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## Title:

Synthesis of  $\pi$ -conjugated systems bearing thiophene and pyrrole heterocycles through palladiumcatalyzed decarboxylative cross-coupling reaction

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**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.)

Thiophene and pyrrole moieties play important roles in synthetic and medicinal chemistry, as they are present in a large number of natural products and biologically active compounds. For this reason, amongst all five-membered aromatic heterocycles, molecules containing the pyrrole nucleus have attracted the greatest attention of researchers and have been studied in most detail. Especially, 2-aryland 2-heteroaryl-substituted pyrroles are of great interest to the pharmaceutical industry, for instance, as precursors in the synthesis of chemotherapeutics. Furthermore, synthetic pyrrole -containing derivatives (e.g. functionalized thienylpyrroles and 2,5-dithienylpyrroles) and  $\pi$ -conjugated oligo- and polypyrrolic systems are of growing relevance in materials science, supramolecular chemistry, and nanotechnology. For example, they have found application in anion binding and cation coordination, conducting organic polymers, liquid crystals, and nonlinear optics.

The wide array of interesting properties has inspired the development of several procedures for the preparation of differently substituted pyrroles. On the other hand, methods for the construction of 2-(2′-thienyl)pyrroles and (oligo)thienylpyrroles remains limited. Therefore the development of efficient methods for the synthesis of these compounds has become an important and topical area of heterocyclic chemistry. In our laboratories we have developed a convenient method for the synthesis of 1-alkyl(aryl)-2-thienylpyrroles, through the combination of the Friedel-Crafts and Lawesson reactions.<sup>3</sup>

The transition-metal-catalyzed decarboxylative cross-coupling has been recently utilized as a new synthetically useful tool for the preparation of heterocyclic systems.<sup>4</sup>

Having in mind our recent work and also our interest in the development of synthetic methodologies for the synthesis of novel heterocyclic systems we report in this communication the synthesis and the characterization of new  $\pi$ -conjugated systems 1 bearing thiophene and pyrrole rings through palladium-catalyzed decarboxylative cross-coupling reaction between 1-methyl-1H-pyrrole-2-carboxylic acid 1 and thienyl bromides 2. Several reaction conditions (catalyst, solvent, additive, base, stoichiometry and temperature) were studied in order to obtain better yields for compounds 3. Some of the precursor thienyl bromides 2 were prepared through Suzuki coupling reaction. The new compounds were completely characterized by the usual spectroscopic techniques.

# Acknowledgments

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## References

- 1. Bellina, F.; Rossi, R. Tetrahedron 2006, 62, 7213.
- 2. (a) Raposo, M. M. M. in Targets in Heterocyclic Systems: Chemistry and Properties, "Recent

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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. (b) 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. (c) Raposo, M. M. M.; Castro, M. C. R.; Schellenberg, P.; Fonseca, A. M. C.; Belsley, M. Tetrahedron 2011, 67, 5189. 3. (a) Raposo, M. M. M.; Sampaio, A. M. B. A.; Kirsch, G. Synthesis 2005, 2, 199. (b) Raposo, M. M.; Sousa, A. M. R. C.; Fonseca, A. M. C.; Kirsch G. Tetrahedron 2006, 62, 3493. 4. Zhao, D.; You, J.; Hu, C. Chem. Eur. J. 2011, 17, 5466.
1. Zhuo, D., 10u, J., 11u, C. Chent. Dar. J. 2011, 17, 5700.