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FORMAL (3+2)-CYCLOADDITION OF DONOR-ACCEPTOR CYCLOPROPANES WITH ISOTHIOCYANIC ACID

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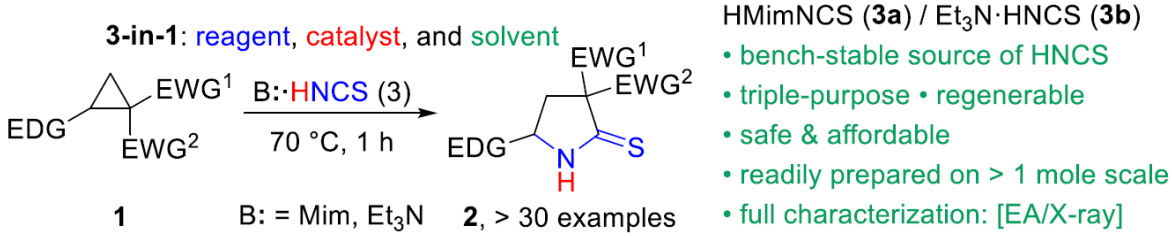
Abstract. Modern demands of synthetic chemistry rely heavily on the development of processes, which meet fundamental concepts of atom and step economy, and, thus, require design and application of less hazardous reagents and catalysts, as well as minimization of waste production. One of the most attractive solutions to all these problems implies the utilization of protic ionic liquids (PILs), i.e., low-melting salts of Brønsted acid and base.[1]

We started this work by the preparation of thiocyanate-containing PILs with organic bases (1-methylimidazole and triethylamine). Using the obtained PILs, we performed chemoselective ring-opening of D–A cyclopropanes **1** *via* nitrogen attack on the three-membered ring affording pyrrolidine-2-thiones **2** – products of the formal (3+2)-cycloaddition of isothiocyanic acid with D–A cyclopropanes.[2] Such behavior of ambident thiocyanate ion differs crucially from the typical reactivity of this nucleophile with a saturated carbon atom, when *S*-attack proceeds predominantly or exclusively.[3]

Thus, we have demonstrated for the first time that PILs containing nucleophilic anions are able to play the triple role: reaction medium, Brønsted acid, initiating the process as a catalyst, and a source of the nucleophile. A broad scope of D–A cyclopropanes have been successfully employed. Scaling up and multiple PIL recovery cycles have been demonstrated; additionally, pyrrolidine-2-thiones **2** were transformed into other valuable *N*-heterocycles.



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This work was supported by the Russian Foundation for Basic Research (project # 20-33-70014) and the President of the Russian Federation scholarship for young scientists, working on R&D in top-priority areas vital to the modernization of the Russian economy (medical technologies area, # СП-4317.2018.4).