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Photocatalytic synthesis of phenanthridine derivatives using Iridium photocatalyst

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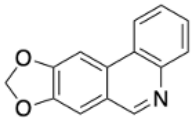
Abstract
Phenanthridine derivatives are one of the most extensively investigated classes of biologically potent compounds. There has been substantial research interest in the turn of this century in the formation of these N- containing heterocyclic compounds as they are widely present in many alkaloids and also exhibit remarkable biological properties including bactericidal, antifungal in nature, anticancer activities. In this regard, a number of synthetic strategies toward the formation of phenanthridine fragments with various substituted groups, and to improve their yield have been devised by the synthetic organic community. Even though many researchers have established various novel methods for the synthesis of phenanthridine derivatives for the past few years, still there is considerable potential for the development of new synthetic methods. In this review, the recent advances in the different photocatalytic approach for regioselective preparation of phenanthridine derivatives using Ir photocatalyst are described. The present review also enlightens the use of different chemicals, the variety of the starting materials identified, and the proposed mechanisms elucidated towards the construction of these biologically significant frameworks.

Keywords: *Nitrogen containing heteroatomic molecule, Ir-photocatalyst, visible/blue/LED light, Phenanthridine*

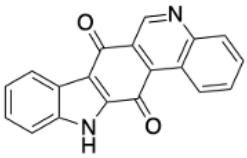
Introduction

Nitrogen-containing heteroaromatic compounds are of considerable interest because of their reactivity and biological characteristics. Phenanthridine is a significant fused heteroaromatic framework present in pharmaceutical agents, natural products, and other functional molecules, and belongs to the quinoline family. The phenanthridine framework is commonly found in natural alkaloids and bioactive pharmaceutical agents including lycobetaine, trispheridine, sanguinarine, chelerythrine, oxyavicine, and nitidine (Figure 1).[1] These alkaloids have received substantial attention owing to their medicinal significance and prospective pharmacological activities.[2]

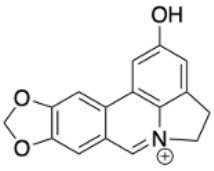
For instance, the monofunctional platinum(II) compound phenanthriplatin has demonstrated notable antitumor and optoelectronic properties.[3,4] Among the most significant and attractive phenanthridine derivatives is 3,8-diamino-5-ethyl-6-phenylphenanthridinium, commonly known as ethidium bromide (EB) (Figure 1), which is widely employed as a standard fluorescent marker for DNA and RNA. Ethidium bromide exhibits both antiparasitic and antitumor activities under in vivo and in vitro conditions.[5,6]



Trisphaeridine
(anti-HIV-I protease activity)



Calothrixn B
(DNA topoisomerase I poisoning activity)



Lycobetaine
(topoisomerase IIβ-selective poision and antitumor activity)

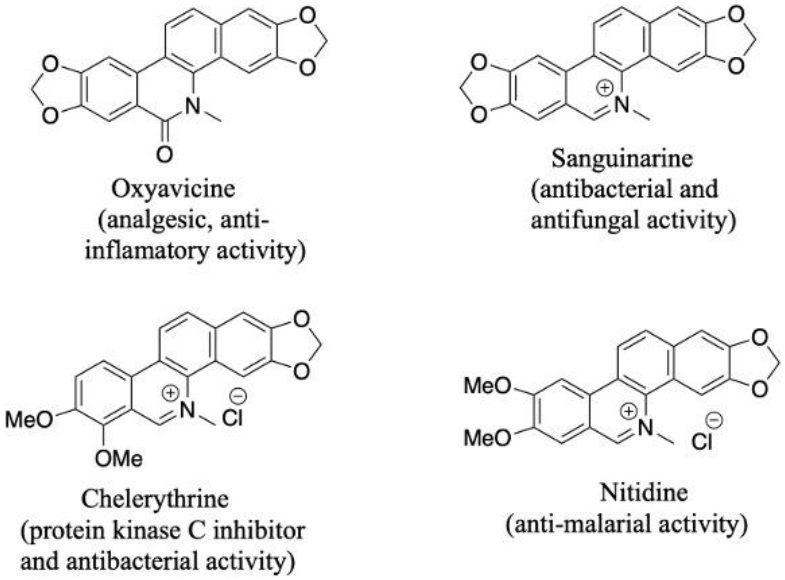
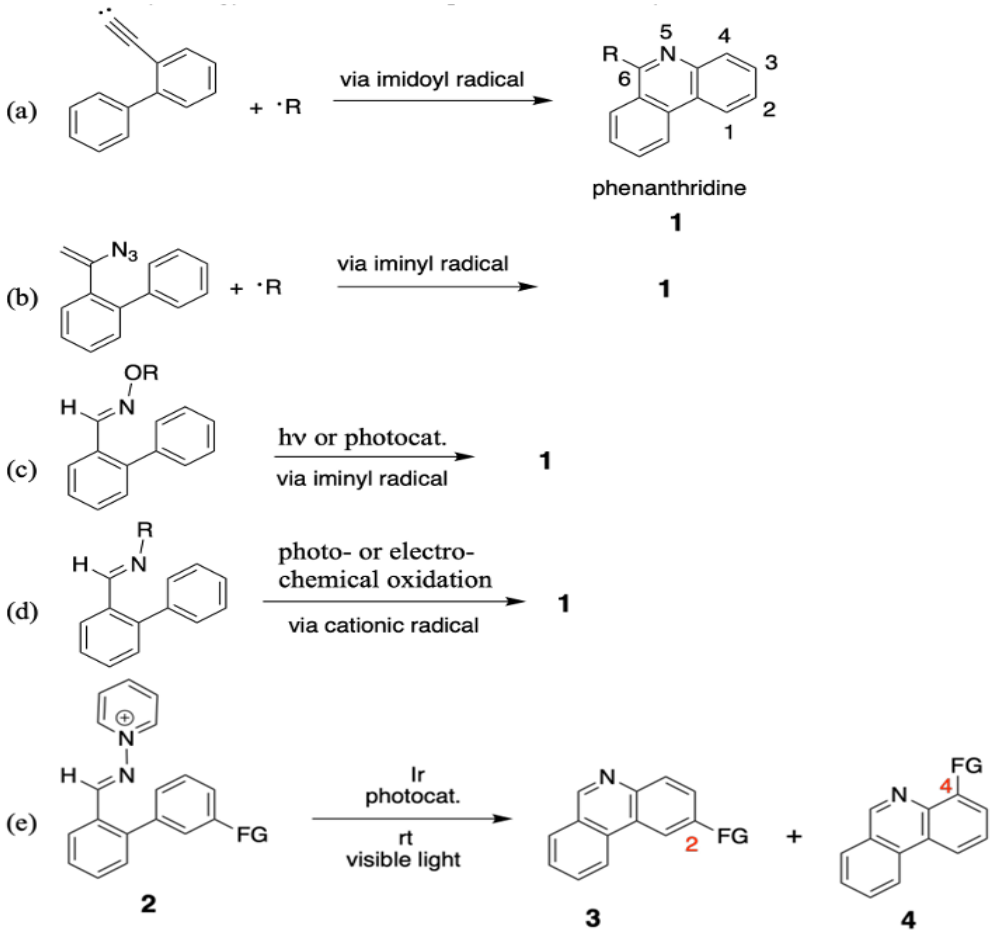


Figure 1. Bioactive phenanthridine derivatives.

The development of phenanthridine alkaloid analogues, together with the utilization of the antiparasitic properties of phenanthridine derivatives, has attracted substantial interest within the scientific community since around the beginning of the twenty-first century.[7] Because of their promising pharmaceutical and materials-related applications, synthetic and medicinal chemists have concentrated on establishing reliable and efficient methodologies for constructing phenanthridine frameworks and their derivatives. In 1889, Pictet and Ankersmit reported the first synthesis of phenanthridine through the pyrolysis of the condensation product obtained from benzaldehyde and aniline.[8] Nevertheless, the Bischler–Napieralski reaction remains one of the most frequently employed approaches for the preparation of phenanthridines.[9]

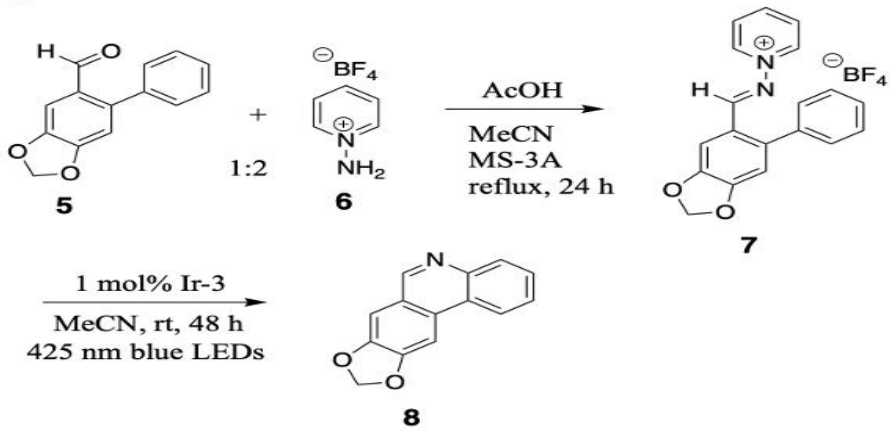
However, many traditional synthetic methodologies suffer from limitations such as restricted substrate scope, poor functional-group compatibility, harsh reaction conditions, and the requirement for multiple synthetic steps. Lately, several radical-based procedures originating from different precursors have been disclosed, as illustrated in Scheme 1. The radical addition to biaryl isonitriles (Scheme 1a)[10, 11] and to vinyl azides (Scheme 1b)[12] with subsequent cyclization offers an appealing approach for preparing phenanthridines, allowing for the selective incorporation of diverse functional groups at the C6 position. Furthermore, one-electron redox transformations of oxime or imine precursors (Scheme 1c and 1d),[13,14,15] which are readily available and considerably safer and less toxic than the aforementioned reagents, have also emerged as valuable tools for building nitrogen-containing polyaromatic systems, including phenanthridines. Consequently, significant efforts have been directed toward developing structurally diverse phenanthridines through milder, simpler, and more convenient synthetic procedures. Accordingly, this review focuses on the radical-mediated synthesis of phenanthridine derivatives under metal-photocatalyzed conditions.[16,17]

Recently, synthetic methods through redox reaction of designed pyridinium salts have been well studied because the system can be applied to generation of the corresponding various C-, O-, and N-centered radicals.[18] We developed aroyloxylation and amidation with the corresponding N- aroyloxy- and amidyl-pyridinium salts by visible-light photoredox catalysis.[19] In this context, we designed N-(2- arylbenzylidenamino)pyridinium salts 1 as the precursors for photocatalytic synthesis of phenanthridines (Scheme 1e). Herein we will describe photocatalytic reaction of 1, leading to regioselective synthesis of functionalized phenanthridines, especially, 2-substituted products. It is notable that the reaction turned out to be initiated by energy transfer from the photoexcited catalyst rather than electron transfer.



Scheme 1. Radical-mediated synthesis of phenanthridines.

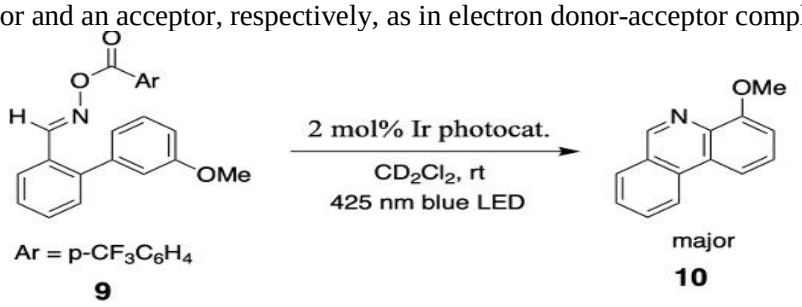
To demonstrate utility of the present reaction system, one- pot synthesis of Trisphaeridine **8** from the corresponding aldehyde was studied (Scheme 2). As a result, **8** was obtained in 67% isolated yield from the corresponding aldehyde without purification at the stage of intermediate 7.[20]



Scheme 2. Application to one-pot synthesis of Trisphaeridine (8).

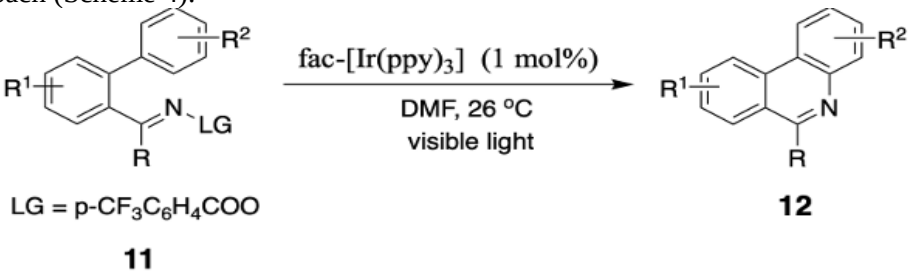
Simple cyclization of the iminyl radical intermediate can be excluded, because the photocatalytic reaction of O-acyl oxime **9** reported by Yu and co-workers under the reaction conditions produced the 4-substituted isomer **10** as a major product Scheme 3).[21] It is noted that **9** did not undergo the E-to-Z photoisomerization under those reaction conditions. An electron-

rich aromatic ring significantly enhanced the present cyclization. In one conformer obtained by DFT calculation, the distance between the nitrogen atom in the pyridinium ring and the ipso carbon atom in the aromatic ring is 3.2 Å, suggesting possible cation-p interaction,[22] which was also supported by a 2D NOESY NMR spectrum. In addition, the electrostatic potential map and frontier orbitals indicate that the aromatic ring A and the pyridinium unit would serve as an electron donor and an acceptor, respectively, as in electron donor-acceptor complex (EDA).[23]



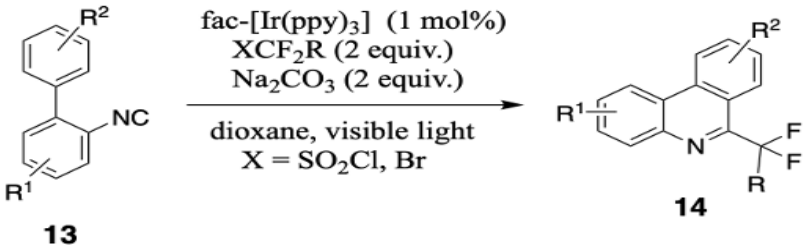
Scheme 3. Photocatalytic reaction of O-acyl oxime using Ir-catalysts.

In 2015, Y u and co-workers reported[24] the visible light-mediated transformation of acyl oximes **11** to iminyl radicals generating a variety of heteroarenes with N-containing six-membered heterocycles, along with quinolines, pyridines, and phenanthridines. These modern N-containing heterocycles were synthesized from a variety of substrates through irradiation of visible light under 1.0 mol% of a photocatalyst at room temperature. Furthermore, the highly effective total synthesis of the alkaloids such as nornitidine and noravicine could be achieved by this approach (Scheme 4).



Scheme 4. Visible light-mediated synthesis of phenanthridines.

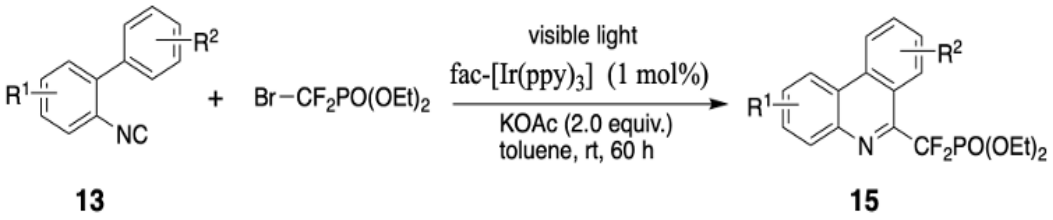
The first example of visible light-promoted difluoromethyl and 1,1-difluoroalkyl radical isonitrile insertion reactions were explored by Dolbier Jr and group.[25] This methodology has successfully derived a series of 6-(difluoromethyl) and 6-(1,1-difluoroalkyl) phenanthridines **14** in presence of fac-Ir(ppy)$_3$ as a photoredox catalyst in wet dioxane at room temperature. The difluoromethyl radical and α,α-difluorobenzyl or 1,1-difluoroethyl radicals showed high reactivity with isonitriles. Also, the sulfonyl chlorides were shown to be good precursors of difluoromethyl and 1,1-difluoroethyl radicals. In this reaction, 2-isocyano- biphenyls **13** bearing both electron-donating and with- drawing groups furnished the products in good yields (Scheme 5).



Scheme 5. Preparation of 6-(difluoromethyl) and 6-(1,1-difluoroalkyl)phenanthridines.

In the same year Liu et al. disclosed[26] a mild and efficient route to synthesise 6-difluoromethylenephosphonated (DFMP) phenanthridines **15** via radical cyclization of 2 isocyanobiphenyl **13** by the use of cheap and readily accessible diethyl bromodifluoromethylphosphonate under

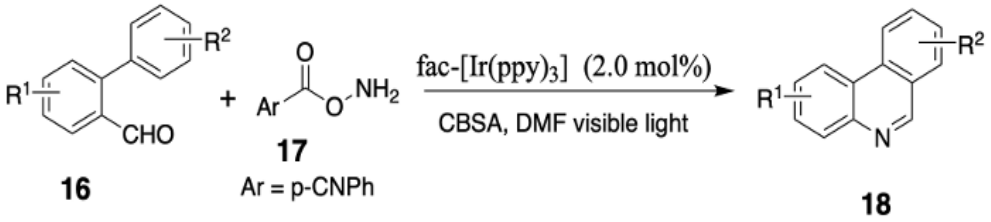
irradiation of visible light. This strategy could be used for the synthesis of DFMP phenanthridines through a practical approach, which is otherwise difficult to be synthesised by direct C H difluoromethylenephosphonation of phenanthridines (Scheme 6).



13 15

Scheme 6. Synthesis of 6-difluoromethylenephosphonated (DFMP) phenanthridines.

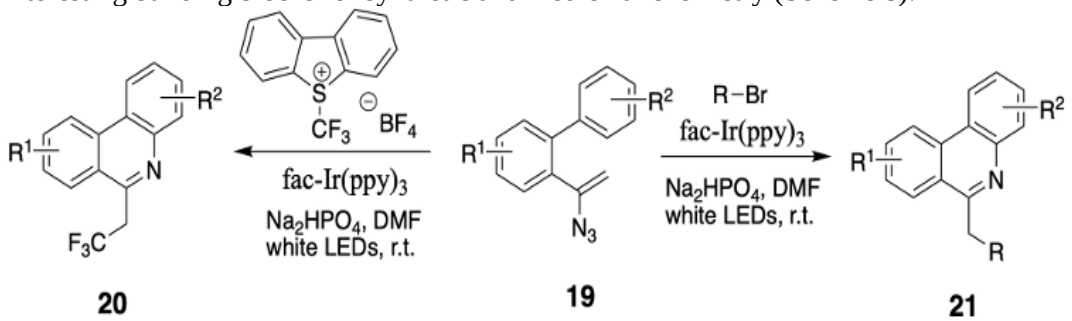
Y u et al. disclosed[27] a photoredox-catalyzed one pot synthetic strategy to construct phenanthridines **18** by the reaction of readily available biphenyl-2-carbaldehyde **16** and (4 cyanobenzoyl)hydroxyl-amine 199 a under visible light conditions. O-(4- cyanobenzoyl)hydr-oxylamine **17** a was employed as the nitrogen source to furnish o-acyl oximes in-situ, which was further subjected to photoredox-catalyzed cyclization through iminyl radicals to generate aza-arenes. p-Cl-benzenesulfonic acid (CBSA) acts as the best additive for this transformation. This methodology was useful for the synthesis of bioactive natural alkaloid trisphaeridine (Scheme 7).



16 17 Ar = p-CNPh 18

Scheme 7. Construction of phenanthridine derivatives.

Again, in 2016 same group disclosed an easy and effective strategy for the preparation of various 6-functionalized phenanthridine derivatives **20** and **21** under visible light photoredox conditions.[28] This transformation proceeds through the generation of iminyl radical from vinyl azides **19**. The addition of alkyl and trifluoromethyl radicals onto vinyl azides produced iminyl radicals followed by homolytic aromatic substitution afforded phenanthridine deriva- tives with good yields. The advantages of this reaction are mild conditions, wide substrate scope and high chemical yields. The resultant phenanthridine scaffolds exhibit several biological activities and are interesting building blocks for synthetic and medicinal chemistry (Scheme 8).

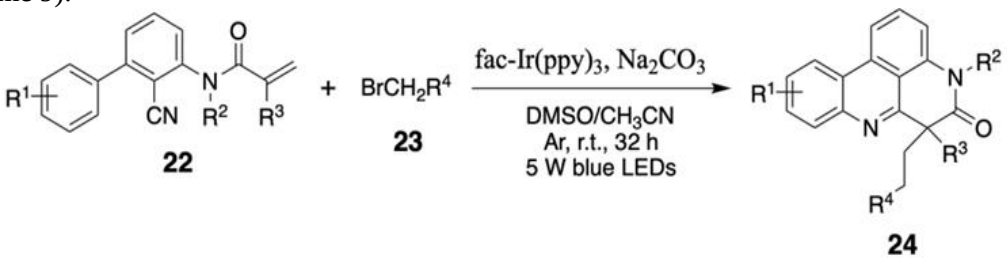


20 19 21

Scheme 8. Construction of 6-(fluoro)alkylated phenanthridines.

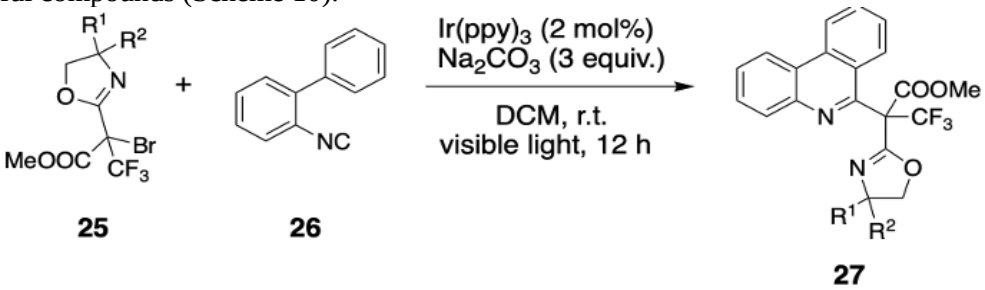
Sun and co-workers developed[29] a visible light-mediated radical cascade reaction to construct diverse phenanthridine derivatives **24**. The 6-quaternary alkylated phenanthridines were obtained in good yields by the photoredox catalyzed addition of the active methylene radicals from ethyl 2-bromoacetate, 2-bromoacetonitrile, or 2-bromo-N,N-dimethylacetamide to the

C=C double bonds of N-arylacrylamides **22** and sequential cyclization. The advantages of the strategy are easy availability of starting material, wide substrate compatibility, and the use of a low amount of catalyst and one-step generation of extremely complex polycyclic scaffolds (Scheme 9).



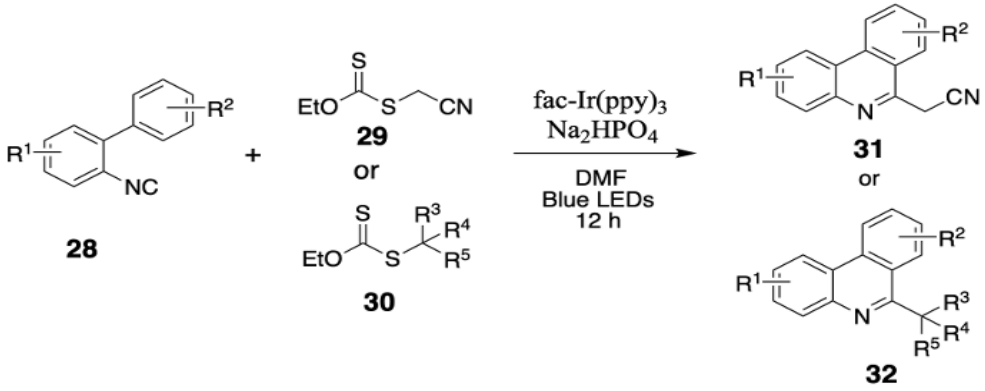
Scheme 9. Synthesis of phenanthridines from N-arylacrylamide by radical cyclization.

Chen et al. in 2018 reported[30] visible light-assisted efficient synthetic route to construct trifluoromethylated quaternary carbon center containing diverse phenanthridine derivatives **27** by the reaction of trifluoromethylated tertiary bromides **25** and 2-isocyano-1,1'-biphenyl derivatives **26** via cyclization. The reaction was carried out in DCM solvent using 2 mol% $Ir(ppy)_3$ catalyst and 3 equiv. Na_2CO_3 as the base. These diverse phenanthridine compounds exhibited highly potent agrochemicals. The key features of this transformation were mild conditions, good func- tional group compatibility, wide substrate scope, good bioactivities and excellent chemical yields. This reaction also shows a suitable transformation of harmful waste into useful compounds (Scheme 10).



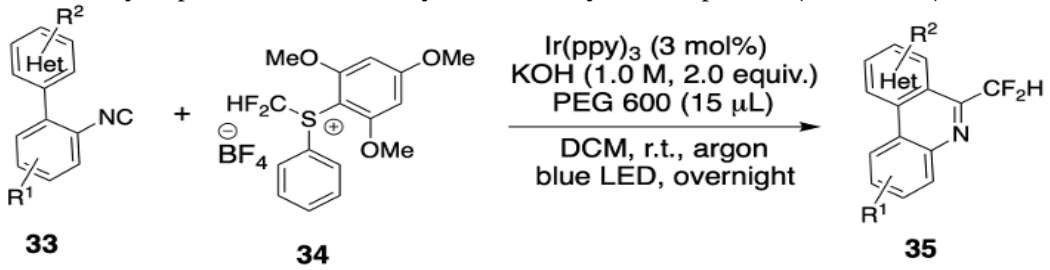
Scheme 10. Synthesis of various phenanthridine derivatives via visible light.

Recently, Miranda and co-workers demonstrated a visible light-induced new synthetic route to various 6-alkylated phenanthridines **31** or **32** using 2-biphenylisocyanides **28** and xanthates **29** or **30** as radical precursors.[31] This xanthate-based radical strategy facilitated the construction of 6-alkylated phenanthridine scaffolds via a photoredox neutral somophilic isocyanide insertion reaction. Electrophilic radicals generated from aromatic and aliphatic ketones, nitriles, amides, and malonates and also from benzylic derivatives and phthalimidome- thyl, were successfully incorporated in this reaction. A wide range of 6-alkylated phenanthrid- ines were synthesized from this protocol with yields ranging from 50 to 78% under mild and oxidant free conditions (Scheme 11).



Scheme 11. Construction of 6-alkylated phenanthridines.

A novel and efficient approach towards the visible light assisted radical difluoromethylation of isocyanides to furnish a diverse difluoromethylated phenanthridines **35** has been disclosed by Liu et al.[32] Stable S-(difluoromethyl)diarylsulfonium salts **34** which act as a highly efficient electrophilic difluoromethyl radical precursor has been used. Based on optimized studies, by using 3.0 mol% fac-Ir(ppy)$_3$ as a photo redox catalyst, 2.0 equiv. 1 M aq. KOH, 15 μL of PEG 600 in dichloromethane solvent at room temperature under irradiation of light and argon atmosphere gave the maximum yield of the reaction. This protocol tolerated a wide range of functional groups to furnish the desired difluoromethylated phenanthridines **35** in moderate to excellent yields. This present method would deliver an efficient route to introduce numerous pharmaceutically important difluoromethylated heterocyclic compounds (Scheme 12).



Scheme 12. Visible light-mediated approach to the synthesis of difluoromethylated phenanthridines.

Conclusions

As clearly demonstrated above, the synthesis of phenanthridine compounds with diverse substituents has attracted considerable attention from numerous research groups in synthetic organic chemistry because of their wide range of pharmacological activities, including anti-inflammatory, antimicrobial, antifungal, and antitumor properties. This review highlights recent advances in various synthetic approaches for preparing phenanthridine derivatives, encompassing Ir-metal-mediated photocatalytic methods. The Ir photocatalyst with higher triplet energy plays vital roles in the sensitization of the precursors through energy transfer. It also discusses the wide variety of reagents and substrates employed in the synthesis of these widely occurring nitrogen-containing heterocycles, which are valuable building blocks for constructing complex molecular frameworks. Most of these transformations take place under relatively mild reaction conditions and exhibit compatibility with a broad range of functional groups. The increasing interest in developing multifunctional phenanthridine frameworks and understanding their underlying reaction mechanisms is expected to lead to further significant advances in the future.

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