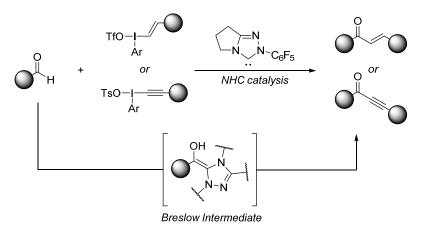
IODONIUM SALTS AS GROUP TRASFER REAGENTS – N-HETEROCYCLIC CARBENE-CATALYZED SYNTHESIS OF VINYL AND PROPARGYL KETONES

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N-heterocyclic carbene (NHC) catalysis has emerged as a powerful tool of synthetic organic chemistry, inter alia allowing for a unique umpolung activation of aldehydes via the formation of Breslow intermediate. An array of electrophiles, including less common ones, have been coupled with this nucleophilic species, giving rise to a number of useful formyl C-H functionalizations of aldehydes.[1]

Using this principle, we have developed two novel methods for the direct C-H olefination[2] and propargylation[3] of aldehydes, via the NHC-catalyzed reaction with aryl(vinyl)- and aryl(propargyl)iodonium salts, respectively. The methodology readily provides a plethora of α , β -unsaturated ketones, highly synthetically useful reagents. Importantly, the reactions employ a simple commercially available NHC precatalyst and they proceed under very mild conditions, enabling the straightforward preparation of compounds not accessible easily by other means. We have also investigated the mechanism of the new processes using both experimental and computational approaches.



^[1] Flanigan, D. M.; Romanov-Michailidis, F.; White, N. A.; Rovis, T. Chem. Rev. 2015, 115, 9307-9387.

^[2] Rajkiewicz, A. A.; Kalek, M. Org. Lett. 2018, 20, 1906-1909.

^[3] Rajkiewicz, A. A.; Wojciechowska, N.; Kalek, M. in preparation.