New photocatalytic strategies for organic synthesis with ketyl radicals

About the project or challenge area: Visible-light photoredox catalysis is becoming an increasingly valuable tool in organic synthesis. This is because it allows versatile free radical intermediates to be formed by single electron transfer (SET) reactions under mild conditions by simply irradiating reaction mixtures with common household lightbulbs or LEDs. However, for particularly challenging SET reactions, photoredox catalysis fails, and therefore stoichiometric amounts of strong oxidants or reductant are required instead. This is often the case for ketyl radicals, which are highly useful synthetic intermediates that can be accessed by single electron reduction of carbonyls, such as aldehydes or ketones. Typically, this challenging reduction requires the use of super-stoichiometric strong metal reductants, which leads to a lot of waste and limits the sustainability of these reactions.

In this project, you will investigate new strategies that allow ketyl radicals to be generated under mild catalytic conditions and without the use of stoichiometric reductants. This will be achieved by designing redox-active derivatives of aldehydes and ketones that can be transformed into ketyl radicals using photoredox catalysis (Figure 1). These new reagents will enable us to significantly expand the scope of ketyl radical chemistry beyond what is currently possible with stoichiometric reductants.

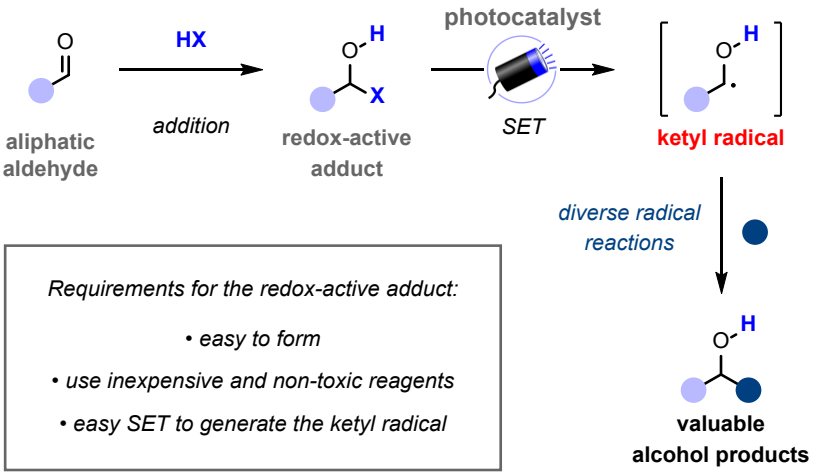

Figure 1

Why choose this opportunity? The focus of your project will be to develop new approaches to ketyl radicals using visible-light photoredox catalysis, which will provide an excellent platform to learn about photochemistry, radical chemistry, and the development of new synthetic methodologies. Your work in this area will provide new, sustainable reactions that can be used to make important organic molecules, such as bioactive natural products, pharmaceuticals, and agrochemicals. You will develop and increase your expertise in broad chemical synthesis and characterization techniques, whilst becoming familiar with the fundamentals of organic synthesis and photocatalysis. Furthermore, this project will require your collaboration with members of other research groups, thus improving your teamwork and networking skills. You will also develop a range of transferable skills, including presentation, scientific writing, and project and time management. Finally, you will be interacting with students from all over the world learning from their culture and skills, adding to your professional and personal development.

Full training will be provided for all aspects of this project. You will be embedded in the Supervisor's research group, who will provide support. In addition, you will be assigned a mentor for the duration of your project, who will provide extra support and help you to identify any additional training needs or opportunities.

About you: Ideally, you will already have skills and knowledge in general synthetic organic chemistry, analytical methods, teamwork and time management.

Bench fees: A bench fee of £10,000 is required.

How to apply: Applications are accepted throughout the Academic Year, and you should complete the online application form for Chemistry (MSc by Research).

Supervisor: Your supervisor for this project will be Adam Noble, Research Fellow in the School of Chemistry. You can contact him at a.noble@bristol.ac.uk

Find out more about your prospective research program: This review article provides an overview of ketyl radical chemistry, including different catalytic methods used for their generation:

Recent advances in the chemistry of ketyl radicals. *Chem. Soc. Rev.* **2021**, *50*, 5349 (https://pubs.rsc.org/en/content/articlepdf/2021/cs/d0cs00358a)