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Photoredox-catalysed nucleophilic α-functionalization of carbonyl compounds via destabilised carbocations

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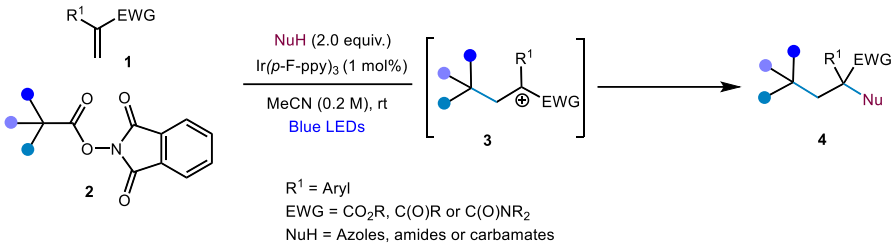
ABSTRACT

Destabilised carbocations, such as those substituted with electron-withdrawing groups, are underexplored majorly due to their inaccessibility under mild reaction conditions.[1,2] While the α-position of carbonyl compounds is known for nucleophilic reactivity,[3] exploiting umpolung α-carbonyl carbocations under a new mechanistic strategy could be valuable to expand the reaction space. Here, we report a photoredox-catalysed *C*-centred radical addition to Michel acceptors **1** that generates an α-carbonyl carbocation **3** upon oxidative radical to polar cross-over by a photocatalyst. These destabilised intermediates were successfully trapped with weak nucleophiles including azoles and amides. This reaction provides a direct method for making valuable α-functionalised carbonyl compounds **4** including α-amino acid derivatives. Readily accessible redox-active phthalimide esters **2** served as precursors for reductively generating 1°, 2° and 3° nucleophilic carbon radicals under mild reaction conditions using Ir-based photocatalyst. Moreover, Michael acceptors other than acrylates can also be used in the transformation, including α,β-unsaturated ketones, and amides.



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