



Metallophthalocyanines and Metalloporphyrins

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Introduction

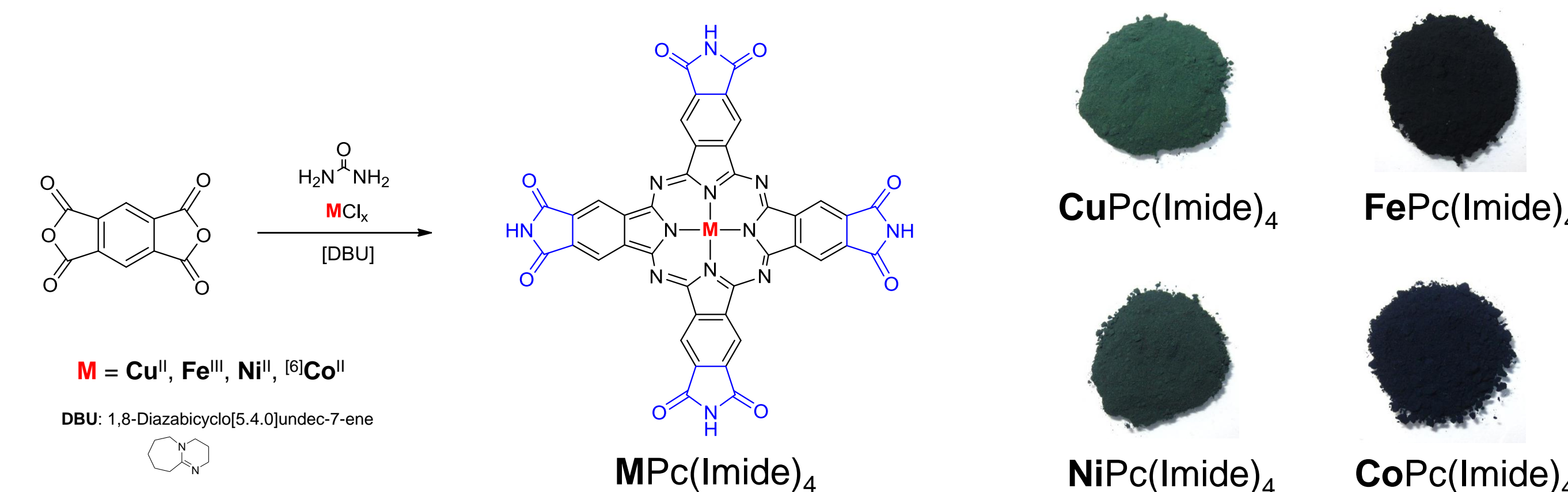
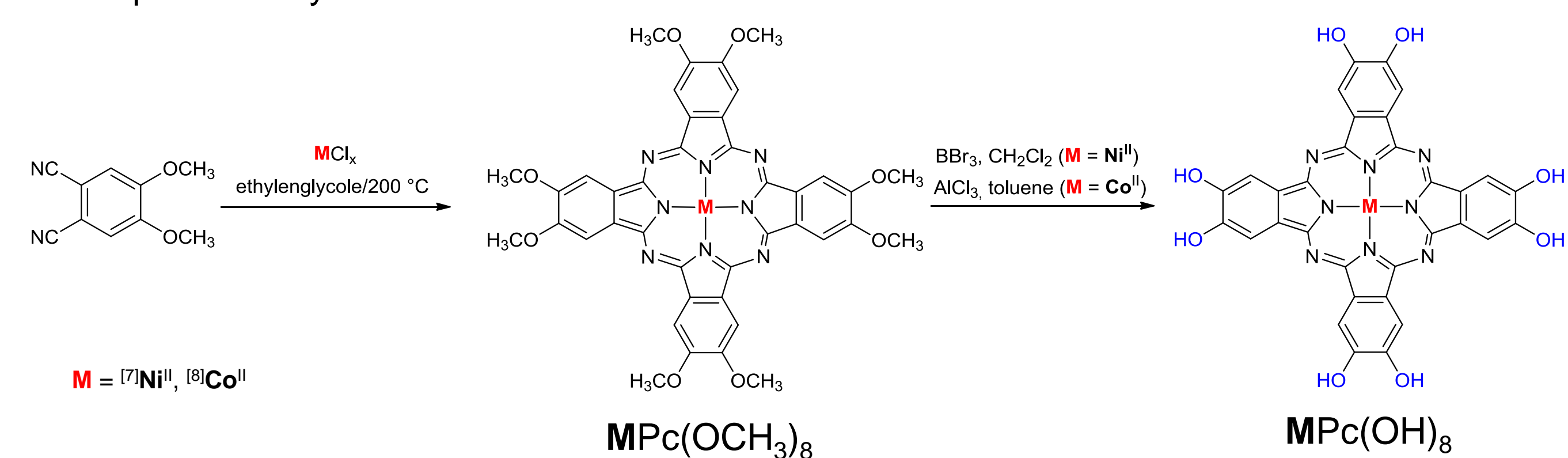
Since the early 20th century phthalocyanines and porphyrins and their appropriate metal complexes have attracted much attention due their distinct aromaticity and planar structure. They exhibit a high chemical and thermal stability, interesting electronic, spectroscopic as well as optical properties. Out of this reason these compounds have gained special interest during the last two decades in the field of material science where they find application in non-linear optics, data storage, as electrochromic substances, gas sensors, in photochemical and photovoltaic cells or in the therapy of cancer.^[1-4]

Motivation

One of the challenges of project SP2 is to synthesize magneto-active molecules, which have the possibility to generate networks formed by hydrogen bond interactions, when deposited on surfaces (e.g. Au(111)). This can be achieved by terminal modification of the phthalocyanine and porphyrin scaffold, using polar substituents, which provides hydrogen donor and/or acceptor functionalities. Here we report on the synthesis and characterization of various substituted (**R** = Imide, COOH, OH) phthalocyanines, porphyrins and their appropriate metal species (**Cu**, **Fe**, **Ni**, **Co**). In cooperation with SP6 the arrangement of this molecules based on the intermolecular hydrogen bond interactions should be determined *via* STM.

Metallophthalocyanines

The metallophthalocyanines are accessible in a one step cyclotetramerization reaction of functionalized phthalic anhydrides and benzodinitriles, respectively, with the corresponding metal salts in high boiling solvents or melts.^[5-8] After appropriate work-up, the thus obtained compounds were fully characterized by ¹H and ¹³C{¹H} NMR, IR and UV/Vis spectroscopy, elemental analysis as well as high resolution mass spectrometry.



Compound	Chemical Shift δ [ppm]
CuPc(Imide)₄	11.81; 8.09
FePc(Imide)₄	11.81; 8.10
NiPc(Imide)₄	11.81; 8.09
CoPc(Imide)₄	11.81; 8.10

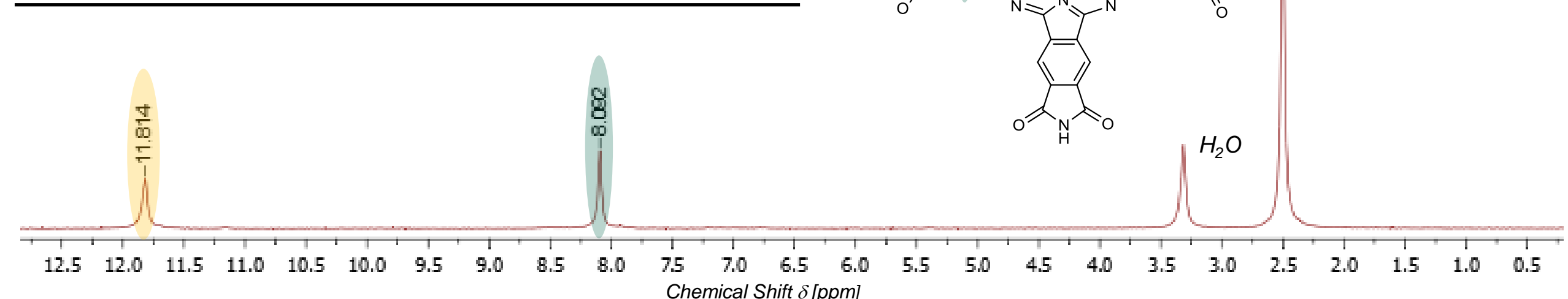


Fig. 1: Part of the ¹H NMR spectrum of **NiPc(Imide)₄** measured in DMSO-*d*₆.

The ¹H NMR spectra all four compounds show the expected signals.

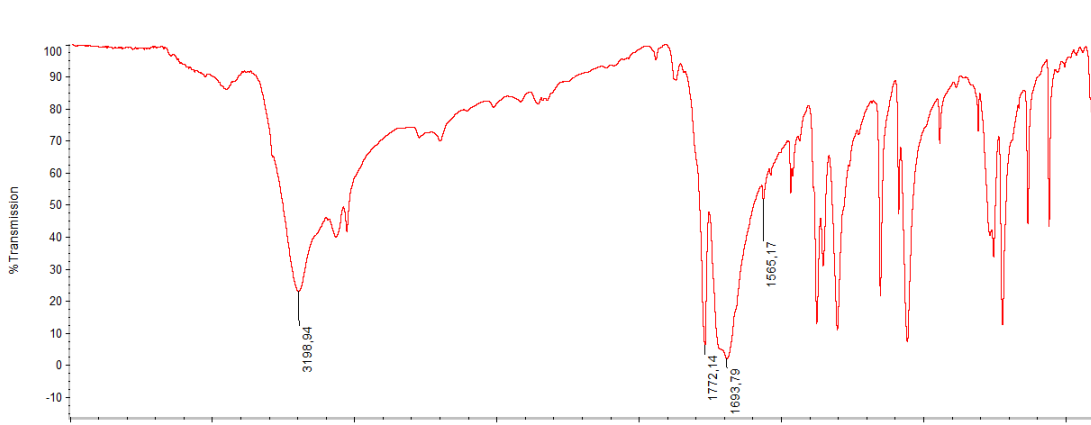
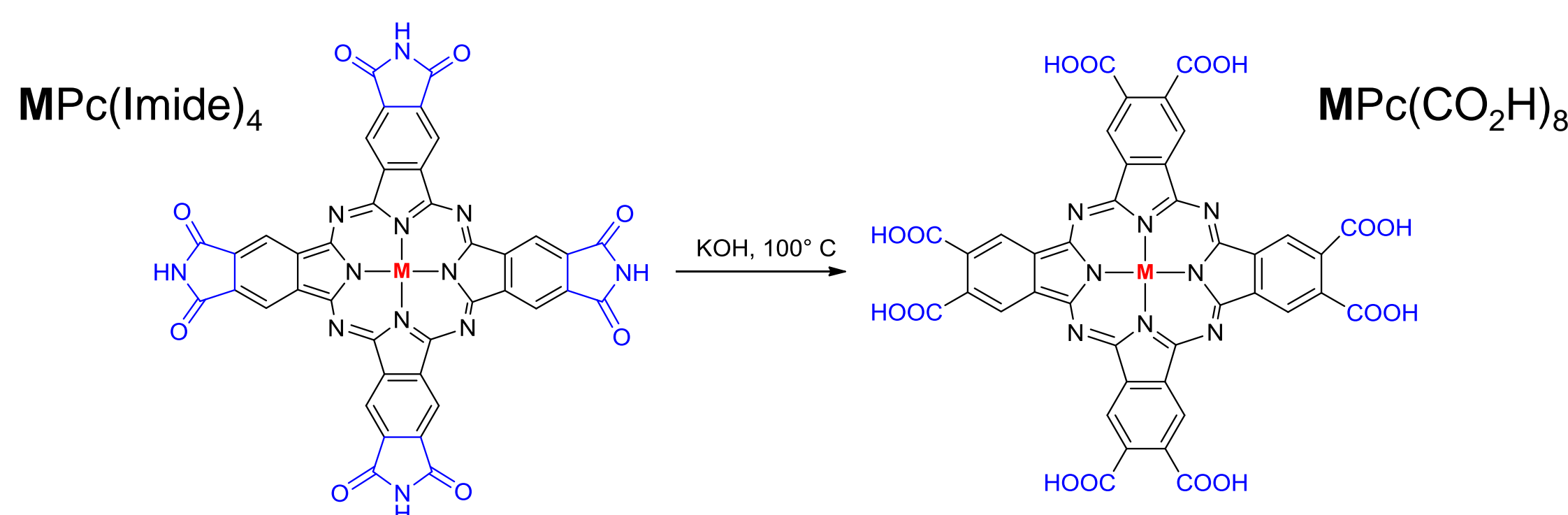


Fig. 2: IR spectrum of **NiPc(Imide)₄** measured with KBr.

From the IR spectra characteristic CO and NH stretching frequencies can be observed. However the compounds offer extremely poor solubility, therefore a more precise characterization is very difficult. *ESI-MS* and *APCI-MS* measurements did not give any results.

The next step is the hydrolysis of the imides to give the carboxylic acid substituted metallophthalocyanines.



Metalloporphyrins

The synthesis of the metalloporphyrins is realized *via* an intermediate step of the appropriate metal free porphyrin systems. Subsequent reaction with the respective metal salt in DMF give the desired metal complexes.^[4] The resulting porphyrins exhibit a good solubility in common organic solvents. This simplifies a detailed characterization of the systems. After appropriate work-up, the obtained compounds were fully characterized by the aforementioned methods.

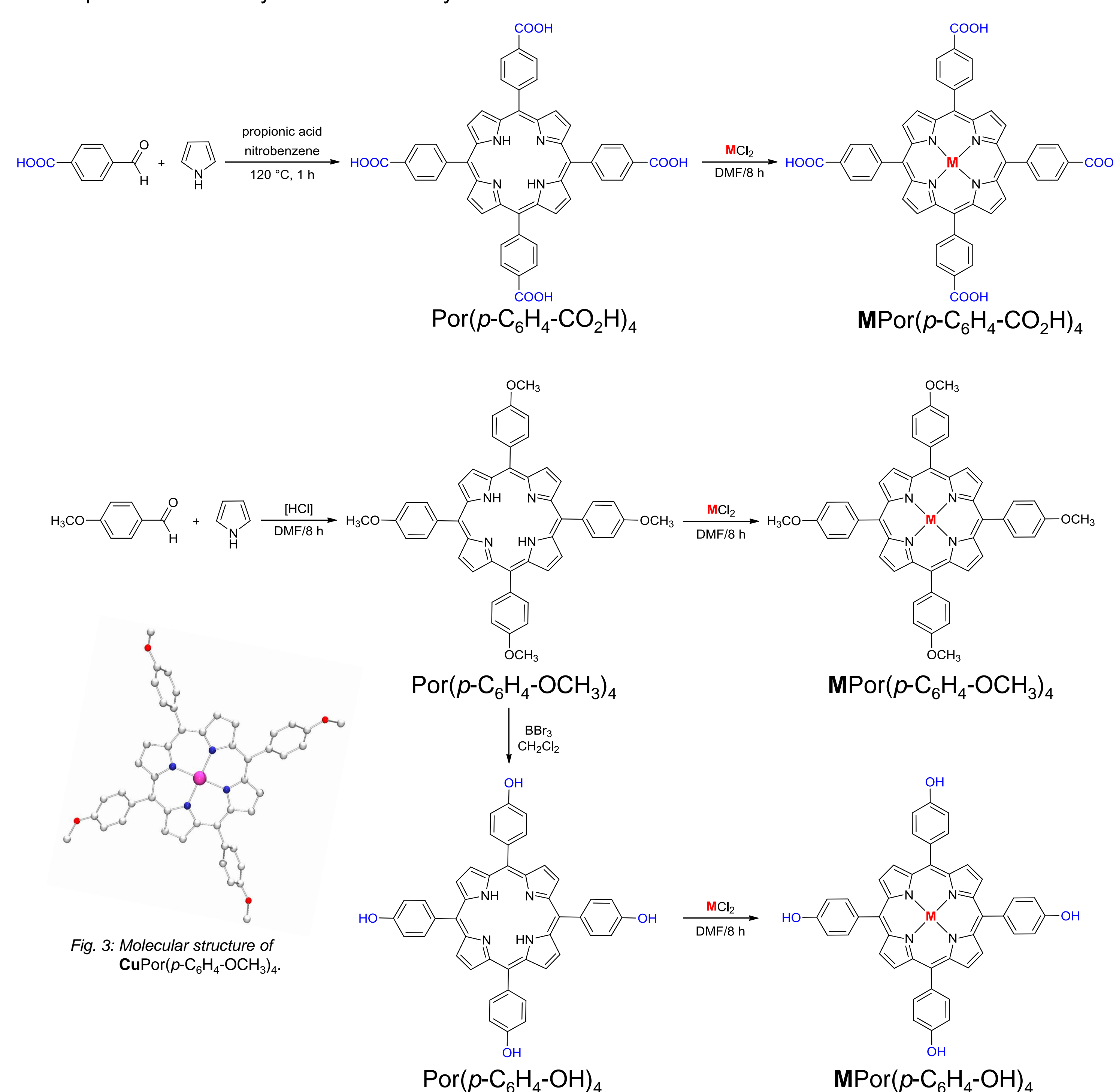


Fig. 3: Molecular structure of **CuPor(p-C₆H₄-OCH₃)₄**.

Via ¹H NMR spectroscopy the complete conversion from **Por(p-C₆H₄-OCH₃)₄** (**A**) to **Por(p-C₆H₄-OH)₄** (**B**) can be observed.

R	Chemical Shift δ [ppm]	Chemical Shift δ [ppm]	Chemical Shift δ [ppm]	Chemical Shift δ [ppm]	Chemical Shift δ [ppm]
(A)	8.86 (s, 8H)	8.13 (d, 8H)	7.40 (d, 8H)	4.06 (s, 12H)	-2.88 (s, 2H)
(B)	8.86 (s, 8H)	8.00 (d, 8H)	7.21 (d, 8H)	9.94 (s, 4H)	-2.88 (s, 2H)

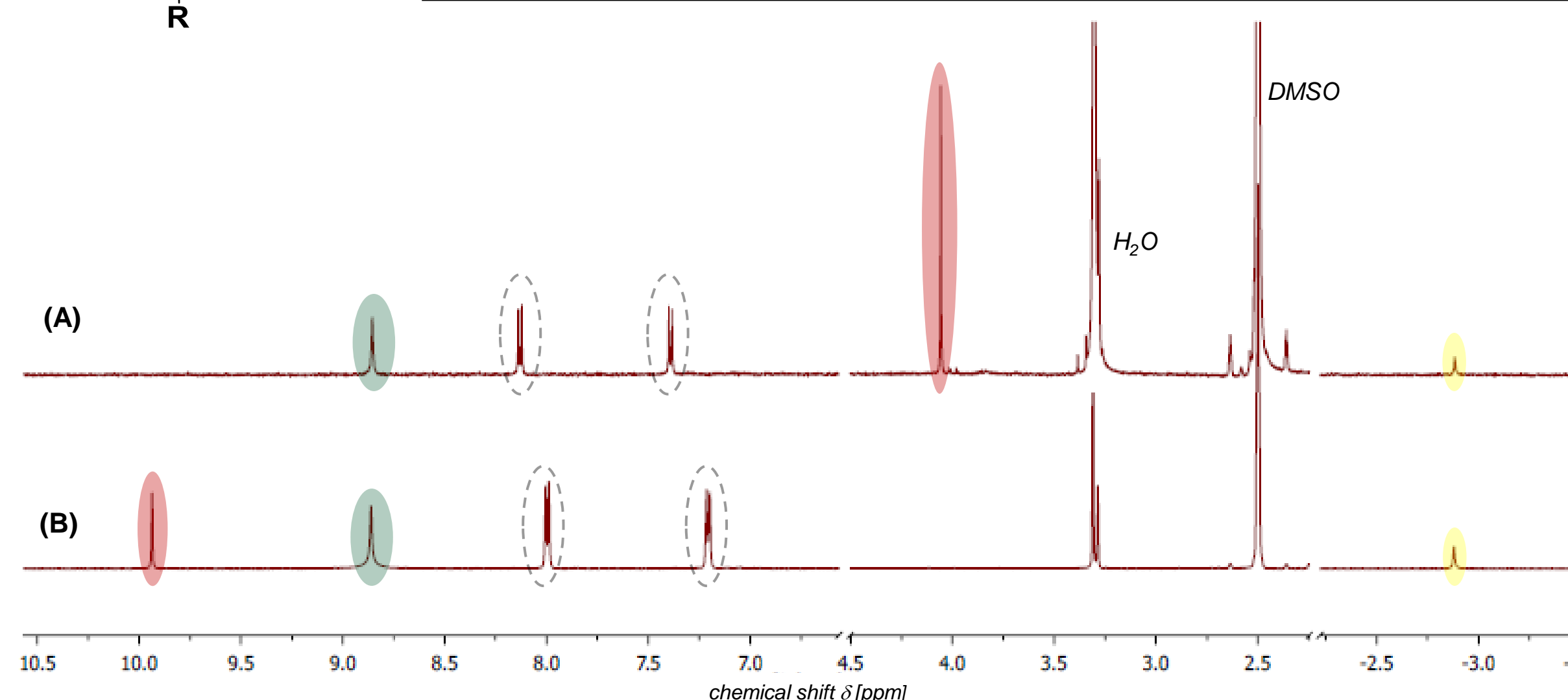


Fig. 4: Part of the ¹H NMR spectrum of **(A)** **Por(p-C₆H₄-OCH₃)₄** and **(B)** **Por(p-C₆H₄-OH)₄** measured in DMSO-*d*₆.

References

- [1] M. Hanack, K. Albert et al., *Chem. Eur. J.* **2001**, 7, 2459–2465. [2] F. Yuksel, S. Tuncel, V. Ahsen, *J. Porphyrins and Phthalocyanines* **2008**, 12, 123–130. [3] M. J. Plater, S. Aiken, G. Bourhill, *Tetrahedron* **2002**, 58, 2415–2422. [4] A. Kumar, S. Maji, P. Dubey, G. J. Abhilash, S. Pandey, S. Sarkar, *Tetrahedron Lett.* **2007**, 48, 7287–7290. [5] M. Hanack, M. Lang, *Adv. Mater.* **1994**, 6, 819–833. [6] K. Sakamoto, E. Ohno, *Progr. in Organic Coatings* **1997**, 31, 139–145. [7] M. Ruf, A. M. Lawrence, B. C. Noll, *Inorg. Chem.* **1998**, 37, 1992–1999. [8] J. Metz, O. Schneider, M. Hanack, *Inorg. Chem.* **1984**, 23, 1065–1071.

Acknowledgment

We are grateful to the DFG for generous financial support.