

SEMINARIO

Lunedì 27 marzo 2023

ore 14:30 15.00

<u>Aula Seminari</u> AULA T5

Dipartimento di Scienze e Tecnologie Chimiche

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Merging methodology and technology: pushing boundaries in photocatalyzed synthesis

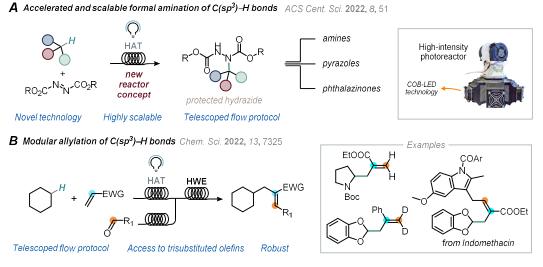
Proponente: Prof. Massimo Bietti

Abstract. Gone are the days when the development of new synthetic methods was the sole driving force in organic chemistry. Nowadays, a strategic blend of methodology and technology holds the key to the future of synthesis. In this seminar, I will demonstrate the potential of this approach by presenting three instances from my recent research.

First, a convenient approach for the accelerated and scalable formal amination of unactivated $C(sp^3)$ – H bonds will be illustrated (Figure 1A). This reaction proceeds via photocatalyzed hydrogen-atom transfer (HAT), where the excited state of a photocatalyst cleaves a C–H bond in the substrate to deliver a C-centered radical; the nascent radical is readily trapped by azodicarboxylates. In this case, I took advantage of an exclusive technology patented by Signify based on high-intensity LEDs (144 W optical power) to enable fast results gathering and scalability in a single device, thus bridging the gap between academic discovery (mmol scale) and industrial production (>2 kg/day productivity).

Second, a telescoped approach for the modular allylation of $C(sp^3)$ –H bonds in continuous-flow will be shown (Figure 1B). Specifically, our sequence featured the merger of a radical hydroalkylation step via photocatalyzed HAT and Horner-Wadsworth-Emmons (HWE) olefination to deliver the targeted allylated compounds. This approach allowed the synthesis of densely functionalized olefins that cannot be prepared via traditional protocols for radical allylation.

Finally, a novel methodology for C–C bond formation based on photoinduced halogen-atom transfer will be presented (Figure 1C). Here, a photocatalyst was used to generate NHC-ligated boryl radicals from the corresponding boranes, thus promoting the homolytic cleavage of a C–X bond (X: halogen) to deliver a C-centered radical. The mildness of the present approach is demonstrated by the fact that derivatives of medicinally-relevant compounds and biologically-active molecules were smoothly functionalized. The key role of the NHC-ligated boryl radicals in the operative reaction mechanism was uncovered through a combination of experimental, spectroscopic and computational studies. Future outlooks for my research will be also given at the end of the talk.



C Photoinduced Halogen-Atom Transfer by NHC-ligated boryl radicals J. Am. Chem. Soc. 2023, 145, 991

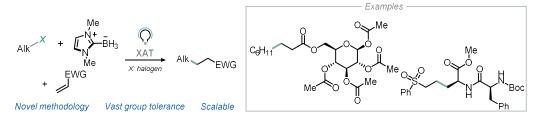


Figure 1. Merging methodology and technology: pushing boundaries in photocatalyzed synthesis.