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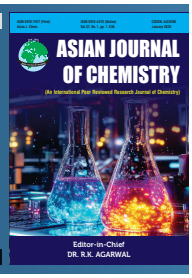

REVIEW

A Review on Visible-Light-Mediated Aziridine Synthesis: Mechanisms and Recent Advances

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Aziridines are highly valued in synthetic chemistry due to their substantial ring strain and reactive C-N bonds, making them remarkably reactive and essential for various transformations in organic synthesis. Their ring-opening ability reactions is crucial for synthesizing complex molecules, including natural products and pharmaceuticals. Over 130 biologically active aziridine-containing compounds exhibit pharmacological activities, including antitumor, antimicrobial and antibacterial effects, making aziridines key sources for drug prototypes and potential leads for drug discovery. In recent decades, numerous innovative and practical methodologies have been developed in the chemistry of aziridines, focusing on their synthesis and transformation into diverse functional forms. Traditional methods typically involve the use of precious transition metals, oxidants and strong acids or bases under harsh reaction conditions. In contrast, photochemistry has emerged as an intriguing approach, enabling the construction of aziridine derivatives from diverse substrates under milder conditions. Consequently, numerous light-driven synthetic approaches featuring high efficiency and mild conditions have been developed. This review focuses on environment-friendly and benign synthetic methods for preparing aziridine compounds, along with mechanistic insights into their formation under photocatalytic conditions.

Keywords: Photocatalysis, Visible light, Aziridine, Mechanism, Radical, Nitrene, Carbene.

INTRODUCTION

Aziridines, the simplest aza-heterocycles, are highly valued in synthetic chemistry due to their significant ring strain and polarized carbon-heteroatom bonds, which make them exceptionally reactive in various kinds of transformations, including cycloadditions, rearrangements and isomerizations [1-3]. Their ability to undergo ring-opening reactions to form 1,2-amino-functionalized products is particularly valuable in the synthesis of complex molecules, including natural products and pharmaceuticals [4-10]. The ring strain in aziridines, estimated at 27 kcal/mol, makes them potent intermediates in organic synthesis [11]. This reactivity is leveraged in various synthetic methodologies to access compounds with diverse functional groups, often in a regio- and stereo-selective manner. For instance, overall, the reactivity of aziridines, coupled with their ability to form complex, biologically active structures, makes them essential tools in both synthetic organic chemistry and drug development.

Various strategies, such as transition-metal catalysts, metal-free method (demands harsh conditions), microwave irradiation [12] and photochemical catalytic systems, offer diverse approaches to synthesizing aziridine scaffolds. Among these, photocatalysis–characterized by electron excitation through optical absorption–has emerged as a particularly environmental friendly method, avoiding the release of organic contaminants or hazardous residues [13-17]. Consequently, the development of photocatalytic processes in aziridine chemistry is of significant interest. This review summarizes recent advances in light-induced methods and mechanisms for aziridine synthesis over the past few decades.

Biological significance of aziridine ring-containing compounds: Aziridine-containing compounds have exhibited substantial biological activities. The aziridine core in mitomycins, which are potent antibiotics and members of the antitumor quinone family, is particularly noteworthy. Mitomycin C, a natural product used clinically as a chemotherapeutic agent, along with mitomycins A and C, has exhibited antimicrobial

activity against *Bacillus subtilis* and *Klebsiella pneumonia* [18]. Moreover, it has shown anthelmintic activity against the gastrointestinal parasites *Hymenolepis microstoma* and *Hymenolepis nana* in *Tribolium confusum* (Coleoptera, Tenebrionidae) [19]. Porfiromycin [20, 21] gained early widespread clinical use due to its superior activity against solid tumors. Mitomycins H, G, K and L have shown antibacterial activity [22]. Additionally, some mitomycins display anticancer activity against the Sarcoma 180 cell line. FR-900482 and FR-073317 exhibit strong cytotoxic effects against *in vitro* cultured B16, P388, HeLa S3 and KB tumor cell lines. *In vivo* experiments revealed that FK-073317 had equivalent antitumor activity against P388, M5076 and MX-1 cell lines and more potent activity against L1210, colon 38 and LX-1 cell lines compared to FK973 [23]. Both FR-900482 and FR-66979 are structurally novel natural products that are highly potent antitumor antibiotics [24] (Fig. 1).

Furthermore, some naturally occurring peptides containing an aziridine ring, such as madurastatin A1 and B1, consisting of serine and salicylic acid moieties, exhibit antibacterial activity against *Micrococcus luteus* indicates that the presence of the aziridine ring is essential for such activity [25] (Fig. 2).

Azinomycin A and B express antitumor activities against P388 leukemia, P815 mastocytoma, B-16 melanoma, Ehrlich carcinoma, Lewis lung carcinoma and Meth A fibrosarcoma [26]. Azicemicin A and B, have well-defined physico-chemical properties and antimicrobial activity [27] (Fig. 3).

General synthetic routes for aziridination: Several strategies are employed for aziridine synthesis, including (i) intermolecular [2+1] cycloaddition of reactive nitrene intermediates with olefins [28]; (ii) [2+1] cycloaddition of imines with carbenes [29]; (iii) reduction of azirines [30]; (iv) aza-darzen reaction [31] and (v) nucleophilic addition to the imino carbon of α-haloimines followed by intramolecular nucleophilic substitution (De Kimpe aziridine synthesis) [32] (**Scheme-I**). Over the past few decades, research has demonstrated that transition metals can effectively stabilize nitrene intermediates derived from precursors like aryl azides, sulfonyl azides, imino iodinanes, halo amines and tosyloxy carbamates leading to

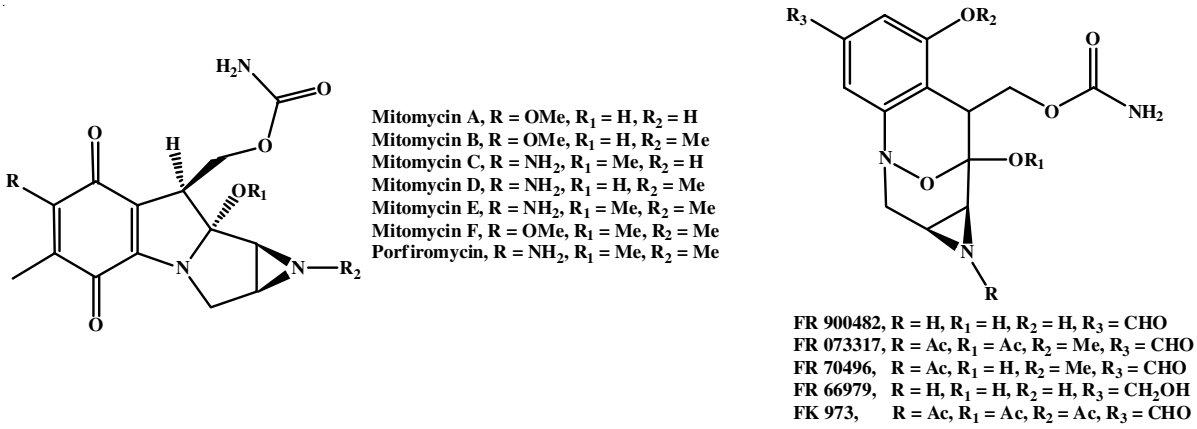


Fig. 1. Biologically active mytomycins, FR and FK compounds

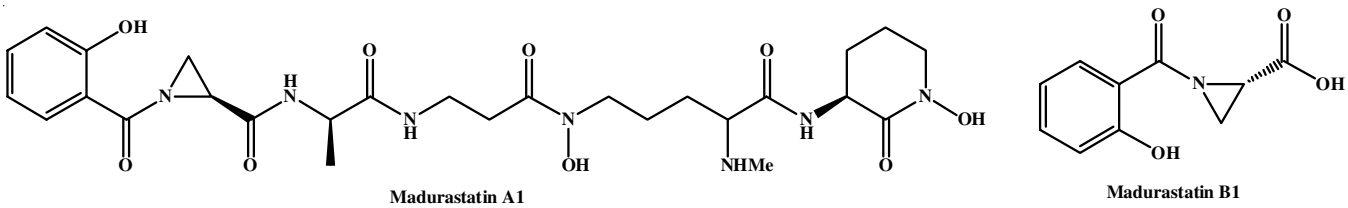


Fig. 2. Biologically active madurastati A1 and madurastati B1

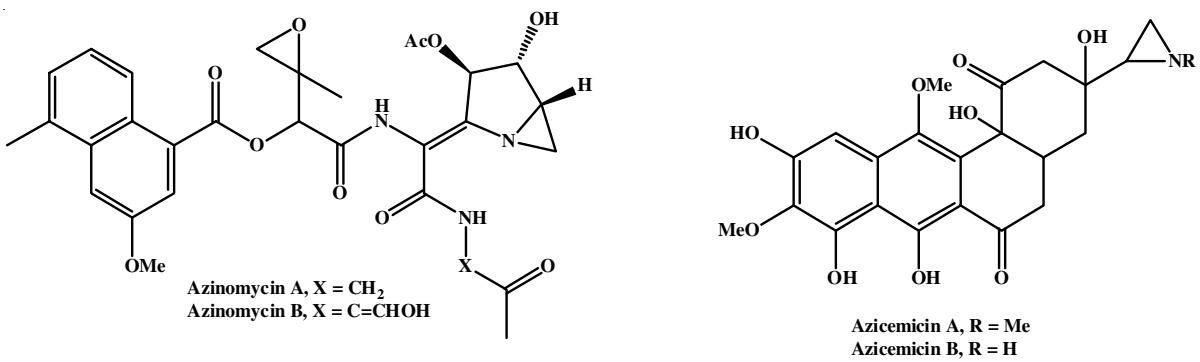
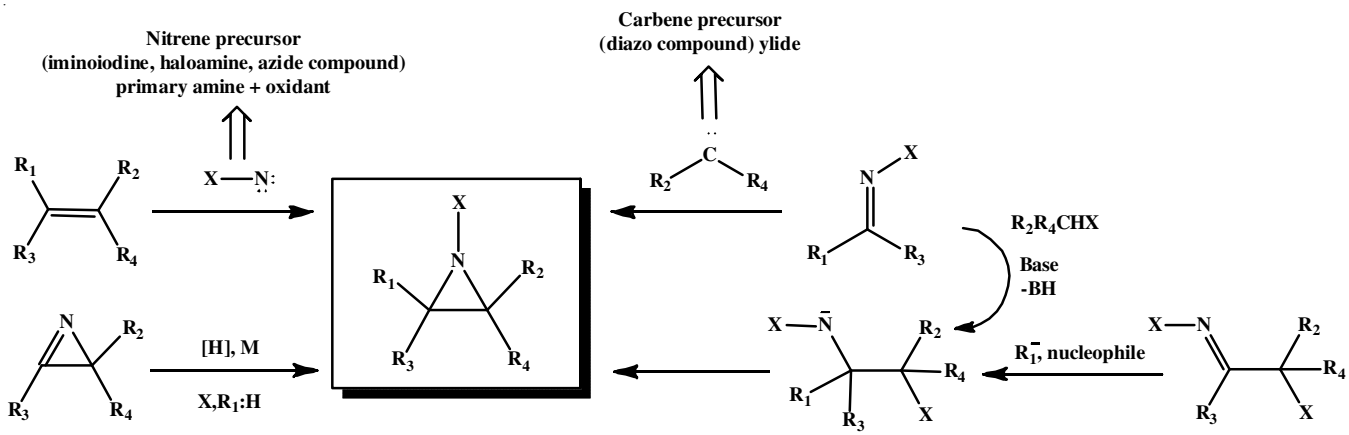


Fig. 3. Biologically active azinomycin and azicemicin compounds



Scheme-I: General strategies for the preparation of aziridines

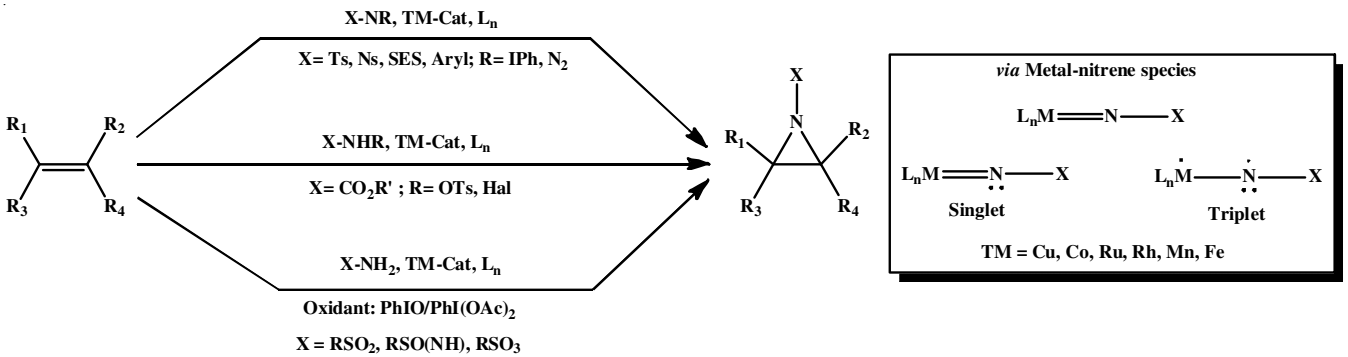
efficient reactivity. Furthermore, transition metal catalysts can stabilize nitrenes derived from sulfonamides, sulfonimidamides and sulfamates in the presence of hypervalent iodine (**Scheme-II**).

Aziridination typically occurs in the presence of a ligand, such as porphyrins, bisoxazolines, acetylacetone, imines or diimines, along with a transition metal catalysts [33-37]. Although metal-nitrene complexes appear to be intermediates, their multiplicity (singlet or triplet) is still questionable but crucial from a stereochemical point of view. Singlet species are generally assumed to react stereospecifically, retaining the stereochemistry of the alkene. In contrast, triplet species are not stereospecific in their reactions. While each approach offers unique advantages, these methods are often conducted under harsh conditions and have a limited substrate scope. Moreover, the more notable milder methods currently still require the use of precious metals such as ruthenium and rhodium [38].

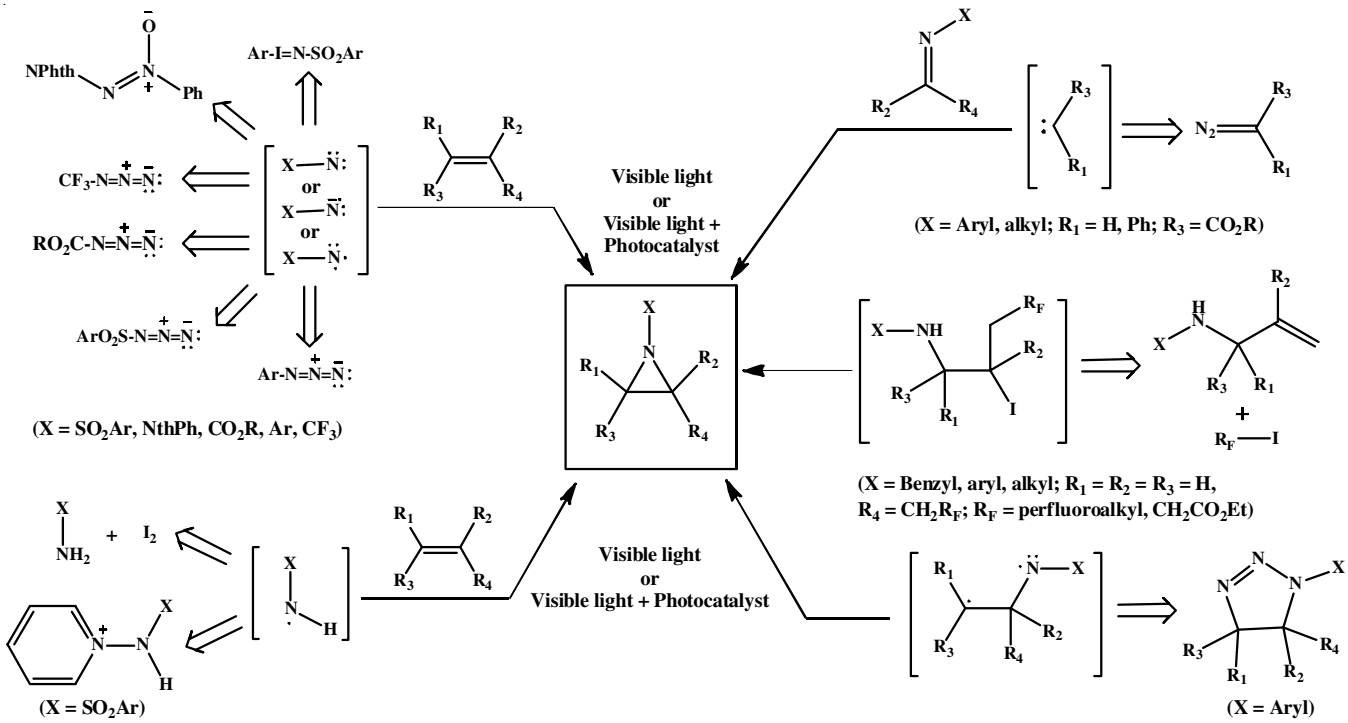
Photocatalytic approaches to aziridine synthesis: Over recent years, various methods have been developed for constructing aziridine derivatives using photocatalytic systems. As depicted in **Scheme-III**, diverse photochemical approaches enable straightforward access to aziridines, utilizing substrates like iodinanes, azidoformates, sulfonyl azide, aryl azide, trifluromethyazide, N-protected 1-aminopyridinium salts, sulphonamides, azoxy-triazenes in conjunction with alkenes, α-diazo esters in combination with *in situ* generated imines, odd electron pairing of *in situ* generated biradical through the photo-denitrogenation of triazolines as well as fluoroalkylation of allylamine followed by intramolecular nucleophilic reaction. These protocols not only unlock new pathways for synthesizing novel aziridines but also enhance accessibility to related molecules. In this context, recent advancements in light-induced synthesis of aziridines are summarized and discussed.

Photo-induced aziridination *via* nitrene addition to olefins: In photochemical aziridination, the primary method involves irradiating a suitable precursor to generate a nitrene near an unsaturated center, similar to metal-mediated nitrene transfer (NT) reactions. The advancement in photogenerated nitrenes has provided significant benefits compared to traditional thermal methods [39,40]. Previously, generating nitrenes required harsh conditions, such as high temperatures, UV light, or transition metals for intermolecular nitrene transfer. Recent developments now include direct photolysis and the use of photocatalysts under mild visible-light conditions to produce free nitrenes [41]. Yoon *et al*. [42] developed a visible-light-mediated method for producing aziridines *via* the spin-selective photogeneration of triplet nitrenes from azidoformates in the presence of transition metal complexes (**Scheme-IV**).

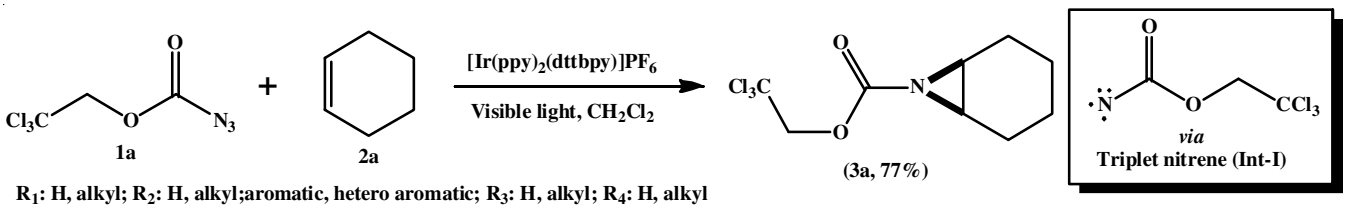
The group investigated the reaction of ethyl azidoformate (0.5 mmol) with cyclohexene (0.1 mmol) using various photoactive Ru^{II} and Ir^{III} complexes. They identified $[Ir(ppy)_2(dttbpy)]$-PF_6 as the most effective photocatalyst, achieving a 17% yield of aziridine after 4 h of irradiation with a 15 W blue LED lamp. Their findings revealed that the introduction of electron-withdrawing substituents accelerated the aziridination process. Notably, when 2,2,2-trichloroethyl azidoformate ($TrocN_3$, **1a**) was utilized, cyclohexene (**2a**) was completely consumed within 4 h, resulting in a 77% yield of aziridine **3a**. Further-



Scheme-II: Metal-nitrene species as a nitrogen source in the aziridination of alkenes



Scheme-III: General methods of photocatalytic synthesis of aziridines



Scheme-IV: Visible-light triplet sensitization for photocatalytic activation of azides

more, increasing the reaction scale to 0.4 mmol yielded partial conversion to aziridine after 4 h, but full conversion was achieved by extending the reaction time to 20 h. These observations suggest that the reaction is likely limited by photon availability, aligning with the high molar absorptivity characteristic of this class of photocatalysts. Finally, the team explored the direct UV-promoted photochemical reaction (λ_{exc} = 310 nm) of azidoformate with cyclohexene, resulting in a complex mixture of allylic amination and aziridination products. This underscores the importance of triplet sensitization for achieving the chemoselective aziridination.

A variety of cyclic alkenes undergo smooth aziridination under the developed conditions. The method yields good quantities of aziridines derived from both aliphatic and styrenic alkenes and internal olefins undergo aziridination as successfully as terminal alkenes. A range of functional groups, including protected amines and alcohols, potentially photosensitive halides and Lewis basic heterocycles, are tolerated (Fig. 4). Electron-deficient alkenes react at a slower rate, consistent with the electrophilic nature of the nitrene intermediate, often requiring somewhat extended reaction times.

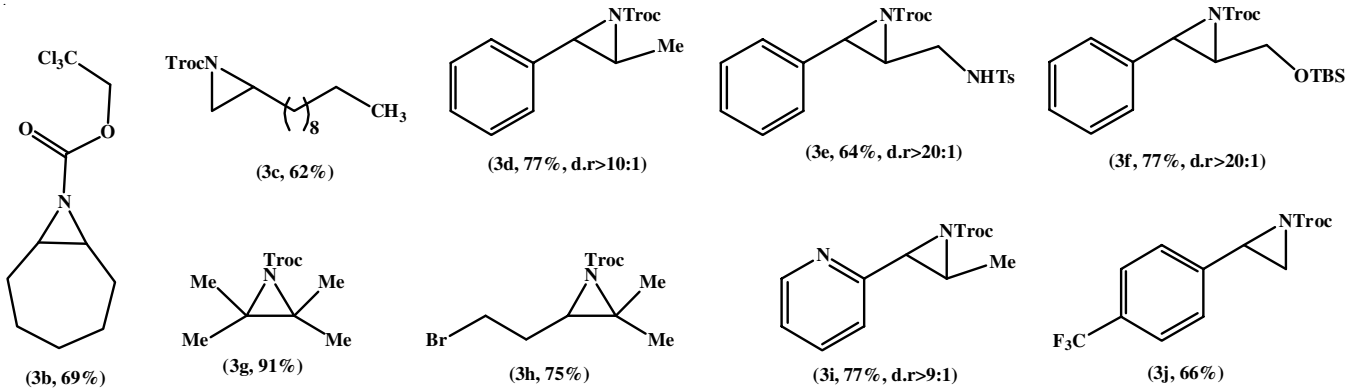
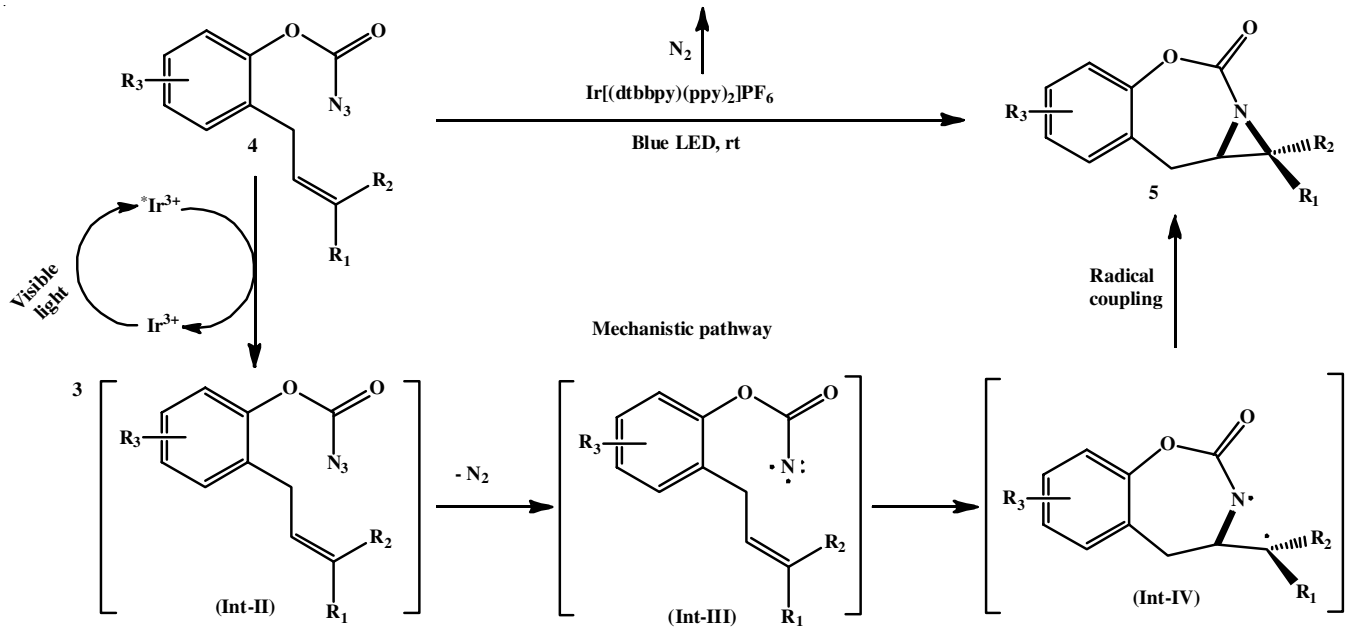


Fig. 4. Selected examples of synthesized *via* aziridines triplet sensitization of azides

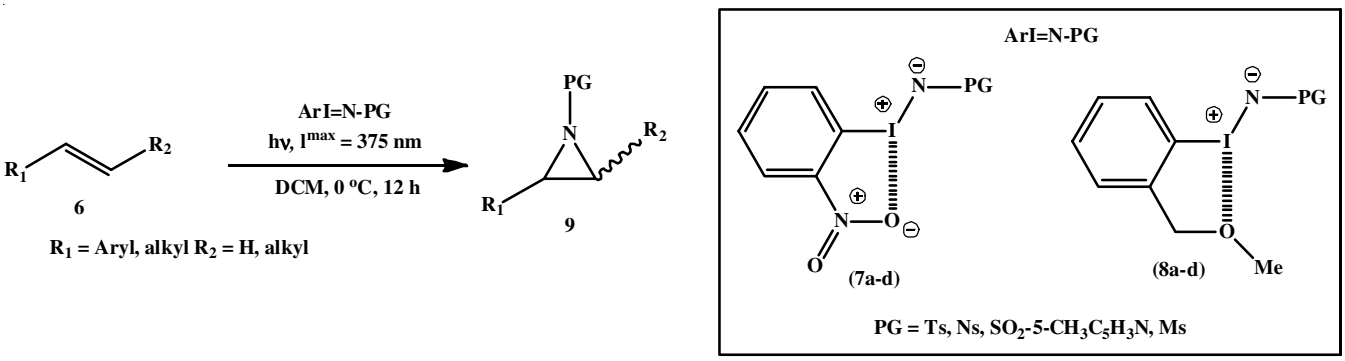
Lu *et al*. [43] reported visible light-induced C (sp^2)–H amination and aziridination of *o*-allylphenyl azidoformates. They exposed substituted phenyl azidoformates to blue light-emitting diode (LED) irradiation in the presence of numerous transition metal photocatalysts to furnish the C–H amination products. Ir[(dtbbpy)$(ppy)_2$]PF_6 was identified as the preferred catalyst; the photocatalyst enables mild generation of the reactive nitrene species that reacts as a free nitrene with a kinetic preference for olefin attack. Exploration of an extensive substrate scope revealed that allylsubstituted substrates preferentially underwent aziridination (**Scheme-V**). Based on prior investigation of similar transformations, the reaction proceeds *via* a triplet energy transfer mechanism wherein photolysis of the azide is the rate-determining step (RDS). The reaction is presumed to be stereospecific, although the single trans-substrate was examined. Regardless, this methodology produces unique fused aromatic systems difficult to obtain in other ways.

Takemoto *et al.* [44] demonstrated a greener methodology for aziridination by activating *o*-substituted N-sulfonyliminoiodinanes (*e.g.* –CH_2OMe, –NO_2) with photo-irradiation at 375 nm, followed by a reaction with various alkenes to produce the corresponding aziridines (**Scheme-VI**). In this study, styrene and iminoiodinane in dichloromethane was used, stirred the reaction mixture at 0 ºC for 12 h under photo-irradiation with LED light (peak wavelength 375 ± 3 nm). This resulted in the formation of aziridine (**9**, Fig. 5).

When the reaction was performed with (*Z*)-oct-4-ene and ArI = N-PG (Ar = *o*-$NO_2C_6H_4$, PG = Ts), it produced the corresponding aziridine with a *syn/anti* ratio of 29:71, whereas (*E*)-oct-4-ene resulted in a *syn/anti* ratio of 24:76. These results



Scheme-V: Photocatalyzed intramolecular olefin aziridination



Scheme-VI: Aziridination *via* activation of *o*-substituted *N*-sulfonyliminoiodinanes with alkenes

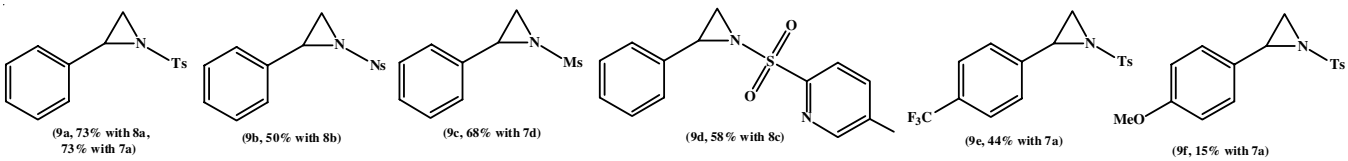


Fig. 5. Selected example of synthesized *N*-sulfonyl aziridines

strongly suggested that the photoinduced aziridination of alkenes with *o*-substituted *N*-sulfonyliminoiodinanes proceeds *via* a stepwise mechanism involving radical intermediates rather than a concerted process.

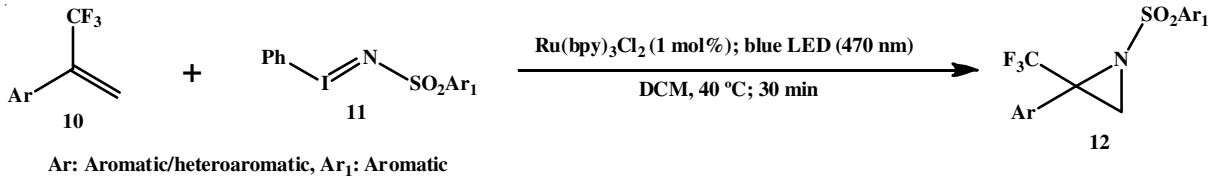
In 2021, Koenigs *et al.* [45] demonstrated that iodinanes undergo oxidative quenching in the presence of the simple $Ru(bpy)_3Cl_2$ catalyst, releasing a nitrene radical anion. This radical anion serves as a reactive intermediate in the direct aziridination reactions of fluorinated olefins, enabling the formation of fluorinated aziridines with diverse substitution patterns, including difluoromethyl and perfluoroalkylated aziridines (**Scheme-VII**). α-Trifluoromethyl styrene (**10a**, 1.0 mmol, 5 equiv) was employed as substrate, PhINTs (**11a**, 0.2 mmol) as nitrene source and $Ru(bpy)_3Cl_2$ (1 mol %) as photocatalyst. The mixture was dissolved in 2 mL of degassed DCM under argon gas and irradiated with a 3 W blue LED (470 nm) to synthesize the trifluoromethylated aziridine (**12**).

The system showed tolerance for diverse Ar_1 groups attached to the sulfonyl iminoiodane substrate, as well as for various substitutions on the phenyl group of the styrene partner. These substitutions included electron-withdrawing nitro groups and sensitive thiophene moieties. However, *ortho* substitution was not tolerated and isolated olefins did not undergo aziridination (Fig. 6). Surprisingly, pyridine derivatives also failed to undergo aziridination, likely due to a single-electron transfer (SET) pathway where the pyridine may quench the radical. Control experiments indicated that reductive quenchers such as DABCO, triethylamine and the Hantzsch dihydropyridine inhibited the reaction.

Experimental and computational studies show that electron transfer from the excited state of the $Ru(bpy)_3^{2+}$ catalyst to PhINTs occurs easily *via* single-electron transfer (SET) with very low activation free energy, forming the iodinane radical anion intermediate Int-V. This formation significantly extends the N-I bond (from 1.99 Å to 3.72 Å), facilitating its cleavage in a barrier-free pathway to produce the nitrene radical anion, which is energetically favoured by 8.3 kcal/mol. The nitrene radical anion then undergoes radical addition to α-trifluoromethyl styrene through a low-lying transition state (ΔG = 14.9 kcal/mol), forming intermediate Int-VI. The subsequent electron transfer to the oxidized form of the photocatalyst $Ru(bpy)_3^{3+}$ is easy, with a very low activation free energy of 1.1 kcal/mol, yielding the zwitterionic intermediate Int-VIII, which can cyclize without any energy barrier to produce the aziridine product **12** (**Scheme-VIII**).

Rastogi *et al*. [46] developed a similar reaction protocol, involving the generation of a nitrene radical anion intermediate from iminoiodinanes using the same photocatalyst, $Ru(bpy)_3Cl_2{\cdot}6H_2O$, for the aziridination of chalcones instead of trifluoromethyl styrene. In this reaction, a mixture of 0.2 mmol of chalcones (**13**), 0.002 mmol of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ in 2 mL of $CHCl_3$ and 0.4 mmol of iminoiodinanes (**11**) were irradiated with 455 nm blue LEDs for 3-6 h under N_2 at room temperature. This method yielded *trans*-3-arylaziridine-2-ketones (**14**) with percentages ranging from 18% to 62% (**Scheme-IX**).

The authors have also explored the reaction's scope in terms of both the substrates and in most cases, *trans*-3-arylaziridine-2-ketones were isolated in good yields. Chalcones with unsubstituted or electron-donating phenyl rings, halogens on one or both phenyl rings and strongly electron-withdrawing nitro groups were well-tolerated under the reaction conditions, yielding products in good amounts. Furthermore, chalcones with



Scheme-VII: Synthesis of trifluoromethylated aziridines *via* photocatalytic amination reaction

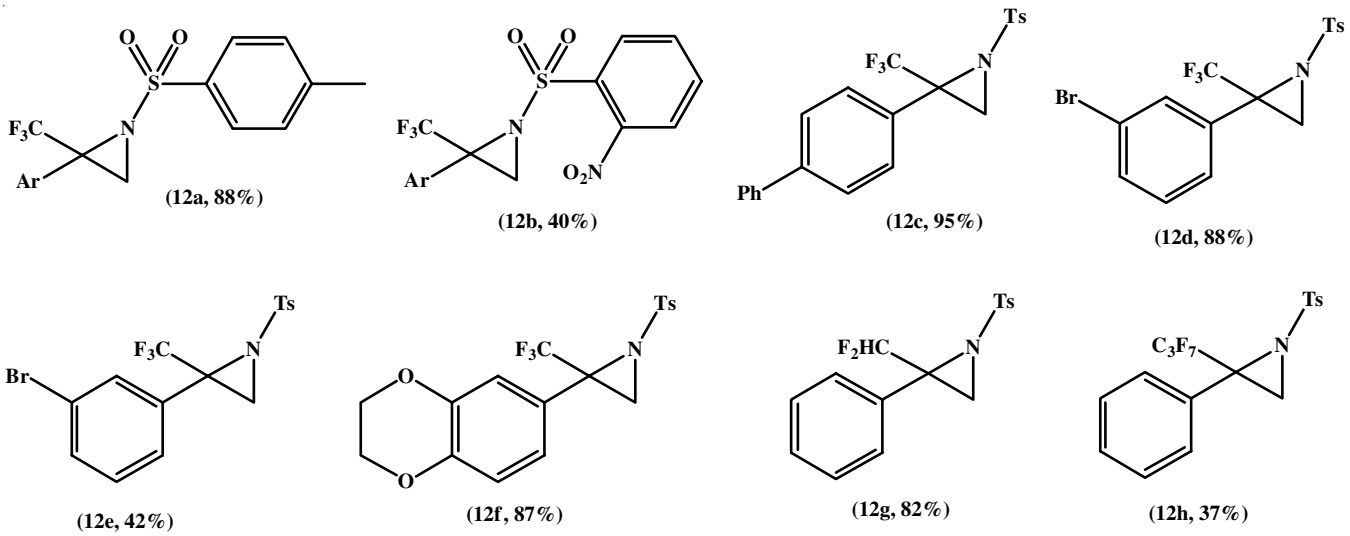
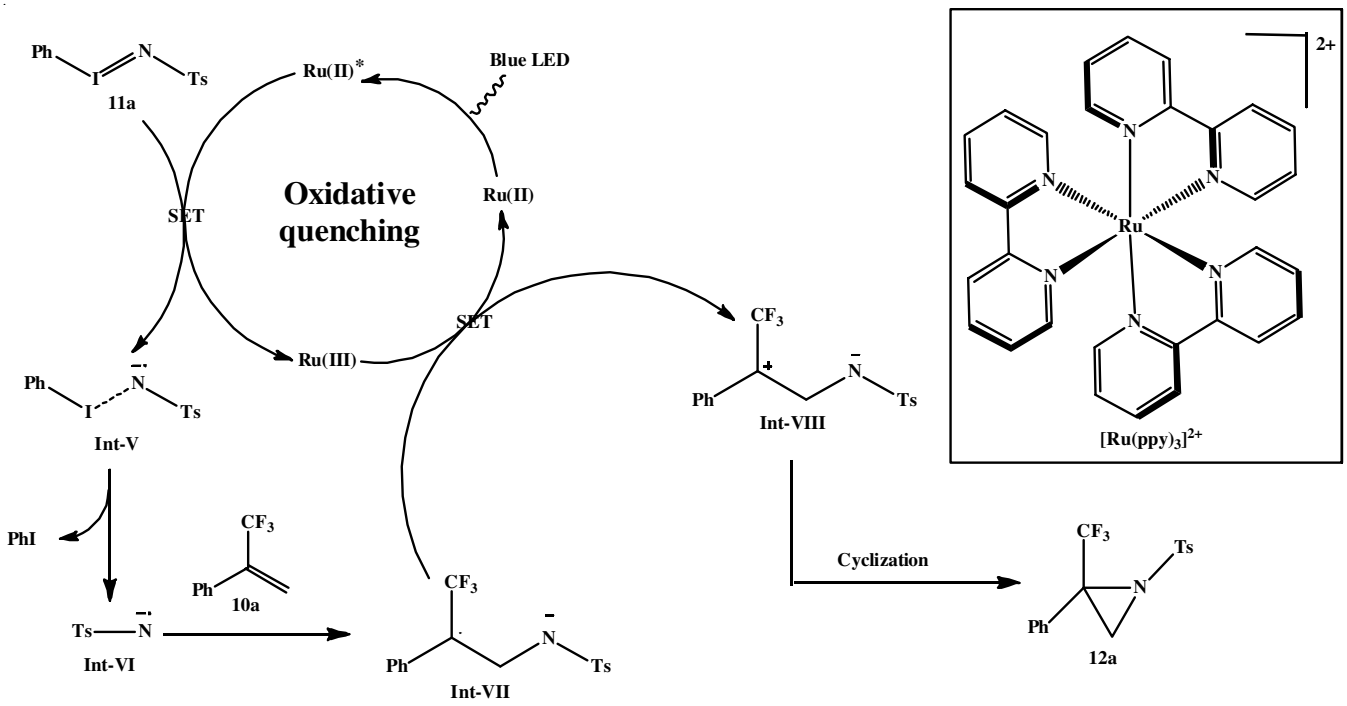
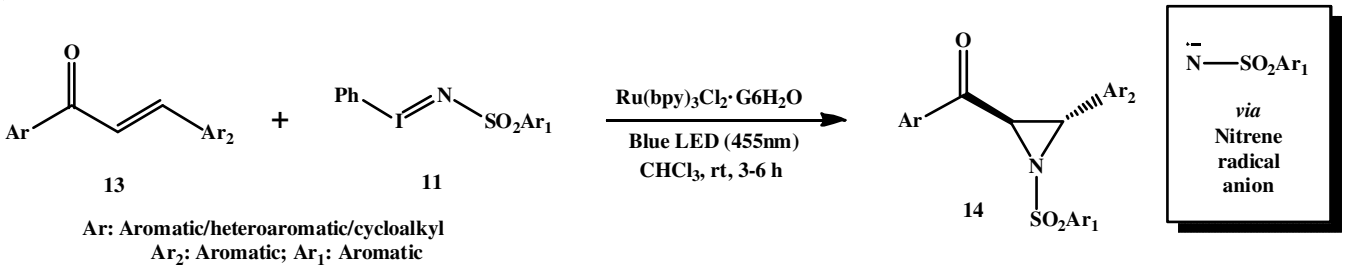


Fig. 6. Structure of synthesized trifluoromethylated aziridines



Scheme-VIII: Reaction pathway of the photocatalytic aziridination



Scheme-IX: Synthesis of trifluoromethylated aziridines *via* photocatalytic amination reaction

bulkier substituents such as arene-bearing phenyl rings, naphthyl rings and those with heteroaryl or alicyclic rings also produced the corresponding aziridine-ketones in significant yields. Not only the chalcones but also various sulfonyl substituents, such as N-(phenyl-λ3-iodaneylidene)benzenesulfonamide, *p*-chloro/*p*-bromo/*p*-trifluoromethyl phenyl sulfonyl-substituted imino-iodinanes, were well tolerated under the optimized conditions (Fig. 7).

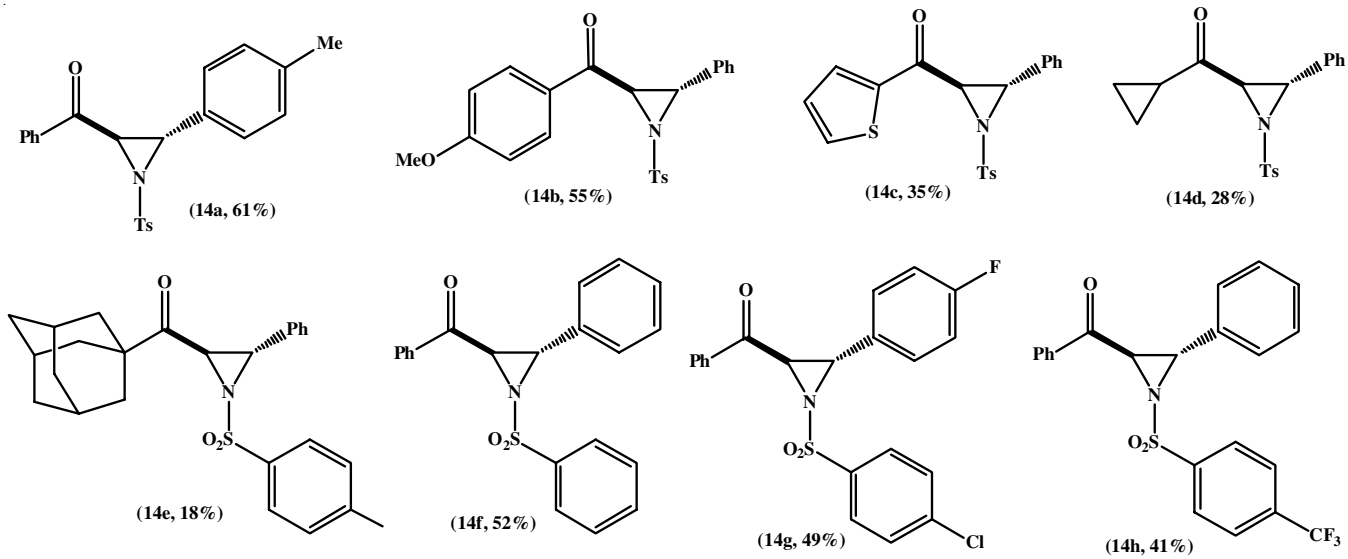


Fig. 7. Few example of trifluoromethylated aziridines

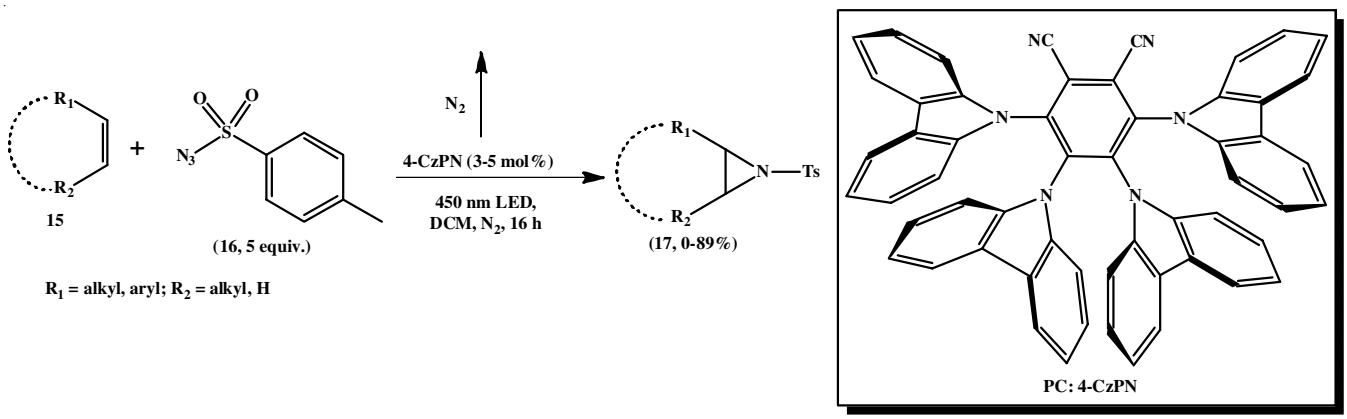
The reaction pathway follows the same mechanism as reported by Koenigs and coworkers [45], involving nitrene radical anion intermediates. This was further supported by trapping experiments, where the addition of the radical scavenger TEMPO completely arrested the reaction. The mechanism starts with the oxidative quenching of the excited photocatalyst $Ru(bpy)_3^{2+}$ (E_{red} = 0.81 V *vs.* SCE in MeCN) [45] by iminoiodinane PhINTs (E_{red} = 0.58 V *vs*. SCE in MeCN) [47], forming an iminoiodinane radical anion. This intermediate then eliminates iodobenzene, generating the nitrene radical anion. The nitrene radical anion adds to the chalcone's double bond and the resulting intermediate transfers a single electron to the oxidized photocatalyst, becoming a zwitterionic species. Finally, the intramolecular cyclization of the zwitterionic species produces *trans*-3-arylaziridine-2-ketone (similar as **Scheme-VIII**).

Unlike metal-based photosensitizers, organic dyes can also function as azide photosensitizers. This was demonstrated by the research group of Dam *et al.* [48], who reported that triplet sensitization of sulfonyl azides results in the formation of triplet nitrenes. These triplet nitrenes were utilized in the chemo-, regio- and diastereoselective aziridination of structurally complex alkenes in the presence of cyanoaryl photosensitizers (**Scheme-X**). They explored the substrate scope of aziridination reaction by examining various simple aliphatic alkenes, substituted styrenes, trisubstituted olefins and olefins containing α,β-unsaturated ketones with sulfonyl azide, obtaining the respective aziridines with significant yields (Fig. 8).

The stereoselection observed when using *cis*- and *trans*-4-octene as substrates, which yielded the same diastereomeric mixture of aziridines, is consistent with a stepwise triplet nitrene insertion mechanism. Notably, even strongly electron-withdrawing trifluoromethyl groups and bulky silyl ethers did not adversely affect the reaction yield. Highly diastereoselective reactions were achieved by using sterically demanding groups, as demonstrated by the excellent diastereocontrol in the formation of aziridines. They demonstrated that the nature of sulfonyl azide, combined with the triplet-excited state energy of the photosensitizer, affects the aziridination yield. Moreover, they also showed that tuning the electronic effects of the substituents on the benzenesulfonyl azides can align them with the triplet excited-state energy of the photosensitizers. This alignment prevents catalyst deactivation pathways that would otherwise lead to diminished yields. The mechanism involves the excitation of an organic dye, which sensitizes the sulfonyl azide into its triplet state. This triplet sulfonyl azide then decomposes to form a triplet nitrene reactive intermediate (Int-IX). The triplet nitrene reacts with alkenes in a stepwise process: it first forms a biradical, which then undergoes radical pairing, ultimately leading to the formation of aziridines (**Scheme-Xa**).

Alike azidoformate a visible light photocatalysis can generate triplet trifluoromethyl nitrene from CF_3N_3, which has a longer half-life and more predictable reactivity. Using CF_3N, Beier *et al*. [49] developed a method to synthesize N-trifluoromethylaziridines *via* radical addition to alkenes in the presence of fac-Ir(PPy)$_3$ as a photocatalyst. Both (*E*)- and (*Z*)-stilbene were used as alkenes under the developed reaction conditions, yielding similar diastereomeric product ratios that favoured the anti-product (**Scheme-XI**).

A control experiment without azide showed that (*E*)-stilbene isomerized to (*Z*)-stilbene at a rate comparable to aziridination. Aziridines from trisubstituted alkenes, tetrasubstituted alkenes and aliphatic terminal alkenes were isolated in excellent to



Scheme-X: Photocatalyzed intramolecular olefin aziridination

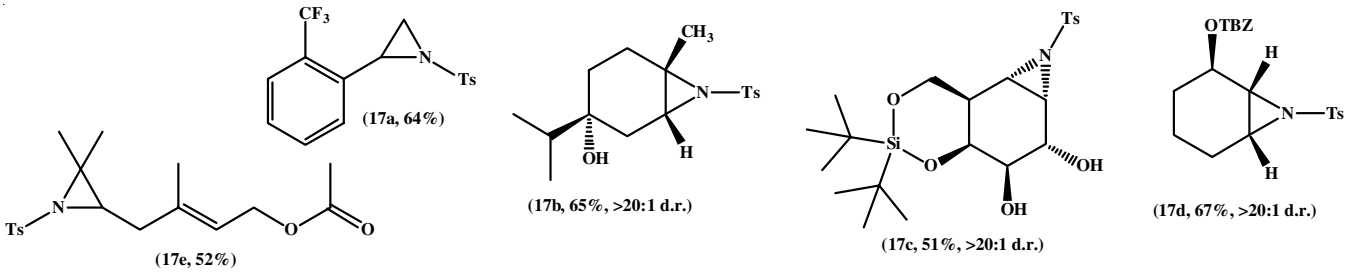
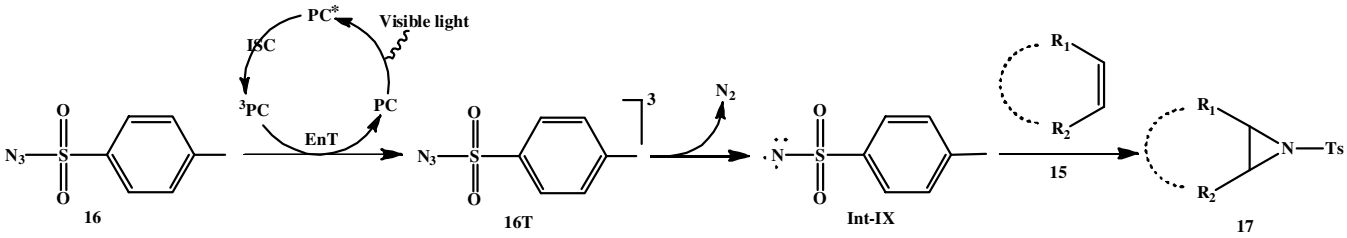
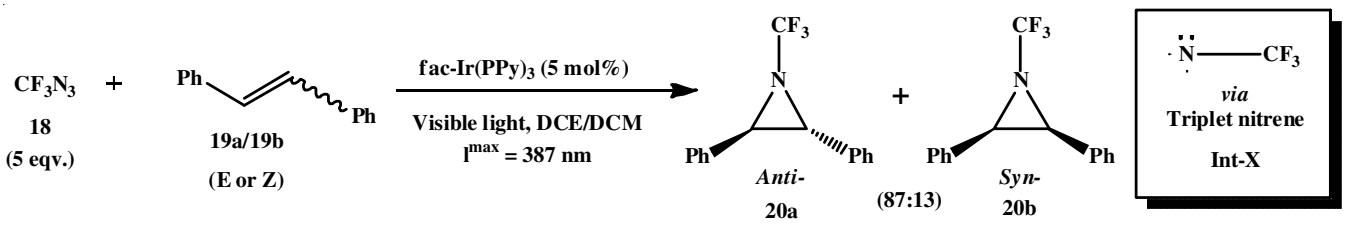


Fig. 8. Example of diasteroselective aziridines



Scheme-Xa: Mechanistic proposal of photocatalyzed intramolecular olefin aziridination



Scheme-XI: Visible-light mediated triplet nitrine generation for aziridination

moderate yields (Fig. 9). Using various experimental techniques such as NMR, EPR, luminescence quenching, transient absorption spectroscopy, cyclic voltammetry and DFT calculations, the group revealed that the excited triplet photocatalyst sensitizes CF_3N_3 into the triplet state, returning itself to the ground singlet state. The excited azide exhibits a local shallow energy minimum in the T_1 state. The energy barrier for nitrogen molecule dissociation is 0.037 eV, comparable to thermal energy. Therefore, upon reaching the triplet state, the azide undergoes decomposition, forming the triplet nitrene reactive intermediate (Int-X). This triplet nitrene then reacts with alkenes, producing an adduct in a biradical triplet state with the nitrogen atom bonded to one of the carbon atoms of the original double bond (**Scheme-XII**). For unsymmetrical alkenes, the two adducts differ in energy and the calculated energy differences between the two biradical isomers indicate a preference for the formation of stabilized secondary or tertiary benzylic radicals. Their experimental studies show that product diastereoselectivity depends on various factors such as (a) isomerization of starting alkene under the given reaction conditions; (b) C-C bond rotation in biradicals and (c) the efficiency of the intersystem crossing (ISC) of biradicals, which precedes the closure of the aziridine ring.

Parasram *et al*. [50] reported that under visible light excitation, azoxy-triazenes can serve as a source of nitrogen atom for the chemoselective phthalimido-protected aziridination of both activated and unactivated alkenes. Through various controlled experiments, including nitrene trapping studies, stereochemical probe studies, kinetic ratio studies and control studies for the photodecomposition of azoxy-triazene, they proposed that the singlet-excited state of the azoxy system, accessed upon visible light excitation, fragments to generate free singlet nitrenes. These nitrenes then undergo a [2+1] cycloaddition with the alkene in a concerted manner, yielding the desired aziridine (**Scheme-XIII** and Fig. 10). This protocol is operationally simple, scalable and adaptable to photo flow conditions.

Che *et al*. [51] reported that iron porphyrin Fe(TF_4DMAP)-Cl effectively catalyzed alkene aziridination with high selectivity using aryl azides as nitrene precursor under blue LED light (469 nm) irradiation (**Scheme-XIV**). Mechanistic studies revealed that Fe(TF_4DMAP)Cl functioned as both a nitrene transfer catalyst and a photosensitizer. This dual role was crucial in enabling a variety of room temperature amination reactions with azides, overcoming the significant limitation of high reaction temperatures typically required in conventional nitrene transfer reactions.

Photo-induced aziridination *via* carbene equivalent reaction with *in situ*-generated imines: Using visible light for the aziridination of imines with diazo carbene sources provides a simpler and more controlled reaction environment, lowering the risk of organic substrate photodecomposition. Moreover, it improves selectivity and efficiency due to the gentler reaction conditions compared to traditional catalytic methods for carbon insertion into the imine double bond. Xuan *et. al.* [52] developed

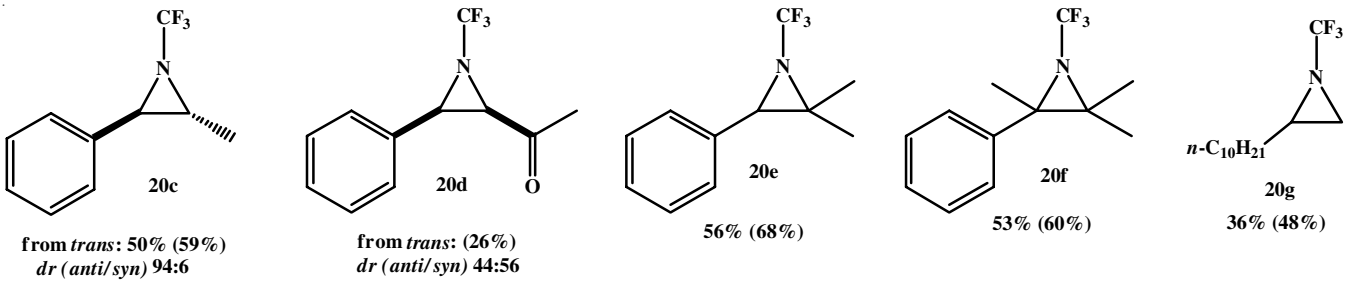
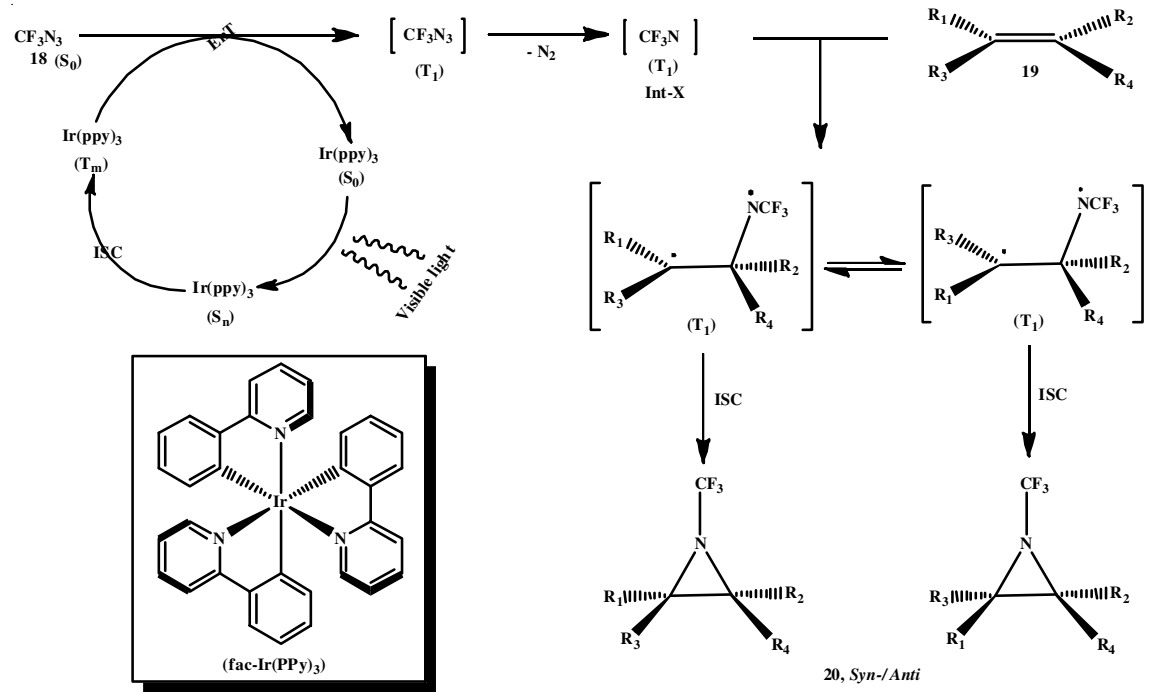
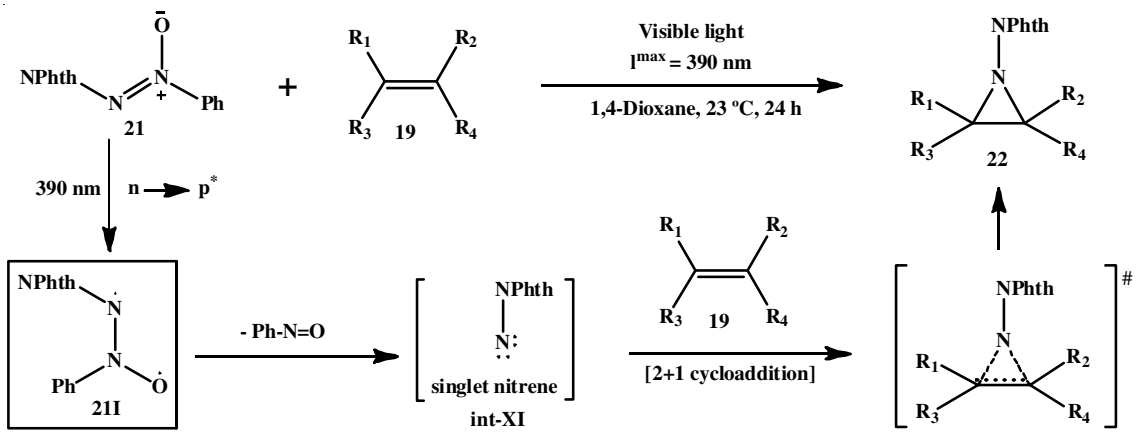


Fig. 9. Example of *N*-trifluoromethylaziridines



Scheme-XII: Probable mechanism of trifluromethy nitrine formation for aziridination



Scheme-XIII: Aziridination of olefins from photoexcited azoxy-triazenes

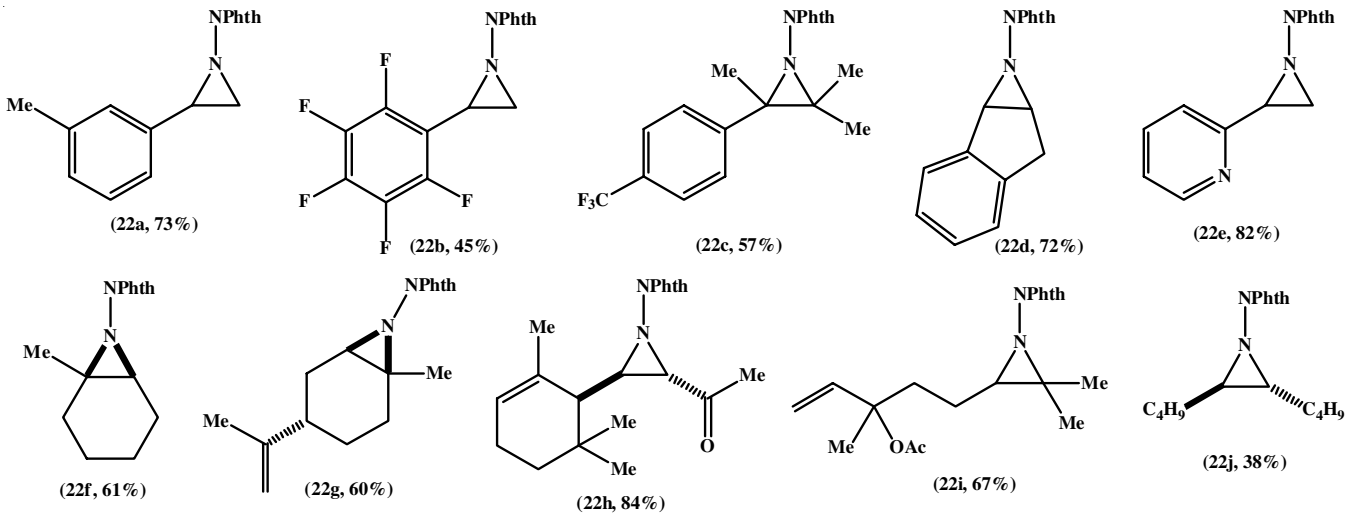
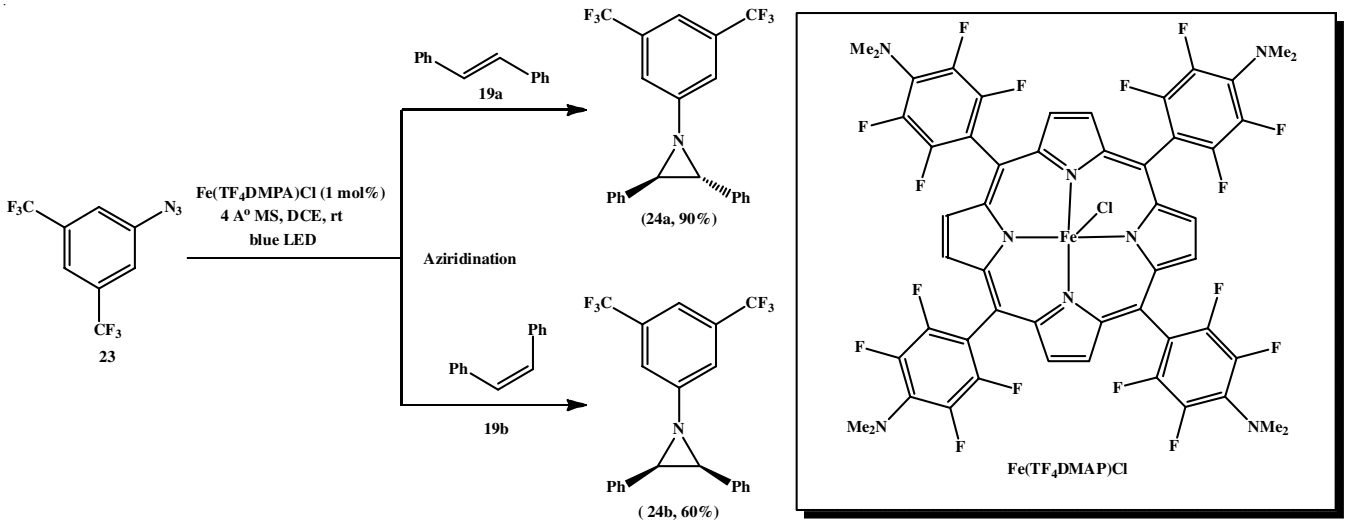


Fig. 10. Selected examples of *N*-phthalimido azidines

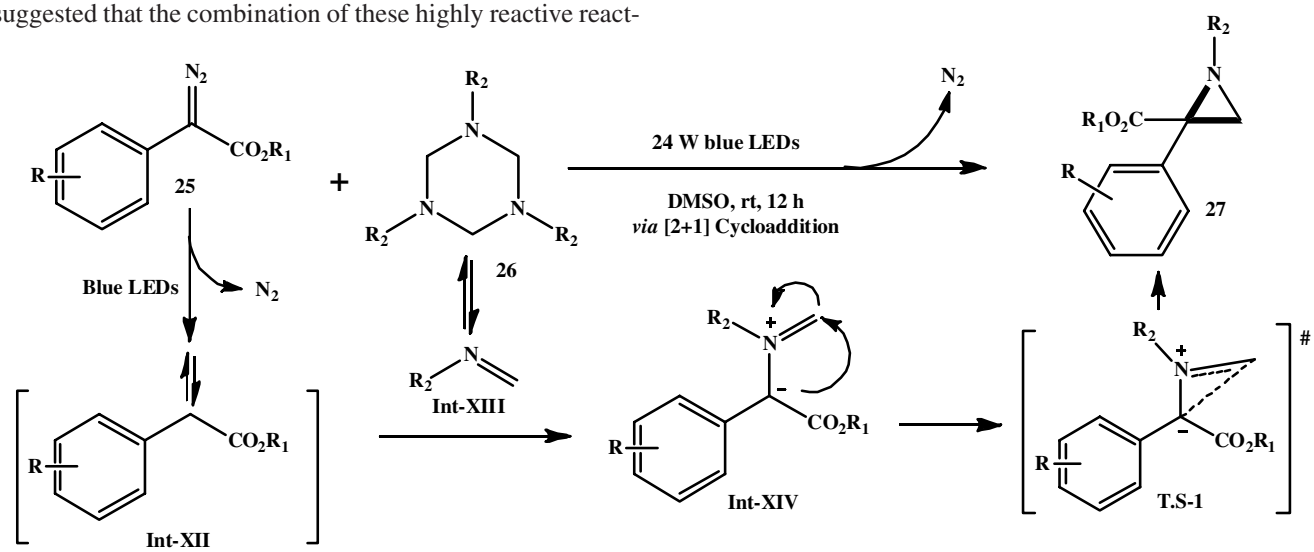


Scheme-XIV: Stereospecific aziridination of alkenes and arylazide catalyzed by $Fe(TF_4DMAP)Cl$

a visible light-promoted divergent cycloaddition of α-diazo esters with hexahydro-1,3,5-triazines, resulting in a series of aziridine frameworks. This reaction occurs under visible light irradiation alone, without the need for photoredox catalysts. They used phenyldiazoacetate and PMP-substituted hexahydro-1,3,5-triazine in DMSO under blue LED irradiation to synthesize aziridine. The mechanistic study revealed that the reaction proceeded through an *in situ* generated singlet carbene intermediate. Initially, under visible light irradiation, photolysis of aryl diazoacetate produces a carbene species (Int-XII) with the release of nitrogen gas. Subsequently, the reaction between the nitrogen atom of formaldimine (Int-XIII), generated *in situ* by the dissolution of 1,3,5-triazine and the carbene species (Int-XII) forms ylide Int-XIV. Consequently, Int-XIV undergoes the intramolecular cyclization *via* TS-1, yielding aziridine (**Scheme-XV**).

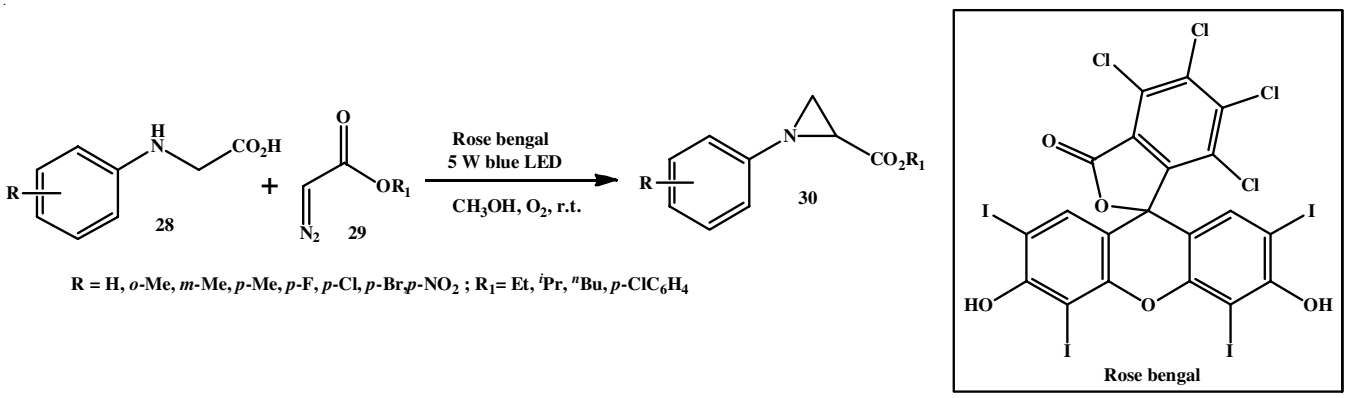
The mechanism was supported by DFT calculations, which suggested that the combination of these highly reactive reactants, Int-XII and Int-XIII, decreases the system's free energy by –38.54 kcal/mol and the cyclization energy barrier is only 8.19 kcal/mol. The Mulliken charge distribution of Int-XIV reveals substantial polarization of the C1=N–C2 bonds [q(C1) = –0.28 and q(C2) = 0.30], indicating the potential for a connection between the two polarized carbon atoms.

Zhou *et al*. [53] demonstrated a visible light-induced decarboxylative aza-darzens reaction between N-aryl glycines and diazo compounds, yielding various monosubstituted aziridines (**Scheme-XVI**). Initially, photoexcited RB* is readily quenched by N-aryl glycine, producing a cation radical. This radical undergoes decarboxylation, forming an α-amino alkyl radical. The α-amino alkyl radical is then further oxidized by a superoxide radical to yield an iminium ion (Int-XVII). This iminium ion deprotonates to generate an active imine (Int-XVIII), which subsequently undergoes nucleophilic addition of diazo compounds at the C=N bond to form Int-XIX. An intra-



R = H, 4-Me, 4-F, 4-Cl, 4-Br, 3-Cl, 2-Cl
R_1 = Me, Et, Hex, ^{i}Pr, cyclobutyl, cyclopentyl
R_2 = PMP, COMe, CO_2Me, *o*-menthyl

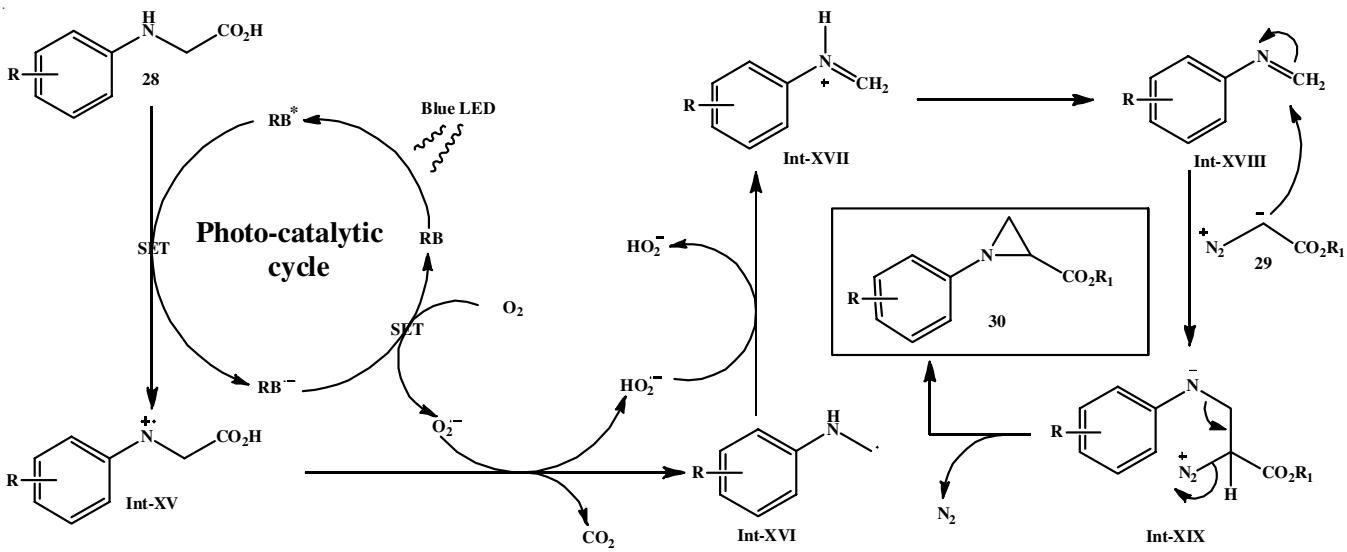
Scheme-XV: Divergent synthesis of aziridine frameworks under blue LED irradiation



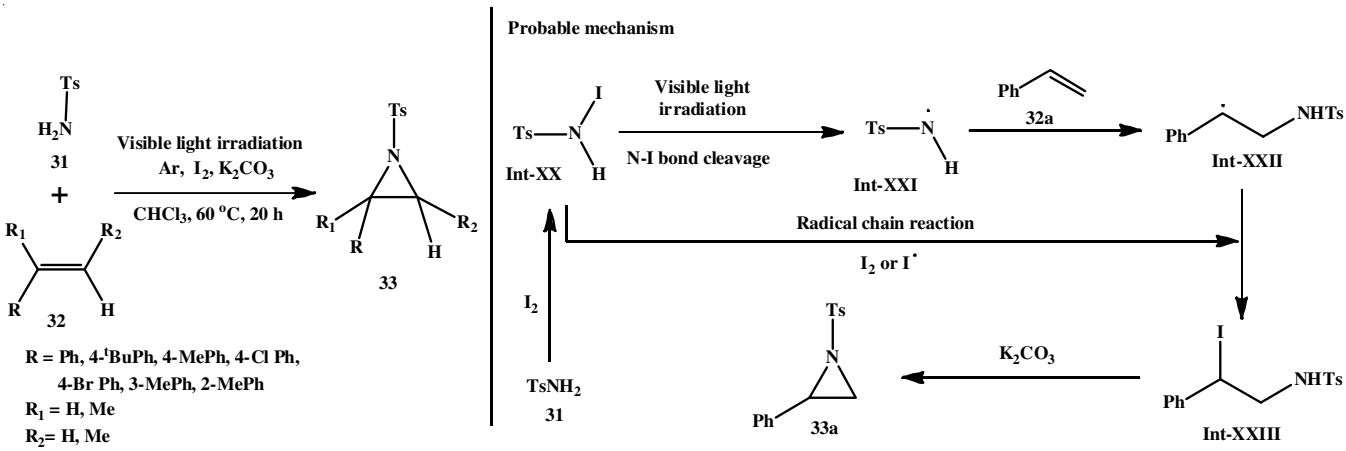
Scheme-XVI: Light-induced decarboxylative cyclization of *N*-aryl glycines and diazo compounds

molecular nucleophilic attack by the nitrogen atom on another carbon atom, with N_2 as leaving group, then gives rise to the desired aziridine (**Scheme-XVIa**).

Photoinduced aziridination *via in situ*-generated nitrogen centered radical addition to olefins: Itoh *et al*. [54] proposed a method for the synthesis of aziridines involving a reaction of styrenes with sulfonamide in the presence of K_2CO_3 and iodine in $CHCl_3$ under visible light irradiation. First, $TsNH_2$ reacts with molecular iodine to produce intermediate Int-XX. Next, photolysis of the N–I bond generates nitrogen-centered radical Int-XXI, which then reacts with styrene to form a carbon centered radical Int-XXII. The resulting radical Int-XXII can react with either molecular iodine or an iodine radical to produce intermediate Int-XXIII. Finally, the target aziridine is formed through a ring-closure reaction of Int-XXIII (**Scheme-XVII**).



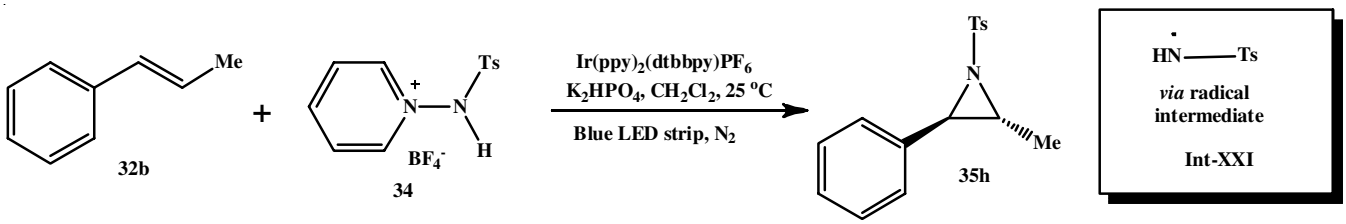
Scheme-XVIa: Mechanism of decarboxylative cyclization of *N*-aryl glycines and diazo compounds



Scheme-XVII: Aziridination of styrenes promoted by visible light

Xu *et al*. [55] developed a novel strategy for visible light-induced functionalization of alkenes, enabling the synthesis of substituted aziridines with excellent diastereoselectivity by using N-protected 1-aminopyridinium salts under mild conditions (**Scheme-XVIII**). The group investigated by the use of (*E*)-β-methylstyrene as alkene substrate and N-Ts-protected 1-aminopyridinium as radical source, in the presence of 1 mol% of fac-Ir(ppy)$_3$, NaOAc (1.5 equiv.), dichloromethane and a 25 W blue LED strip as visible light source. This reaction yielded *trans*-1-phenyl-2-methylaziridine (**35a**) as a single diastereoisomer (dr > 20:1) with a 56% yield. Upon optimizing the reaction conditions, they found that photocatalyst Ir(ppy)$_2$(dtbbpy)PF$_6$ (II) was superior in terms of reaction efficiency. The choice of base additive was crucial, with K_2HPO_4 providing the best results. Furthermore, the non-polar solvent DCM proved to be the optimal medium, while polar solvents such as DMF inhibited the reaction. Under the optimized conditions, the group has demonstrated that several substituted alkenes and nitrogen radical precursors are well-tolerated (Fig. 11).

A proposed reaction mechanism is illustrated in **Scheme-XIX**. Initially, the photocatalyst Ir(ppy)$_2$(dtbbpy)PF$_6$ (Ir^{3+}) undergoes a metal-to-ligand charge-transfer (MLCT) process under visible-light irradiation, forming the excited state (*Ir^{3+}). This excited state is then oxidatively quenched by N-Ts-protected 1-aminopyridinium, generating the nitrogen-centered radical species (XXI) and Ir(ppy)$_2$(dtbbpy)$^+$ (Ir^{4+}). The electrophilic radical adds to the alkene, forming intermediate XXIV, which is oxidized by Ir^{4+} to create the stabilized carbocation intermediate XXV and regenerate Ir^{3+}. Finally, the nitrogen of the sulfonamide acts as a nucleophile, initiating an intramolecular nucleophilic reaction. The final product **35** is formed through deprotonation.



Scheme-XVIII: Alkene functionalization for the stereospecific synthesis of substituted aziridines

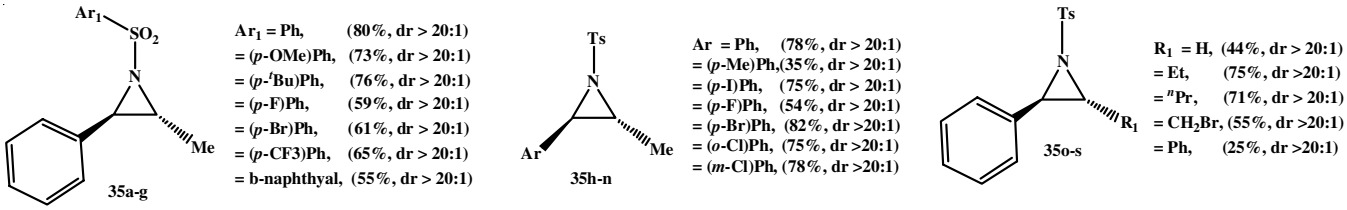
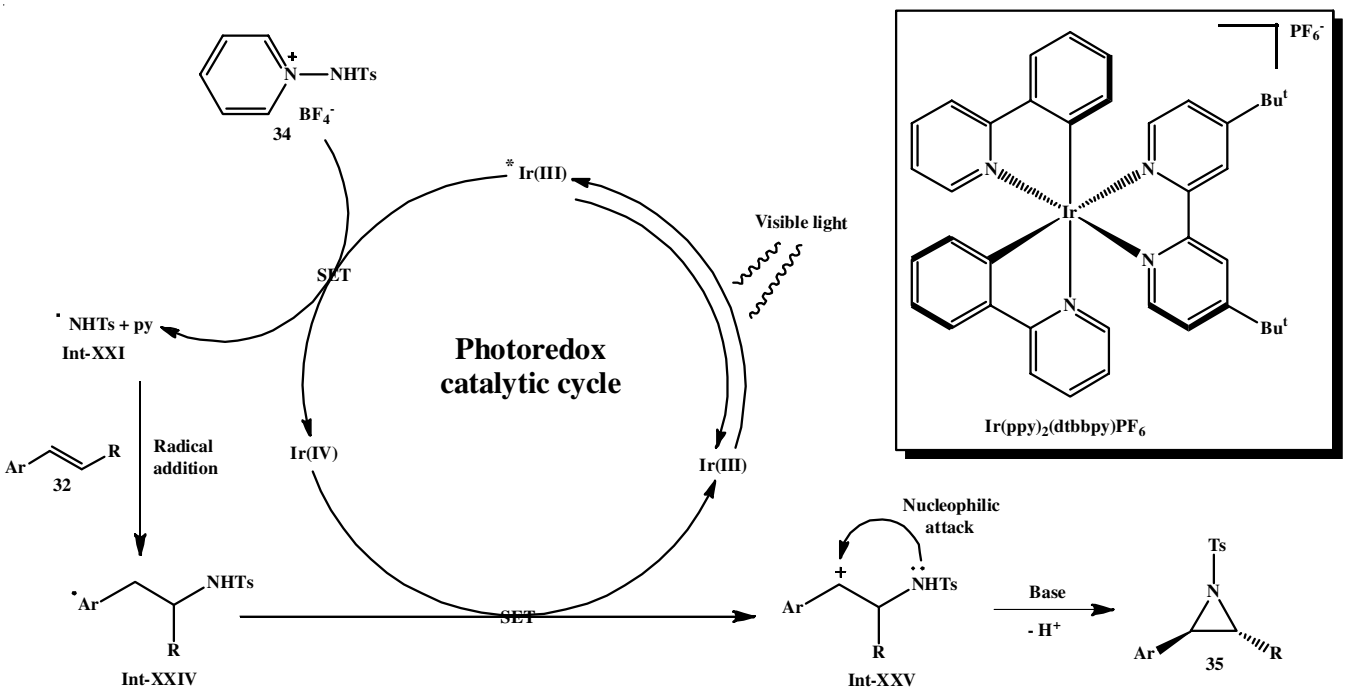


Fig. 11. Scope of nitrogen radical precursors and alkenes in aziridination



Scheme-XIX: Reaction pathway of the photocatalytic aziridination

Visible light-assisted [2+1] aza-cyclization for aziridination: Samanta *et al*. [56] have established a facile, visible light-assisted [2+1] aza-cyclization reaction involving cyclic N-sulfonyl imines and α-aryl-substituted vinyl azides. This process utilizes an *in situ* generated Cu^{I} complex as a photocatalyst to access synthetically valuable sulfamidate-fused aziridines in acceptable chemical yields with excellent diastereoselectivities. The optimal reaction conditions were achieved using a CuI catalyst (10 mol%) and 2,2′-bpy ligand (10 mol%), with 0.2 mmol of N-sulfonyl imines and 0.4 mmol of vinyl azides in a CH_3CN:H_2O (2.0 mL, 50:1) solvent system under irradiation by four 5 W blue LEDs at room temperature in an argon atmosphere for 16 h. This investigation revealed that the [1C1N+1C] aza-cyclization reaction tolerates azides with both electron-donating and electron-withdrawing substituents on the aryl rings, as well as cyclic imines with various electron-donating (Me, MeO and EtO) and electron-poor halogen atoms (F, Cl and Br) on the benzene rings, producing the corresponding aroyl-substituted fused aziridines with excellent diastereoselectivities (up to 99:1 dr). However, alkyl-substituted vinyl azides and vinyl azides or cyclic imines containing strong electron-withdrawing NO_2 groups did not participate in this aza-cyclization reaction (**Scheme-XX**).

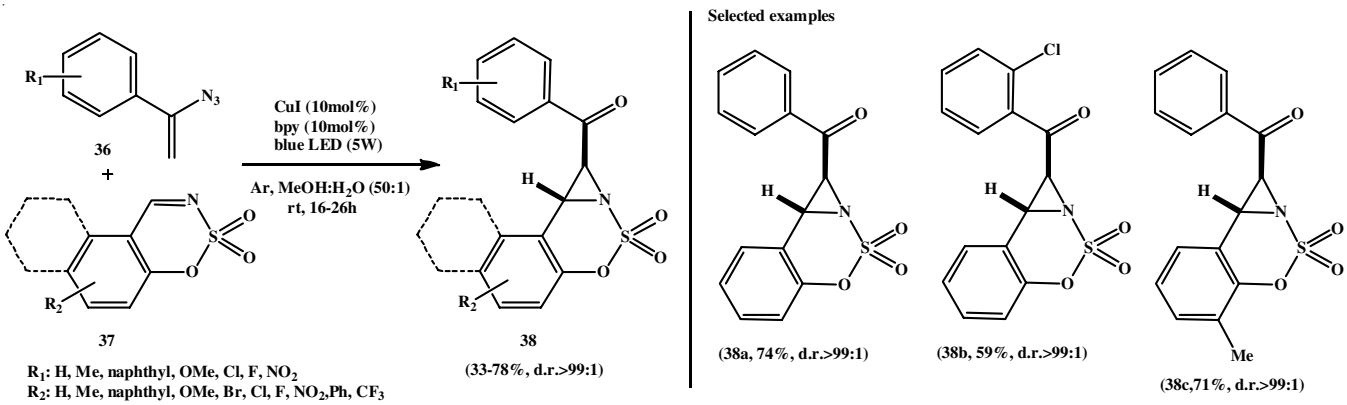
They proposed that the mechanism starts with CuI complexing with ligand bpy to form a Cu(I)bpy-complex. This complex absorbs blue LED light, forming an electron-rich photoexcited Cu(I)bpy* species ($E_{CuI/CuII}$ = 0.75 V), which triggers a single electron transfer (SET) to reduce vinyl azide (**36a**) (E_{red} = 0.53 V) to vinyl azide anion radical (Int-XXVI). This radical undergoes denitrogenative decomposition to form an iminyl-Cu(II) radical (Int-XXVII). The nucleophilic carbon-centered radical then attacks the C=N bond of (**37a**), forming another iminyl-Cu(II) radical (Int-XXVIII). An intramolecular 1,3-Cu(II) migration and HAT (hydrogen-atom-transfer) of (Int-XXVIII) may produce an organocopper(II) species (Int-XXIX), which undergoes hydrolysis to yield a radical intermediate (Int-XXX). This intermediate undergoes oxidative cyclization to produce aziridine (**38a**) and regenerate the Cu(I)-complex for the next cycle (path a). Alternatively, it may form a stable four-membered organocopper(III) transition state TS-II (path b), where the orientation of benzoyl and aryl parts of sulfamidate minimizes steric repulsion, leading to the desired *trans*-isomer **38a** with excellent diastereoselectivity (**Scheme-XXa**).

Photo-assisted aziridination *via* aminofluoroalkylation and intramolecular nucleophilic reaction: In 2013, Cho *et al*. [57] presented a perfluoroalkylation method using visible light-induced photocatalysis to prepare aziridines containing CF_3, C_3F_7 and C_4F_9 groups from unactivated allylic amines. The reaction involves an allylic amine, fluorinated alkyl iodide as fluorinated alkyl radical source, 0.5 mol% $[Ru(phen)_3]Cl_2$ (where phen = 1,10-phenanthroline) and TMEDA in MeCN, under a 14 W fluorescent lamp, leading to the formation of aziridines through the selective nucleophilic reaction of XXXI (**Scheme-XXI**).

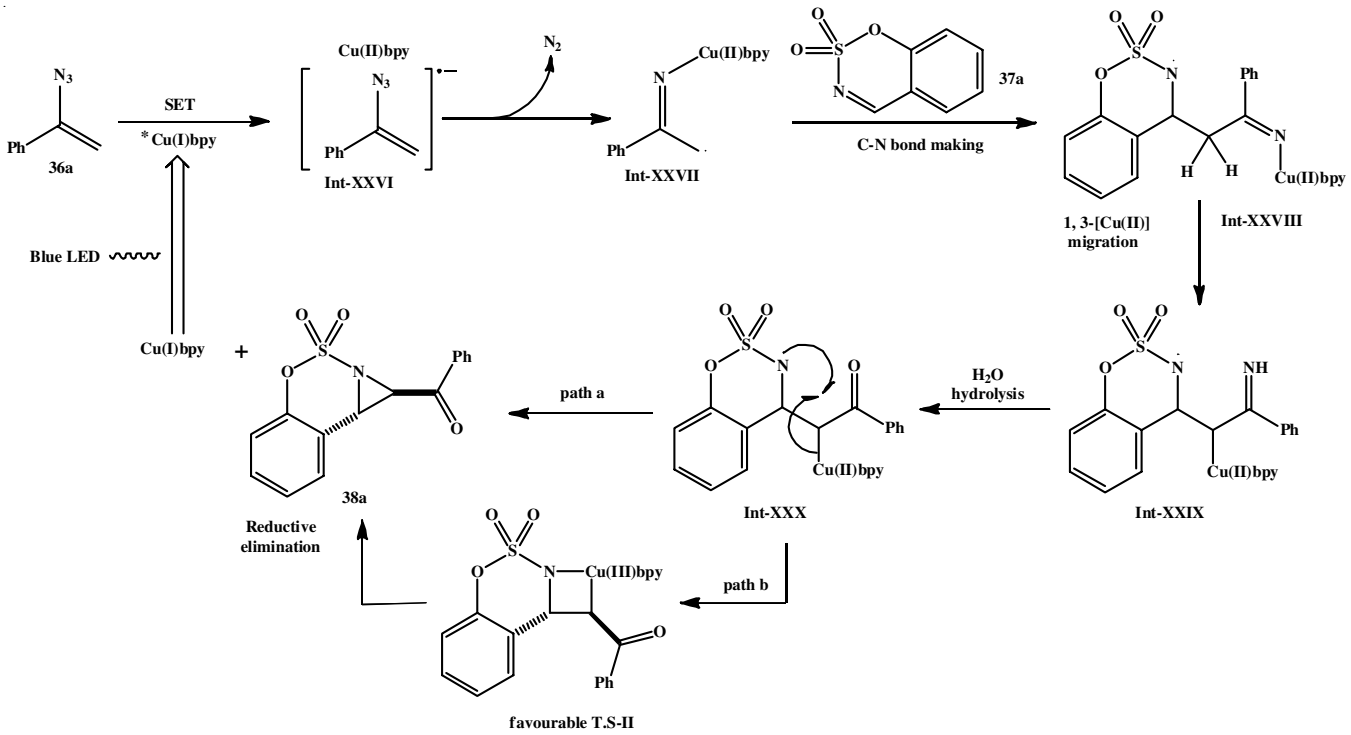
Furthermore, Liu *et al*. [58] further developed a similar type of strategy to synthesize fluorinated aziridines. The reactions employed N-allylaniline (42, 0.2 mmol, 1.0 equiv.) and fluoroalkyl iodides (39, 0.6 mmol, 3.0 equiv.) in the presence of KOH (0.8 mmol, 4.0 equiv.) in a *t*-BuOH:THF (2:1, 1.0 mL) solvent system under argon. The mixture was then irradiated with 12 W blue LEDs. For the use of ICF_2COOEt as fluoroalkyl iodide, KOAc (0.8 mmol, 4.0 equiv.) and a DMSO:DCM = 1:3 (1.0 mL) solvent system were employed to obtain the corresponding aziridines (**Scheme-XXII**). They introduced a catalyst free photochemical transformation for the direct aminofluoroalkylation of olefins, driven by non-covalent interactions between N-allylanilines and fluoroalkyl iodides, demonstrating high functional group tolerance (Fig. 12).

The proposed mechanism involves initial non-covalent interactions between amine **42** and the C–I bond of **39**. This interaction leads to the generation of a fluoroalkyl radical (Int-XXXIII) upon visible light irradiation. The newly formed radical then abstracts an iodine atom from R_FI, resulting in the formation of intermediate (Int-XXXIV) and the regeneration of the R_F radical. The desired products (**43** or **44**) are obtained through further cyclization in the presence of bases (**Scheme-XXIII**).

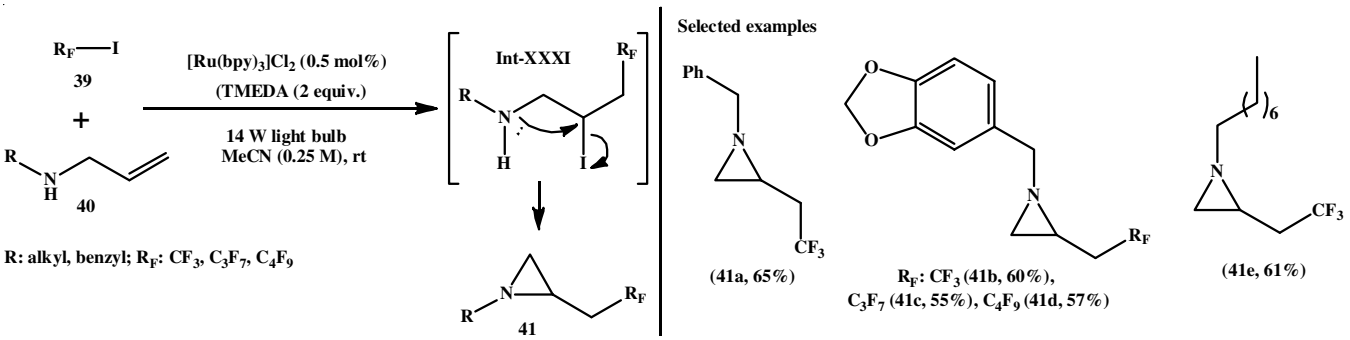
Photoinduced aziridination *via* coupling of *in situ* generated biradicals: Loera & Garcia-Garibay [59] investigated the solid-state photodenitrogenation of crystalline triazolines, demonstrating a high-efficiency formation of corresponding aziridines under photoirradiation (**Scheme-XXIV**). They showed that these solid-to-solid reactions proceed *via* the formation of products in metastable crystalline phases. The experiments, using chlorosubstituted triazoline, were conducted with a medium-pressure Hg lamp equipped with a quartz filter transmitting light at λ = 200 nm. The formation of aziridine was



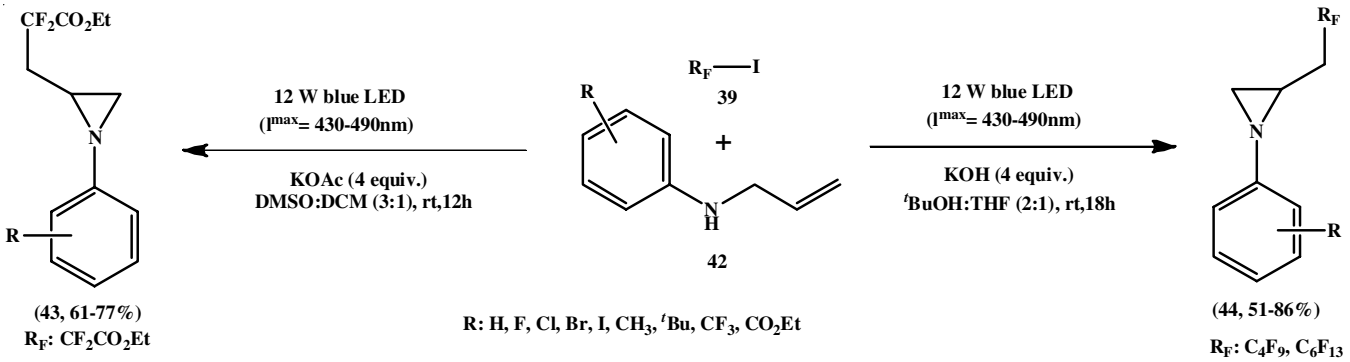
Scheme-XX: Copper(I)-photocatalyzed diastreoselective synthesis of fused aziridines



Scheme-XXa: Proposed mechanism of copper(I)-photocatalyzed diastreoselective synthesis of fused aziridines



Scheme-XXI: Photocatalyzed aziridination of allylic amine



Scheme-XXII: Visible light promoted aminofluoroalkylation of unactivated olefins

monitored every 15 min through ^{1}H NMR spectroscopy. The photoreaction, occurring entirely in the solid phase, reached completion after 60 min with an 80% yield, alongside some unidentified byproducts likely resulting from secondary photoreactions of the aziridine under the reaction conditions.

Conclusion

Aziridines, with their inherent ring strain and high reactivity, serve as essential building blocks in the construction of complex organic molecules, playing a pivotal role in the development of pharmaceuticals and natural products. In recent decades,

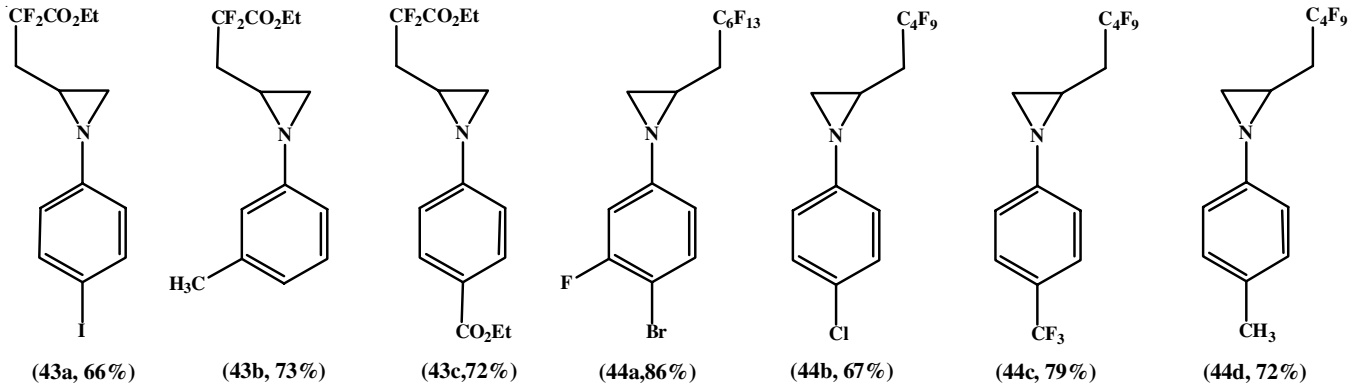
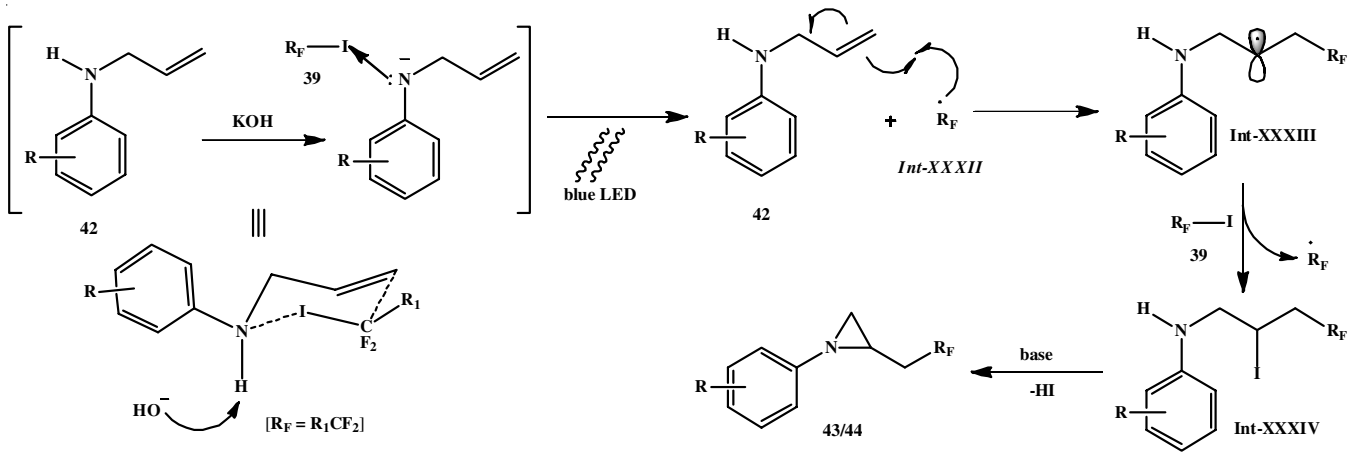
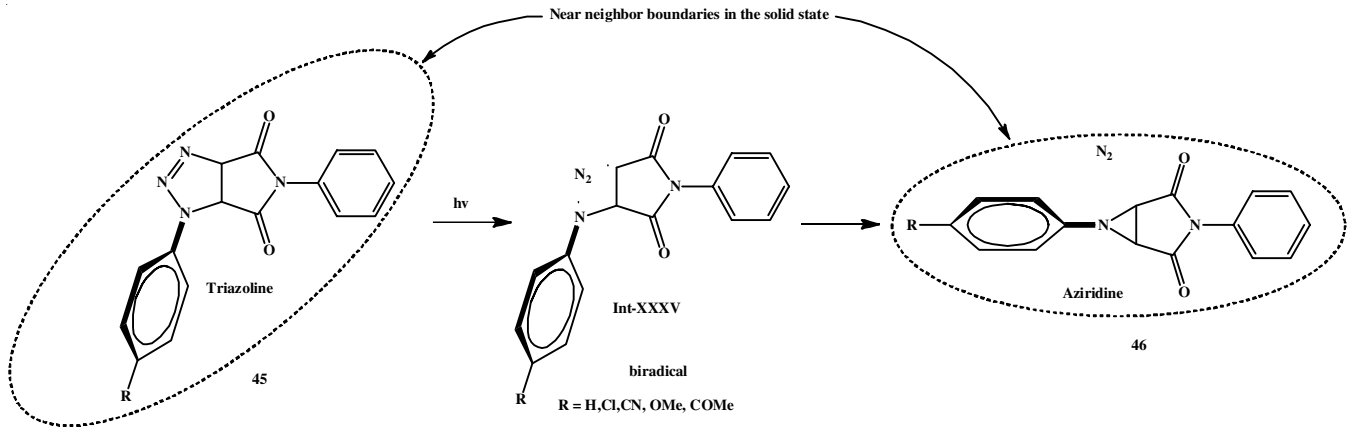


Fig. 12. Selected examples of fluoroalkyl group containing aziridines



Scheme-XXIII: Mechanistic proposal of light driven aminofluroalkylaton of unactivated olifins



Scheme-XXIV: Photoinduced aziridination through solid-state denitrogenation of triazoline

significant advancements have been achieved in aziridine chemistry through photochemical methods. Photocatalysis has introduced a range of efficient strategies for synthesizing these three-membered nitrogen heterocycles, offering greener and more selective alternatives to traditional approaches. This review highlights the major progress in the photocatalytic aziridination, emphasizing the development of novel radical, nitrene and carbene precursors. Despite these achievements, discovering new photocatalysts to improve the stereospecificity and stereoselectivity of the products is an ongoing challenge. Nevertheless, it is anticipated that significant progress will continue in photocatalytic transformations, with newly developed protocols offering efficient and selective strategies, advancing aziridine chemistry and its applications in the synthesis of complex molecules, including natural products and pharmaceuticals.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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