

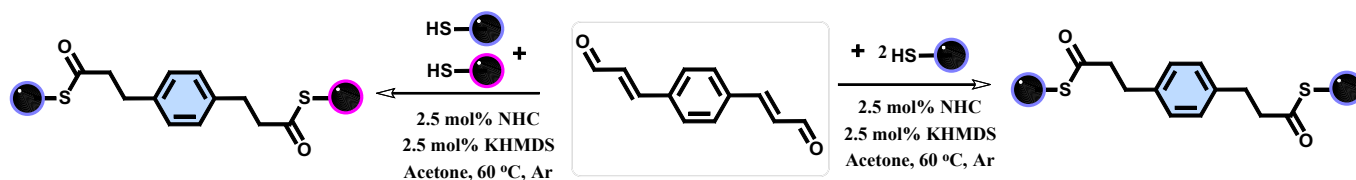
Bulky carbenes in chemoselective synthesis of bis(thioesters) from acroleins

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Organosulfur compounds can have huge variety of different applications in medicine^[1] or pharmacy.^[2] Among them, thioesters are especially interesting due to their potential application as synthetic scaffolding in many reactions^[3] or as catalysts in cascade reactions.^[4] Unfortunately, the synthetic procedures for obtaining thioesters struggle with many drawbacks, e.g., the need of use of harmful transition metal complexes, oxidants, high temperature and most importantly lack of sufficient selectivity [5-6]. The potential solution to these problems lies within the organocatalysis that utilises small organic molecules, like *N*-heterocyclic carbenes, in catalytic reactions. What is worth mentioning, bulky carbenes, that provide great steric hindrance, are especially important due to their ability to provide great selectivity under mild conditions.^[8-10]

Here we present a new, fully optimized and chemoselective method of obtaining bis(thioesters) from a commercially available acrolein derivative. The proposed method permits introduction of two sulfur groups to the thioesterification reaction that can lead to symmetrically and unsymmetrically functionalized products. For all combinations of reagents, the reactions proceeded effectively, with high chemoselectivity, leading to formation of the expected materials. All products, that constitute a scientific novelty, have been comprehensively described using available techniques, such as ¹H NMR, ¹³C NMR, ESI-MS. The XRD analyses have been performed to confirm the structures of the obtained materials.



The presented methodology is characterized with simplicity, high chemoselectivity and isolation yields, mild reaction conditions (metal-free catalyst, green solvent, low temperature) and because of that it perfectly cooperates with the rules of green chemistry that is of great importance in contemporary science.

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