

## Electronic Supplementary Information (ESI)

### ***N*-Heterocyclic Carbene Ligand based on a $\beta$ -cyclodextrin-Imidazolium Salt: Synthesis, Characterization of Organometallic Complexes and Suzuki Coupling.**

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## Materials and apparatus.

$\beta$ -cyclodextrin was obtained from Roquette Frères (Lestrem, France).  $\beta$ -CD-OTs was obtained from the native  $\beta$ -cyclodextrin.<sup>i</sup> PM- $\beta$ -CD-OTs was synthesized from  $\beta$ -CD-OTs.<sup>ii9</sup> ( $\beta$ -CD-MIM,Cl was synthesised in three steps starting from  $\beta$ -cyclodextrin as already described in the litterature.<sup>iii</sup> The most of chemical products, reagents and solvents used in this study were purchased from Acros Organics and Sigma-Aldrich in their highest purity and used without further purification. Metal precursors and deuterated solvents were purchased respectively from Strem Chemicals and Euriso-Top in their highest purity and used without further purification. Ultrapure water was used for surface tension measurements (Fresenius Kabi;  $\gamma = 72.0$  mN/m at 25°C) and distilled water was used in all other experiments. Analytical thin-layer chromatography plates (TLC Silica gel 60 F<sub>254</sub> Aluminium) and silica (Geduran® Si 60 (0.063 - 0.200 mm)) for preparative column chromatography were purchased from Merck. Compounds were identified by using UV fluorescence and/or staining with a solution of phosphomolybdic acid in aqueous sulphuric acid and EtOH.

Characterization and structure determinations were achieved by NMR experiments on different spectrometers (a 300 MHz Bruker Avance DRX spectrometer, operating at 300.13 MHz for <sup>1</sup>H nuclei and 75.47 MHz for <sup>13</sup>C nuclei, equipped with a QNP probe; a 600 MHz Bruker Avance spectrometer, operating at 599.94 MHz for <sup>1</sup>H nuclei and 150.9 MHz for <sup>13</sup>C nuclei or a 700 MHz Bruker Avance spectrometer, operating at 700.13 MHz for <sup>1</sup>H nuclei and 176.06 MHz for <sup>13</sup>C nuclei, equipped with a TCI cryo-probe). 1D and 2D NMR experiments were obtained using the pulse programs available from the Bruker library. The off-resonance ROESY experiment<sup>iv</sup> used a rf field strength of 10 kHz shifted by 7080 Hz (effective angle = 54.7°) and were acquired in the phase sensitive mode using the TPPI method. The adiabatic version of the sequence using a trapezoidal spin-lock pulse during the mixing time of a NOESY experiment was employed.<sup>v</sup> Details concerning experimental conditions are given in

the figure captions. All NMR measurements were performed under careful temperature regulation using a Bruker BVT variable temperature unit. Chemical shifts are given in parts per million (ppm) relative to external reference using internal capillary (sodium salt of 3-(trimethylsilyl)-2,2,3,3-tetradeuteropropionic acid (98% atom D) in D<sub>2</sub>O for <sup>1</sup>H and <sup>13</sup>C NMR and calibration was performed using the signal of the residual signals of the solvent as a secondary reference while taking into account temperature effects. The MALDI-TOF mass spectra were recorded on a MALDI-TOF-TOF Bruker Daltonics Ultraflex II spectrometer in positive reflectron mode by using 2,5-dihydroxybenzoic acid as matrix and external peptide calibration standard kit (Bruker Daltonics) within 750-4200 mass range. The acceleration voltage was fixed at 25 keV, the delayed extraction time at 10 ns and the number of laser shots at 200. The samples were dissolved either in H<sub>2</sub>O, acetone or MeOH and equally mixed with the matrix solution (10 mg.mL<sup>-1</sup> of 2,5-dihydroxybenzoic acid in water/0.1 % TFA:MeCN, 70:30 (v/v)) and spotted onto a ground style MALDI target according to the dried droplet method. Electrospray ionization mass spectroscopy experiments were performed on a Thermoquest Finnigan LCQ Duo. The samples were introduced through the fused silica inlet capillary at a flow rate of 5 mL.min<sup>-1</sup>. The ion spray needle potential and the orifice potential were set at 3100 V and 10-120 V, respectively. Positive ion detection mode was used and calibration was performed with polypropylene glycol. Optical rotations were measured at 20°C with a Perkin-Elmer 341 digital polarimeter by using a 1 mL cell with a path length of 1 dm. The UV-Vis experiments were performed by using a Varian Cary 50 UV-Vis spectrophotometer at ambient temperature (293.15 K) with a 10 mm quartz cell. Gas chromatographic analyses were carried out on a Shimadzu GC-17A gas chromatograph equipped with a methyl silicone capillary column (30 m × 0.32 mm) and a flame ionization detector.

### Determination of the association constant of 1:AdOH inclusion complex.

The evaluation of the host inclusion ability towards 1-adamantanol (AdOH) was determined by UV-vis spectroscopy, combined with the direct titration method. This method was applied for a fixed concentration of CD (0.05 mM) and varying concentrations of AdOH.

Assuming a 1:1 stoichiometry, the calculation of the formation constant  $K_f$  was developed as follows:

$$K_f = \frac{[\text{CD/AdOH}]}{[\text{CD}] \times [\text{AdOH}]} = \frac{[\text{CD/AdOH}]}{([\text{CD}]_0 - [\text{CD/AdOH}]) \times ([\text{AdOH}]_0 - [\text{CD/AdOH}])}$$

and  $[\text{CD/ACNa}]$  can be estimated by

$$[\text{CD/AdOH}] = -\frac{1}{2} \times \sqrt{\left( \frac{1}{K_f} + [\text{CD}]_0 + [\text{AdOH}]_0 \right)^2 - 4 \times [\text{CD}]_0 \times [\text{AdOH}]_0} + \frac{1}{2} \times \left( \frac{1}{K_f} + [\text{CD}]_0 + [\text{AdOH}]_0 \right)$$

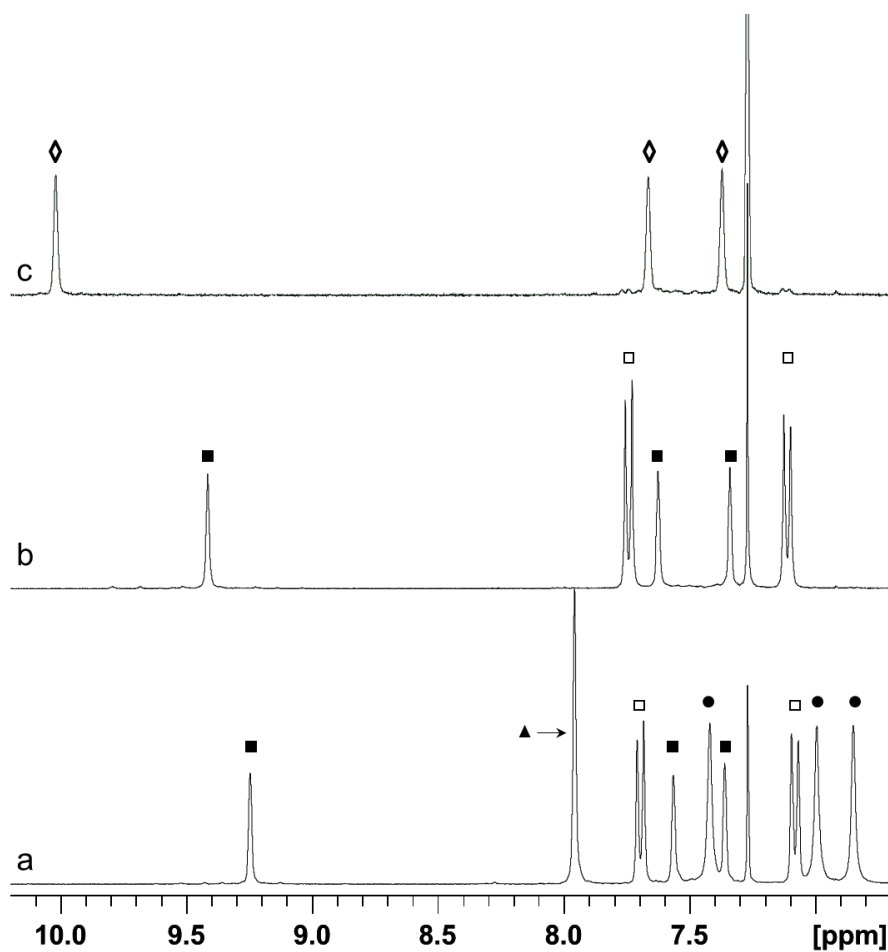
For a given value of  $K_f$ , the  $[\text{CD/AdOH}]$  concentration was known and thus the molar absorptivity of the complex can be calculated. An algorithm treatment was then applied to minimize the difference between the experimental and the theoretical values of the spectral characteristics for each concentration of AdOH.<sup>vi</sup> The association constant was determined by computer fitting of the experimental titration curve.

### Surface tension measurements.

The processor tensiometer Sigma 70 (KSV) and the Wilhelmy plate method for air-water interface have been used for the surface tension measurements at 293.15 K. A concentrated solution of the cyclodextrin derivative is installed in a syringe and the addition of small volumes to ultrapure water enhances the solution concentration. After each addition, the solution is gently stirred for 30 s. Equilibrium surface tension is measured for each

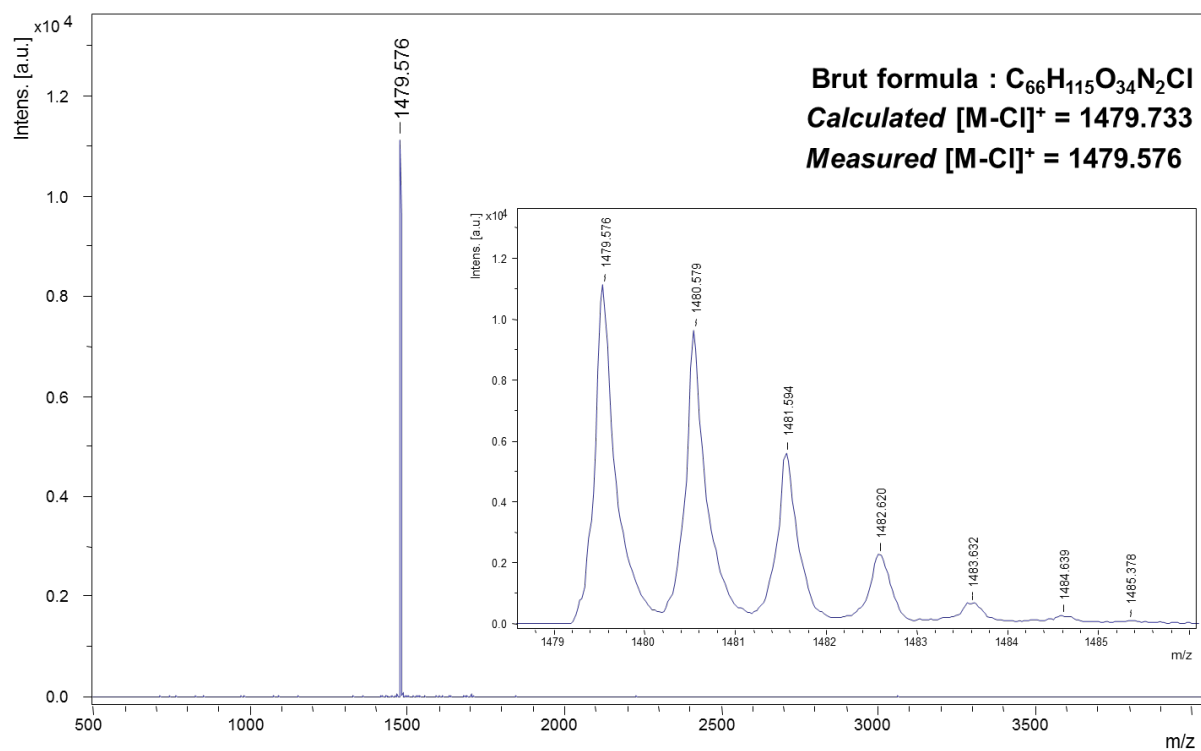
concentration. All surface tension values were mean quantities of at least three measurements. The standard deviation of the mean never deviated  $\pm 1.5$  % of the mean. The precision of the force transducer of the surface tension apparatus was  $0.1 \text{ mN.m}^{-1}$ . Before each experiment, the platinum plate was cleaned in red/orange colour flame. The temperature stabilisation can be estimated as better than  $\pm 0.05 \text{ K}$  with a thermoregulated bath Lauda RC6.

Figure S1:  $^1\text{H}$  NMR partial spectra (293.15 K; 300.13 MHz;  $\text{CDCl}_3$ ) of the crude reaction mixture (a), of the product after dialysis (b) and of the product 1 after ion exchange (c).



| Symbol | Compound                      |
|--------|-------------------------------|
| ▲      | <i>N,N</i> -dimethylformamide |
| ●      | 1-methylimidazole             |
| □      | tosylate ion                  |
| ■      | PM- $\beta$ -CD-MIM,OTs       |
| ◇      | PM- $\beta$ -CD-MIM,Cl        |

**Figure S2: MALDI-TOF mass spectrum of 1 (matrix: 2,5-dihydroxybenzoic acid).**



**Figure S3: UV-visible spectrum of an aqueous solution of 1 (293.15 K; 0.2 mM in water).**

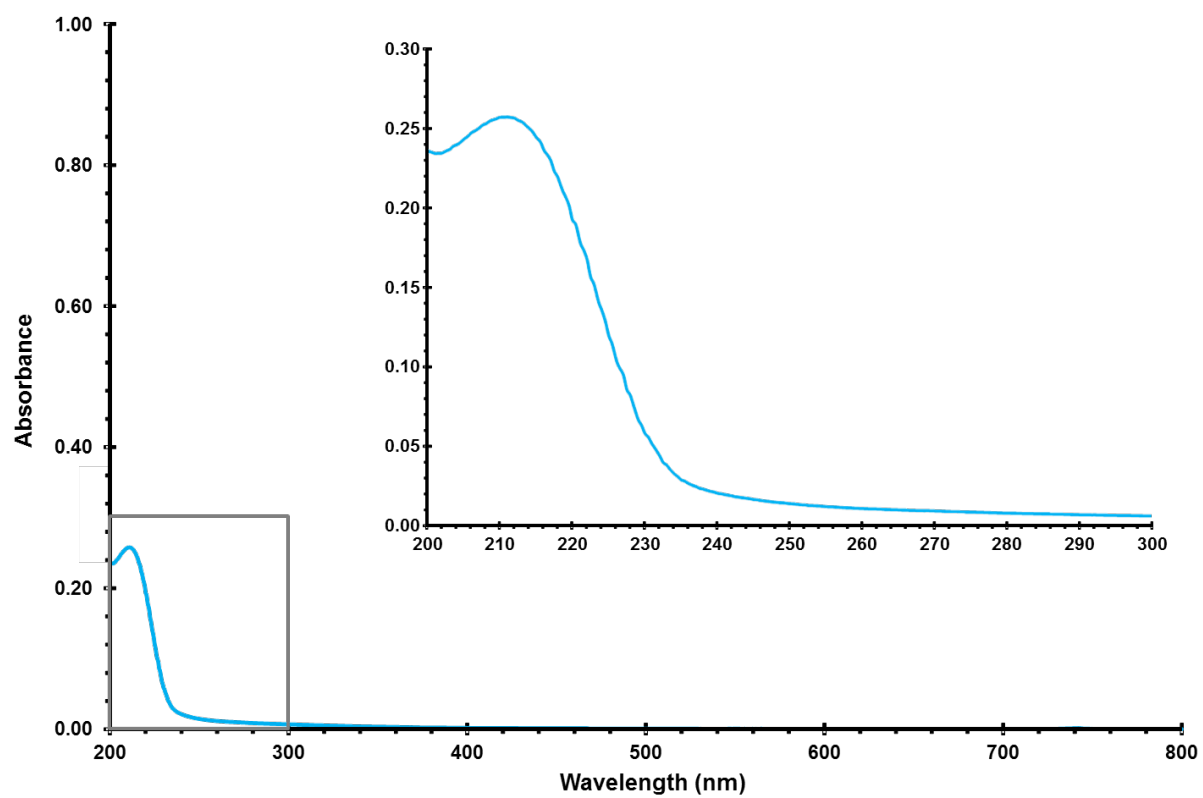




Figure S4:  $^1\text{H}$  NMR spectrum of **1** (293 K; 700.13 MHz; 8 mM in  $\text{CDCl}_3$ ).

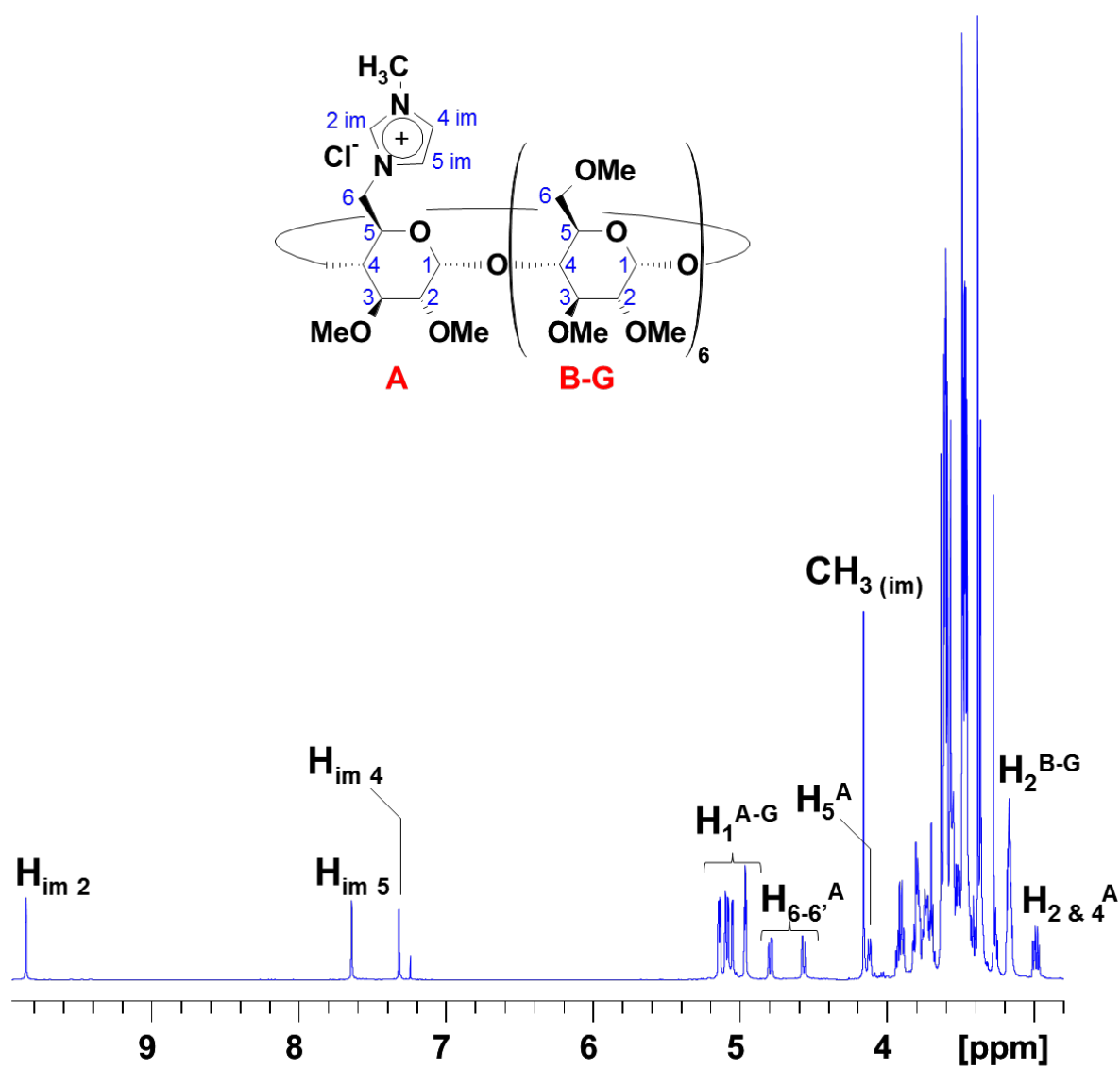


Figure S5:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 1 (293 K; 176.06 MHz; 8 mM in  $\text{CDCl}_3$ ).

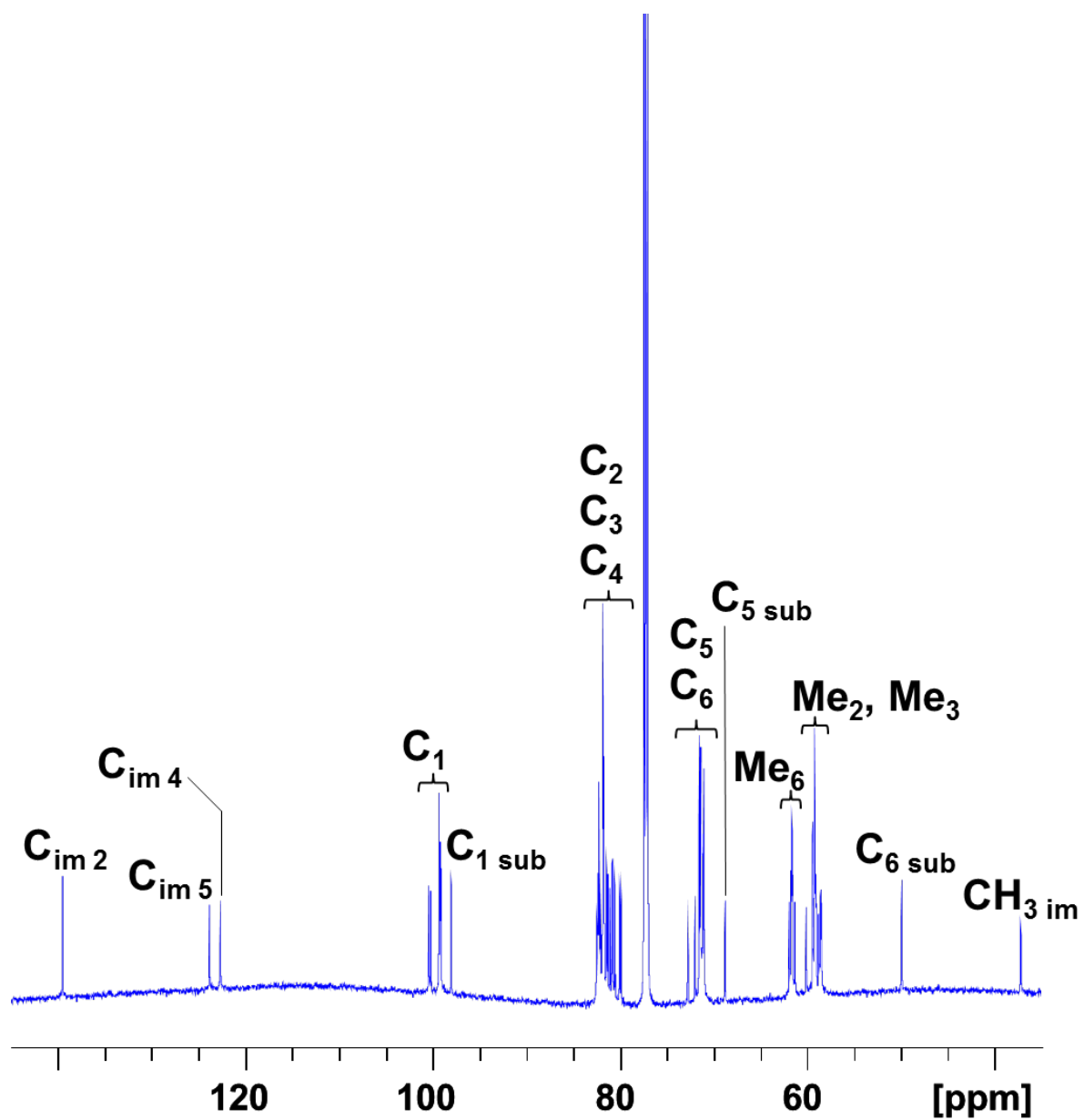
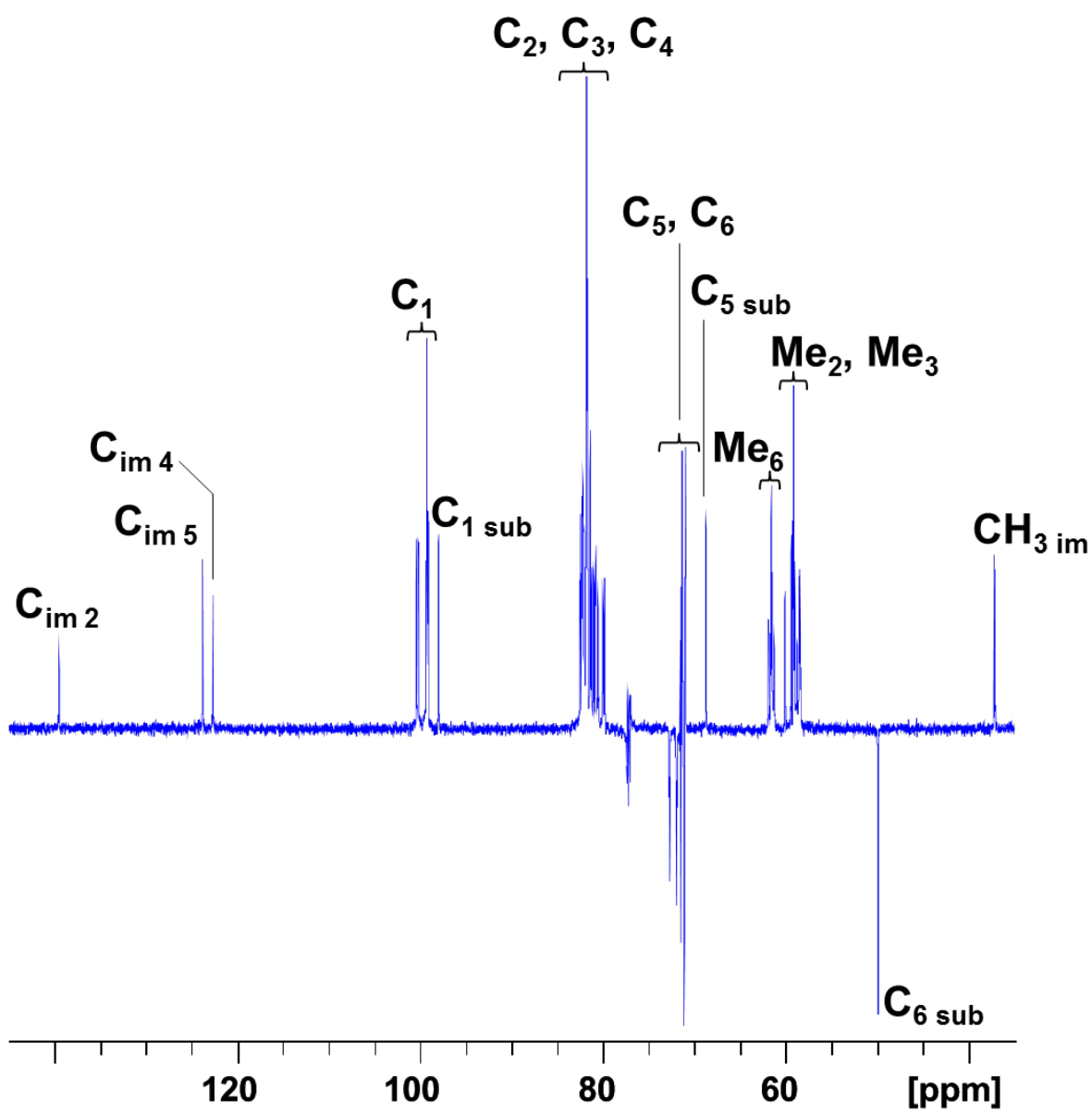
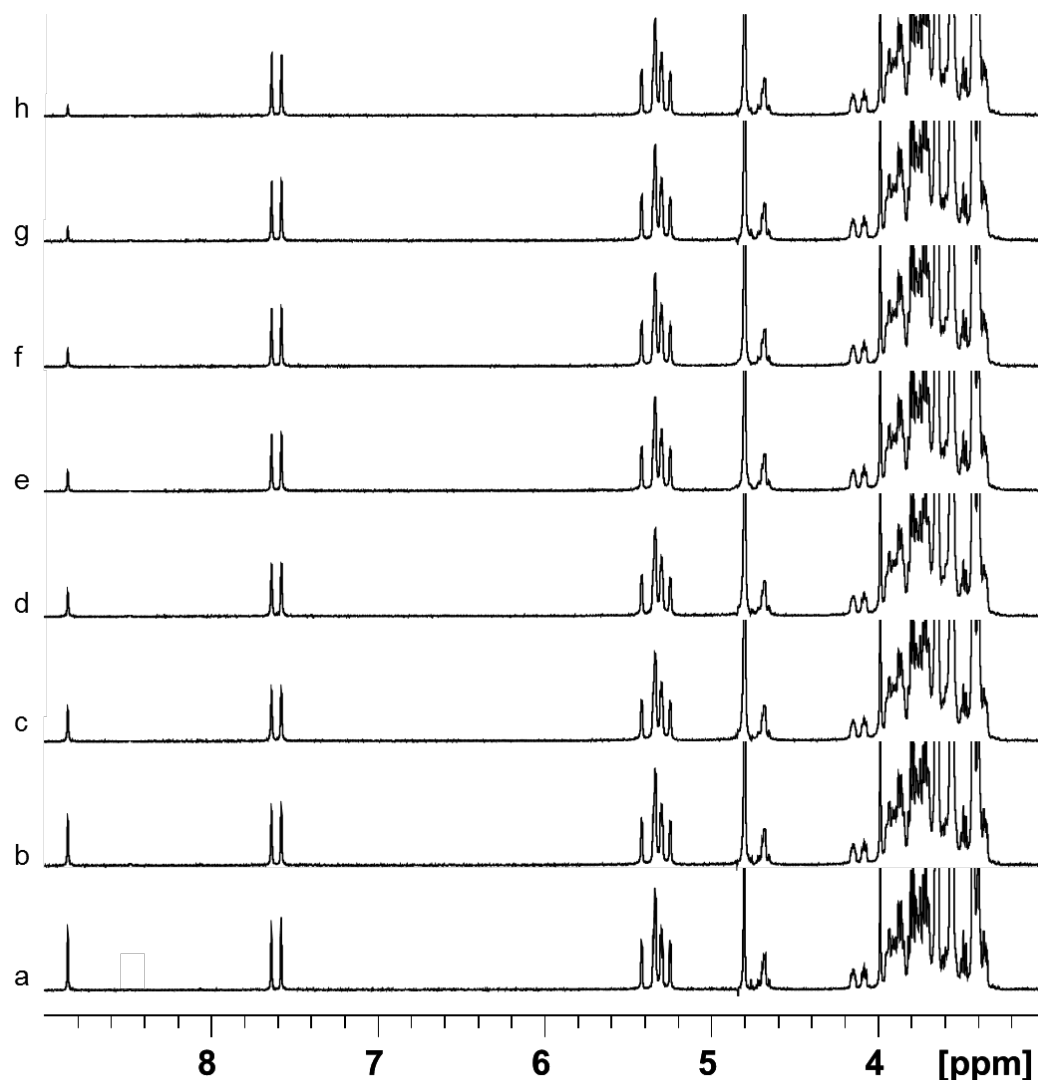


Figure S6: DEPT 135 NMR spectrum of **1** (293 K; 176.06 MHz; 8 mM in CDCl<sub>3</sub>).



**Figure S7:  $^1\text{H}$  NMR spectra in  $\text{D}_2\text{O}$  at 20 °C of **1** (2.0 mM) recorded initially (a) and after 45 (b), 105 (c), 165(d), 225 (e), 285 (f), 345 (g), 405 min (h).**



#### **Determination of the kinetic constant of the H/D exchange.**

600  $\mu\text{L}$  of a solution of **1** (2.0 mM in heavy water, pD 7.42) were introduced into a standard 5 mm NMR tube. Proton spectra were recorded regularly during one day at 293.15 K. The temperature control of the probe was approximately  $\pm 0.1$  °C. The kinetic of the H/D exchange was investigated by integration of the signal of the exchanging proton  $\text{H}_2$  at different times (the calibration of integral was performed from the value of the integral of an

unexchangeable proton, *i.e.* the proton H<sub>4</sub> or the proton H<sub>5</sub>; the deuteration of **1** during the acquisition of the spectra (around 5 min) must be negligible).

For a first-order H/D exchange reaction, the reaction kinetic follows the integrated rate law

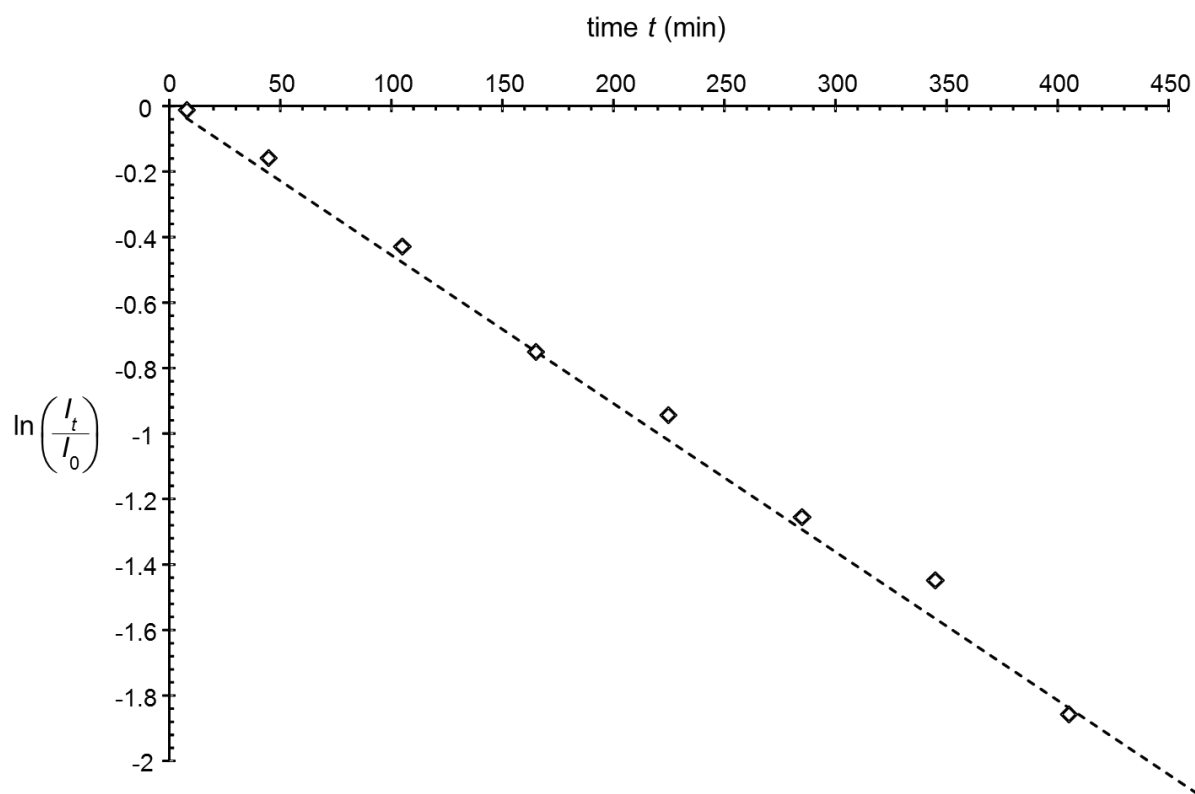
$\ln\left(\frac{[1]_t}{[1]_0}\right) = -k_{\text{H/D}} \times t$ . So, by plotting  $\ln\left(\frac{I_t}{I_0}\right)$  according to time  $t$ , with  $I_t$  the integral of the

exchanging proton at time  $t$  and  $I_0$  the integral of the exchanging proton at time 0, we can

determined the apparent constant ( $k_{\text{H/D}} = -$  slope) and the half-life time of the

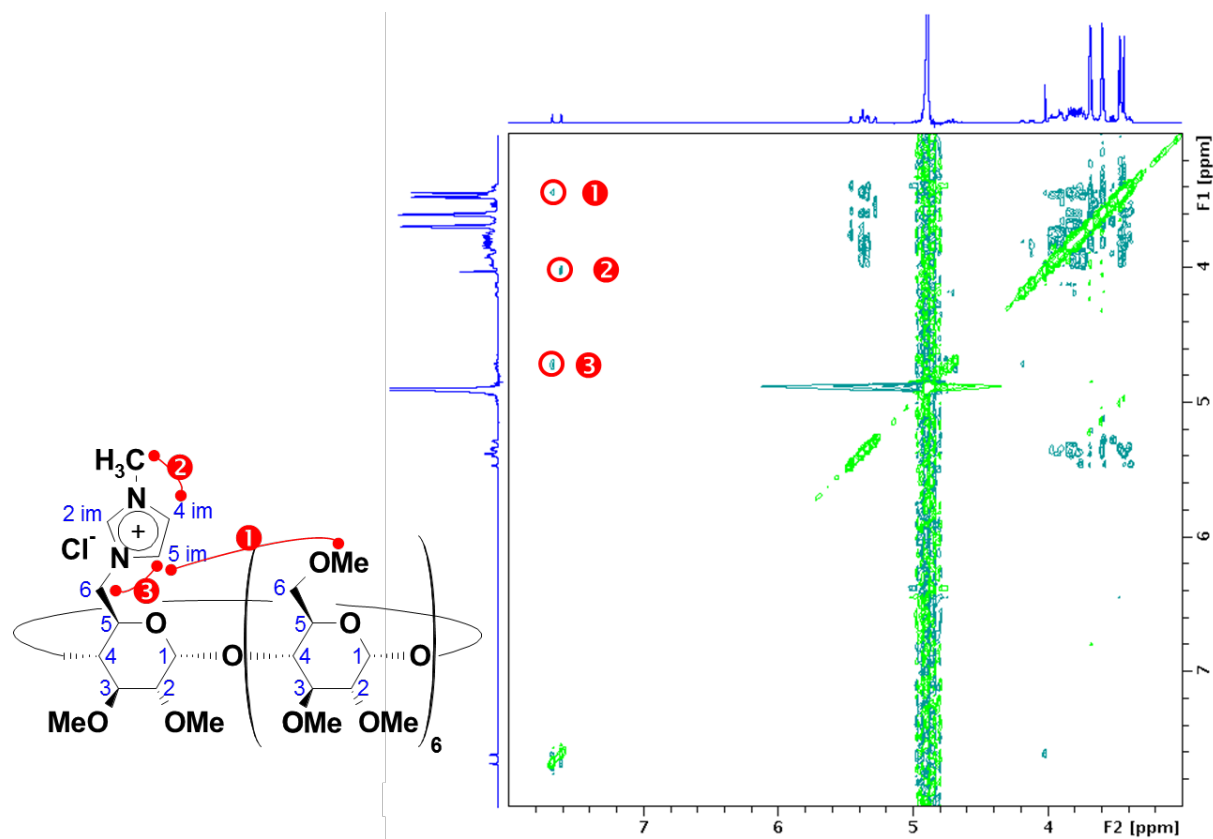
hydrogen/deuterium exchange . Since the plot obtained is linear ( $r^2 = 0.990$ ), we

can concluded that the hydrogen/deuterium exchange is of first-order.



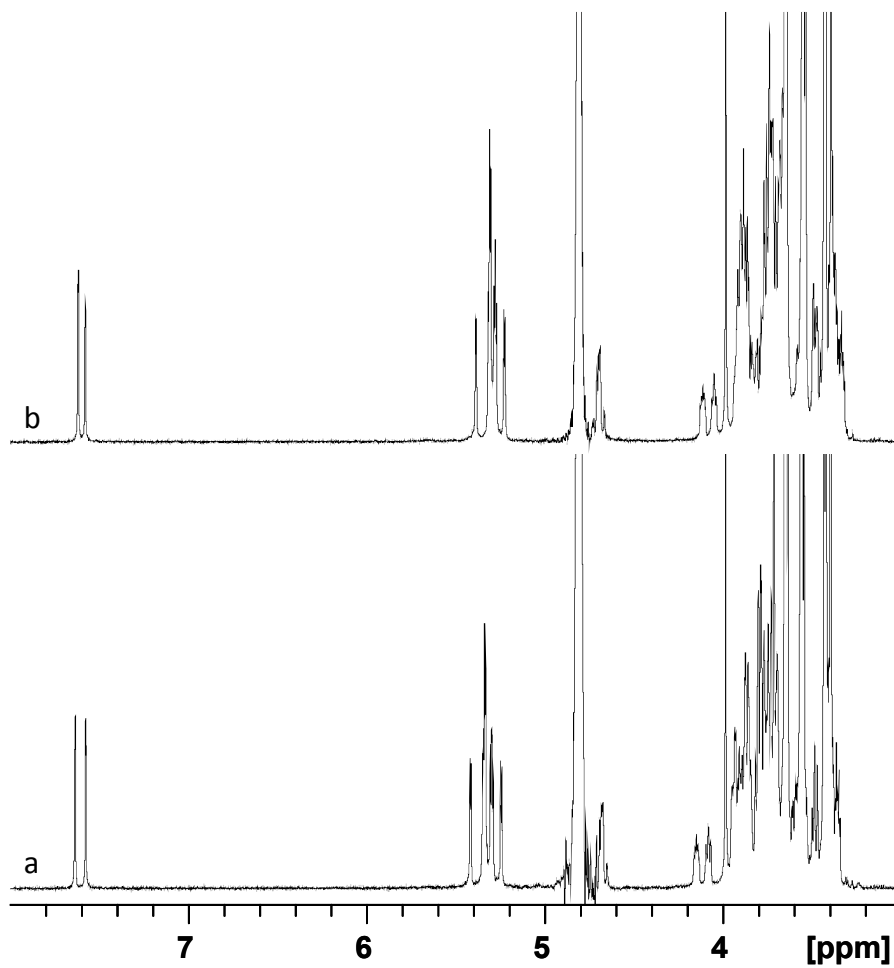
Fit between experimental (dots) and theoretical (line) evolution of  $\ln\left(\frac{I_t}{I_0}\right)$  against time.

**Figure S8: Off-resonance ROESY NMR spectrum of 1 (288 K; 600 MHz; 0.75 mM in D<sub>2</sub>O, mixing time: 400 ms).**

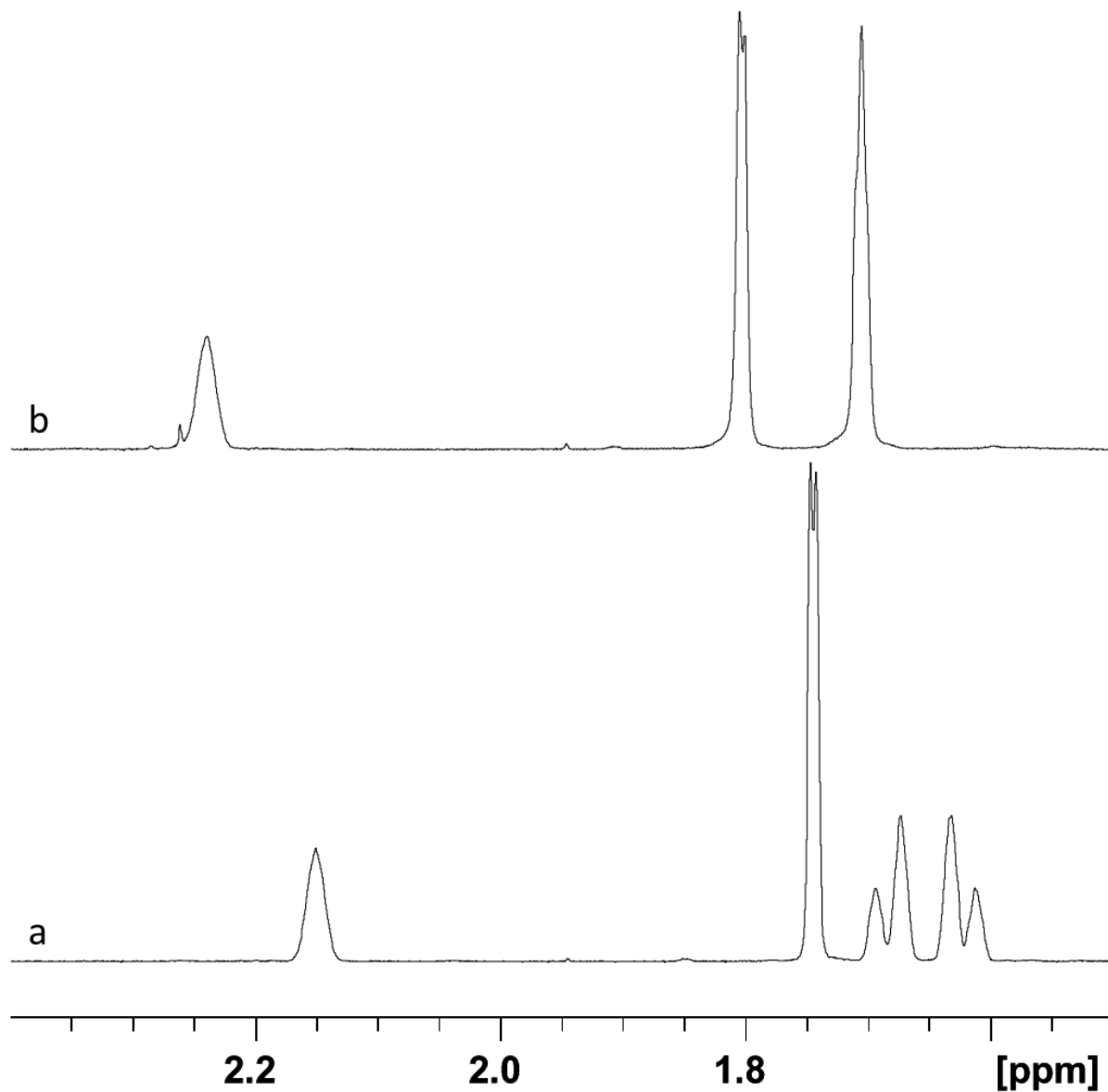


As explained on the scheme, no dipolar contact is observed between the imidazolium ring and internal protons of cyclodextrin moiety.

**Figure S9:  $^1\text{H}$  NMR spectra (293 K; 600 MHz;  $\text{D}_2\text{O}$ ) of 1 (0.75 mM; spectrum a) and of a mixture of 1/1-adamantanol (0.75 mM/2.25 mM; spectrum b).**



**Figure S10:**  $^1\text{H}$  NMR spectra (293 K; 600 MHz;  $\text{D}_2\text{O}$ ) of 1-adamantanol (2.25 mM; spectrum a) and of a mixture of 1/1-adamantanol (0.75 mM/2.25 mM; spectrum b).



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