



Digest paper

# Asymmetric induction in photocatalysis – Discovering a new side to light-driven chemistry

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## ABSTRACT

The state of asymmetric photocatalysis is exceptionally promising, as chemists from different fields and backgrounds have converged to solve a longstanding issue: stereocontrol in photochemistry. As a strategy that relies heavily on the elevated reactivity of radical intermediates, managing to suppress the background racemic reactions in favor of the stereoselective processes is a challenging endeavor many researchers have embarked on. In order to tackle this matter, conceptually diverse activation modes have been developed, obtaining valuable results across mechanistically-distinct types of reactions, all while setting the stage for future breakthroughs in the field.

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## Introduction

Photo-induced transformations have been at the forefront of chemical research for many years, yet lately they have received enormous interest.<sup>1</sup> The basis for modern photocatalytic methodologies is set on the transmission of photons to a specific molecule – a photosensitizer, which can be parlayed into the population of the molecule's excited state. This energy can then be transferred to other substrates via energy or electron transfer, wherein the

pairing of excited-state energies and of redox potentials, respectively, of the sensitizer and the reactive substrate is crucial for a successful outcome in photochemical reactions.

Light absorption strategies are frequently employed across organic chemistry to construct bonds that are somewhat difficult to build through traditional two-electron pathways. Conventional formation of carbon-carbon bonds is fundamentally based on reagents that require a preactivation step. However, many photochemical procedures allow the researcher to work with substrates that are simple, diverse, and commercially available. The straightforwardness of these reactions is also latent in the mild conditions under which they usually take place, leading to immense potential in functional group tolerance. Furthermore, the photogeneration of open-shell intermediates is an exciting aspect as well, as they are ideal species to interact with highly-congested carbons in

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unusually complex molecules. Therefore, direct synthetic routes, which yield novel bond constructions in intricate environments, are discovered.

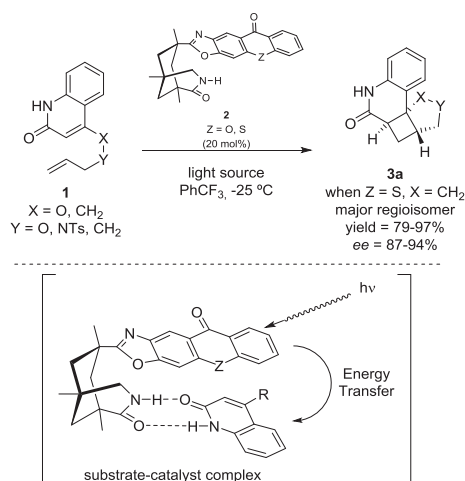
Photocatalytic approaches repeatedly depend on either an external photosensitizer or a photoactive species generated *in situ* by means of substrate-catalyst interactions. As shown in the increasing body of published work in photochemistry, new synthetic pathways can be opened through visible light irradiation, a benign energy source under which organic molecules tend to be inert. Consequently, the more powerful UV irradiation can be avoided.

Asymmetric induction in photochemical reactions is a formidable challenge that has recently been rediscovered by the scientific community.<sup>2</sup> The involvement of high-energy intermediates is translated into short lifetimes for these species and quick follow-up reactions featuring low energetic barriers. For this reason, the implementation of an asymmetric catalyst capable of controlling the sterics of the reaction while also suppressing the background racemic process is the quintessential issue. If the structural variety of these reaction intermediates is considered as well, the development of optimal chiral catalysts that should fit the geometrical prerequisite for each species can be labeled as arduous.

Nevertheless, organic chemists have recognized this challenge by developing a wide array of truly remarkable strategies based on different concepts and applied to several kinds of reactions and substrates. Herein, the most noteworthy contributions to the field of asymmetric photocatalysis are presented.

### The advent of energy transfer processes. Photocycloadditions and other reactions

An initial report on enantioselective photocatalysis surfaced in 2005, wherein Bach's group displays initial studies on a photo-induced electron transfer (PET), employing a chiral organocatalyst equipped to fulfil two roles.<sup>3</sup> Firstly, it presents two hydrogen bonding sites to establish a chiral environment around the substrate. Secondly, a benzophenone-type unit can act as a photosensitizer under UV irradiation. This approach was further investigated, yielding excellent results for intramolecular [2 + 2] photocycloadditions (PCAs) completed with quinolones **1**, presumably catalyzed through an energy transfer process.<sup>4</sup> The substrate-catalyst complex shown in Scheme 1 enables the energy transfer from the light-harvesting xanthone sensitizer **2** to the substrate, which then undergoes the ensuing PCA in enantioselective fashion



**Scheme 1.** Bach's PCA strategy employing chiral photo-organocatalysts **2**. Z = O (366 nm), Z = S (400–700 nm).

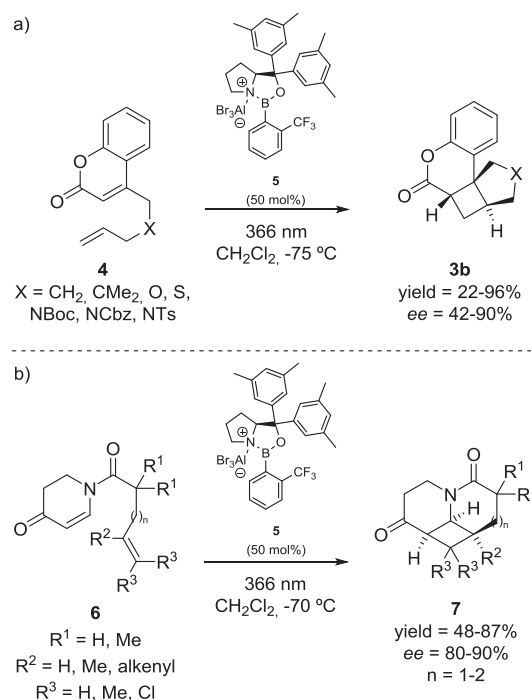
because of the control element inherent of the rigid oxazole structure. An interesting variant was introduced when the xanthone moiety was replaced by a thioxanthone group, allowing the reaction to proceed under visible light irradiation.<sup>5</sup>

Additionally, Sibi and Sivaguru introduced a different form of H-bond organocatalysis in this field by developing atropisomeric binaphthyl-derived thioureas to catalyze the intramolecular [2 + 2] PCA of 4-alkenyl-substituted coumarins.<sup>6</sup> The interaction between the organocatalyst and the substrate leads to a bathochromic shift of the mixture when compared to each component on its own. Irradiation at the appropriate wavelength delivers an enantioselective energy-transfer-driven transformation, while stifling the background racemic reaction.

Bach and co-workers had already disclosed an enantioselective intramolecular PCA of coumarins **4**, featuring in this case the unexplored use of chiral Lewis acids in photochemical reactions (equation a, Scheme 2).<sup>7</sup> Oxazaborolidines activated by AlBr<sub>3</sub> (**5**) display exceptional behavior, inducing a bathochromic shift upon coordination to the substrates. Application of these highly-stereoregulating Lewis acids to the intramolecular [2 + 2] PCA of synthetically useful enones, such as 5,6-dihydro-4-pyridones **6**, was later reported by Bach (equation b, Scheme 2).<sup>8</sup> The strong absorption of the enone-Lewis acid complex prevents any background reaction of uncomplexed enones **4** or **6**.

A broader synthetic approach towards cyclobutanes **10** was described in 2014 by Yoon's group (Scheme 3).<sup>9</sup> Lanthanide-based Lewis acids **9** proved to be effective cocatalysts for the promotion of intermolecular [2 + 2] PCAs, involving  $\alpha,\beta$ -unsaturated ketones **8a** and **8b**. The independent photocatalyst [Ru(bpy)<sub>3</sub>]<sup>2+</sup> used in this transformation gives way to a wider substrate scope since the reaction is no longer dependent on the spectral properties of the starting material.

Lewis acid-coordination to the substrate to induce a bathochromic shift in the energy of its singlet excited state represented an alternative to stereoselective energy transfer PCAs (Bach's strategy).<sup>7,8</sup> Yoon expanded this concept, triggering a similar effect on the energy of the triplet excited state of the Lewis acid-substrate



**Scheme 2.** Lewis acid-enabled PCAs reported by Bach's group.

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