



Synthesis of *meso*-tetra-(5-iodo-thien-2-yl)-porphyrin; an intermediate for cross-coupling reactions

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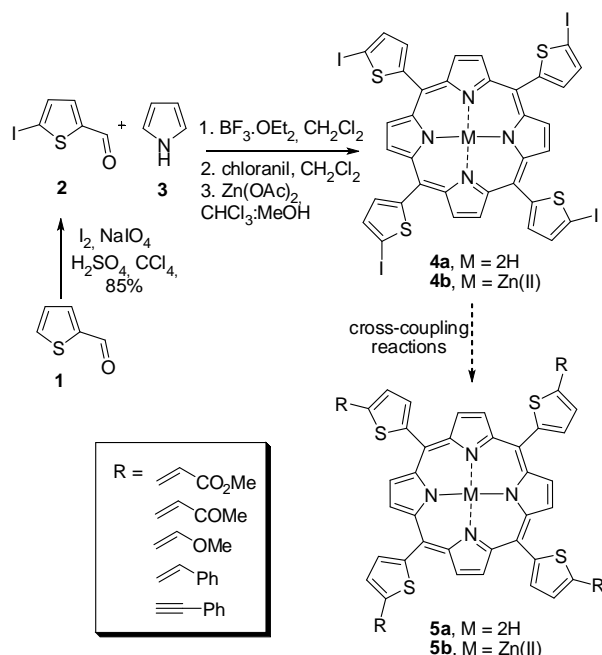
Keywords: *meso*-porphyrins, Heck-Mizoroki reactions, Sonogashira reactions.

INTRODUCTION

The synthesis of new porphyrins has become a major challenge, mainly due to their wide range of applications, including photochemical cells and photodynamic therapy (PDT).¹ With the advent of *one-pot* processes^{2,3} for the synthesis of *meso* substituted porphyrins, the number of these compounds has increased considerably. Porphyrins with *meso*-thienyl groups can also be used as building blocks for new porphyrins. One way to functionalize these compounds is the Heck-Mizoroki and Sonogashira cross coupling reactions.⁴ We now propose the synthesis of *meso*-thien-2-yl-porphyrins functionalized with iodine, ready for cross-coupling reactions.

RESULTS AND DISCUSSION

Iodination of the known thiophene-2-carbaldehyde **1** with iodine in the presence of periodate gave the 5-isomer **2** (85%) after crystallization.⁵



Scheme 1: Synthesis of *meso*-tetra-iodothien-2-yl-porphyrins **3** and **4**.

The compound **2** was tetramerized with pyrrole (**3**) using $\text{BF}_3 \cdot \text{OEt}_2$, followed by oxidation with chloranil, thus furnishing the porphyrin **4a** (Scheme 1). These conditions were shown to be more efficient, with a 20% yield, than conventional treatment with propionic acid in 12%. Porphyrin **4a** was metallated using $\text{Zn}(\text{OAc})_2$ in a $\text{CHCl}_3:\text{MeOH}$ (1:1) solution, thereby obtaining the desired porphyrin **4b** in 90% yield. Presently, we are studying some cross coupling reactions between the porphyrins **4a** and **4b** and alkenes and alkynes in order to produce new functionalized thienyl-porphyrin derivatives such as **5a** and **5b**.

CONCLUSION

We have demonstrated the synthesis of a new *meso*-tetra-iodo-thien-2-yl-porphyrin, and thus the possibility of further functionalizations via cross-coupling reactions.

ACKNOWLEDGEMENTS

The authors thank FAPESP (grant numbers 2011/13993-2, 2013/06532-4), CNPq and CAPES for financial support and fellowships.

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