

Photosensitized Intermolecular Carboimination of Alkenes through the Persistent Radical Effect

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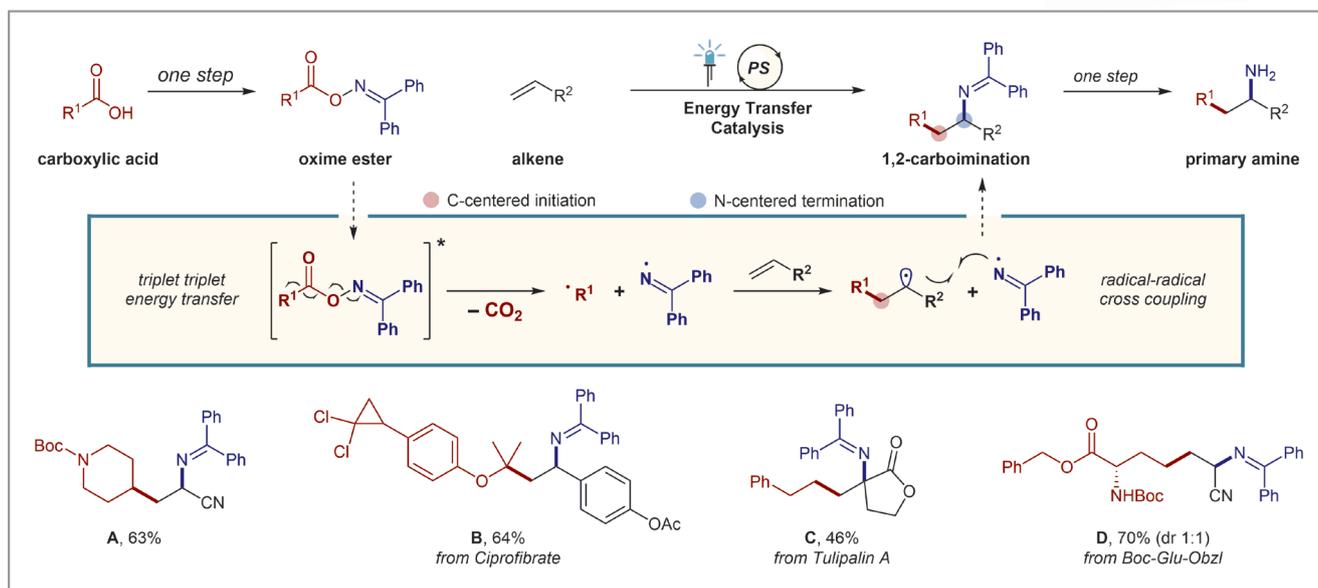
Aliphatic amines are amongst the most prevalent functionalities in organic molecules, including natural products, drugs, peptides, bioactive compounds and agrochemicals. Owing to their favorable physical and chemical properties, the introduction of amine functionalities in small molecules can increase their likelihood of success as pre-clinical candidates. “In this regard, a powerful strategy to synthesize complex primary amines from accessible feedstocks is even more important, since primary amines are the common precursor for amides as well as for secondary and tertiary amines,” said Professor Frank Glorius from the Westfälische Wilhelms-Universität Münster (Germany). “In this work, we developed a 1,2-carboimination strategy for alkenes, resulting in the concurrent installation of both carbon and nitrogen functionalities on the alkenyl framework. For this purpose, we used benzophenone-based oxime esters as bifunctional C- and N-radical sources.” He continued: “Expediently, these oxime esters can be easily prepared from highly abundant and inexpensive aliphatic carboxylic acids to afford the corresponding C-radicals. The N-centered benzophenone iminyl radical is concurrently generated, to participate in a radical–radical cross-coupling pro-

cess providing the final 1,2-carboiminated product. Importantly, the benzophenone iminyl functionality can be readily converted into primary amines by hydrolysis.”

Professor Glorius noted that in general, almost all known N-centered radicals are highly reactive and tend to add first to the alkene C=C bond, which would require the subsequent addition of carbon functionalities. Professor Glorius said: “In contrast, the realization of relatively long lifetimes of the N-centered benzophenone iminyl radical is remarkable. As a result, selective C-radical addition to the alkene indeed occurs first, followed by the N-radical addition to give an overall regioselectivity switch. Importantly, the overall process is highly atom-economic and generates carbon dioxide as the sole byproduct.”

Professor Glorius concluded: “Most radicals generally applied in synthesis are transient (short-lived) in nature. Hence, the key discovery of the high lifetimes of the N-centered benzophenone iminyl radicals has a great potential, as it allows for radical recombinations in alkene difunctionalization chemistry and beyond.”

Master's thesis



About the authors



Dr. T. Patra

Tuhin Patra obtained his B.Sc. degree in chemistry from University of Calcutta (India). After his M.Sc. in chemistry from Indian Institute of Technology Bombay, in 2011, he joined the group of Prof. Debabrata Maiti to explore the field of distal C–H activation. Soon after the completion of his PhD in 2017 from IIT Bombay (India), he moved to Münster (Germany) to join the group of Prof. Frank Glorius as an Alexander von Humboldt post-

doctoral fellow. His postdoctoral research has centered on the development of new methods through visible-light photocatalysis.



P. Bellotti

Peter Bellotti received his B.Sc. degree in chemistry from the University of Milan (Italy) under the supervision of Prof. Cesare Gennari. While completing his M.Sc. in advanced synthesis and catalysis at the University of Regensburg (Germany) in the research group of Prof. Burkhard König working on visible-light carboxylation reactions, he joined Hoffmann–La Roche pRED, Basel (Switzerland) for one year in industry, focusing on

cancer and neurodegenerative diseases. In 2019, he started his PhD in the group of Prof. Frank Glorius, focusing on visible-light photocatalysis and N-heterocyclic carbenes (NHCs) on surfaces.



F. Strieth-Kalthoff

Felix Strieth-Kalthoff studied chemistry at the University of Münster (Germany), where he obtained his BSc degree under the supervision of Prof. J. Neugebauer in 2015. After a six-month research stay with Prof. T. F. Jamison at the Massachusetts Institute of Technology (USA), he joined the group of Prof. F. Glorius at the University of Münster, where he received his MSc in 2017. Currently, he is a doctoral student in the same

group, focusing on the development of photocatalytic reactions and screening methodologies for their discovery.



Prof. F. Glorius

Frank Glorius is a Full Professor of Organic Chemistry at the Westfälische Wilhelms-Universität Münster (Germany). His research program focuses on the development of new concepts for diverse areas of catalysis such as photocatalysis, C–H activation, smart screening and data-based technologies, and N-heterocyclic carbenes (NHCs) in organocatalysis and as surface modifiers and in (asymmetric) arene hydrogenation.