

Synthesis of octa- β -formylporphyrins as templates for functionalized tetrabenzoporphyrins

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INTRODUCTION

Porphyrins with benzene rings fused at the β positions are named benzoporphyrins (Figure 1).¹ These structures have been investigated in a wide range of applications like: light-emitting diodes, photodynamic therapy, biomedical sensing and imaging.² Synthetic modifications of β -functionalized porphyrins have been proposed as an interesting way to synthesize such molecules.¹ Working with this idea, we are investigating the synthesis of an octa- β -formylporphyrin, which will be used for the preparation of new functionalized tetrabenzoporphyrins, to be studied as photosensitizers in photodynamic therapy (PDT).

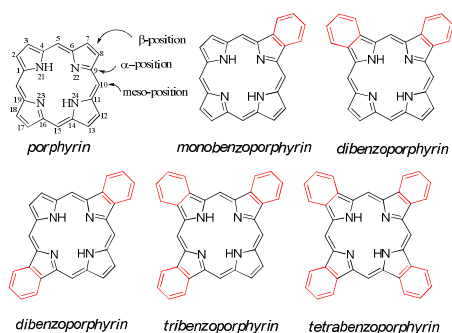
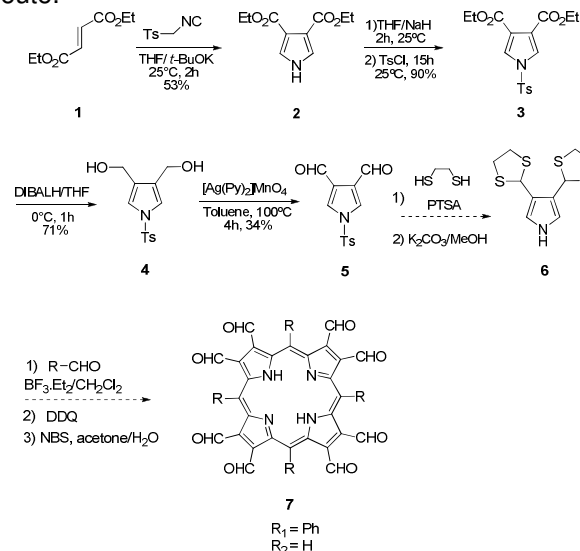


Figure 1. Benzoporphyrin derivatives.

RESULTS AND DISCUSSION

The synthesis started with the preparation of the pyrrole **2** (scheme 1). The 1,3-dipolar addition of *p*-toluenesulfonylmethyl isocyanide to diethyl fumarate (**1**), in anhydrous THF and *t*-BuOK, led to the compound **2** in 53% yield after purification in silica gel. The following step was the protection of **2** with a tosyl group in order to avoid by-products. The reaction was carried out in anhydrous THF, with sodium hydride and *p*-toluenesulfonyl chloride and the compound **3** was obtained in 90% yield after purifications. Reduction of the ethyl ester groups was accomplished using DIBALH in anhydrous THF in 71% yield. The mild oxidation of the dialcohol **4** to dialdehyde **5** was performed using the silver-pyridyl

complex ($[\text{Ag}(\text{Py})_2]\text{MnO}_4$) in toluene at 100 °C (34% yield).³ Currently, we are investigating improvements in the yield of this last step since **5** may be very sensitive to silica gel. We will check the use of the crude product **5** for obtaining of **6** in the synthetic route.



Scheme 1. Synthesis of an octa- β -formylporphyrin.

CONCLUSION

The synthesis of 3,4-substituted pyrrole (**2**) was performed by 1,3-dipolar cycloaddition. Functionalizations in order to obtain suitable pyrroles for the synthesis of porphyrin **7** were also accomplished.

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REFERENCES

- Silva, A. M. G.; de Oliveira, K. T.; Faustino, M. A. F.; Neves, M.; Tome, A. C.; Silva, A. M. S.; Cavaleiro, J. A. S.; Brandao, P.; Felix, V. *Eur. J. Org. Chem.* **2008**, 704.
- Deshpande, R.; Jiang, L.; Shimidt, G.; Rakovan, J.; Wang, X.; Wheeler, K. e Wang, H. *Org. Lett.* **2009**, *11*, 4251.
- Firozabadi, H.; Vessal, B. e Naderi, M. *Tetrahedron Lett.* **1982**, *23*, 1847.