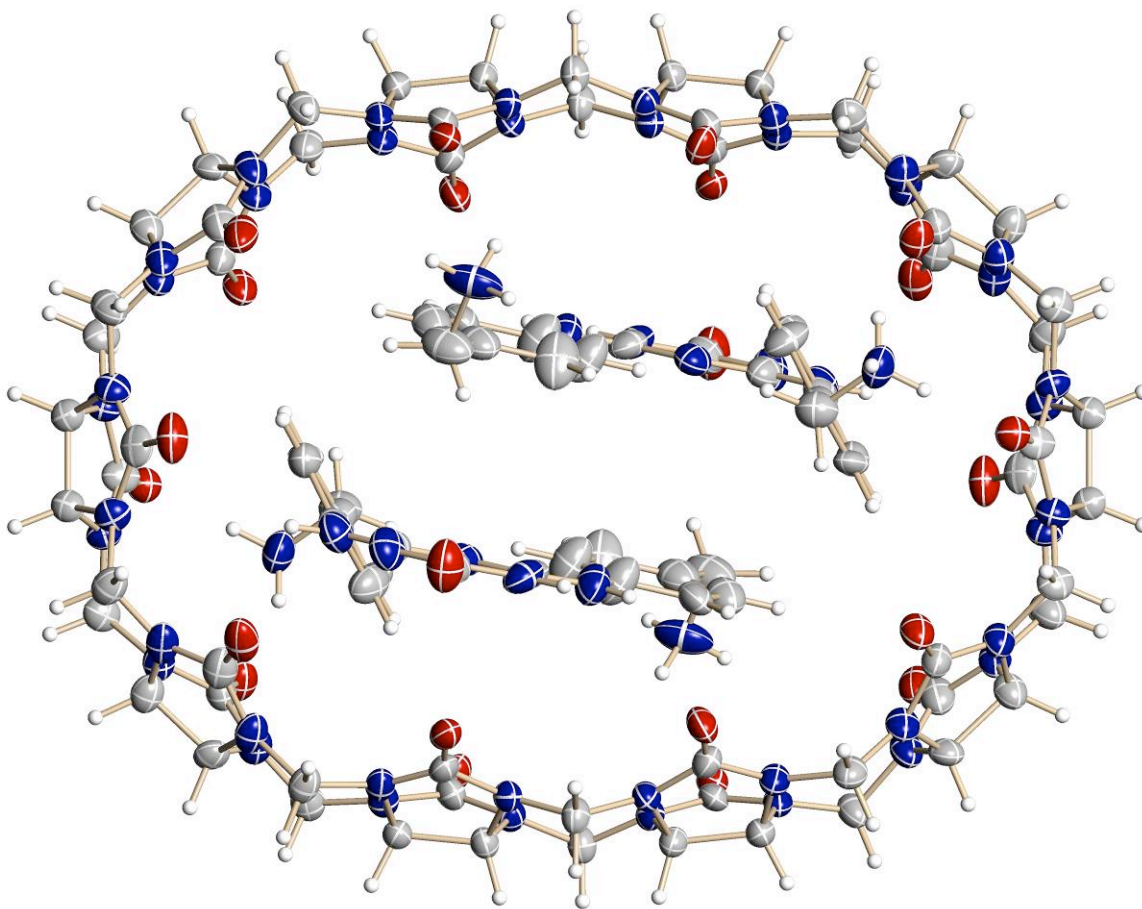


Figure S20. A view of a molecule of CB10@diamine2.14.nH₂O from the crystal structure showing the numbering scheme employed. Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 25% probability level. Hydrogen atoms are displayed with an arbitrarily small radius.

A colorless prism of C₉₄H_{167.87}I₄N₅₄O_{54.94}, approximate dimensions 0.200 × 0.285 × 0.315 mm³, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 233(2) K on a three-circle diffractometer system equipped with Bruker Smart1000 CCD area detector using a graphite monochromator and a MoK α fine-focus sealed tube ($\lambda = 0.71073$ Å) operated at 50 kV and 40 mA. The detector was placed at a distance of 4.99 cm from the crystal.

A total of 1868 frames were collected with a scan width of 0.3° in ω and an exposure time of 15 sec/frame using SMART (Bruker, 1999). The total data collection time was 11.5 hours. The frames were

integrated with SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Orthorhombic unit cell yielded a total of 41685 reflections to a maximum θ angle of 22.50° , of which 4924 were independent (completeness = 99.5%, $R_{\text{int}} = 8.87\%$, $R_{\text{sig}} = 5.06\%$) and 3619 were greater than $2\sigma(I)$. The final cell dimensions of $a = 19.476(4) \text{ \AA}$, $b = 20.192(4) \text{ \AA}$, $c = 18.567(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 7302(3) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 5532 reflections with $2.3 < \theta < 21.0^\circ$ using SAINT. Analysis of the data showed 1.52 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.680 and 0.826.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group $Pn\bar{m}$ with $Z = 2$ for the formula unit $\text{C}_{94}\text{H}_{167.87}\text{I}_4\text{N}_{54}\text{O}_{54.94}$. The final anisotropic full-matrix least-squares refinement on F^2 with 623 variables converged at $R_1 = 8.74\%$ for the observed data and $wR_2 = 23.75\%$ for all data. The goodness-of-fit was 1.001. The largest peak on the final difference map was $2.632 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-1.003 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.565 g/cm^3 and $F(000)$, 3523 e^- .

Table S1. Sample and crystal data for CB10@diamine2.I4.nH2O.

| | | |
|-------------------------------|---|---------------------|
| X-ray labbook No. | 1234 | |
| Crystal ID | Isaacs/Liu 1050B+KI #2 @ -40C redo from non-split crystal | |
| Empirical formula | C ₉₄ H _{167.87} I ₄ N ₅₄ O _{54.94} | |
| Formula weight | 3441.25 | |
| Temperature | 233(2) K | |
| Wavelength | 0.71073 \AA | |
| Crystal size | 0.315 × 0.285 × 0.200 mm ³ | |
| Crystal habit | colorless prism | |
| Crystal system | Orthorhombic | |
| Space group | Pn \bar{m} | |
| Unit cell dimensions | $a = 19.476(4) \text{ \AA}$ | $\alpha = 90^\circ$ |
| | $b = 20.192(4) \text{ \AA}$ | $\beta = 90^\circ$ |
| | $c = 18.567(4) \text{ \AA}$ | $\gamma = 90^\circ$ |
| Volume | 7302(3) \AA^3 | |
| Z | 2 | |
| Density, ρ_{calc} | 1.565 g/cm ³ | |
| Absorption coefficient, μ | 0.957 mm ⁻¹ | |
| F(000) | 3523 $\bar{\text{e}}$ | |

Table S2. Data collection and structure refinement for CB10@diamine2.I4.nH2O.

| | |
|---------------------------------------|--|
| Diffractometer | Bruker Smart1000 CCD area detector |
| Radiation source | fine-focus sealed tube, MoK α |
| Generator power | 50 kV, 40 ma |
| Detector distance | 4.99 cm |
| Detector resolution | 8.33 pixels/mm |
| Total frames | 1868 |
| Frame size | 512 pixels |
| Frame width | 0.3 ° |
| Exposure per frame | 15 sec |
| Total measurement time | 11.5 hours |
| Data collection method | ω scans |
| θ range for data collection | 2.19 to 22.50° |
| Index ranges | $-20 \leq h \leq 20, -21 \leq k \leq 21, -19 \leq l \leq 19$ |
| Reflections collected | 41685 |
| Independent reflections | 4924 |
| Observed reflection, $I > 2\sigma(I)$ | 3619 |
| Coverage of independent reflections | 99.5 % |
| Variation in check reflections | 1.52 % |
| Absorption correction | Semi-empirical from equivalents SADABS (Sheldrick, 1996) |
| Max. and min. transmission | 0.826 and 0.680 |
| Structure solution technique | direct |
| Structure solution program | SHELXS-97 (Sheldrick, 1990) |
| Refinement technique | Full-matrix least-squares on F^2 |
| Refinement program | SHELXL-97 (Sheldrick, 1997) |
| Function minimized | $\sum w(F_o^2 - F_c^2)^2$ |
| Data / restraints / parameters | 4924 / 283 / 623 |
| Goodness-of-fit on F^2 | 0.980 |
| Δ/σ_{\max} | 0.000 |
| Final R indices: | |
| $R_1, I > 2\sigma(I)$ | 0.0874 |
| $wR_2, \text{all data}$ | 0.2375 |
| R_{int} | 0.0887 |
| R_{sig} | 0.0506 |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 122.7P],$ $P = [\max(F_o^2, 0) + 2F_o^2]/3$ |
| Largest diff. peak and hole | 2.632 and $-1.003 \bar{e}/\text{\AA}^3$ |

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$