

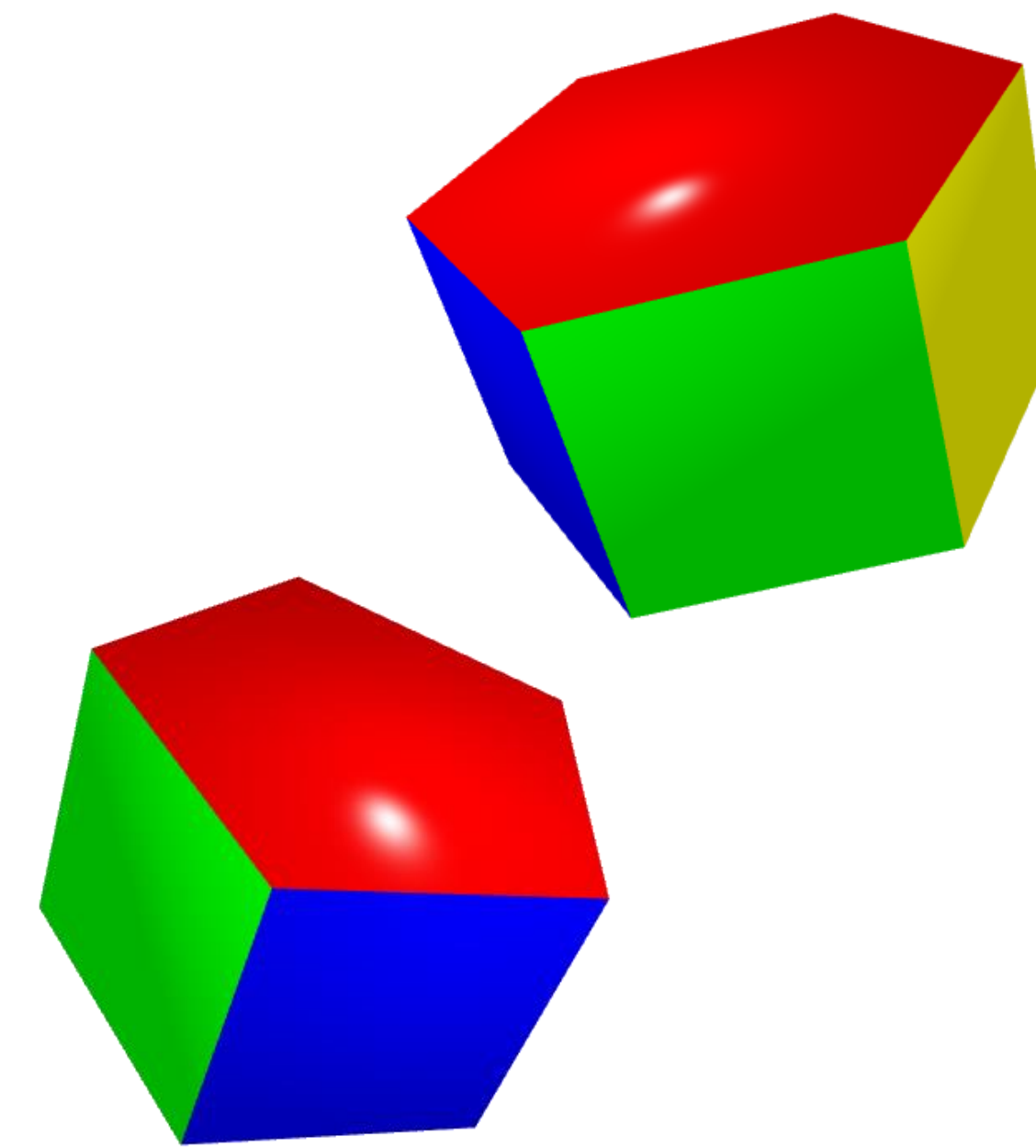


Synthesis and Characterization of Pillar[n]arenes

M. Da Pian^a, F. Fabris^a, A. Scarso^a

^aDipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari di Venezia,

Dorsoduro 2137 I-3012, Venezia, e-mail: marta.dapian@unive.it



INTRODUCTION

In the last decade supramolecular chemistry has been focused on macrocyclic molecules for their applications in recognition processes and catalysis. With similar characteristics to cyclodextrins, resorcin[n]arenes and calix[n]arenes, the recently discovered pillar[n]arene is emerging as a new class of cyclic semi-rigid arenes whose potentialities are still under-investigated. Since its discovery, this class of molecules showed impressive host-guest properties due to the rigid, symmetric and electron-donating structure that promotes selective complexation of different guest molecules. Although the chemistry of pillar[5]arenes has been much more investigated, synthesis and characterization of pillar[6]arenes has been rarely explored. However, in the last two years, several groups focused their attention to this class of tubular hosts with larger cavity.^[1]

Guest molecules can stabilize pillararene structure and concomitantly inhibit the host rotation. In addition, both size and length of the alkoxy chains affect the complexation stability. pillar[6]arenes have different host-guest properties compared to pillar[5]arenes due to larger cavities (internal diameter ca. 7.5 Å and ca. 5.5 Å, respectively).^[2] Our goal was to optimize the synthesis of pillar[6]arene to make it the main product of the cyclization reaction and to study more in detail its supramolecular and host-guest properties aiming at applications in supramolecular catalysis..

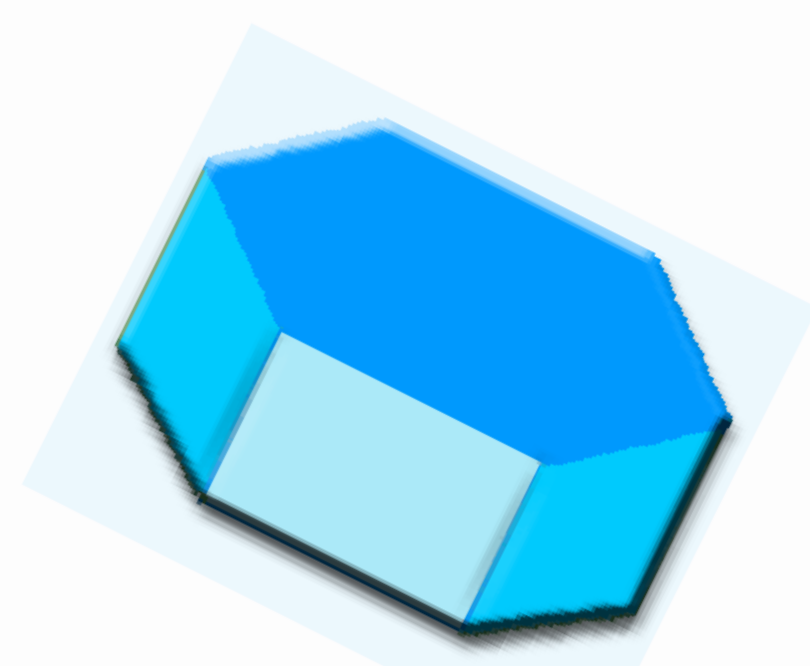
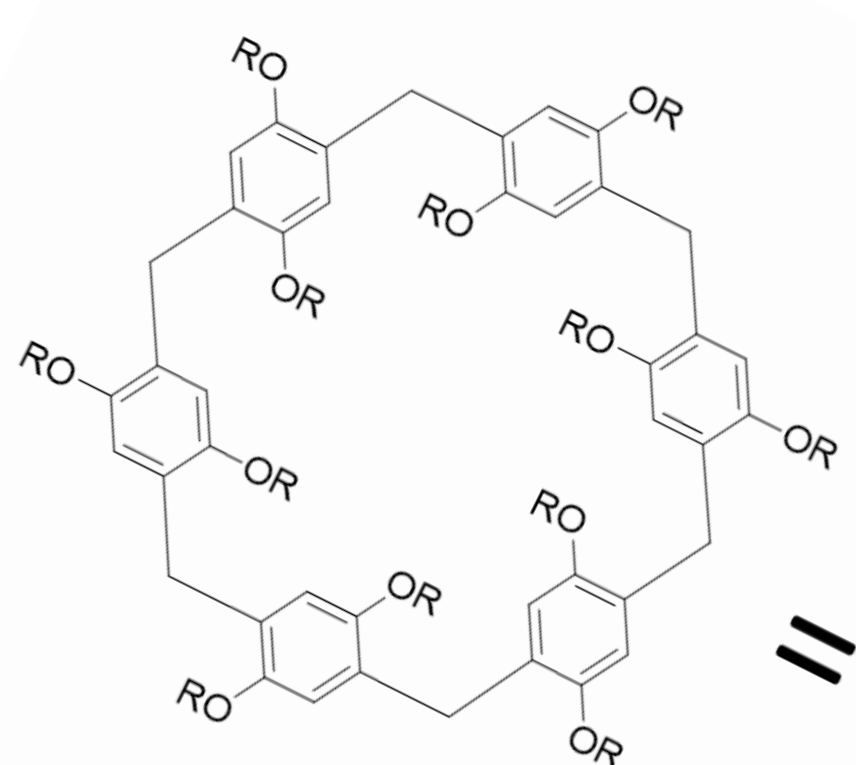


Figure 1: Chemical structure (left) and chemical representation (right) of pillar[6]arene. R = Alkyl

OPTIMIZATION OF LITERATURE EXPERIMENTS

Preliminary studies focused on the reproduction of the experiment present in literature, starting from the reaction of 1,4-diethoxybenzene with paraformaldehyde in the presence of a Lewis acid under mild reaction condition. Both the 5 and 6 membered pillararenes were formed in yield lower than 10%. Different temperature and alkoxy substituents were taken into account to improve the yield with poor results. Alternative synthetic strategies are now under currently investigation, involving p-toluenesulfonic acid as catalyst for the formation of the CH₂-bridge of the arene units.

The two main products can be characterized by NMR spectroscopy showing differences in chemical shift of the aromatic protons (6,72 ppm for pillar[5]arene and 6,70 ppm for pillar[6]arene). They can be separated by TLC (petroleum ether/ diethyl ether:8/2) with R_f of 0,65 for pillar[5]arene and R_f of 0.37 for pillar[6]arene.

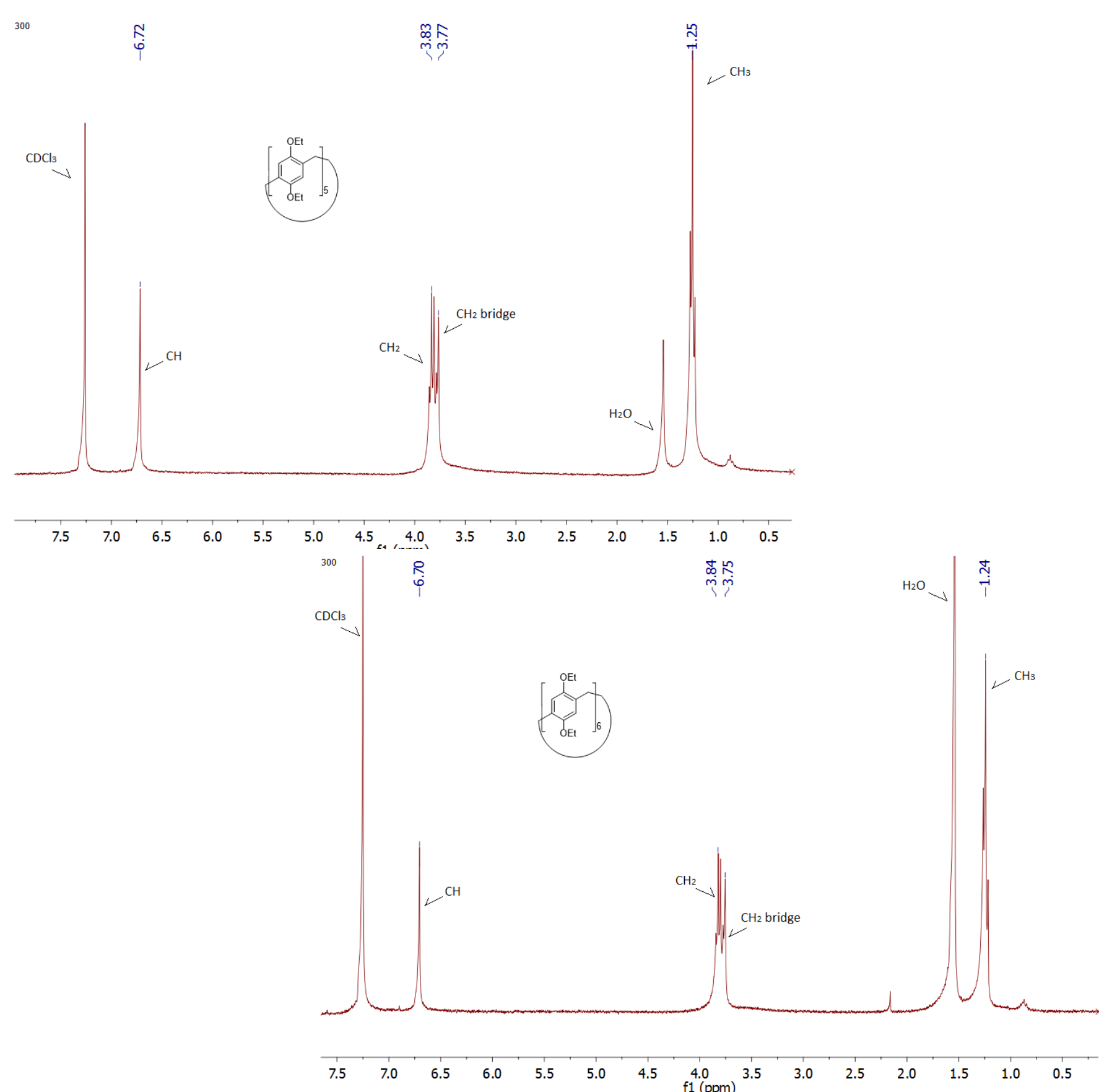


Figure 3: ¹H-NMR spectra of pillar[5]arene (up) and pillar[6]arene (down).

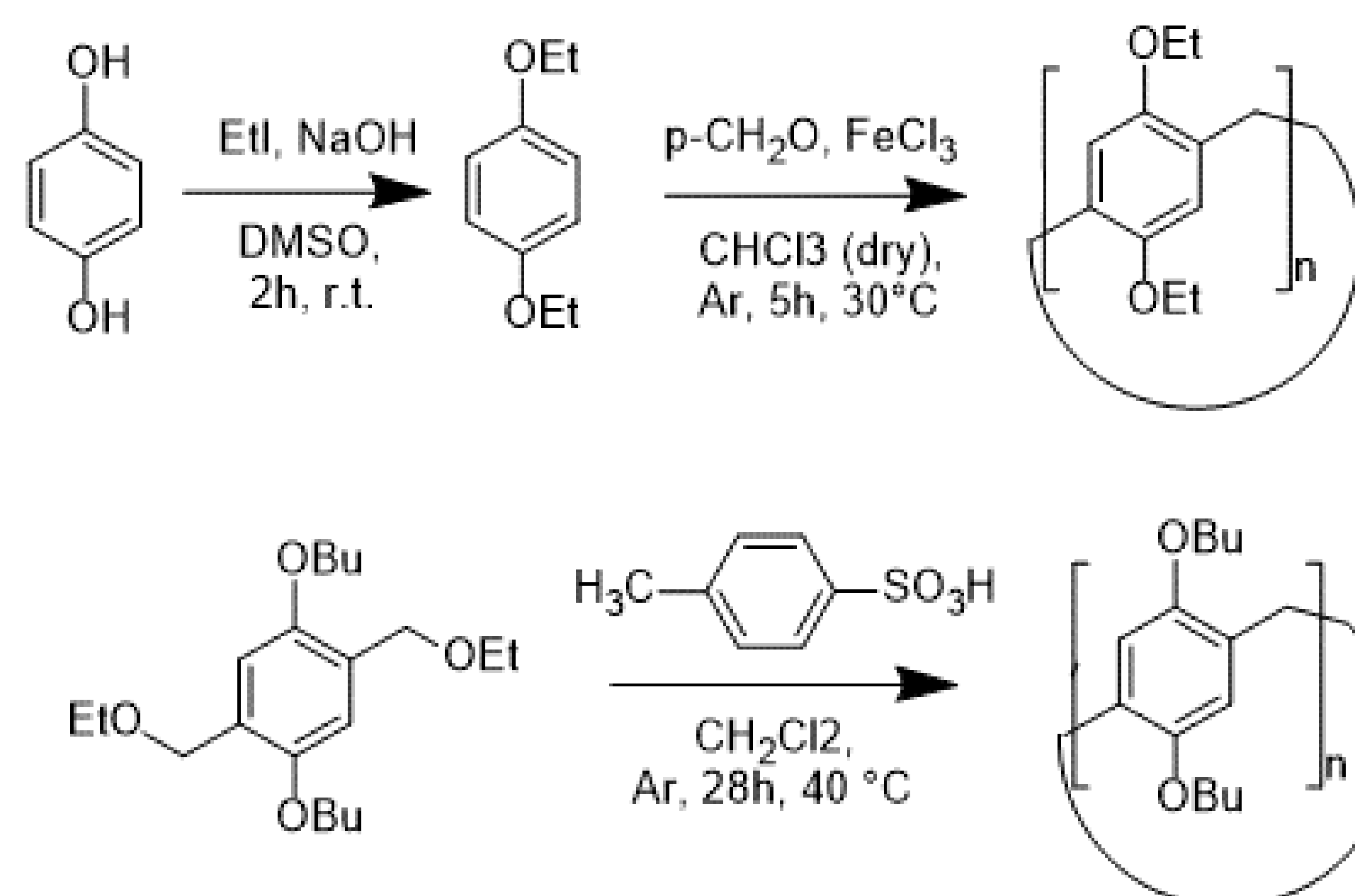


Figure 2: The two synthetic route proposed by D. Cao group (up)^[3], (down).^[4]

FUTURE OUTLINE

Other studies will be focused on the maximization of the pillar[6]arene yield and on the optimization of the purification steps are currently underway.



REFERENCES

- T. Ogoshi et al. *Chem. Commun.*, 2014, 5774-5777
- H. Zhang, *Chem. Eur. J.* 2013, 19, 16862 – 16879
- Cao, D. R. et al. *Angew. Chem. Int. Ed.*, 2009, 48, 9721-9723.
- Cao, D. R. *Sci. China Chem.*, 2012, 55, 223-228.

Acknowledgements: This work was funded by Università Ca' Foscari di Venezia