**Electronic Supplementary Information for:**

# A Well-Behaved Dynamic Library of Cyclophane Formaldehyde Acetals Incorporating Diphenylmethane Units

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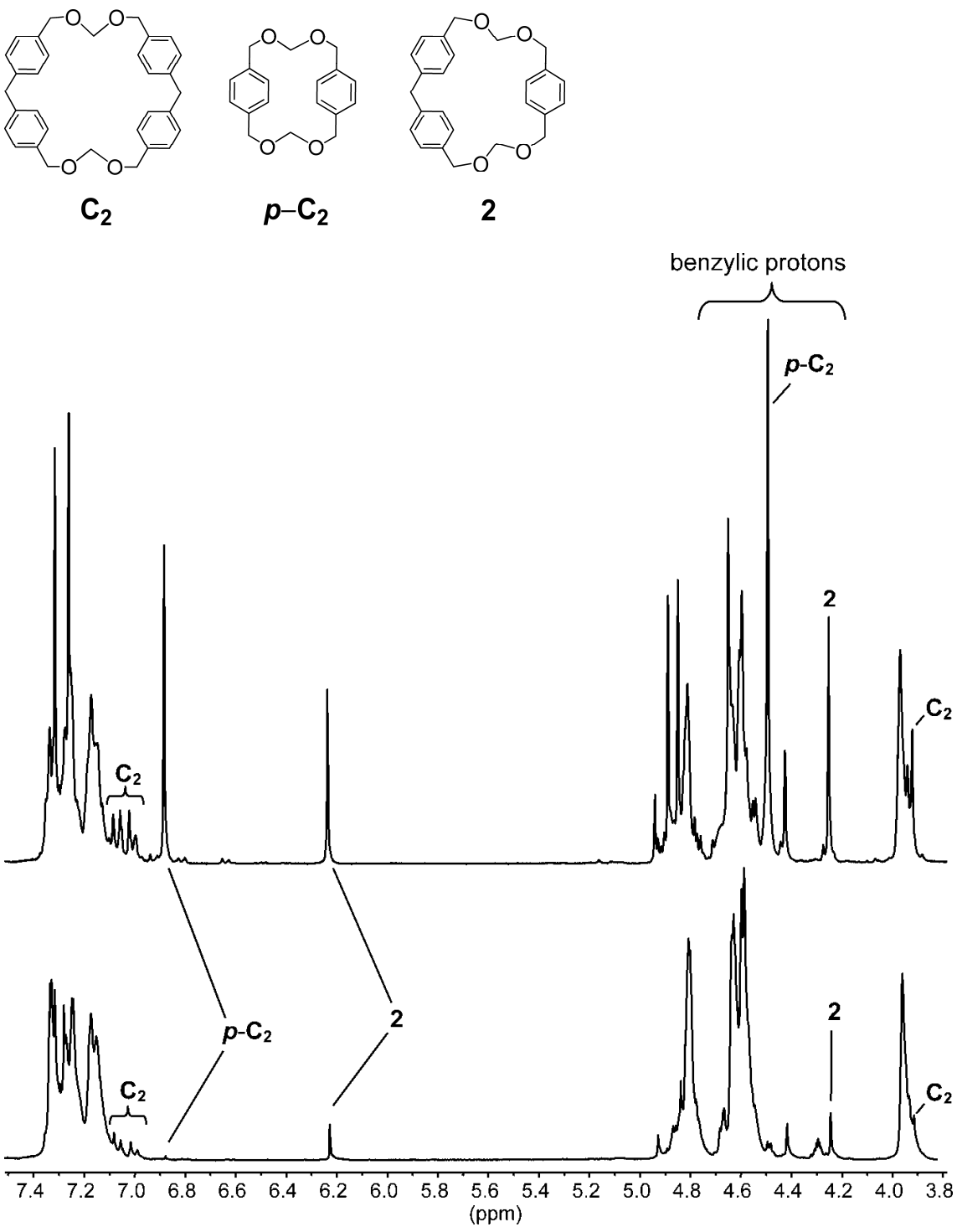
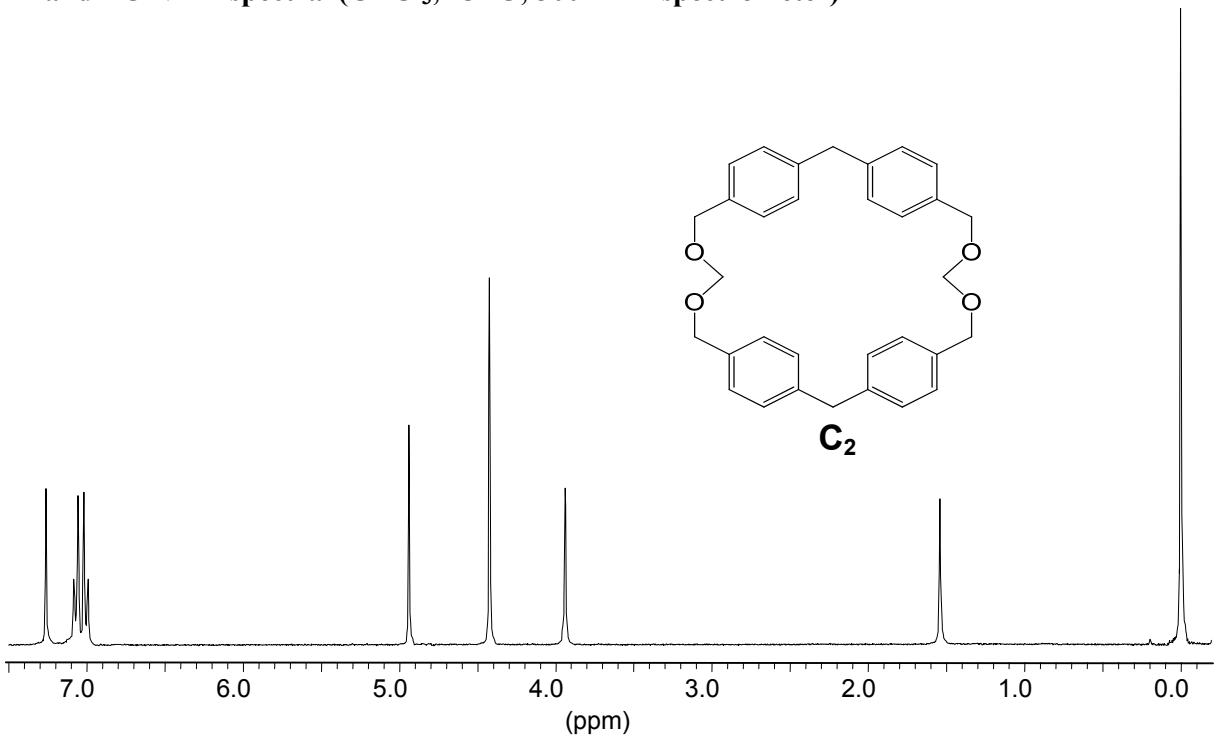
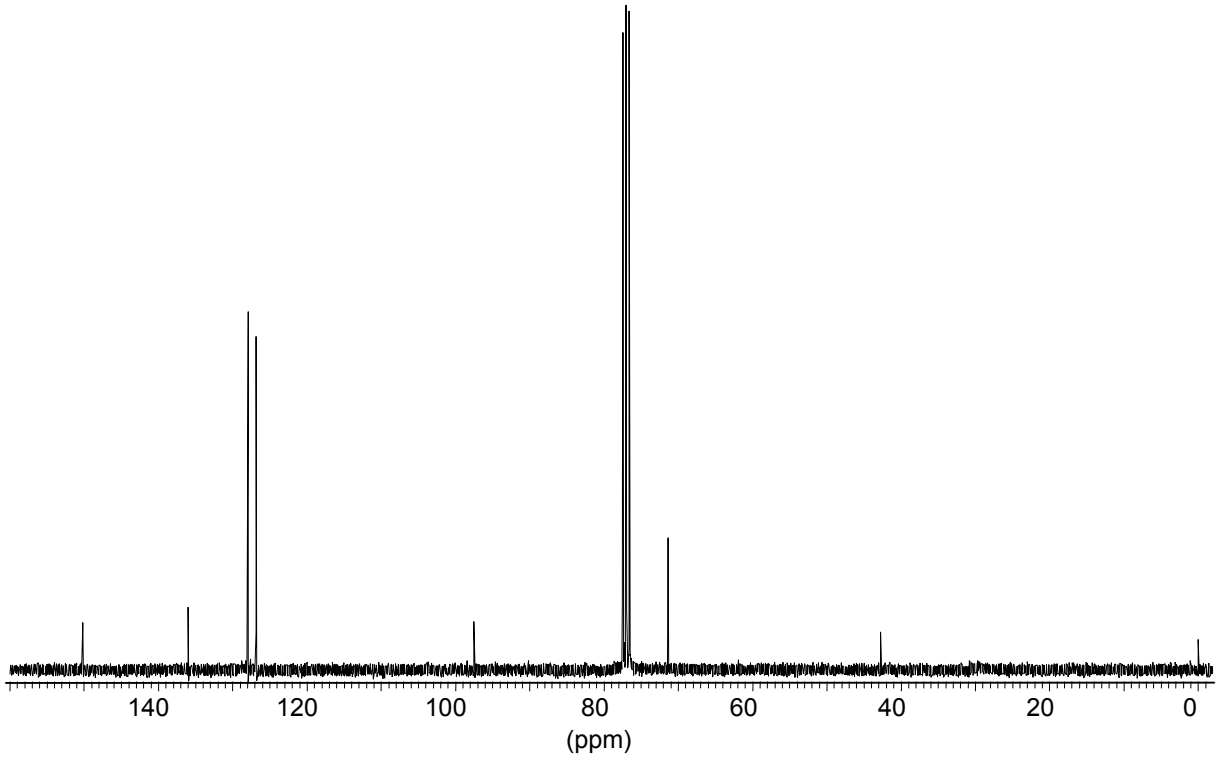
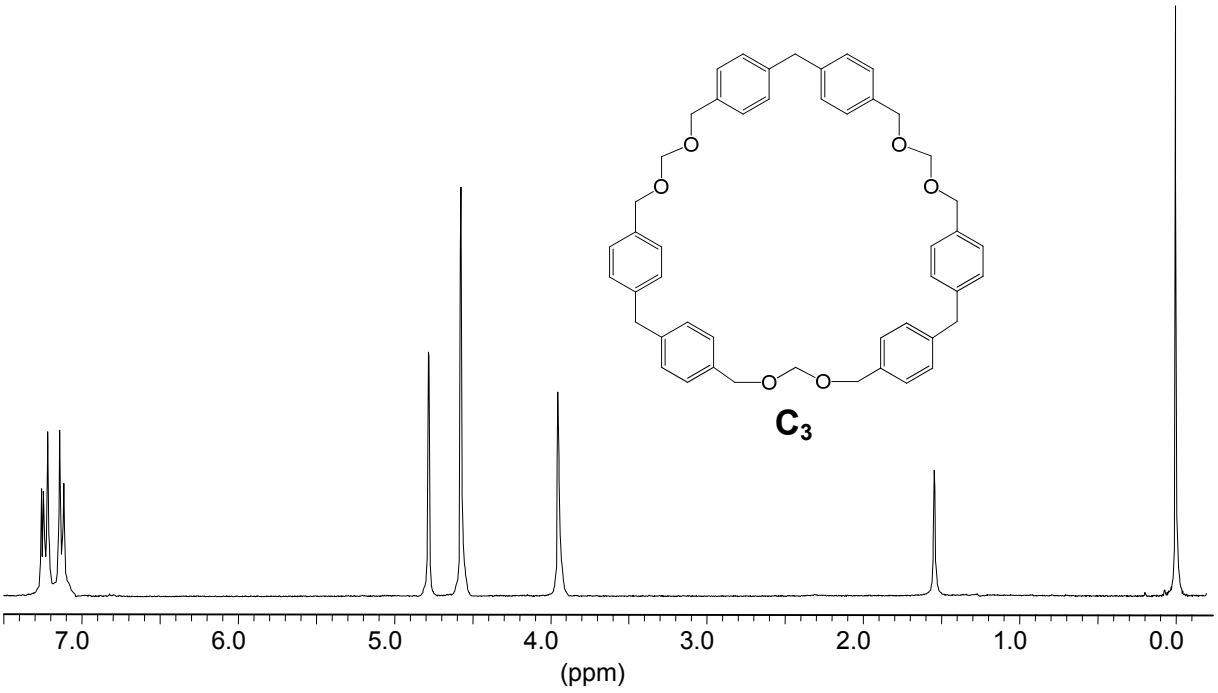


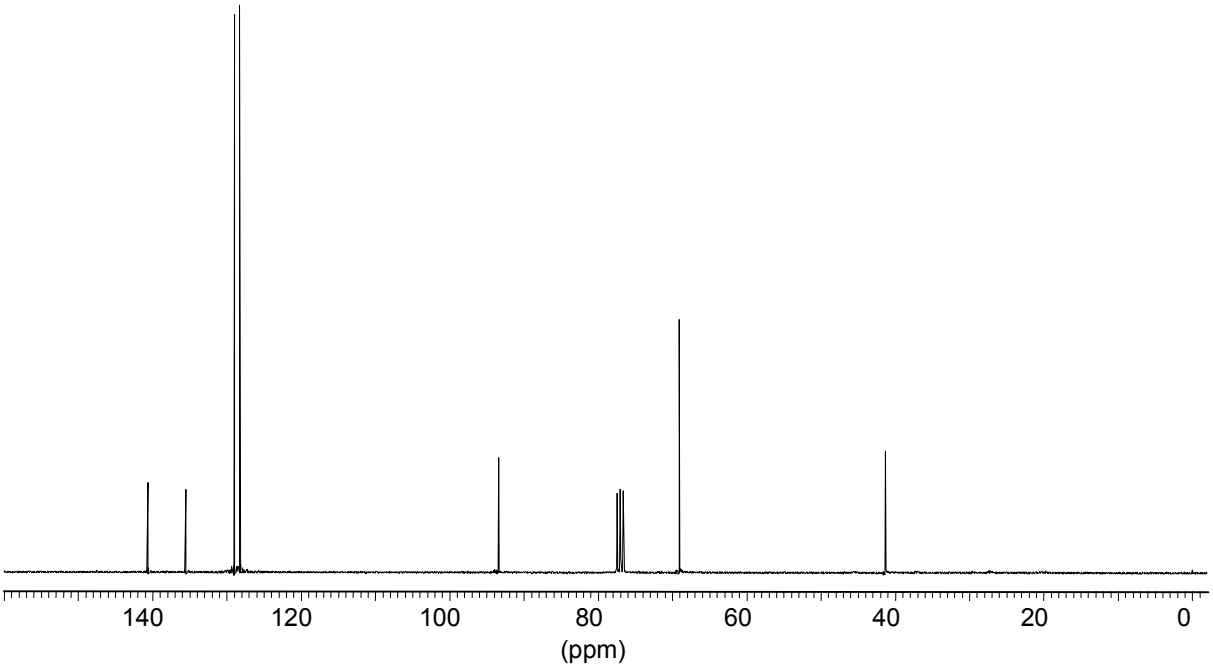

**Figure ESI1.** $^{1}$H NMR spectra ($CDCl_3$, 25 °C) of equilibrated solutions obtained from: 12.5 mM **C₂** + 12.5 mM ***p*-C₂**, TfOH catalyst; (bottom); 12.5 mM **C₂** + 12.5 mM ***p*-C₂** equilibrated in the presence of TfOH catalyst and excess solid $AgNTf_2$, after removal of $Ag^+$ template by extraction with aqueous ammonia (top).

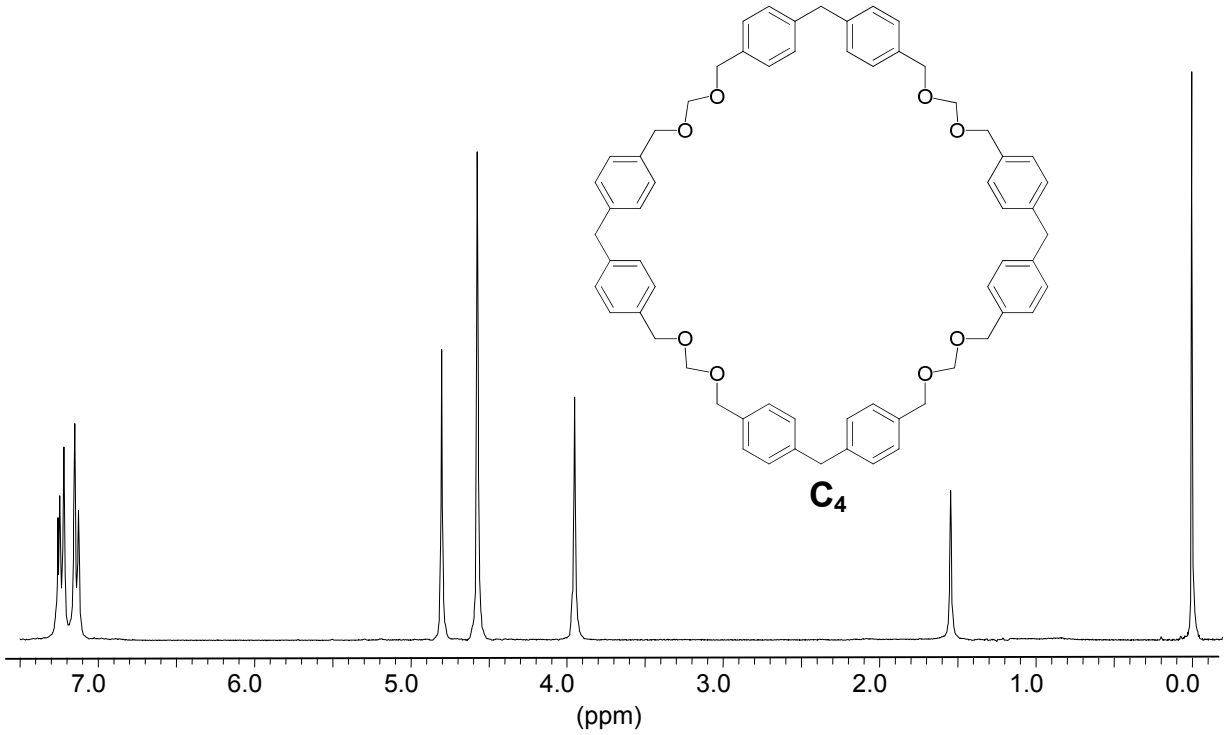
**$^{1}$H and $^{13}$C NMR spectra (CDCl$_3$, 25 °C; 300 MHz spectrometer)**

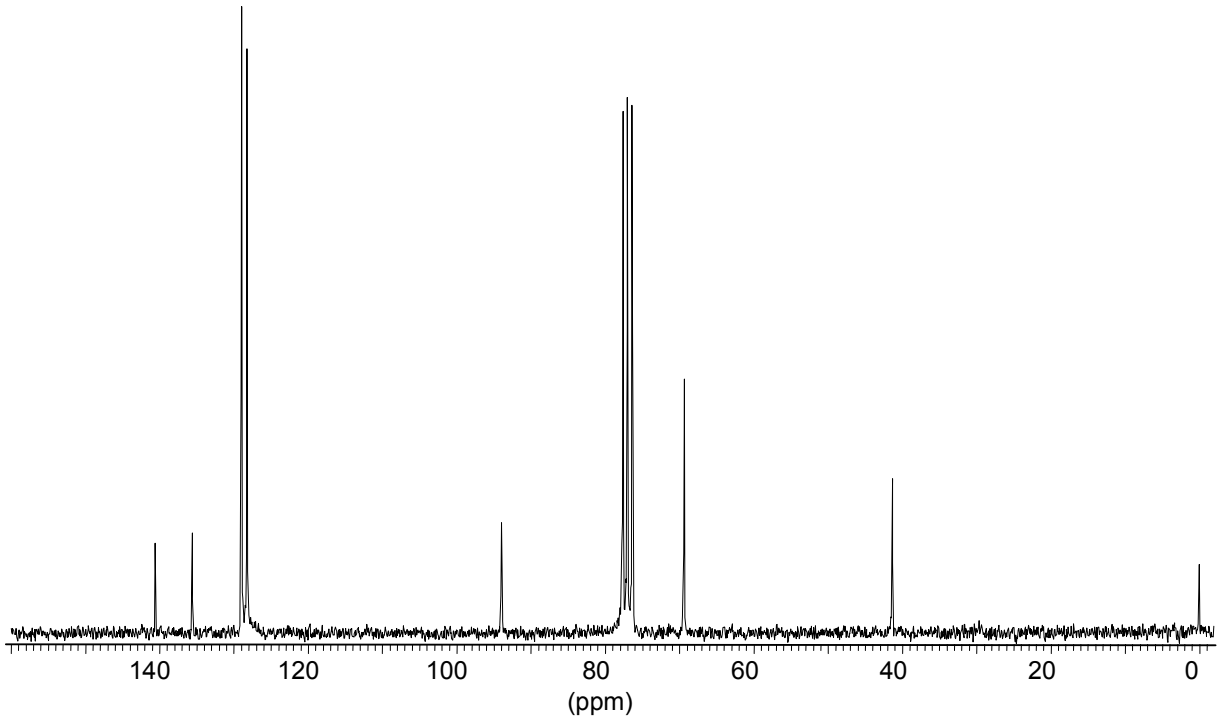


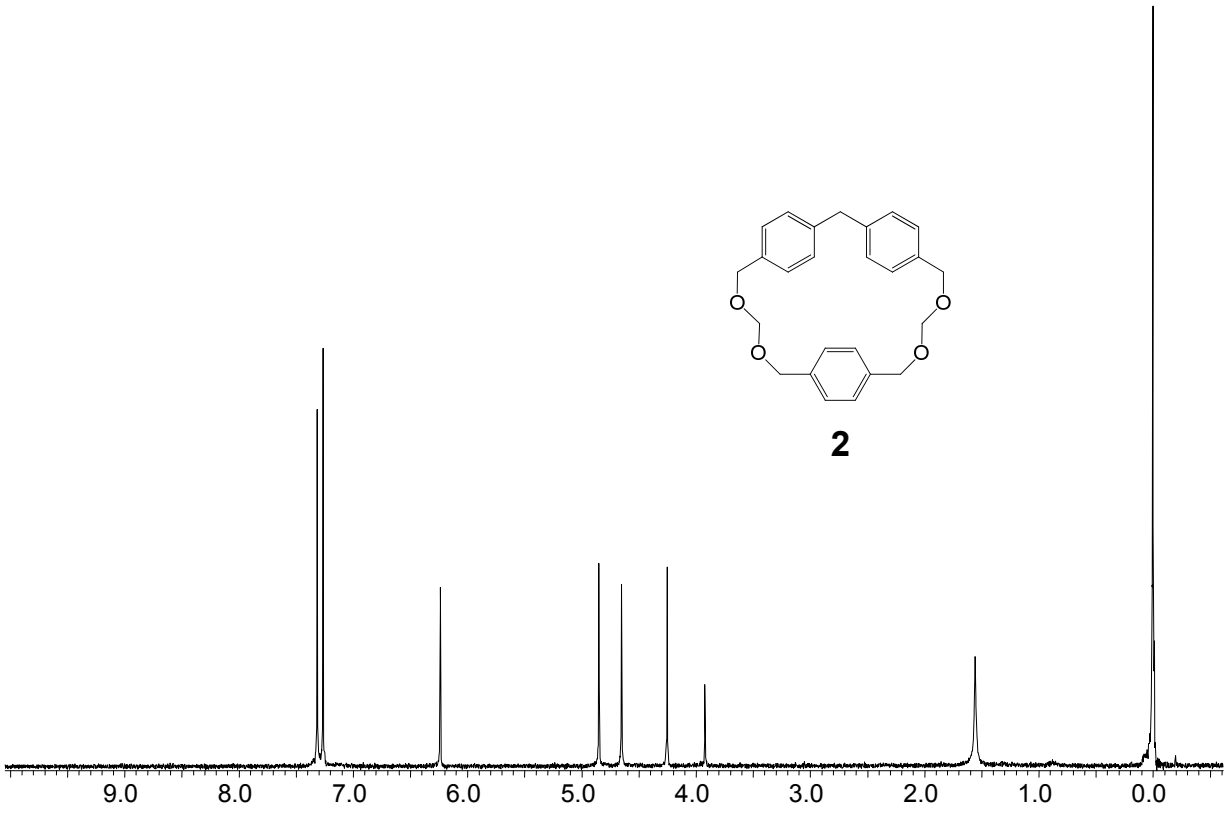





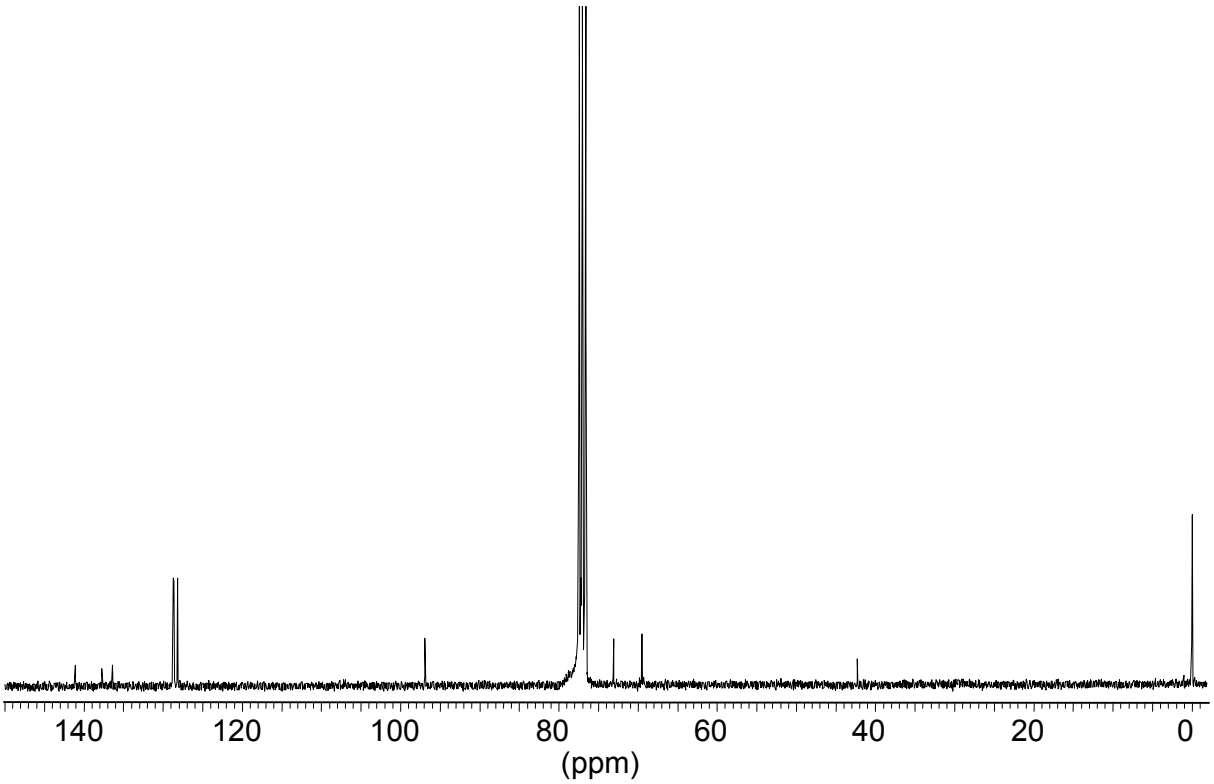








**2**



**Evaluation of *EM* and of Strain Energy**

According to the Jacobson-Stockmeyer theory[1] the limiting values of the saturation profiles reported in Figure 3 coincide with the *EM*'s of the macrocycles. The analytical form for the relation between $\mathbf{C_i}$ and $c_{mon}$ cannot be derived by the theory but surprisingly the simple exponential equation fits remarkably well the experimental points. Thus, the equation $[\mathbf{C_i}] = EM_i\,[1 - \exp(-a\,c_{mon})]$, where $EM_i$ and $a$ are adjustable parameters, was used to fit the experimental data in the plot of $[\mathbf{C_i}]$ vs. $c_{mon}$. The optimized values of $EM_i$ and of $a$, together with the rms deviations are reported below:

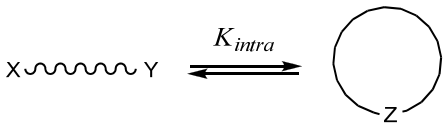
$\mathbf{C_2}$: $EM$ = 4.36 mM, $a$ = 0.0485 $mM^{-1}$ ; rms = 0.12 mM.

$\mathbf{C_3}$: $EM$ = 1.45 mM, $a$ = 0.0364 $mM^{-1}$ ; rms = 0.033 mM.

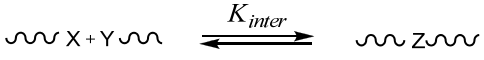
The obtained values of *EM* have been used to estimate the strain energy of the two macrocycles resorting to the extrathermodynamic treatment of *EM*'s due to Mandolini.[2] Eqs 1 and 2 can be derived from this treatment and are related to the hypothetical intramolecular and intermolecular reactions described in Eqs 3 and 4 respectively. Eq 2 is a compact form of Eq 1, where the quantities $EM_H$ and $EM_S$, defined in the given order by the exponential terms of Eq 1, are the enthalpic and entropic component of the *EM*.

$$EM = \exp\left[-\left(\Delta H^{\circ}_{intra} - \Delta H^{\circ}_{inter}\right)/RT\right]\exp\left[\left(\Delta S^{\circ}_{intra} - \Delta S^{\circ}_{inter}\right)/R\right] \qquad (1)$$

$$EM = EM_H \times EM_S \qquad (2)$$




(3)




(4)

The quantity $(\Delta H^{\circ}_{intra} - \Delta H^{\circ}_{inter})$ is a measure of the strain energy of the given macrocycle. For a strainless macrocycle $EM_H$ = 1, and the *EM* is solely determined by the entropic component, $EM = EM_S$.

The pertinent $EM_S$ values for $\mathbf{C_2}$ and $\mathbf{C_3}$ were taken from a compilation[2,3] of the entropic component of *EM* as a function of the number of rotatable bonds *r* in the linear precursor of the given macrocycle. For the present $\mathbf{C_i}$ system, $r_i = 8i-1$. Division of these $EM_S$ values by the symmetry number $\sigma$ of the investigated macrocycle $\mathbf{C_i}$, namely, $\sigma_i = 2i$, gave the symmetry corrected values *EM** of the entropic component of the effective molarity. The strain energy of the macrocycles $\mathbf{C_2}$ and $\mathbf{C_3}$ was then calculated as $RT \ln(EM_i^*/EM_i)$.


1 (*a*) H. Jacobson and W.H. Stockmayer, *J. Chem. Phys.*, 1950, **18**, 1600–1606; (*b*) G. Ercolani, L. Mandolini, P. Mencarelli and S. Roelens, *J. Am. Chem. Soc.*, 1993, **115**, 3901–3908; (*c*) S. Di Stefano, *J. Phys. Org. Chem.*, 2010, **23**, 797–805 and references cited therein.

2 L. Mandolini, *Adv. Phys. Org. Chem.*, 1986, **22**, 1–111.

3 C. Galli and L. Mandolini, *Eur. J. Org. Chem.*, 2000, 3117-3125.