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A green synthesis of 2,5-disubstituted thiophenes from terminal alkynes: a telescopic approach

Jonatan B. S. de Paula and Marcio C. S. de Mattos

Departamento de Química Orgânica, Instituto de Química, UFRJ, 21941-909, Rio de Janeiro

*e-mail: jonatan.barreto@gradu.iq.ufrj.br

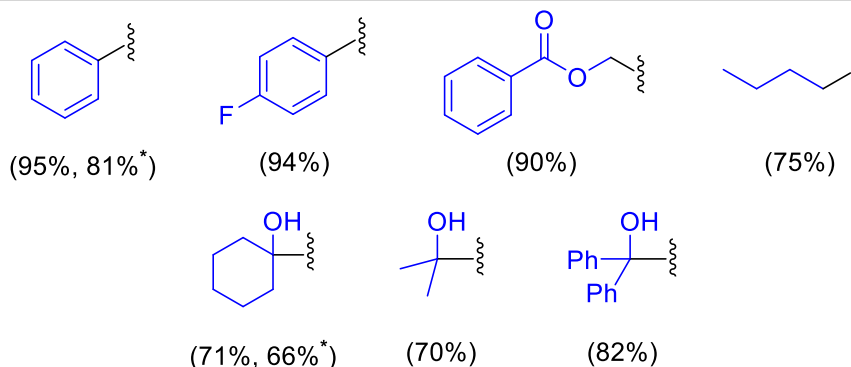
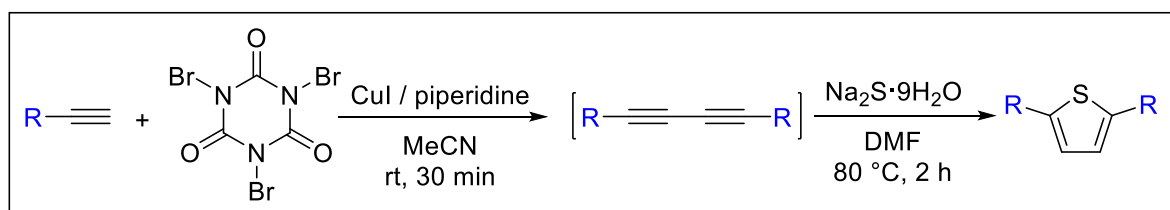
Keywords: thiophenes, Glaser coupling, tribromoisocyanuric acid.

ABSTRACT

The present work focuses on the one-pot synthesis of 2,5-disubstituted thiophenes from terminal alkynes. The method uses a greener version of the Glaser coupling, utilizing copper(I) iodide, piperidine and tribromoisocyanuric acid (TBCA).¹ TBCA proved to be an excellent source of electrophilic bromine,² can also be used as an oxidant,³ has a facile synthesis,⁴ and a great atom economy. This reagent also allows the Glaser reaction to be conducted under mild conditions and no catalyst is needed.

The reaction then proceeds in a telescopic manner, without the isolation step of the recently formed 1,3-diynes, to the formation of the corresponding thiophene through heterocyclization using sodium sulfide in DMF at 80 °C for 2 h.

Therefore, the proposed method gives 2,5-disubstituted thiophenes in 70-95% yield, higher than the usual two-steps approach, with a range of terminal aliphatic or aromatic alkynes.



* Two steps reaction

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REFERENCES

- (1) de Andrade, V.S.C.; de Mattos, M.C.S. Tribromoisocyanuric acid as a useful oxidant for the synthesis of 1,3-diynes via Glaser coupling. *Monatsh Chem* **2020**, *151*, 1403–1408. DOI: 10.1007/s00706-020-02673-8
- (2) Mishra, A.K.; Nagarajaiah, H.; Moorthy, J.N. Trihaloisocyanuric Acids as Atom-Economic Reagents for Halogenation of Aromatics and Carbonyl Compounds in the Solid State by Ball Milling. *Eur. J. Org. Chem.* **2015**, *12*, 2733-2738. DOI: 10.1002/ejoc.201403463
- (3) Zolfigol, M.A.; Niknam, K.; Bagherzadeh, M.; Ghorbani-Choghamarani, A.; Koukabi, N.; Hajjami, M.; Kolvari, E. Tribromoisocyanuric Acid (TBCA) and Oxone®-MX Systems as Oxidizing Agents: Oxidative Coupling of Thiols to Their Corresponding Disulfides under Mild and Heterogeneous Conditions. *Jnl Chinese Chemical Soc.* **2007**, *54*, 1115-1118. DOI: 10.1002/jccs.200700159
- (4) de Almeida, L. S.; Esteves, P. M.; de Mattos, M. C. S. Tribromoisocyanuric Acid: A New Reagent for Regioselective Cobromination of Alkenes. *Synlett* **2006**, *10* 1515-1518. DOI: 10.1055/s-2006-941601