

### **Important notes:**

Do **NOT** write outside the grey boxes. Any text or images outside the boxes **will** be deleted.

Do **NOT** alter the structure of this form. Simply enter your information into the boxes. The form will be automatically processed – if you alter its structure your submission will not be processed correctly.

Do not include keywords – you can add them when you submit the abstract online.

#### **Title:**

**Reactivity studies of thienyl and (oligo)thienylpyrroles**

#### **Authors & affiliations:**

M. C. R. Castro\*, A. M. C. Fonseca, M. M. M. Raposo  
*Centre of Chemistry, University of Minho, Braga, Portugal*

**Abstract:** (Your abstract must use **Normal style** and must fit in this box. Your abstract should be no longer than 300 words. The box will 'expand' over 2 pages as you add text/diagrams into it.)

Currently, a variety of synthetic approaches to substituted pyrroles exist, although their synthesis, in general, remains challenging. Often, the yields are rather low and a significant number of by-products, such as undesired regioisomers, are obtained. Furthermore, pyrroles are susceptible to chemical degradation as they are rather easily oxidized; this further hampers their synthesis and especially their isolation and purification.<sup>1</sup>

The chemistry of thienylpyrroles is a very recent field in the chemistry of heterocyclic compounds. In the last few years, synthetic 2-thienylpyrrole derivatives have come in focus. However, even more than 60 years since the first 2-thienylpyrrole: *bis*-2-[5-(2-thienyl)pyrrole]azametine dihydrochloride) has been reported by Edward Knott<sup>2</sup> at Kodak, the synthesis of functionalized thienyl and (oligo)thienylpyrroles remains challenging. Often, the yields are low and the regioselectivity is only modest.<sup>3</sup>

Before our recent work,<sup>3-4</sup> only a few papers were published concerning the regioselectivity studies of 1-(alkyl)aryl-2-thienylpyrrole systems. Following our interest in the chemistry and optical applications of new functionalized systems bearing thiophene and pyrrole rings we have used heterocyclic systems **1** bearing pyrrole and thiophene rings (1, 2 or 3) as precursors for the synthesis of functionalized pyrrole derivatives. Compounds **1** have proved to be versatile substrates in several reactions (aromatic electrophilic substitutions: azo coupling, direct tricyanovinylolation reaction, Vilsmeier-Haack formylation) and metalation followed by reaction with DMF, allowing the preparation of interesting new donor-acceptor substituted heterocyclic systems, selectively functionalized on the pyrrole **2** or on the thiophene **3** rings. Precursors **1** were prepared through a palladium-catalyzed decarboxylative cross-coupling reaction. The structures of the new compounds were unambiguously confirmed by their analytical and spectral data.

#### **Acknowledgments**

Thanks are due to the *Fundação para a Ciência e Tecnologia* (Portugal) and FEDER-COMPETE for financial support through the Centro de Química - Universidade do Minho, Project PTDC/QUI/66251/2006 (FCOMP-01-0124-FEDER-007429), Project PEst-C/QUI/UI0686/2011 (FCOMP-01-0124-FEDER-022716) and a PhD grant to M. C. R. Castro (SFRH/BD/78037/2011). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

#### **References**

1. Schmuck, C.; Rupprecht, D. *Synthesis* **2007**, 3095.
2. Knott, E. B. *J. Chem. Soc.* **1947**, 1196.
3. (a) Raposo, M. M. M. in *Targets in Heterocyclic Systems: Chemistry and Properties*, "Recent developments in the chemistry of 2-thienylpyrroles: synthesis, reactivity and applications", Attanasi, O. A.; Spinelli, D. Eds.; Royal Society of Chemistry: London, 2008, Vol. 11, pp 122-154.
4. (a) Raposo, M. M. M.; Sousa, A. M. R. C.; Fonseca, A. M. C.; Kirsch, G. *Tetrahedron* **2005**, *61*,

**Important notes:**

Do **NOT** write outside the grey boxes. Any text or images outside the boxes **will** be deleted.

Do **NOT** alter the structure of this form. Simply enter your information into the boxes. The form will be automatically processed – if you alter its structure your submission will not be processed correctly.

Do not include keywords – you can add them when you submit the abstract online.

8249. (b) Raposo, M. M. M.; Sousa, A. M. R. C.; Kirsch, G.; Ferreira, F.; Belsley, M.; Matos Gomes, E.; Fonseca, A. M. C. *Tetrahedron* **2005**, *61*, 11991. (c) Raposo, M. M. M.; Sousa, A. M. R. C.; Fonseca, A. M. C.; Kirsch G. *Tetrahedron* **2006**, *62*, 3493. (d) Raposo, M. M. M.; Sousa, A. M. R. C.; Kirsch, G.; Cardoso, P.; Belsley, M.; Matos Gomes, E.; Fonseca, A. M. C. *Org. Lett.* **2006**, *8*, 3681. (e) Raposo, M. M. M.; Castro, M. C. R.; Schellenberg, P.; Fonseca, A. M. C.; Belsley, M. *Tetrahedron* **2011**, *67*, 5189.