

## Modular self-assembled multiporphyrin cages with tunable shape

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### Electronic Supplementary Information

1D and 2D NMR experiments were recorded at 500 MHz on a Varian 500 spectrometer. Proton peak positions were referenced to the peak of residual non deuterated solvent (set at  $\delta$  7.26 for CDCl<sub>3</sub>).

Solvents for spectroscopic measurements were of spectroscopic grade, all the other solvents were of reagent grade quality, and used as received. CDCl<sub>3</sub>, used in NMR experiments, was treated with basic alumina prior to use.

Abbreviations: 4'-*cis*DPyP = 5,10-bis(4'-pyridyl)-15,20-diphenylporphyrin, 4'-*trans*DPyP = 5,15-bis(4'-pyridyl)-10,20-diphenylporphyrin, 4'-*trans*PyPDI = *N,N'*-di(4-pyridyl)-perylene-3,4:9,10-tetracarboxylic acid bisimide, tpt = 2,4,6-tris(4-pyridyl)triazine, 4'-TPyP = 5,15,10,20-(4'-pyridyl)-porphyrin, 4'-TPhPyP = 5,15,10,20-(4'-pyridylphenyl)-porphyrin.

4-(4-formylphenyl)pyridine and pyrrole were purchased from Aldrich. Metallacycle **1** was synthesized as previously reported.<sup>9</sup> tpt was synthesized as reported in the literature.<sup>1S</sup> 4'-TPhPyP was synthesized according to literature procedures, via condensation of 4-(4-formylphenyl)pyridine and pyrrole.<sup>2S</sup>

Synthesis of **2** - **4**: metallacycle **1** (20 mg,  $1.1 \times 10^{-2}$  mmol) and tpt (5 mg,  $1.65 \times 10^{-2}$  mmol) were dissolved in CHCl<sub>3</sub> (20 mL) and the solution was stirred at room temperature for 15 min. Concentration *in vacuo* to *ca.* 5 mL followed by addition of *n*-hexane induced the precipitation of **2** as a violet solid, that was isolated by filtration, washed with *n*-hexane and vacuum dried (21 mg, 95%). A similar procedure was followed for **3** and **4**: equimolar amounts of **1** (20 mg,  $1.1 \times 10^{-2}$  mmol) and 4'-TPyP (3 mg,  $5.49 \times 10^{-3}$  mmol) or 4'-TPhPyP (5 mg,  $5.49 \times 10^{-3}$  mmol) yielded **3** (22 mg, 95%) or **4** (24 mg, 95%), respectively, as a dark-violet solids.

[ $1_3(\mu\text{-tpt})_2$ ] (**2**).  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ;  $-20\text{ }^\circ\text{C}$ ; see text for labels): 2.11 (6H, d,  $\text{py}_o$ , tpt), 5.87 (6H, d,  $\text{py}_m$ , tpt), 7.68 (12H, m,  $\text{mH}'$ , **1**), 7.78 (24H, m,  $\text{mH}+\text{pH}$ , **1**), 8.02 (12H, d,  $\text{oH}'$ , **1**), 8.17 (12H, d,  $\text{oH}$ , **1**), 8.27 (12H, d,  $\text{py}_b$ , **1**), 8.50 (12H, d,  $\text{py}_b'$ , **1**), 8.72 (12H, s,  $\beta\text{H}$ , **1**), 8.77 (12H, s,  $\beta\text{H}$ , **1**), 9.05 (12H, d,  $\beta\text{H}$ , **1**), 9.09 (12H, d,  $\beta\text{H}$ , **1**), 9.61 (12H, d,  $\text{py}_a$ , **1**), 9.76 (12H, d,  $\text{py}_a'$ , **1**).

[ $1_4(\mu\text{-4}'\text{-TPyP})_2$ ] (**3**).  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ; see text for labels): -5.19 (4H, s,  $-\text{NH}$ ), 2.30 (8H, d,  $\text{py}_o'$ , 4'-TPyP), 2.49 (8H, d,  $\text{py}_o$ , 4'-TPyP), 5.33 (8H, d,  $\text{py}_m'$ , 4'-TPyP), 5.70 (8H, d,  $\text{py}_m$ , 4'-TPyP), 6.54 (8H, br d,  $\beta\text{H}$ , 4'-TPyP), 7.72 (8H, br d,  $\beta\text{H}$ , 4'-TPyP), 7.83 (48H, m,  $\text{mH}+\text{mH}'+\text{pH}$ , **1**), 8.26 (32H, br m,  $\text{oH}+\text{oH}'$  **1**), 8.58 (32H, dd,  $\text{py}_b'+\text{py}_b$ , **1**), 9.82 (32H, dd,  $\text{py}_a'+\text{py}_a$ , **1**).

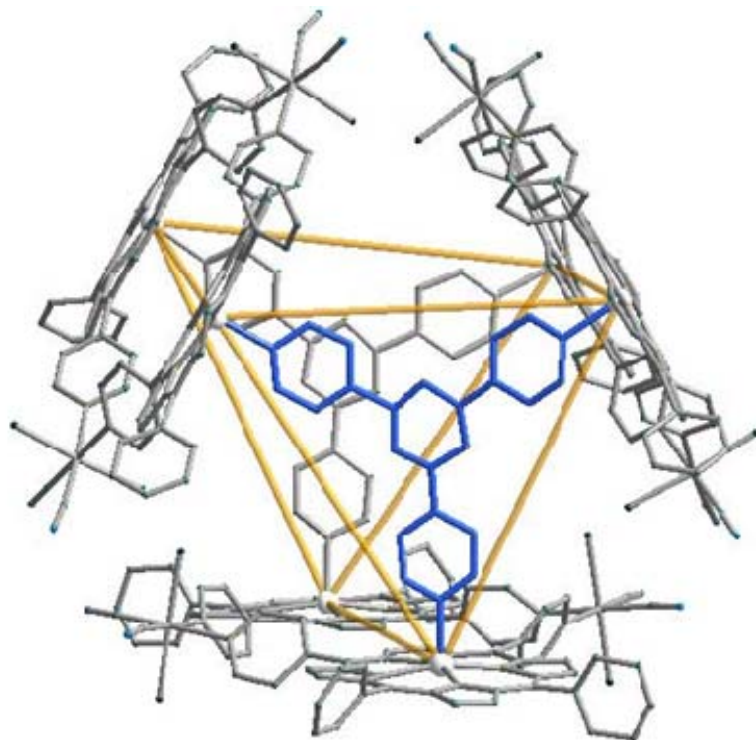
[ $1_4(\mu\text{-4}'\text{-TPhPyP})_2$ ] (**4**).  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ): -3.87 (4H, s,  $-\text{NH}$ ), 2.40 (16H, d,  $\text{py}_o$ , 4'-TPhPyP), 5.79 (4H, d,  $\text{py}_m$ , 4'-TPhPyP), 6.62 (8H, d,  $\text{Ph}_o'$ , 4'-TPhPyP), 6.81 (8H, d,  $\text{Ph}_o$ , 4'-TPhPyP), 7.22 (8H, d,  $\text{Ph}_m'$ , 4'-TPhPyP), 7.47 (8H, d,  $\text{Ph}_m$ , 4'-TPhPyP), 7.79 (16H, m,  $\text{mH}'$ , **1**), 7.86 (48H, m,  $\text{mH}+\text{pH}$ , **1**  $\beta\text{H}$  4'TPyP), 8.28 (32H, d,  $\text{oH}+\text{oH}'$  **1**), 8.49 (16H, d,  $\text{py}_b'$ , **1**), 8.66 (16H, d,  $\text{py}_b$ , **1**), 9.10 (64H, m,  $\beta\text{H}$ , **1**), 9.57 (16H, d,  $\text{py}_a'$ , **1**), 9.74 (16H, d,  $\text{py}_a$ , **1**).

### X-ray structure determination

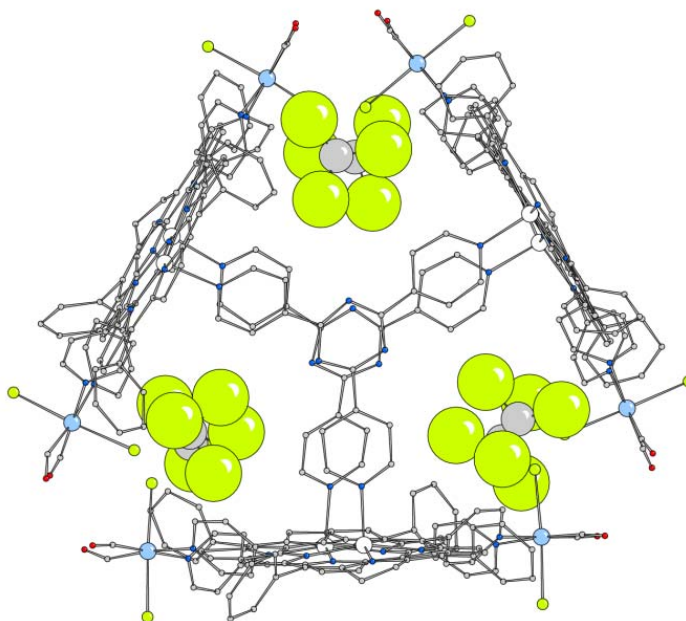
Crystals of **2** suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a chloroform solution of **2**.

Diffraction data were collected at 100 K on a CCD MAR detector at the X-ray diffraction beamline of the Elettra Synchrotron, Trieste (Italy), with monochromatic wavelength of 1.0000 Å. Cell refinement, indexing and scaling of the data set were carried out using Denzo and Scalepack programs.<sup>3S</sup> The structure was solved by direct methods and subsequent Fourier analyses,<sup>4S</sup> and refined by the full-matrix least-squares procedure.<sup>4S</sup> A  $\Delta$ Fourier analysis revealed six molecules of  $\text{CHCl}_3$  (four of which at half occupancy, for a total of four per  $\text{Ru}_6\text{Zn}_6$  unit, Figure S2). Due to the large void volume in the unit cell the SQUEEZE procedure (program PLATON)<sup>5S</sup> applied to the data allowed to estimate the presence of 30 additional molecules of  $\text{CHCl}_3$  per  $\text{Ru}_6\text{Zn}_6$  unit, therefore a total of 34  $\text{CHCl}_3$  molecules were included in the formula, formula weight, density and  $F(000)$ . All the calculations were performed using the WINGX SYSTEM, version 1.80.05.<sup>6S</sup>

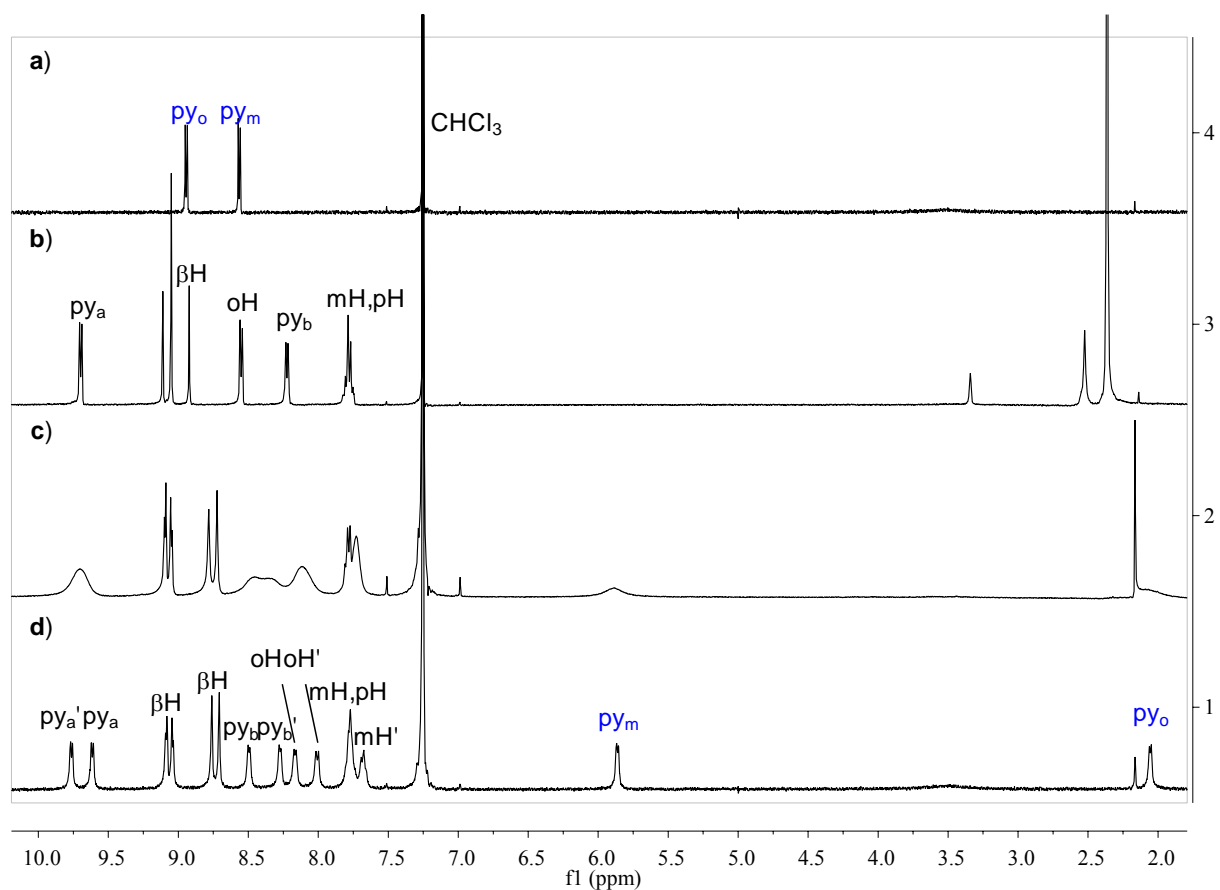
The ruthenium ions have an octahedral coordination geometry, with normal Ru–C, Ru–Cl and Ru–N bond. Each zinc ion inside the porphyrin has a square pyramidal geometry, with equatorial Zn–N(porphyrin) and axial Zn–N(pyridyl) bond lengths in the range 2.035(12)-2.101(14) Å and 2.086(12)-2.181(12) Å, respectively.



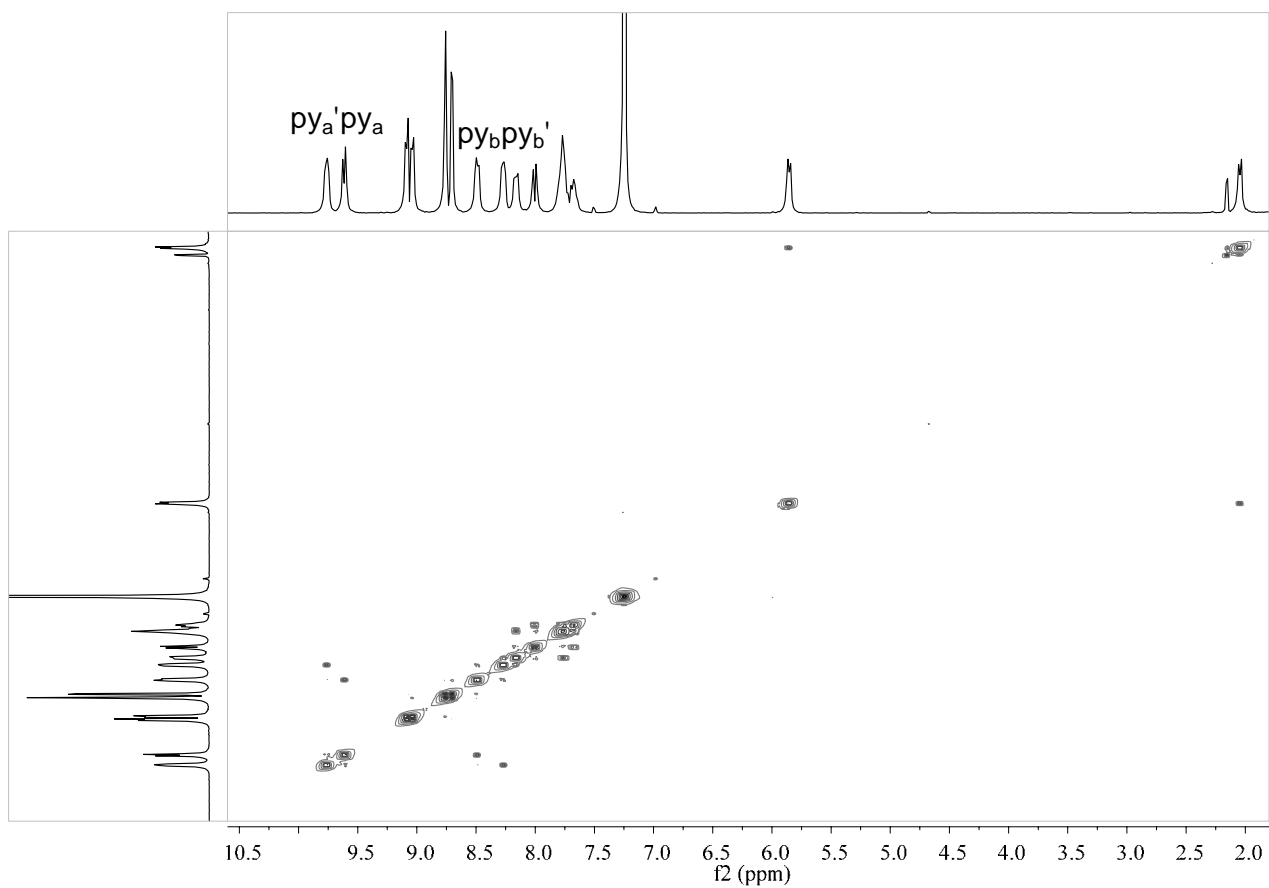
**Fig S1** X-ray structure of **2**, with highlighted the inner prism, delimited by the two tpt lids and the six Zn atoms.



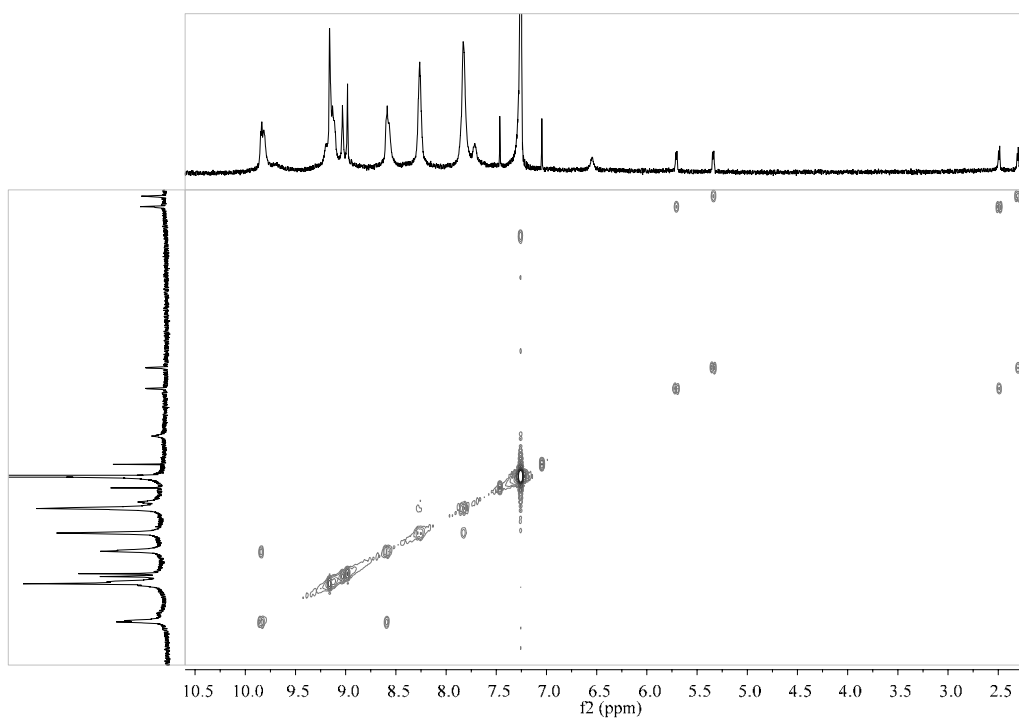
**Fig S2** X-ray structure of **2**, with highlighted the six solvent molecules (CHCl<sub>3</sub>, four of which at half occupancy) that were located inside the trigonal prismatic cavity.



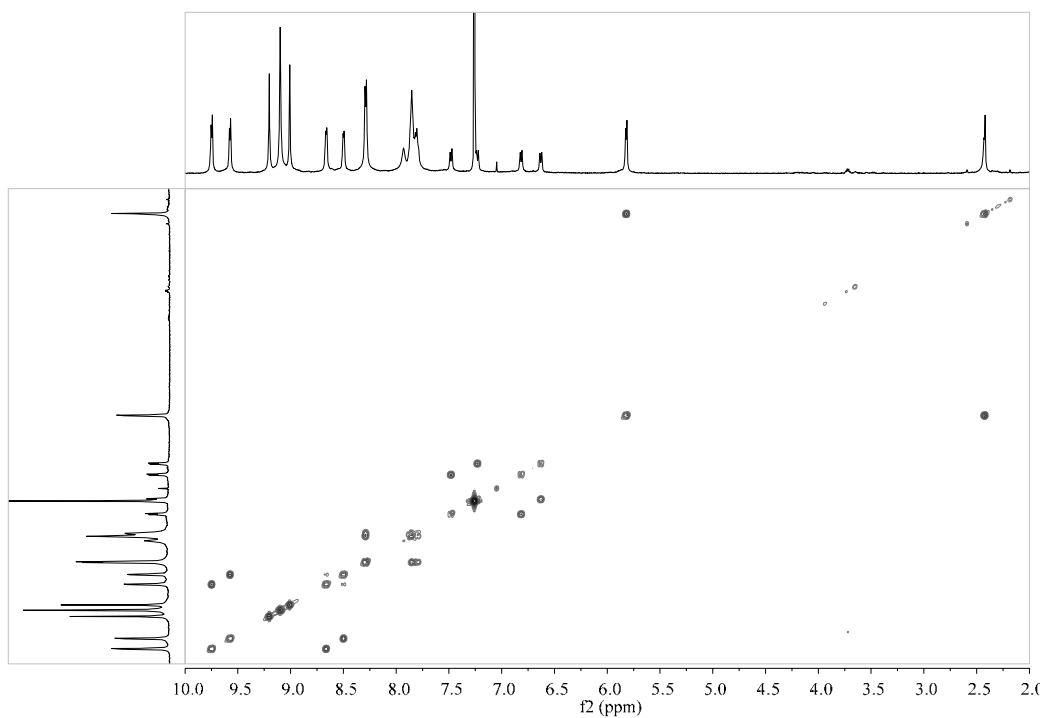
**Fig S3** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of a) tpt, b) **1**, c) [1<sub>3</sub>(μ-tpt)<sub>2</sub>] (**2**) (0 °C) and d) [1<sub>3</sub>(μ-tpt)<sub>2</sub>] (**2**) (-20 °C), see text for labelling scheme.



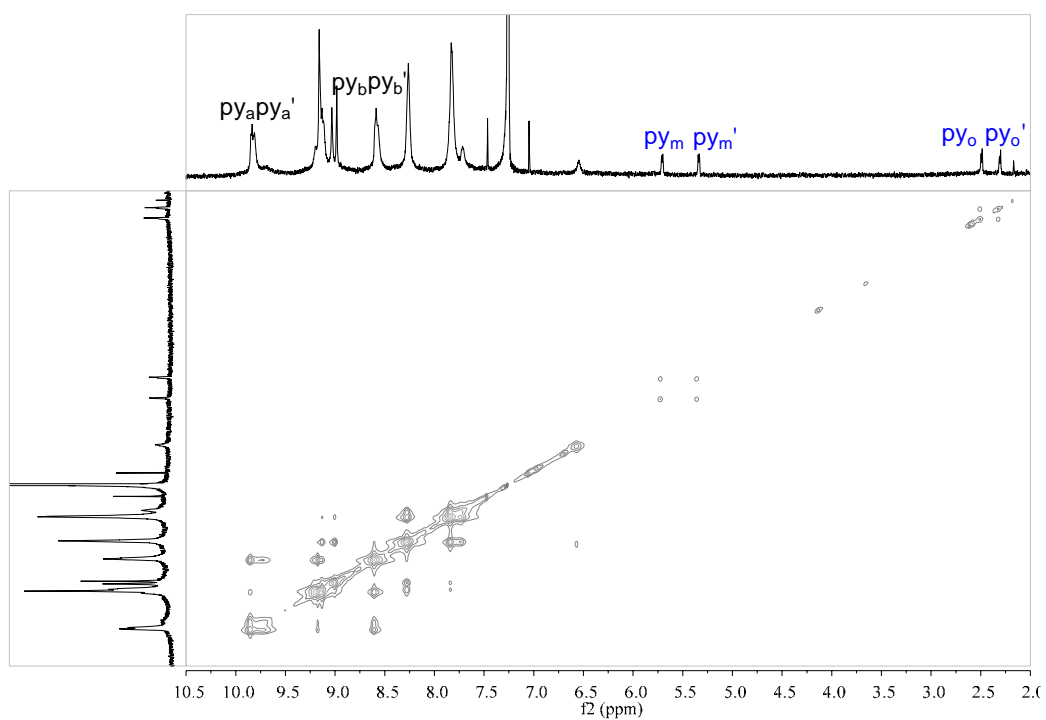
**Fig S4** H-H COSY spectrum (CDCl<sub>3</sub>, -20 °C) of **2**.



**Fig S5** H-H COSY spectrum (CDCl<sub>3</sub>, +25 °C) of **3**.



**Fig S5** H-H COSY spectrum (CDCl<sub>3</sub>, +10 °C) of **4**.



**Fig S6** NOESY spectrum (CDCl<sub>3</sub>, +25 °C) of **3**.

## References

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