

# Visible Light-Mediated Organic reactions using Iridium based Photoredox Catalyst

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**MASTER OF SCIENCE**

By

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Indian Institute of Technology Hyderabad

to the

**DEPARTMENT OF CHEMISTRY**

**INDIAN INSTITUTE OF TECHNOLOGY HYDERABAD**

India

April, 2016

## Declaration

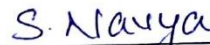
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## Approval Sheet

This thesis entitled –Visible light-Mediated Organic reactions using Iridium based photoredox catalyst. –by S.Navya –is approved for the degree of Master of Science in Chemistry from IIT Hyderabad.



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Dedicated to

**My Parents**

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# **Visible Light-Mediated** **Organic reactions using Iridium based photoredox catalyst**

## **Abstract**

Proposal to employ visible light in a process to initiate organic reactions is appealing because of its reducing side reactions and products which are related with photochemical reactions conducted in the presence of high energy UV light. This literature review gives a broad overview of visible light photoredox catalysis using iridium based catalyst in organic synthesis followed by some recent examples which emphasize its potential to commence an organic transformation [1].

## **1. Introduction**

In the last few decades, organic reactions were performed by following synthetic methodology or by total synthesis to achieve highest optimum yield thereby enhancing the reactivity of the reaction. Renewable source of energy which is “light” is an abundant source which could accomplish greener reactions. Therefore, photochemistry and photocatalysis have greater efficacy and potential in organic reactions. Application of photochemical synthesis through visible-light absorbing photo-catalyst has utilized electron or energy transfer in organic reactions to sensitize molecules for performing photochemical synthesis and thereby achieving greener chemistry [1].

### **1.1 Photocatalysis**

Photocatalysis is composed of two words, i.e. photo and catalysis in which photo means light and catalysis is a process in which rate of the chemical reaction is being increased by reducing the activation energy. Thermal catalysts (which are different from photo-catalysts) are only effective



in excited state and activate the molecule by means of a chemical process, namely Single Electron Transfer (SET) process [2] thereby regenerating the catalyst.

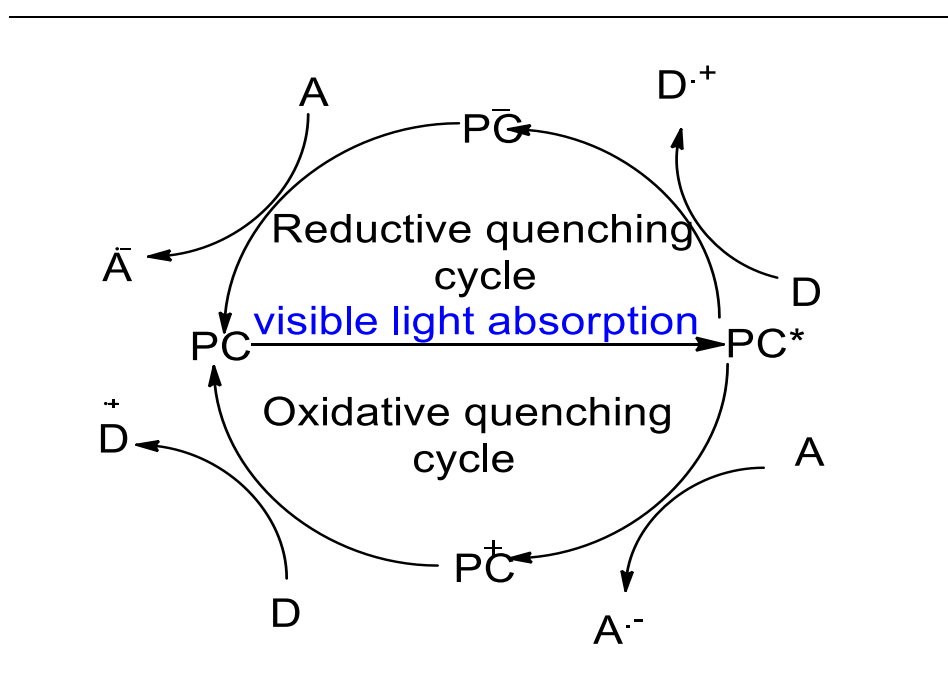
## **1.2 Visible light mediated photoredox catalysis**

Visible light energy is an inexpensive, renewable, clean source which is found infinitely for synthesizing many reactions in day to day life. Hundred years ago, Ciamician had recognized that sunlight could be used as a renewable, clean, abundant and inexpensive energy source in chemical reactions. In the field of photocatalyst (which has a wide research scope) especially with photoredox catalyst, visible light has been used in many areas, one of which is transformation of solar energy into electrical energy and fuel. This process helped in emitting lesser chemical pollutants than seen in the last few years. Till recently, almost all the photocatalysts used were metallic compounds [2]. The photocatalyst has been divided into three catalytic methods: light which is being absorbed, metal to ligand charge transfer in excited states and oxidative or reductive quenching cycle [2]. Photoredox catalyst uses transition metal complexes for commencing organic reactions in which it uses 4d or 5d coordinating metal complexes like Ru(II) polypyridine complexes or Ir(III) cyclometalated complexes which are being used as a catalyst in several transformations [3]. Primary Ir complex used is tris-[2-phenylpyridinato-C<sup>2</sup>,N] iridium(III) or Ir(ppy)<sub>3</sub> by single electron transfer or atom transfer radical addition mechanistic pathway. Iridium based catalyst has indeed enhanced the reactivity and selectivity of the reactions. Ir(III) complex has a maximum absorption in the UV region of approx. 370 nm of wavelength which is significant for the chemical reactions [3]. Ir(III) cyclometalated complexes which has a pseudo octahedral geometry in which it has two isomers and the facial isomer is used as a catalyst for the photocatalytic reactions in which it is coordinated to monoanionic bidentate species to occupy the six sites of Ir(III) complex [4]. Application of cyclometalated Ir(III) complexes like in phosphorescence sensors, bioimaging, photo voltaics cells due to its high quantum yields and wide spectral tuning ability has recently emerged in many research fields. Many research groups have been using iridium based complexes in photoredox catalysis and in phosphorescent staining of intracellular nuclei in organelles, endoplasmic reticulum, plasma membranes and in cytoplasm due to its higher quantum yields, maximum spin-orbit coupling efficiencies which enables non zero transition probability and spin restriction of phosphorescence transition which is being overcome by the

iridium core complexes [5]. In the year 2008, MacMillan and Yoon made a milestone in the research area of photoredox catalyst which uses visible light for the driving of organic synthesis in the making of newer chemical bond which are carbon-carbon or carbon hetero atom bond formation taking place in the process [6].

## 2. Schematic representation of photoredox catalysis using visible light

### light



### PHOTOREDOX CATALYSIS USING VISIBLE LIGHT

PC=photocatalyst, A=electron acceptor

D=electron donor

The mechanistic pathway cycle is composed of a sequence of first electron being transferred from an electron donor to an excited state i.e. PC<sup>\*</sup> which is associated with the formation of

reduced state  $PC^-$  and second from an  $e^-$  acceptor which is A, reduction takes place that's linked with the regeneration of the catalyst i.e. to the ground state (PC) also known as reductive quenching cycle. Another side of this cycle is known as oxidative cycle which is expressed as a series of third electron transfer taking place from an excited state i.e.  $PC^*$  to an electron acceptor which is A being connected with the making of higher oxidation state which is  $PC^+$  and last fourth one is the oxidation of an electron donor i.e. D connected with the reproduction of the ground state of the catalyst which is PC and this cycle is known as oxidative quenching cycle. Reductive cycle and oxidative cycle both will form radical species i.e.  $D^+$  and  $A^-$  in a single reactor by a process known as SET which is single electron transfer process to produce redox-neutral transformation. The words - oxidative and reductive might be slightly confusing therefore to make it meaningful let us associate reductive term as the reducing process of the photoexcited species  $PC^*$  and unlike to this oxidation of the electron donor i.e. D which is taking place in same process. Oxidative would then refer to the photoexcited species oxidation i.e.  $PC^*$  which is associated with the external electron acceptor which is A – leading to reduction taking place in this process [7]

### 3. Homolytic aromatic substitution

1. In 2013, Pixu Li with co-workers, worked on arylation of arenes or heteroarenes with aryl halides which could be carried out in the presence of potassium t-butoxide and DMSO using Ir based photoredox catalyst (figure 1) at room temperature. The aryl radicals react with arenes or heteroarenes intermolecularly to give optimum yields and mechanistic pathway as shown in figure 2 [10].

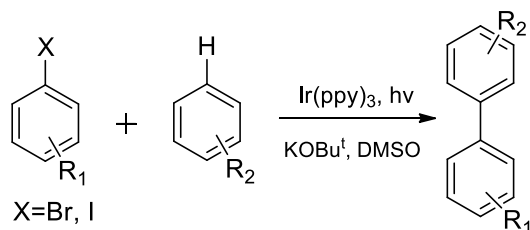


Figure 1

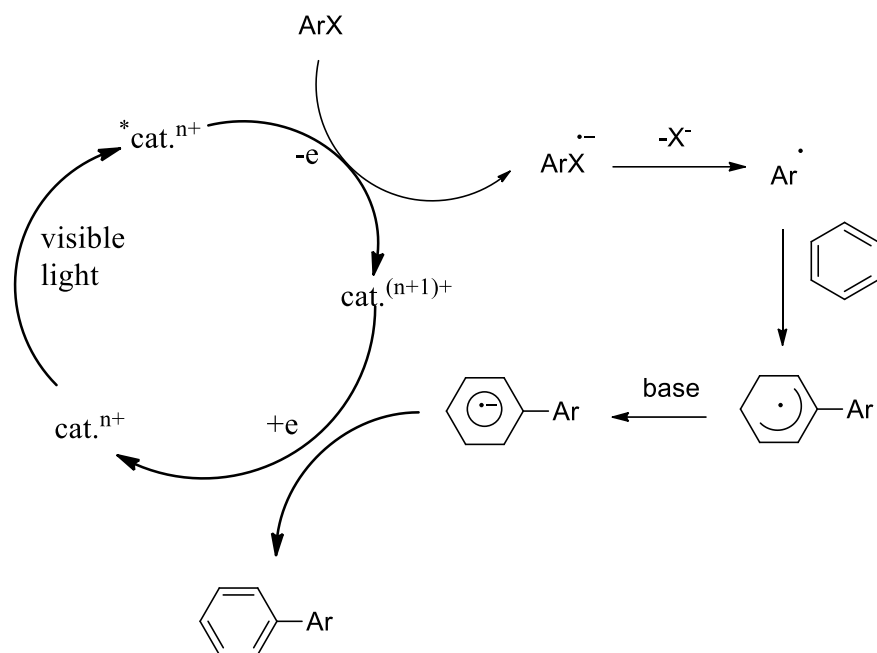


Figure 2:- mechanistic pathway

#### 4. Intermolecular synthesis of $\gamma$ -lactones

1. In 2013, Li-Zhu Wu, Qiang Liu with co-workers synthesized a novel method for preparation of  $\gamma$ -lactone (figure 1) through visible light photoredox catalyst. This photocatalyst is considered to have a good protocol for regioselectivity and compatibility affording a novel way to intermolecular  $\gamma$ -lactone synthesis. Using Ir(ppy)<sub>3</sub> single electron transfer mechanism  $\gamma$ -lactones are obtained (as figure 2 shows) through mechanistic pathway of this reaction [12].

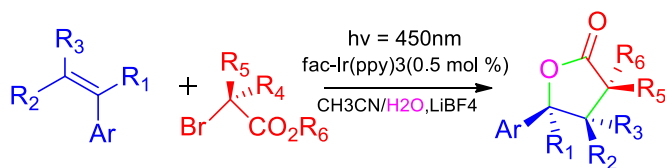


Figure 1

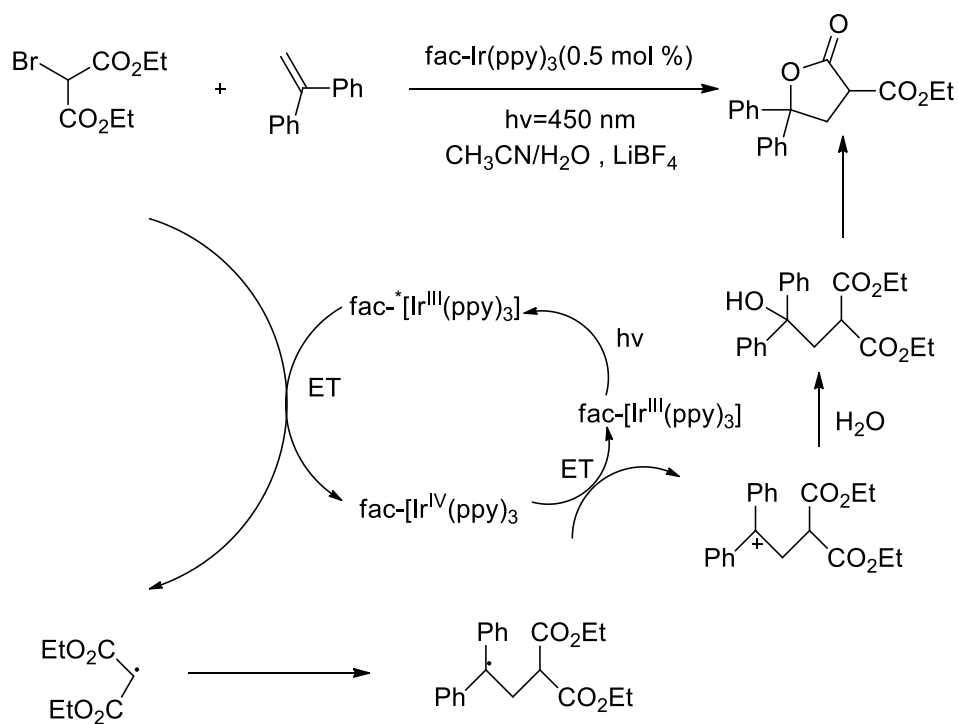


Figure 2:- mechanistic pathway

## 5. Photoredox catalysed multicomponent reaction

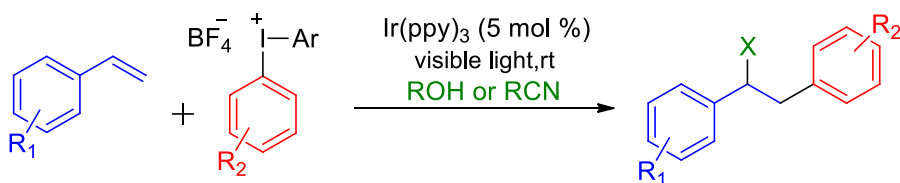


Figure 1

1. In 2013, Micheal F. Greaney with co-workers reported coupling of styrenes via three component system using photocatalyst (as seen in figure 1). They screened with different catalysts and the best one that gave the highest optimum yield was  $\text{fac-Ir(ppy)}_3$  with simultaneous arylation and CO or CN bond formation across styrene double bond [13].

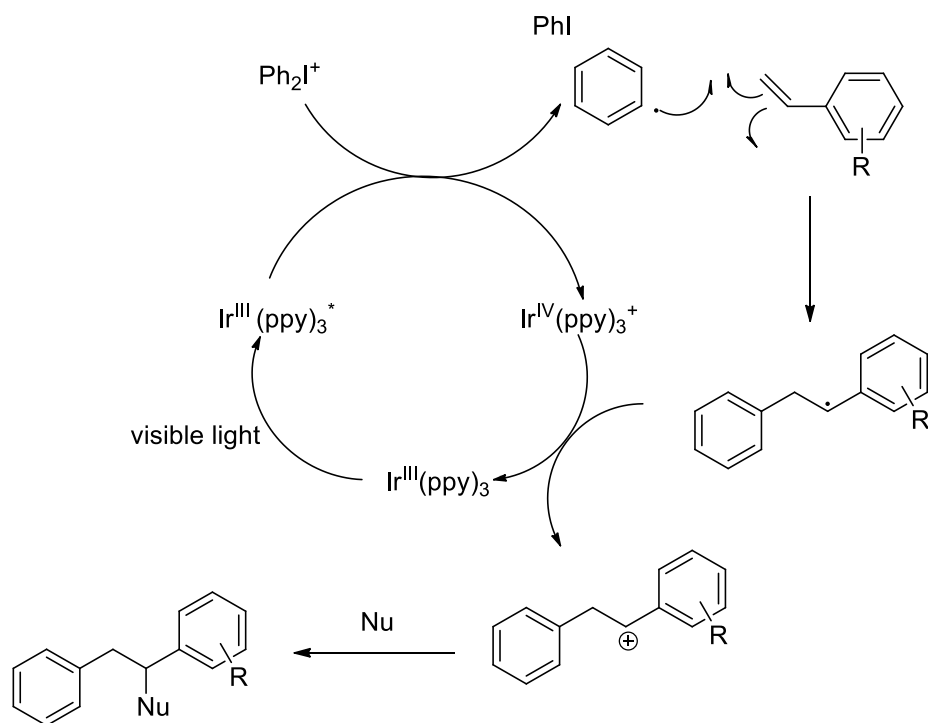


Figure 2:- mechanistic pathway

It is a mild and facile coupling of styrene with aryl and heteroatom nucleophiles such as alcohol,  $\text{H}_2\text{O}$  and  $\text{RCN}$ . Figure 2 gives a brief mechanistic pathway [13].

2. In 2013, Magnus Rueping and Carlos Vila synthesized amino amides and imides from  $\alpha$ -amines by oxidative three component system (figure 1) which involves functionalization of  $\text{sp}^3$  hybridized carbon-hydrogen bond adjacent to nitrogen atom via mild aerobic oxidation using visible light photoredox catalyst. Figure 2 shows mechanistic catalytic cycle by reductive quenching of R-amino amides [14].

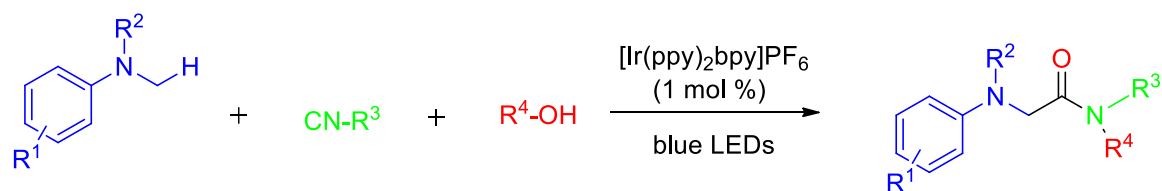


Figure 1

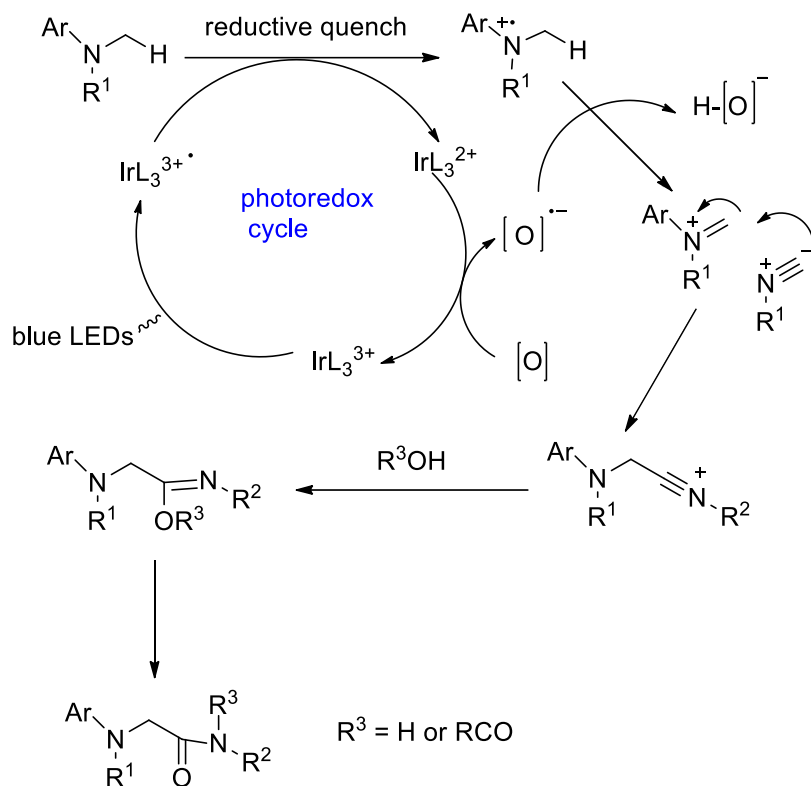


Figure 2:- mechanistic pathway

3. In 2014, Aiwen Lei with co-workers performed synthesis of  $\gamma$ -alkoxynitriles via three component alkoxylation of alkenes (figure 1).  $\text{fac-Ir}(\text{ppy})_3$  catalyst is used for this transformation. It is a one pot difunctionalized catalytic radical alkylation and alkoxylation of alkenes. Figure 2 shows substrate scope of  $\gamma$ -alkoxynitriles [15].

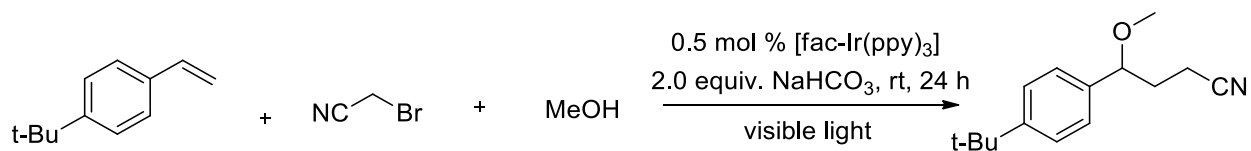


Figure 1

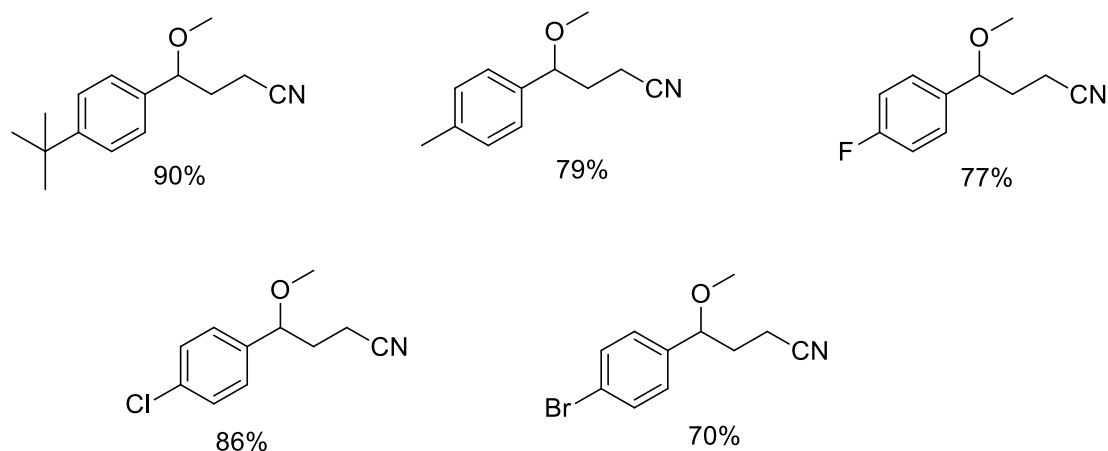
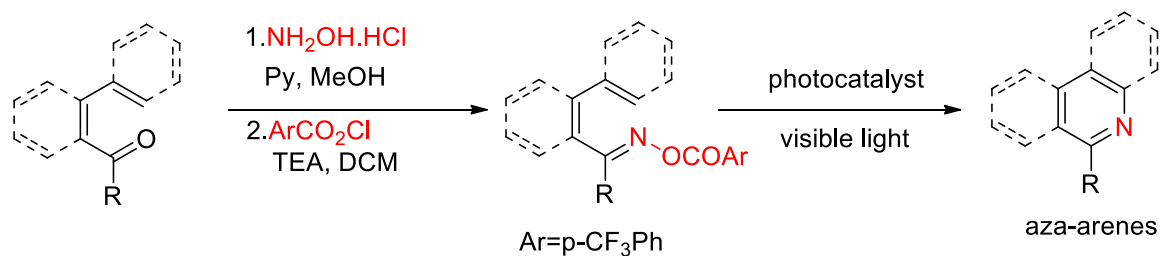


Figure 2:- substrate scope

## 6. One pot synthesis using visible light

1. In 2015, Xiao-De and Shouyun Yu worked on synthesis of phenanthridines and quinolines from aldehydes and O-acyl hydroxylamine using visible light photoredox catalyst via cyclization and iminyl radical to furnish aza arenes. Substrate scope can be seen in figure 1 by changing the R groups of aza-arenes [22].

Previous work was performed on three steps synthesis of aza-arenes from aldehydes or ketones via acyl oximes





This work on one pot synthesis of aza-arenes

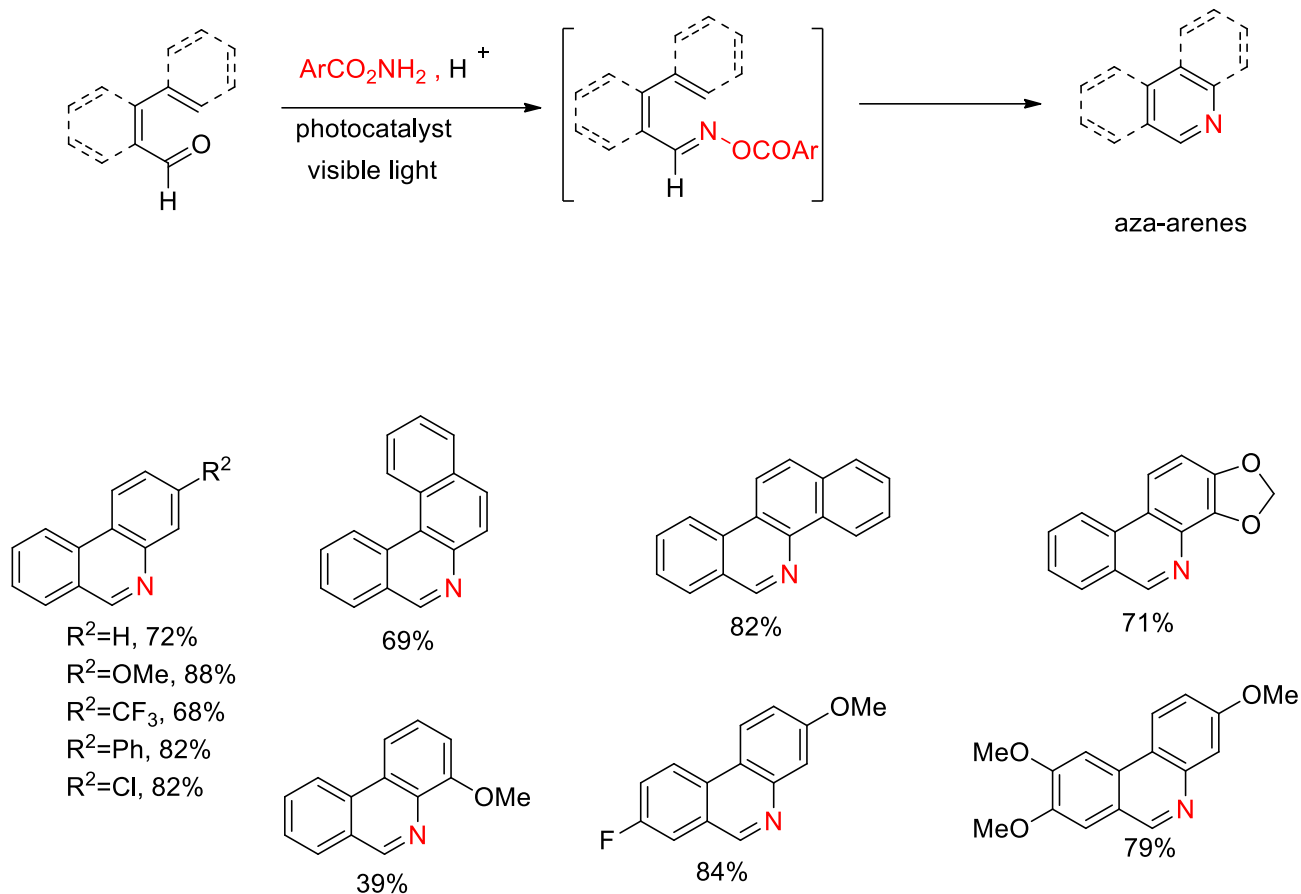


Figure 1:- substrate scope

## 7. Decarboxylative reactions

1. In 2015, David W. C. MacMillan and his co-workers synthesized ketone by decarboxylative arylation of  $\alpha$ -oxo acids using visible light iridium photoredox catalyst and Ni based organo catalyst (figure 1). Achieved from an  $\alpha$ -oxo acid precursor through acyl radical intermediate. This mild decarboxylative arylation is efficient for many medicinal chemistry. Nickel catalytic cycle and photoredox catalytic cycle is shown below (figure 2) [23].

Decarboxylative keto acid arylation

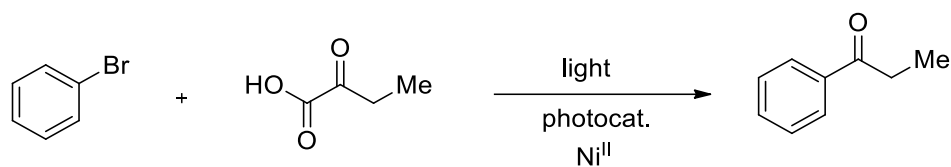


Figure 1

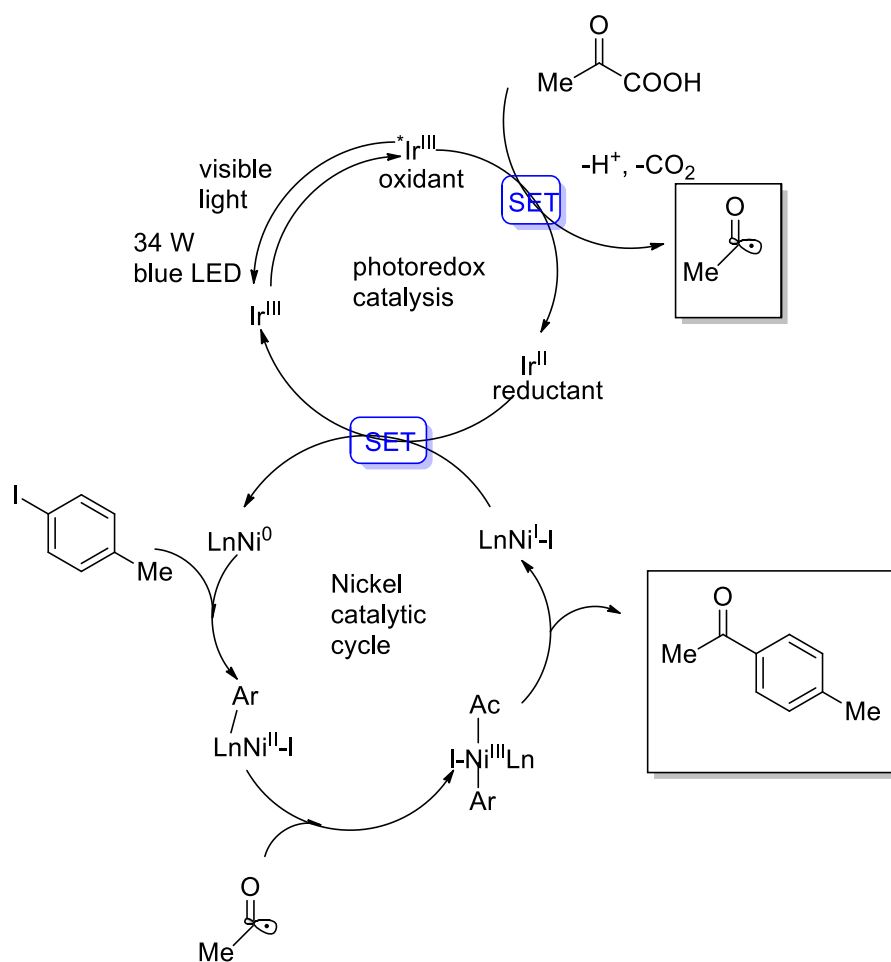


Figure 2:- mechanistic pathway of photoredox catalyst and nickel catalyst

2. In 2015, MacMillan with co-workers performed fluorination of aliphatic carboxylic acids through visible light iridium catalyst (figure 1) via oxidative quenching pathway in which photon

induced oxidation of carboxylates led to carboxyl radical with rapid CO<sub>2</sub> extrusion and F radical transfer to fluorinating agents led to fluoroalkanes with highest optimum yield [24].

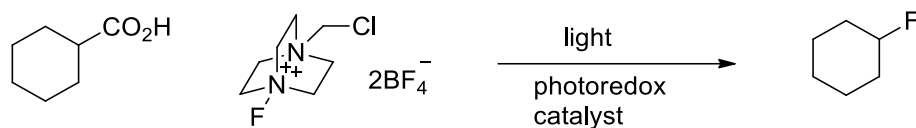
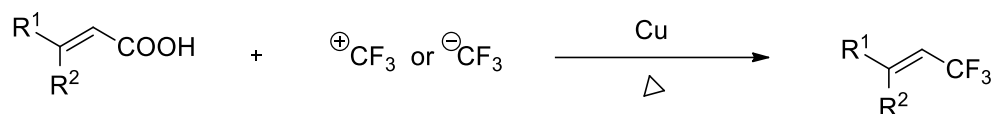


Figure 1:- decarboxylative radical coupling

3. In 2014, Chengjian Zhu with co-workers performed trifluoromethylation of  $\alpha,\beta$  unsaturated carboxylic acid by decarboxylative method using togni reagent (figure 1). Trifluoromethylated alkenes were obtained in highest yield with radical mechanism [25].

Previous work reported with Cu



This work reported with photoredox catalyst

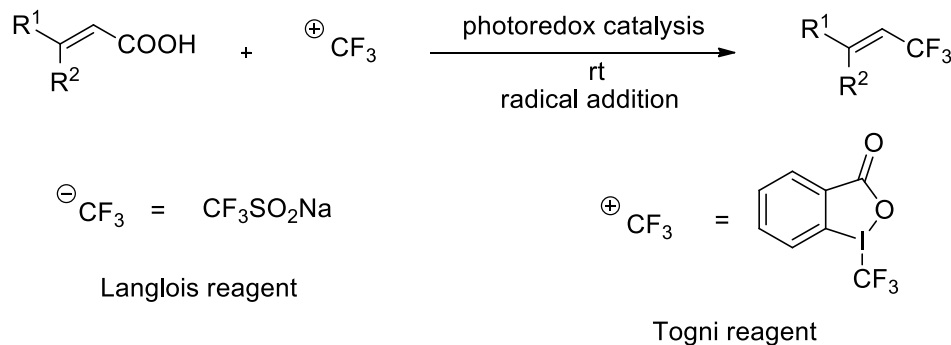


Figure 1:- trifluoromethylation of  $\alpha,\beta$ -unsaturated carboxylic acid

4. In 2014, Jon A. Tunge with co-workers performed decarboxylative allylation of amino alkanic acid and ester with combination of palladium and photoredox catalysis at room temperature (figure 1). The reactions gives  $\text{CO}_2$  as a byproduct with allylated alkanes. By varying the R group substrate scope can be seen (figure 2) [26].

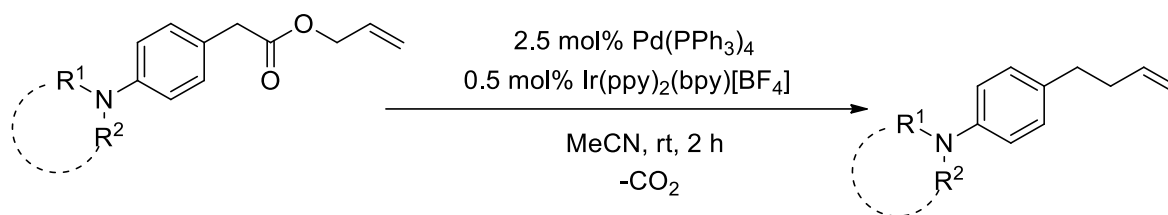


Figure 1

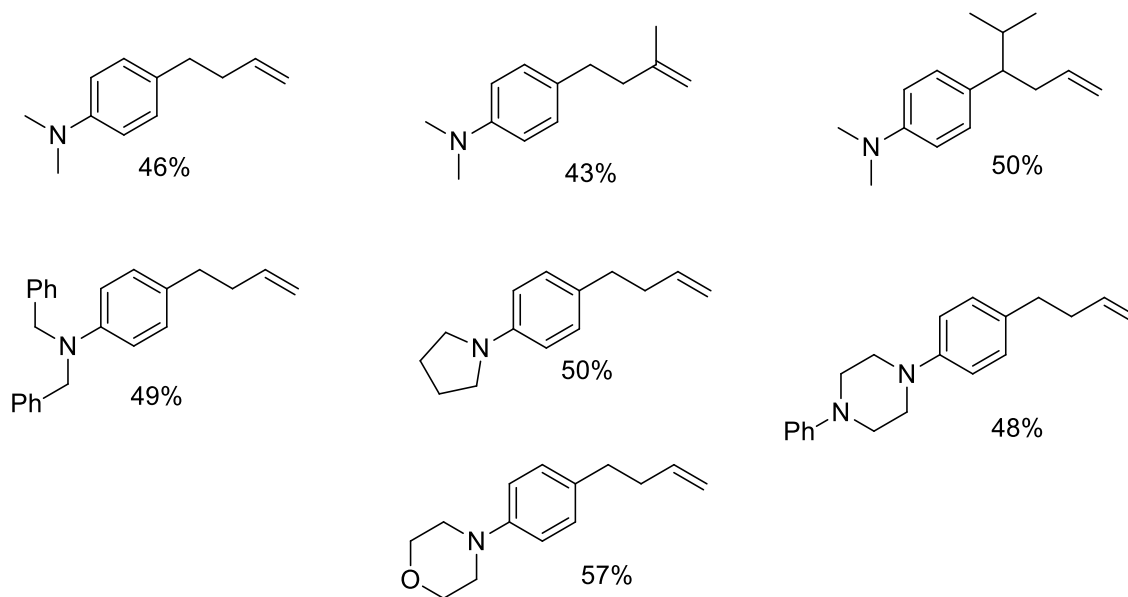


Figure 2:-substrate scope

5. In 2014, David W. C. MacMillan with co-workers performed three step synthesis of Pregabalin (figure 1). Application of carboxylic acid for radical activation by Micheal addition through visible light based iridium photoredox catalysis. Different substrate scope can be seen in figure 2 [27].

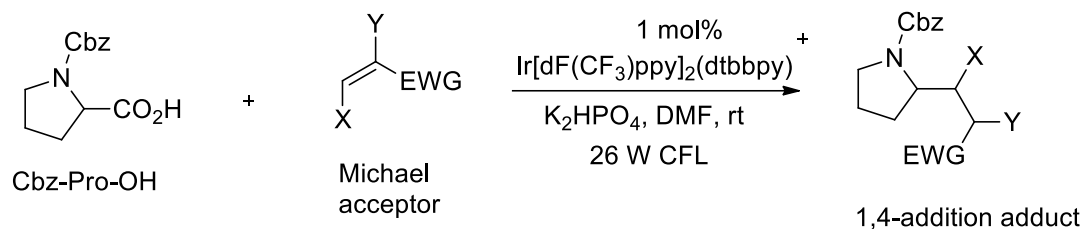


Figure 1

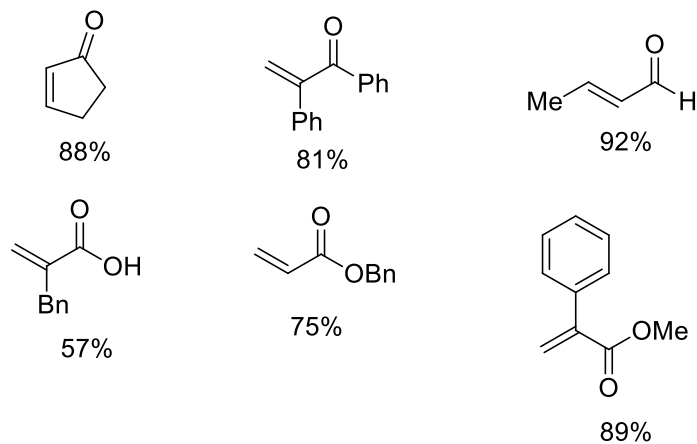


Figure 2:- substrate scope

6. In 2013, Yoshiaki Nishibayashi, Yoshihiro Miyake with co-workers performed oxidative decarboxylation of arylacetic acid into benzyl radicals through polypyridyl iridium based

photoredox catalyst via alkyl radical as intermediate in the reaction process (figure 1). It is a mild and efficient method for decarboxylative reaction with highest optimum yield [28].

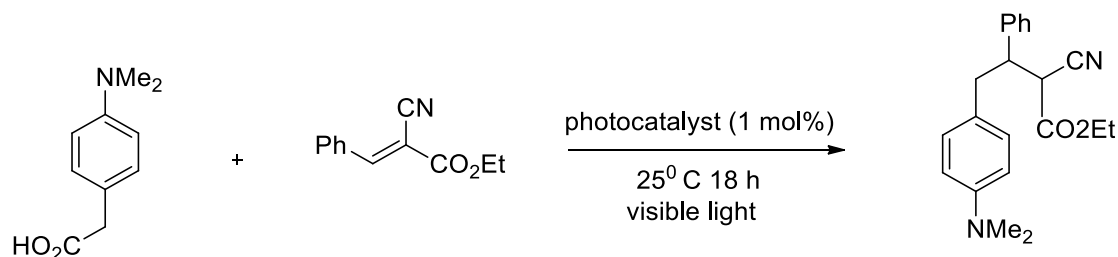


Figure 1

7. In 2014, MacMillan with his co-workers performed decarboxylative reaction in which coupling of  $\alpha$ -amino acids and benzonitriles using visible light by means of photoredox catalysis in figure 1. This reaction is done by reduction of benzonitriles by single electron transfer mechanism using iridium based photocatalyst in the excited state and generating radical anion. Regeneration of photocatalyst by oxidation of amino acid. Maximum yields are obtained by trying various substrate scope [29].



Figure 1

## 8. Asymmetric catalysis

1. In 2015, Eric Meggers and his co-workers performed photoactivation and asymmetric catalysis in the presence of dual catalyst under mild condition. Asymmetric catalysis with chiral iridium complex. Reaction between 2-acyl imidazoles with benzyl bromides give  $\alpha$ -alkylated 2-acyl imidazoles in high optimum yields by varying the R(aryl) group with high enantioselectivity (figure 1) using chiral iridium complex. Substrate scope can be seen in figure 2 [30].

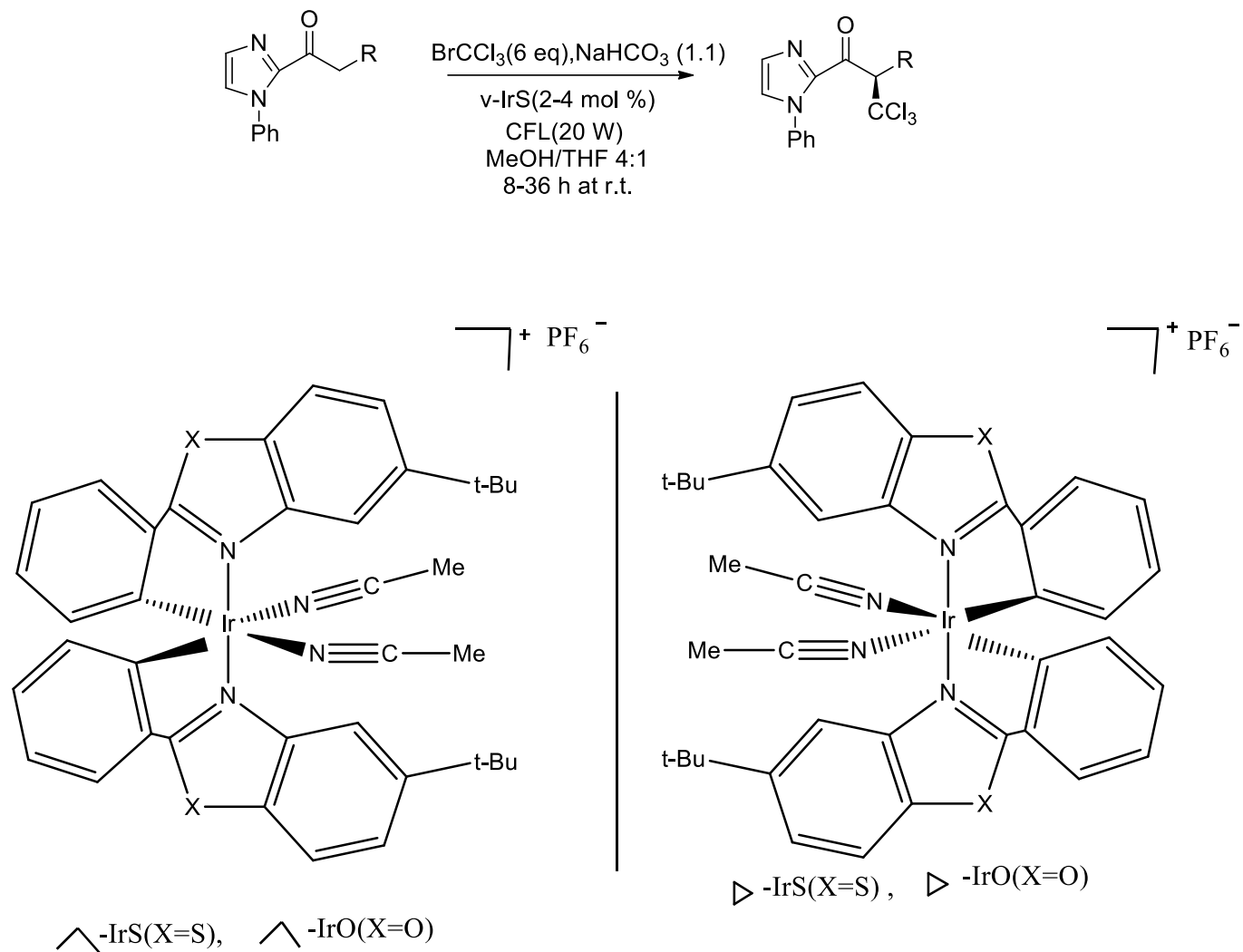


Figure 1

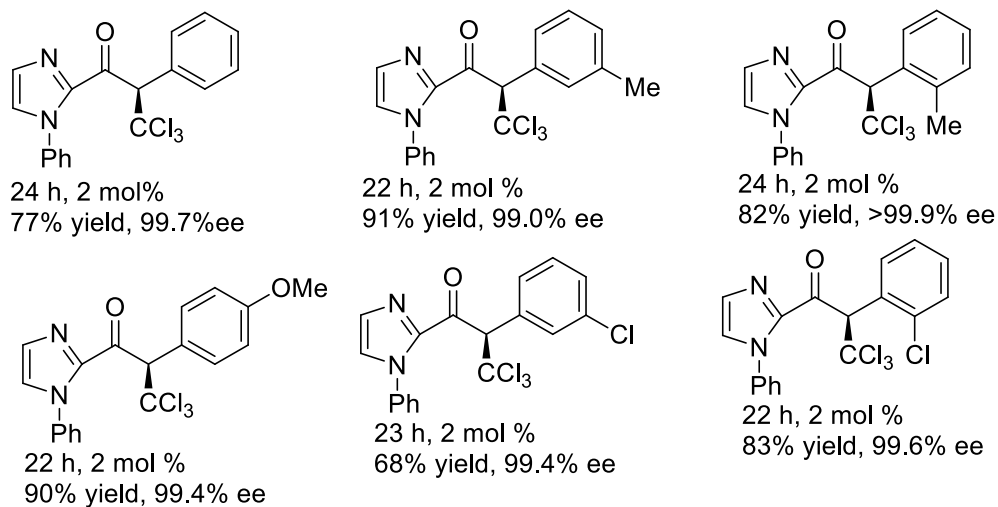


Figure 2:-substrate scope

## 9. Diaryliodonium salts

1. In 2014, Yan Zhang, Shouyun Yu with their co-workers performed multi-substituted isoquinoline derivatives using visible-light mediated vinyl isocyanide insertion with diaryliodonium salts at room temperature (figure 1). Isoquinoline synthesis through somophilic isocyanide insertion. By changing R group substituted products with different optimum yields are obtained (figure 2) [31].

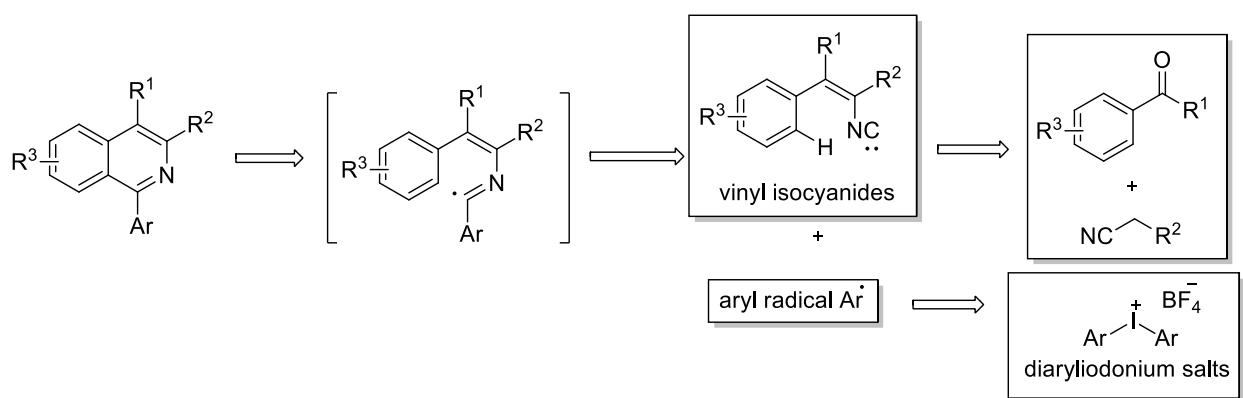


Figure 1

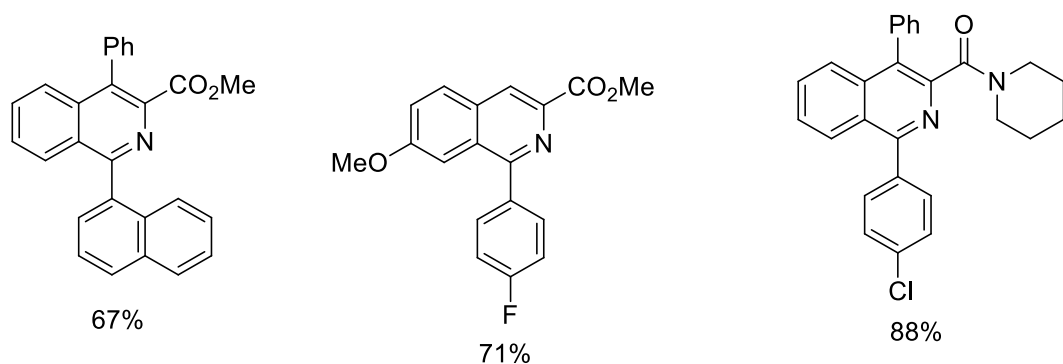


Figure 2:- substrate scope



## 10. Visible light induced Deoxygenation reaction

1. In 2014, Louis Fensterbank, Jean-Philippe Goddard, Cyril Ollivier performed Barton-McCombie deoxygenation which is important for organic transformation. The deoxygenation of secondary and tertiary alcohols from thiocarbamate under visible light photoredox catalyst is shown in figure 1 [32].

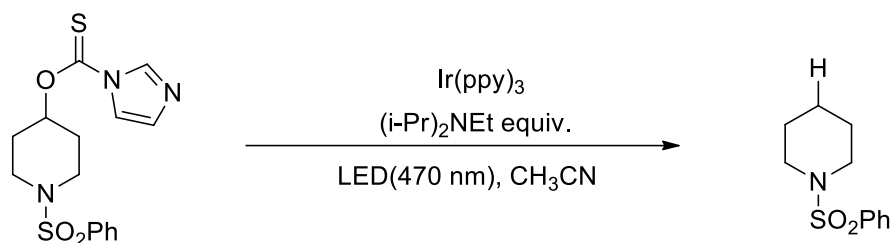


Figure 1

## 11. Visible light mediated Fluoroalkylation reactions

1. In 2014, Eun Jin Cho with his co-workers performed difluoroalkylation of alkenes using photoredox catalyst (figure 1) [33].

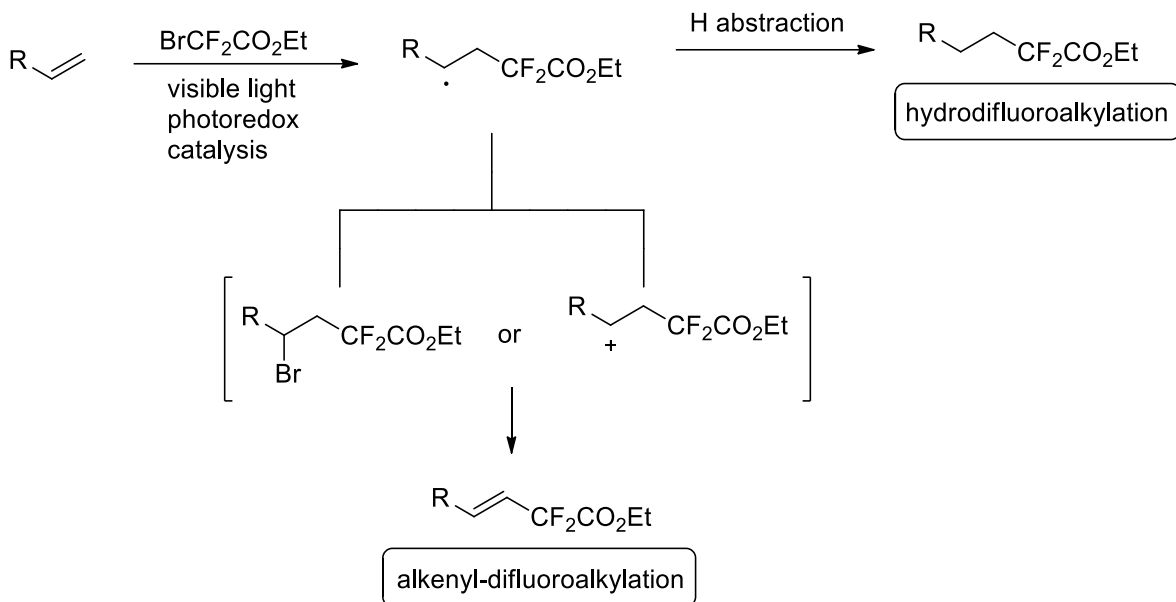


Figure 1

2. In 2014, Shouyun Yu and Xiaoyang worked on fluoroalkylation of isocyanides and ethyl bromofluoroacetates through visible light mediated photoredox catalyst (figure 1). The reaction was done at room temperature with excellent yields, proper solvent stepwise and with one-pot synthesis. By changing different aryl substituted groups substrate scope can be seen (figure 2) [34].

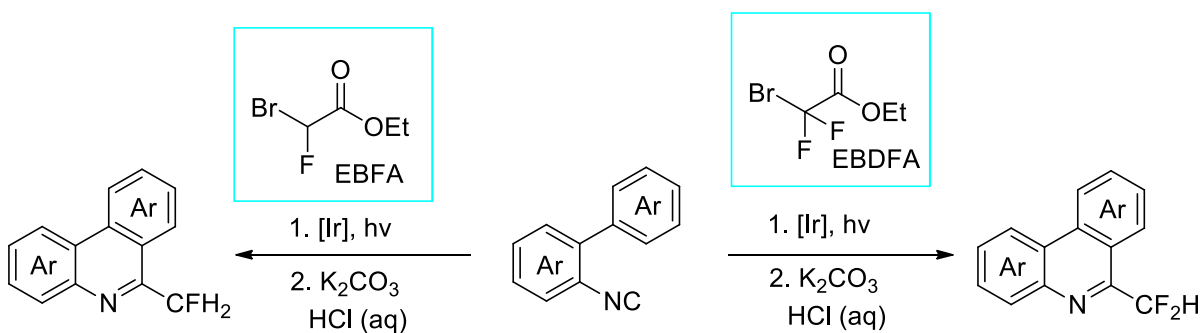


Figure1

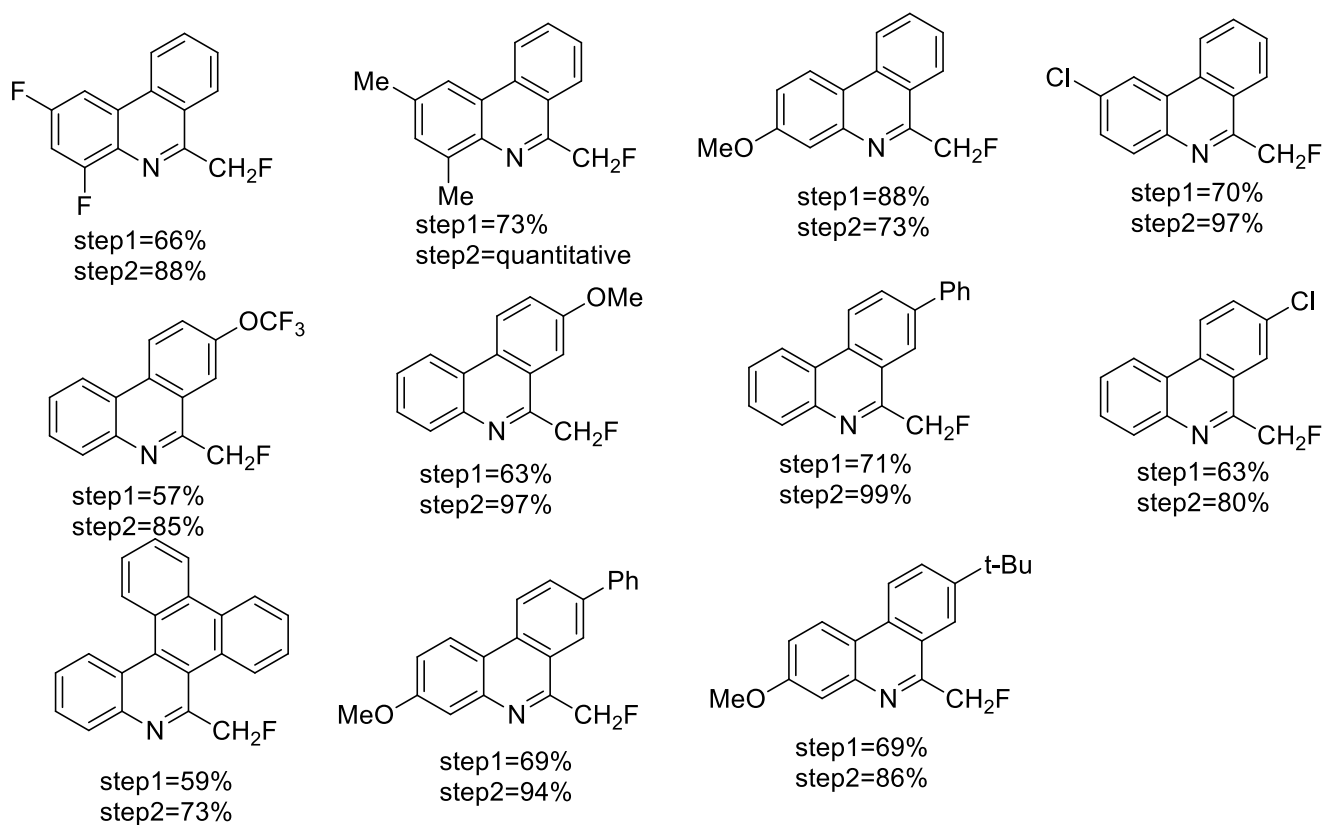


Figure 2:- scope of isocyanides with monofluoroalkylation

3. In 2014, Shouyun Yu with co-workers performed synthesis of trifluoromethylisoquinoline via somophilic vinyl isocyanide insertion through photoredox catalyst with the help of Umemoto's reagent (figure 1). This method is highly regioselective and gave good yields under mild condition. Substrate scope could be seen by changing the R<sup>1</sup> group in figure 2 [35].

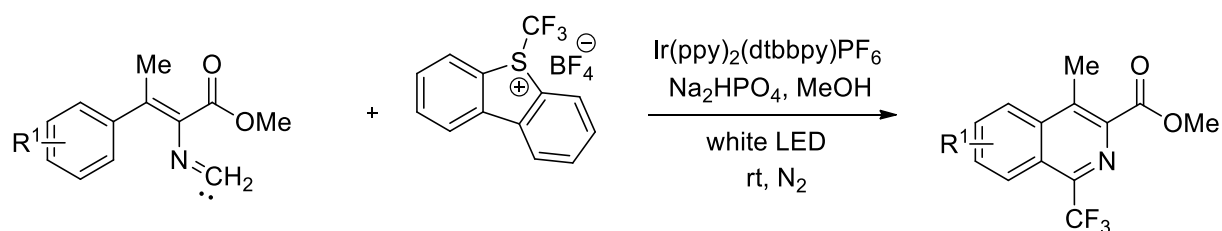


Figure 1

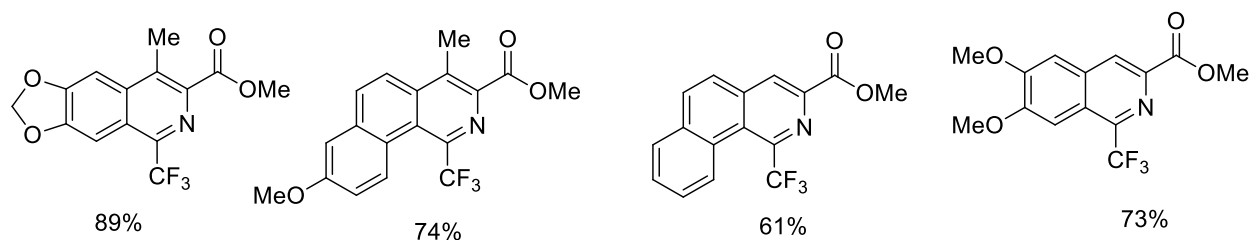


Figure 2:- substrate scope

4. In 2014, Youngmin You, Eun Jin Cho with co-workers performed synthesis of aromatic difluoroalkylation through visible light photoredox catalyst (figure 1) at room temperature with optimum yield and high reactivity [36].

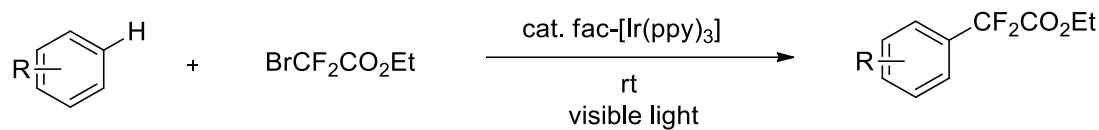


Figure 1

5. In 2014, Takashi Koike, Munetaka Akita with their co-workers performed hydroaminomethylation of olefins with aminomethyltrifluoroborate using photoredox catalyst (figure 1) [37].

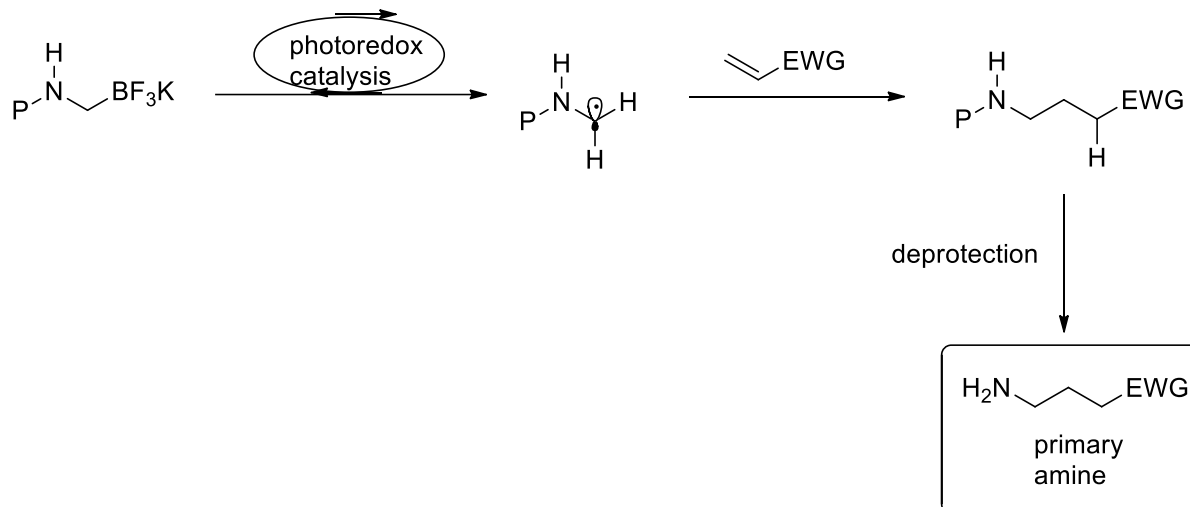


Figure 1

6. In 2014, Takashi Koike and Munetaka Akita with co-workers synthesized  $\alpha$ -trifluoromethylated ketones from alkenes through oxidation of dimethyl sulfoxide (figure 1). It is a facile synthesis using iridium based photocatalyst. By varying  $\text{R}_1$  and  $\text{R}_2$  groups substrate scope could be seen (figure 2) [38].

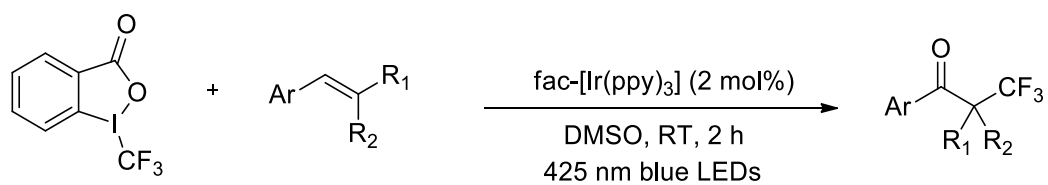


Figure 1

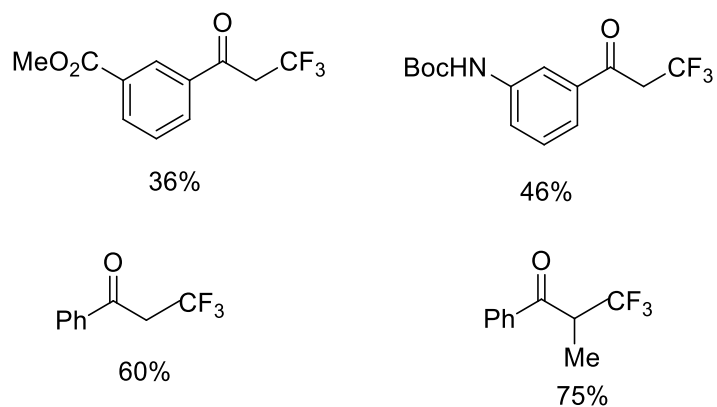


Figure 2:- substrate scope

7. In 2013, Yan Zhang, Shouyun Yu with their co-workers performed trifluoromethylation and sulphonation of ethyl acetate with sulfonyl chlorides using photoredox catalyst. It is a facile method for the preparation of trifluoromethylated ketones and sulfonyl with excellent yields [39].

8. In 2015, Shuhua Li, Chengjian Zhu with co-workers performed C-H difluoroalkylation of hydrazones with photoredox catalyst via aminyl radical or through polar mechanistic pathway (figure 1). It requires mild reaction conditions for its substrate scope and high efficiency for one pot synthesis [40].

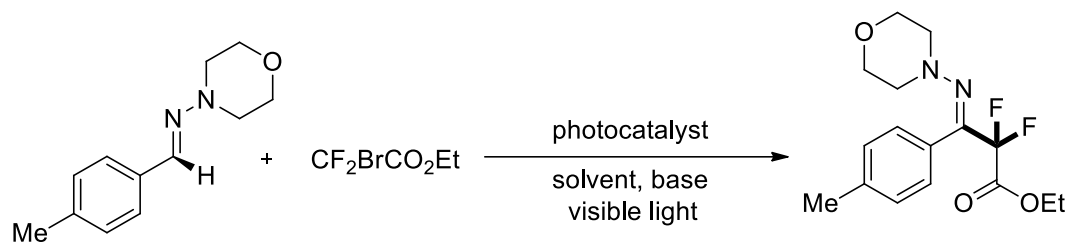


Figure 1

9. In 2015, Takashi Koike, Munetaka Akita with co-workers performed synthesis of aryl or alkyl-thioalkylation of olefins through organotrifluoroborates using iridium based photocatalyst in visible light (figure 1). It gave good yields and wide range of alkylsulphides are made under mild and efficient conditions [41].

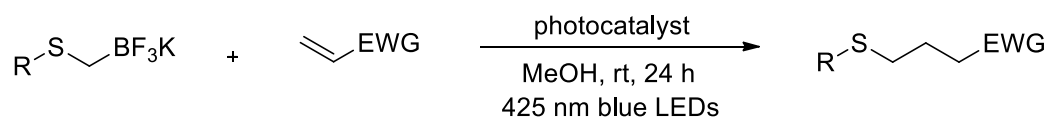


Figure 1

10. In 2014, Feng-Ling Qing with co-workers performed trifluoromethylation of styrenes through (SET) and triplet-triplet energy transfer (TTET) process, a significant method of chemo, regio, and stereoselective photocatalytic trifluoromethylation of styrenes using visible light method. With ruthenium based photoredox catalyst thermodynamically stable E-trifluoromethylated alkenes were prepared by Togni's reagent and less stable thermodynamically Z-trifluoromethylated alkenes were prepared using iridium based photocatalyst by Umemoto's reagent (figure 1). A series of substrate scope were seen with ruthenium and iridium based photocatalyst under trifluoromethylation of styrenes (figure 2 and 3) which was a mild, facile and efficient method for this process [42].

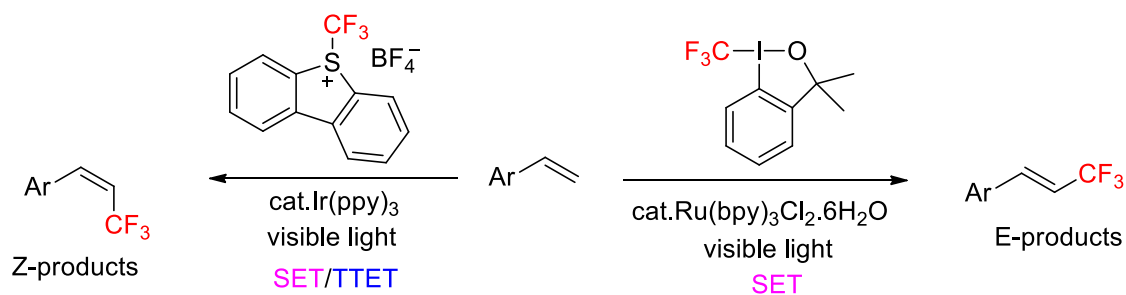


Figure 1

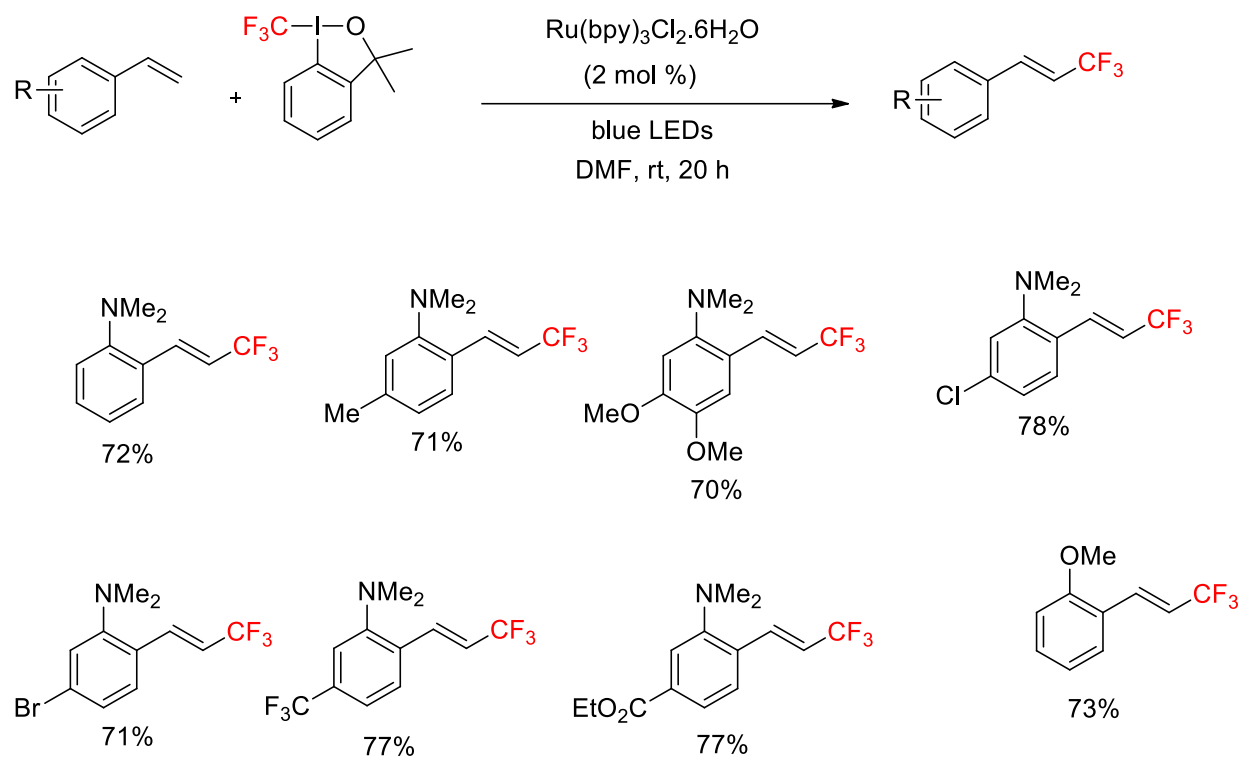


Figure 2:- substrate scope with Ru-catalysed trifluoromethylation of styrenes

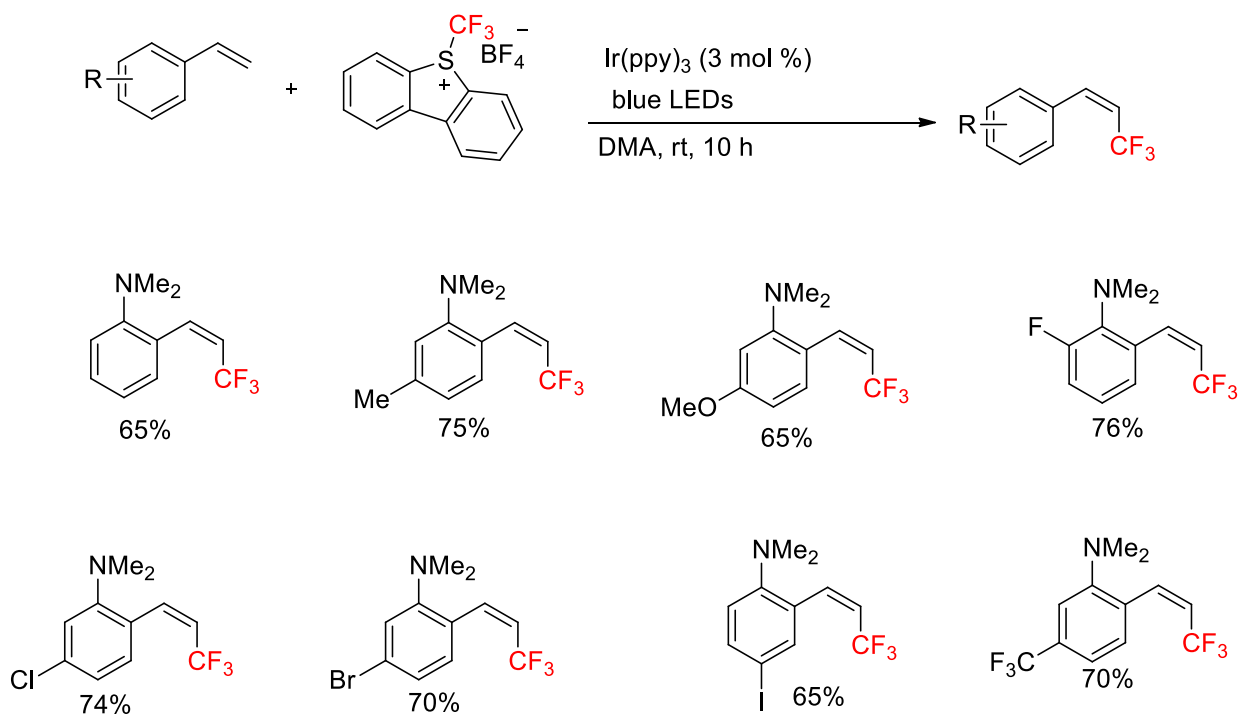




Figure 3:- substrate scope with Ir-catalysed trifluoromethylation of styrenes

11. In 2015, Munetaka Akita with co-workers performed synthesis of stereoselective and regioselective conversion from alkynes to tetrasubstituted trifluoromethylated alkenes with electrophilic  $\text{CF}_3$  reagent named as Umemoto reagent using iridium based photoredox catalyst in visible light leading to trifluoromethylated alkenes in a stereoselective manner (figure 1). It is a facile one-pot synthesis method. By substituting various group on phenyl ring, different yields are obtained (figure 2) [43].

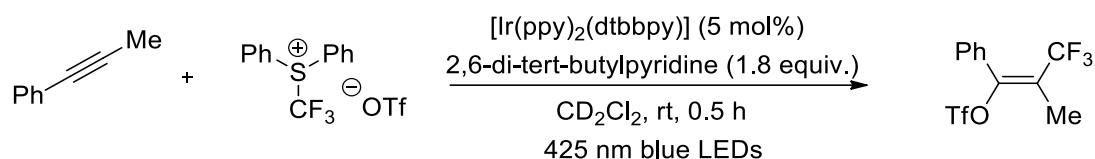


Figure 1

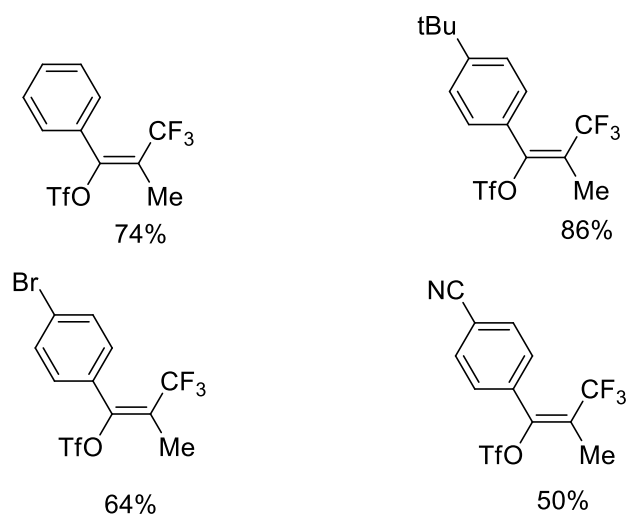


Figure 2:- substrate scope

12. In 2015, Weijun Fu with co-workers synthesized 3-difluoroacetylated Coumarin using visible light (figure 1). C-C bond formation via Tandem radical cyclization. Substrate scope of various alkynoates with  $\text{BrCF}_2\text{COOEt}$  (figure 2) and the mechanistic pathway of this catalytic cycle is described in figure 3 [44].

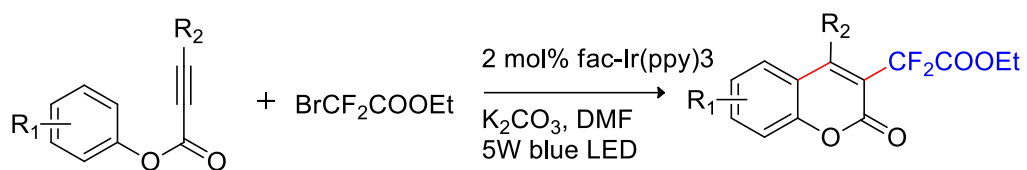


Figure 1

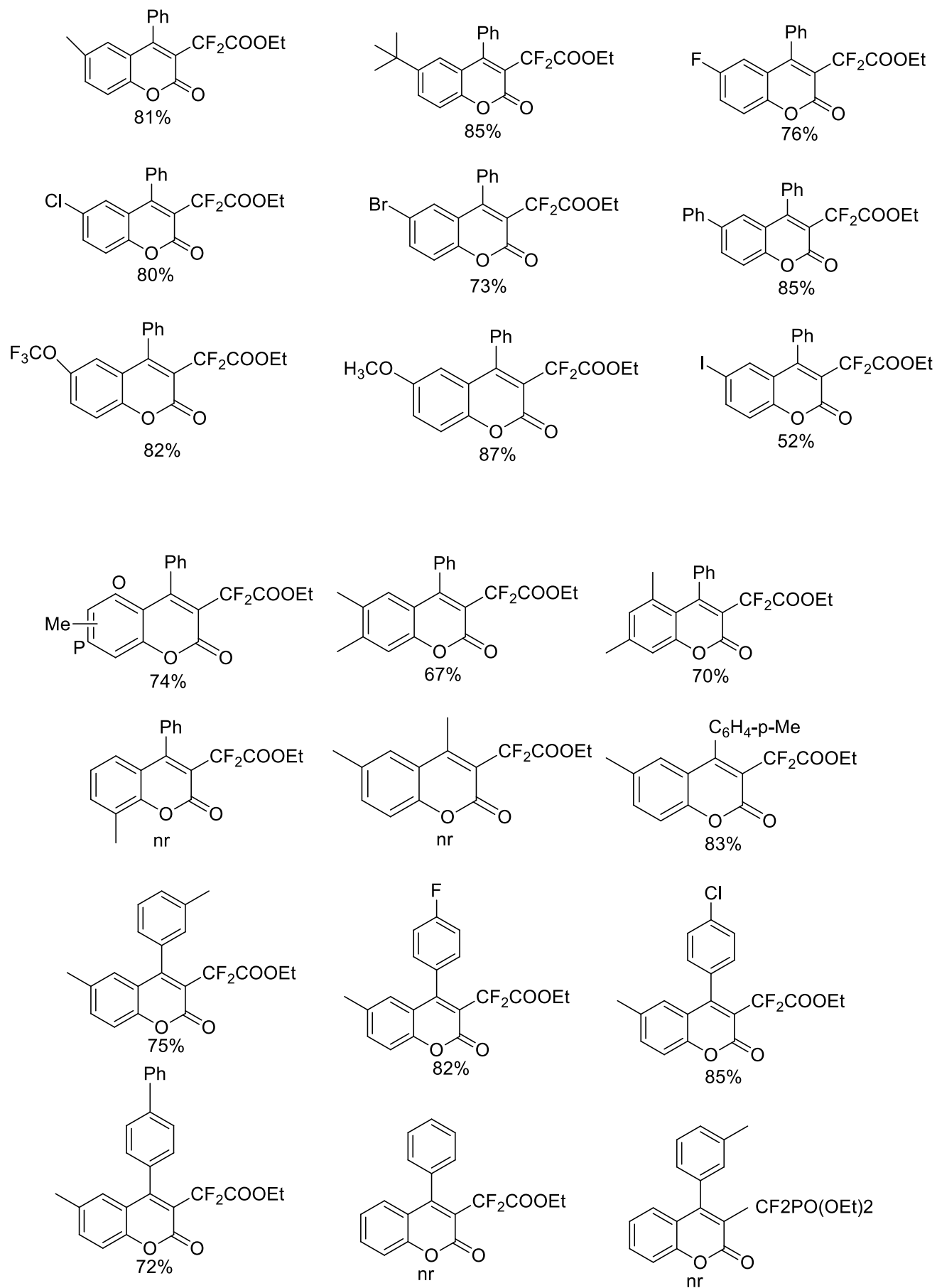


Figure 2:- cyclization of various alkynoates with BrCF<sub>2</sub>COOEt

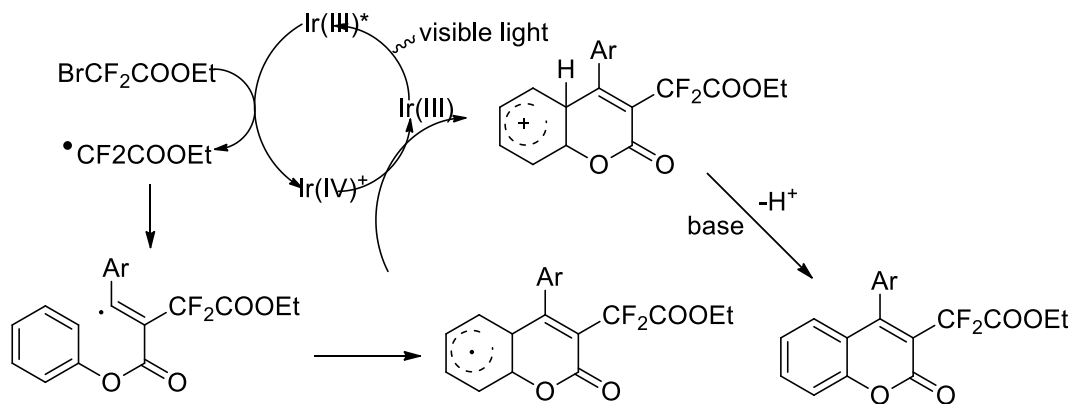


Figure 3:- mechanistic pathway of catalytic cycle

In catalytic transformation first, Ir(III) is irradiated to an excited state of Ir(III)\* then it is oxidatively quenched by BrCF<sub>2</sub>COOEt with the generation of Ir(IV)<sup>+</sup> and  $\cdot$ CF<sub>2</sub>COOEt radical species. The radical adds to alkynoates to produce a radical intermediate species after which the species is oxidized to form cyclohexadienyl cation by Ir(IV)<sup>+</sup> catalyst with the regeneration of catalyst Ir(III). The final product is formed by deprotonation of a base [44].

13. In 2015, Qing-Yun Chen, Yong Guo with co-workers performed difunctionalization reaction of styrenes with 1,1,1-trifluoro-2-iodoethane under molecular oxygen in the presence of water to give  $\gamma$ -trifluoromethyl alcohol (figure 1). By substituting various aryl substituted group substrate scope could be seen in figure 2 [45].

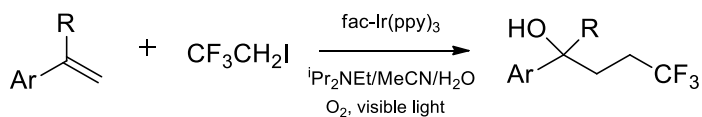


Figure 1

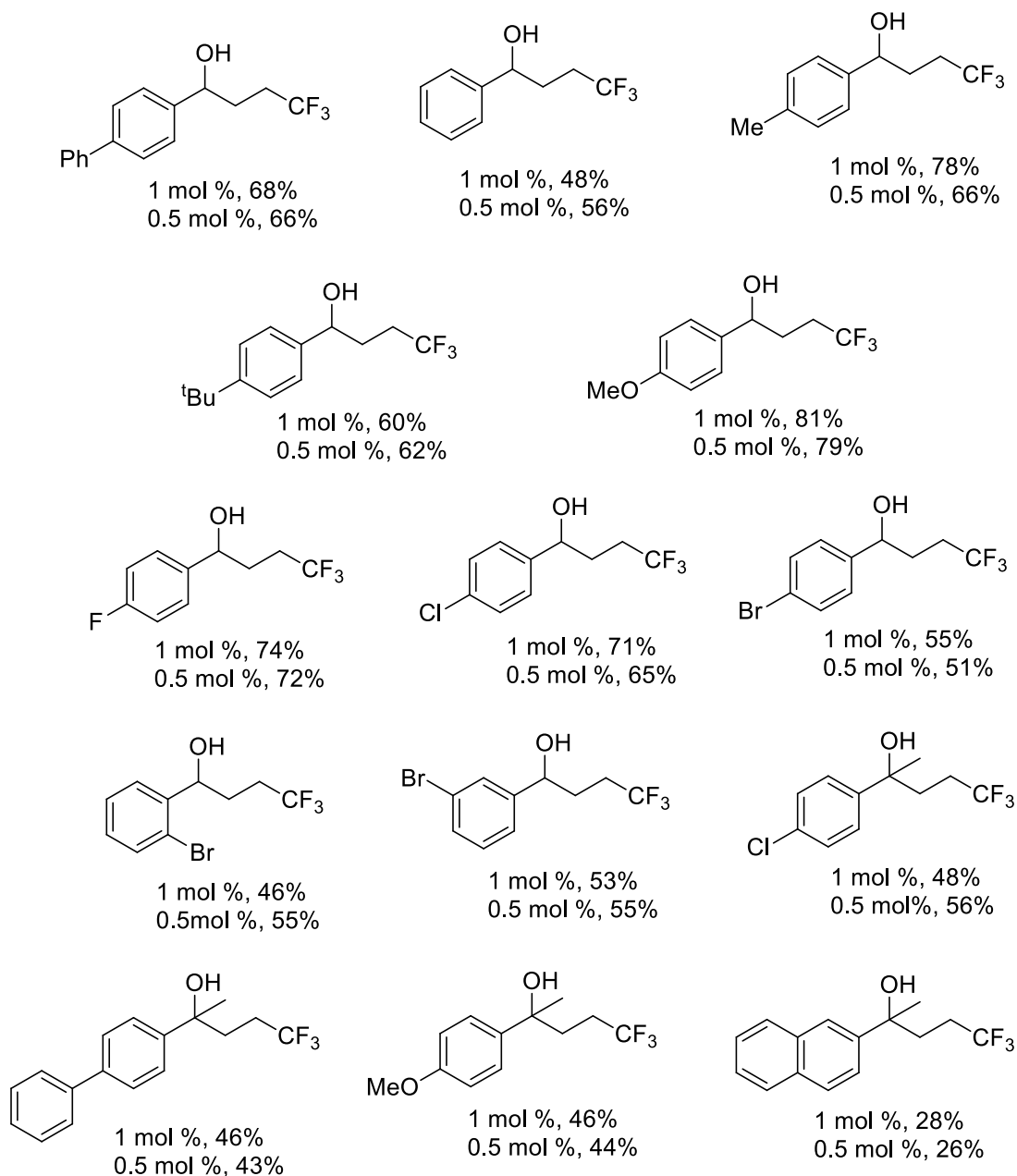


Figure 2:- substrate scope

## 12. Intermolecular atom transfer radical addition

1. In 2012, Corey R. J. Stephenson with co-workers performed atom transfer radical addition which is done intermolecularly by oxidative or reductive quenching process of haloalkanes into alkenes or alkynes by this process (figure 1). In this method iridium or ruthenium based

photoredox catalyst are used with various solvents and wide range of substrate scope are obtained [46].

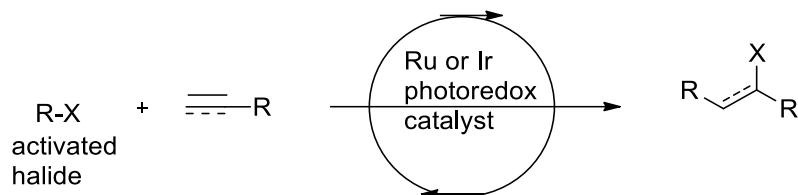


Figure 1

2. In 2011, Corey R. J. Stephenson with his co-workers performed ATRA of haloalkanes and  $\alpha$ -halocarbonyls to alkenes through Iridium based catalyst  $\text{Ir}[(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  in a mild condition at ambient temperature with optimum yields (figure 1). Excellent efficiency and atom economy are seen in this transformation [47].

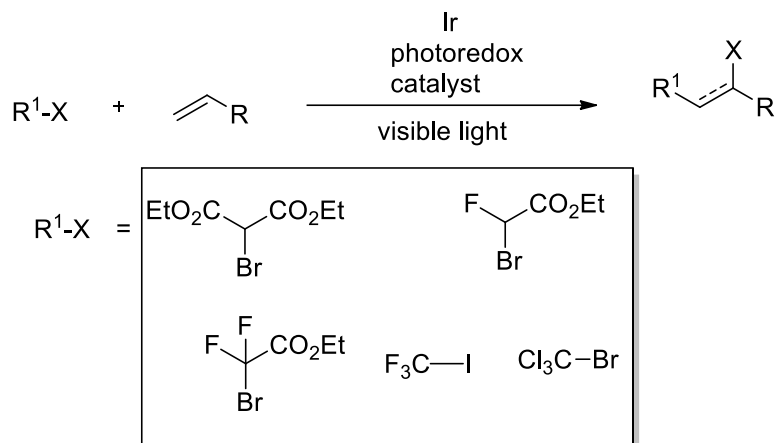


Figure 1

### 13. Reductive transformation

1. In 2012, Chulbom Lee and Hyejin Kim performed reductive transformation of organohalides through visible light mediated photoredox catalyst (figure 1). It is a mild and facile method for the generation of single electron transfer (SET) process. Its mechanistic pathway is ideal for greener chemistry reaction and is efficient for various reactions [48].

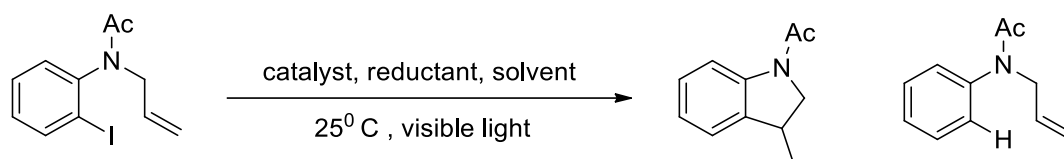
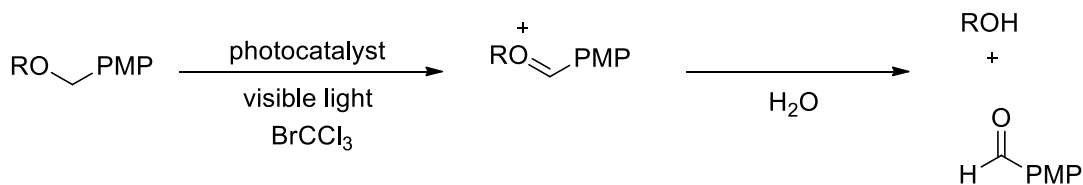


Figure 1

### 14. Oxidative transformation

1. In 2013, Takashi Koike, Munetaka Akita with co-workers performed hydroalkoxymethylation of electron deficient alkenes by means of alkoxyethyltrifluoroborates through visible light mediated photoredox catalyst (figure 1). Alkoxyethyl radical is generated from oxidation of alkoxyethyltrifluoroborates using visible light induced single electron transfer. Substrate scope can be seen in figure 2 [49].

1. Work by Stephenson



2. This work:- C-C bond formation through alkoxyethyl radical

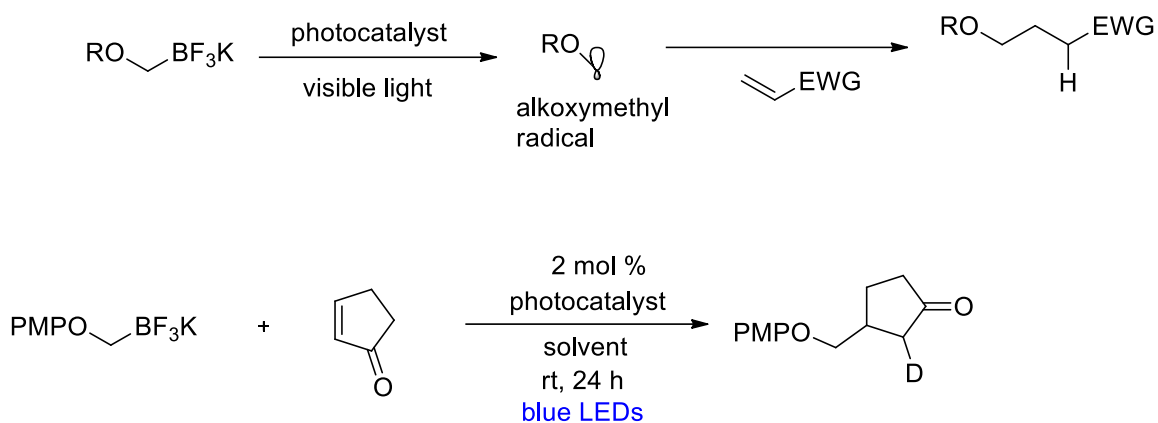
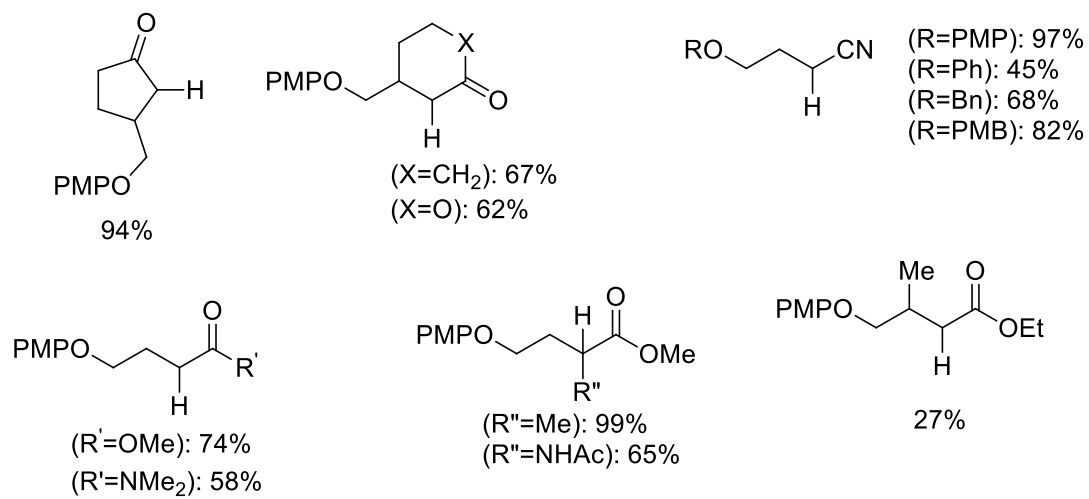


Figure 1





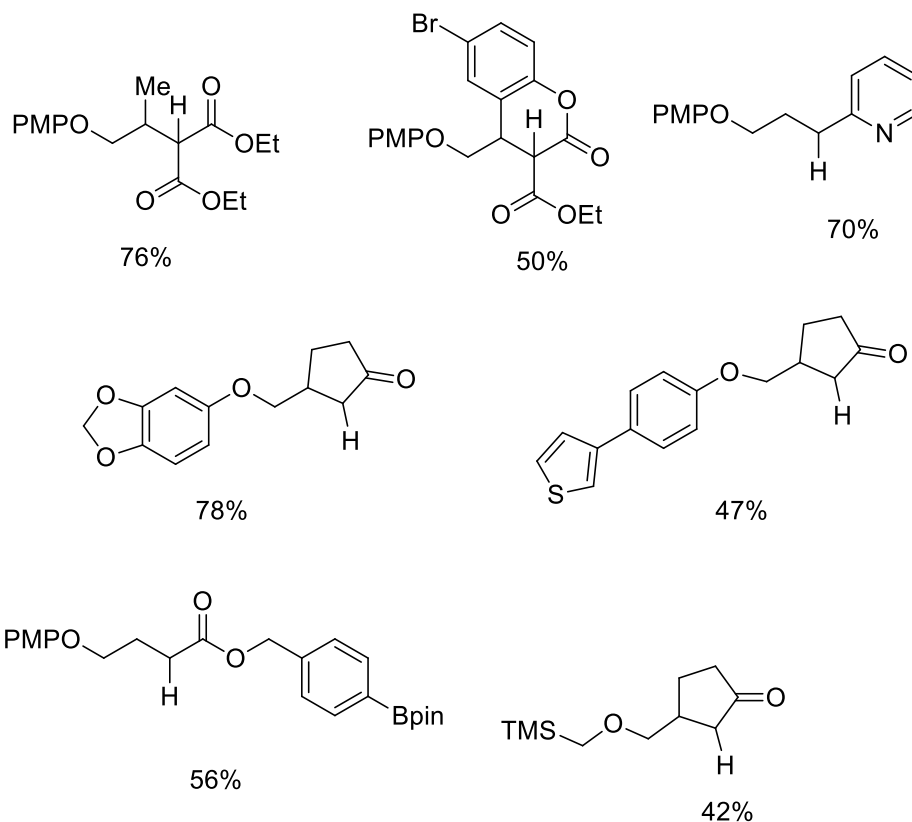


Figure 2:- substrate scope

2. In 2011, Corey R. J. Stephenson and his co-workers performed the application of photoredox catalyst using electron rich oxidation of arenes for selectively deprotonation of para-methoxybenzyl (PMB) ethers (figure 1). The photoredox catalyst through oxidative quenching of visible light induced excited state, may promote the generation of oxocarbenium intermediate under mild condition by oxidation of benzyl ethers. Mechanistic catalytic cycle is briefly described in figure 2 [50].

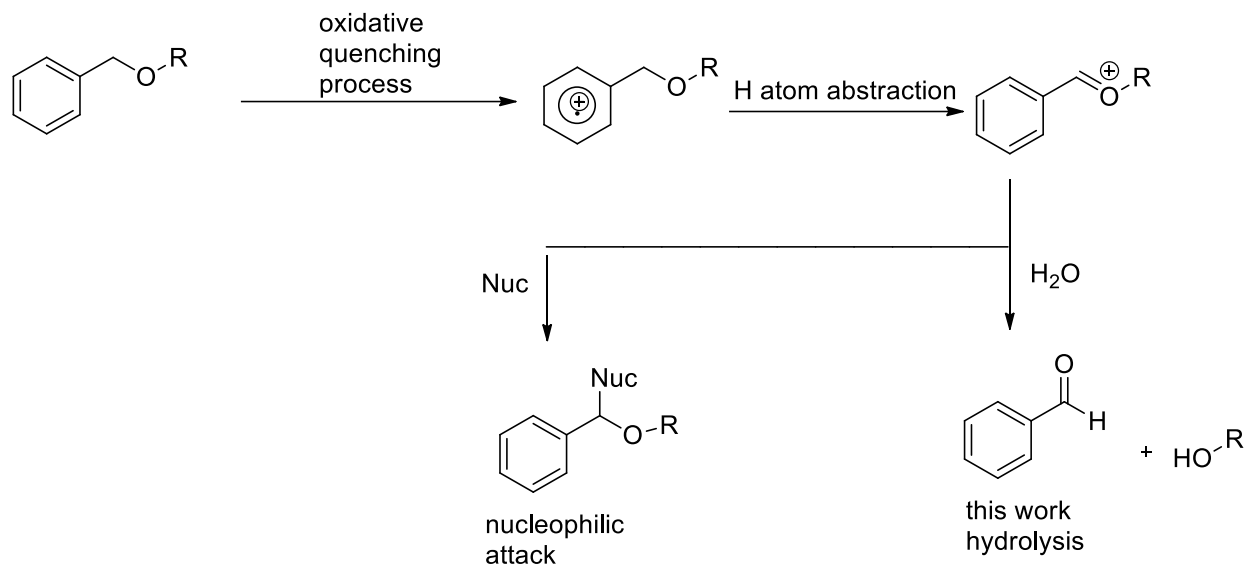


Figure 1

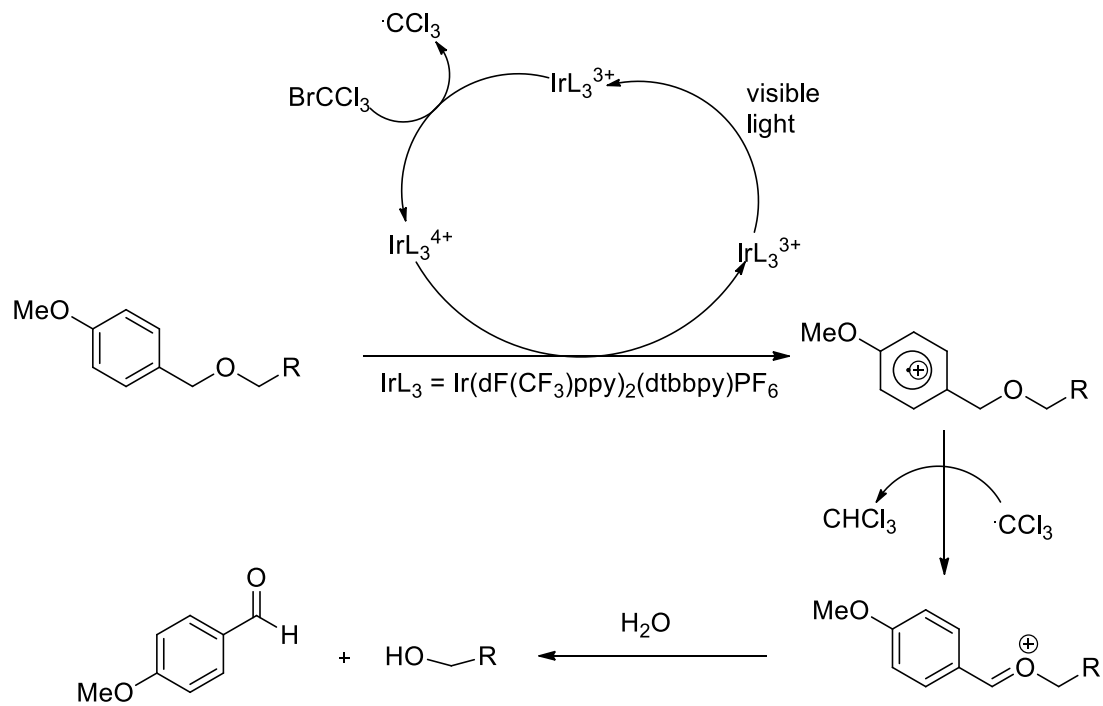


Figure 2:- mechanistic pathway of oxidative cleavage of PMB ethers

## 15. Visible light induced cyclization

1. In 2011, Corey R. J. Stephenson with co-workers performed tandem cyclization of divinylcyclopropane rearrangement to tricyclic pyrrolidinones through single electron reduction of bromocyclopropyl by photoredox catalyst (figure 1). It is a novel method for the tandem radical cyclization /sigmatropic rearrangement for the generation of tricyclic pyrrolidinones at ambient temperature with diverse substrate scope [51].

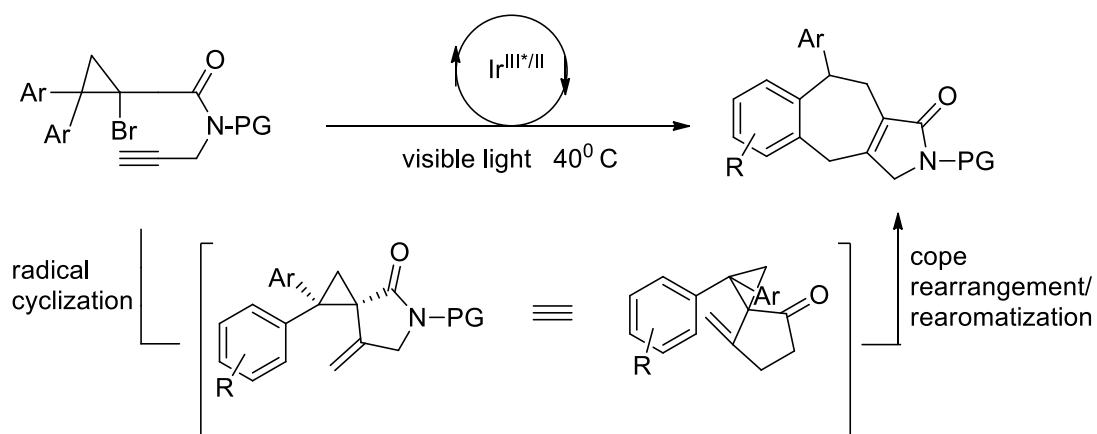


Figure 1

2. In 2013, Chengjin Zhu with his co-workers performed cascade reaction by decarboxylation/C-H functionalisation using visible light mediated photoredox catalyst (figure 1). It is a mild, efficient and facile method for the formation of C-C bond in organic reaction through tandem process. Substrate scope could be seen in figure 2 by varying the branching groups and obtaining different yields [52].

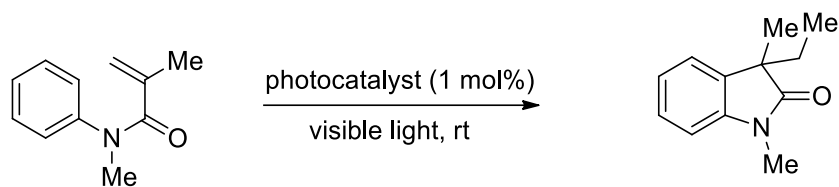


Figure 1

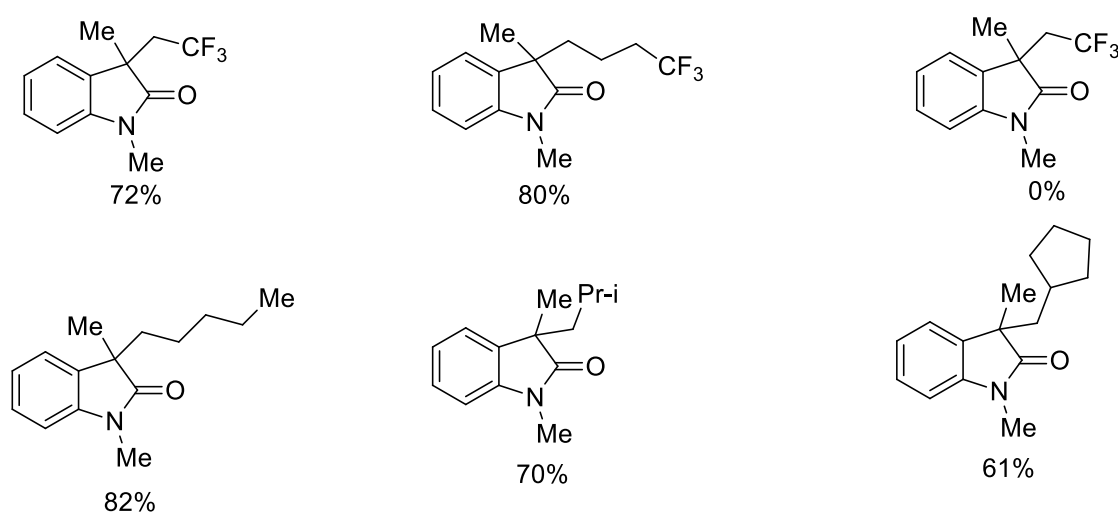


Figure 2:- substrate scope

3. In 2015, Chengjin Zhu with co-workers performed synthesis of cinnamamides through radical tandem Aryldifluoroacetylation with ethyl Bromodifluoroacetate as  $\text{CF}_2$  precursor through synthetic method (figure 1) [53].

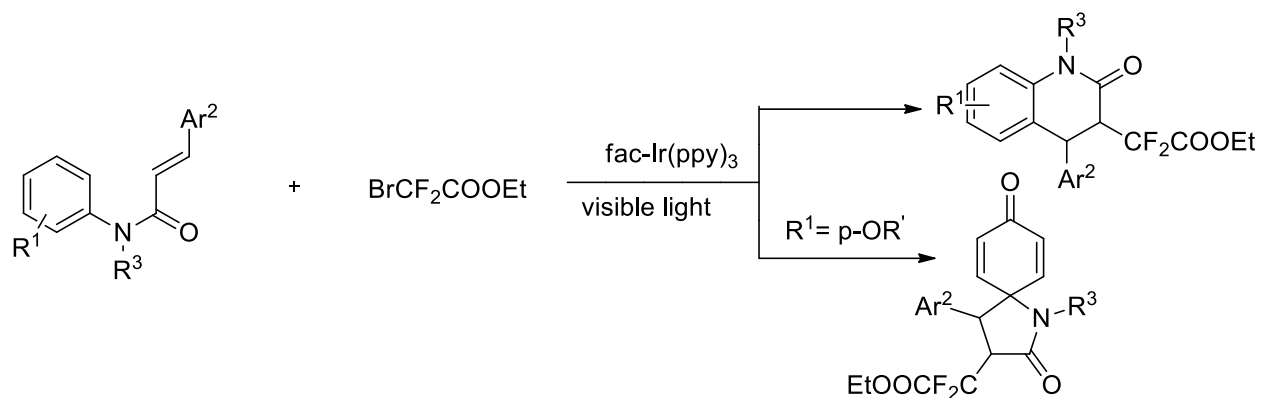


Figure 1

4. In 2013, David W. C. MacMillan with his co-workers performed  $\beta$  functionalisation of cyclic ketones with aryl ketones through photoredox catalyst and organocatalyst resulting in highest optimum yields in figure 1 as described below [54].

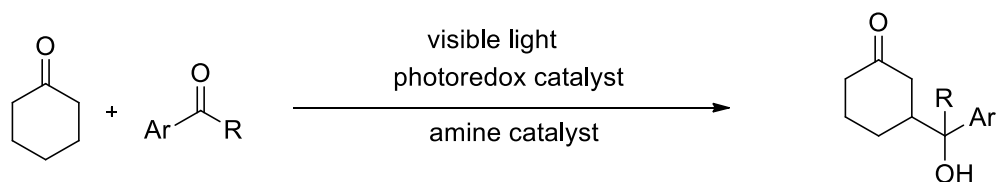


Figure 1

5. In 2015, Chengjian Zhu with his co-workers performed a novel synthesis of enol lactones through visible light mediated photoredox catalyst through radical cyclization. Resulting in fluorinated  $\gamma$ -butyrolactones in excellent yields with diastereoselectivity shown in figure1 and by varying different R group substrate scope could be seen in figure2 [55].

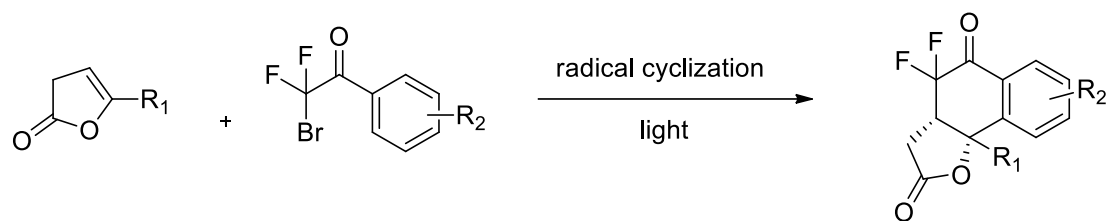


Figure 1

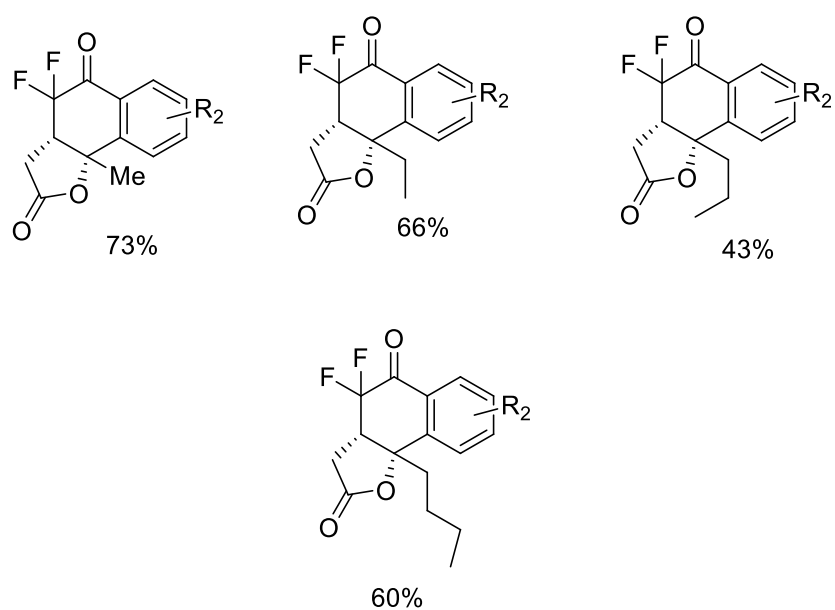


Figure 2:- substrate scope

6. In 2014, Timothy F. Jamison with his co-workers performed polycyclic quinoxaline derivative through visible light mediated photoredox catalyst (figure 1). It is a facile method for the preparation of high range of heterocyclic quinoxaline resulting in excellent yields [56].

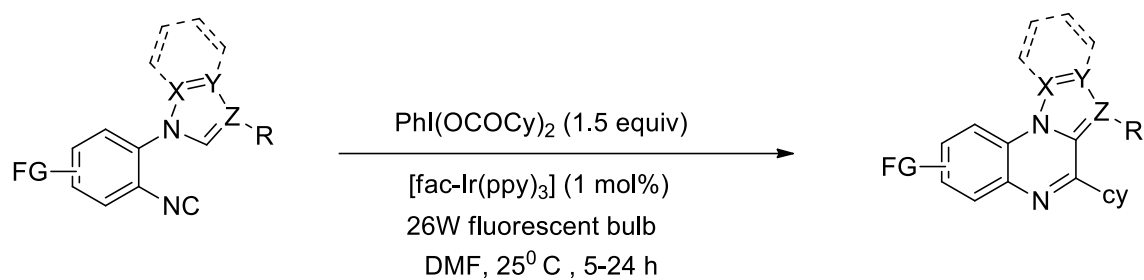


Figure 1

7. In 2015, Zuxiao Zhang, Xiaojun Tang and William R. Dolbier performed a photoredox reaction using difluoromethylation and 1,1-difluoroalkylation of biphenyl isocyanides (figure 1) which allowed synthesis of various 6-(Difluoromethyl)- and 6-(1,1-difluoroalkyl)phenanthridines through tandem addition/cyclization/oxidation process. The reaction is carried out in dioxane with suitable base in the presence of room temperature and fac-Ir catalyst as photoredox catalyst gave good yields (figure 2). Figure 3 shows mechanistic pathway of this catalytic cycle [9].

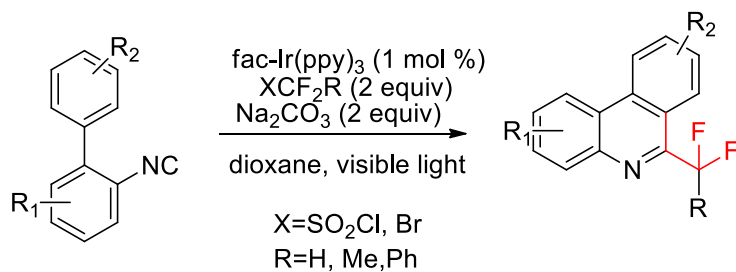


Figure 1

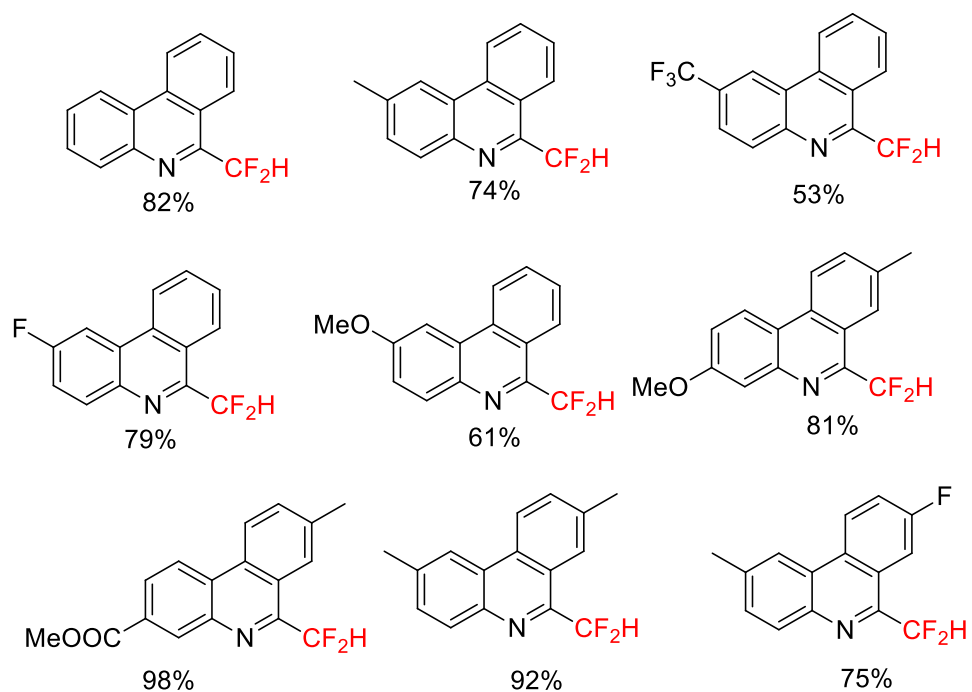


Figure 2:- substrate scope

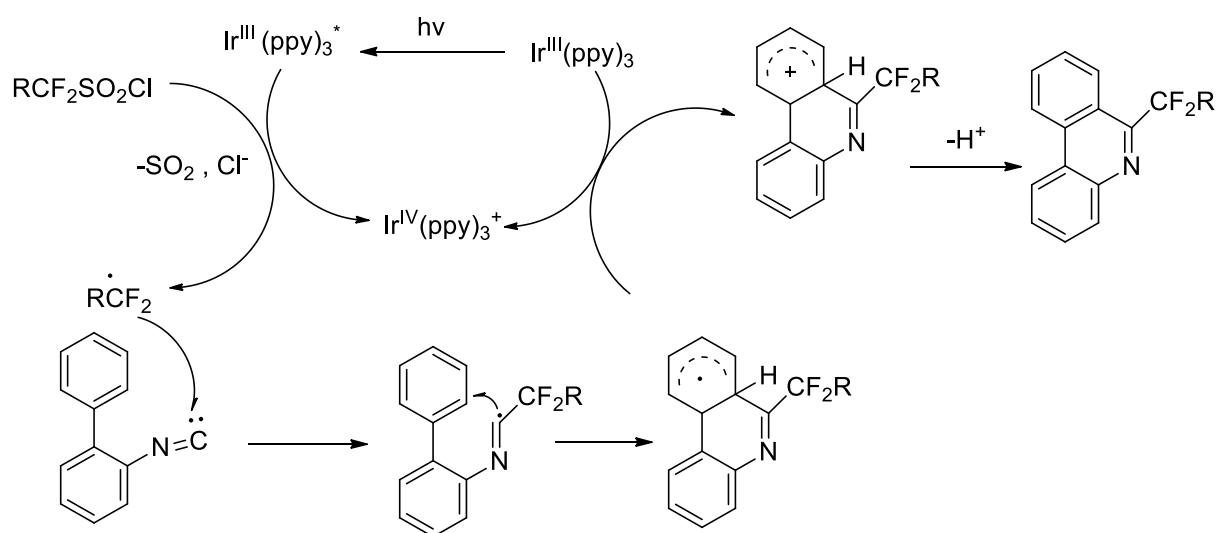


Figure 3:- mechanistic pathway



8. In 2015, Shi Tang and their co-workers worked on a novel method of visible light mediated carboperfluoroalkylation of alkenes using perfluoroalkyl bromides and iodides as  $R_f$  source, leading to isoquinoline-1,3-diones (figure 1). By changing different R(alkyl) groups substrate scope could be seen (figure 2). Below described is the Mechanistic pathway for the catalytic cycle as seen in figure 3 [16].

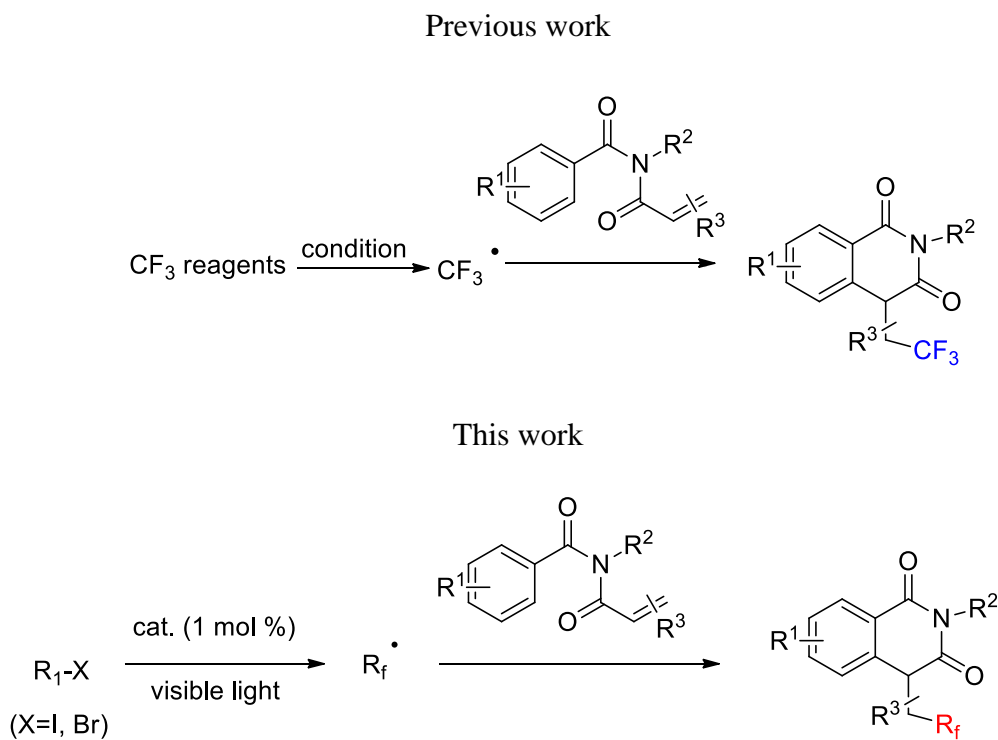


Figure 1

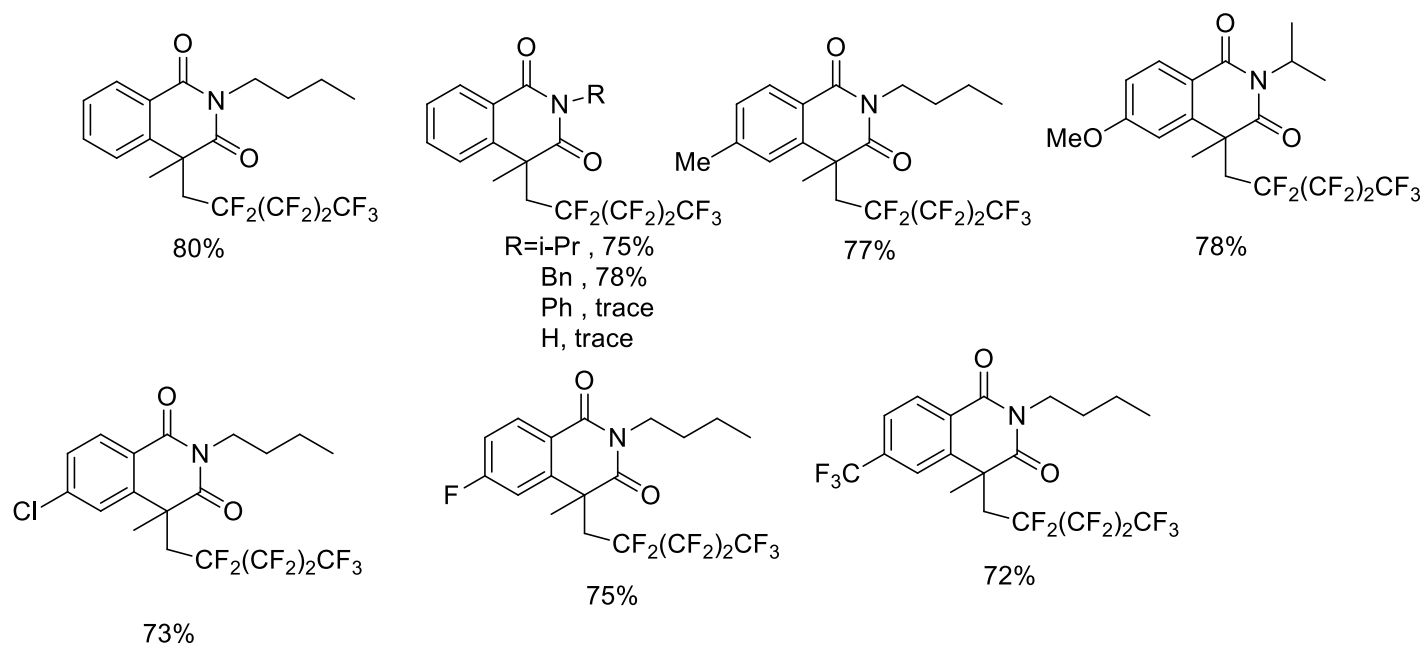


Figure 2:- substrate scope

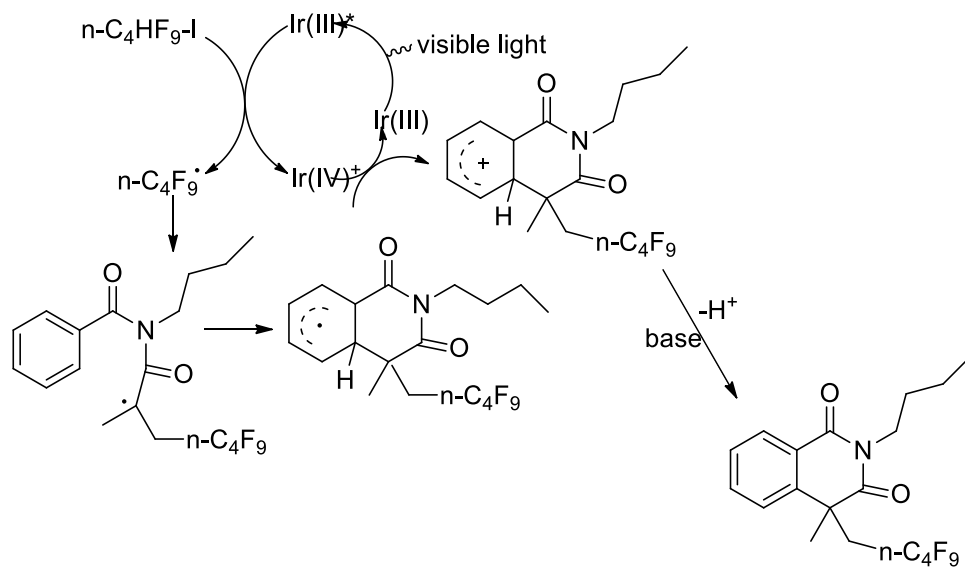


Figure 3:- mechanistic pathway

In conclusion, it is a mild, facile and efficient alkylation of alkenes leading to isoquinoline using  $R_f$  source under visible light induced photoredox reaction [16].

## 16. Visible light mediated radical chemistry

1. In 2012, Yoshiaki Nishibayashi with his co-workers synthesized  $\alpha$ -aminoalkyl radical through single electron oxidation of amines (figure 1). In electron deficient alkenes,  $\alpha$ -aminoalkyl are added through visible light mediated photoredox catalyst [57].

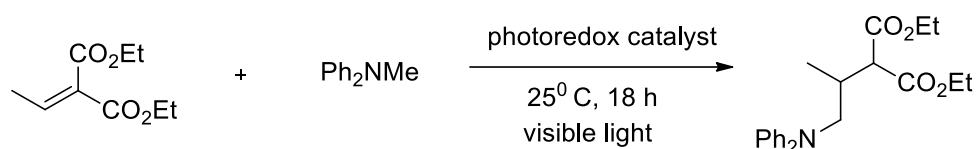


Figure 1

2. In 2015, Daniele Leonori with his co-workers synthesized nitrogen centered radicals through visible light mediated photoredox catalyst. It is a novel method for the cyclization of hydroimination and iminohydroxylation reaction [58].

3. In 2012, Yoshiaki Nishibayashi with his co-workers performed addition of  $\alpha$ -aminoalkyl radical generated from  $\alpha$ -silylamines to  $\alpha,\beta$ -unsaturated carbonyl compounds through photoredox catalyst (figure 1). It is a mild and efficient method which resulted in good yields [59].

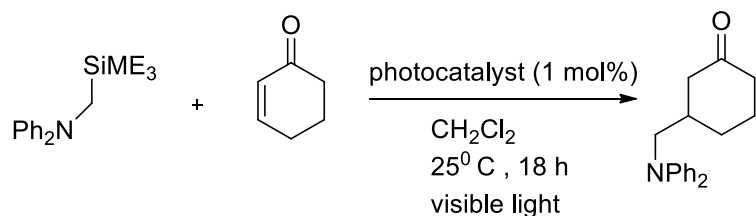
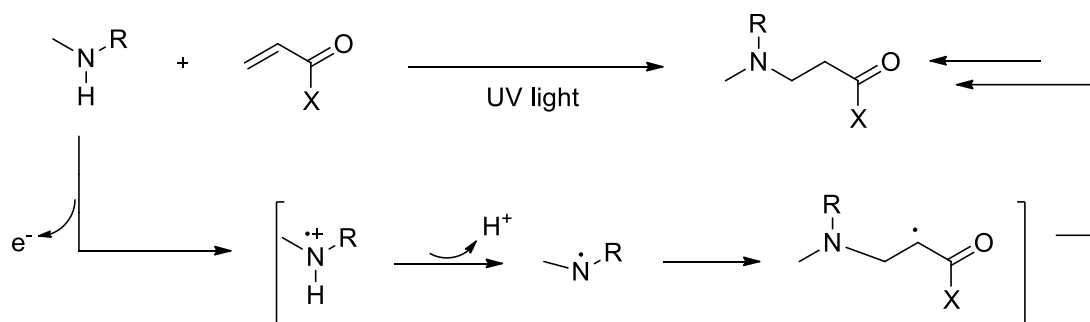


Figure 1

4. In 2014, Yoshihiro Miyake, Yoshiaki Nishibayashi with co-workers performed synthesis of nitrogen heterocycle. In visible light mediated  $\alpha$ -aminoalkyl radical generation through  $\alpha$ -silyl secondary amines in one pot synthesis by formation of pyrroles and  $\gamma$ -lactams through  $\gamma$ -aminocarbonyl compounds (figure 1). It gave us a mild and facile method with excellent yields [60].

- Previous report



- This report

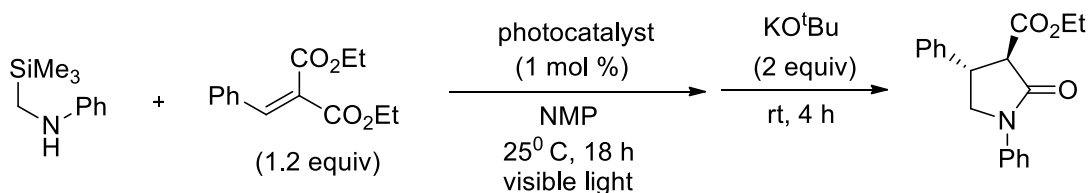
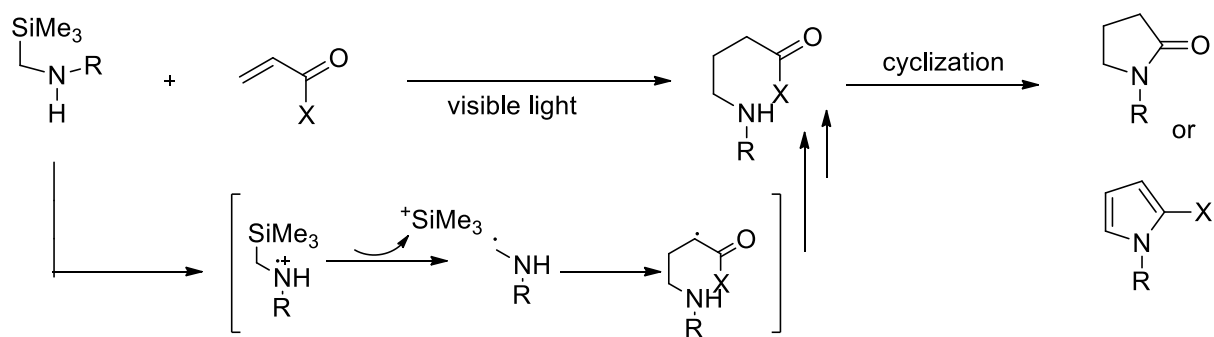


Figure 1

5. In 2013, Magnus Rueping with his co-workers performed oxygen switch which activates two different reaction products by two different reaction ways, cyclization and C-C bond cleavage reactions in *N,N*-dimethylaniline to an alkenes which is electron deficient by getting a  $\gamma$ -amino nitriles in optimum yields as shown below (figure 1) [61].

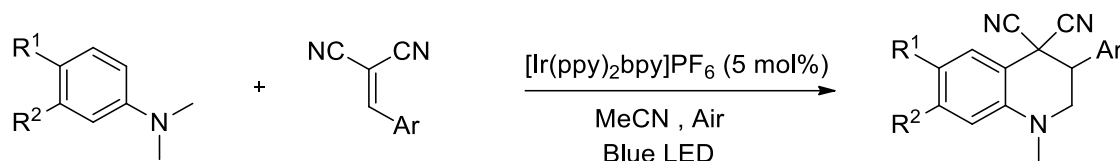


Figure 1

6. In 2014, Magnus Rueping with his co-workers performed intermolecular radical addition of  $\alpha$ -halo amides to alkenes through visible light photoredox catalyst (figure 1). It is an anti-markovnikov reaction of  $\alpha$ -alkylation to various olefins. It resulted in good yields to various alkylated amines through reductive atom transfer radical addition (ATRA) [62].

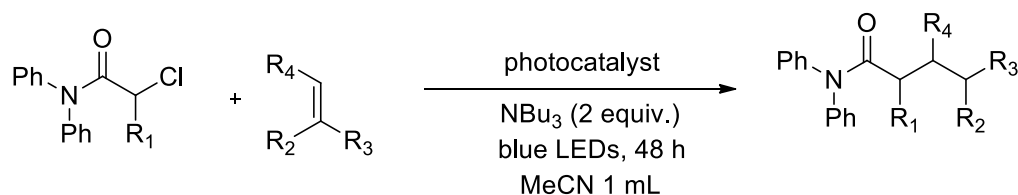


Figure 1

7. In 2013, Pixu Li and co-workers works on preparation of *R*-amino amide or *R*-amino thioamide from *N,N*-dimethylaniline derivatives and isocyanate or aryl isothioyanate (figure 1). Bis[2-(4,6-difluorophenyl)pyridinato- $\text{C}_2$ , $\text{N}$ ](picolinato)iridium(III) (FIrpic) was shown best

catalyst for the preparation. It was an effective and mild catalyst for the synthesis. Figure 2 shows the mechanistic pathway of this reaction [11].

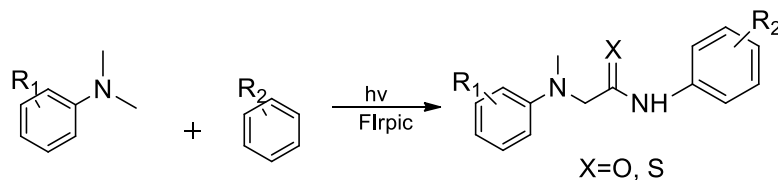


Figure 1

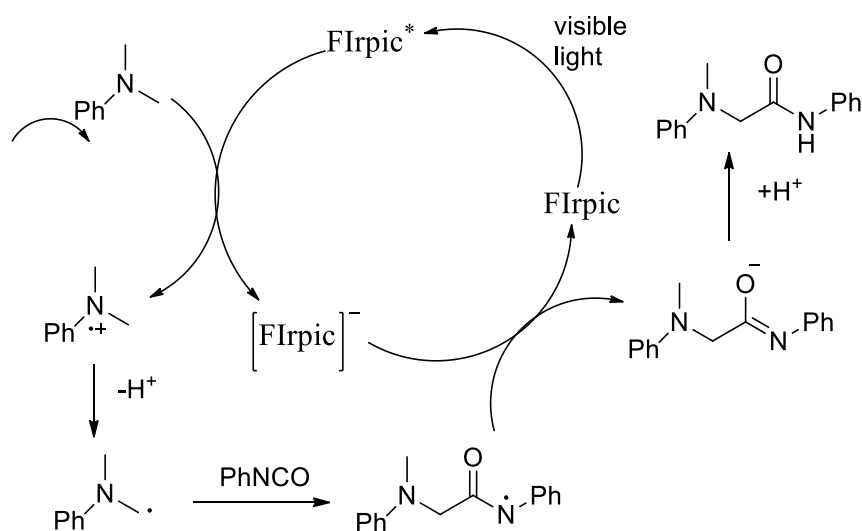


Figure 2:- mechanistic pathway for the catalysis

## 17. Visible light mediated cycloaddition reactions

1. In 2012, Tehshik P. Yoon and Zhan Lu performed synthesis of [2+2] styrenecycloaddition reaction by energy transfer through visible light mediated photoredox catalyst shown in figure 1. By substituting various groups on phenyl ring substrate scope could be seen as mentioned in figure 2 [63].

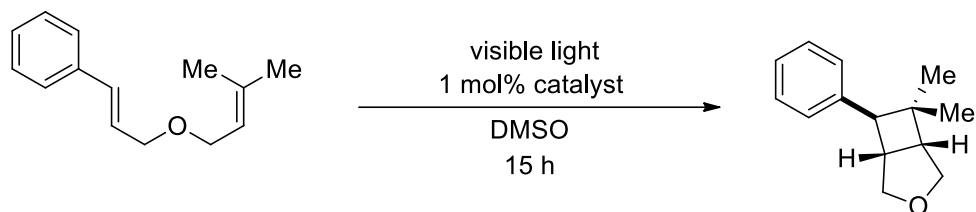


Figure 1

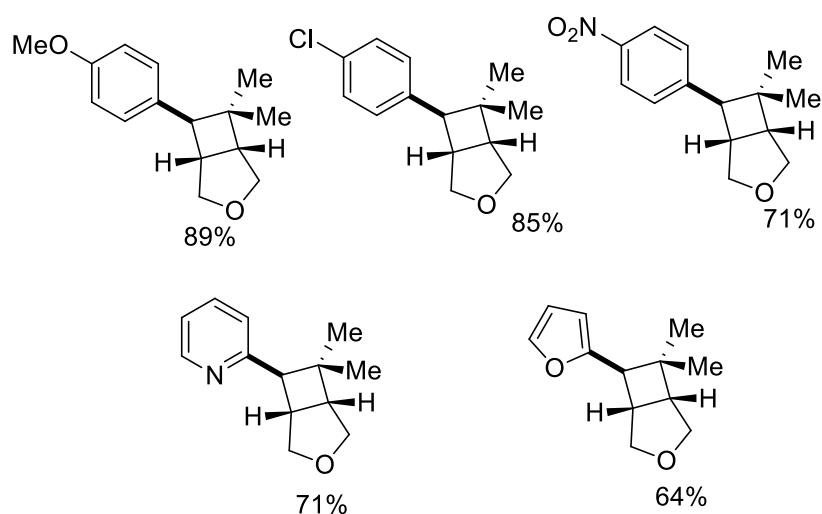


Figure 2:- substrate scope

2. In 2014, Tehshik P. Yoon with his co-workers did visible light mediated reaction of 1,3-Dienes by [2+2] cycloaddition photoredox catalyst (figure 1). In this synthesis, longer wavelength is useful because of the presence of the sensitive functional groups that might readily get decomposed by high energy radiation for direct photo-excitation of 1,3-dienes. Substrate scope could be seen in figure 2 with different optimum yields [64].

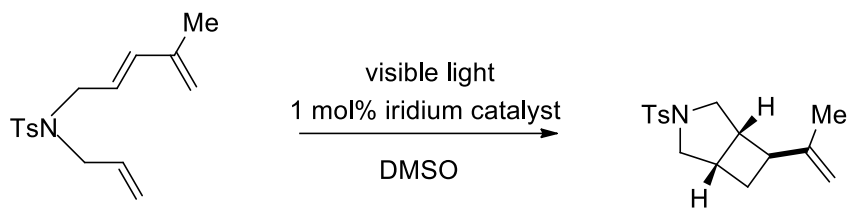


Figure 1

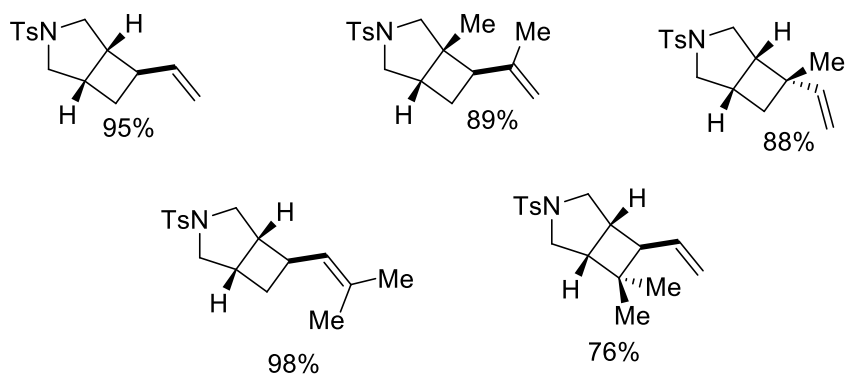


Figure 2:- substrate scope

3. In 2014, Magnus Rueping with his co-workers performed synthesis of nitrones. Oxidative [3+2] cycloaddition of N-substituted hydroxylamine with alkenes through visible light mediated photoredox catalyst (figure 1). It is a mild, efficient and effective method for the preparation of five member ring isoxazolidines heterocycles [65].

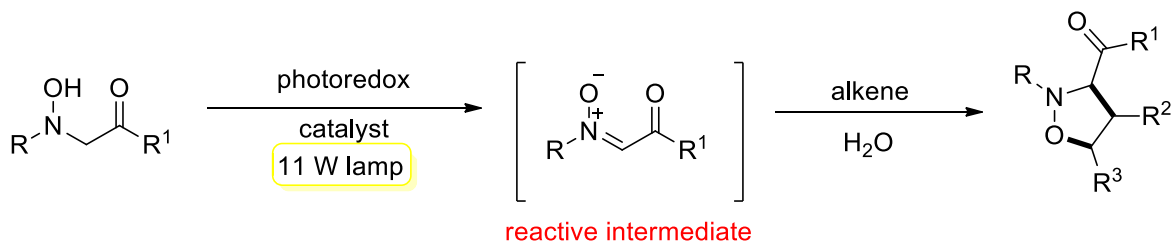




Figure 1

## **18. Spin-selective generation of triplet nitrene**

1. In 2016, Tehshik P. Yoon with his co-workers performed synthesis of nitrene through visible light photoredox catalyst (figure 1). Visible light mediated transition metal complex can be triplet sensitizer that could selectively produce aziridines through spin generation of triplet nitrenes from azidoformates [66].

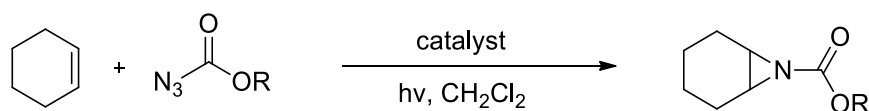


Figure 1

## **19. Visible light mediated Cross-Coupling reactions**

1. In 2014, David W. C. MacMillan and Christopher K. Prier performed synthesis of amine  $\alpha$ -heteroarylation through visible light photoredox catalyst (figure 1). It is done through homolytic aromatic substitution pathway in which catalytically  $\alpha$ -amino radical generated undergo direct addition to electrophilic chloroarene [67].

C-C bond formation amine heterocycle coupling can be seen below:

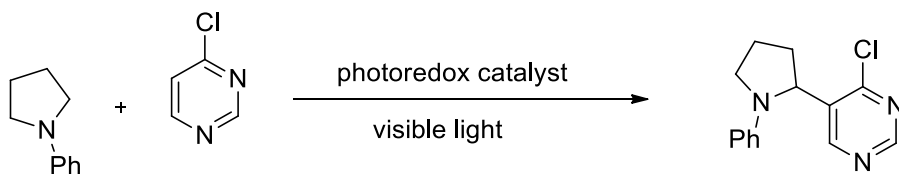


Figure 1

2. In 2013, Shouyun Yu, Yan Zhang with co-workers performed De Novo synthesis of polysubstituted furans and naphthols by neutral coupling of alkynes with 2-bromo-1,3-dicarbonyl through photoredox catalyst (figure 1). It is a mild and efficient method for the preparation of furans and naphthols at room temperature with good yields without any external stoichiometric ratio. By varying different electron withdrawing groups and R groups, different substrate scope could be seen as shown in figure 2 [68].

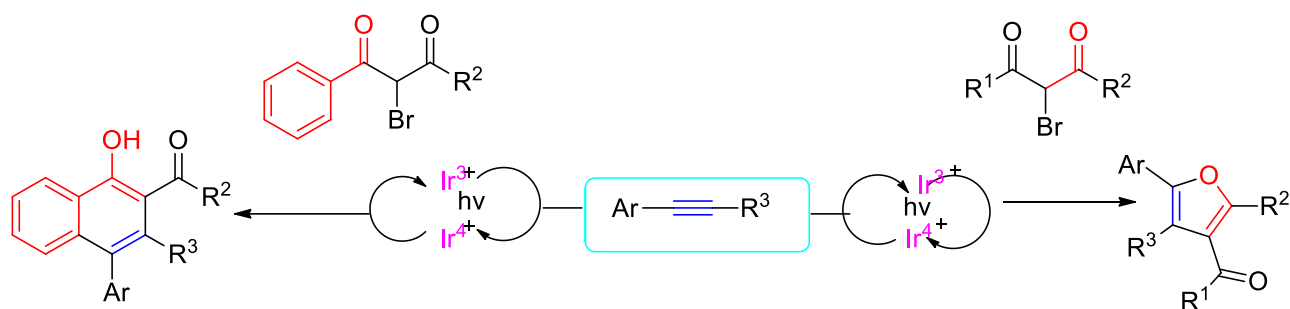
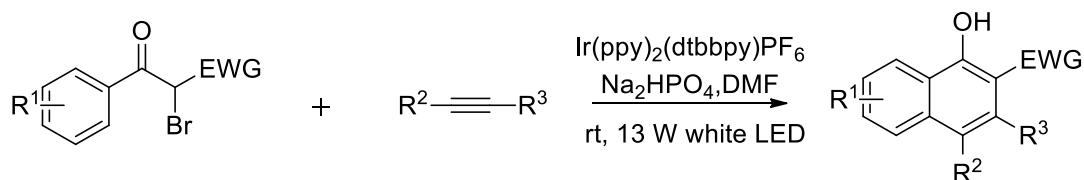


Figure 1



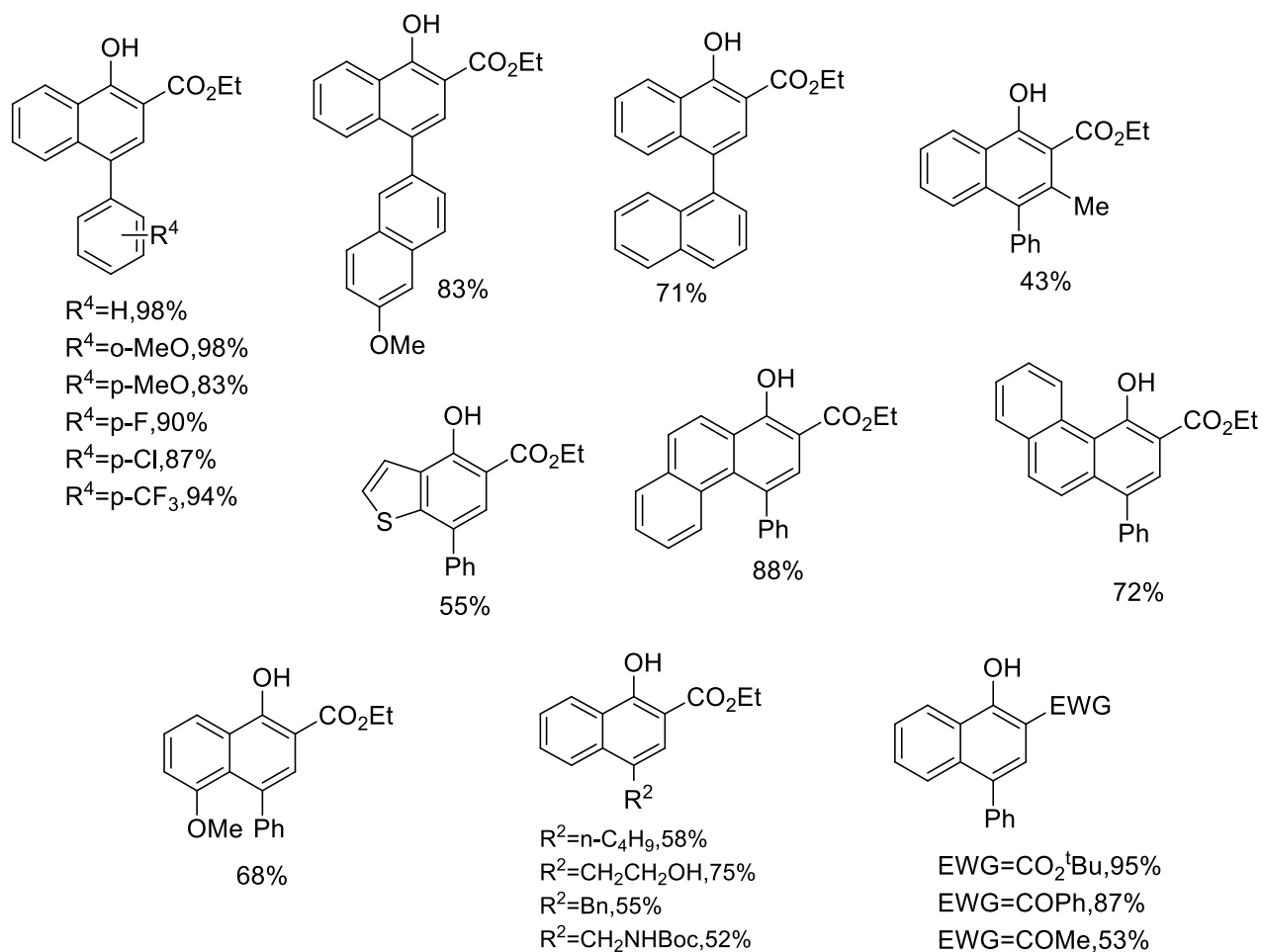


Figure 2:- substrate scope

3. In 2016, Eric Meggers with his co-workers performed asymmetric radical-radical cross coupling by iridium catalyst using visible light. It is a synthetic methodology for the production of amino alcohols from electron acceptor and electron donor i.e from trifluoromethyl ketones and tertiary amines to form catalytic enantioselectivity and diastereoselectivity (figure 1). Carbon-carbon bond formation through (SET) mechanism [69].

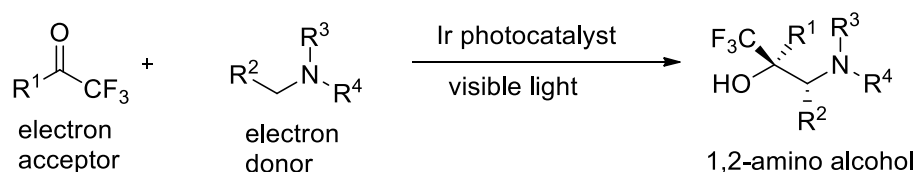


Figure 1

4. In 2014, Oliver Reiser with co-workers performed coupling of  $\alpha$ -bromochalcones with olefins using visible light (figure 1). It is an intermolecular coupling to alkenes with iridium based photoredox catalyst, vinyl radicals were generated as an intermediate efficiently in [4+2] cyclization with various olefins [70].

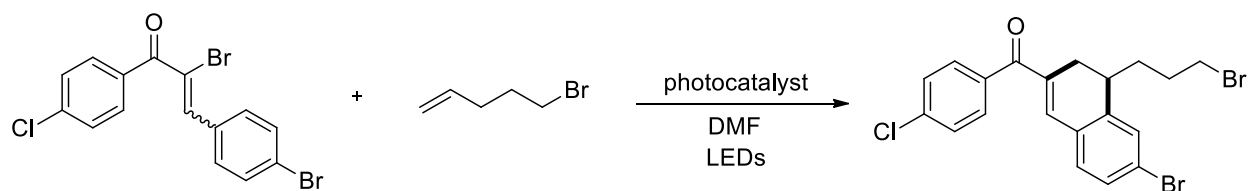


Figure 1

5. In 2014, David W. C. MacMillan with co-workers performed decarboxylative cross-coupling of carboxylic acids with vinyl halides in the presence of photoredox catalyst and nickel catalyst (figure 1). It is a mild and efficient method under optimum conditions [71].

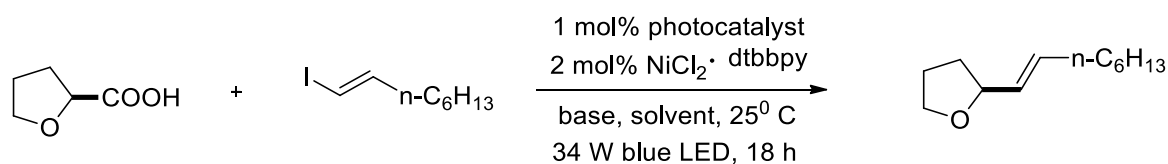


Figure 1

6. In 2015, Shu Kobayashi with co-workers performed Chan-Lam coupling reaction of aryl boronic acid and aniline derivative using visible light mediated iridium based photocatalyst (figure 1). This oxidative Chan-Lam reaction has various substrate scope to boronic acids as their starting material [72].

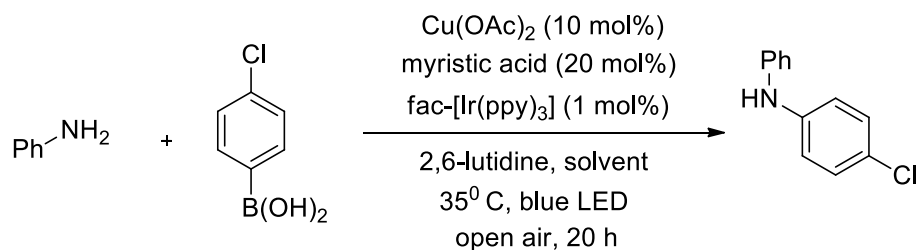


Figure 1

7. In 2014, Shu Kobayashi with co-workers performed dehydrogenative cross-coupling of tertiary amines by polymer-immobilized iridium photocatalyst using visible light through radical polymerization method [73].

8. In 2015, David W. C. MacMillan with co-workers performed radical-radical cross coupling reaction by  $\beta$ -Mannich mechanism (figure 1). It is a synergistic effect of combination of photocatalyst and organocatalysis. This protocol allows direct synthesis of  $\beta$ -Mannich products through chemoselective three component coupling of aryl aldehydes, amines and ketones. Substrate scope could be seen in figure 2 [74].

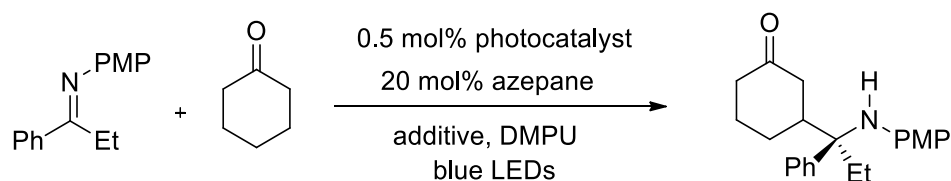


Figure 1

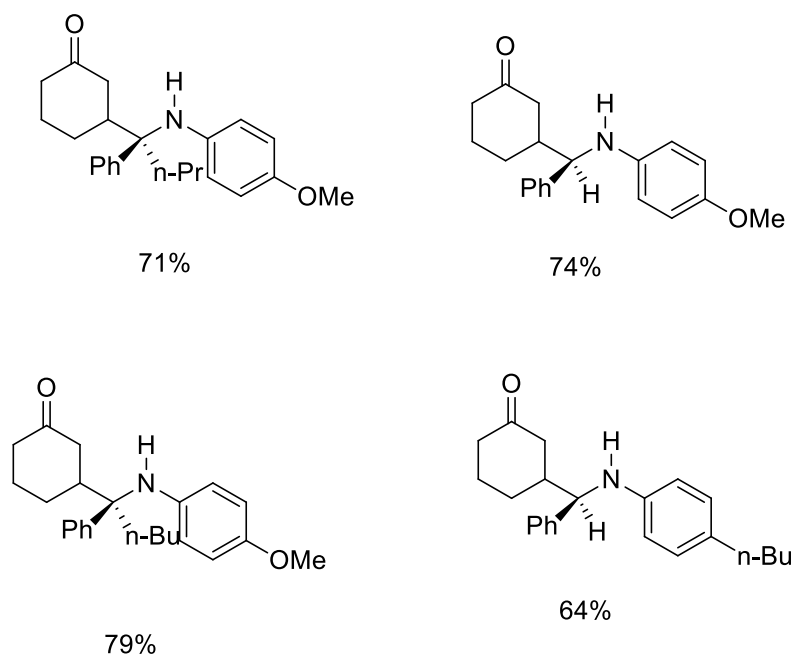


Figure 2:- substrate scope

9. In 2015, Gary A. Molander with co-workers performed single electron transmetalation of alkyl transfer through this mechanism enabling cross-coupling under mild conditions (figure 1). Cross-coupling of secondary alkyltrifluoroborates was achieved with alkyl bromides using iridium based photocatalyst and nickel catalyst [75].

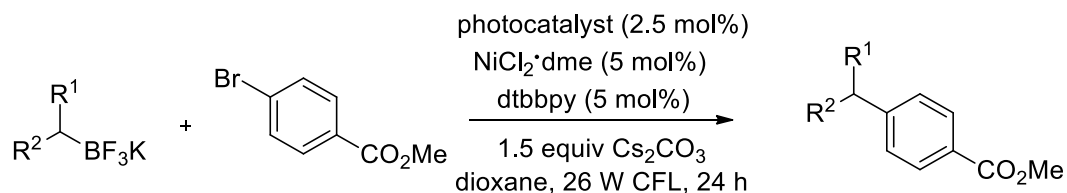


Figure 1

10. In 2015, Jeffrey W. Johannes with co-workers performed dual catalyzed cross-coupling reaction with the effect of molecular oxygen, solvent and light (figure 1). In this reaction, C-C bond formation via dual catalysis. Also, we could see that molecular oxygen promotes reduction of Ni(II) precatalyst by Ir(II) to Ni(0) [76].

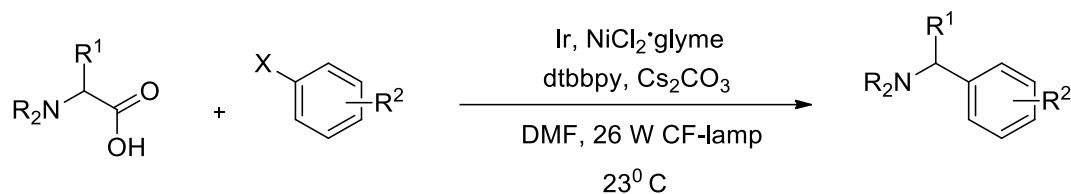


Figure 1

11. In 2015, Gary A. Molander with co-workers performed synthesis of Benzylic ethers with dual-catalysis in visible light by single electron transmetalation method (figure 1). It is a mild and efficient method to carry out the reaction at room temperature. Various substrate scope could be seen in figure 2 [77].

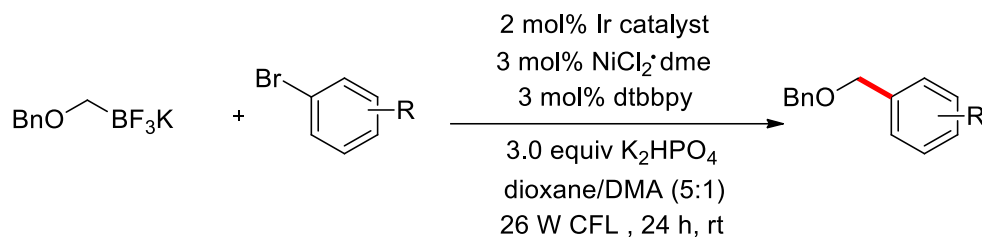


Figure 1

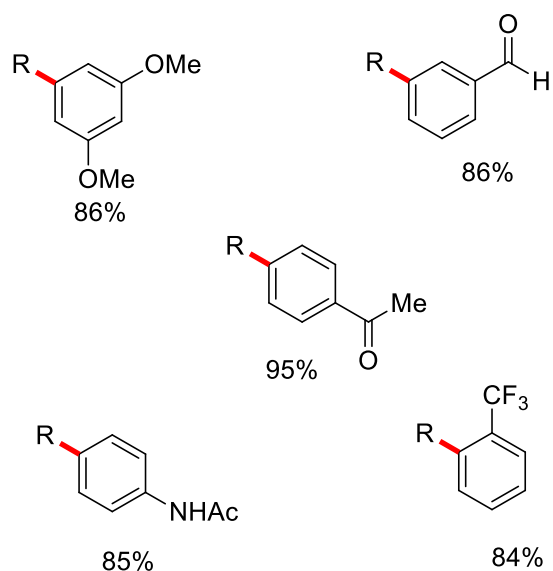


Figure 2:- substrate scope

12. In 2016, Gary A. Molander with co-workers performed synthesis of  $\alpha$ -alkoxyketones via cross-coupling of acyl chlorides with potassium alkoxymethyltrifluoroborates in visible light through photoredox catalyst (figure 1). By single electron transfer mechanism,  $\alpha$ -alkoxyketones are produced. It is a mild protocol with maximum number of yields for desired ketones generation and is a dual catalysis method for this process. By substituting various groups different yields with substrate scope could be seen in figure 2 [78].

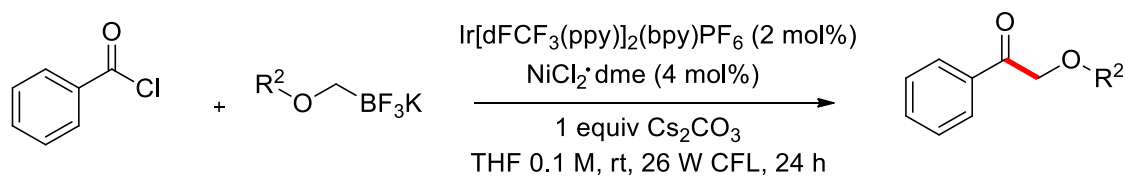


Figure 1



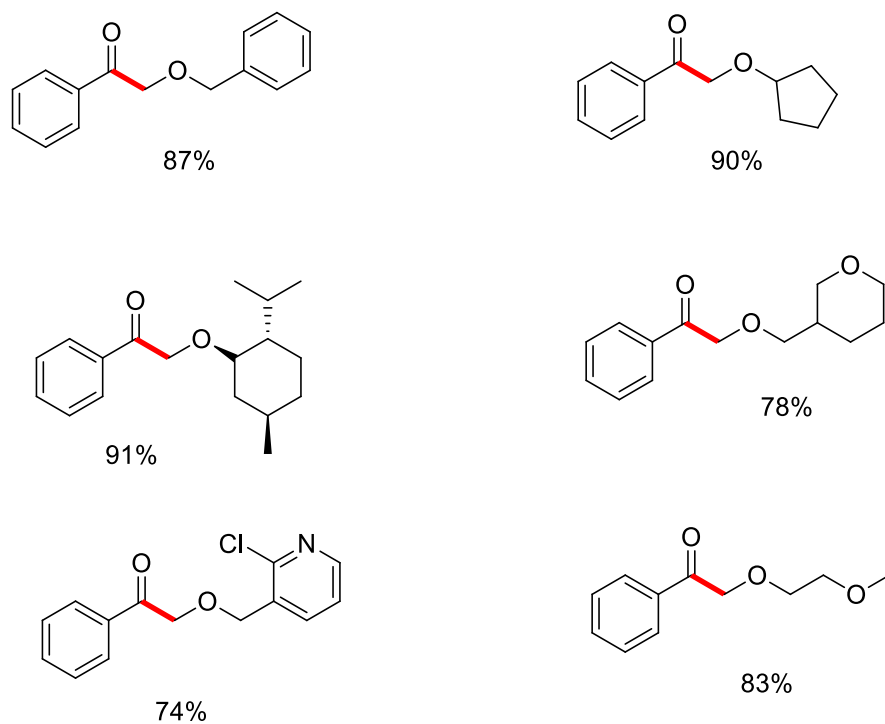
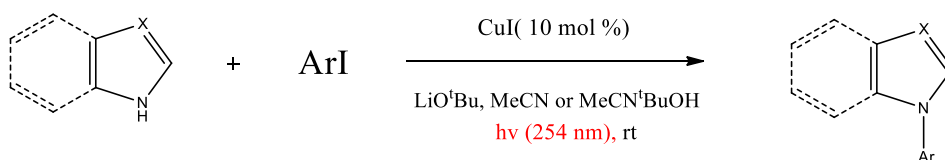


Figure 2:- substrate scope

13. In 2015, Shu Kobayashi with co-workers performed Ullmann-type C-N coupling reaction in which Transition metal can mediate single electron transfer (SET) processes of various organic functional groups (figure 1) to produce reactive charged radical intermediate. Nitrogen containing organic compounds found in the agrochemical and material sciences were used for the development of efficient method to construct C-N bond. Various substrate scope could be seen in figure 2 [79].

**Previous report:-**photoinduced, Cu catalyzed Ullmann coupling reaction.



**This work:-** Cu catalyzed C-N coupling reaction under photoredox condition.

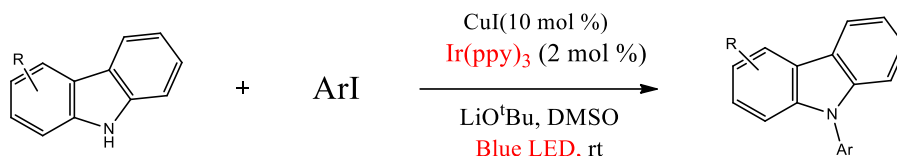


Figure 1

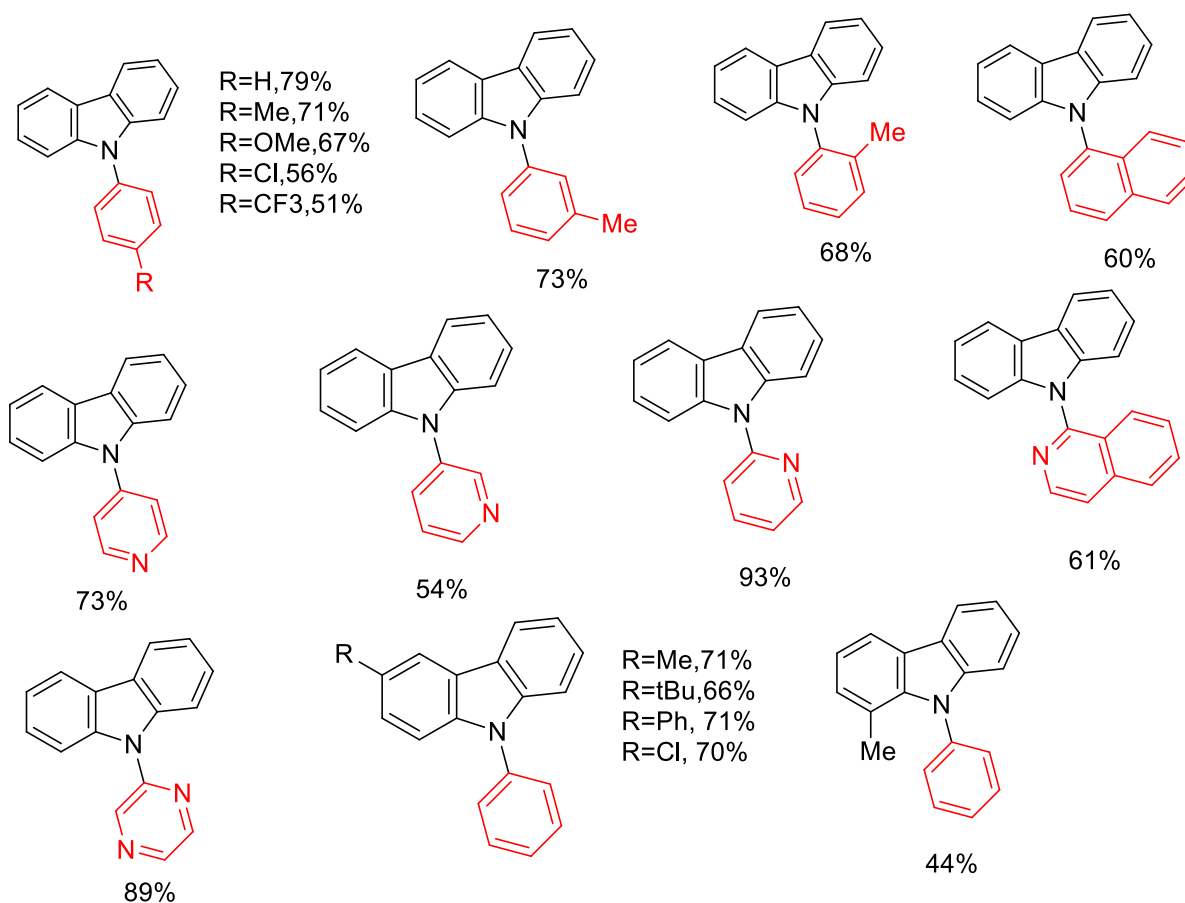


Figure 2:- substrate scope

Copper iodide can form copper(I) amide in the presence of Carbazole under basic conditions. Then Ir(III) is irradiated to excited state Ir(III)\* after which the complex would be quenched to afford excited copper carbazolidine and Ir(III) complex. Iodobenzene could experience a single electron transfer from excited state copper complex to generate radical disproportionation which would result in the formation of an aryl radical thereby reacting with copper(II) amide to produce 9-phenylcarbazole and copper catalysis. In conclusion, copper catalysis and photoredox catalysis work in concerted fashion to facilitate Ullmann coupling reaction [79].

## **20. Visible light-mediated Activation of C-H bond**

1. In 2014, David W. C. MacMillan with co-workers performed arylation of benzylic ethers via activation of C-H bond through photoredox catalyst (figure 1). Excellent yields are produced by this method [80].

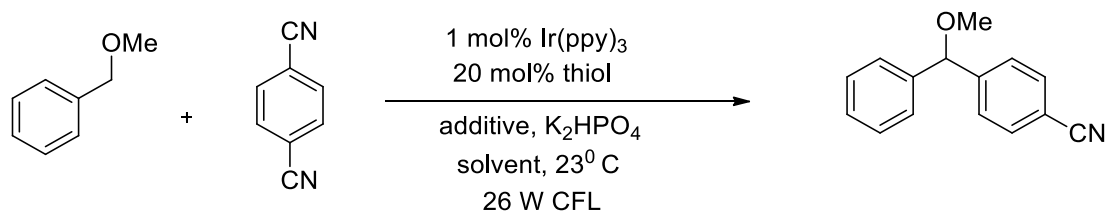


Figure 1

2. In 2016, Qiang Liu with co-workers performed intramolecular difluoroacetamidation using visible light. It is a facile and efficient reaction for the production of oxindole (3,3-difluoro-2-oxindoles) from iridium based photocatalyst and bromodifluoroacetamides using iridium based photoredox catalyst (figure 1). It is great for the preparation of intramolecular C-H activation of arenes at room temperature [81].

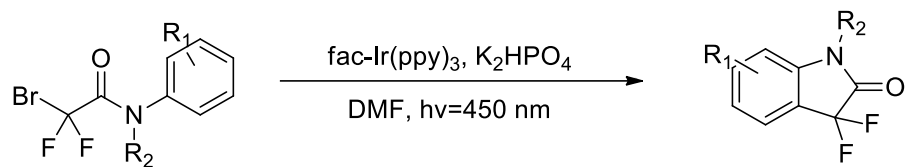


Figure 1

3. In 2014, David W. C. MacMillan and Jian Jin performed  $\alpha$ -arylation of ethers through C-H functionalization using photoredox catalyst and Minisci reaction as shown in figure 1. By differencing various substituents different yields could be seen in figure 2 [82].

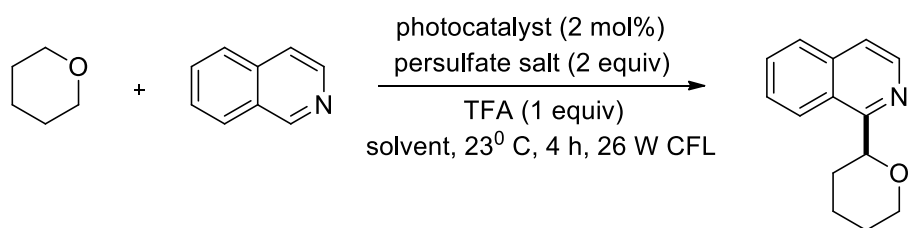


Figure 1

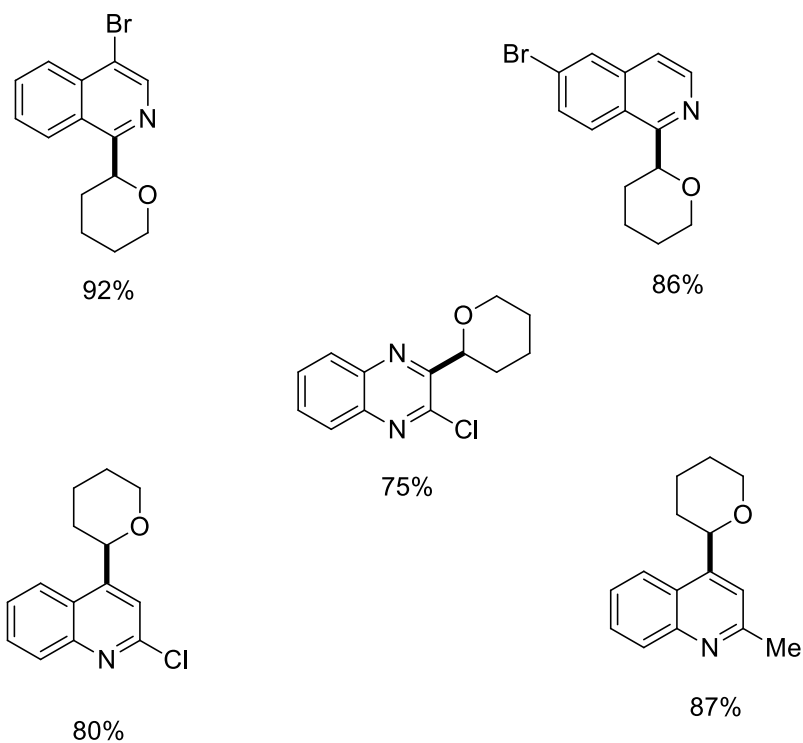


Figure 2:- substrate scope

4. In 2014, Daniel A. DiRocco with co-workers performed functionalization of biologically active heterocycles using iridium based photoredox catalyst (figure 1). It is a simple protocol with mild conditions at room temperature [83].

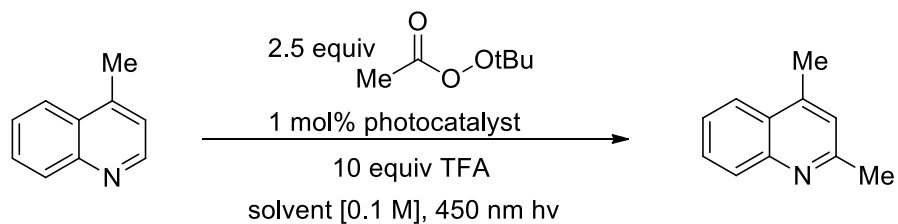


Figure 1

5. In 2014, David W. C. MacMillan and Adam Noble performed  $\alpha$ -vinylation of amino acid and N-aryl amines using photoredox catalyst (figure 1). C-H vinylation of N-aryl tertiary amines and decarboxylative vinylation lead to high optimum yields [84].

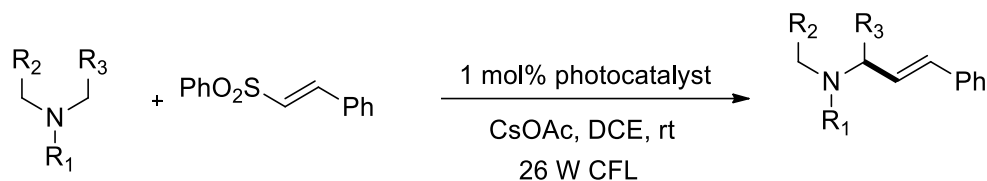


Figure 1

6. In 2014, Chulbom Lee with co-workers performed imidation of arenes and heteroarenes using visible light with iridium based photocatalyst (figure 1). The reactions were performed at an ambient temperature via nitrogen-centered radical mediated aromatic substitution [85].

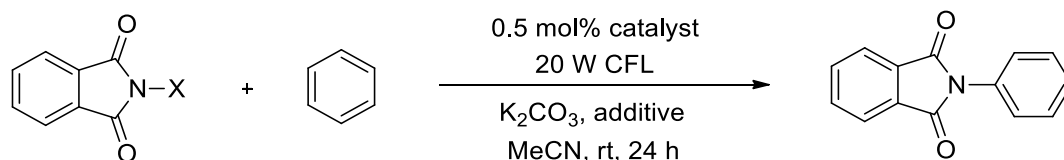


Figure 1

7. In 2014, Melanie S. Sanford with co-workers performed C-H amination of arenes and heteroarenes at room temperature via photocatalyst under visible light (figure 1). N-acyloxyphthalimides as nitrogen radical intermediates were used for this transformation. A large range of substrate scope were seen in (figure 2) with radical aromatic substitution mechanism as shown in figure 3 giving us a brief mechanistic catalytic cycle for this reaction [86].

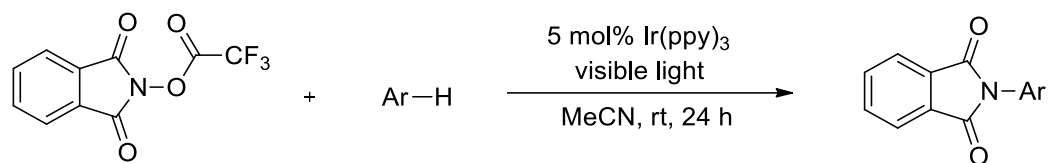


Figure 1

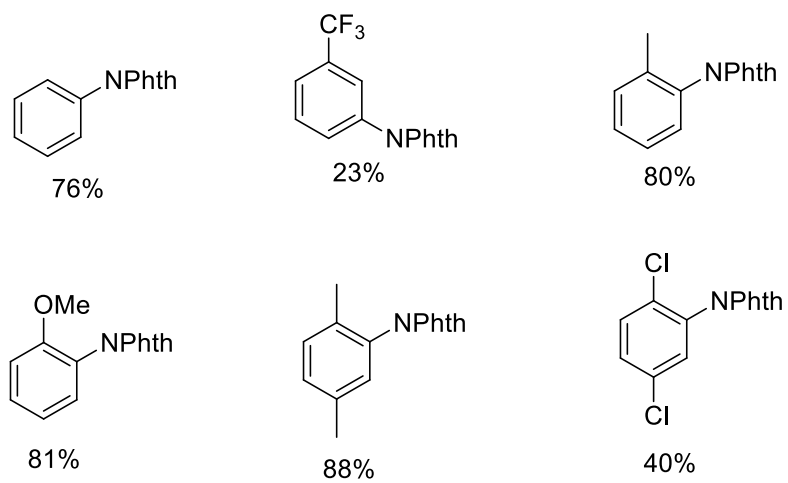


Figure 2:- substrate scope

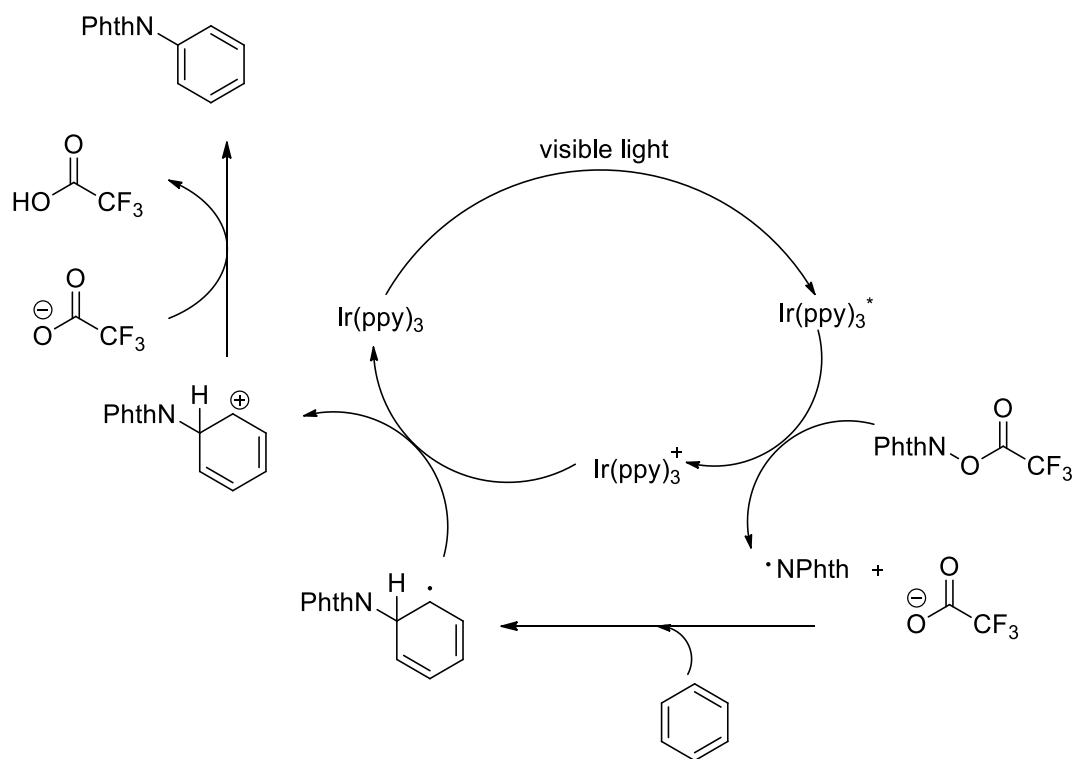


Figure 3:- mechanistic pathway

8. In 2015, De-Cai Xiong and Xin-Shan Ye with co-workers performed a mild and efficient transformation of C-H trifluoromethylation of glycol using visible light photoredox catalyst (figure 1). The best catalyst used for the highest optimum yield was *fac*-Ir(ppy)<sub>3</sub> with Umemoto's reagent as its CF<sub>3</sub> source for the reaction. Substrate scope could be seen by glycols having an e<sup>-</sup> withdrawing and e<sup>-</sup> donating groups which were seen for suitable substrate for the reaction condition (figure 2) [17].

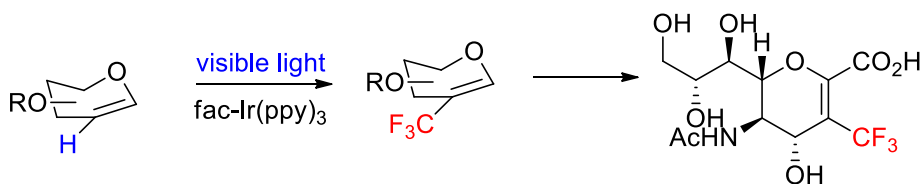




Figure 1

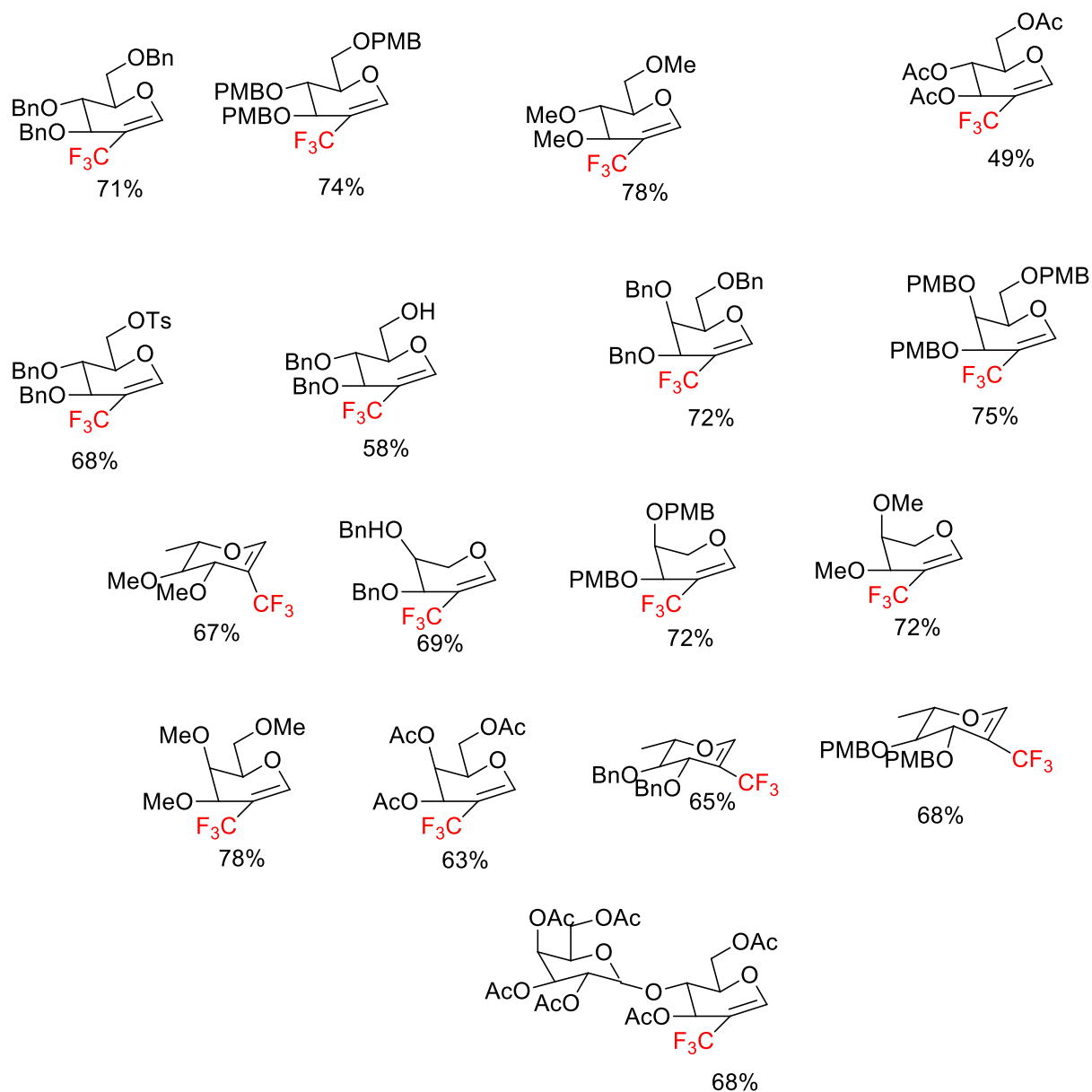


Figure 2 substrate scope

9. In 2015, Pixu Li with co-workers performed the conversion of alkyl benzyl ether to alkyl ester or alcohol through radical chain reaction in visible light involving homolytic cleavage of O- $\alpha$ -sp<sup>3</sup> C-H bond in the propagation process (figure 1) [18].

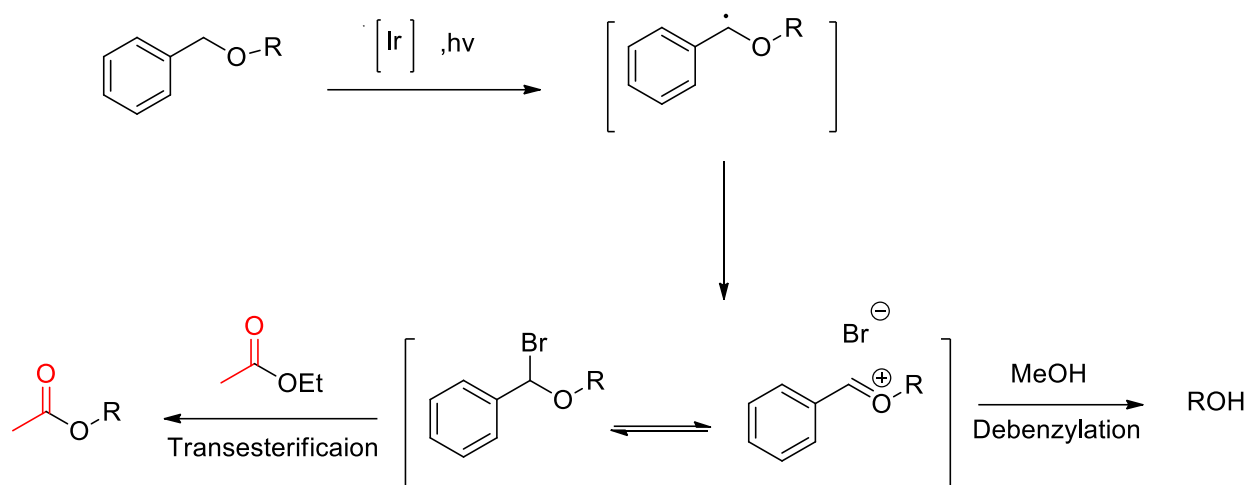


Figure 1

10. In 2014, Lin Wang with his co-workers performed work on difluoroacetamidation of unactivated arenes and heteroarenes with bromodifluoroacetamides using visible light mediated photoredox catalyst at room temperature (figure 1). Wide range of substrate scope on difluoroacetamidation of arenes and heteroarenes with bromodifluoroacetamides could be seen in figure 2 and 3 [19].

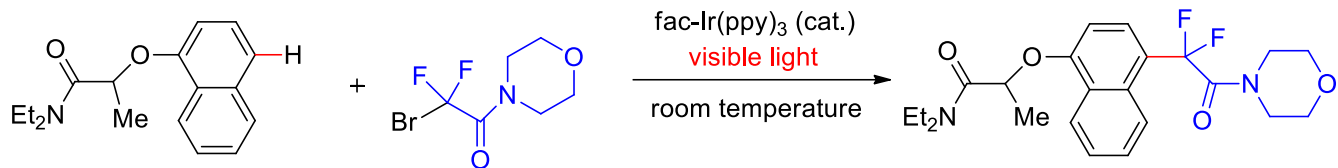


Figure 1

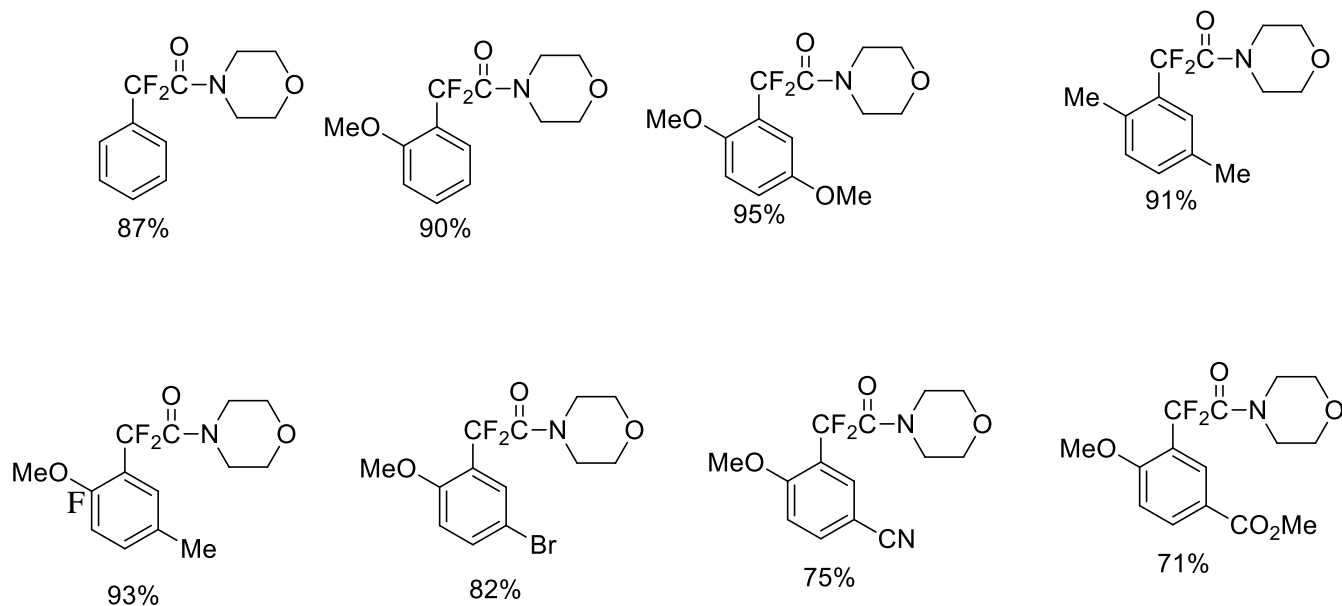


Figure 2:- substrate scope of difluoroacetamidation of arenes using bromodifluoroacetamides

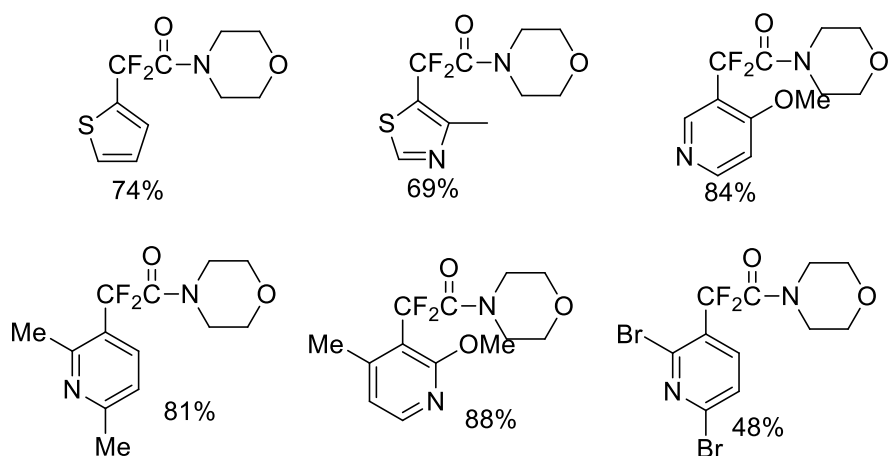


Figure 3:- scope of difluoroacetamidation of heteroarenes using bromodifluoroacetamides

11. In 2014, Qixeu Qin and Shouyun Yu performed neutral C-H activation of amidation of heteroarenes with hydroxylamine derivatives through visible light promoted single electron transfer without directing groups (figure 1). These reactions are much more regioselective and

only single regio isomer is obtained. By changing R group scope for the substrate could be seen (figure 2) [20].

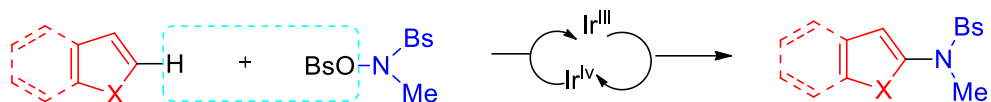


Figure 1

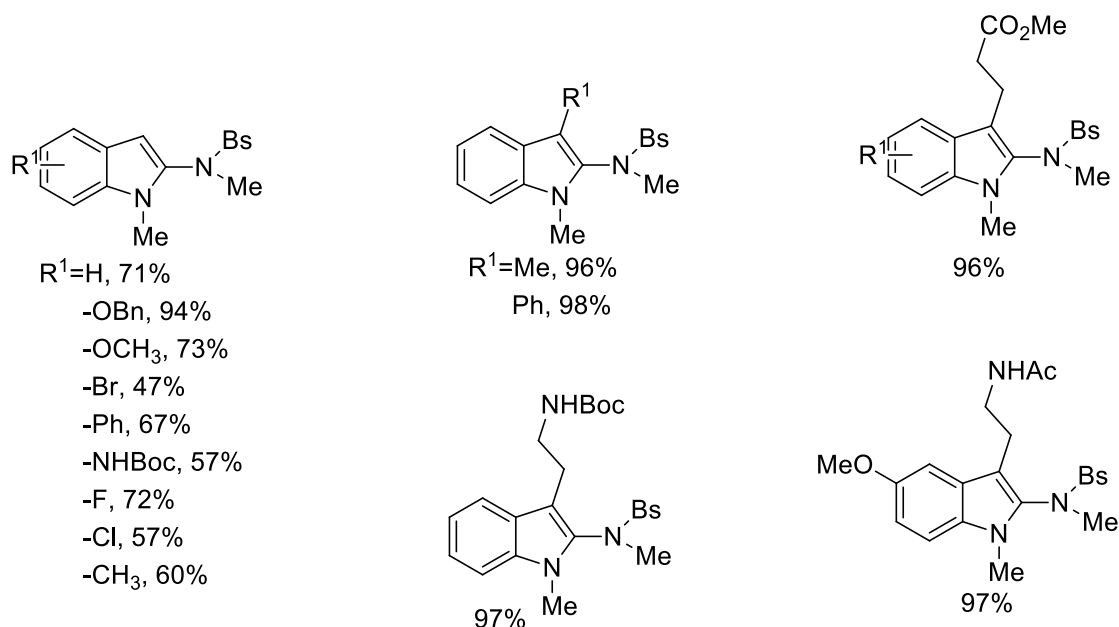


Figure 2:- substrate scope

12. In 2014, Jing Ma and its co-workers worked on radical promoted C-H trifluoromethylation of free anilines through iridium based photoredox catalyst (figure 1). This protocol is efficient and economical to prepare various substituted trifluoromethylated free anilines by changing R group which are high for synthetic and biological value (figure 2) [21].

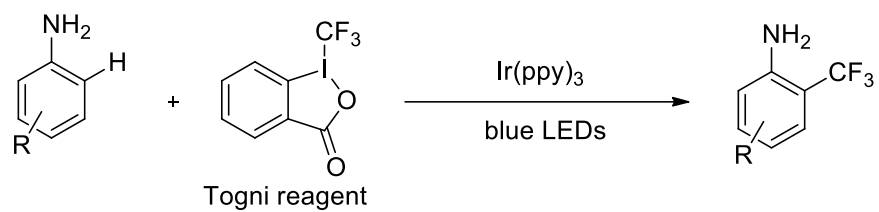
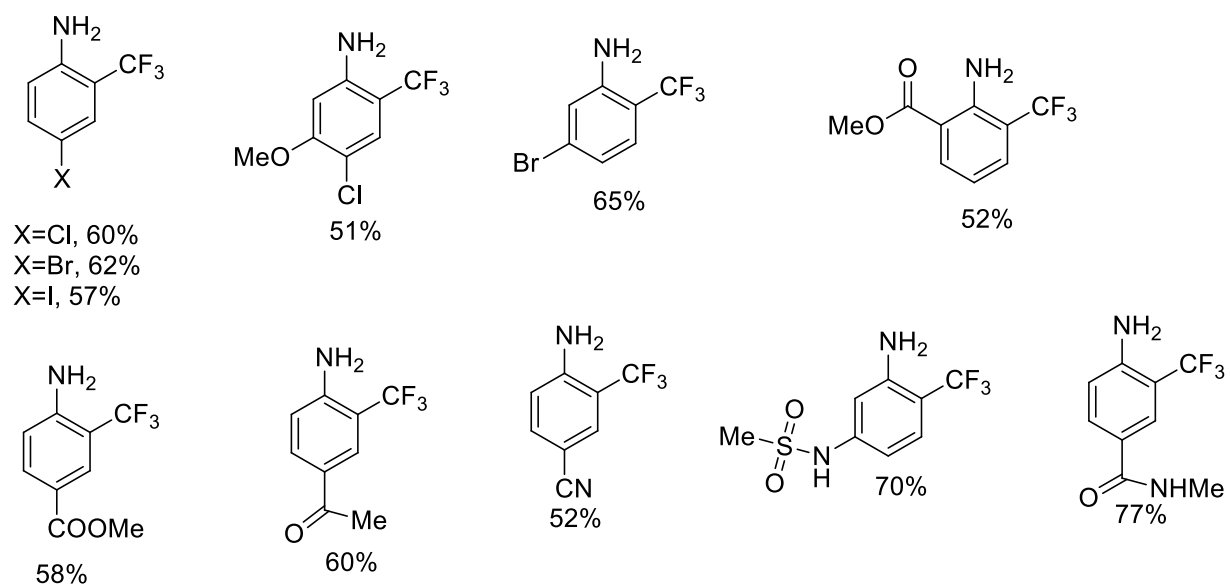


Figure 1



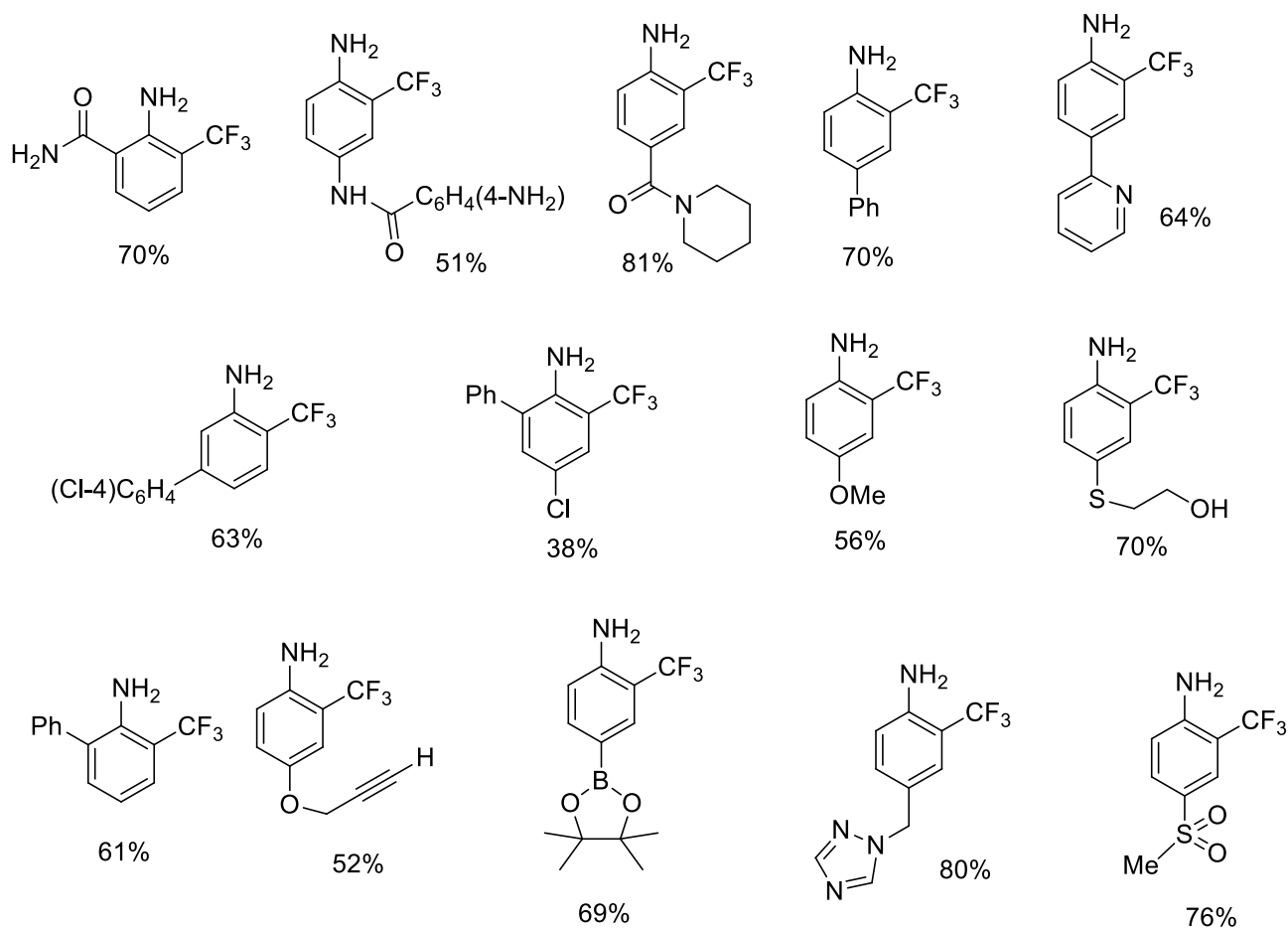


Figure 2:- substrate scope

## Conclusion

Year 2015 is claimed by the United Nations as the “International Year of Light” and the main aim of this thesis is “Light for Change”. No other science can match this dictum other than chemistry itself; as it clearly states that “Chemistry is responsible for change of matter” [87]. Until year 2010, visible light mediated organic reactions have become an emerging field to academics and industrial chemists due to its overall sustainability. All reactions were carried out at low-energy LEDs, or with the help of sunlight in the absence of any purposeful use of photochemical instruments [88]. In organic reactions, the usage of productive visible light for the photoredox catalysis makes a better approach for greener alternative synthesis [89]. Only in the excited state after irradiation of light iridium(III) based complexes possess versatile properties which are useful for photoelectrochemical applications. Ir(III) complexes have been fruitful in

research for its photophysical and electrochemical properties and yield emission band spanning in the spectrum range of near ultraviolet region to the near infrared region. Its applications are seen in water photolysis, photocatalysis, biosensing and bioimaging [90]. Its distinctive ability of ‘activating’ molecules in a photoredox catalysis brings substantial capabilities towards production of a perfect method for the chemical reactivity and moderativity leading to well organised conversion due to its unique regio, chemo and stereoselectivity under gentle and favourable environmental conditions (presuming that the answers are for long-lasting). Reductive and oxidative quenching pathways constitute the visible light photoredox catalysis. Another characteristic of visible light photoredox catalyst is the energy transfer in many organic transformations. Photoredox catalyst can perform two jobs such as electron transfer and atom transfer which can vary the substrate scope and, the combination of photoredox catalysis and organo catalysis can be seen as driving force for production of novel organic reactions [91]. With the astonishing advancement in the combination of photoredox catalyst and organo catalyst, the boundaries delineating new emergent horizon of catalytic chemical reactions are getting vague [92]. In the advancement of visible light, photocatalysis sets unique interests in fields of material science, chemical biology, drug discovery which are recognized by various researchers who believe that the photochemical synthesis will proceed to grow with synergistic relationship with intellectual adjacent fields. It is said that the coming generation of photocatalytic reactions remains bright and greener [93].

## **References**

- [1.] Corey R. J. Stephenson, Jagan M. R. Narayanam, *Chem. Soc. Rev.*, 2011, **40**, 102-113
- [2.] Al Postigo, Sergio M. Bonesi, Sebastian Barata-Vallejo, *Org. Biomol. Chem.*, 2013, **11**, 2387-2403
- [3.] Sebastian Barata-Vallejo, Sergio M. Bonesi and Al Postigo, *Org. Biomol. Chem.*, 2015, **13**, 11153-11183, [3'] Sofia Telitel, Frederic Dumur, Siham Telitel, Olivier Soppera, Marc Lepeltier, Yohann Guillaneuf, Julien Poly, Fabrice Morlet-Savary, Philippe Fioux, Jean-Pierre Fouassier, Didier Gigmes and Jacques Lalevee, *Polym. Chem.*, 2015, **6**, 613-624
- [4.] Youngmin You, Wonwoo Nam, *Chem. Soc. Rev.*, 2012, **41**, 7061-7084

- [5.] Wonwoo Nam, Youngmin You, Somin Cho, *Inorg. Chem.* 2014, 53, 1804-1815
- [6.] Chengjian Zhu, Jin Xie, Hongming Jin, Pan Xu, *j.tetlet*.2013.10.090
- [7.] Munetaka Akita, Takashi Koike, *Inorg. Chem. Front.*, 2014, **1**, 562-576
- [9.] Zuxiao Zhang, Xiaojun Tang, William R. Dolbier, *Org. Lett.* **2015**, 17, 4401-4403
- [10.] Yannan Cheng, Xiangyong Gu, Pixu Li, *Org. Lett.*, Vol. 15, No. 11, **2013**
- [11.] Hongxia Zhou, Ping Lu, Xiangyong Gu, Pixu Li, *Org. Lett.*, Vol. 15, No. 22, **2013**
- [12.] Xiao-Jing Wei, Deng-Tao Yang, Lin Wang, Tao Song, Li-Zhu Wu, Qiang Liu, *Org. Lett.*, Vol. 15, No. 23, **2013**
- [13.] Gabriele Fumagalli, Scott Boyd, Michael F. Greaney, *Org. Lett.*, Vol. 15, No. 17, **2013**
- [14.] Magnus Rueping and Carlos Vila, *Org. Lett.*, Vol. 15, No. 9, **2013**
- [15.] Hong Yi, Xu Zhang, Chu Qin, Zhixiong Liao, Jie Liu and Aiwen Lei, *Adv. Synth. Catal.* **2014**, 356, 2873-2877
- [16.] Shi Tang, You-Lin Deng, Jie Li, Wen-Xin Wang, Guo-Liang Ding, Ming-Wei Wang, Zhu-Ping Xiao, Ying-Chun Wang and Rui-Long Sheng, *J. Org. Chem.* 2015, 80, 12599-12605
- [17.] Bang Wang, De-Cai Xiong, Xin-Shan Ye, *Org. Lett.* 2015, 17, 5698-5701
- [18.] Ping Lu, Tianyuan Hou, Xiangyong Gu and Pixu Li, *Org. Lett.* 2015, 17, 1954-1957
- [19.] Lin Wang, Xiao-Jing Wei, Wen-Liang Jia, Jian-Ji Zhong, Li-Zhu Wu and Qiang Liu, *Org. Lett.* 2014, 16, 5842-5845
- [20.] Qixue Qin and Shouyun Yu, *Org. Lett.* 2014, 16, 3504-3507
- [21.] Jin Xie, Xiangai Yuan, Ablimit Abdukader, Chengjian Zhu and Jing Ma, *Org. Lett.* 2014, 16, 1768-1771
- [22.] Xiao-De An and Shouyun Yu, *Org. Lett.* 2015, 17, 2692-2695



- [23.] Lingling Chu, Jeffrey M. Lipshultz and David W. C. MacMillan, *Angew. Chem. Int. Ed.* **2015**, 54, 7929-7933
- [24.] Sandrine Ventre, Filip R. Petronijevic and David W. C. MacMillan, *J. Am. Chem. Soc.* 2015, 137, 5654-5657
- [25.] Pan Xu, Ablimit Abdukader, Kaidong Hu, Yixiang Cheng and Chengjian Zhu, *Chem. Commun.*, 2014, **50**, 2308-2310
- [26.] Simon B. Lang, Kathryn M. O'Nele and Jon A. Tunge, *J. Am. Chem. Soc.* 2014, 136, 13606-13609
- [27.] Lingling Chu, Chisa Ohta, Zhiwei Zuo and David W. C. MacMillan, *J. Am. Chem. Soc.* 2014, 136, 10886-10889
- [28.] Yoshihiro Miyake, Kazunari Nakajima and Yoshiaki Nishibayashi, *Chem. Commun.*, 2013, **49**, 7854-7856
- [29.] Zhiwei Zuo and David W. C. MacMillan, *J. Am. Chem. Soc.* 2014, 136, 5257-5260
- [30.] Haohua Huo, Chuanyong Wang, Klaus Harms, Eric Meggers, *J. Am. Chem. Soc.* 2015, 137, 9551-9554
- [31.] Heng Jiang, Yuanzheng Cheng, Ruzhi Wang, Yan Zhang and Shouyun Yu, *Chem. Commun.*, 2014, **50**, 6164-6167
- [32.] Ludwig Chenneberg, Alexandre Baralle, Marion Daniel, Louis Fensterbank, Jean-Philippe Goddard and Cyril Ollivier, *Adv. Synth. Catal.* 2014, 356, 2756-2762
- [33.] Chunghyeon Yu, Naeem Iqbal, Sehyun Park and Eun Jin Cho, *Chem. Commun.*, 2014, **50**, 12884-12887
- [34.] Xiaoyang Sun and Shouyun Yu, *Org. Lett.* 2014, 16, 2938-2941
- [35.] Yuanzheng Cheng, Xiangai Yuan, Heng Jiang, Ruzhi Wang, Jing Ma, Yan Zhang and Shouyun Yu, *Adv. Synth. Catal.* **2014**, 356, 2859-2866
- [36.] Jaehun Jung, Eunjin Kim, Youngmin You, Eun Jin Cho, *Adv. Synth. Catal.* **0000**, 000, 0-0

- [37.] Kazuki Miyazawa, Takashi Koike and Munetaka Akita, *Adv. Synth. Catal.* **2014**, 356, 2749-2755
- [38.] Ren Tomita, Yusuke Yasu, Takashi Koike and Munetaka Akita, *Angew. Chem. Int. Ed.* **2014**, 53, 1-6
- [39.] Heng Jiang, Yuanzheng Cheng, Yan Zhang and Shouyun Yu, *Eur. J. Org. Chem.* **0000**, 0-0
- [40.] Pan Xu, Guoqiang Wang, Yuchen Zhu, Weipeng Li, Yixiang Cheng, Shuhua Li and Chengjian Zhu, *Angew. Chem. Int. Ed.* 2015, 54, 1-6
- [41.] Yanjie Li, Kazuki Miyazawa, Takashi Koike and Munetaka Akita, *Org. Chem. Front.*, 2015, **2**, 319-323
- [42.] Qing-Yu Lin, Xiu-Hua Xu and Feng-Ling Qing, *J. Org. Chem.* 2014, 79, 10434-10446
- [43.] Ren Tomita, Takashi Koike and Munetaka Akita, *Angew. Chem. Int. Ed.* **2015**, 54, 12923-12927
- [44.] Weijian Fu, Mei Zhu, Guanglong Zou, Chen Xu, Zhiqiang Wang and Baoming Ji, *J. Org. Chem.* 2015, 80, 4766-4770
- [45.] Lun Li, Meiwei Huang, Chao Liu, Ji-Chang Xiao, Qing-Yun Chen, Yong Guo and Zhi-Gang Zhao, *Org. Lett.* **2015**, 17, 4714-4717
- [46.] Carl-Johan Wallentin, John D. Nguyen, Peter Finkbeiner and Corey R. J. Stephenson, *J. Am. Chem. Soc.* 2012, 134, 8875-8884
- [47.] John D. Nguyen, Joseph W. Tucker, Marlina D. Konieczynska and Corey R. J. Stephenson, *J. Am. Chem. Soc.* 2011, 133, 4160-4163
- [48.] Hyejin Kim and Chulbom Lee, *Angew. Chem. Int. Ed.* **2012**, 51, 12303-12306
- [49.] Kazuki Miyazawa, Yusuke Yasu, Takashi Koike and Munetaka Akita, *Chem. Commun.*, 2013, **49**, 7249-7251
- [50.] Joseph W. Tucker, Jagan M. R. Narayanam, Pinkey S. Shah and Corey R. J. Stephenson, *Chem. Commun.*, 2011, **47**, 5040-5042

- [51.] Joseph W. Tucker and Corey R. J. Stephenson, *Org. Lett.*, Vol. 13, No. 20, **2011**
- [52.] Jin Xie, Pan Xu, Huamin Li, Qicai Xue, Hongming Jin, Yixiang Cheng and Chengjin Zhu, *Chem. Commun.*, 2013, **49**, 5672-5674
- [53.] Zhangxi Gu, Honglin Zhang, Pan Xu, Yixiang Cheng and Chengjian Zhu, *Adv. Synth. Catal.* **2015**, 357, 3057-3063
- [54.] Filip R. Petronijevic, Manuel Nappi and David W. C. MacMillan, *J. Am. Chem. Soc.* 2013, 135, 18323-18326
- [55.] Chuanhua Qu, Pan Xu, Wujiang Ma, Yixiang Cheng and Chengjian Zhu, *Chem. Commun.*, 2015, **51**, 13508-13510
- [56.] Zhi He, Minwoo Bae, Jie Wu and Timothy F. Jamison, *Angew. Chem. Int. Ed.* **2014**, 53, 1-6
- [57.] Yoshihiro Miyake, Kazunari Nakajima and Yoshiaki Nishibayashi, *J. Am. Chem. Soc.* 2012, 134, 3338-3341
- [58.] Jacob Davies, Samuel G. Booth, Stephanie Essafi, Robert A. W. Dryfe and Daniele Leonori, *Angew. Chem. Int. Ed.* **2015**, 54, 14017-14021
- [59.] Yoshihiro Miyake, Yuya Ashida, Kazunari Nakajima and Yoshiaki Nishibayashi, *Chem. Commun.*, 2012, **48**, 6966-6968
- [60.] Kazunari Nakajima, Mai Kitagawa, Yuya Ashida, Yoshihiro Miyake and Yoshiaki Nishibayashi, *Chem. Commun.*, 2014, **50**, 8900-8903
- [61.] Shaoqun Zhu, Arindam Das, Lan Bui, Hanjun Zhou, Dennis P. Curran and Magnus Rueping, *J. Am. Chem. Soc.* 2013, 135, 1823-1829
- [62.] Masaki Nakajima, Quentin Lefebvre and Magnus Rueping, *Chem. Commun.*, 2014, **50**, 3619-3622
- [63.] Zhan Lu and Tehshik P. Yoon, *Angew. Chem. Int. Ed.* **2012**, 51, 1-5
- [64.] Anna E. Hurtley, Zhan Lu and Tehshik P. Yoon, *Angew. Chem. Int. Ed.* **2014**, 53, 1-5

- [65.] Hong Hou, Shaoqun Zhu, Fangfang Pan and Magnus Rueping, *Org. Lett.* 2014, 16, 2872-2875
- [66.] Spencer O. Scholz, Elliot P. Farney, Sangyun Kim, Desiree M. Bates and Tehshik P. Yoon, *Angew. Chem. Int. Ed.* **2016**, 55, 2239-2242
- [67.] Christopher K. Prier and David W. C. MacMillan, *Chem. Sci.*, 2014, **5**, 4173-4178
- [68.] Heng Jiang, Yuanzheng Cheng, Yan Zhang and Shouyun Yu, *Org. Lett.*, Vol. 15, No. 18, **2013**
- [69.] Chuanyong Wang, Jie Qin, Xiaodong Shen, Radostan Riedel, Klaus Harms and Eric Meggers, *Angew. Chem. Int. Ed.* **2016**, 55, 685-688
- [70.] Suva Paria, Viktor Kais and Oliver Reiser, *Adv. Synth. Catal.* **2014**, 356, 2853-2858
- [71.] Adam Noble, Stefan J. McCarver and David W. C. MacMillan, *J. Am. Chem. Soc.* 2015, 137, 624-627
- [72.] Woo-Jin Yoo, Tatsuhiro Tsukamoto and Shu Kobayashi, *Angew. Chem. Int. Ed.* **2015**, 54, 1-5
- [73.] Woo-Jin Yoo and Shu Kobayashi, *Green Chem.*, 2014, **16**, 2438-2442
- [74.] Jenna L. Jeffrey, Filip R. Petronijevic and David W. C. MacMillan, *J. Am. Chem. Soc.* 2015, 137, 8404-8407
- [75.] David N. Primer, Idris Karakaya, John C. Tellis and Gary A. Molander, *J. Am. Chem. Soc.* 2015, 137, 2195-2198
- [76.] Martin S. Oderinde, Adrian Varela-Alvarez, Brian Aquila and Daniel W. Robbins, *J. Am. Chem.* 2015, 80, 7642-7651
- [77.] Idris Karakaya, David N. Primer and Gary A. Molander, *Org. Lett.* 2015, 17, 3294-3297
- [78.] Javad Amani, Esmat Sodagar and Gary A. Molander, *Org. Lett.* XXXX, XXX, XXX-XXX
- [79.] Woo-Jin Yoo, Tatsuhiro Tsukamoto and Shu Kobayashi, *Org. Lett.* **2015**, 17, 3640-3642

- [80.] Katrine Qvortrup, Danica A. Rankic and David W. C. MacMillan, *J. Am. Chem. Soc.* 2014, 136, 626-629
- [81.] Xiao-Jing Wei, Lin Wang, Shao-Fu Du, Li-Zhu Wu and Qiang Liu, *Org. Biomol. Chem.*, 2016, **14**, 2195-2199
- [82.] Jian Jin and David W. C. MacMillan, *Angew. Chem. Int. Ed.* **2014**, 53, 1-6
- [83.] Daniel A. DiRocco, Kevin Dykstra, Shane Krska, Petr Vachal, Donald V. Conway and Matthew Tudge, *Angew. Chem. Int. Ed.* **2014**, 53, 1-6
- [84.] Adam Noble and David W. C. MacMillan, *J. Am. Chem. Soc.* 2014, 136, 11602-11605
- [85.] Hyejin Kim, Taehoon Kim, Dong Gil Lee, Sang Weon Roh and Chulbom Lee, *Chem. Commun.*, 2014, **50**, 9273-9276
- [86.] Laura J. Allen, Pablo J. Cabrera, Melissa Lee and Melanie S. Sanford, *J. Am. Chem. Soc.* 2014, 136, 5607-5610
- [87.] Richard Brimiouille, Dominik Lenhart, Mark M. Maturi and Thorsten Bach, *Angew. Chem. Int. Ed.* **2015**, 54, 2-21
- [88.] Jin Xie, Hongming Jin, Pan Xu and Chengjian Zhu, *J. Xie et al./Tetrahedron Letters* 55 (2014) 36-48
- [89.] Jagan M. R. Narayanam and Corey R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102-113
- [90.] Youngmin You and Wonwoo Nam, *Chem. Soc. Rev.*, 2012, **41**, 7061-7084
- [91.] Yumeng Xi, Hong Yi and Aiwen Lei, *Org. Biomol. Chem.*, 2013, **11**, 2387-2403
- [92.] Cheng Zhong and Xiaodong Shi, *Eur. J. Org. Chem.* **2010**, 2999-3025
- [93.] Danielle M. Schultz and Tehshik P. Yoon, *Science* **343**, 1239176 (2014)