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Supporting Information

for

Bambusuril analogs based on alternating glycoluril and xylylene units

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MS and NMR spectra, computational details and crystallographic data for macrocycles 1a and 1b

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MALDI:

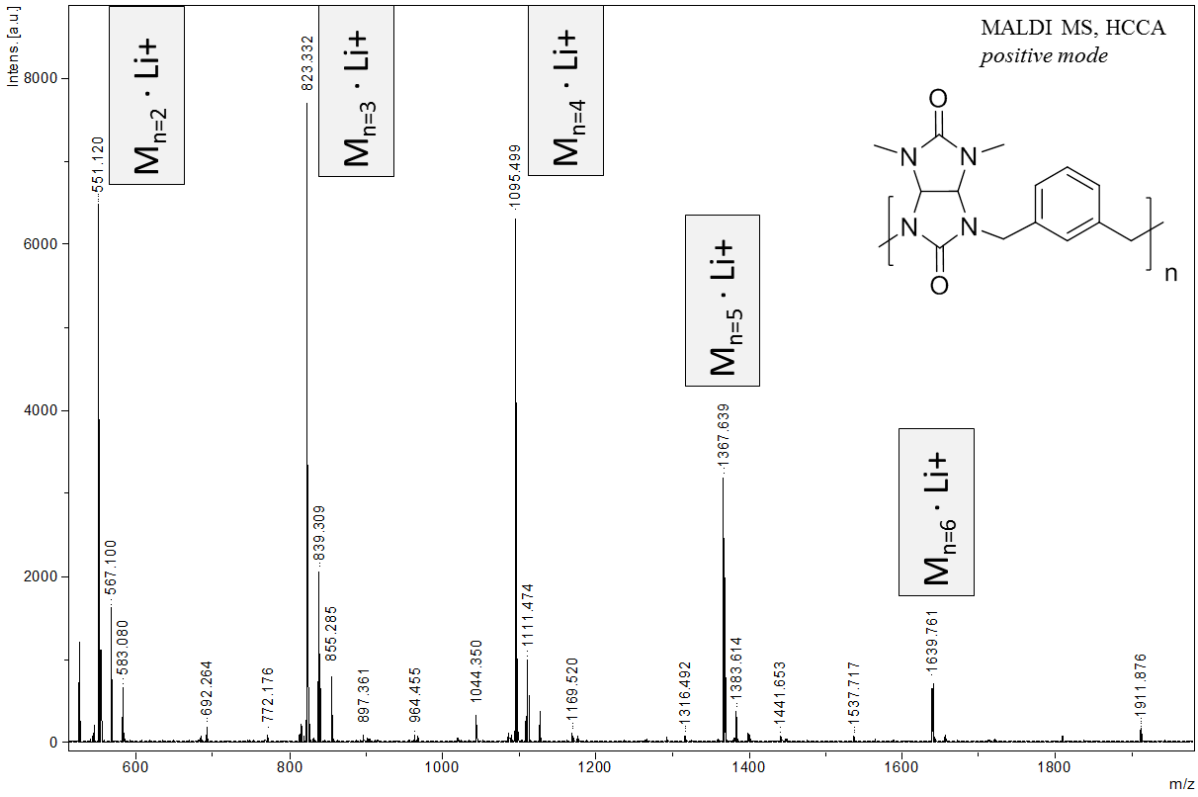

Figure S1: MALDI MS spectra of the crude product.

HPLC

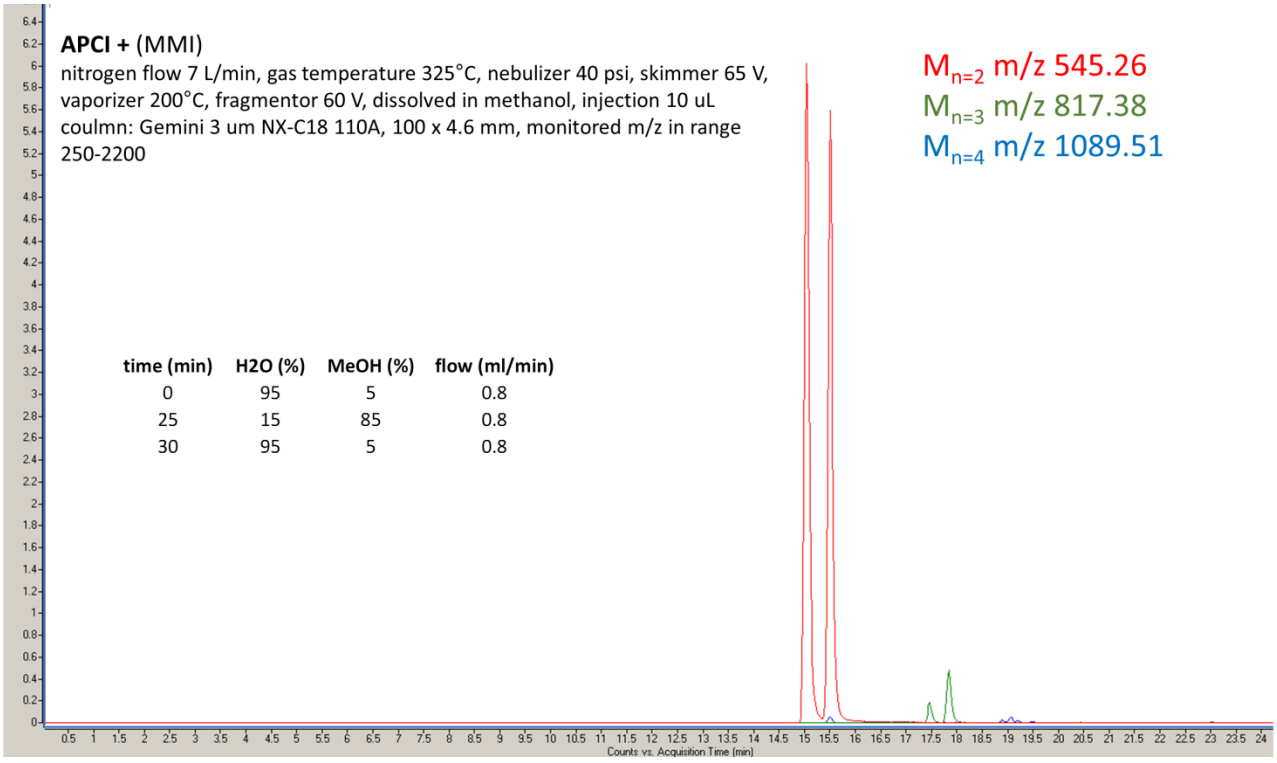

Figure S2: HPLC-MS analysis of the crude product.

HR-MS:

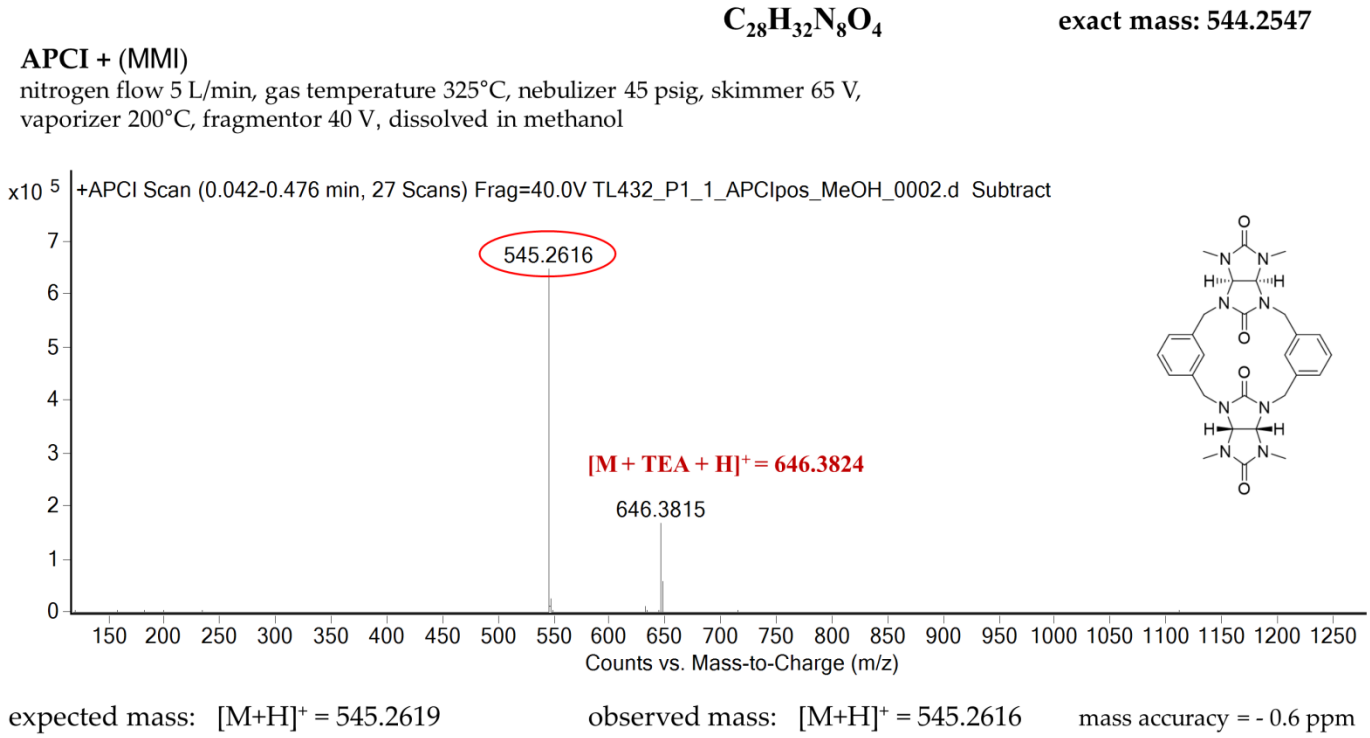

Figure S3: HR-MS analysis of **1a**.

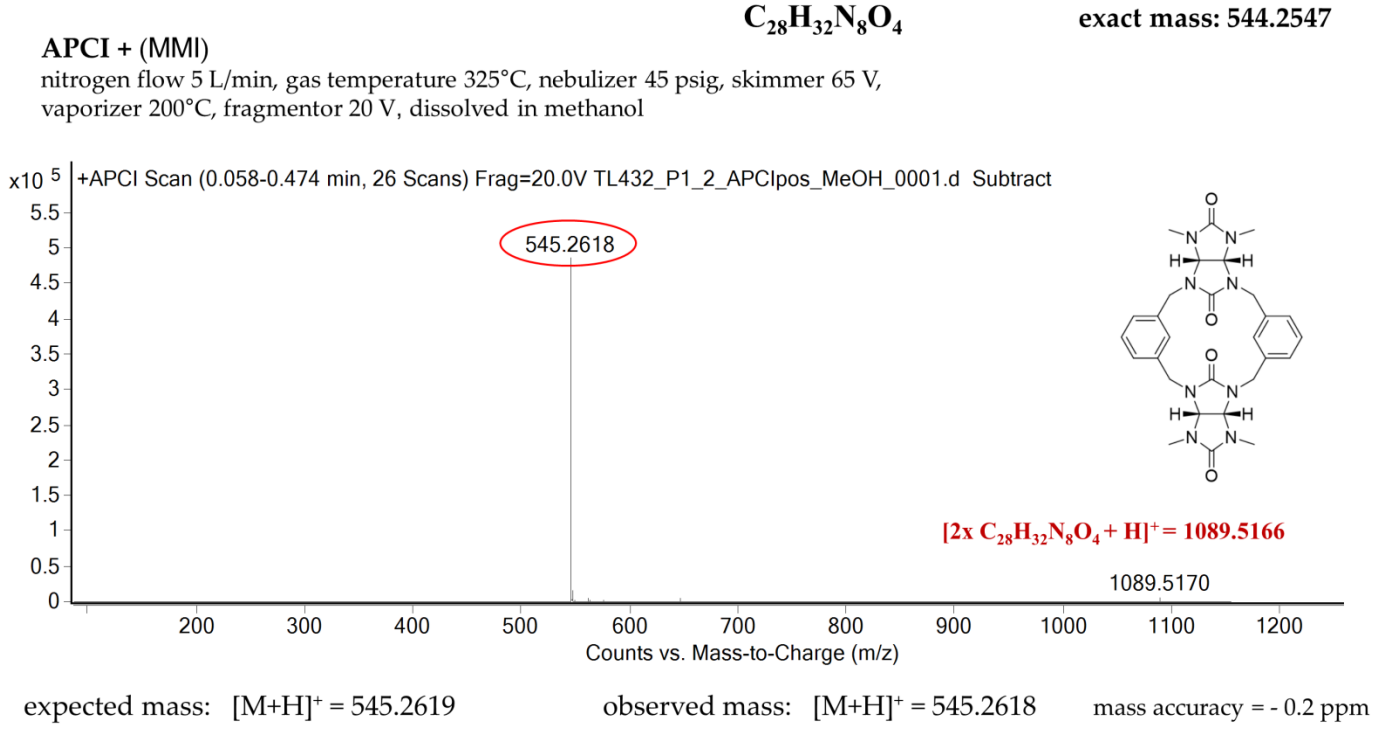

Figure S4: HR-MS analysis of **1b**.

NMR:

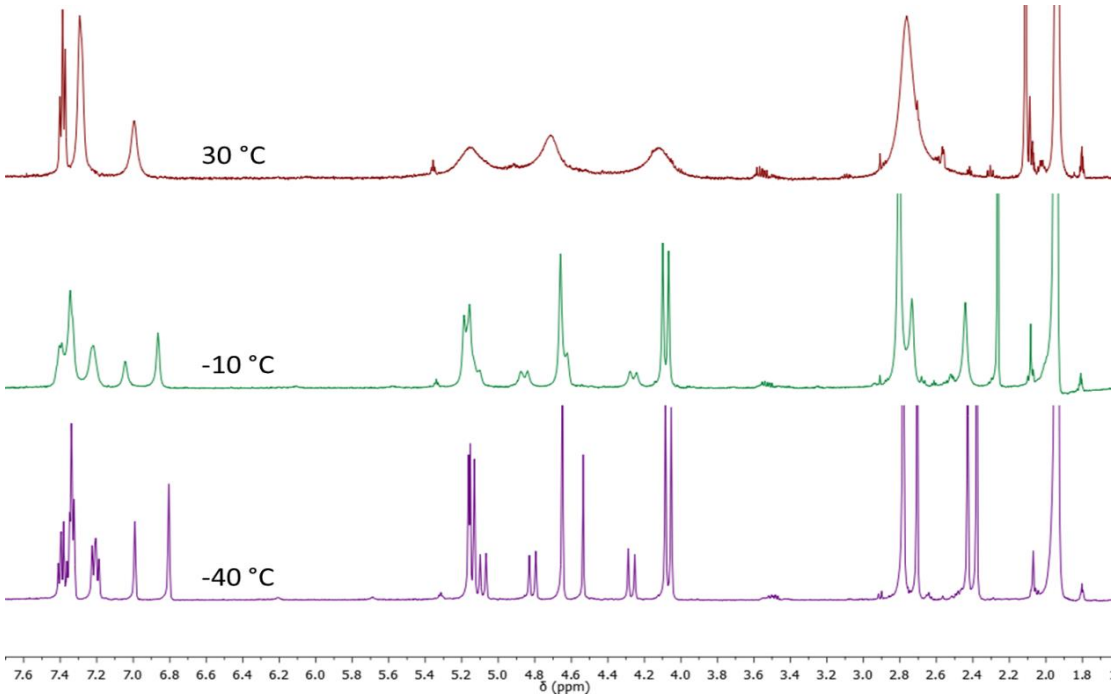

Figure S5: Variable-temperature ^{1}H NMR spectrum of **1a** measured at 30 °C, −10 °C and −40 °C in MeCN-d_3.

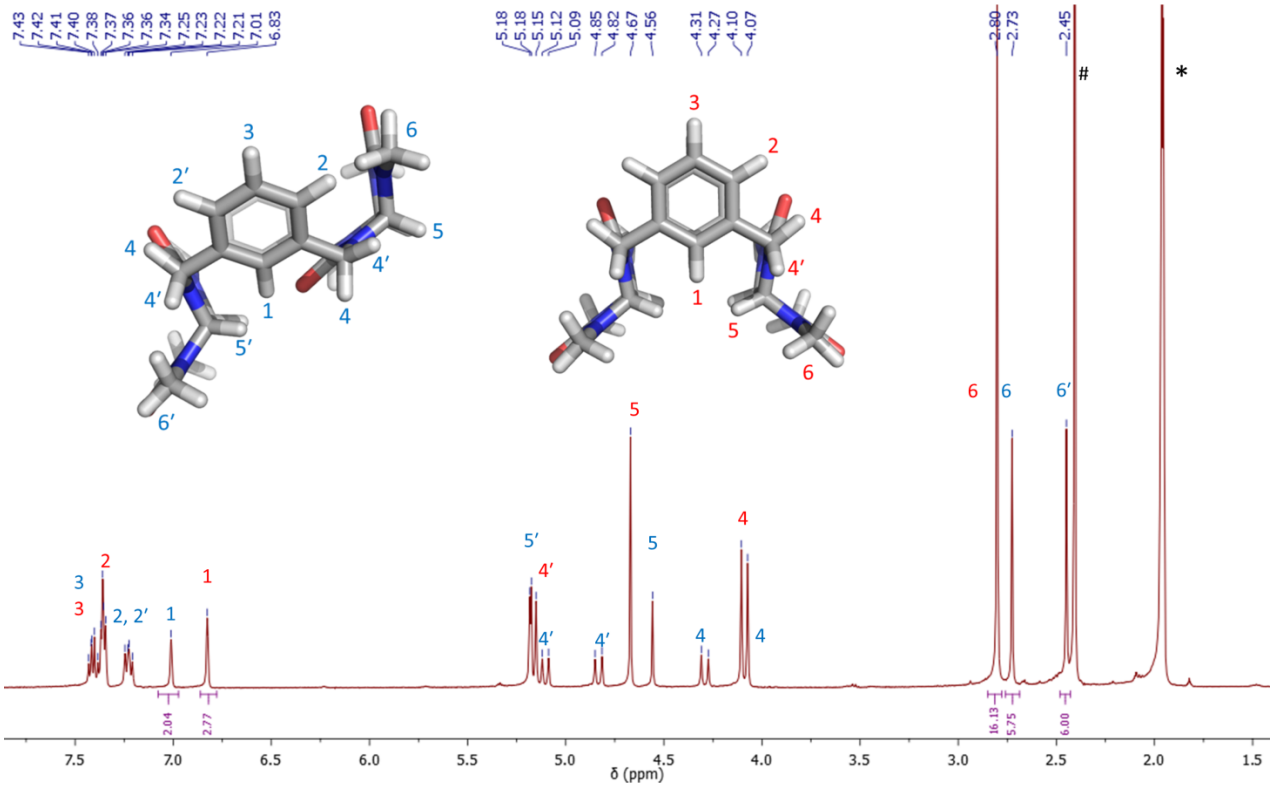

Figure S6: ^{1}H NMR spectrum of **1a** measured at −40 °C in MeCN-d_3 , $^{\#}$HDO signal, *MeCN signal.

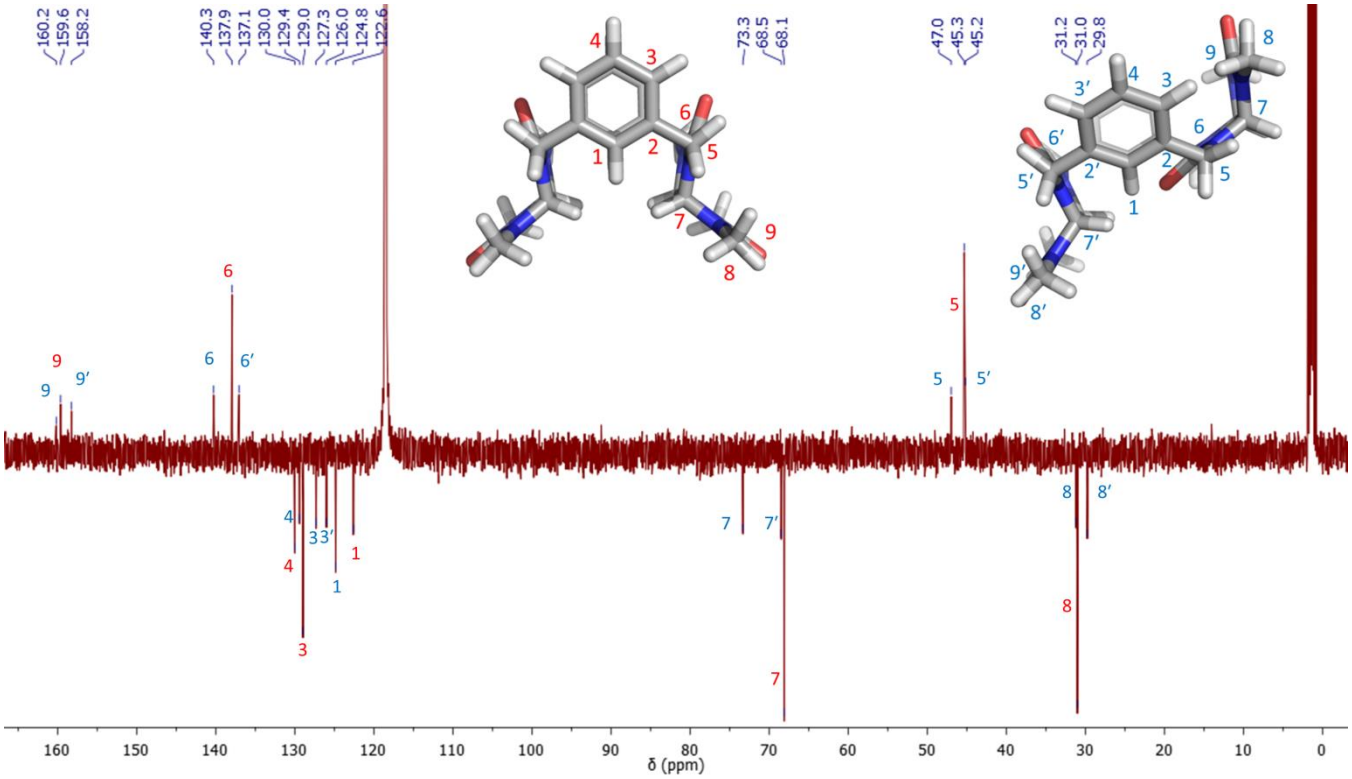

Figure S7: ^{13}C APT NMR spectrum of **1a** measured at −40 °C in MeCN-d_3.

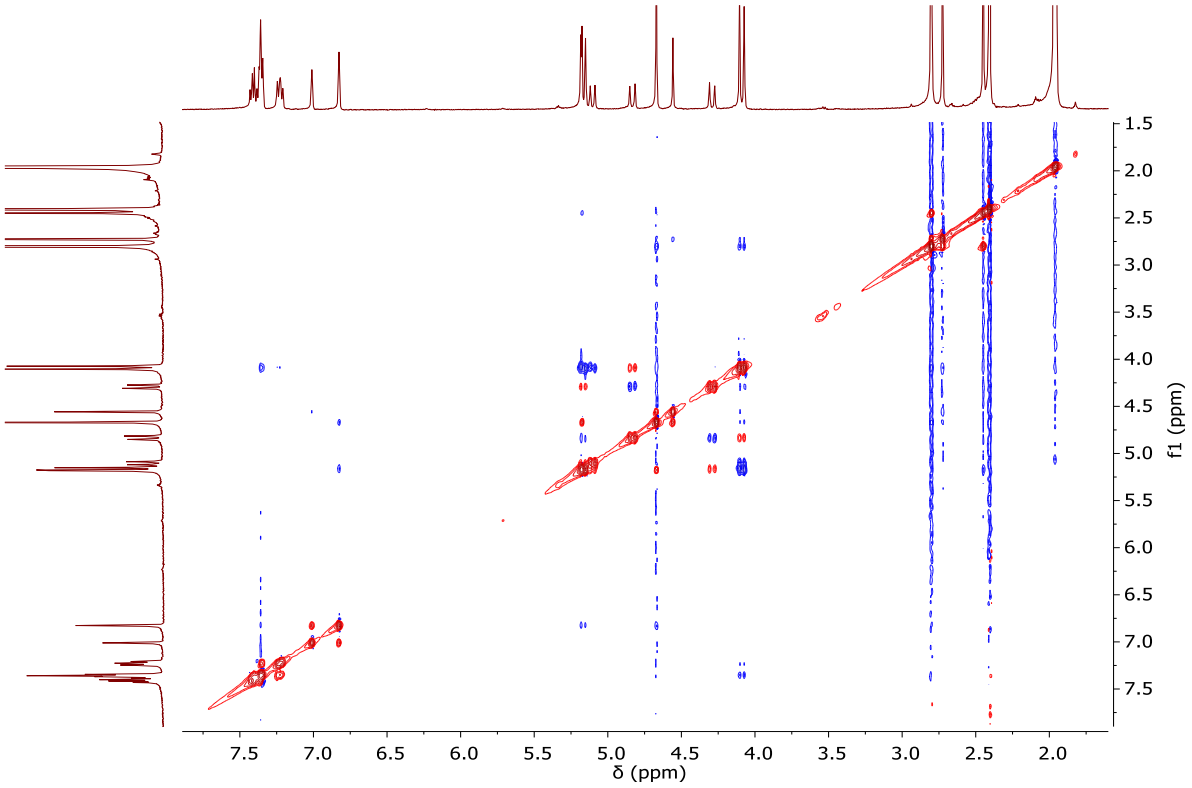

Figure S8: ROESY NMR spectrum of **1a** measured at −40 °C in MeCN-d_3.

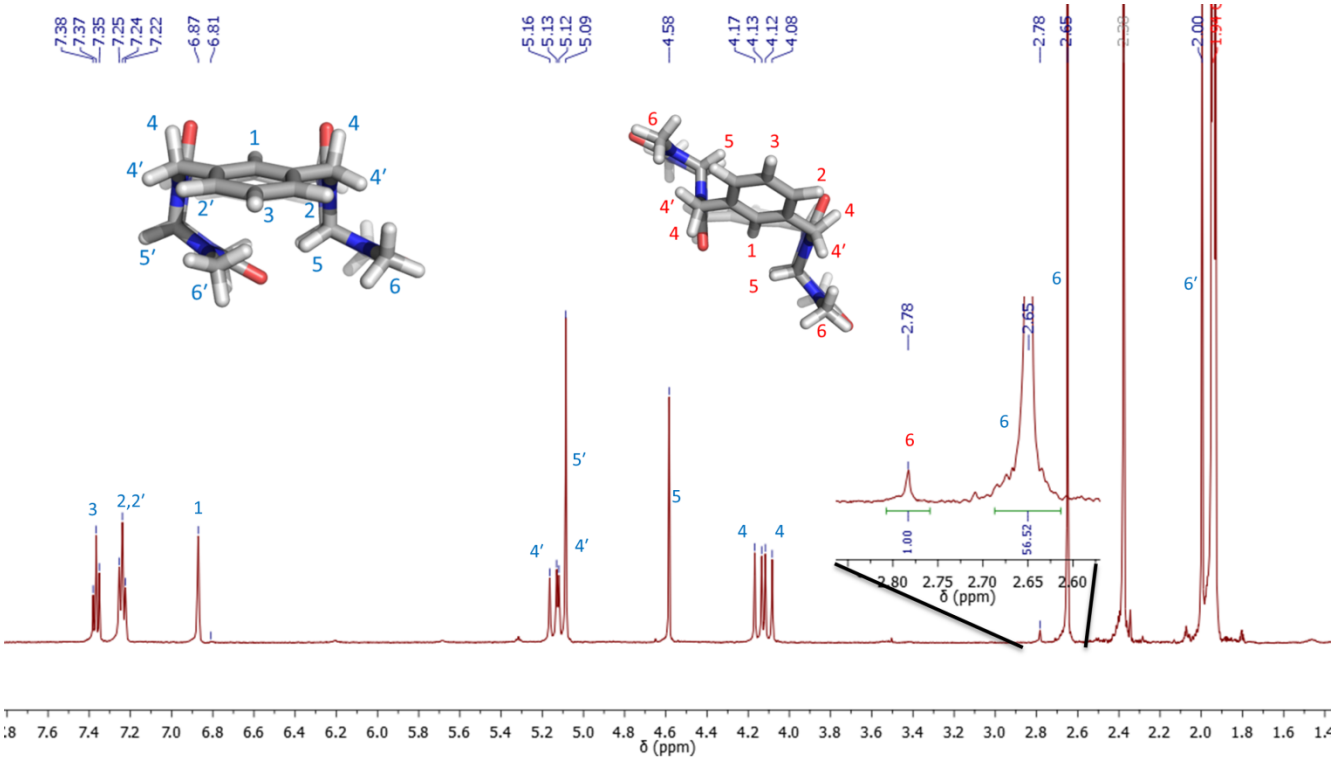

Figure S9: ^{1}H NMR spectrum of **1b** measured at −40 °C in MeCN-d_3.

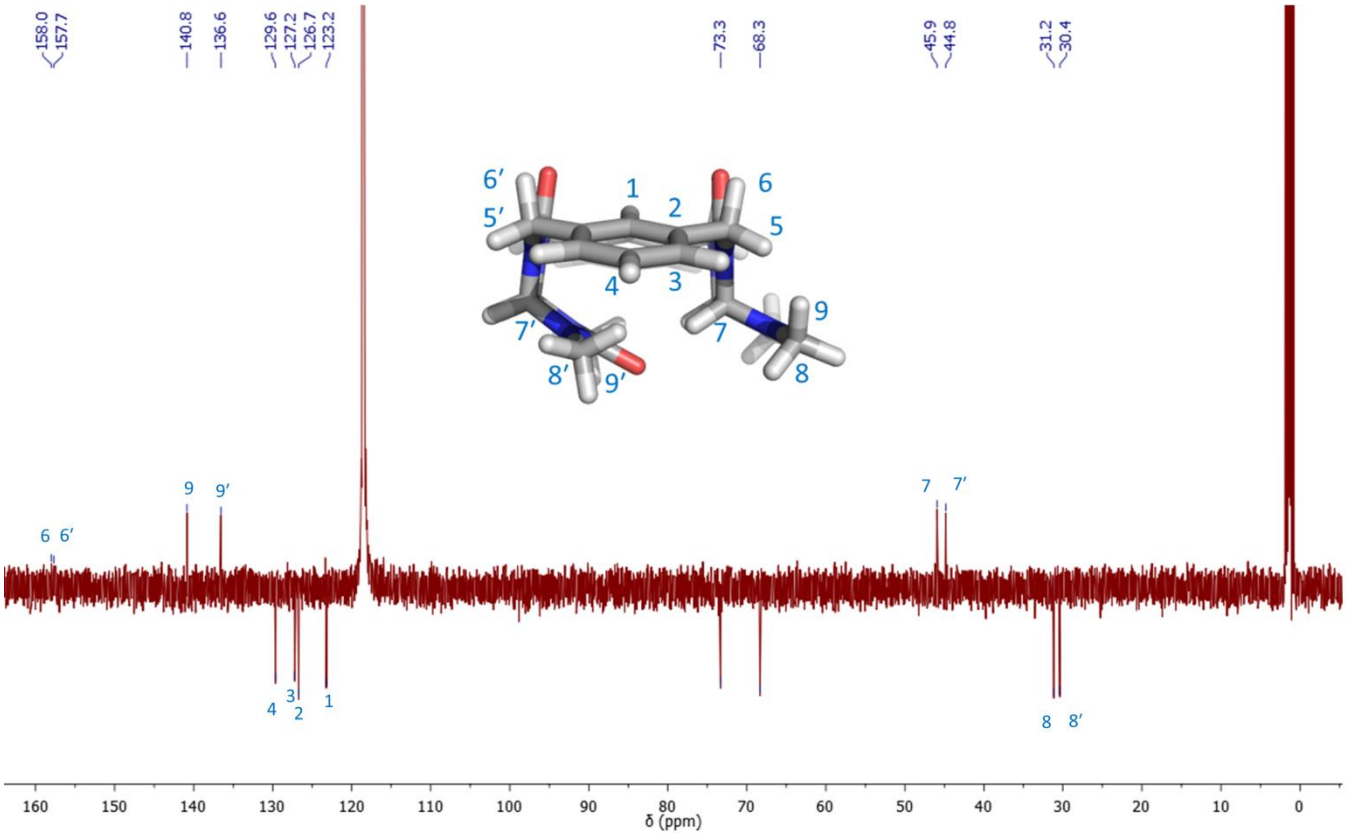

Figure S10: ^{13}C APT NMR spectrum of **1b** measured at −40 °C in MeCN-d_3.

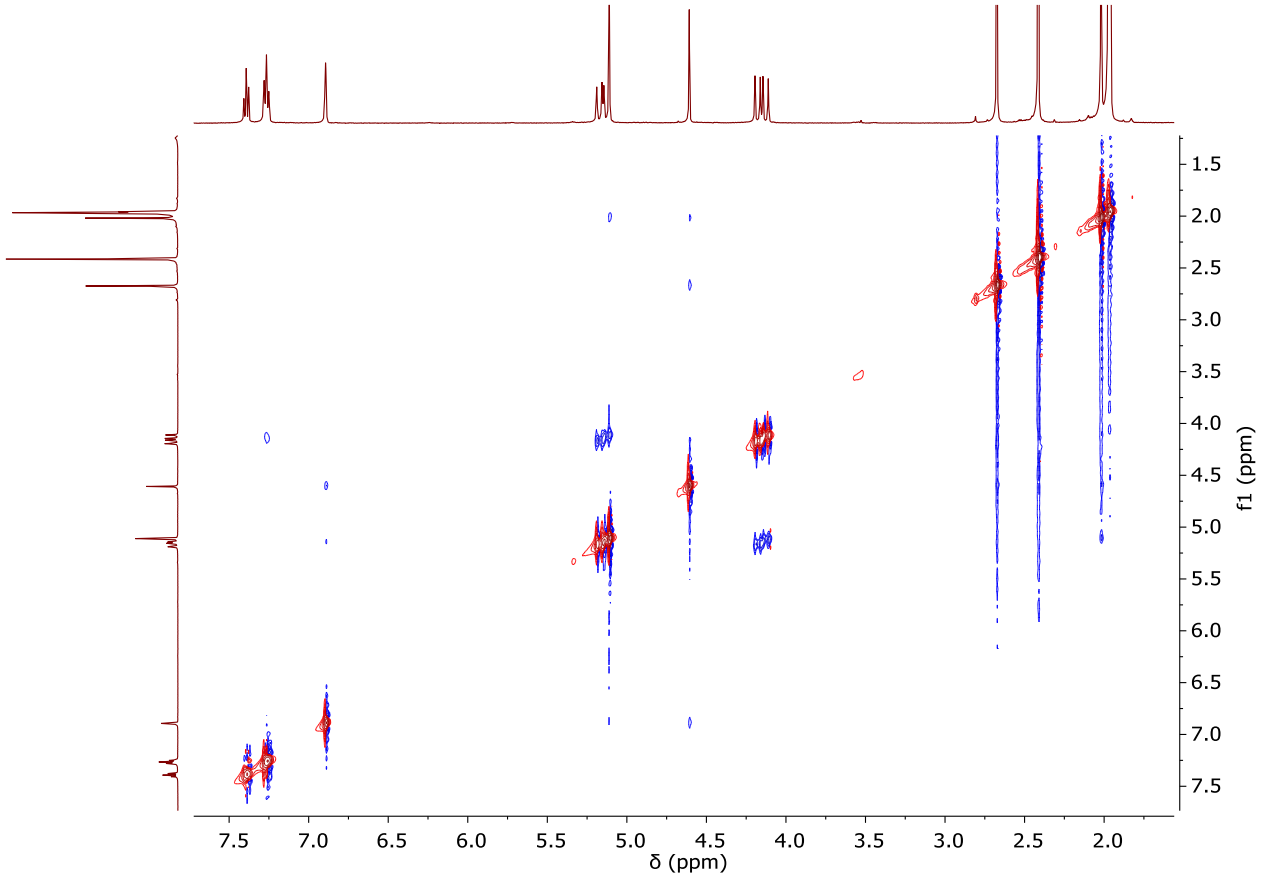

Figure S11: ROESY NMR spectrum of **1b** measured at −40 °C in MeCN-d_3.

Determination of energy difference of conformers:

Application of Boltzmann equation:

The energy differences in of the conformers were calculated using equation (1)[1],

$$\frac{N_i}{N_j} = e^{\frac{-(E_i - E_j)}{kT}} \rightarrow \ln\frac{N_i}{N_j} kT = -(E_i - E_j) \qquad (1)$$

where N_i is the population of conformer *i*, N_j is the population of conformer *j*, k is the Boltzmann constant (kcal mol^{-1}), T is the temperature of measurement (233.15 K).

1a (MeCN, -40 °C): $\ln\frac{4}{3}\, 0.001987 \times 233.15 = -(E_i - E_j) = 0.13\, kcal/mol$

1b (MeCN, -40 °C): $\ln\frac{82}{1}\, 0.001987 \times 233.15 = -(E_i - E_j) = 2.04\, kcal/mol$

Computational details

Computational methods available in Spartan '18 software[2] were employed to determine geometries and properties of macrocycle conformers. The structures of **1a-1**, **1a-2, 1b-1 and 1b-2** were built in silico. The geometry of the structures were optimized at the CAM-B3LYP/6-31G(d) level of theory using C-PCM solvation model of acetonitrile.

X-ray crystallography

Diffraction data were collected at 120 K on Rigaku Saturn944+ diffractometer with graphite-monochromated Mo Kα radiation. The structures were solved by direct methods and refined using ShelXTL software package[3].

CCDC No.	1898386
Empirical formula	$C_{30}H_{36}Cl_4N_8O_4$
Formula weight	714.47
Crystal system	Orthorhombic
Space group	$Pca2_1$
a [Å]	30.482(10)
b [Å]	9.034(3)
c [Å]	22.961(7)
Volume [Å^3]	6323(4)
Z	8
μ [mm^{-1}]	0.426
Crystal size [mm]	0.18 × 0.13 × 0.10
θ range [^{o}]	1.1–27.5
Reflections collected/unique	19956/ 9563
R_{int}	0.042
Data/restraints/parameters	9563/745/837
Final *R* indices [$I>2\sigma(I)$]	0.045
$\Delta\rho_{max}$ /$\Delta\rho_{min}$ [e Å^{-3}]	0.47/ −0.47

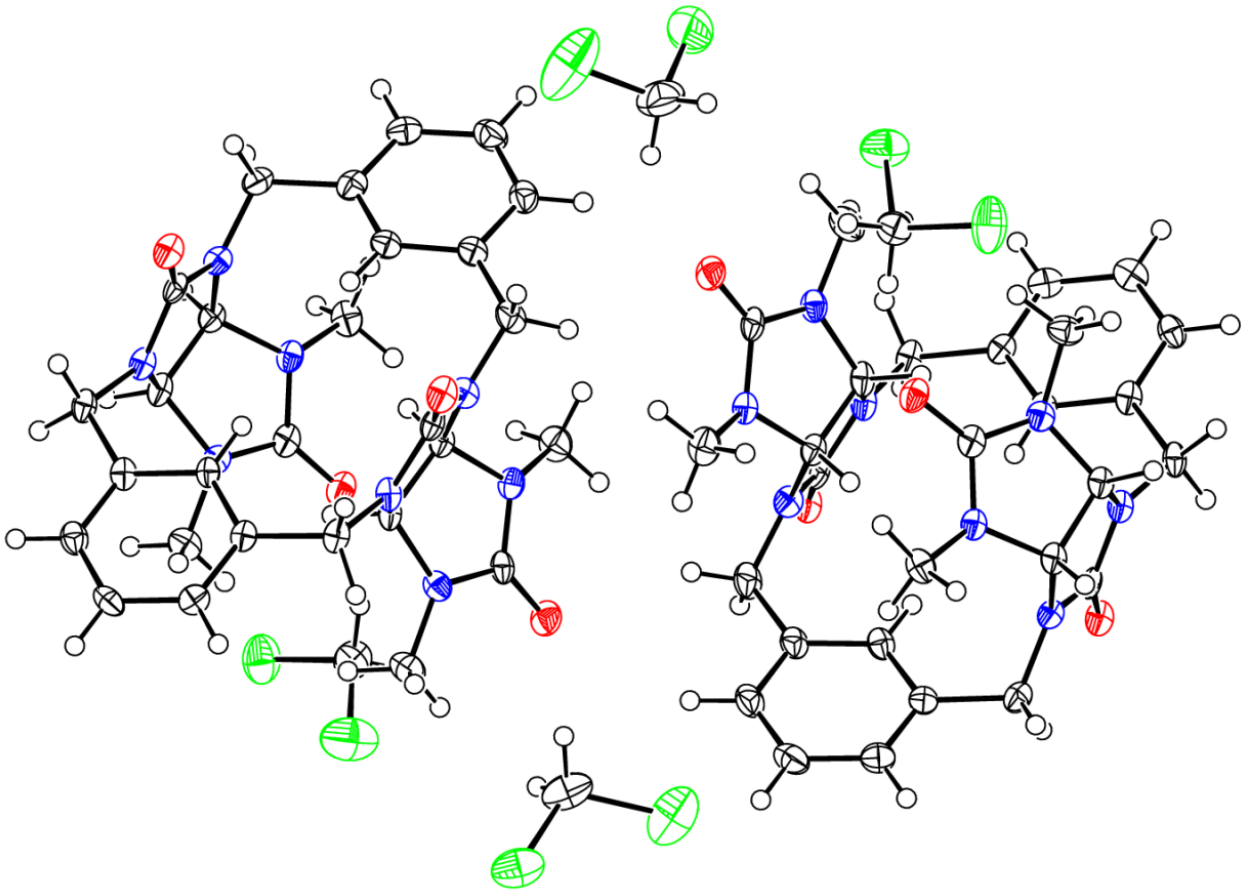

Figure S12: Molecular structure of **1b-1**. Thermal ellipsoids are drawn at the 50% probability level.

References:

(1) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science, 2006.
(2) *Spartan'18*; Wavefunction: Irvine, CA, USA, 2018.
(3) Sheldrick, G. M. Crystal Structure Refinement with *SHELXL*. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71* (1), 3–8. https://doi.org/10.1107/S2053229614024218.