Synthesis of substituted phthalonitrile building blocks for the preparation of non-aggregating phthalocyanines

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Keywords: thiophene-1,1-dioxide, Diels-Alder, phthalocyanine synthesis

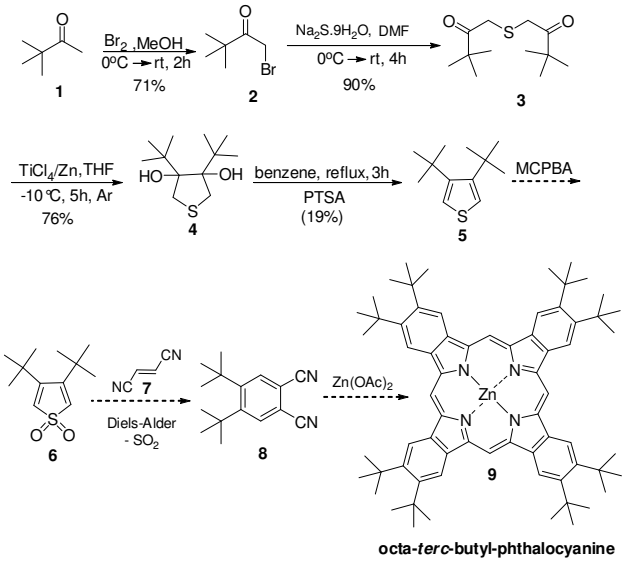
INTRODUCTION

Phthalocyanines since their discovery, have been the focus of much research because of wide applications in different areas of science, namely photodynamic therapy (PDT), semiconductors, liquid crystals, photovoltaic and solar cells.[1-3] The most important challenge in phthalocyanine synthesis is the production of a macrocycle with low aggregation and adequate photophysical proporieties.[3] The introduction of bulky groups on the periphery of the phthalocyanines core structure has been used to avoid aggregation,[3] and has yielded promising biological activities.

In this work, we describe our first attempts to synthesize a series of substituted phthalonitrile building blocks, using the Diels-Alder reaction between 3,4-substituted thiophene-1,1-dioxide and fumaronitrile as key step. As is well known, phthalonitriles are the main building blocks to synthesize phthalocyanines.[1-3] To start the development of this methodology, the 3,4-*ditert*-butyl-thiophene (**5**) was prepared (Scheme 1).

RESULTS AND DISCUSSION

Bromination of pinacolone (**1**) was performed in methanol (0°C→rt, 4h, 71% yield) (Scheme 1). Then, compound **2** was reacted with sodium sulfide nonahydrate by bimolecular nucleofílic substitution in DMF yielding **3** (90%). After that, intramolecular reductive coupling was carried out using low-valent titanium reagent prepared from titanium(IV) chloride and zinc powder in THF at -10°C to give the 3,4-di-*terc*-butyl-*cis*-thiolane (**4**) (76% yield).[4] Aromatization was performed using (PTSA) furnishing **5** in 19% yield. A product of pinacol-pinacolone rearrangement was also observed. We are investigating this reaction, in order optimize this last result.



Scheme 1. Synthetic purpose for non-aggregating phthalocyanines.

CONCLUSION

Thiophene **5** was synthesized in four steps from pinacolone (**1**). We are now trying to improve the yield of **5**, and carry out the remaining steps of the proposed synthesis.

ACKNOWLEDGEMENTS

The authors thank FAPESP (2008/06619-4), CNPq (470338/2010-5) and CAPES for financial support. Thanks are also due to FAPESP for scholarship of Nicholas R. S. Gobo. (2010/12549-9)

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