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REVIEW ARTICLE

Utilization of photocatalysts in decarboxylative coupling of carboxylic N-hydroxyphthalimide (NHPI) esters

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Metal photocatalyst;
Organic photocatalyst

Abstract Recently, the visible-light photoredox decarboxylative couplings of N-(acyloxy) phthalimides (NHPI esters) and its derivatives have become an efficient chemical transformation. Under visible light, the NHPI esters undergo a single-electron transfer (SET) process to afford the corresponding carbon or nitrogen radicals that participate in many chemical transformations. The photoredox decarboxylative couplings have been applied to achieve construction of an array of carbon–carbon and carbon–heteroatom bonds as well as the synthesis of carbocycles and heterocycles. This review categorises photocatalysts, discusses the application and catalysis mechanisms of NHPI esters, and details recent progress in this field.

1. Introduction

Carboxylic acids are a comparatively abundant, stable, and structurally diverse class of molecules. They are inexpensive, easy to store, and attractive raw starting materials for pharmaceuticals, agrochemicals, and organic materials (Gooβen et al., 2008). One of the most fascinating transformations of carboxylic acids is decarboxylative cross-coupling, which has been applied widely in various types of organic synthesis (Murarka et al., 2018; Karmakar et al., 2021). These decarboxylative transformations undergo cleavage of C–C bonds to extrude carbon dioxide with concomitant formation of an active species, such as an organometallic intermediate (R-M) or radical intermediate. Carboxylic acids or their salts can react with transition-metal catalysts to afford a R-M, which is employed with organic functional entries to complete redox-neutral or oxidative couplings. In addition, carboxylic acids and their derivatives undergo single electron transfer (SET) processes to offer radical intermediates under visible-light irradiation

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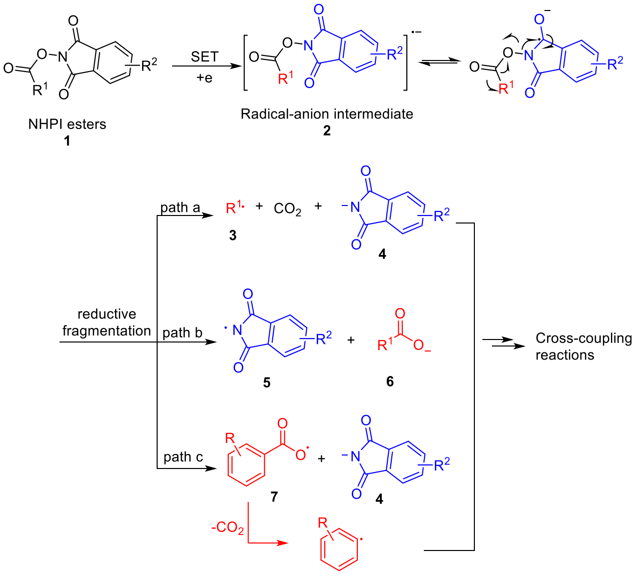
or strong oxidation (Niu et al., 2020). Classic radical decarboxylative reactions include the Hunsdiecker-Borodin reaction and Barton decarboxylative rection (Johnson et al., 1956; Barton et al., 1980). Great achievements have been achieved in radical decarboxylative couplings, but the development of more convenient, environmentally friendly, and efficient methods under mild conditions are needed urgently (Zhu et al., 2021). To improve the reactivity of carboxylic acids, prefunctionalisation of carboxylic acids (e.g., ester, thioester, or amide derivatives) is an attractive alternative to carry out radical-mediated decarboxylative cross-couplings (Li et al., 2017). Carboxylic N-hydroxyphthalimide (NHPI) esters, as efficient radical precursors, are usually employed to construct carbon–carbon or carbon–heteroatom bonds. NHPI esters-mediated decarboxylation has been adapted by photoredox catalysis (**PC**) (Fu et al., 2017; Ma et al. 2021), transition-metal catalysis (Parida et al., 2021) and electrochemical methods (Ramadoss et al., 2021). This review discusses and analyses the redox properties, photocatalysis mechanisms, and application of various types of photocatalysts in decarboxylative coupling of carboxylic N-hydroxyphthalimide (NHPI) esters. Depending on the reaction conditions employed, the couplings have been categorised into metal-photoinduced and organic-photoinduced cross couplings.

2. Decarboxylation of NHPI esters

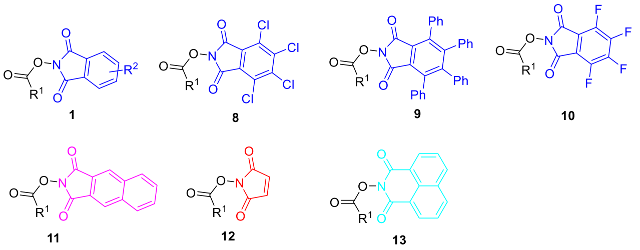
In 1988, Oda and co-workers reported pioneering research on the decarboxylative cross-couplings of NHPI, but that research was ignored for a long time (Okada et al., 1988). Recently, the redox properties of NHPI esters have been investigated intensively, along with the use of photoredox catalysis. As a type of redox-active compound, NHPI esters **1** can accept one electron through a SET process to give the corresponding radical-anion intermediate **2**. Depending on the electronic nature of the carboxylic-acids moiety or phthalimide moiety, the intermediate **2** undergoes cleavage of the N – O bond to produce carbon-centred radicals **3** ($\mathrm{R}^1\bullet$), N-centred radicals **5** (PhthN•) (Niu et al., 2020) or aryl carboxyl radicals **6** (Shih et al., 2019). In general, the intermediate **2** undergoes fragmentation of the N-O bond to generate a carbon-centred radical **3** ($\mathrm{R}^1\bullet$) with the extrusion of CO_2 and phthalimide anion **4** (Phth^-, path a). More electron-withdrawing substituents (R^1) with a carboxylic-acid moiety will enhance the leaving-group ability of the carboxylate anion, thereby intermediate **2** can release the N-centred phthalimide radical **5** (PhthN•) and carboxylate anion **6** (path b). Sometimes, under special conditions aryl carboxylic acids can enable the aryl carboxyl radicals **7** (path c) which furtherly release CO_2 and generate aryl radicals (Candish et al. 2017). Finally, the resulting carbon-centred radicals, aryl carboxyl radicals, aryl radicals, or N-centred radicals participate in formation of C-C and C-X bonds under thermal, electrochemical, and photolytic conditions (Scheme 1).



Scheme 1 Decarboxylation of NHPI esters.

3. Redox properties of NHPI esters

NHPI esters **1** are synthesised by carboxylic acids or corresponding acid chlorides and NHPIs. The different NHP-type esters are shown in Scheme 2 (Xia et al., 2020).



Scheme 2 Different NHP-type esters.

Great progress has been made regarding the utility of carboxylic acid-derived NHP-type esters as radical precursors in radical decarboxylative cross-coupling reactions. Phthalimide esters derivatives **1** and tetrachlorophthalimide esters derivatives (TCNHPI esters) **8** have been reported to participate in a multitude of transformations under visible-light or electrochemical conditions. Based on the cyclic voltammetry experiments of Bach and colleagues, the value of the potential of phthalimide esters **1** has been documented to be $E_{1/2} = -1.24$ to -1.37 V *vs.* SCE (Zhang et al., 2020) and the potential of the corresponding tetrachlorophthalimide esters **8** to be $E_{1/2} = -0.70$ to -0.54 V *vs.* SCE (Bosque et al. 2019). The potential of phthalimide esters **1** has been observed to be lower than the potential of the corresponding tetrachlorophthalimide esters **8**. Thus, TCNHPI esters appear to be beneficial for decarboxylation coupling. Besides **1** and **8**, Liu reported the value of the potential bench-stable N-hydroxy 2,3-naphthalimide-derived ester (**11**) to have an Ep value of – 1.174 V. Based on their experiments, compared with TCNHPI esters, the corresponding 2,3-naphthalimide esters as substrates had enhanced reaction efficiency and inhibited the side-dimerization products (Xia et al., 2020). Further study on the redox potential of NHPI esters is under progress.

4. Photoredox catalysis-mediated decarboxylative couplings of NHPI esters

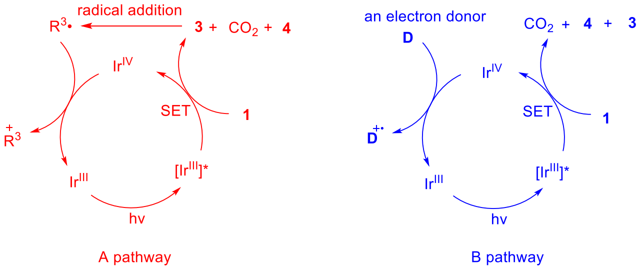
Visible-light photoredox catalysis has enabled novel approaches for the construction of carbon–carbon or carbon-heteroatom bonds under mild reaction conditions through high-energy intermediates such as carbon or heteroatom-centred radicals. Convenient photoredox catalysts such as ruthenium (Ru) complexes, iridium (Ir) complexes have been utilised in organic synthesis: they have remarkable excited-state lifetimes and visible-light absorption (Prier at al., 2013). In addition, the use of nickel (Ni) (Zhu et al., 2019) and copper (Cu) (Zhang et al., 2020) species as photocatalysts has been reported frequently. Organic photoredox catalysts can participate in photoinduced decarboxylative couplings, and we have categorised them under "transition-metal catalysis" and "metal-free catalysis", as detailed below. Each part has been further divided into subsections.

4.1. Transition-metal-mediated decarboxylative couplings of NHPI esters

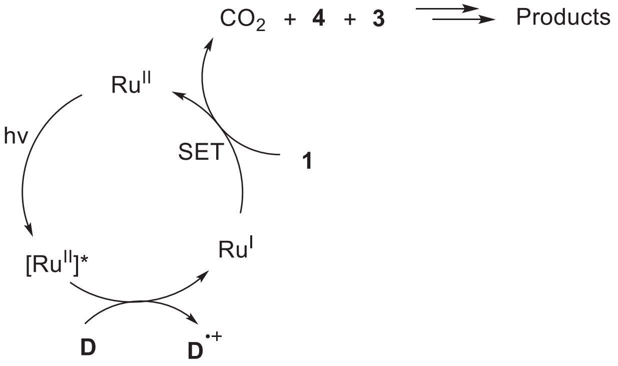
4.1.1. Ir/Ru-mediated coupling

Decarboxylative coupling of NHPI esters has been shown to occur readily under Ir/Ru-mediated photocatalysis. Alemán's group measured the redox potential of Ir/Ru-photoredox catalysts (*fac*-Ir(ppy)$_3$: $E_{1/2}^{IV/*III}$ = − 1.73 V *vs.* SCE; [Ru (bpy)$_3$]$^{2+}$: $E_{1/2}^{*II/I}$ = 0.77 V *vs.* SCE, $E_{1/2}^{II/I}$ = − 1.33 V *vs.* SCE; $E_{1/2}^{III/II}$ = 1.29 V *vs.* SCE, $E_{1/2}^{III/*II}$ = − 0.81 V *vs.* SCE) (Garrido-Castro et al., 2017) and redox active ester ($E_{1/2}$ = − 1.26 to − 1.37 V *vs.* SCE). They concluded that an Ir^{III} catalyst ($E_{1/2}^{IV/*III}$ = − 1.73 V, compared with $E_{1/2}$ = − 1.26 to − 1.37 V) and a Ru^{I} catalyst ($E_{1/2}^{II/I}$ = − 1.33 V, compared with $E_{1/2}$ = − 1.26 to − 1.37 V) could reduce the redox-active ester, but a Ru^{II} catalyst ($E_{1/2}^{III/*II}$ = − 0.81 V, compared with $E_{1/2}$ = − 1.26 to − 1.37 V *vs.* SCE) (Zheng et al., 2018) could not. Hence, *Ru^{II} had to accept one electron to generate its reduced form Ru^{I}. A Ru^{II}/Ru^{I} redox mechanism is feasible whereby the Ru^{I} reduces the redox-active ester to generate alkyl radicals, and an electron-donor reduces the excited *Ru^{II} to Ru^{I}. According to the results stated above and other investigations, a plausible mechanism for the Ir/Ru-catalysed decarboxylative is suggested in Schemes 3 and 4.

Under visible-light irradiation, Ir^{III} is converted to the excited state Ir^{III*}, which offers an electron to the NHPI ester. The radical anion of the NHPI ester undergoes fragmentation to produce an alkyl radical (**3**), the phthalimide anion (**4**), and CO$_2$. The alkyl radical (**3**), as an active intermediate, undergoes radical addition to form a new radical R^3•. The latter is oxidised by Ir^{III} to afford the alkyl cation $^+$R^3 and regenerates Ir^{III}. Finally, $^+$R^3 is trapped by a nucleophile to afford the desired product (Scheme 3, pathway A). When R^1 fails to reduce Ir^{IV} to Ir^{III}, the photocatalytic cycle is completed with reduction of the Ir^{IV} species by an extra electron-donor **D**, such as DIPEA (Scheme 3, pathway B) (Akita and Koike 2016).



Scheme 3 Mechanism of Ir -catalysed decarboxylative coupling.

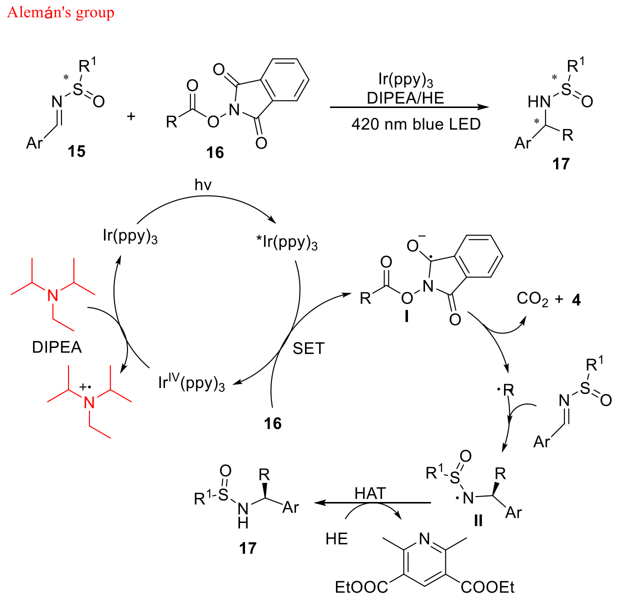


Scheme 4 Mechanism of Ru-catalysed decarboxylative coupling.

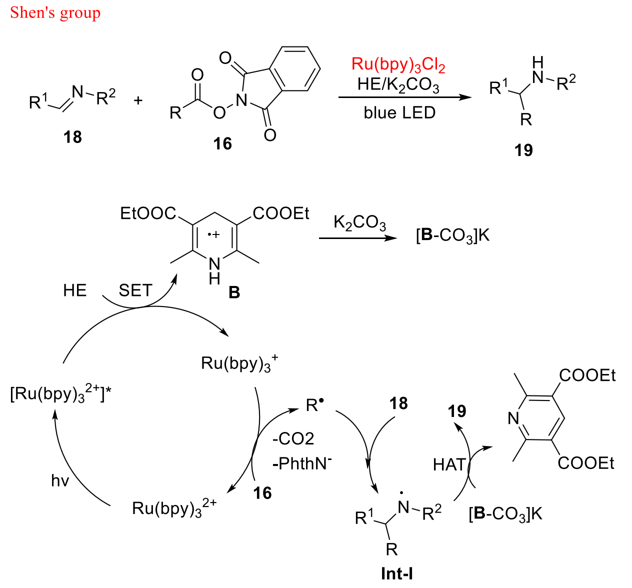
Under visible-light irradiation, Ru^{II} is converted to the excited state Ru^{II*}. The photoexcited Ru^{II*} obtains an electron from **D** to afford the radical cation **D**$^{•+}$ and Ru^{I}. As mentioned above, the redox potential of the photoexcited Ru^{II*} catalyst can enable reduction electron-donors **D** ($E_{1/2}^{*II/I}$ = +0.77 V, DABCO $E_{1/2}^{red}$ = + 0.6 V, DIPEA $E_{1/2}^{red}$ = +0.65 V, Hantzsch ester (HE), $E_{1/2}^{red}$ = +0.79 V) but reduction of NHPI esters cannot occur. Subsequently, Ru^{I} ($E_{1/2}^{II/I}$ = − 1.33 V *vs.* SCE in MeCN) delivers an electron to the NHPI ester ($E_{1/2}$ = − 1.26 to − 1.37 V *vs.* SCE) to give the alkyl radical **3** and regenerate Ru^{II}. Finally, the alkyl radical **3** participates in a multitude of transformations (Scheme 4) (Xu et al., 2017; Gao et al., 2016).

4.1.1.1. Formation of C-C bonds. 4.1.1.1.1. Formation of C (sp^3)- C(sp^3) bonds. Several research teams have designed convenient and efficient methods to construct new C-C bonds by utilising NHP-type esters. Under visible-light, carbon radicals generated from NHPI esters can undergo conjugated addition with alkenes to construct C(sp^3)–C(sp^3) bonds. This strategy provides an efficient and mild way to construct C (sp^3)–C(sp^3) bonds. In 2017, a photo-induced, Ir-catalysed, highly enantioselective alkylation of N-sulfinimines was described by Alemán et al. (Garrido-Castro et al. 2017). This was the first description of enantioselective photocatalytic addition to *N*-sulfinimines. In an initial experiment, they tested N-sulfinimines **15** with different radical donors, such as isobutyric acid and isopropyl oxalate, but this approach was unsuccessful. Gratifyingly, the reaction with NHPI esters gave rise to the desired product in an acceptable yield. A plausible mechanism is depicted in Scheme 5. The highly reducing excited *Ir (ppy)$_3$ species deliver one electron to NHPI esters, leading to Ir^{IV} and an anion radical **I**, which undergoes fragmentation to produce an alkyl radical R•, CO$_2$, and phthalimide **4**. Subsequently, R• undergoes radical addition with N-sulfinimines to afford the N-centred radical **II**. The latter abstracts one hydrogen atom from the HE *via* a hydrogen atom-transfer process, giving rise to sulfonamide **17**.

Subsequently, Shen group reported photoinduced decarboxylative coupling of NHPI esters with aldimines **18** to synthesise α-amino esters **19** in the presence of Ru(bpy)$_3$Cl$_2$ and



Scheme 5 Asymmetric radical addition of *N*-sulfinimines with NHPI esters.



Scheme 6 Decarboxylative radical addition of NHPI esters with aldimines.

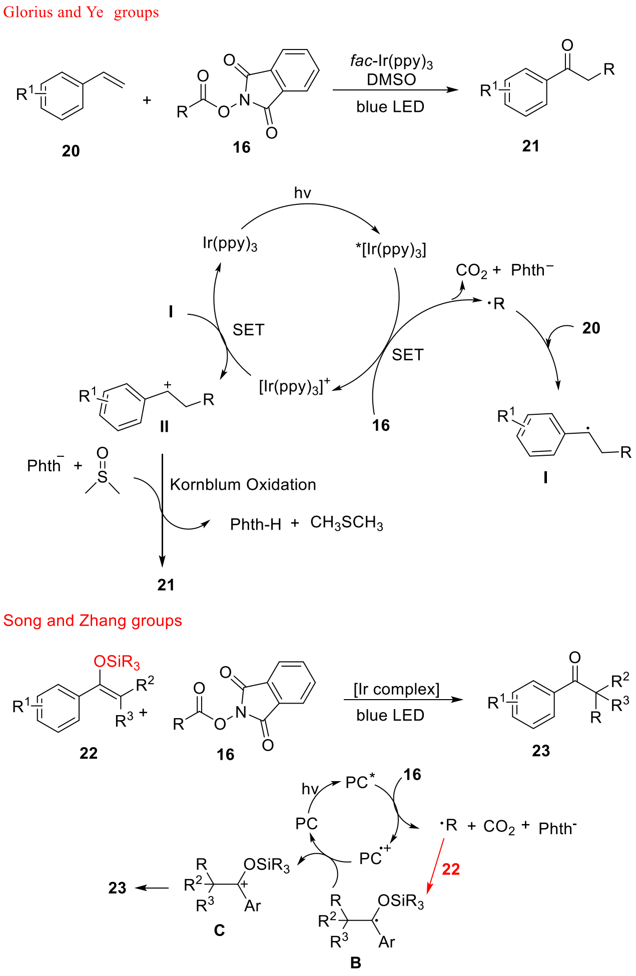
HE (Wang et al., 2020a,b,c). A computation study suggested that inorganic bases could suppress an umpolung side reaction and complete formation of the desired product. According to the proposed mechanism, the photo-excited [Ru(bpy)$_3^{2+}$]* is reduced by HE to generate the reduced form Ru(bpy)$_3^+$, which delivers one electron to **16** to afford an alkyl radical. The latter is trapped by **18** to provide the N-centred radical **Int-I**, which abstracts one hydrogen atom from the radical cation of HE **B** to generate products **19**. In fact, the reduced form Ru(bpy)$_3^+$, as the reductant delivers one electron to the NHPI ester, not Ru(bpy)$_3$Cl$_2$ (Scheme 6).

Later on, several research groups developed a decarboxylative radical conjugation addition between NHPI esters and electron-deficient carbon – carbon double bonds. In 2018, photoinduced radical addition of NHPI esters with styrenes was disclosed by Glorius, and Ye (Tlahuext-Aca et al., 2018; Xia et al., 2018). They documented photoinduced decarboxylative coupling of NHPI esters with a wide range of styrenes for synthesising α-alkyl-acetophenones in good yields. Based on their assays and the literature reports, dimethyl sulfoxide as a mild terminal oxidant, was found to be important for this transformation. After accepting one electron from photo-excited **fac*-Ir(ppy)$_3$, NHPI esters **16** followed by decarboxylation offer a reactive alkyl radical R•, which adds to the styrene **20** to deliver a new benzyl radical **I**. The generated [*fac*-Ir(ppy)$_3$]$^+$ ($E_{1/2}^{IV/III}$ = +0.77 V *vs.* SCE in MeCN) oxidised intermediate **I** (E^{ox} = +0.37 V *vs.* SCE in MeCN) to give rise to the carbocation **II**, which is oxidised by DMSO *via* a Kornblum-type mechanism to afford the desired α-alkyl-acetophenone product (Scheme 7). Simultaneously, Song and Zhang documented a cross-coupling of silyl enol ethers with NHPI esters to furnish diverse functionalized aryl alkyl ketones in optimum yields (Kong et al., 2018; Song et al., 2020). The proposed mechanism is similar to that reported by Glorius and co-workers (Tlahuext-Aca et al., 2018). Mechanistically, the corresponding alkyl radical derived from NHPI esters was trapped by silyl enol ether to deliver a new alkyl radical **B**, which is oxidised by the photocatalyst to form a carbon cation species **C**. Finally, the intermediate **C** undergoes desilylation to produce the desired ketone **23** (Scheme 7).

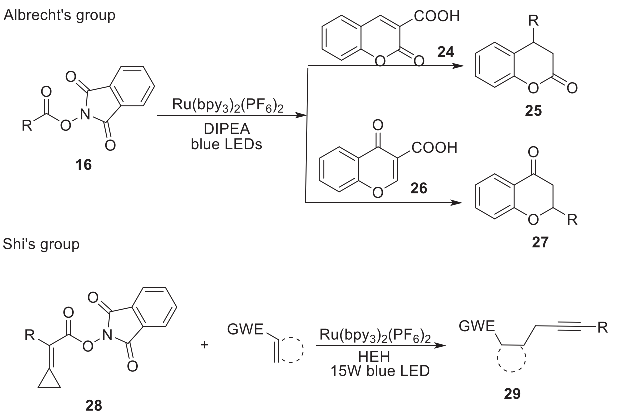
Meanwhile, Albrecht developed a doubly decarboxylative photocatalytic Giese reaction toward synthesis of 4-substituted-chroman-2-ones **25** and 2-substitutedchroman-4-ones 27 utilizing NHPI esters and chromone-3-carboxylic acids derives (**24**, **26**) (Moczulski et al., 2021). Simultaneously, Shi's group provided a new synthetic route for preparation of a variety of alkynyl derivatives **29** through a coupling of NHPI esters bearing alkylidenecyclopropanes (ACPs) **28** with electron-deficient alkenes (Zhang et al., 2021a,b). This new synthetic routes inspired by a practical classical ring-opening radical clock reaction. The radicals derived from **28** undergo the ring-opening, radical rearrangement to generate the corresponding radical species containing an alkynyl moiety and subsequently added to electron-deficient alkenes to form the functionalized alkyne **29** (Scheme 8).

Styrene is a key synthon in many synthetic transformations. Difunctionalisation of alkenes (which can introduce two chemical bonds in one step) is a powerful tool in this regard (Li et al., 2020). Recently, much attention has been paid to the photoredox transformation of NHPI esters by means of a strategy based on three-component alkene difunctionalisation because it increases the molecular complexity rapidly in one step. In 2017, Glorius and co-workers developed an Ir-catalysed oxyalkylation of styrenes using NHPI esters as the radical precursor and water or primary alcohols as a nucleophile (Tlahuext-Aca et al., 2017). With the aid of visible-light photoredox catalysis, the NHPI ester decomposes and affords the alkyl radical, CO$_2$, and phthalimide anion. The alkyl radical undergoes radical conjugate addition on styrenes to form a new alkyl radical **I**, which is oxidised subsequently by [Ir(ppy)$_2$(dtbbpy)]$^{2+}$ to afford the alkyl cation intermediate **II** and leads to regeneration of the ground-state photocatalyst. Finally, the intermediate **II** is trapped by water or primary alcohols to afford the oxyalkylated product **30** (Scheme 9).

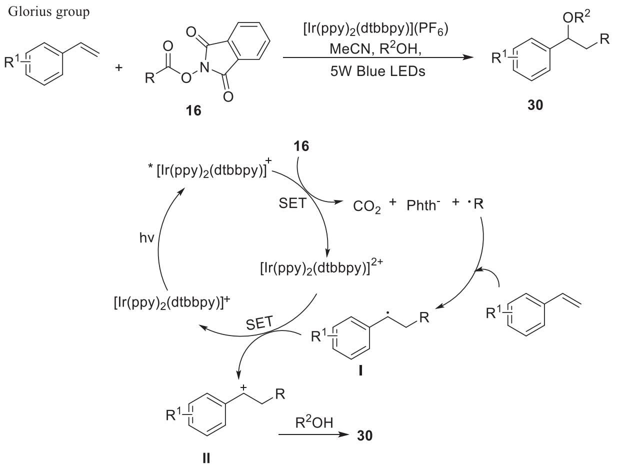
In 2018, Li et al. (Ouyang et al. 2018) reported a Ru- catalysed 1,2-alkylamination of styrenes **31** with NHPI esters **16**



Scheme 7 Photoinduced synthesis of α-alkyl-acetophenone.



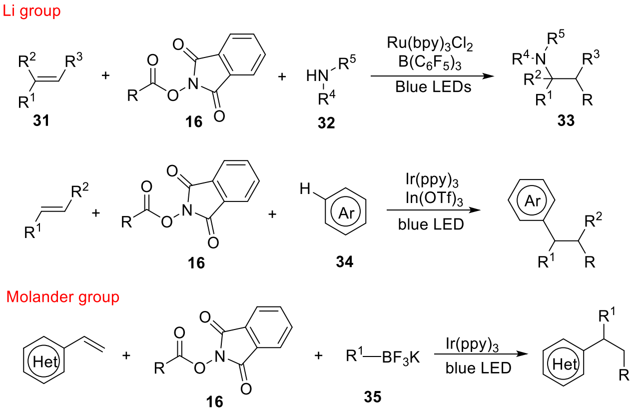
Scheme 8 Conjugate additions of NHPI esters to electron-deficient alkenes.



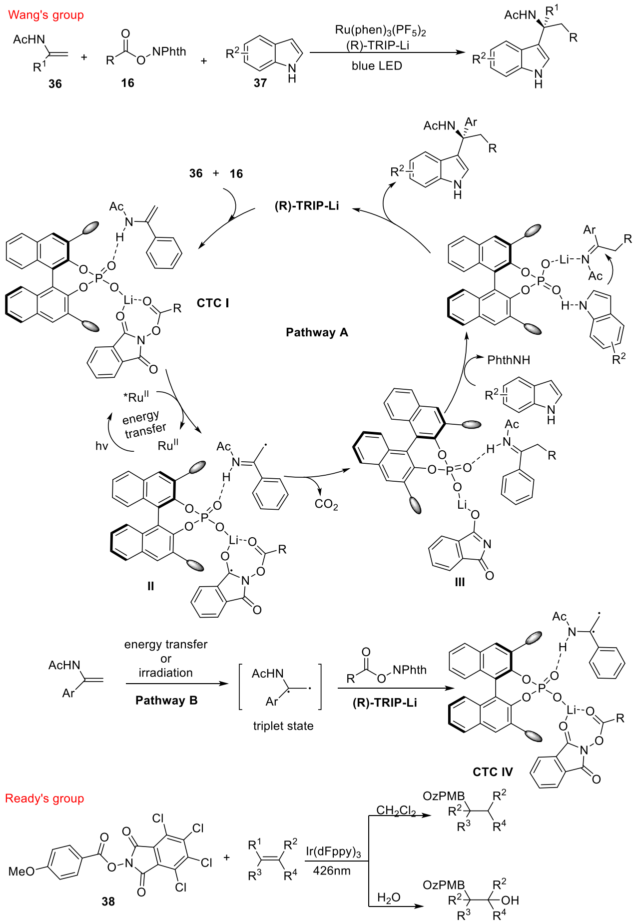
Scheme 9 Multicomponent oxyalkylation of styrenes.

and amines **32** as a nucleophile. This methodology features high selectivity and a broad scope of substrates with excellent tolerance of functional groups. The mechanism of this transformation is similar to the mechanism discussed in Scheme 9. Under visible-light irradiation, the alkyl radical generated from **16** adds to the styrenes **31** to deliver a new alkyl radical. This reactive species is then oxidised by the reduced form Ru^{III} to afford an alkyl cation intermediate, which reacts with the nucleophilic amines **32** to offer the desired product **33**. Following this study, several nucleophiles were developed by Li and Molander; indoles **34** and potassium organotrifluoroborate salt **35** were applied as nucleophiles in this methodology, respectively (Scheme 10) (Wang et al., 2019; Cabrera-Afonso et al., 2021).

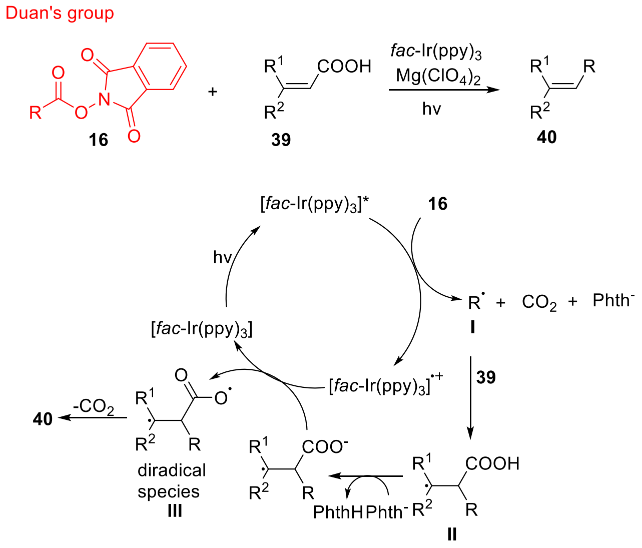
In 2020, Wang and colleagues demonstrated an asymmetric alkylarylation of enamides **36** with NHPI esters and indoles **37** (Shen et al., 2020). Mechanistic studies suggested that the chiral lithium phosphate **(R)-TRIP-Li**, enamide **36**, and NHPI esters **16** coordinated a charge-transfer complex (**CTC**, **I**), which could be excited by direct irradiation or the catalyst Ru^{II} to provide intermediate **II** *via* electron transfer from the enamide to NHPI esters (Scheme 11, pathway A). In pathway B, after direct irradiation or energy transfer, the triplet state of enamide reacted with chiral lithium phosphate and NHPI to give complex **CTC IV**, which also underwent electron transfer to generate the intermediate **II**. The latter underwent decarboxylation and radical recombination to afford the intermediate **III**. Finally, intermediate **III** reacted with indoles **37** to furnish alkylarylation of enamides. This mechanism is different from the mechanisms described in the studies of the research teams of Glorius, Li, and Molander. Recently, Ready



Scheme 10 Difunctionalisation of alkenes with NHPI esters and nucleophiles.



Scheme 11 Difunctionalization of Olefins.



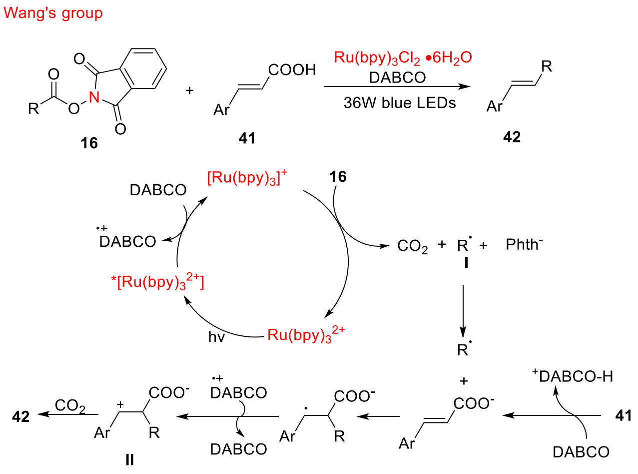
Scheme 12 Dual-decarboxylative alkyl–vinyl cross-coupling.

et al. (Leng et al. 2021) presented a regioselective, anti-Markovnikov hydroesterification of unactivated olefins using aryl N-(acyloxy)phthalimides **38**. In the presence of added water, it observed difunctionalization of olefins (Scheme 11).

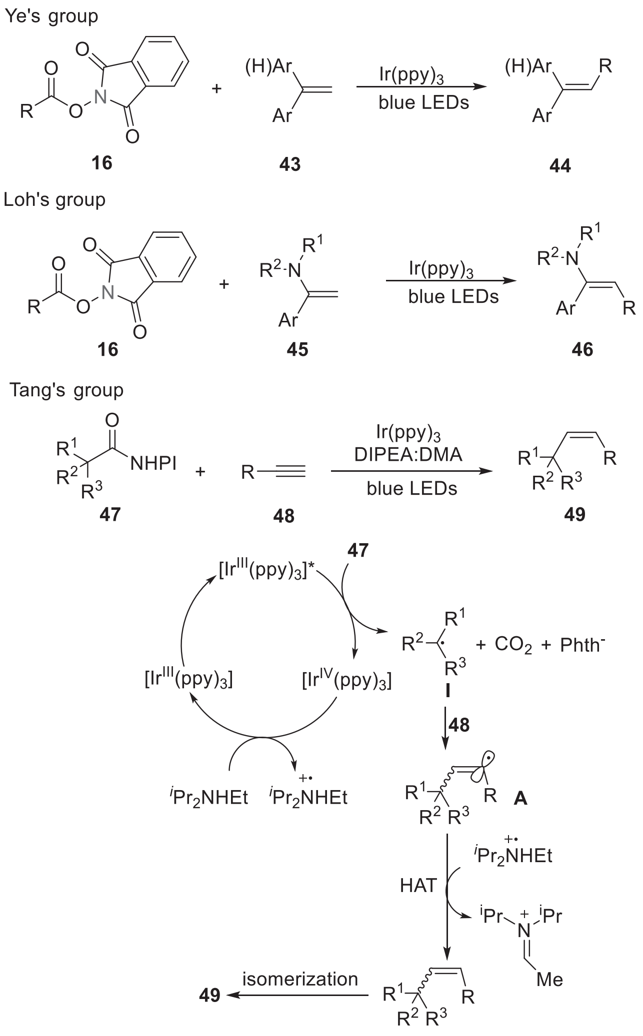
4.1.1.1.2. Formation of C(sp^3)-C(sp^2) bonds and C(sp^3)-C (sp) bonds. Inspired by the formation of Csp^3-Csp^3 bonds using NHP esters as an alkyl source, a novel alkyl–vinyl cross-coupling reaction was developed by Duan, Wang, Ye, Loh and Tang (Zhang et al., 2017a,b; Xu et al., 2017; Xia et al., 2018; Guo et al., 2019; Dai et al., 2019). A diverse range of NHPI esters derived from primary, secondary, and tertiary carboxylic acids provided the corresponding substituted alkene products in moderate-to-excellent yields. In 2017, Duan and co-workers developed a photoinduced dual-decarboxylative alkenylation of α,β-unsaturated carboxylic-acids **39** and NHPI esters, which provided a photocatalytic strategy to synthesise substituted alkenes (Zhang et al., 2017a,b). Based on previous reports, the excited-state [Ir(ppy)$_3$]* facilitates decarboxylative fragmentation to form an alkyl radical R• (**I**). Addition of the alkyl radical **I** to the α,β-unsaturated carboxylic acids generates a new radical **II**. Then, deprotonation and oxidation give the diradical species **III**. The iradical species **III** is oxidised by [Ir(ppy)$_3^+$] and then releases CO$_2$ to deliver the desired product **40** (Scheme 12).

Simultaneously, Wang and co-workers documented a Ru-catalysed decarboxylative alkyl–vinyl cross-coupling between alkenyl carboxylic acids **41** and NHPI esters (Xu et al., 2017). Analyse of the redox potential of Ru-photoredox catalyst (shown in section **4.1.1.1**) showed that the Ru$^{\mathrm{I}}$ is sufficiently strong to reduce the NHPI ester ($E_{1/2}^{\mathrm{II/I}}$ = –1.33 V compared with $E_{1/2}$ = –1.26 to –1.37 V *vs*. SCE), so a Ru$^{\mathrm{II}}$/Ru$^{\mathrm{I}}$ redox mechanism is suitable. The general mechanism is depicted in Scheme 13. The reaction is initiated through generation of highly reducing [Ru(bpy)$_3$]$^+$, which fragments the NHPI ester to generate the alkyl radical **I**. The latter follows a pathway similar to the one described above, and affords the benzylic cation **II**. Finally, the desired olefin product **42** is generated through a decarboxylative-elimination process (Scheme 13).

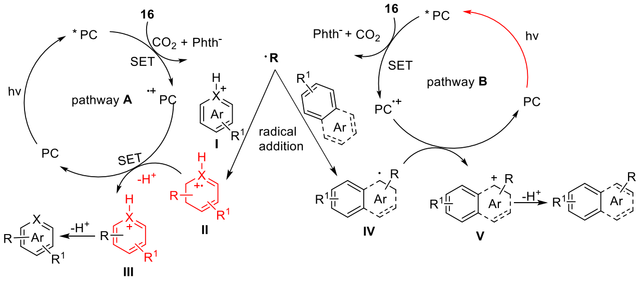
An alternative way to achieve alkenylation of NHPI esters was achieved independently by several research groups exploiting decarboxylative coupling of NHPI esters with various alkenes or alkynes (Scheme 14). Ye and Loh explored the alkyl radicals generated from NHPI esters coupled with various alkenes (**43**, **45**) to achieve the corresponding alkenylation products (**44**, **46**) (Xia et al., 2018; Guo et al., 2019). Dai et al. reported a decarboxylative coupling of NHPI esters **47**



Scheme 13 Photoinduced decarboxylative alkenylation of NHPI esters with alkenyl carboxylic acids.



Scheme 14 Photoinduced decarboxylative alkenylation of NHPI esters with alkenes or alkynes.



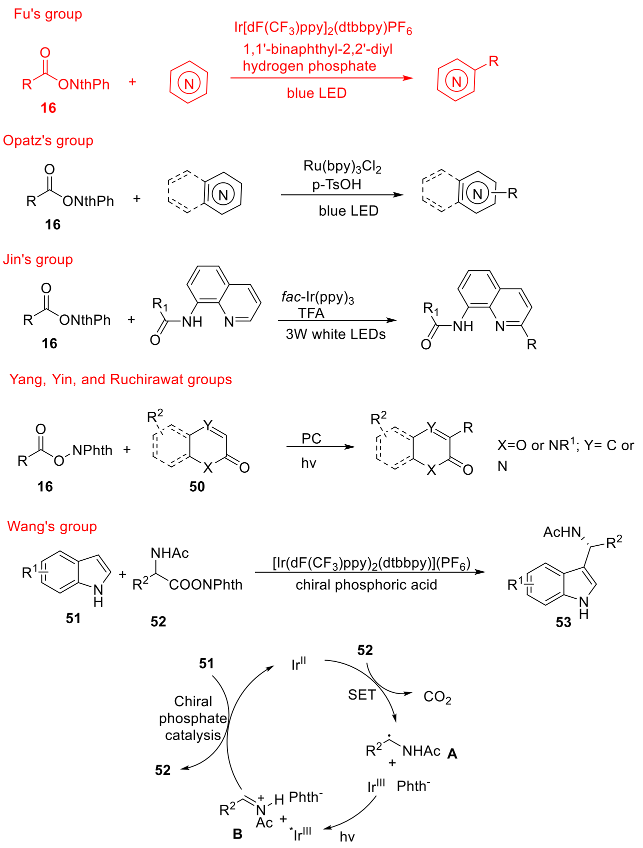
Scheme 15 Mechanisms for Minisci-type alkylation of NHPI ester.

with terminal arylalkynes **48** for the synthesis of Z alkenes **49** (Dai et al., 2019). The methodology presented showed a broad scope of substrates with regard to arylalkyne components and carboxylic acid. The photo-excited state catalyst, through oxidative quenching, delivers the alkyl radical **I** and then is oxidised to the reductive formation of Ir^{IV}. Then, the Ir^{IV} species is reduced to Ir^{III} to complete the photocatalytic cycle by a SET process from DIPEA. Meanwhile, the alkyl radical **I** adds to the terminal alkyne **48** to offer the vinyl radical **A**, which abstracts one hydrogen atom from DIPEA$^{\bullet +}$ to form Z (E) alkenes **B**. Finally, isomerisation of **B** gives Z-alkenes **49** (Scheme 14).

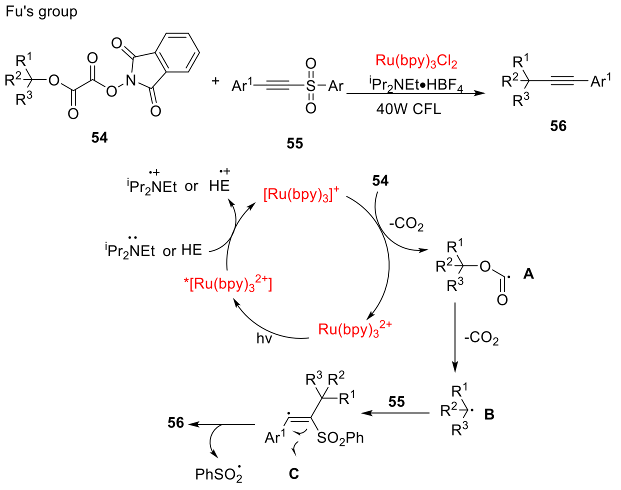
Quinoxalin-2-ones and coumarins are common structural motifs. They are found widely in natural products, and their synthesis has attracted considerable attention (Srikrishna et al., 2018). Some classical reactions have been developed: redox-neutral cross-coupling reactions, and oxidative arylations (especically the Minisci reaction). Very recently, Minisci-type alkylation of these heteroaromatic compounds employing an alkyl radical generated from NHPI esters under mild redox-neutral conditions was developed by the research teams of Opatz, Phipps, Yang, Yin and Jin (Kammer et al., 2018; Reid et al., 2019; Jin et al., 2019; Liu et al., 2019a,b; Sun et al., 2020a,b). A stoichiometric amount of a BrØnsted acid or catalytic amount of Lewis acid has crucial roles in these transformations. On the basis of those reports, two mechanisms for a Minisci-type alkylation are shown in Scheme 15. Under visible light irradiation, the redox-active ester is one-electron reduced by the photoexcited catalyst to give the radical intermediate R•. This resulting radical R• is tracked by a protonated heteroarene **I** to generate adduct **II**, which is oxidized further to the carbocation intermediate **III** by PC$^{\bullet +}$. Intermediate **III** can deliver the desired product immediatedly through a deprotonation process (Scheme 14, pathway A) (Cheng et al. 2017a,b; Kammer et al., 2018). In the case of pathway B, this alkyl radical R• then undergoes addition to a heteroarene and follow-up oxidation to provide **IV**. The final product is delivered by successive deprotonation (Scheme 14, pathway B) (Jin et al., 2019).

In 2018, Fu, Opatz and Jin demonstrated that an Ir/Ru photocatalyst in combination with a Lewis acid could catalyse the decarboxylative alkylation of N-heteroarenes using NHPI esters (Cheng et al. 2017a,b; Kammer et al., 2018; Sun et al., 2020a,b). The Lewis acid was employed for activation of heteroarenes to afford a protonated heteroarene, therby facilitating the nucleophilic attack of the alkyl radical. The general mechanistic cycle is similar to the mechanisms discussed in pathway A of Scheme 15. Subsequently, Yang, Yin and Ruchirawat independently developed a 3-position alkylation of non-aromatic heterocycles **50** such as coumarins, quinolinones, and quinoxalinones, thereby providing convenient access to the corresponding medicinally important motifs (Jin et al., 2019; Liu et al., 2019a,b; Niwetmarin et al., 2021). The catalysis mechanism is similar to the mechanisms discussed in pathway B of Scheme 15. Furthermore, this protocol features a broad scope of substrates and good tolerance of functional group. Subsequently, Wang and co-workers established an asymmetric Friedel-Crafts reaction of indoles derives **51** and α-amino acid-derived NHPI esters **52**, which is different from the Minisci reaction (Shen et al., 2019). Under irradiation, Ir^{III*} oxidised the α-aminoalkyl radical **A** derived from NHPI esters to afford the protonated N-acyl imine **B**. Finally, indole derives **51** attack the imine **B** to afford the asymmetric products **53** in the presence of chiral phosphate (Scheme 16).

Traditionally, formation of C(sp^3)-C(sp) bonds is through Pd/Cu-catalysed Sonogashira couplings of terminal alkynes with halides. Recently, visible-light photoredox catalysis has emerged, and great achievements have been made for photoredox decarboxylative alkynylation of carboxylic acids and their derivatives. In 2016, Fu et al. (Gao et al. 2016) revealed a Ru-catalysed alkynylation using NHPI esters **54** and 1-(2-(arylsul



Scheme 16 Alkylation of heteroarenes and non-aromatic heterocycles.

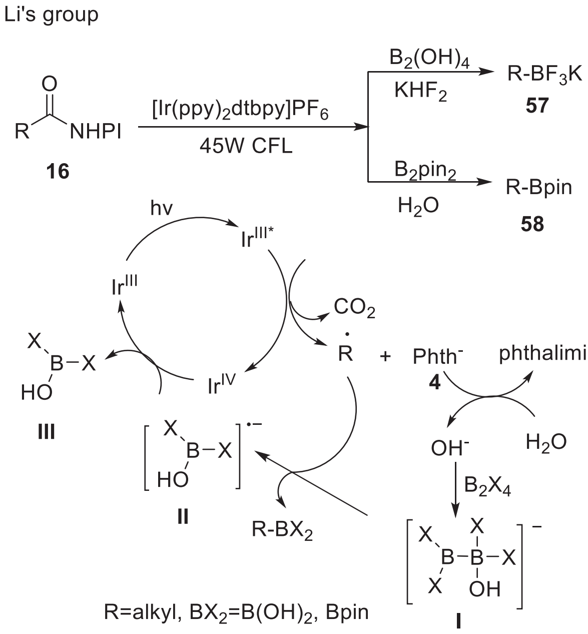


Scheme 17 Decarboxylative alkynylation of NHPI esters.

fonyl)ethynyl)benzenes **55**. This reaction was efficient for constructing a series of internal alkynes **56** containing quaternary carbons. They proposed that the photoexcited *Ru(bpy)$_3^{2+}$ is quenched reductively by HE, and thereafter transfers one electron to NHPI esters **54** to provide a carbonyl radical **A** and to regenerate the catalyst Ru(bpy)$_3^{2+}$. The alkyl radical **B** undergoes regioselective addition on 1-(2-(arylsulfonyl)ethynyl)benzenes **55** to generate a vinyl free radical **C**, after releasing a second molecule of carbon dioxide. Finally, the resulting radical **C** eliminates an aryl sulfonyl radical *via* homolytic cleavage of the C-S bond to provide the desired product **56** (Scheme 17).

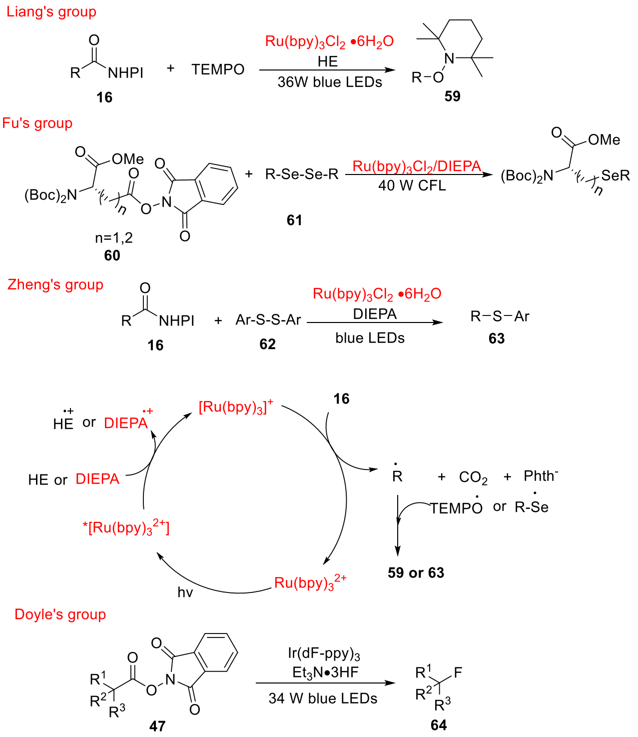
4.1.1.2. Formation of C-X bonds. Decarboxylative transformation is a powerful tool for the construction of carbon-heteroatoms. It has garnered considerable attention for the organic synthesis of bioactive molecules and functional materials. In particular, the rapid development of photo-catalysed reactions enables a series of diverse decarboxylative transformations of NHPI esters: decarboxylative borylation, thiolation, selenylation, oxygenation, and fluorination. In 2017, Li et al. reported the conversion of carboxylic acids into pinacol boronates **58** and tetrafluoroborates **57** (Hu et al. 2017). They described an Ir-mediated decarboxylative borylation between redox-active NHPI esters and bis(pinacolato)diboron or tetrahydroxydiboron. The method tolerated various primary and secondary carboxylic acid-derived NHPI esters. However, tertiary carboxylic acid-derived NHPI esters and aryl acid-derived NHPI esters provided only trace yields. A plausible mechanism is outlined in Scheme 18. Initially, a SET from photoexcited Ir^{III*} triggers reductive fragmentation of NHPI esters **16** to generate alkyl radicals and the phthalimide anion **4**. Subsequently, the **4** extracts hydrogen from water to generate the hydroxide ion that thereafter reacts with the boron source B_2X_4 to give borate **I**. Finally, the borate **I** reacts with an alkyl radical to generate an alkyl-boron compound (**57**, **58**) and boryl radical anion **II**, which reduces Ir^{IV} species and regenerates the catalyst Ir^{III} (Scheme 18).

Contemporaneously, Liang and co-worker documented a novel Ru-induced decarboxylative aminoxylation of NHPI esters with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (Zheng et al. 2018). A diverse range of primary, secondary, tertiary, α-amino, and α-hydroxy alkyl-NHPI esters participated in this process to afford the corresponding alkoxyamines. Analyses of the redox potential of Ru^{II} suggested that the transformation undergoes a Ru^{II}/Ru^{I} redox mechanism in which Ru^{I} is stronger than *Ru^{II} in terms of reducing N-(acyloxy)phthalimide. Thus, a photoexcited *Ru^{II} catalyst is reduced by HE in a SET process to generate Ru^{I}, which reduces **16** to give alkyl radicals. The resulting radicals are trapped by TEMPO to afford corresponding alkoxyamines **59**. Fu group reported photoredox coupling between the amino acid-derived NHPI esters **60** and diphenyl diselenide **61** to provide selenodipeptide (Jiang et al., 2016). Coded proteinogenic amino acids, and natural α-amino acids (e.g. glutamic acid and L-aspartic acid) were tolerated. Besides decarboxylative borylation, oxygenation, and selenylation, decarboxylative thiolation (Xiao et al., 2020) and fluorination (Webb et al., 2020) were developed by Zheng and Doyle. In 2020, Zheng and co-workers developed visible light-induced decarboxylative arylthiolation of NHPI esters derived from alkyl carboxylic acids or amino acids with diaryl disulfides **62**. DIPEA served as a reductant, and had crucial roles in this process. DIPEA transfers one electron to the excited-state Ru^{II} to furnish Ru^{I}. Then, the latter reduces the NHPI ester and affords alkyl radicals, which react with diaryl disulfide **62** to provide diverse aryl alkyl sulfides **63**. Simultaneously, Doyle group reported a novel method for fluorination of NHPI esters. The strategy was applied successfully to the synthesis of alkylated fluorides, including tertiary benzylic fluorides and unactivated tertiary fluorides. Use of alkylated fluorides is less likely to be successful because the benzylic/tertiary car-



Scheme 18 Iridium photoredox-catalysed synthesis of alkyl boronates and tetrafluoroborates.

bocation tends to be eliminated during nucleophilic fluorination. Mechanistic investigations showed that the fluorination proceed a two-electron-transfer between the Ir catalyst and NHPI esters. First, NHPI esters undergo a single-electron transfer to afford a carbon-centred radical. Then, the resulting radical intermediate is oxidised by the photocatalyst Ir^{IV} to afford the photocatalyst Ir^{III} and a carbocation, which becomes trapped by the fluoride anion to provide the desired alkyl fluoride **64** (Scheme 19).

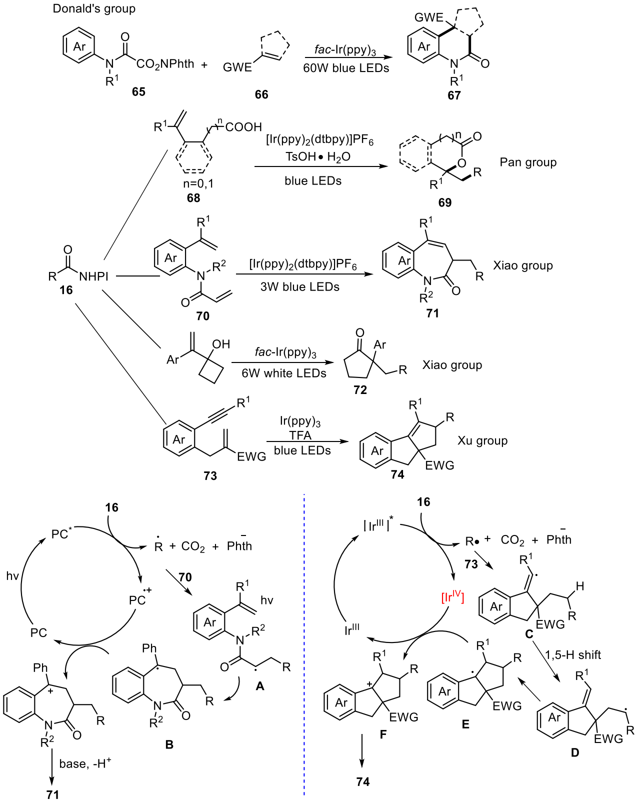


Scheme 19 C-X decarboxylative coupling of NHPI esters.

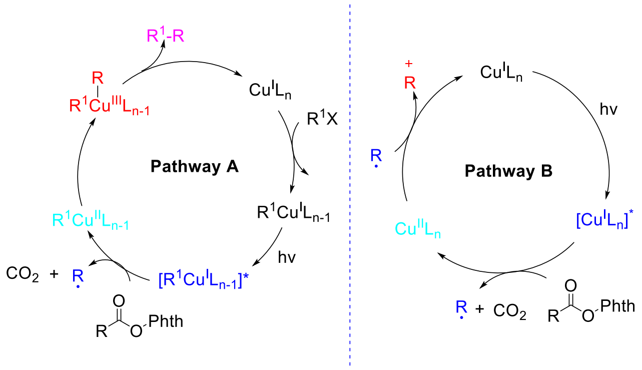
4.1.1.3. Cascade annulations. Alkyl radicals from NHPI esters undergo a cascade process involving intramolecular radical addition, cyclisation, migration, or deprotonation, to provide heterocycles or carbocycles in good yield. An interesting consecutive radical cascade annulation between NHPI esters and broad substrates containing unsaturated bonds (Petersen et al., 2017; Sha et al., 2017) was developed by Petersen and Sha. In 2017, Donald group documented an intermolecular addition/cyclisation coupling between N-hydroxyphthalimido oxamides **65** and electron deficient olefins **66** towards the synthesis of 3,4-dihydroquinolin-2-ones **67** (Petersen et al., 2017). The carbamoyl radical from **65** is added to the electron-deficient alkene **66** to form the electrophilic conjugate radical which, upon addition and cyclisation, delivers the 3,4-dihydroquinolin-2-one product **67**. Concomitantly, this strategy has been applied to the synthesis of alkyl substituted lactones **69** by Pan group. They reported Ir photoredox-catalysed alkylation/lactonisation cascade annulation of the unsaturated carboxylic acid **68** with NHPI esters **2**. The reaction features a range of alkenoic acids **68** as well as primary, secondary, and tertiaryl alkyl carboxylic redox esters. Thereafter, Xiao and co-worker (Zhao et al., 2018) developed an Ir-catalysed alkyl radical addition cascade annulation of NHPI esters **2** with acrylamide-tethered styrenes **70** to deliver benzazepine derivatives **71**. The process was initiated through the generation of alkyl radicals R• from NHPI esters under excited-state *fac*-Ir(ppy)$_3$*. Subsequently, the radical R• undergoes a chemoselective radical addition cascade to afford a stable benzyl radical **B** which upon oxidation and hydrogen abstraction, furnishes the desired product **71**. Xiao group also developed tandem alkyl radical addition/semipinacol rearrangement reactions toward cyclic ketones **72** (Yao et al., 2018). Recently, Xu and co-workers developed an Ir photoredoxcatalysed [2 + 2 + 1] cascade annulation of 1,6-enynes **73** with NHPI esters for the synthesis of indene-containing polycyclic frameworks **74** (Jiao et al., 2019). The reaction was triggered by the photoinduced SET reduction of the NHPI by the excited state Ir^{III*} to generate the radical R• and oxidising-state Ir$^{IV\bullet+}$. The resulting R• undergoes an intermolecular addition and intramolecular cyclisation process to form the vinyl radical **C**. Due to the reactivity and instability of vinylic radicals, an intramolecular 1,5-H atom shift occurs to generate a second radical **D**, which undergoes intramolecular cyclisation and oxidation to produce cationic **F**. Finally the desired product **74** is delivered through a deprotonation process (Scheme 20).

4.1.2. Cu-mediated coupling

Copper salts have become popular materials as photoredox catalysts due to their abundance, low cost, and ability to provide strong photoexcited reducing power (Zhang et al., 2021a, b). Copper salts have special roles in promoting the transfer of electrons to organic substrates as an attractive alternative to Ru or Ir photocatalysts. One area in which copper salts have potential utility is photoredox-catalysed decarboxylative coupling of redox-active esters. The redox process startes with a SET from the photoexcited Cu^{I*}or RCu^{I*} to NHPI esters. Cu^{I} is one-electron oxidised to Cu^{II} and NHPI esters are reduced to the corresponding radical (R•) with the release of



Scheme 20 Cascade annulations involving NHPI.



Scheme 21 Mechanisma of copper-catalysed photoinduction.

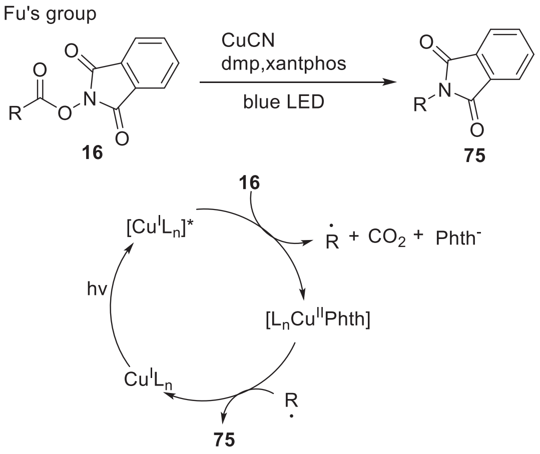
CO_2. Rejoining of Cu^{II} and the internal radical (R•) provides a Cu^{III} complex, which undergoes reductive elimination to deliver products R^1-R with regeneration of the Cu^I catalyst (Scheme 21 pathwayA) (Zhang et al., 2020). Alternatively, R• is oxidised to a cationic intermediate R^+, along with regeneration of Cu^I. Then, R^+ participates in a multitude of transformations (Scheme 21 pathway B) (Lyu et al., 2019).

In 2017, Fu and co-workers reported a photoinduced, copper-catalysed decarboxylative $C-N$ coupling that provides an alternative to the classic Curtius rearrangement (Zhao et al., 2017). The methodology features a wide scope of substrates and good acceptance of functional groups. A dual-ligand catalyst system consisting of 2,9-dimethyl-1,10-phenanthroline(dmp) and xantphos along with a CuCN catalyst was key to the success of the reaction. Under visible light irradiation, the coupling is initiated through the oxidative quenching of the photo-excited Cu^I by the NHPI ester to give Cu^{II} and radical R•. Finally, recombination of R• and a Cu^{II} – phthalimide complex affords the C–N coupling product **75** and regenerates the Cu^I complex. According to this mechanism, the Cu-based catalyst has a dual role both photosensitiser for SET and a catalyst for formation of $C-N$ bonds (Scheme 22).

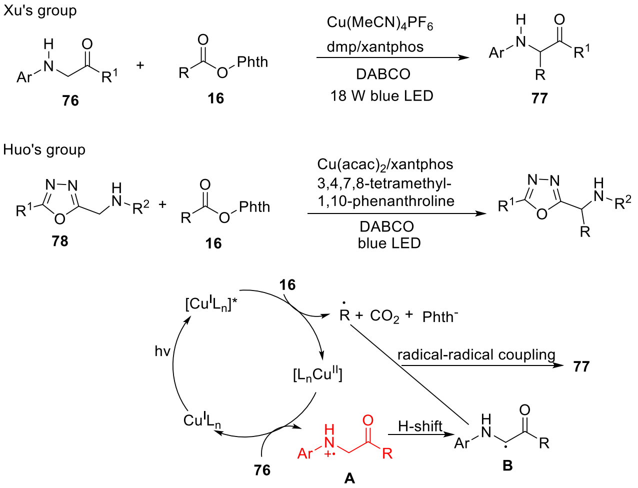
In 2018, Xu and co-workers disclosed Cu-catalysed decarboxylative $C(sp^3)$-H alkylation of glycine derivatives and peptides **76**. The mechanistic study revealed a radical–radical coupling pathway (Wang et al., 2018a,b). The photo-excited Cu^{I*} transfers one electron to **16** to trigger reductive disintegration, thereby leading to an alkyl radical R• and a Cu^{II} intermediate. The resulting Cu^{II} intermediate then oxidises glycine derivatives to the radical cation intermediate **A**, along with regeneration of Cu^I. Under basic conditions, a subsequent deprotonation and 1, 2-H-shift forms a stable a-carbon radical **B**, which couples with R• to construct an alkyl-alkyl cross-coupling product **77**. Along these lines, Huo et al. disclosed a similar $C(sp^3)$-H alkylation between NHPI esters and heteroaryl methenamine derivatives **78** (Scheme 23) (Niu et al 2021).

In 2019, Wang and co-workers developed copper-catalysed decarboxylative $C(sp^3)-H$ heteroarylation between NHP esters **16** and N-heteroarenes **79** (Lyu et al., 2019). Under visible light irradiation, $[Cu(dmp)(xantphos)]BF_4$ formed *in situ* serves as the photoactive species, and is excited to $*[Cu(dmp)(xantphos)]BF_4$, which transfers a single electron to the NHPI ester **16** to generate an alkyl radical intermediate **A**. The Lewis acid cocatalyst enhances the reactivity of the heteroarene, which is attacked by the alkyl radical **A** to give an aromatic substitution intermediate **B**. Subsequently, **B** is oxidized by Cu^{II} to generate the intermediate **C** and regenerate Cu^I. By means of dehydroaromatization, **C** delivers the desired product **80** (Scheme 24).

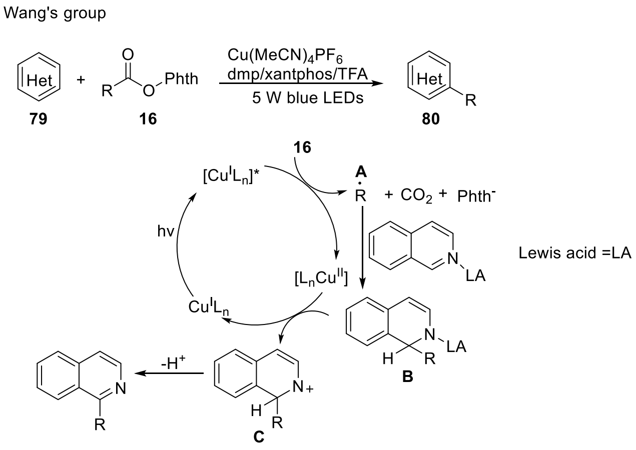
Later on, several research groups developed photoinduced copper-catalysed decarboxylative alkenylation and alkynylation, thereby providing a new powerful platform to construct C-C unsaturated bonds. Recently, a copper-catalyzed decarboxylative alkenylation was carried out by Lu group using α, β-unsaturated carboxylic acids and NHPI esters. This transformation enabled vinyl bond formation and afforded a variety of valuable alkene derivatives (Lu et al., 2021). In 2020, Zhang and Pan groups demonstrated $C(sp^3)$-C(sp) coupling of terminal alkynes (**82**,**84**) with NHPI esters (**81**, **16**) (Zhang and Zhang, 2020; Mao et al., 2020). According to the literature and density functional theory (DFT) calculations, in the presence of a base, the alkyne reacts with the Cu^I salt to afford photosensitive Cu^I-acetylide **A,** which is irradiated to excited state $*Cu^I$-acetylide **A***. Subsequently, the **A*** undergoes a SET process with an NHPI ester, leading to an alkyl radical **B** and Cu^{II}-acetylide **C**. Then, **B** combines with **C** to provide an alkylcopper(III) species **D**, which undergoes reductive elimination and subsequently delivers the cross-coupling product (**83**, **85**) along with the regeneration of Cu^I species. Following the report from Zhang group, Liu et al. (Xia et al. 2020) applied this methodology towards the synthesis of the chiral alkynes (**88**). They disclosed copper-catalysed asymmetric decarboxylative alkynylation of NHPI esters **86** with terminal alkynes (**87**) utilizing chiral cinchona alkaloid-derived N, N, P-ligand. This methodology exhibits a broad scope and tolerance of functional groups. The investigations stated above suggest that the copper-induced catalytic cycle has key roles as a pho-



Scheme 22 Photoinduced, Cu-catalysed decarboxylative C – N coupling.



Scheme 23 Decarboxylative C(sp^3)-H alkylation.

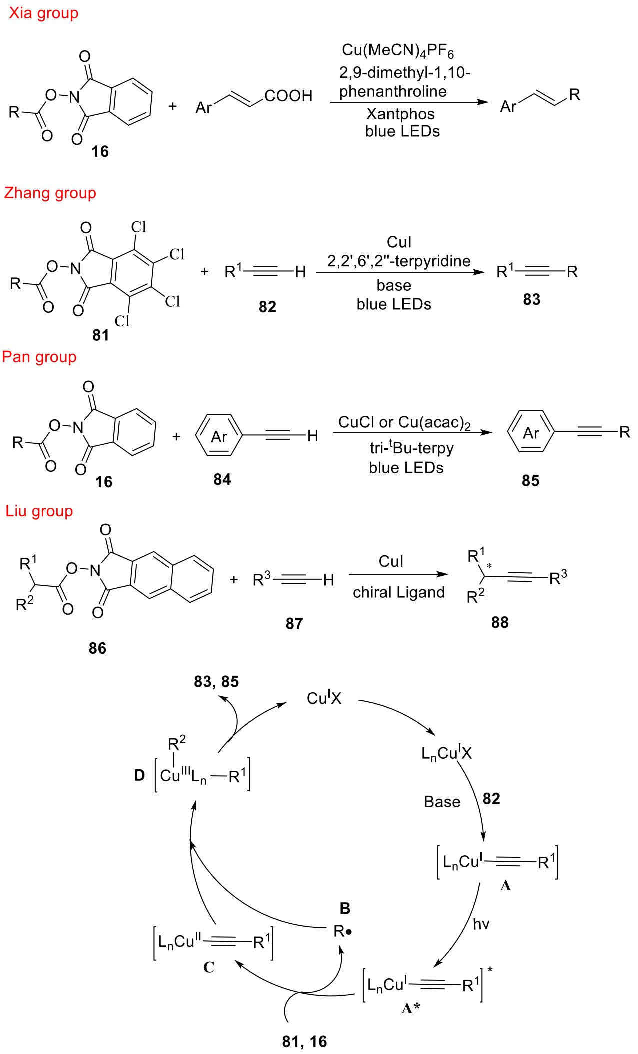


Scheme 24 Copper-catalysed photoinduced decarboxylative heteroarylation.

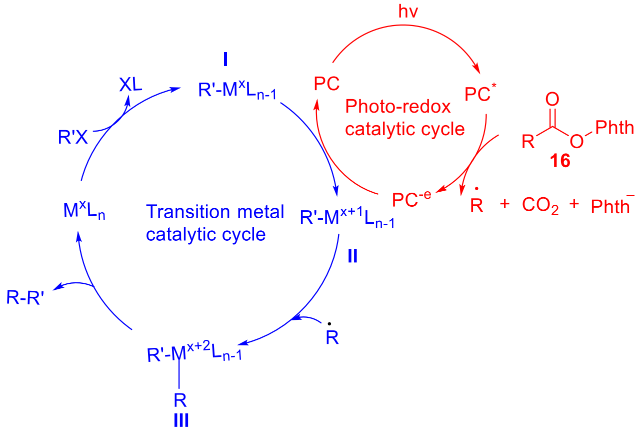
tosensitiser for SET and/or a catalyst for asymmetric control. Moreover, external oxidants or reductants are not needed for the catalytic cycle. Despite such remarkable achievements, more copper-based catalytic reactions need to be developed (Scheme 25).

4.1.3. Dual-metal-mediated coupling

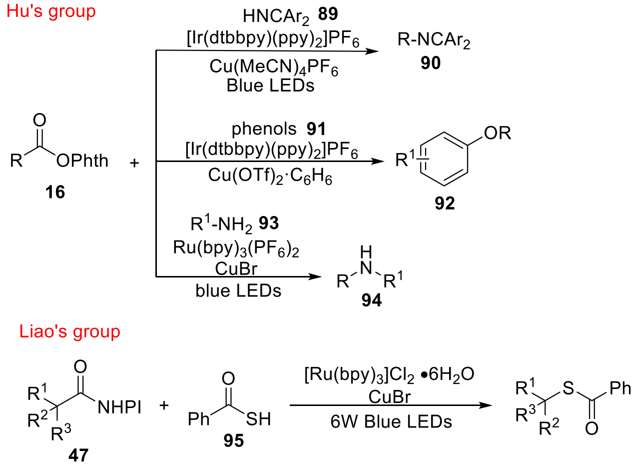
Decarboxylative radical transformations can be facilitated by a dual-metal catalytic system employing photocatalysis and metal catalysis. The dual-metal catalytic system provide for decarboxylative cross-coupling involves two catalytic cycles: a photoredox catalytic cycle ("red cycle") and transition-metal catalytic cycle ("blue cycle") (Niu et al., 2020). The photocatalytic cycle has a dual role: (i) the conversion of an alkyl NHPI ester into an alkyl radical; (ii) one-electron oxidation of a low-valency metal–substrate complex. Metal complexes have been shown to play a key part in the catalytic cycle, which is intended to facilitate the difficult reductive elimination. A plausible catalytic mechanism for a dual-metal system is proposed in Scheme 26, which provides a fundamental understanding of tandem photoredox reactions and metal



Scheme 25 Copper-catalysed photoinduced decarboxylative alkynylation.



Scheme 26 Mechanism of dual catalysis.



Scheme 27 Decarboxylative C(sp^3) – heteroatom coupling.

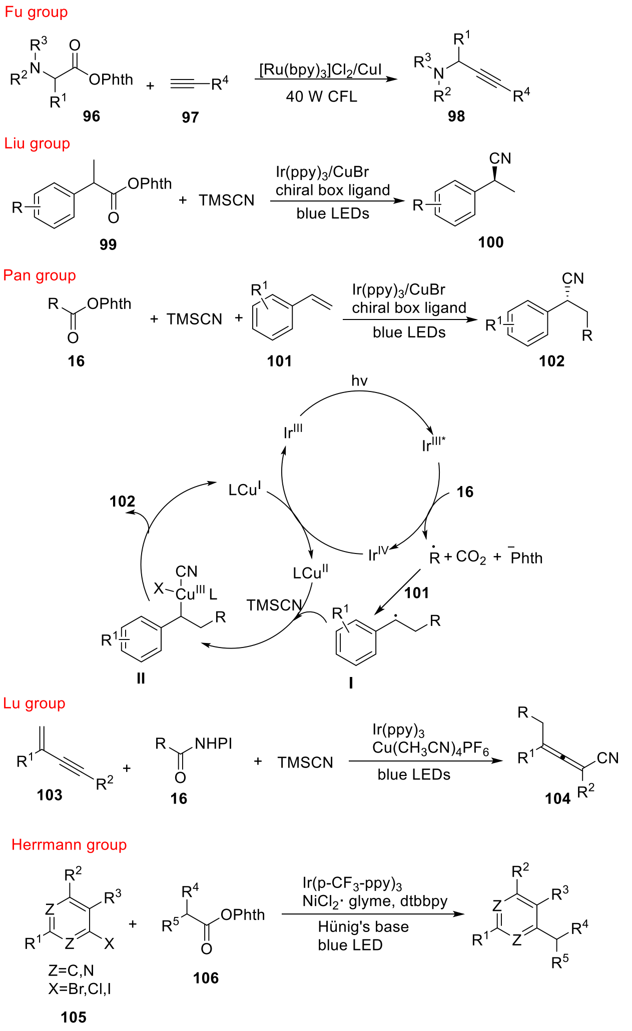
catalysis. The key alkyl radical R• and PC^{-e} are generated through one-electron reduction of NHPI ester 1 by a photoexcited PC*. Meanwhile, the photocatalytic cycle is closed by a SET process between M^xL_{n-1}-R′ species **I** and the PC^{-e}, thereby providing $M^{x+1}L_{n-1}$-R′ species **II**. Then, the radical R• is trapped by a low-valency metal catalyst intermediate **II** to generate the intermediate $M^{x+2}L_{n-1}$-R′R **III**. Finally, the intermediate **III** proceeds to reductive elimination to give the final product RR′ and regeneration of the metal catalyst M^xL_n (Scheme 26).

Several research groups have constructed carbon – carbon and carbon – heteroatom bonds using alkyl NHPI esters with the dual-metal catalytic system. This dual-catalytic strategy was extended by Mao group. In 2018, Mao group developed an Ir or Ru with copper catalysed C–X (X = N, O) coupling of NHPI esters with nucleophiles (**89**, **91**, **93**) (Mao et al., 2018a,b,c). These methods allow rapid transformation of readily available alkyl carboxylic acids into amines (**90**, **94**) (Mao et al., 2018a,b,c) or alkyl aryl ethers (**92**) (Mao et al., 2018a, b,c). Under optimal reaction conditions, the scope of alkyl redox-active esters and amines (**89**, **93**) was explored. Tertiary alkyl NHPI esters had low conversions and yields. Secondary amines and the bulky amines did not allow a product to be formed. A DFT-based computational study was carried to demonstrate the mechanism of C-N coupling of alkyl redox-active esters with anilines (Liu et al., 2020a,b). Those results indicated that steric hindrance prevented C-N coupling. In contrast, C–O coupling had a broad scope of substrates and good tolerance of functional groups. Not only C-N coupling but C-O coupling, the photocatalyst, copper catalyst, and light were essential because a desired product was not obtained if any one of the those three elements was absent. In 2020, Liao et al. published Ru/Cu dual catalyzed decarboxylative thioesterification between NHPI esters (**47**) and thioacids (**95**) (Xu et al., 2020). The reaction is applicable to primary, secondary, and tertiary alkyl carboxylic acids, as well as several amino acids and drugs (Scheme 27).

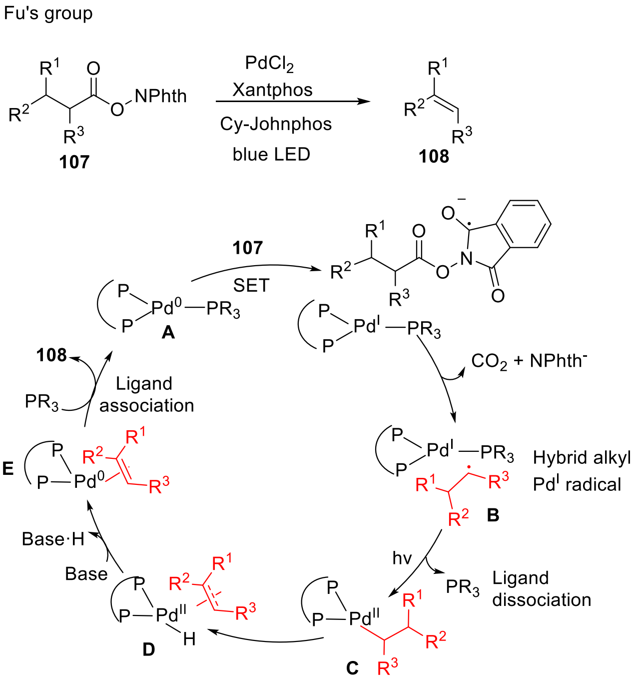
Methodologies involving a dual-metal catalytic system have been applied for the construction of carbon–carbon bonds. In 2016, an efficient decarboxylative alkynylation of α-amino acid-derived NHPI esters **96** with terminal alkynes **97** was displayed by Fu and co-workers (Zhang et al., 2017a,b). A series of amino acids containing propargyl amines **98** was synthesised in the presence of $[Ru(bpy)_3]Cl_2$/CuI dual catalysis. In 2017, Liu et al. revealed an Ir/Cu-dual catalysed asymmetric cyanation using NHPI esters **99** and TMSCN (Wang et al., 2017). This protocol provided straightforward access to chiral alkyl nitriles **100** with high enantioselectivity and yields. Contemporaneously, a similar highly enantioselective cyanoalkylation reaction was carried out by Pan and co-workers using NHPI esters **16**, alkenes **99** and TMSCN (Sha et al., 2018). Under blue LEDs, the alkyl radical R• and oxidised state Ir^{IV} were generated by the same process detailed in Scheme 26. Subsequently, the radical was added to styrene **101** to form the key benzylic radical **I**. Meanwhile, Ir^{IV} was reduced by Cu^I to regenerate the photocatalyst Ir^{III} and give the chiral Box/Cu^{II} state **II**. The resulting intermediate **II** was trapped by **III** and further reacted with TMSCN to offer the chiral intermediate Box/Cu^{III} that underwent reductive elimination to furnish the products **102** and regenerated the Cu^I catalyst. In 2021, Lu group disclosed a copper/photoredox dual catalysed decarboxylative 1,4-carbocyanation of 1,3-enynes **103**, which enabled access to tetra-substituted allenes **104** (Chen et al., 2021). Moreover, Herrmann group reported a decarboxylative arylation of NHPI esters by Ir(p-CF_3-ppy)$_3$ photocatalysis and nickel catalysis. The method was applicable for the cross-coupling of pyrimidine and pyridine heteroaryl halides **105** with alkyl NHPI esters **106** in good yield (Scheme 28) (Behnke et al., 2021).

4.1.4. Other metal-mediated coupling

Besides Ir, Ru, and Cu, other metals (e.g., Pd, Ni) are amenable catalysts. In 2018, Fu and co-workers reported photoinduced Pd-catalysed decarboxylative desaturation of NHPI esters by a dual phosphine ligand system (Cheng et al., 2018). UV–Vis spectrum experiments, stern–volmer quenching experiments, and electron paramagnetic resonance (EPR) experiments revealed that Cy-JohnPhos and Xantphos have essential roles in this transformation. The reaction involves a SET and dynamic ligand dissociation/association process. As depicted in Scheme 29, one electron transfers from the dual phosphine-coordinated Pd^0 complex **A** to NHPI esters **107** to provide alkyl radicals. Meanwhile, the resulting alkyl radical is oxidised to a hybrid alkyl Pd^I radical intermediate **B,** which dissociates one weakly coordinate phosphine ligand (PR_3, Cy-JohnPhos) and then binds an alkyl group to provide intermediate **C**. The intermediate **C** undergoes β-H elimination to



Scheme 28 Dual-metal catalytic decarboxylative C – C coupling.



Scheme 29 Palladium-catalysed decarboxylative desaturation of NHPI esters.

form the Pd^{0} catalyst **E**. Finally, the dissociated phosphine Cy-JohnPhos rebinds to the Pd^{0} catalyst **E** to generate complex **A** after releasing the olefin product **108**. This activation principle opens up new avenues for Pd catalysts.

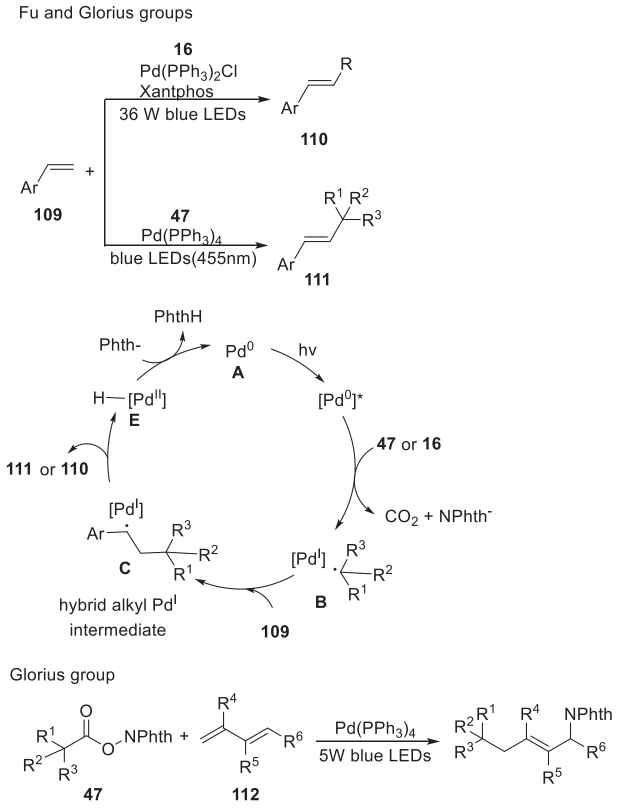
Subsequently, Fu and Glorius demonstrated an irradiation-induced, Pd-catalysed decarboxylative Heck reaction of NHPI esters with vinyl arenes and vinyl heteroarenes **109** (Wang et al., 2018a,b; Koy et al., 2018). The Heck reaction features a wide scope of substrate and high tolerance of functional groups. From a mechanistic viewpoint, the Pd-catalysed transformations are similar to the mechanisms discussed in Scheme 29. The Pd^{0} catalyst **A** undergoes a SET process with an NHPI ester to afford the alkyl radical and putative Pd$^{\mathrm{I}}$ species **B**. Addition of the radical to vinyl arenes **109** gives a hybrid alkyl Pd$^{\mathrm{I}}$ intermediate **C**, which undergoes β–H elimination to offer the corresponding allylic product **110, 111** and palladium(II) hydride species **E**. The presence of phthalimide closes the catalytic cycle. Very recently, Glorius group reported a radical strategy of 1,4-aminoalkylation of dienes **112** using NHPI esters as dual functionalising reagents in combination with 1,3-dienes (Scheme 30). More metal catalysis may find further applications in photoredox coupling reactions (Huang et al., 2020).

4.2. Organic photoinduced decarboxylative coupling of NHPI esters

Transition metal-photoinduced decarboxylative couplings of NHPI esters have been appreciated as a powerful tool in organic synthesis for many years. Significant advances have been achieved in this field by employing ruthenium(II) and iridium(III) complexes, Cu and Pd as photocatalysts. Intriguingly, some excited organic molecules could be employed to promote a chemical reaction (just as a metal catalyst does) and be regenerated in the process. Thus, organic molecules acting as organic photocatalysts have been employed in photochemical reactions. An “ideal” photo-organocatalyst (in analogy with ruthenium(II) or iridium(III) complexes) should absorb in the visible-light region (Ravelli and Fagnoni, 2012). The different styles of organic photocatalysts are shown in Scheme 31. The properties and reactivity of the organic molecules employed in such syntheses have been explored by many groups. They found that organic photoredox catalysis offers far more than “metal-free” alternatives to transition metal-catalysed examples. Their potent reactivity allows access to unique chemistries and a broad range of substrates that are unreactive in most synthetic contexts (Romero and Nicewicz, 2016).

4.2.1. A general mechanism of organic photoredox catalysts

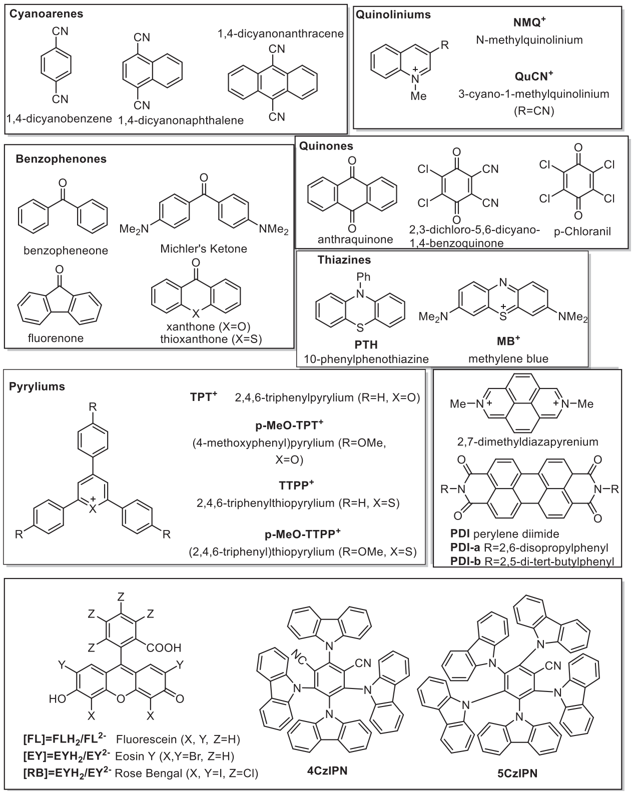
To understand catalysed photoredox processes, a discussion of the general mechanism of organic photoredox catalysts is needed (Scheme 32). Under irradiation, the organic photoredox catalysts (**OPC**) are converted to the excited state



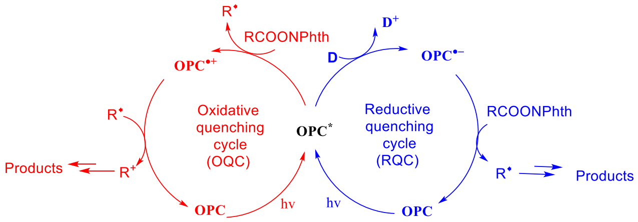
Scheme 30 Palladium-catalysed decarboxylative Heck reaction of NHPI esters.

OPC*, which offers electrons to an external acceptor **A** (NHPI esters) or receive electrons from a ‘‘sacrificial’’ donor **D** (often a tertiary amine, HE). The photoexcited **OPC*** transfers electrons to **A** and thereby yields oxidised **OPC**$^{\bullet+}$, which subsequently accepts one electron from an external donor (**D**) to regenerate the ground-state catalyst **OPC**. This type of reaction mechanism is called an ‘‘oxidative quenching cycle’’ (**OQC**). Correspondingly, the photoexcited **OPC*** accepts electrons from **D** to form **OPC**$^{\bullet-}$, which then undergoes electron transformation to regenerate **OPC**, which is called the ‘‘reductive quenching cycle’’ (**RQC**) (Akita and Koike 2016). In **OQC**, the excited-state **OPC*** offers an electron to NHPI esters to facilitate the decarboxylative fragmentation to form the alkyl radical R•. The **OPC*** is one electron-oxidised to the radical cation **OPC**$^{\bullet+}$. Subsequently, **OPC**$^{\bullet+}$ accepts one electron from the resulting R• (or its derived radical) to form the ground-state **OPC**. Meanwhile, the R• is oxidised to the cation R^{+}, which reacts with an electrophile to offer the desired product. Alternatively, in **RQC**, the excited-state **OPC*** is one electron-reduced to give the corresponding radical anion **OPC**$^{\bullet-}$. Subsequently, the photoredox cycle is closed by a SET process between **OPC**$^{\bullet-}$ and NHPI ester to afford the alkyl radical R• with the regeneration of **OPC**. Finally, the R• is trapped and generates the desired products (Ravelli and Fagnoni, 2012).

Similar to organic photoredox catalysts, the chromophore triphenylphosphine-sodium iodide-NHP esters or electron–donor–acceptor (**EDA**) complex HE-alkyl NHP esters can convert to a photoexcited species to induce electron transformation.



Scheme 31 Common organic photoredox catalysts.



Scheme 32 Mechanism of organic photoredox catalysts.

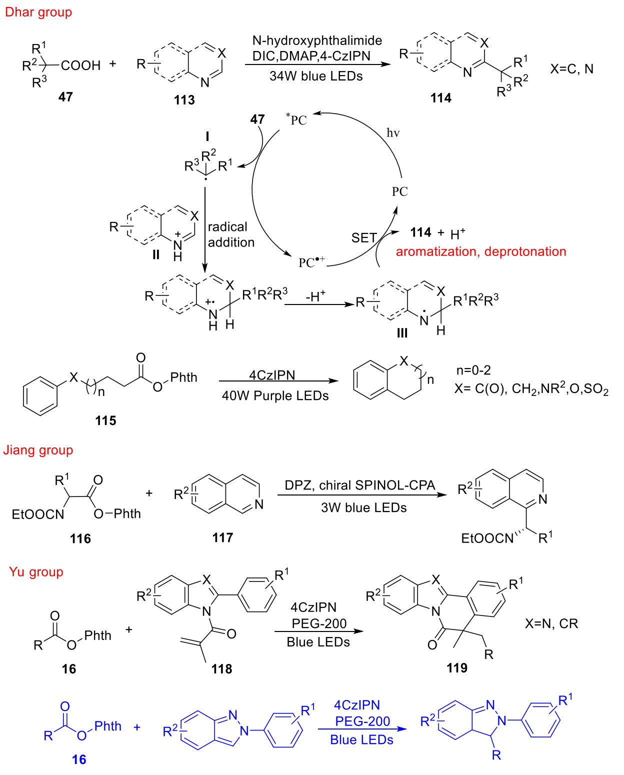
4.2.2. Organic photoredox-mediated decarboxylative coupling

Very recently, inexpensive organic dyes, such as Rose Bengal, 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4-CzIPN) and Eosin Y, have been applied as effective visible light photoredox organocatalysts.

4.2.2.1. Decarboxylative coupling mediated by 4-CzIPN and its analogues. Recently, Minisci reactions have been developed by visible-light-driven organic photoredox catalysis. Dhar group independently developed 4-CzIPN-catalytic alkylation of heteroarene **107** with NHPI esters **47**. The methodology displayed high tolerance of functional groups. Quinoline, isoquinoline, nucleosides, phthalazine, and quinoxaline possessing multiple reactive sites were investigated to afford the desired products in moderate-to-good yields (Sherwood et al., 2018). The common mechanism for this transformation is described in Scheme 33. Mechanistically, the photo-activated PC* undergoes oxidative quenching to deliver the alkyl radical **I**, which subsequently attacks the protonated heteroarene **II** and forms the radical intermediate **III** by enabling deprotonation.

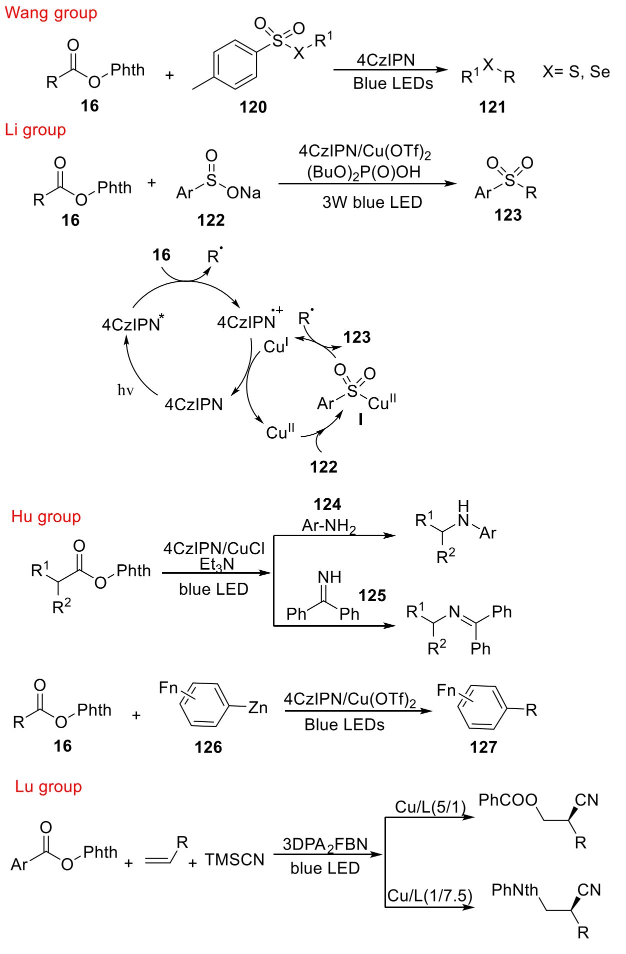
Finally, the radical intermediate **III** undergoes SET and deprotonation to deliver the desired product **114**, thereby completing the catalytic cycle. Simultaneously, an analogous intramolecular arene alkylation is carried out in the same group (Sherwood et al., 2019). As shown in Scheme 33, the aryl ketone and non-ketone arene **115** are tolerated. A mechanistically similar alkylation of isoquinolines **117** with α-amino acid-derived-NHPI esters **116** was reported by Jiang and co-workers (Liu et al., 2018). Subsquencely, Yu group applied the photocatalyst 4-CzIPN for the synthesis of alkylated benzimidazo[2,1-a]isoquinoline-6(5H)-ones and indolo[2,1-a]isoquinolin-6(5H)-ones **119** through the coupling of substituted 2-arylbenzimidazoles **118** with NHPI esters **16** (Scheme 33) (Li et al., 2021). Various primary, secondary, and tertiary alkylated 2-aryl-2H-indazoles were synthesized in the similar method (Ma et al., 2021).

Subsequently, several research teams developed versatile methods for constructing carbon–heteroatom bonds using 4CzIPN as an organic photocatalyst. In 2020, Wang group and co-workers disclosed a mild photoredox synthetic method for constructing a C(sp^3) – S/Se bond between NHPI esters **16** and thio/selenosulfonates **120** (Dong et al., 2020). They hypothesised that the thiosulfonates **120**, as radical acceptors, reacted with the radicals R• derived from NHPI esters to deliver the thioethers **121**. Simultaneously, Li and Hu showed independently that 4-CzIPN in combination with copper salt can catalyse the decarboxylative C-X (S, N) coupling of alkyl radicals derived from NHPI esters (He et al., 2020, 2021; Barzanò et al., 2020). The proposed mechanism for C-S coupling starts with the photo-excitation of 4CzIPN, and subsequent SET triggers cleavage of the N – O bonds in NHPI esters to afford alkyl radicals. In the meantime, transmetalation of the sulfinate anion ArSO$_2^-$ (**122**) leads to formation of the Cu^{II}–SO$_2$Ar intermediate **I**. Then, the alkyl radical is trapped by intermediate **I** to provide the desired product **123** and Cu^{I}. Finally, Cu^{I} is oxidised and regeneration of Cu^{II} and 4CzIPN catalysts occurs (Scheme 34). 4CzIPN-catalysed decarboxylative C(sp^3) – N coupling of anilines **124** and imines**125** developed by Hu is similar to decarboxylative C-S coupling. Later in 2021, the Hu group described a photo- and Cu catalyzed decarboxylative coupling of NHPI esters with polyfluoroaryl zinc reagents **126**. This method enabled the synthesis of a wide variety of polyfluoroarenes **127**, which could have variable F-substitution patterns on the aryl groups (Yi et al., 2021). Contemporaneously, Lu developed a dual 2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile (3DPA2FBN) and Cu^{I}-catalyzed three-component oxocyanation or aminocyanation of alkenes with NHPI ester and TMSCN through tuning the metal-to-ligand ratio(Scheme 34) (Zheng et al., 2021).



Scheme 33 Heteromation and cyclisation of NHPI esters.

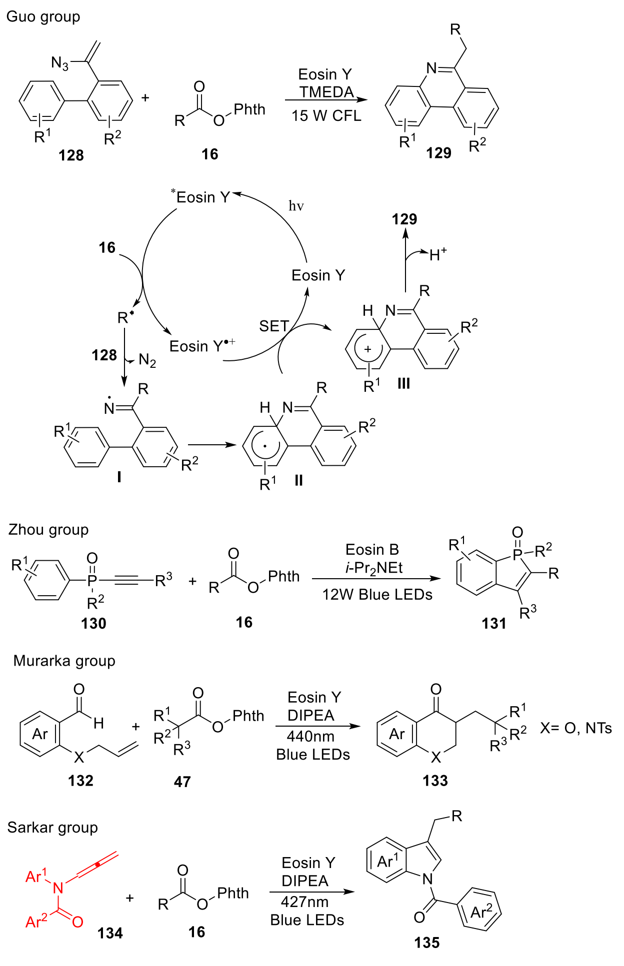
4.2.2.2. Decarboxylative coupling mediated by eosin Y and its derives. An eosin Y-catalysed decarboxylative cyclisation of NHPI esters with alkenes and alkynes was developed independently by the Guo, Zhou and Murarka (Yang et al., 2018; Liu et al., 2019a,b; Das et al., 2020). In 2018, Guo and co-workers reported eosin Y catalysed decarboxylative cyclisation of NHPI esters with vinyl azides **128**. The excited-state eosin Y* undergoes single-electron transfer to generate the alkyl rad-



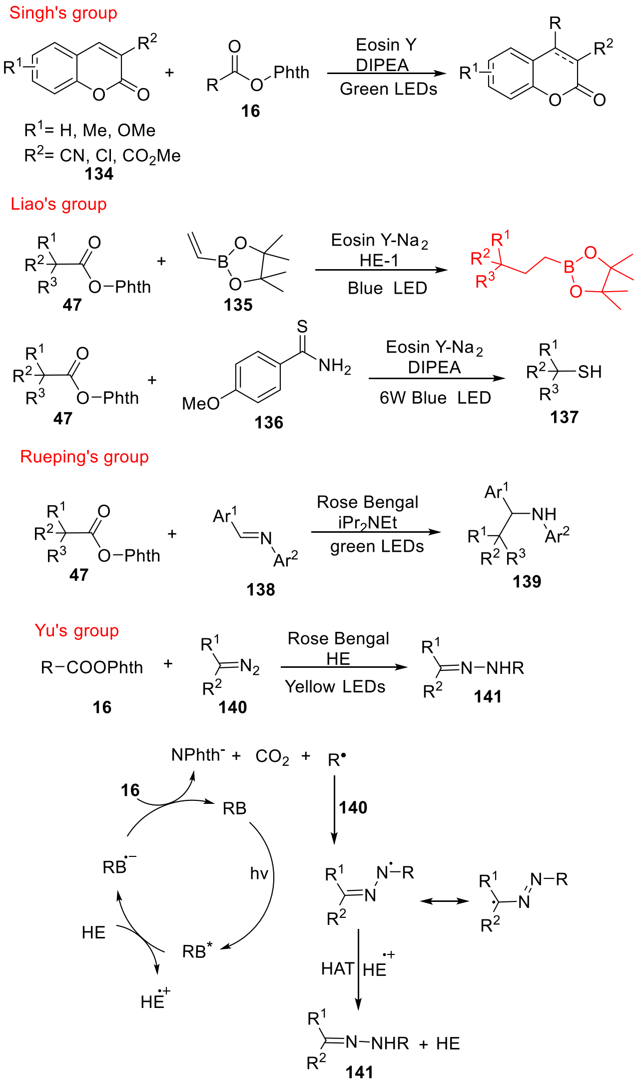
Scheme 34 Decarboxylative C-X (S, N, C) coupling of NHPI esters.

ical along with eosin Y$^{\bullet+}$. The resulting alkyl radical adds to the C = C bond of vinyl azides **128**, furnishing the iminyl radical **I** with releasing dinitrogen. The iminyl radical **I** undergoes an intramolecular cyclisation and SET process to produce the cation intermediate **III,** which upon deprotonation, furnishes the corresponding products **129**. Inspired by this innovative strategy, Zhou et al. and Murarka group introduced a similar decarboxylative cyclisation of alkynylphosphoryl compounds **130** or 2-(allyloxy)arylaldehydes **132** with NHPI esters. Liu group found the alkyl radicals generated from NHPI esters added to the α-position of the P = O bond rather than the β-position to form the alkenyl radical. Finally, the alkenyl radical undergoes the 5-*exo*-ring pathway or 4-*exo*-ring pathway to eventually deliver product **131**. Murarka group introduced a method for preparing a 3-alkyl substituted chroman-4-one scaffold **133**. Recently, Sarkar et al. applied an eosin Y-catalyzed couping of NHPI esters and various N-arylated allenamides **134** in the synthesis of alkylated indoles **135** (Scheme 35) (Das et al., 2021a,b).

Subsequently, several research teams developed decarboxylative radical addition of alkyl radicals derived from NHPI esters to different electron-deficient alkenes (Scheme 36). In 2019, Singh group investigated eosin Y-catalysed decarboxylative addition of NHPI esters **16** with coumarins **134**. The reaction employs a primary alkyl radical derived from an NHPI ester to generate 4-alkylated 3-substituted saturated coumarins, while secondary and tertiary alkyl radicals produce 4-alkylated 3-substituted unsaturated coumarins (Tripathi et al., 2020). In 2020, Liao and co-workers demonstrated decarboxylative radical addition of NHPI ester **16** with vinyl boronic ester **135** utilising eosin Y-Na$_2$ as the organophotocatalyst and stoichiometric HE as the reductant (Shu et al., 2020). Simultaneously, they disclosed an eosin Y-Na$_2$-catalysed synthesis of free thiols **137** by the decarboxylative thiolation between NHPI esters **47** and benzothioamides **136**, thereby providing a convenient conversion of aryl thioamides into important thiol derivatives (Cao et al., 2020). Very recently, Rueping et al. extended decarboxylative radical addition to imines using Rose Bengal as the organo-photocatalyst (Jia et al., 2020). Under green LEDs, the corresponding radical derived from NHPI esters adds to the C = N double bond of the imine **138** to generate α-branched secondary amines **139**. A similar Rose Bengal-catalysed protocol was utilised for the synthesis of diverse N-alkyl hydrazones **141** from α-diazoacetates **140** and NHPI esters **16** by Yu and co-workers (Chan et al., 2019). Radical trap experiments, deuteriumIsotope experiments, and luminescence quenching experiments



Scheme 35 Eosin Y catalysed cascade radical annulation of NHPI esters.

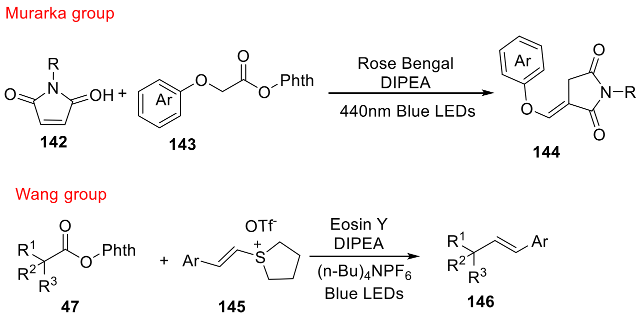


Scheme 36 Decarboxylative radical addition of NHPI esters.

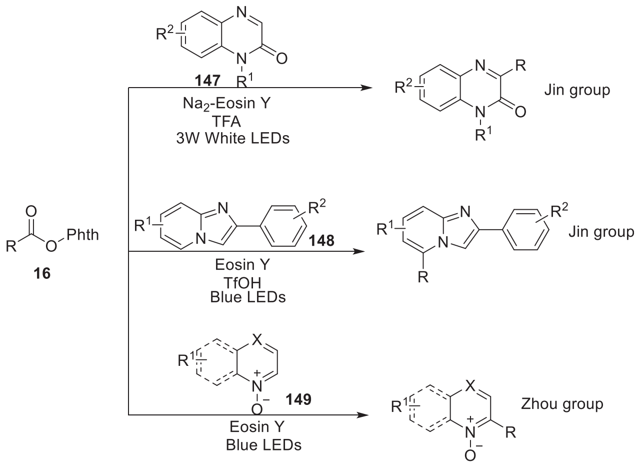
provided a plausible mechanism. Initially, the photoexcited Rose Bengal is quenched reductively by HE. Thereafter, a SET from the radical anion RoseBengal$^{\bullet-}$ triggers reductive fragmentation of NHPI esters to generate an alkyl radical. The latter undergoes addition on the terminal nitrogen of the diazo compound to generate a nitrogen-centred radical intermediate. Finally, the intermediate receives one hydrogen atom from radical-cationic HE to deliver the desired product **141** (Scheme 36). Recently, a metal-free decarboxylative alkenylation (**144**, **146**) of NHPI esters (**47**, **143**) was developed by Murarka and Zhang groups (Das et al., 2021a,b; Zhang et al., 2020) using N-protected maleimides **142** and vinyl sulfonium salts **145** as a radical acceptor (Scheme 37).

Furthermore, an eosin Y-catalysed protocol utilised for the alkylation of heteroarenes such as quinoxalin-2(1H)-ones **147**, imidazo[1,2-a]pyridines **148,** and heterocyclic N-oxides **149** was developed by Jin and Zhou (Yan et al., 2019; Sun et al., 2020a,b; Qin et al., 2020) (Scheme 38). Mechanistic studies indicated that addition of an alkyl radical derived from NHPI to heteroarenes produces a radical or radical cation, which can be oxidised further to give the desired product and the regenerated photocatalyst eosin Y.

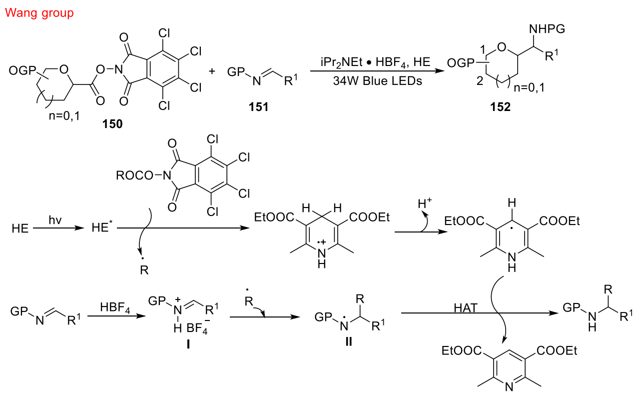
4.2.2.3. Decarboxylative coupling mediated by HE and phenothiazines (PTH). Besides the above organic photoredox catalysts (4-CzIPN, eosin Y, HE), organosulfide complexes (e.g., PTH), as organic photoredox catalysts, also catalysed decarboxylative reactions. In 2019, Wang group reported HE-catalysed decarboxylative addition of NHPI esters **150** with α-imino esters **151** for the preparation of C-glycosyl amino-acid derivatives **152** (Ji et al., 2019). Some preliminary experiments showed that HE is a photosensitiser and a hydrogen-atom source. In the presence of light, HE undergoes photoexcitation to generate HE*, which delivers one electron to the redox-active esters of saccharides, leading to the cation radical HE$^{\bullet+}$ and C-glycosyl radicals R•. Subsequent addition of glycosyl radicals R• to the activated imine **I** leads to formation of the N-centred radical intermediates **II**, and a follow-up hydrogen atom-abstraction from HE releases the desired product (Scheme 39). Contemporaneously, Ohmiya and co-workers demonstrated a PTH-catalysed decarboxylative coupling between NHPI esters **47** with heteroatom nucleophiles **153** such as azole and aliphatic alcohol (Shibutani et al., 2020; Kobayashi et al., 2021). In the presence of visible light, a single electron transfers from the excited-state PTH* to NHPI esters to generate the radical cation PTH$^{\bullet+}$ and alkyl radicals. Subsequently, PTH$^{\bullet+}$ reacts with alkyl radicals to afford the alkylsulfonium intermediates **A** by single-electron oxidation or radical–radical coupling. Finally, a carbocation from alkylsulfonium intermediates **A** is attacked by **153** to give the desired products **154**. In 2021, the same group successfully extended their methodology to three-component coupling of nucleophiles, alkenes, and NHPI esters (Scheme 40) (Shibutani et al., 2021).



Scheme 37 Decarboxylative alkenylation of NHPI esters.

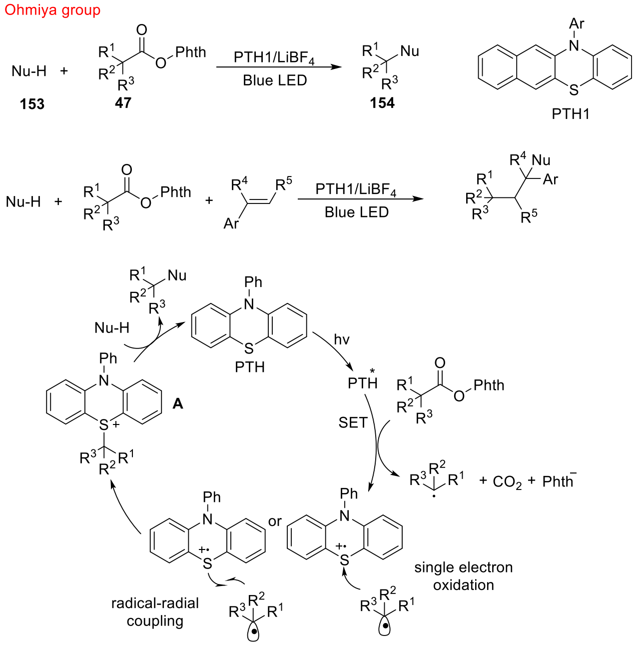


Scheme 38 Alkylation of heteroarenes.



Scheme 39 HE catalysed decarboxylative coupling.

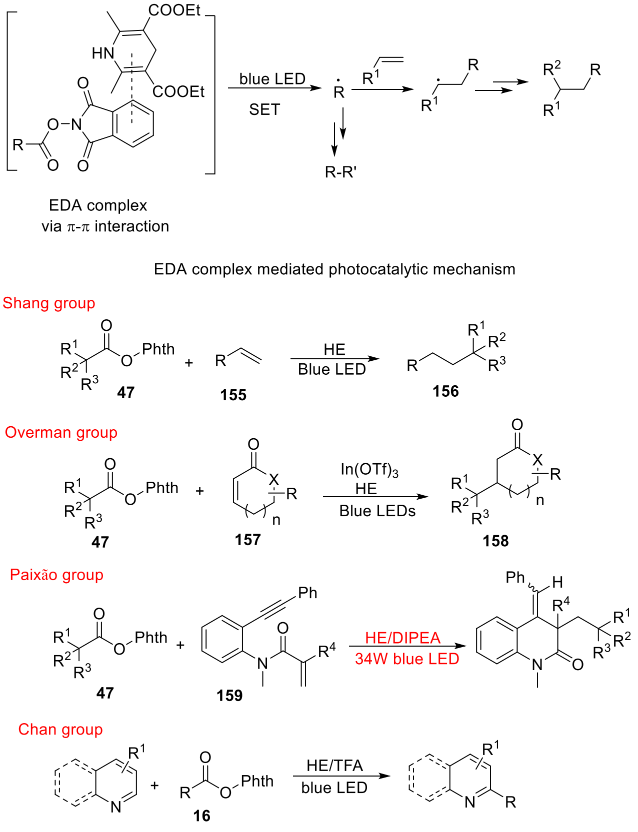
4.2.2.4. EDA complex-mediated decarboxylative coupling. Recent studies have revealed that decarboxylative coupling of NHPI esters could be activated efficiently by an "encounter" EDA complex such as NHPI esters in combination with HE or NHPI esters with PPh3/NaI. UV–vis absorption spectra provided evidence of EDA-complex formation (Correia et al., 2020). Under irradiation, NHPI esters with HE (or PPh_3/NaI) informed an encounter EDA complex which was photoactivated to facilitate photoelectron transfer from a donor moiety (HE or PPh_3/NaI) to an acceptor moiety (NHPI esters) to generate an alkyl radical. The alkyl radical was trapped and then participated in a multitude of transformations (Fawcett, et al. 2017; Fu et al. 2019). In 2019, Shang and co-workers reported a decarboxylative Giese addition of aliphatic NHPI esters with olefins **155** by photoactivation of an EDA complex consist ing of HE and NHPI esters (Zheng et al., 2019). The EDA complex underwent a SET and N – O bond cleavage to produce an alkyl radical. This radical reacted with electron-deficient



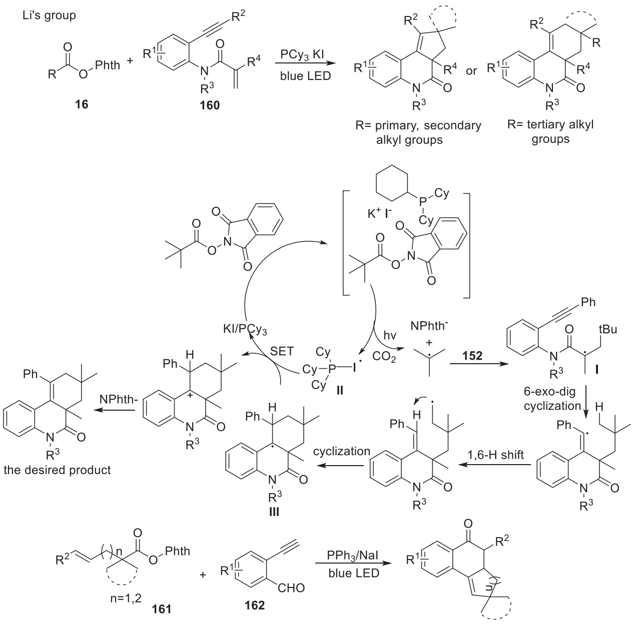
Scheme 40 PTH catalysed decarboxylative coupling.

olefins **155** to provide coupling products **156** in good yields. Later on, Overman et al. presented a decarboxylative Giese addition of NHPI esters with cyclic α, β-unsaturated ketones **157** through photoactivation of a ternary complex between the NHPI ester, HE, and Ln(OTf)$_3$ (Pitre et al., 2021). In this protocol, a range of tertiary alkyl-NHPI esters served as the tertiary carbon radical precursor reacting with α, β-unsaturated carbonyl acceptors to construct quaternary carbons products **158**. Formation of an encounter EDA complex has been to be crucial for the high reactivity and substrate generality. Recently, a radical cascade hydroalkylation of 1,7-enynes **159** with NHPI esters was disclosed by Paixão a groups (Correia et al., 2020). HE-mediated Minisci-type C2-alkylation of N-Heteroarenes such as quinolines, isoquinolines and pyridines with NHPI esters was carried out by Chan group (Li et al., 2022). These reactions presented a broad substrate scope and functional group tolerance without recourse to an expensive photocatalyst (Scheme 41).

In a recent report, Liu et al. presented a catalyst-free [2 + 2 + m] cyclisation of a similar 1,7-enyne scaffold **160** through photoactivation of an EDA complex (Liu et al., 2020a,b). PCy$_3$/NaI formed an EDA complex with an NHPI ester which, under photo-excitation, underwent a SET from iodide to NHP esters and subsequent decarboxylative fragmentation to produce a *tert*-butyl radical. The generated *tert*-butyl radical added to the C = C bond in 1,7-enyne to afford the radical intermediate **I**. Meanwhile, the iodine radical is stabilised by PCy$_3$ to form Cy$_3$P – I• species **II**. Then, intermediate **I** undergoes 6-*exo*-dig cyclisation, 1,6-H atom shift, and cyclisation to produce the radical intermediate **III** which, upon deprotonation, delivers the desired product (Scheme 42). In 2021, a similar decarboxylative annulation transformation was achieved by the same group by employing a combination of γ,σ-unsaturated N (acyloxy)phthalimides **161** and enynals **162** (Scheme 42) (Liu et al., 2021a,b).



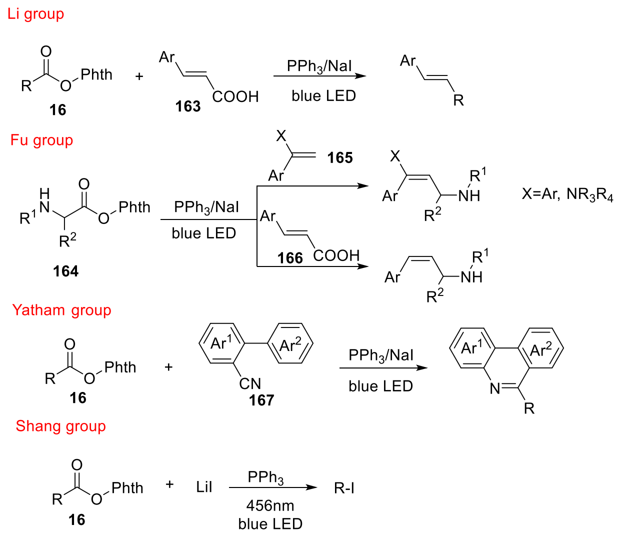
Scheme 41 Decarboxylative coupling catalysed by an HE-NHPI esters complex.



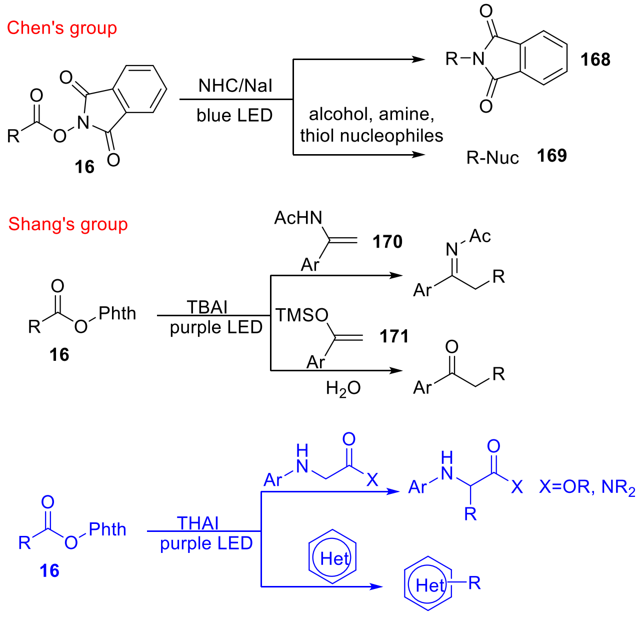
Scheme 42 PCy$_3$/NaI-mediated decarboxylative annulation.

The efficient and practical EDA complex-mediated method has also been documented to be applicable in decarboxylative alkenylation, alkylation, and iodination. In 2020, Li and Fu groups reported an efficient photocatalytic decarboxylative alkenylation of alkyl NHPI ester (**16**, **164**) with α,β-unsaturated carboxylic acids (**163**, **166**) or aromatic olefins (**165**) mediated by triphenylphosphine and sodium iodide. Importantly, alkenylation of NHPI esters with α,β-unsaturated carboxylic acids is a dual-decarboxylative coupling (Wang et al., 2020a,b,c). Subsequently, Yatham group disclosed a photocatalytic decarboxylative alkylarylation radical cascade of 2-isocyanobiaryls (**167**) (Wadekar et al., 2020). The decarboxylative cascade cyclisation reaction showed a broad scope and was proposed to occur *via* formation of a charge-transfer complex between triphenylphosphine, sodium iodide, and NHP-ester. Recently, Shang et al. reported PPh_3 catalysed decarboxylative iodination of NHPI esters using LiI as an iodide source in the absence of alkenes (Scheme 43) (Fu et al., 2020).

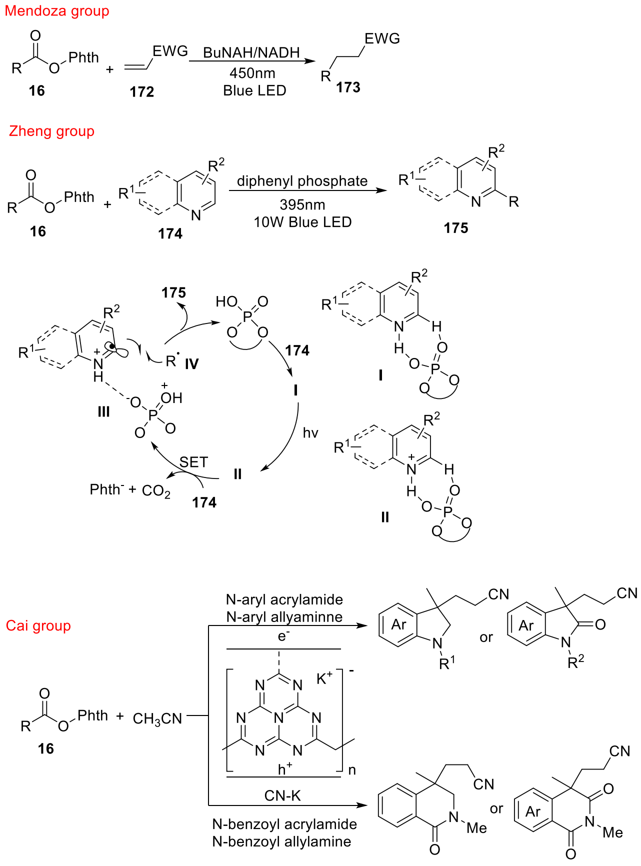
New types of EDA complexes have been developed by several groups. N Heterocyclic Carbene (NHC), NaI formed a new type EDA complex with NHPI esters was developed by Chen group (Chen et al., 2020). The EDA complex catalysed decarboxylative carbon-heteroatom bond formation of NHPI esters **16** with the *in situ*-generated phthalimide anion or nucleophiles (alcohol, amine, and thiol). Under irradiation, the photoexcited EDA undergoes a SET process to afford the phthalimide anion, alkyl radical R•, and iodine radical I•. NHC further facilitates alkyl iodide products which, thereafter, are attacked by nucleophiles to afford the final products (**168**,**169**). In 2021, Shang and co-workers demonstrated a tetrabutylammonium iodide (TBAI) catalysed decarboxylative alkylation of enamide **170** and silyl enol ether **171**. TBAI associates with the NHPI esters to assemble an EDA complex *via* anion–π interactions. Photoactivation of this EDA complex results in electron transfer from the iodide anion to NHPI esters (Scheme 44) (Liu et al., 2021a,b). Subsequent, the same group developed ammonium iodide salt (THAI) catalyzed decarboxylative alkylation of C(sp^3)-H bonds of N-aryl glycine derivatives, of C(sp^2) – H bond of heteroarenes (Wang et al. 2021).



Scheme 43 PPh_3/NaI (or LiI)-mediated decarboxylative coupling.



Scheme 44 Decarboxylative coupling mediated by new types of EDA complexes.



Scheme 45 Decarboxylative coupling mediated by other photocatalysts.

4.2.2.5. Other reactions. Dihydronicotinamide (NADH derivatives), diphenyl phosphate, and heterogeneous semiconductor photocatalysts have been used for decarboxylative transformation of NHPI esters. In 2020, Mendoza and co-workers explored a NADH-catalysed decarboxylative alkyl coupling between NHPI ester (**16**) and electron-deficient double bonds (**172**) (Chowdhury et al., 2020). Under light irradiation, photo-excited NADH transfers one electron and one proton to the NHPI ester to produce alkyl radicals. The resulting radicals undergo radical addition on electron-deficient alkenes to eventually produce a new radical which abstracts a hydrogen atom from NADH to form the desired product **173**. Simultaneously, Zheng group developed a phosphoric acid mediated Minisci C- H alkylation of N-heteroarenes (Jin et al., 2021). Compared with the intensively studied photoredox catalysts, a proposed mechanism is depicted in Scheme 45. Under irradiation, NHPI esters can be activated efficiently through a photosensitive intermediate **I** which forms from the phosphoric acid and N-heteroarene derivative **174**. Photoinduced electrons transfer from the excited state **II** to NHPI esters to produce the corresponding alkyl radical **IV** along with the aromatic radical **III**. Then, the desired product **175** is obtained through radical–radical cross-coupling. In 2021, Cai et al. demonstrated a semiconductor material (K-modified carbon nitride (CN-K))-catalysed cyanomethylarylation of N-arylallylamines and N-benzoylallylamines with acetonitrile (Scheme 45) (Pan et al., 2021).

5. Conclusions

Radical mediated decarboxylative coupling reactions of NHPI esters have emerged as an important synthetic methodology. Importantly, NHPI ester-based radical transformations not only provide a shortcut to known complex molecules, but also pave the way for exploration of new chemical spaces. In this review, based on the types of photocatalysts, advancements made in the field of radical decarboxylative processes have been summarised. Metal-photocatalysts and organic-photocatalysts show high efficiency and practicability. Furthermore, the corresponding mechanisms for photocatalysts have also been described. Despite these advancements and accomplishments, four main challenges remain to be explored.

First, future studies should explore more novel redox-active esters, not just NHPI esters. Second, aromatic redox-active esters as aryl radical precursors are limited to specific molecular modes, while other type reactions such as aryl alkylation, aryl alkynylation are rare. Hence, future studies should be undertaken to explored general arylation methods. Third, the new strategies for utilising NHPI esters as oxygen or nitrogen radical precursors should be expanded. Fourth, examples of asymmetric synthesis and applications in total synthesis of diverse natural products are limited. Future studies should focus on a diverse range of asymmetric transformations involving NHPI esters.

Looking forward, we anticipate the development of highly efficient catalysts, new ligands, and novel catalytic strategies. We believe that various other cross-coupling reactions of redox-active esters will flourish which, in turn, will expand applications of redox-active esters further.

Funding

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