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Review

Recent Advances of Dicyanopyrazine (DPZ) in Photoredox Catalysis

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Abstract: Visible light organophotoredox catalysis has emerged as an invaluable tool for organic synthetic transformations since it works brilliantly in tandem with organic substrates and has been known to create unique chemical environment for organic transformations. Dicyanopyrazine (DPZ), a relatively lesser researched organophotoredox catalyst, has shown great potential through its catalytic activity in organic synthesis and necessitates attention of synthetic community.

Keywords: visible light; organophotoredox; dicyanopyrazine

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1. Introduction

Visible light photoredox catalysis is conceivably one of the most exponentially growing areas of viable and economical synthetic organic chemistry [1–10]. Continuous investigation of this field has substantiated that it can be applied to accomplish several innovative molecular transformations, otherwise inaccessible by traditional methods of organic synthesis [11–14]. Based on its broad synthetic scope, exceptional tolerance to wide range of functional groups, easy activation of even poorly reactive bonds within molecules, and the different kinds of unique bond constructions that have been achieved using this system, researchers are now attempting to synthesize increasingly complex target molecules through the use of visible light. Apart from organic synthesis, the efficacy of photoredox catalysis has also been successfully implemented for late-stage functionalization of several advanced drug candidate intermediates [15] and for solving longstanding challenges of pharmaceutical chemistry [16]. Visible light-mediated photocatalysis has undergone major breakthroughs and many novel activation modes, catalytic systems, and synthetic protocols have been developed.

In order to direct the potential of visible light toward maximum usefulness and to ensure the productive exploitation of visible light as a reaction inducer, effective photoredox catalysts are a definite prerequisite. The role of transition metal complexes as photoredox catalysts is already well established [17]. However, as the focus on sustainability is increasingly becoming the central idea around which synthetic protocols are developed, organic photoredox catalysts have attained center-stage. Organophotoredox catalysts are excellent catalytic tools that can act as both strong oxidants and strong reductants in their excited state, work really well with organic substrates, and can lead to unprecedented forms of organic transformations [13,18–24]. Organic photocatalysts, however, present a challenge of restricted tunability in their properties. It is extremely desirable for a photocatalyst to possess some scope for modifications as per a reaction requirement. 4,5-disubstituted-pyrazine-2,3-dicarbonitrile (dicyanopyrazine, DPZ) presents itself as an organic photocatalyst that can be tuned for specific objectives in a synthetic protocol. The push-pull molecules derived out of DPZ serve as better charge transfer chromophores and exhibit elegant photocatalytic capabilities in several organic transformations. The possibilities of structural modifications, particularly involving the remodeling of donor and acceptor and installation of new functionalities in these push-pull family of molecules, promises development of several novel efficient photocatalysts. DPZ is practical as a SET (single electron transfer) as well as EnT (energy transfer) based photoredox catalyst. By using different π systems in DPZ derivatives, its catalytic properties such as effectiveness of electron transport and stability of the photocatalyst can also be tuned to requirement. One of the most remarkable properties of DPZ is its ability to enable chemoselectivity control in certain reactions. The desirable photoelectronic properties of DPZ such as its high chemical and photo-stability, HOMO-LUMO gap and its polarizable π system, ascertain usefulness in different radical cascade pathways. Photosensitizer DPZ-derived chromophores have also been effectively employed in various enantioselective synthetic protocols, radical coupling reactions, and cooperative photocatalysis. The combinations of DPZ with other chiral catalysts to produce unique chiral H-bonding catalytic systems for stereocontrol of reactions has been a budding research area. DPZ and its derivatives, therefore, have emerged as outstanding organic photoredox catalysts for diverse synthetic organic transformations. As part of our ongoing work in the field of photocatalyzed synthesis, [25–42] in this review, we aim to highlight reports that demonstrate the catalytic activity of DPZ as an organophotoredox catalyst (Figure 1).

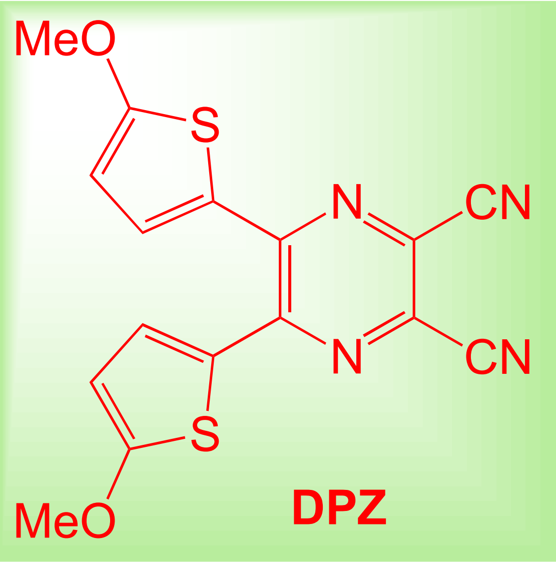
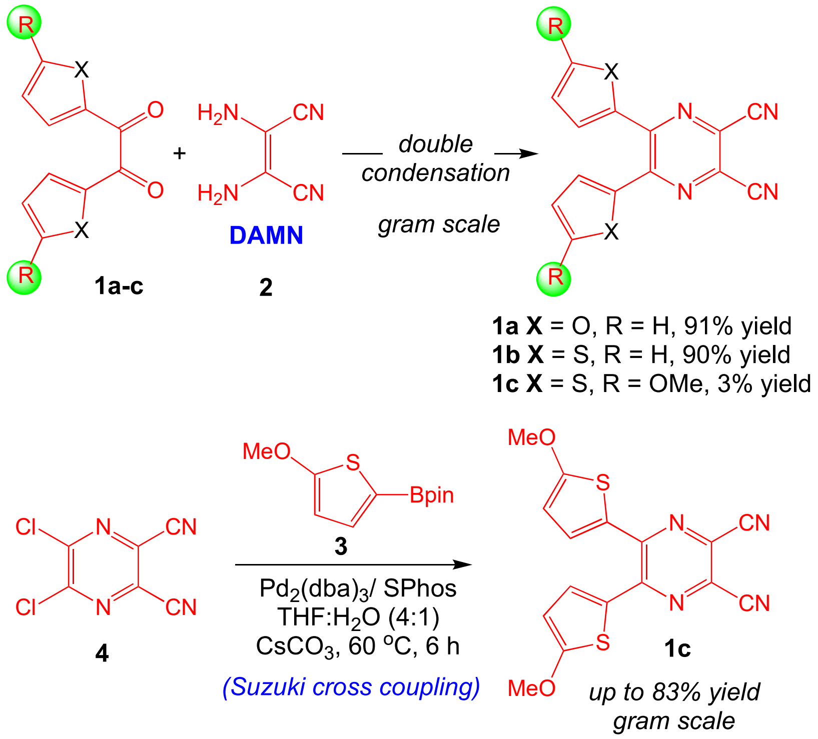


Figure 1. Structure of dicyanopyrazine (DPZ).

2. Synthesis of DPZ

In 2012, F. Bureš and co-workers [43,44] presented push–pull molecules based on 5,6-disubstituted pyrazine-2,3-dicarbonitrile (dicyanopyrazine, DPZ) and their nonlinear optical properties were investigated by Jiang group [45,46]. These organic photocatalysts can be readily prepared from available starting materials such as diaminomaleodinitrile (DAMN) in excellent yields (Scheme 1).



Scheme 1. Synthetic protocols for the synthesis of DPZ.

3. Photochemistry of DPZ

The photochemistry of DPZs reveals that the LUMO is localized in the pyrazine core whereas at the center of the donor groups HOMO is situated at position 5 and 6. [45,46] This polarized system exhibits an effective CT (charge transfer) character (Figure 2) and a short S1 lifetime (<1 ns) that is generated due to their weak fluorescence [47]. Therefore, DPZ photocatalyst exclusively reacts in their T1 state. Two structural features participate in the optimization of the DPZ photocatalyst: (i) the EDGs (electron withdrawing groups) at positions 5 and 6, and (ii) the EW (electron withdrawing) heterocyclic core. Among these two features, the second one has the lesser impact.

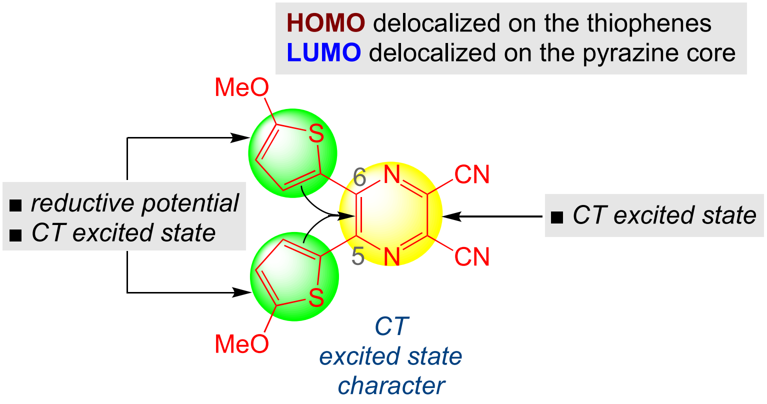
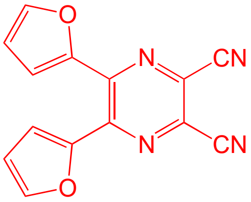
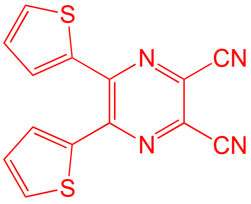
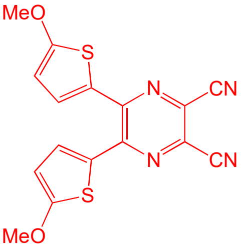


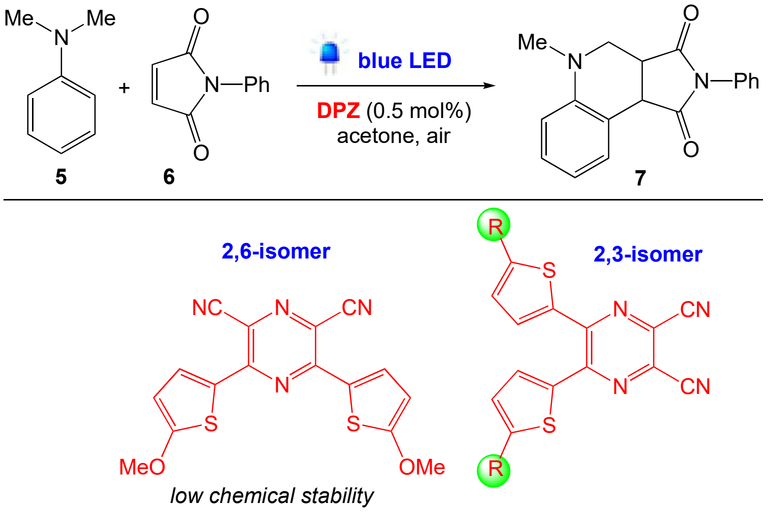
Figure 2. The structure–property relationship of the DPZ.

The main strategy to regulate the reduction potential depends on the modification of the donor groups [47]. The furyl group (1a) decreases the energy of the HOMO and it is a photocatalyst with a balanced distribution of the oxidative and reductive power, which mainly depends on the absorption of UV-light (Table 1). In 1b, the substitution of the furyl group for its sulfur analogue reduces its $E_{0,0}$ while red-shifting (bathochromically) its absorption. Furthermore, the presence of more electron-donating groups (EDGs) renders 1c an excellent visible-light photocatalyst, with an λ_{max} centered at 448 nm, sustaining good level of E_{red} and E_{ox}. The charge transfer (CT) character also increases along the series (Scheme 2).

Table 1. Impact of electron-donating groups at positions 5 and 6.

	 **1a**	 **1b**	 **1c**
λ_{abs} (nm)	379	391	448
ε[$M^{-1}cm^{-1}$]	17,400	14,600	21,500
E^*_{red} (V)	−1.36	−1.00	−1.07
E_{ox} (V)	1.95	1.32	1.32
increasing donor ability			***red shift absorption***

Povarov cyclization (Scheme 2) [48] represents a comparison of the synthetic performances of the different scaffolds. The initial key step of this reaction is the oxidation of the amine 5 by the photocatalyst. Because of low chemical stability of photocatalyst 8, containing the methoxy-substituted thienyl ring, its utilization was unsuccessful, whereas the use of the 2,3-dicyanopyrazine photocatalysts 1b and 1c afforded 7 in good to excellent yields (73% and 95% respectively). The authors explained these results of higher absorption of 1c, able to generate higher amount of photocatalyst-excited state in solution.

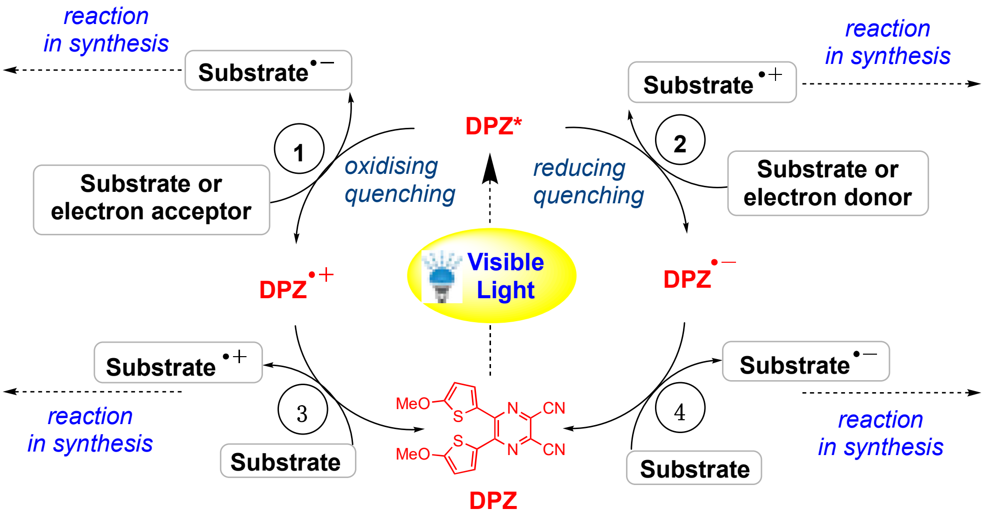


	8	R= H, **1b**	R= OMe, **1c**
E^*_{red} (V)	1.55	1.79	1.36
E_{ox} (V)	1.57	1.75	1.32
yield (%)	<1	73	95

increasing stability & λ *improved performance*

Scheme 2. Structural tuning of the DPZ.

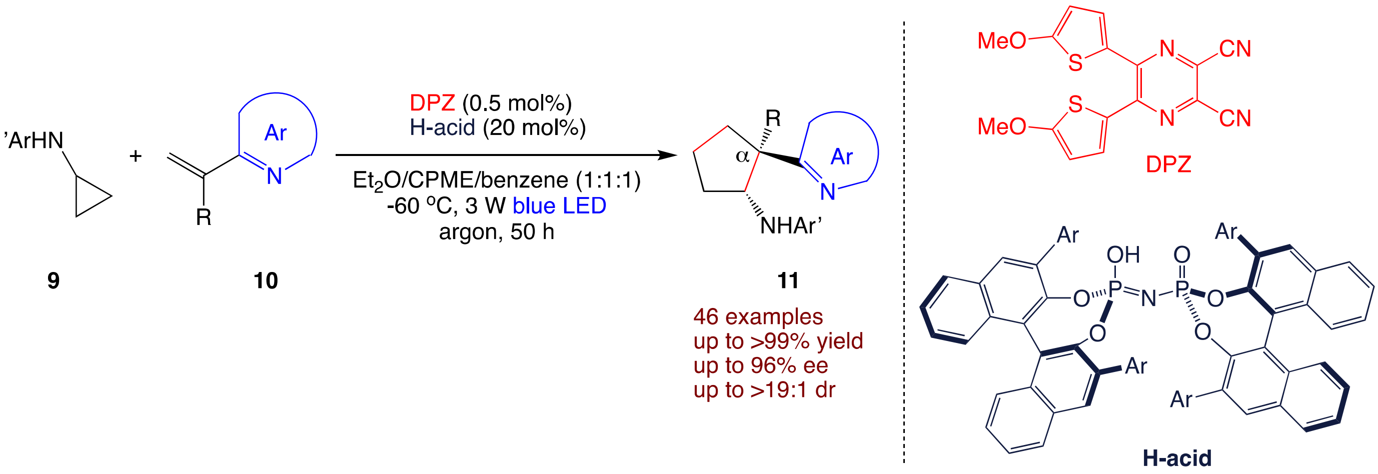
In presence of visible light, DPZ undergoes quenching process to generate DPZ$^+$/DPZ$^-$, subsequently followed by a substrate to form substrate radical cation or anion in the chemical reaction to give the desire product. The general mechanistic pathway for DPZ photocatalysis has been depicted in Scheme 3.



Scheme 3. The general mechanistic pathway for DPZ photocatalysis.

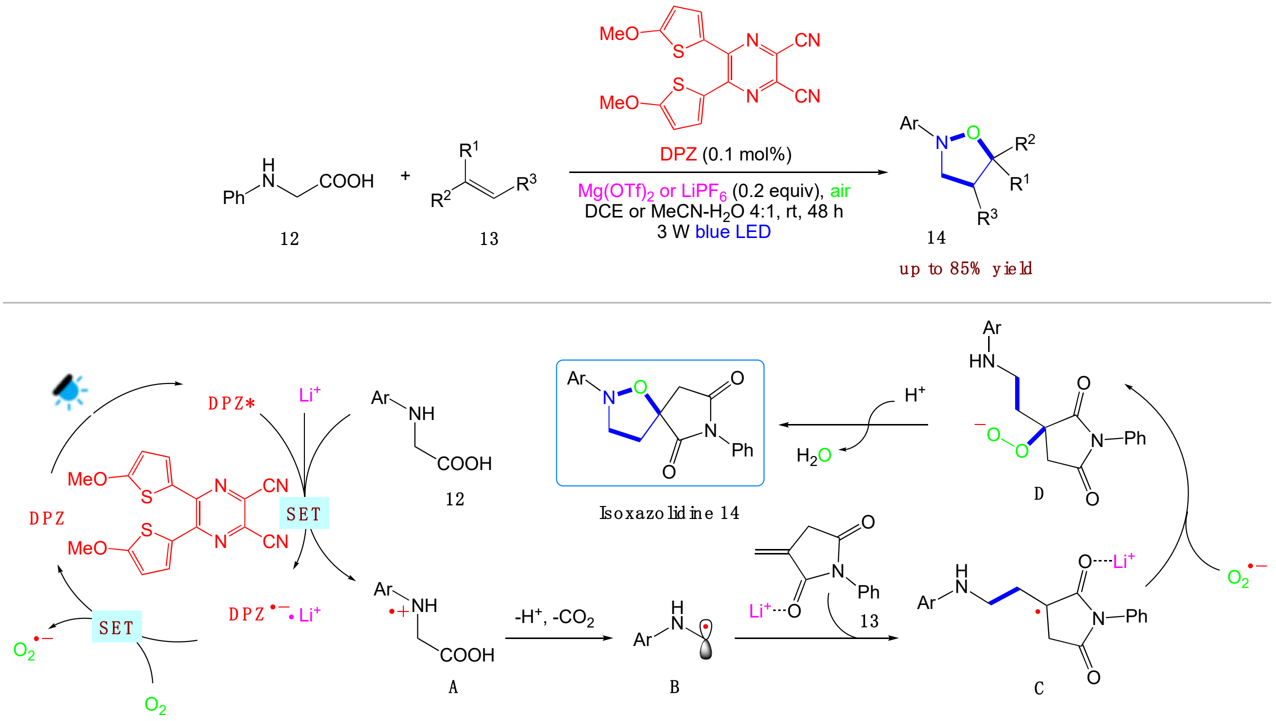
4. Applications in Photoredox Chemistry

A rapidly growing number of chemical transformations employs DPZs as photocatalysts [49–63]. In 2020, Jiang et al. reported a radical-based asymmetric olefin difunctionalization strategy for rapidly forging all-carbon quaternary stereocenters α to diverse azaarenes (Scheme 4) [64]. Under cooperative DPZ as photoredox and chiral Brønsted acid catalysis, cyclopropylamines 9 with α- branched 2-vinylazaarenes 10 can undergo a sequential two-step radical process, furnishing various valuable chiral azaarene-substituted cyclopentanes 11. The use of the rigid and confined C2-symmetric imidodiphosphoric acid catalysts achieves high enantio- and diastereo-selectivities for these asymmetric [3 + 2] cycloadditions.



Scheme 4. Enantioselective construction of all-carbon quaternary stereocenters α to azaarenes.

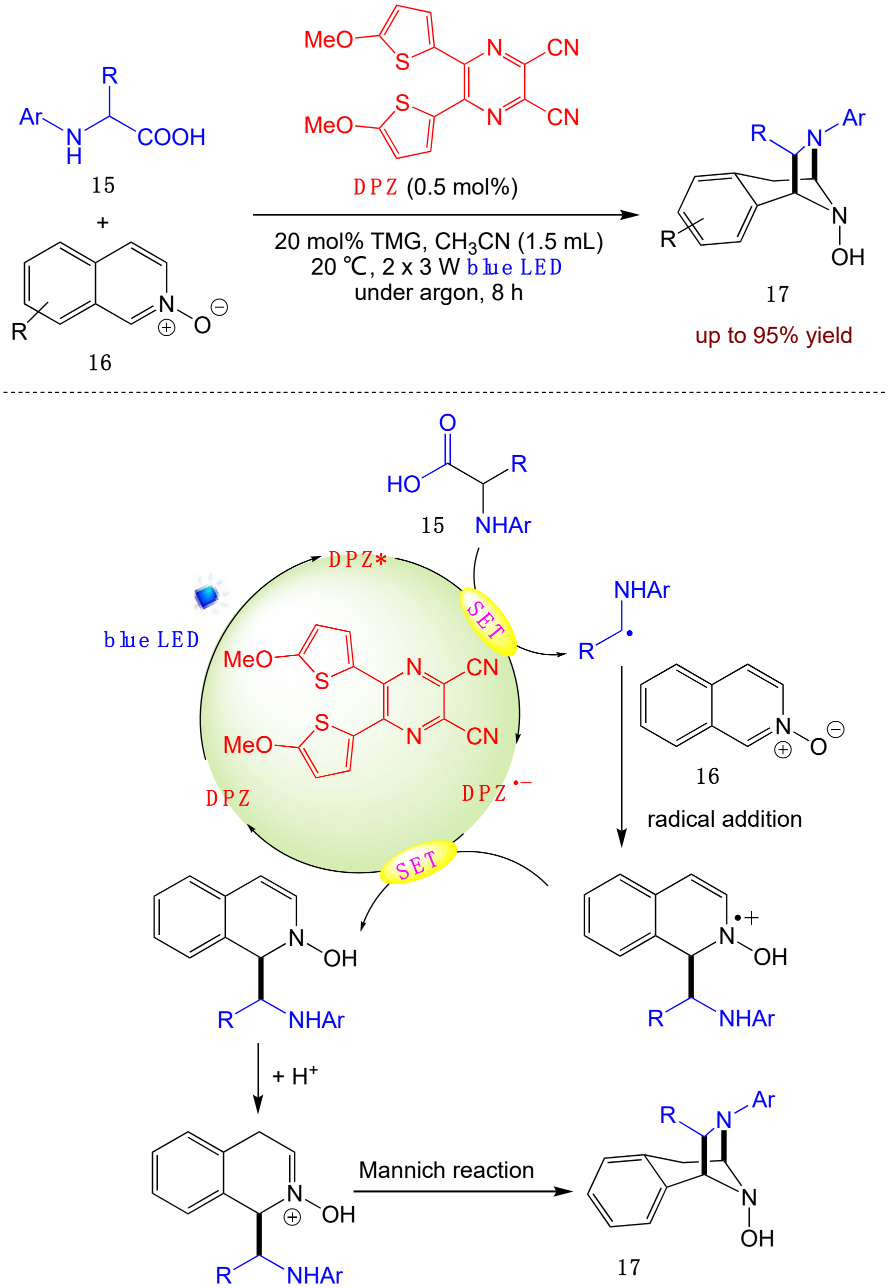
In 2019, Jiang et al. reported an access to isoxazolidines featuring visible-light induced aerobic difunctionalization of alkenes. α-Amino radicals generated via oxidative decarboxylation of *N*-aryl glycines add to alkenes and the resulting radical intermediates are trapped by superoxide. The peroxides undergo swift intramolecular amine oxidation to provide valuable isoxazolidines. Alkenes with varied functionalization can be applied. The isoxazolidine ring can be readily opened via reduction by zinc in acetic acid to afford γ-lactams in high yield (Scheme 5) [65].



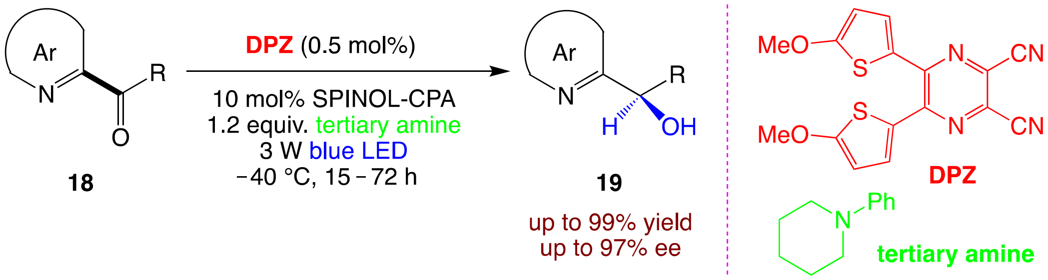
Scheme 5. Access to isoxazolidines through visible-light-induced difunctionalization of alkenes.

In 2019, Jiang et al. reported a formal [3 + 2] cycloaddition of *N*-aryl α-amino acids with isoquinoline N-oxides via visible light-driven using a dicyanopyrazine-derived chromophore (DPZ) as the photoredox catalyst. The transformation was efficient and led to a series of important diazabicyclo[3.2.1]octane-based *N*-heterocyclic compounds. They demonstrate the synthetic utility of *N*-aryl α-amino acids as 1,2-synthons and provides a new strategy for the dearomatization of isoquinolines (Scheme 6) [66].

In 2019, Jiang et al. also reported an enantioselective reduction of azaarene-based ketones through photoredox asymmetric catalysis. With a dual catalytic system including DPZ as a phoredox catalyst and SPINOL-CPA as a Brønsted acid catalyst and using a tertiary amine as the terminal reductant, these transformations underwent a tandem process involving double SET reductions and then enantioselective protonation, providing valuable chiral alcohols in high yields (up to >99%) with good to excellent enantioselectivities up to 97% yield (Scheme 7) [67].



Scheme 6. Photoredox DPZ catalyzed formal [3 + 2] cycloaddition of *N*-aryl α- amino with isoquinoline *N*-oxides.



Scheme 7. Enantioselective reduction of azaarene-based ketones via visible light-driven photoredox asymmetric catalysis.

5. Conclusions

DPZ has demonstrated its catalytic potential in synthetic transformations, has led to unique chemical transformations, has tunable photocatalytic properties, and has definite advantages over some other photocatalysts. Being an organophotoredox catalyst, its applications in organic transformations are a very promising area for exploration. However, research on the properties and possible synthetic applications of DPZ is still in its preliminary stage and needs to be further explored to realize its full potential. Continuous interest in such photocatalysts will potentially enable organic chemistry to achieve sustainability and efficiency goals.

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