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

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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 processes2,3 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

The compound 2 was tetramerized with pyrrole (3) using BF3.OEt2, 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 Zn(OAc)2 in a CHCl3: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-iodothien-2-yl-porphyrin, and thus the possibility of further functionalizations via cross-coupling reactions.

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REFERENCES