

Review

Advances in Visible-Light-Mediated Carbonylative Reactions via Carbon Monoxide (CO) Incorporation

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Abstract: The abundant and inexpensive carbon monoxide (CO) is widely exploited as a C1 source for the synthesis of both fine and bulk chemicals. In this context, photochemical carbonylation reactions have emerged as a powerful tool for the sustainable synthesis of carbonyl-containing compounds (esters, amides, ketones, etc.). This review aims at giving a general overview on visible light-promoted carbonylation reactions in the presence of metal (Palladium, Iridium, Cobalt, Ruthenium, Copper) and organocatalysts as well, highlighting the main features of the presented protocols and providing useful insights on the reaction mechanisms.

Keywords: carbon monoxide; carbonylation; photochemical reactions; visible light; carbonyl-containing compounds



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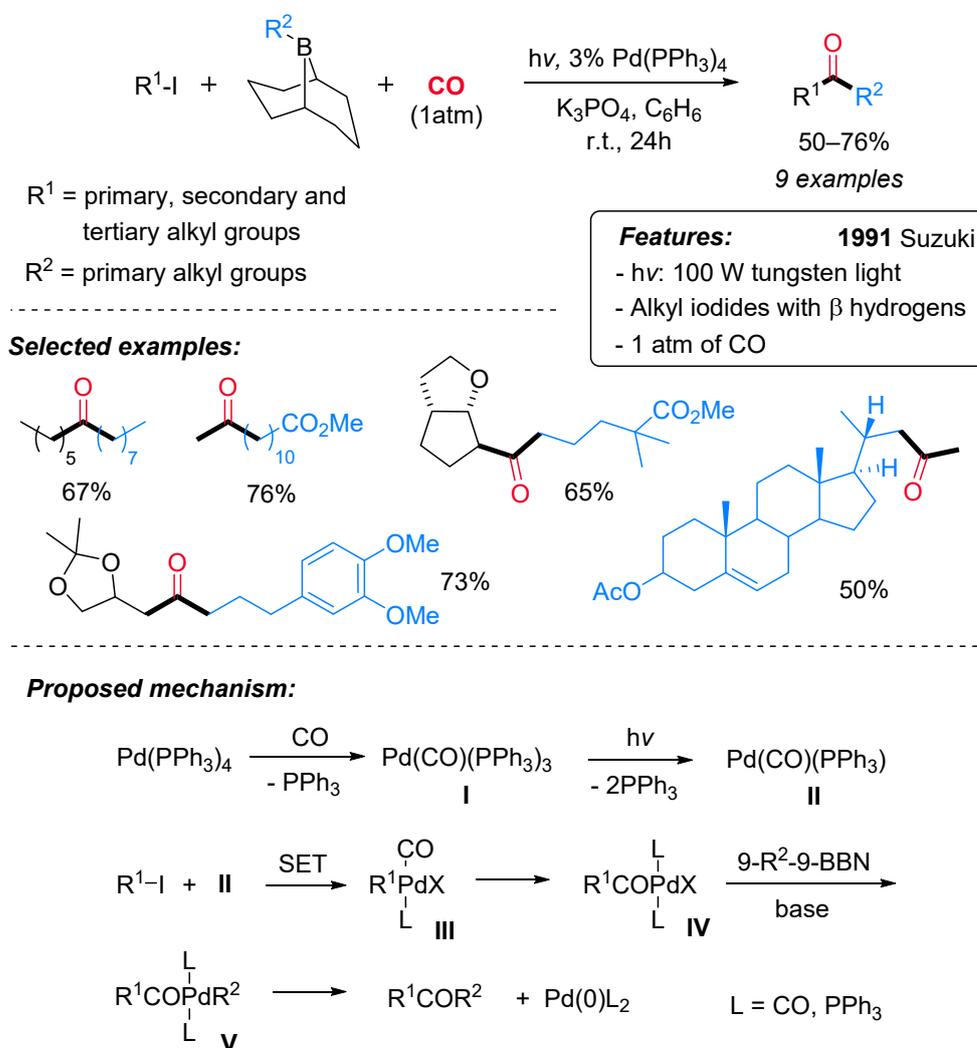
1. Introduction

Carbon monoxide (CO) is largely used in the chemical industry for manufacturing bulk chemicals (i.e., methanol, acetic acid) and fine chemicals (i.e., ibuprofen) and is frequently employed as an inexpensive and readily available C1 source in a wide range of carbonylative transformations for the synthesis of high-value-added carbonyl-containing compounds, such as acids, esters, amides and ketones [1–6]. The carbonyl unit is ubiquitous in a myriad of bioactive molecules, such as natural products, pharmaceuticals and agrochemicals, as well as materials. It can be also manipulated and transformed into a series of other functional groups, including amines, alcohols and olefins. In the era of sustainability, the development of economically improved and environmentally friendly catalytic protocols is highly recommended. In recent years, visible-light photocatalysis has received much attention from the synthetic chemists' community since, unlike traditional thermal and catalytic reactions, it enables unprecedented reaction pathways, high selectivities and mild reaction conditions [7–10]. The combination of carbon monoxide-based carbonylation strategy with the advantages that come from the application of photocatalysis can potentially lead to a highly sustainable process [11–15]. However, the first reports displayed problems connected with a limited generality, poor selectivity and/or efficiency, high pressure of carbon monoxide or high energy of light irradiation [16–23]. Over the last two decades, new and more performing catalytic systems allowed to solve in part these issues. The present review will cover the major advances in the area of visible light-mediated catalyzed carbonylations from 2000, with a focus on CO-based carbonylation methodologies. Sometimes, for a better and more general overview, less recent reports will be mentioned. The review is organized into different sections; each one is related to a

different metal, and one section is dedicated to metal-free protocols, which include the use of organic photocatalysts.

1.1. Visible-Light-Promoted Palladium-Catalyzed Carbonylations

The major achievements in the area of visible-light-driven photocatalysis have been reached with palladium, thanks to its superior versatility. One of the first reports was related to the synthesis of unsymmetrical ketones, which were readily accessed by means of a palladium-catalyzed cross-coupling reaction of iodoalkanes and 9-alkyl-9-borabicyclo[3.3.1]nonane derivatives (9-alkyl-9-BBN) under atmospheric pressure of CO (Scheme 1) [24]. The presence of K_3PO_4 was essential, while the reaction was significantly accelerated by the irradiation of light. Alkyl halides bearing β hydrogens often lead to competitive pathways in traditional cross-coupling reactions, such as the formation of alkenes by β -hydride elimination. In this case, various primary, secondary and tertiary alkyl iodides afforded unsymmetrical ketones in moderate to good yields. Different functional groups (i.e., acetal, nitrile, carbomethoxy groups) were well tolerated on both iodoalkanes and 9-alkyl-9-BBN under the optimized reaction conditions. Selected examples are shown in Scheme 1.

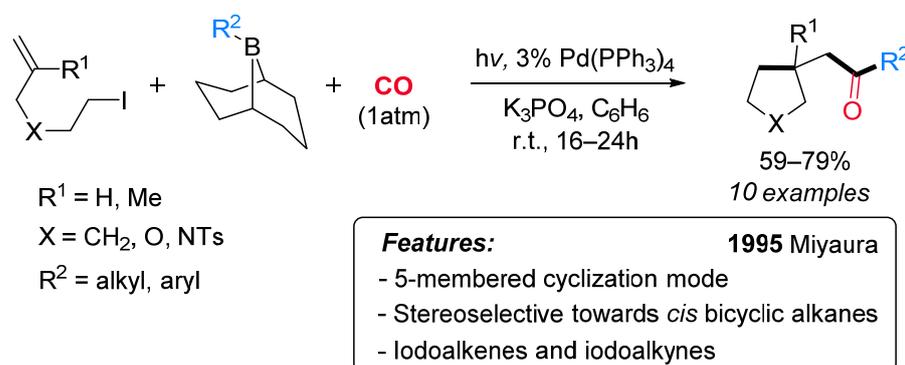


Scheme 1. The synthesis of ketones from iodoalkanes, 9-alkyl-9-BBN derivatives and CO via a light-accelerated Pd-catalyzed reaction.

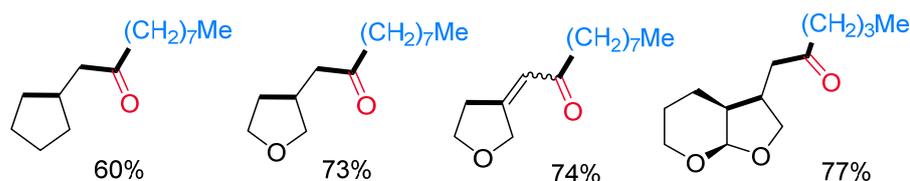
The reaction is supposed to proceed through a free radical mechanism at the oxidative addition step [25]. Firstly, $Pd(PPh_3)_4$ likely converts to the low reactive $Pd(CO)(PPh_3)_3$ complex I under CO atmosphere. In the presence of light irradiation, complex I undergoes

dissociation of ligands to give the unsaturated palladium species **II**. The latter enables an electron transfer to the alkyl iodide with the formation of a radical pair ($\text{Pd(I)X} + \text{R}^\cdot$) that could provide the oxidative intermediate RPdX (**III**). The migration of the alkyl group to a coordinated CO molecule affords complex RCOPdX **IV**. Then, the base facilitates the transfer of the R^2 group from 9- R^2 -9-BBN to palladium providing **V**, which yields the ketone and a palladium(0) species through a reductive elimination step (Scheme 1, proposed mechanism).

Based on their previous studies [25], Miyaura and co-workers developed a palladium-catalyzed three-component reaction between iodoalkenes, carbon monoxide and 9-alkyl- or 9-aryl-9-BBN derivatives to obtain cyclized unsymmetrical ketones under photoirradiation conditions (Scheme 2) [26]. Analogously to the previously reported mechanism (Scheme 1), the iodoalkenes provided cyclized ketones via radical cyclization, carbon monoxide insertion and coupling with 9- R^2 -9-BBN derivatives. Iodoalkynes led to the corresponding cyclized unsaturated ketones as a 1:1 mixture of *E* and *Z* isomers. Interestingly, iodocycloalkenes resulted in the formation of *cis*-fused bicyclic alkanes starting from *trans* iodides as well (Scheme 2). This, together with the predominance of 5-membered over the 6-membered annulation mode, can further confirm the radical nature of the reaction pathway.



Selected examples:

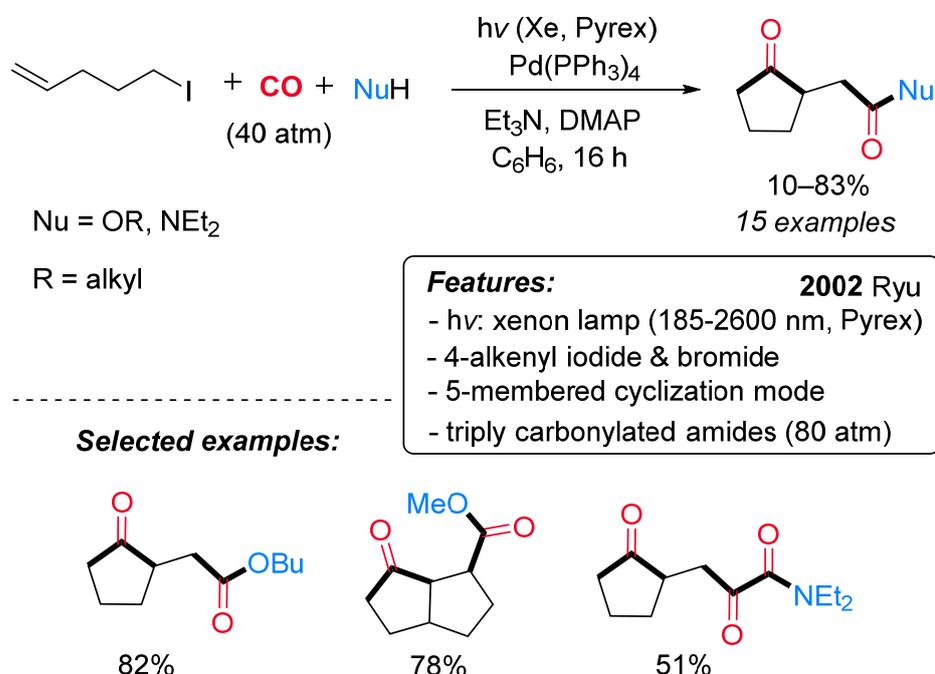


Scheme 2. The synthesis of ketones from iodoalkenes, 9- R^2 -9-BBN derivatives and CO via a light-accelerated Pd-catalyzed reaction.

Palladium-catalyzed photochemical carbonylation reactions aimed at the synthesis of ketones, α,β -unsaturated ketones, esters, lactones and carbamoylacetates have been extensively studied by Ihyong Ryu and co-workers [15,27,28]. The initial idea was to insert carbon monoxide on an alkyl iodide by homolytic cleavage of the C–I bond. The idea has been successfully realized under irradiation and metal-free conditions (*vide infra*, Section 1.6) [29].

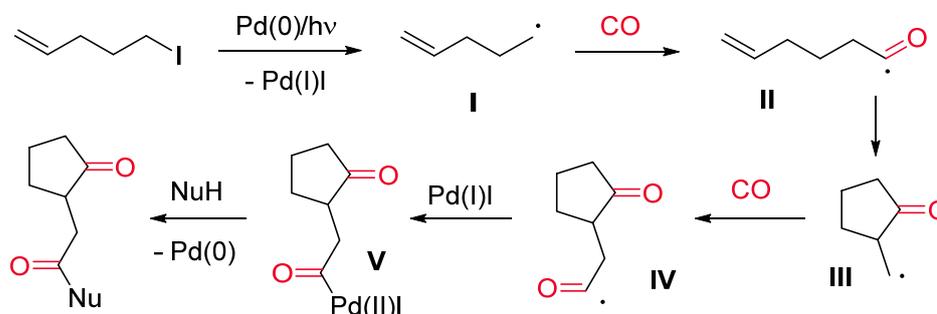
The combination of palladium catalysis with irradiation conditions was crucial for the carbonylation-cyclization-carbonylation sequence reported in 2002 by Ryu and co-workers [30]. A variety of 4-alkenyl iodides were efficiently converted to the desired ketones in the presence of alcohol, $\text{Pd(PPh}_3)_4$ (5 mol %), Et_3N , DMAP (5–10 mol %) under irradiation (500 W xenon lamp, 185–2600 nm, Pyrex) and 40 atm of CO pressure (Scheme 3). When the transformation was performed with diethyl amine in place of alcohol, the triply carbonylated α,δ -diketo amides were obtained as the major product. Alkyl bromides

gave promising but lower yields if compared with the corresponding iodides. This free-radical-based methodology complements the traditional palladium-catalyzed carbonylative reactions that are extensively employed for aromatic and vinylic halides [31].



Scheme 3. Pd-catalyzed/light-induced Cyclizative Carbonylation to esters and amides.

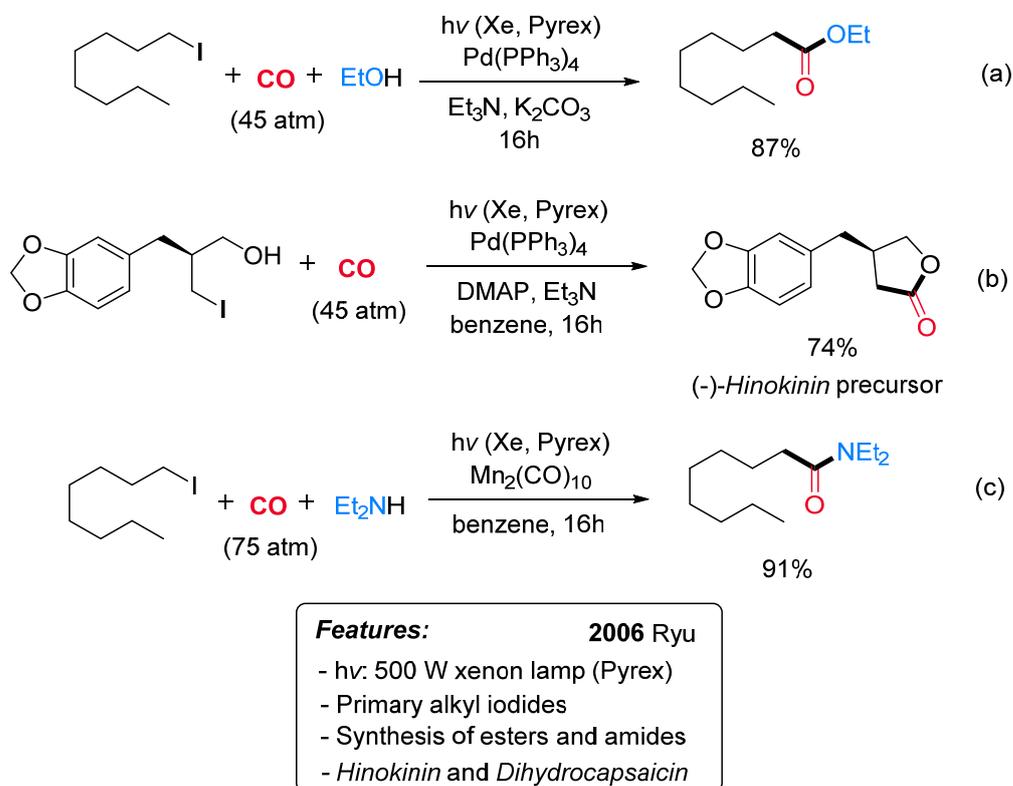
The efficiency of the reaction was improved by the presence of palladium catalysts; however, the stereoselectivity observed with cyclic substrates was identical with those found in palladium-free radical carbonylation sequences. The interplay of organometallic species and radicals can be explained by the mechanism depicted in Scheme 4. As previously observed [25], the palladium(0) species can be active in the C–I bond cleavage providing the radical pair Pd(I)I and alkyl radical I. The high pressure of carbon monoxide favors the formation of the acyl radical II, which undergoes cyclization and further CO insertion to IV. Then, intermediate IV can recombine with the Pd(I)I species leading to V, which affords the desired product by reaction with an alcohol.



Scheme 4. The proposed mechanism for the Pd-catalyzed/Light-induced Cyclizative Carbonylation to ketones and amides.

Based on their previous report [30], Ryu and co-workers reported a general method for the synthesis of esters and amides [32] and, in particular, described the acceleration effect of light-induced atom transfer carbonylation reactions obtained in the presence of Pd(0) complexes and $\text{Mn}_2(\text{CO})_{10}$. Therefore, for example, when 1-iodooctane was caused to

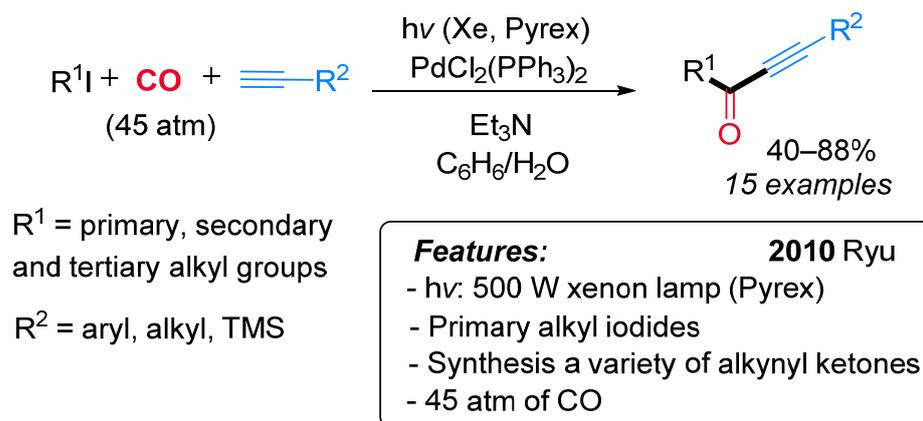
react with CO and ethanol under photoirradiation conditions (Xenon lamp, 185–2600 nm), ethyl nonanoate was obtained in a moderate yield of 54% even with prolonged reaction time (50 h). However, the same reaction in the presence of Pd(PPh₃)₄ (5 mol %) afforded the expected ethyl ester in 87% yield after 16 h (Scheme 5a). Under similar conditions, the synthesis of a precursor of the (-)-*Hinokinin* was efficiently achieved (Scheme 5b).



Scheme 5. Palladium tetrakis-accelerated photo-irradiated atom transfer carbonylation of alkyl iodides to esters (a), lactones (b) and amides (c).

The atom transfer carbonylation of secondary and tertiary alkyl iodides proceeded smoothly, affording moderate to high yields of esters in a shorter reaction time (6.5 h). In this case, the use of Mn₂(CO)₁₀ in place of Pd(PPh₃)₄ was found to be even more effective. The selective synthesis of the corresponding amides was again achieved in the presence of Mn₂(CO)₁₀ (Scheme 5c), while a palladium(0) precursor led to mixtures of amides and ketoamides. Later, highly functionalized linear ester and lactone derivatives were obtained by means of four and three-component photocatalytic methodologies, respectively, under similar reaction conditions [33].

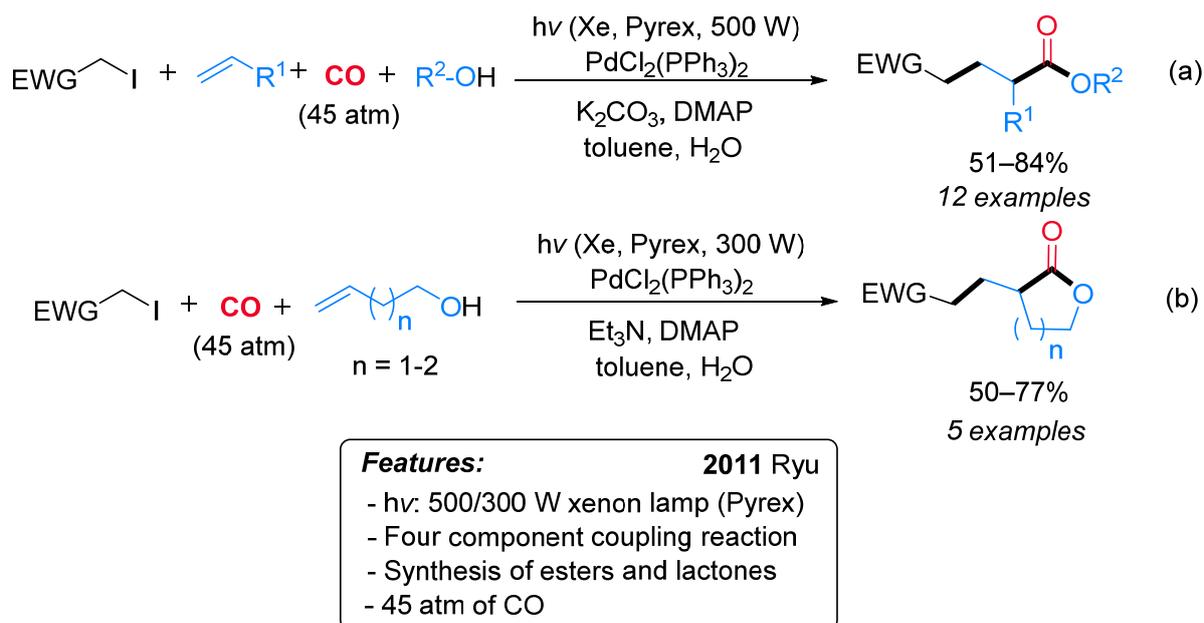
In 2010, a three-component approach for the synthesis of alkynyl ketones was proposed by the Ryu research group [34]. This new methodology, which is an alternative to the acylation of alkynyl organometallic reagents with acid chlorides, is based on the reaction of alkyl iodides, CO and terminal alkynes in the presence of a palladium catalyst and xenon light, under mild reaction condition (Scheme 6).



Scheme 6. The synthesis of alkynyl ketones via a Pd-catalyzed/light-induced three-component cross-coupling reaction.

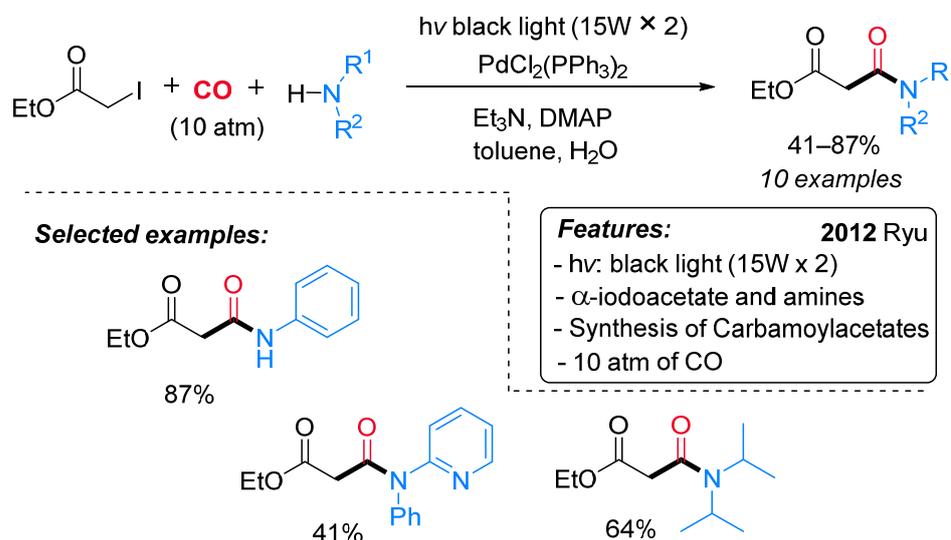
Remarkably, the source of light, the palladium catalyst ($PdCl_2(PPh_3)_2$) and the aqueous medium proved to be crucial for this transformation. Various substituents on the alkyl iodide, such as chloro, methyl ester and ether (TBS) groups, were well tolerated under standard conditions, while aryl, as well as alkyl fragments, can be efficiently employed in the alkyne partner. Once again, this methodology, which starts from a variety of alkyl iodides, is complementary to the transition metal-catalyzed coupling reactions, which are mainly restricted to the use of aryl and vinyl halides [31].

Later, Ryu and co-workers reported versatile four-component coupling reactions leading to functionalized esters using α -substituted iodoalkanes, alkenes, CO and alcohols under photoirradiation conditions (500 W xenon lamp), 45 atm of CO pressure in the presence of $PdCl_2(PPh_3)_2$ (5 mol %) as catalyst (Scheme 7a) [35]. Several electron-withdrawing groups were tolerated (EWG = COOR, CN, $PhSO_2$) on the iodoalkane coupling partner, and both terminal and internal alkenes gave satisfactory results. When alkenyl alcohols were employed in place of alkene/ROH mixture, lactone derivatives were obtained via intramolecular esterification (Scheme 7b).



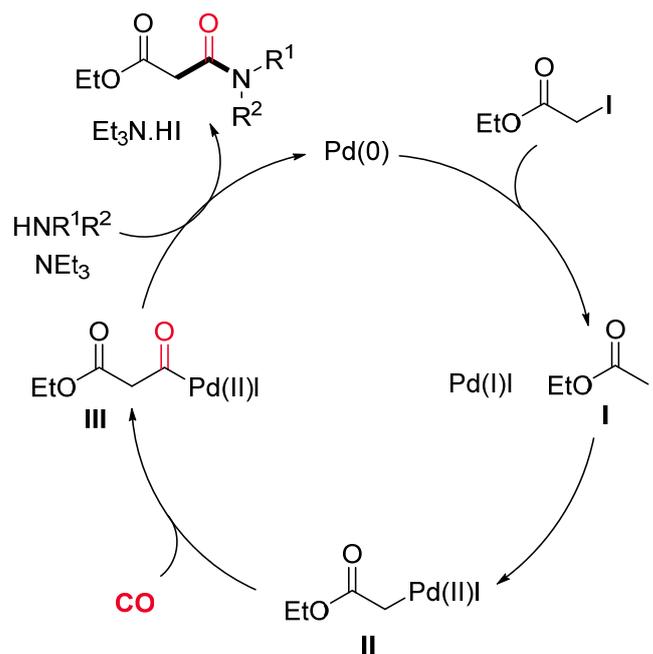
Scheme 7. Pd-catalyzed/Light-induced four and three-component coupling reactions to esters (a) and lactones (b).

The same research group has also reported a novel synthetic method of carbamoylacetates from α -iodoacetate, carbon monoxide and amines under 15 W black light conditions in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ as the catalyst [36]. The methodology was restricted to the use of α -iodo ethyl acetate, while a wide variety of amines, including primary and secondary amines as well as aryl, heteroaryl and aliphatic amines, were employed (Scheme 8).



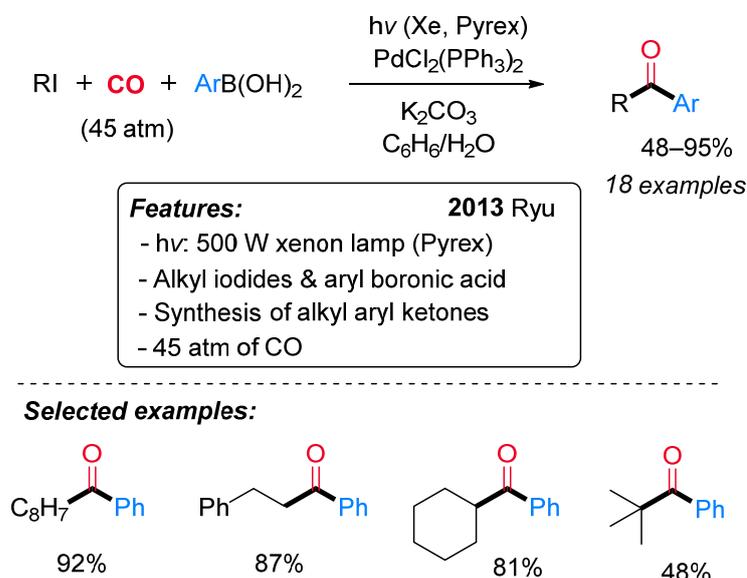
Scheme 8. Palladium-catalyzed/light-induced synthesis of carbamoyl acetates.

A mechanism based on the combined action of radical species and organometallic intermediates was proposed (Scheme 9). The acetate radical **I** is initially formed through the cleavage of the C–I bond, which can be promoted by single-electron transfer from the photo-excited Pd complex. The subsequent coupling between **I** and Pd(I)I leads to an α -pallado ester **II**, which undergoes aminocarbonylation to carbamoyl esters with the regeneration of Pd(0) (Scheme 9).

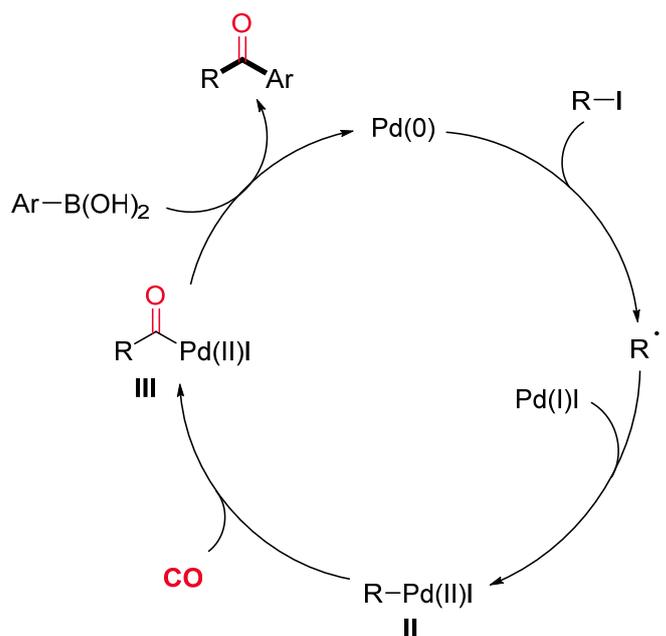


Scheme 9. A plausible reaction mechanism.

Inspired by the work of Suzuki and Miyaura [24,26], the same research group reported a $\text{PdCl}_2(\text{PPh}_3)_2$ -catalyzed light-promoted synthesis of alkyl aryl ketones via carbonylative cross-coupling reaction of alkyl iodides, CO and arylboronic acids [37]. Basic conditions (K_2CO_3), 45 atm of CO and the presence of water were essential for the success of the reaction (Scheme 10). Primary, secondary and tertiary alkyl iodides were successfully coupled with CO and a series of substituted arylboronic acids, bearing both electron-withdrawing and electron-donating groups. The mechanism can likely pass through the formation of an acylpalladium complex via carbonylation of the alkyl radical **I**, which is generated by the action of Pd(0) and light from the alkyl iodide (Scheme 11). The transmetalation of an arylboronic acid with the acylpalladium intermediate **III** leads to the corresponding acyl(aryl)palladium species, which undergoes reductive elimination to the desired alkyl aryl ketone and Pd(0) (Scheme 11).

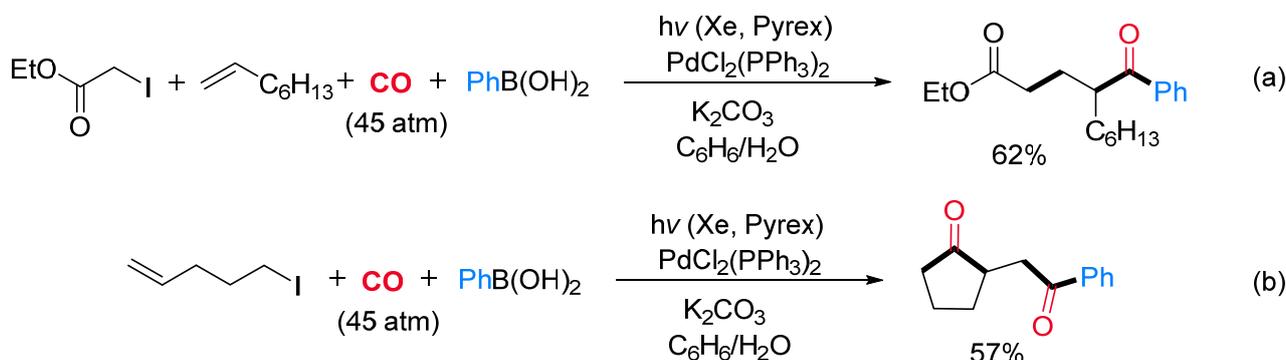


Scheme 10. The synthesis of alkyl aryl ketones via a Pd-catalyzed/light-induced three-component cross-coupling reaction.



Scheme 11. The proposed reaction pathway.

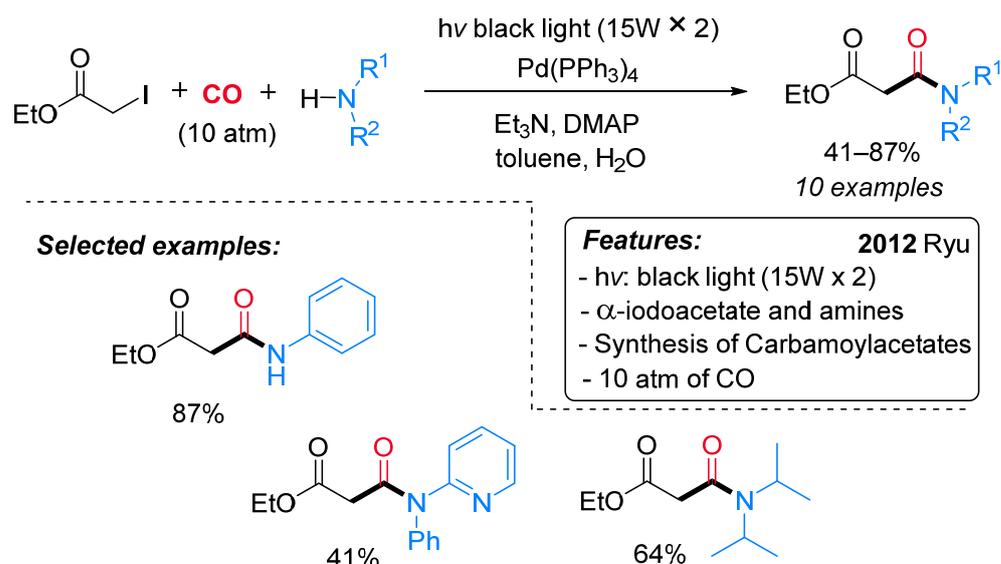
Impressively, this protocol was also applied to the four-component coupling reaction between ethyl iodoacetate, 1-octene, CO and phenylboronic acid to give the corresponding functionalized ketone derivative in 62% yield under the standard optimized conditions (Scheme 12a). The analogous cyclizative double-carbonylation reaction, where 5-iodo-1-pentene replace the couple iodo alkyl/alkene, took place, leading to the aryl ketone with a cyclopentanone moiety, in 57% yield (Scheme 12b).



Scheme 12. The synthesis of diketones *via* Pd-catalyzed/light-induced cross-coupling reactions.

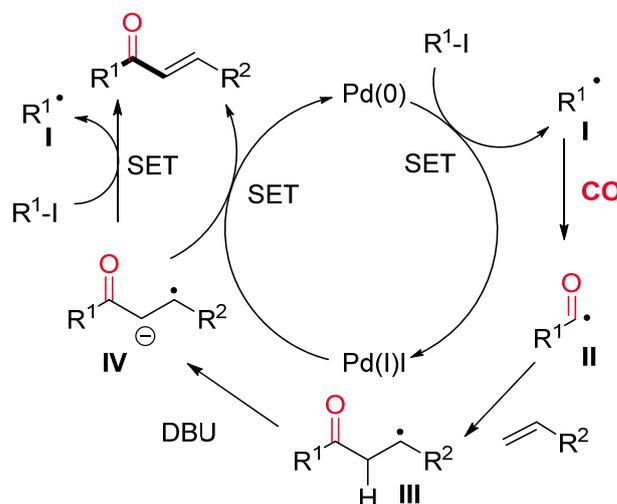
More recently, a similar approach was employed to synthesize aromatic β -keto esters from α -iodoesters, CO and arylboronic acids under lower CO pressures (10 atm) [38]. Taking advantage of this strategy, Li and co-workers developed a protocol to synthesize aryl ketones from aryl iodides and aryl boronic acids by carbonylative Suzuki–Miyaura coupling using DMF as CO surrogate. In this case, TiO_2 was found essential in the in situ generation of CO from DMF and also in the reduction of Pd(II) to Pd(0) species, as it was able to start the catalytic cycle [39].

A carbonylative Mizoroki–Heck reaction was also developed under palladium catalysis and photo-induced conditions [40]. The reaction of alkyl iodides, CO and aryl alkenes leading to α,β -unsaturated ketones was carried out in the presence of $\text{Pd}(\text{PPh}_3)_4$ as a catalyst and DBU as a base under irradiation of a xenon lamp (500 W) (Scheme 13).



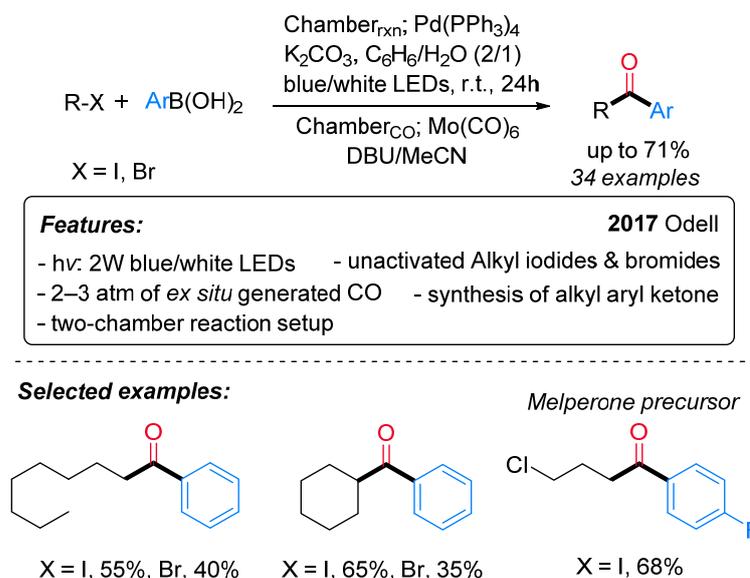
Scheme 13. The synthesis of ketones *via* the Pd-catalyzed/light-induced carbonylative Mizoroki–Heck reaction.

In this approach, alkyl radicals (I) were formed from alkyl iodides via single-electron transfer (SET) and underwent a sequential addition to CO and alkenes to give β -keto radicals (II). It is proposed that DBU would abstract a proton in α to the carbonyl to form radical anions (IV), giving α,β -unsaturated ketones via SET (Scheme 14).



Scheme 14. The proposed reaction pathway.

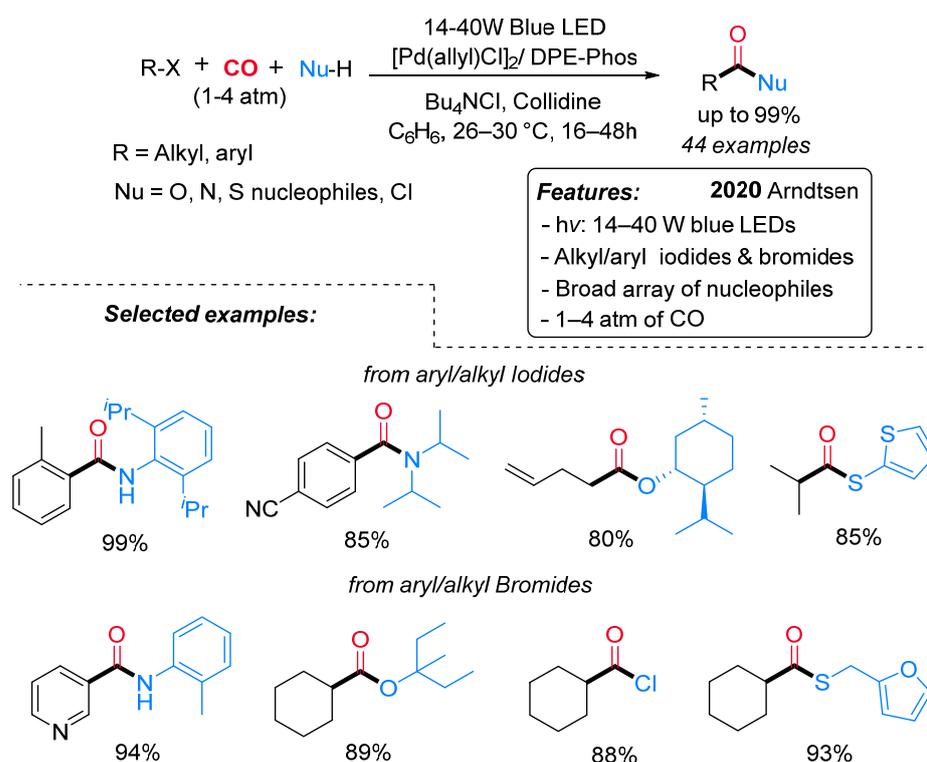
Recently, Odell and co-workers have developed a $\text{Pd}(\text{PPh}_3)_4$ -catalyzed carbonylative Suzuki–Miyaura coupling of unactivated alkyl halides with aryl boronic acids by means of visible-light irradiation with low CO pressure (2–3 atm) at room temperature for the synthesis of aryl alkyl ketones [41]. This methodology features the use of solid CO-source instead of gaseous CO, readily available LED lights and a double-chamber system, one for the CO generation and the other for the palladium-catalyzed reaction (Scheme 15). Under the optimized conditions, various alkyl iodides and bromides reacted with CO and differently substituted aryl boronic acids to provide the desired ketones with moderate to good yields. The same protocol was successfully applied for the synthesis of a precursor of melperone, an antipsychotic drug.



Scheme 15. The synthesis of alkyl aryl ketones via the Pd-catalyzed/light-induced carbonylative Suzuki–Miyaura coupling.

Based on control experiments, the authors verified the crucial role of the visible light as well as of the palladium catalyst. Moreover, the addition of TEMPO completely prevented the product formation while, at the same time, the R-TEMPO adduct was detected.

A recent report by Arndtsen's group has brought a breakthrough in the area of palladium-catalyzed carbonylation reactions. A new palladium-catalyzed/light-induced methodology for the synthesis of a broad array of carbonylated compounds (acid chlorides, esters, amides and ketones) starting from aryl/alkyl iodides and bromides has been reported (Scheme 16) [42]. Compared to previous protocols, this method features high versatility, high functional group tolerance, an impressive reaction scope and mild reaction conditions. In particular, this protocol is compatible with aldehydes, protected amines, esters, nitriles, thioethers and heterocyclic substrates on aryl iodides and bromides. The synthesis of β -amino acid derivatives was achieved with high efficiency. In addition, electron-rich arenes and heteroarenes were successfully employed in place of nitrogen or oxygen nucleophiles. The importance of palladium catalyst and visible light in this radical reaction has been consistently demonstrated, and, in particular, mechanistic studies revealed that light acts as two different roles in this transformation, enabling, together with the palladium catalytic system, both the oxidative addition and reductive elimination steps.

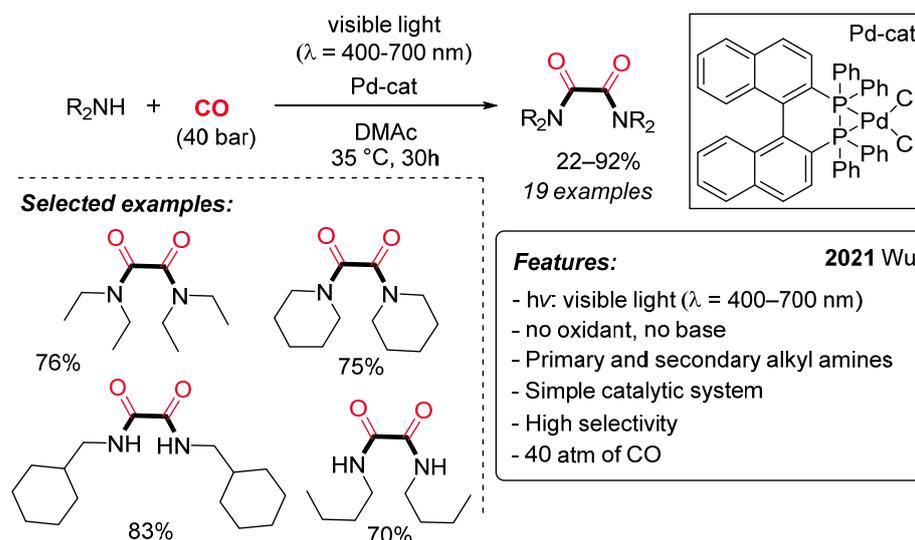


Scheme 16. The general synthesis of carbonylated compounds via the palladium-catalyzed/light-induced carbonylative approach.

Recently, the palladium-catalyzed aminocarbonylation of aliphatic and aromatic iodides under visible-light irradiation has been reported by Sardana and co-workers [43]. The methodology, based on the employment of COgen (9-methyl-9H-fluorene-9-carbonyl chloride, 1 equiv) in a two-chamber system, can be extended to the synthesis of ^{14}C -amides starting from the corresponding ^{14}C ogen. Despite the moderate yields, tertiary amides and C-14-labeled pharmaceutical products were successfully accessed.

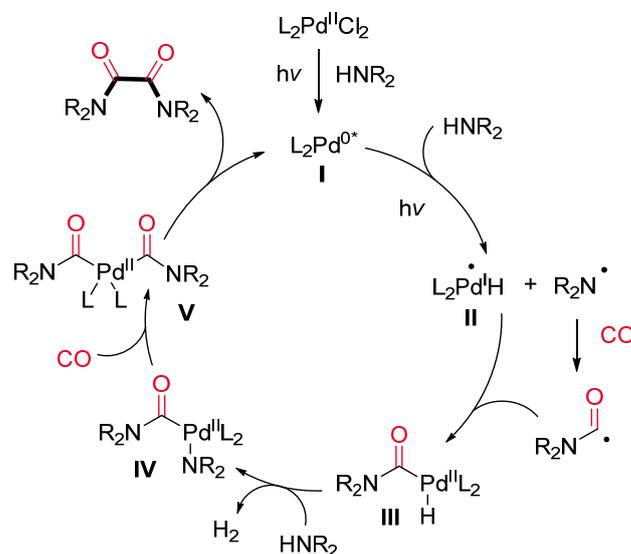
Oxalamides represent a class of relevant compounds frequently found in bioactive and pharmaceutical molecules [44] and used as a ligand in asymmetric catalysis [45]. Wu and co-workers have recently developed a novel, highly sustainable visible-light-induced

palladium-catalyzed method for the synthesis of oxalamides from amines and carbon monoxide [46]. The versatile and green methodology relies on the use of visible light in combination with palladium/BINAP catalysts (Scheme 17) without any oxidant or base. In addition, the protocol features high selectivity (no urea byproducts were detected) and the possibility to reuse the Pd complex without loss of efficiency. Notably, in some cases, the presence of methylene blue as photosensitizer led to a significant improvement in the yield.



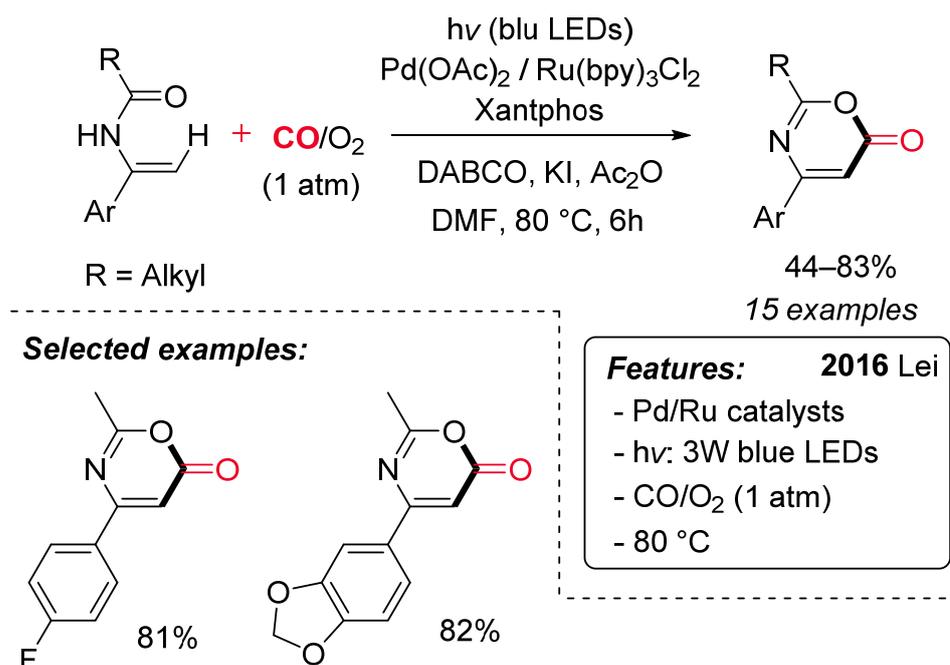
Scheme 17. The general photocatalytic synthesis of oxalamides via the palladium-catalyzed dehydrogenative carbonylation of amines.

Based on control and EPR experiments, the authors propose that the active $L_2Pd(0)^*$ species **I** is first generated in situ from $L_2Pd(II)Cl_2$ in the presence of the amine under visible-light irradiation (Scheme 18). Then, after a SET process with the amine, a nitrogen-radical and a Pd(I)-radical species **II** are generated. The reaction of CO with the nitrogen radical leads to an acyl radical, which recombines with **II** delivering intermediate **III**. The latter undergoes a ligand exchange to provide complex **IV** and molecular hydrogen, which was detected by gas GC. The insertion of another CO molecule provides a bis(carbamoyl)palladium intermediate **V**, which undergoes a reductive elimination step to give the expected oxamide and a Pd(0) species.

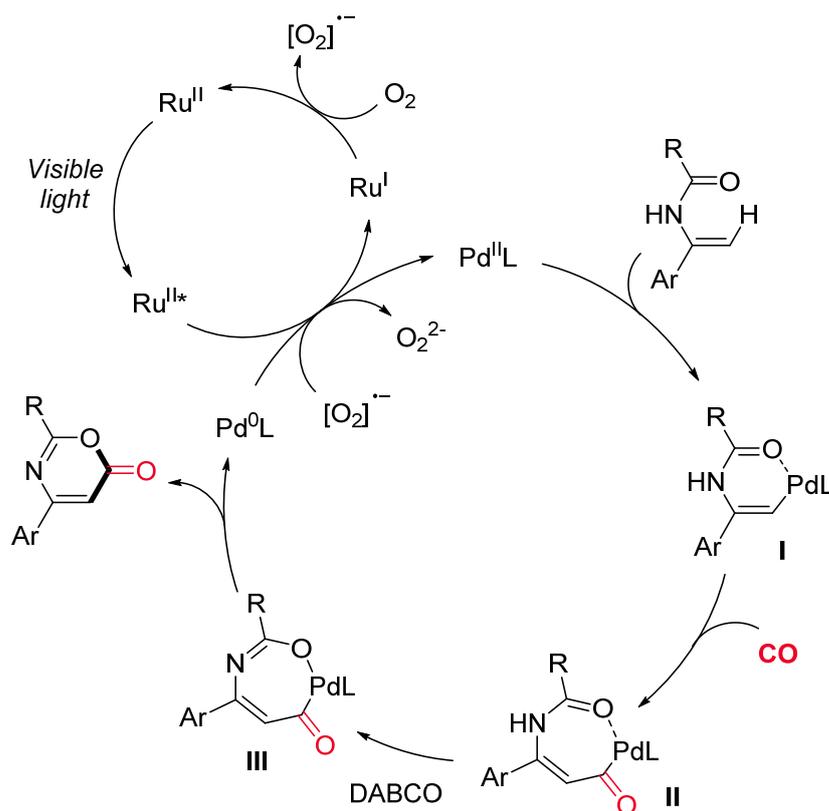


Scheme 18. The proposed reaction mechanism.

In 2016, Lei et al. disclosed a new intramolecular oxidative carbonylation of enamides as a mild and environmentally friendly protocol for the synthesis of 1,3-oxazin-6-ones. Oxygen was employed as a terminal oxidant, avoiding the need for stoichiometric amounts of metal salts, such as Cu(II) salts [47]. The success of the strategy relies on the combination of palladium and photoredox catalysis and, in particular, Pd(OAc)₂ and Ru(bpy)₃Cl₂ were both used in catalytic amounts together with Xantphos as phosphine ligand (Scheme 19). The generality of the reaction was demonstrated as both electron-withdrawing and electron-donating groups, including heteroaromatic rings (furan and thiophene), were well tolerated under the optimized conditions. The authors suggest that the photocatalyst is exclusively involved in the reoxidation of palladium, as described in Scheme 20. Firstly, taking advantage of the amide group, a Pd catalyzed alkenyl C–H activation affords a vinylpalladium complex **I**. Then, a molecule of CO coordinates and inserts, leading to the acylpalladium intermediate **II**. Subsequently, DABCO enables the formation of complex **III**, and, finally, a reductive elimination step delivers the oxazinone product and Pd(0) species. Re-oxidation of palladium(0) can be exerted by the excited Ru(II)* leading to Pd(II)L, which restart a new catalytic cycle, and Ru(I), which, in its turn, can be oxidized back to Ru(II) by molecular oxygen. The generated superoxide anion may also oxidize the Pd(0) species by electron transfer. The presence of KI was found to improve the efficiency of this transformation, likely through coordination of palladium(II) species, while Ac₂O was suggested to reduce the possible formation of inactive palladium(0) species under the CO atmosphere.



Scheme 19. Visible-light-promoted Pd/Ru-catalyzed intramolecular oxidative carbonylation of enamides to 1,3-oxazin-6-ones.



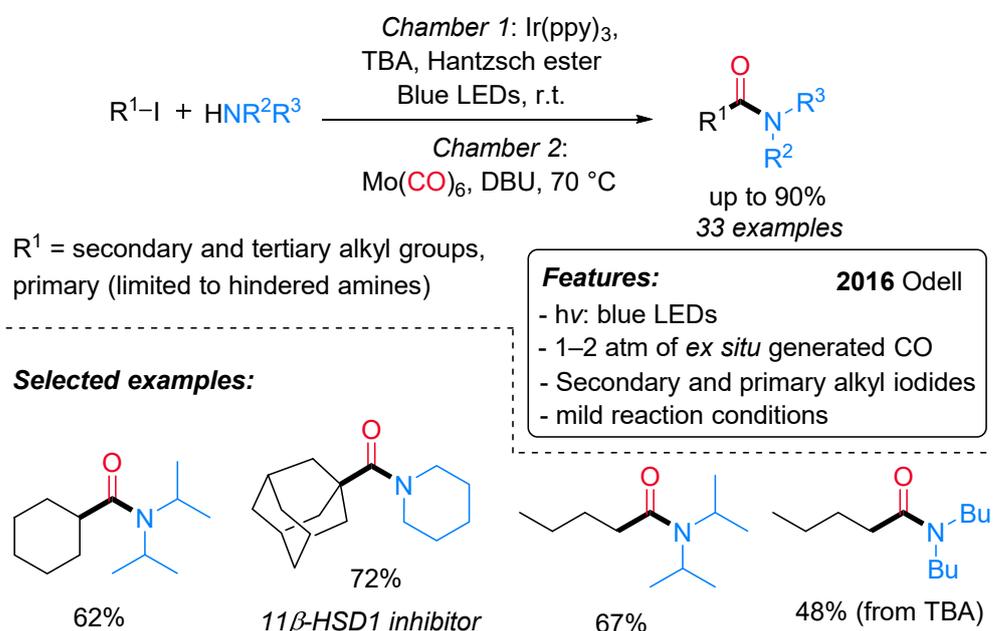
Scheme 20. The proposed reaction pathway.

1.2. Visible-Light-Promoted Iridium-Catalyzed Carbonylations

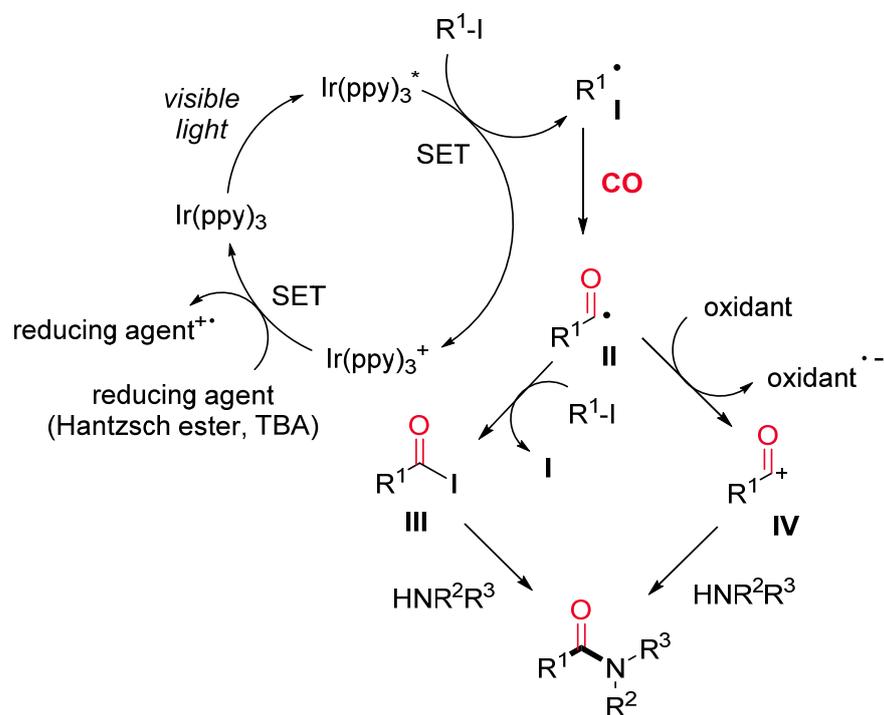
Amides are ubiquitous in both natural and synthetic compounds, including pharmaceutical products. Odell and co-workers have recently developed a visible light-mediated *fac*-Ir(ppy)₃ catalyzed amino carbonylation of unactivated alkyl iodides under mild reaction conditions [48]. The desired amides are produced in moderate to excellent yields through a two-chamber system (H-tube), where the CO is released *ex situ* from Mo(CO)₆ (Scheme 21). Secondary and tertiary iodides can be successfully aminocarbonylated with a wide range of amine nucleophiles, whereas primary iodides provide satisfactory results in combination with hindered amines only. Remarkably, a dealkylative-aminocarbonylation pathway occurs when alkyl halides react with tertiary amines. The reaction mechanism starts with the reductive dehalogenation of an alkyl halide (R-X) to give the alkyl radical **I**, followed by CO insertion with the formation of an acyl radical intermediate **II**. The latter is either quenched by the starting alkyl iodide to produce an acyl iodide **III** or oxidized to an acylium ion **IV**. The nucleophilic attack of the amine on the acyl iodide or the acylium ion affords the final amide (Scheme 22).

A variety of acetate-containing 2,3-dihydrobenzofurans have been synthesized by Polyzos et al. through a visible light-mediated Ir-catalyzed radical carbonylation process under continuous flow conditions [49]. Overcoming the traditional limitations of both Pd-catalyzed alkoxy carbonylation reactions and classical radical-free carbonylation processes in terms of regioselectivity, the pressure of CO and sustainability [50], alkenyl-tethered arenediazonium salts underwent a versatile and stereoselective (exclusive 5-*exo-dig* cyclization) cyclization and alkoxy carbonylation cascade to a wide range of 2,3-dihydrobenzofuran derivatives in the presence of [Ir(dtbbpy)(ppy)₂PF₆] as catalyst under blue LEDs (14 W) at room temperature (Scheme 23). Electron-donating and electron-withdrawing substituents on the arenediazonium salt moiety were nicely tolerated under the standard conditions. Regardless of steric bulk, alkyl alcohols were successfully employed as coupling partners to produce the desired esters in moderate to good yields. This continuous flow methodology also features a very short reaction time (200 s), moder-

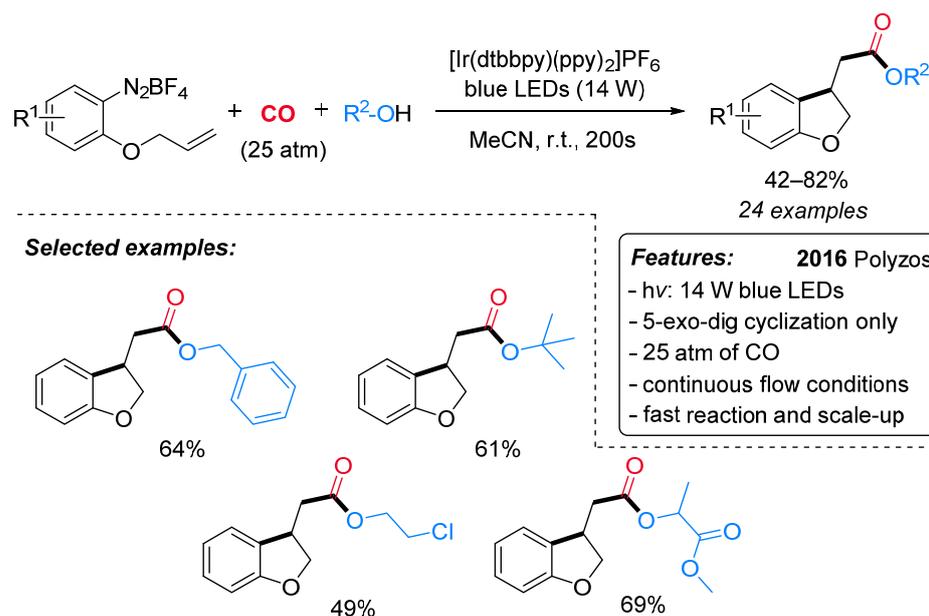
ate CO pressures (25 atm) and a straightforward scale-up. Interestingly, the commercial $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ was found to be slightly less efficient in this transformation.



Scheme 21. Visible light-mediated *fac*- $\text{Ir}(\text{ppy})_3$ -catalyzed aminocarbonylation of alkyl iodides.

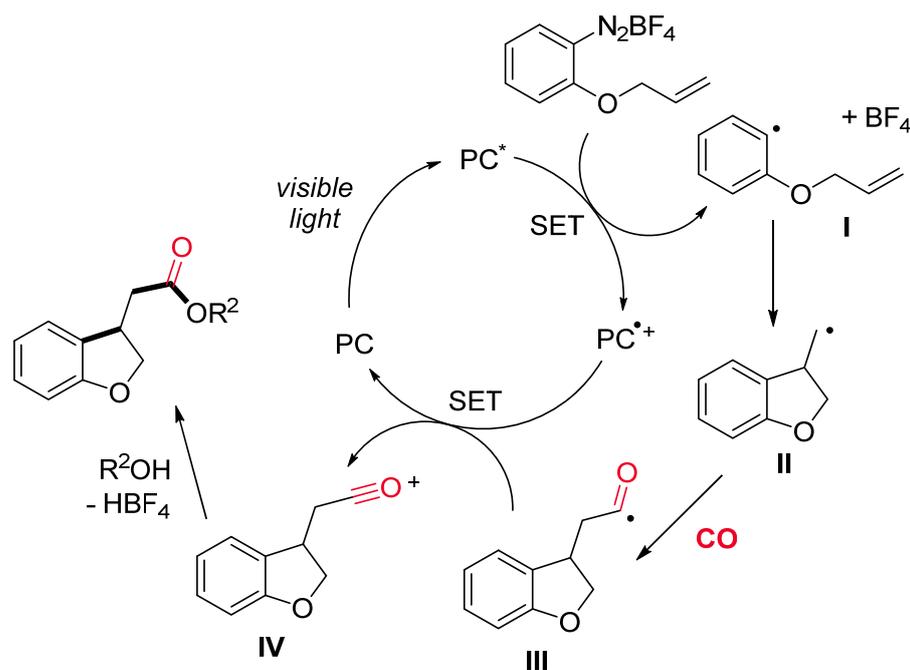


Scheme 22. The proposed reaction pathway.



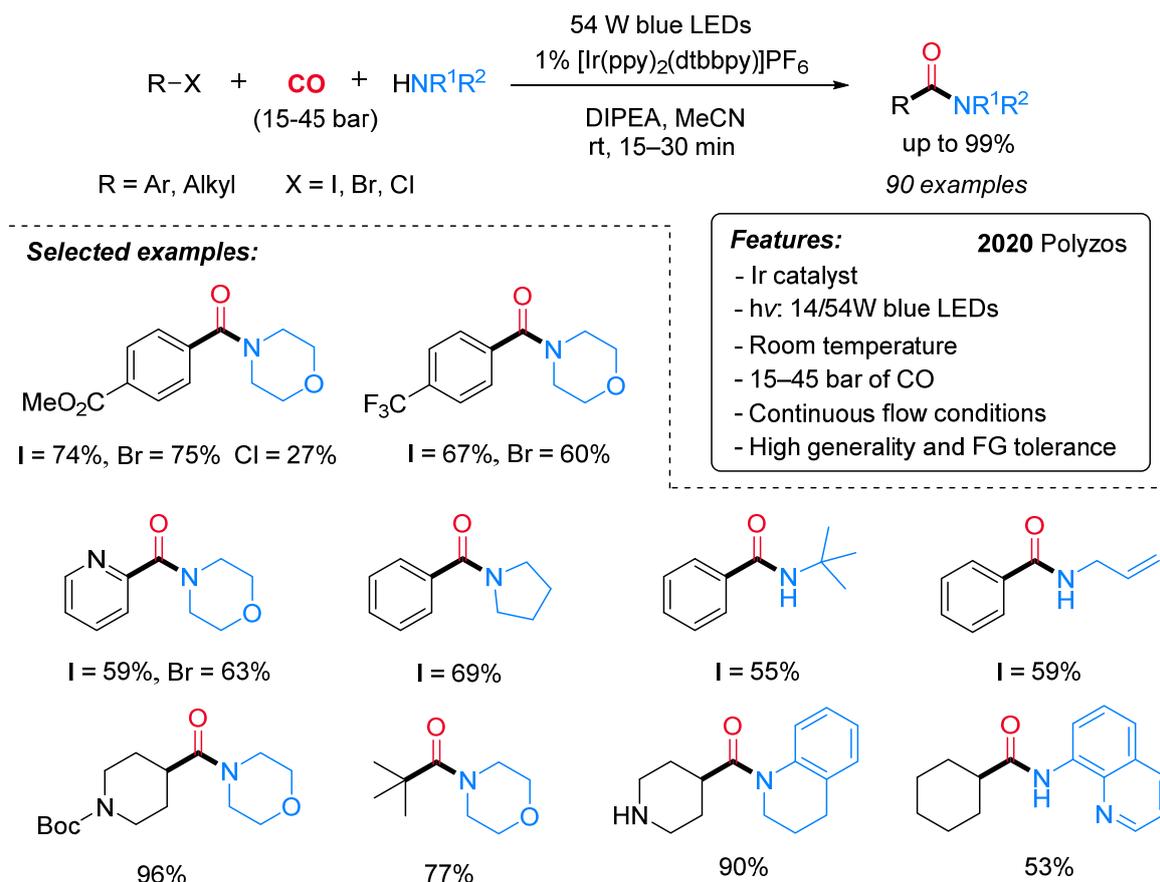
Scheme 23. Visible light-mediated $[Ir(dtbbpy)(ppy)_2]PF_6$ -catalyzed cyclizative alkoxy carbonylation of alkenyl-tethered arenediazonium salts under continuous flow conditions.

The mechanism is supposed to start with the homolytic cleavage of the C–N bond of the allyloxy-tethered arenediazonium salt by single-electron transfer from the photocatalyst in its excited state (PC^*), with the generation of an aryl radical **I** and the oxidized photocatalyst $PC^{\bullet+}$ (Scheme 24). An intramolecular radical alkene addition provides the primary alkyl radical **II**, which, after CO insertion, gives the acyl radical **III**. Oxidation of the acyl radical by the oxidized photocatalyst $PC^{\bullet+}$ results in the formation of an acylium ion **IV** and the regeneration of the photocatalyst PC . Lastly, the reaction of **IV** with alcohol leads to the final product.



Scheme 24. A plausible reaction pathway.

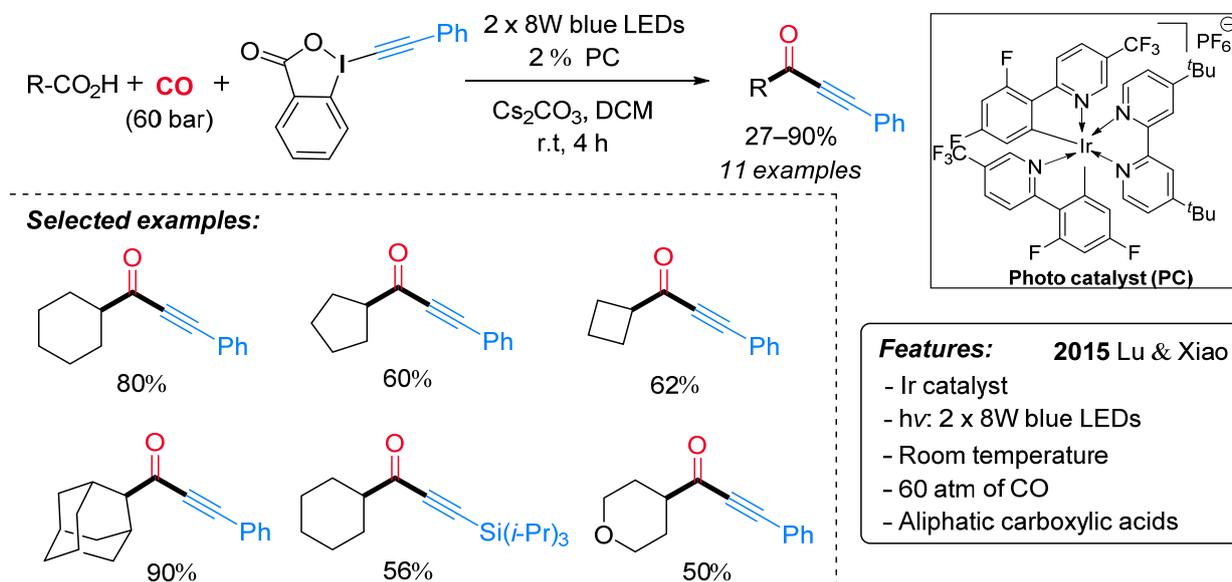
In 2020, Polyzos and co-workers reported an Ir-catalyzed visible-light-promoted aminocarbonylation of alkyl and aryl halides with CO and amines under continuous flow conditions (Scheme 25) [51]. The iridium-based photocatalyst ($[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$) was used in combination with DIPEA (*N,N*-diisopropylethylamine) as a sacrificial reductant and under blue LED (54 W) irradiation. A large variety of aryl halides (I, Br, Cl) and alkyl iodides (primary, secondary and tertiary) reacted successfully with CO and an array of alkyl and aryl amines to provide the expected amides in good to high yields. The continuous flow system was assembled from commercially available components, featuring operational simplicity, high applicability, improved safety and easy scalability.



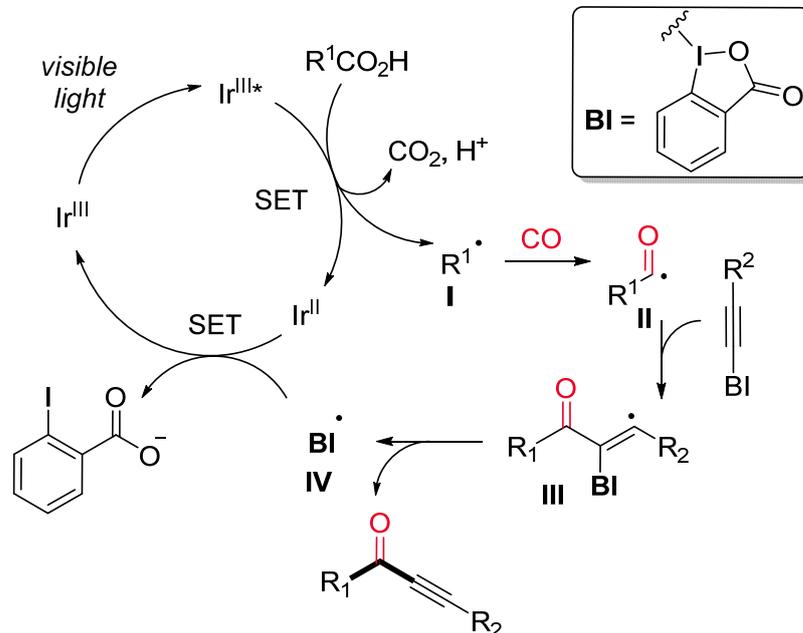
Scheme 25. Visible light-mediated $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ -catalyzed aminocarbonylation of aryl and alkyl halides under continuous flow conditions.

Ynones represent an important motif present in bioactive compounds and are useful intermediates in the synthesis of heterocycles [52]. Alternative to the previously described Ryu's method [34], Lu and Xiao et al. have recently developed an efficient protocol for the synthesis of ynones through a visible-light-induced photocatalytic decarboxylative carbonylative alkylation of carboxylic acids in the presence of carbon monoxide (CO) at room temperature [53]. The decarboxylative alkylation reaction was carried out using ethynylbenziodoxolones (EBX) as the alkylating agent, carboxylic acid, in the presence of $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ as a photocatalyst and Cs_2CO_3 as a base (Scheme 26). A range of aliphatic carboxylic acids gave the corresponding ynones in good to excellent yields under mild conditions but extremely high pressure of CO. Mechanistically, it is proposed that the excited photocatalyst $\text{Ir}(\text{III})^*$, generated from $\text{Ir}(\text{III})$ under visible-light irradiation, is able to oxidize the substrate with the formation of an alkyl radical **I** (Scheme 27). Then, the latter, after CO insertion, gives rise to an acyl radical **II**, which undergoes radical addition to the alkylating agent affording the radical intermediate **III**. The subsequent

radical elimination reaction yields the desired ynone and the benziodoxonyl radical **IV**. Finally, radical **IV** is reduced to *ortho*-iodobenzoate by Ir(II), which, in turn, is oxidized to Ir(III) for a new catalytic cycle.



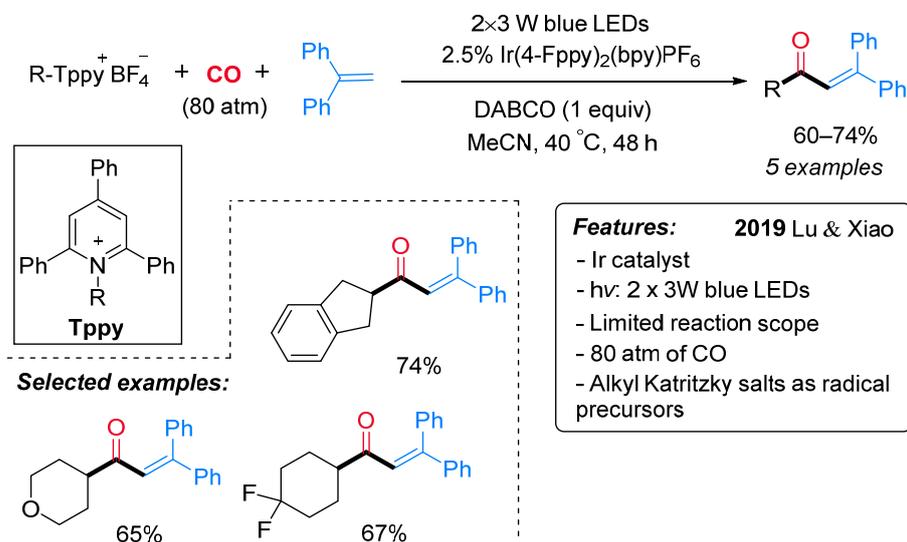
Scheme 26. Visible light-promoted photo-catalyzed decarboxylative carbonylative alkylation of carboxylic acids to ynones.



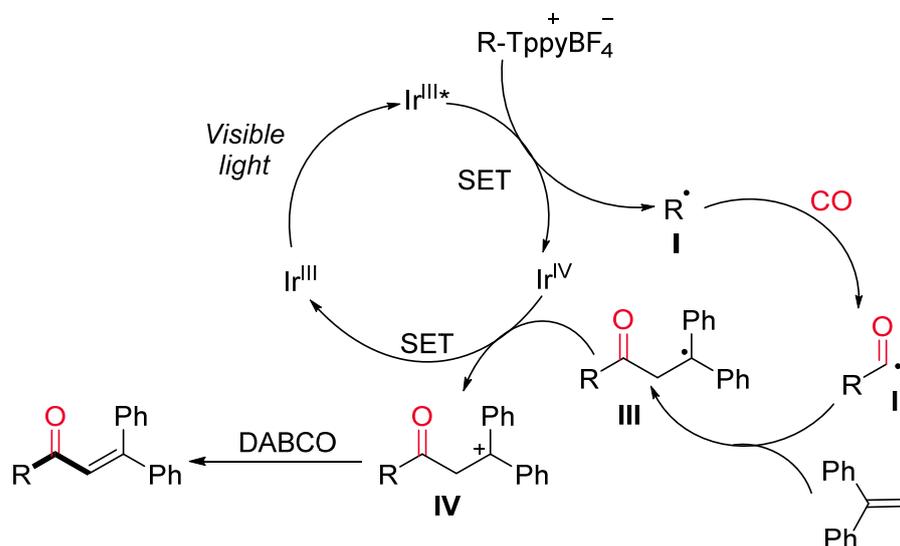
Scheme 27. The proposed reaction mechanism.

More recently, the same research group developed a visible-light-driven photocatalyzed synthesis of α,β -unsaturated ketones starting from alkyl Katritzky salts as a source of radicals [54]. In the context of a more general reactivity, a limited number of alkyl Katritzky salts reacted with 1,1-diphenylethylene in the presence of [Ir(4-Fppy)₂(bpy)]PF₆ and DABCO in MeCN under CO atmosphere and blue LEDs irradiation, leading to α,β -unsaturated ketones (Scheme 28). In the proposed reaction mechanism, the excited photocatalyst Ir(III)* is supposed to reduced alkyl Katritzky salts through a SET process

(Scheme 29). The generated radicals **I** inserts one molecule of CO with the formation of an acyl radical **II**, which reacts with 1,1-diphenylethylene yielding the radical species **III**. Intermediate **III** is then reduced by the photocatalyst Ir(IV) with the formation of the cationic intermediate **IV**, which, lastly, undergoes a DABCO-mediated deprotonation step to deliver the final ketone.



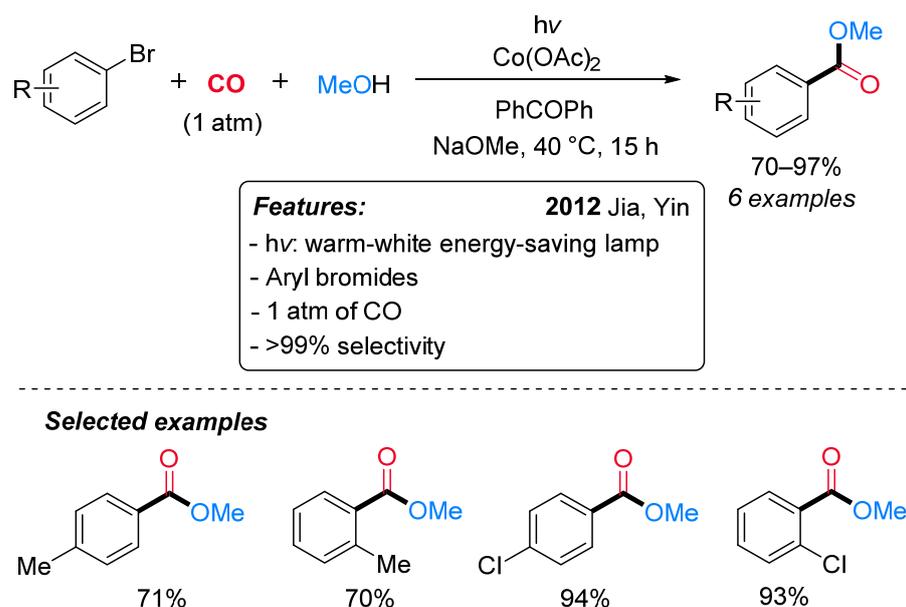
Scheme 28. Visible light-promoted Ir-catalyzed carbonylative alkyl-Heck-type reactions to α,β -unsaturated ketones.



Scheme 29. The proposed reaction mechanism.

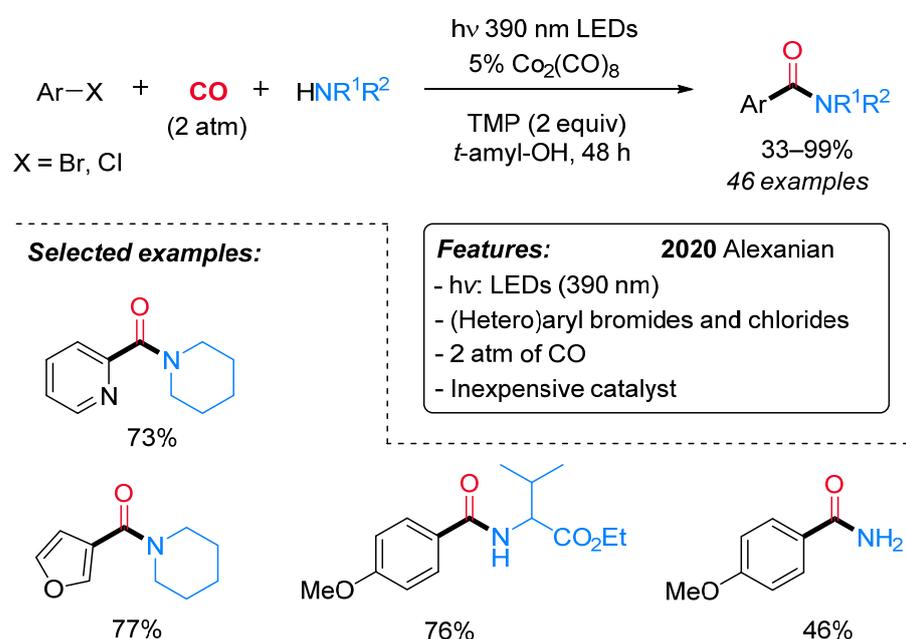
1.3. Visible-Light-Promoted Cobalt-Catalyzed Carbonylations

Cobalt salts have been found to efficiently catalyze the carbonylation of alkenes, chloro and bromoalkanes under UV irradiation [55–59]. The first report on visible-light-mediated cobalt-catalyzed carbonylation reaction appeared in 2012, when Jia, Yin and colleagues, based on their previous findings [60], developed a $\text{Co}(\text{OAc})_2$ -catalyzed alkoxy carbonylation of aryl bromides under visible-light irradiation and mild conditions (Scheme 30) [61]. The use of a strong base (NaOMe) and an organic sensitizer (PhCOPh) was essential to the reaction's success. Aryl bromides with a chloro substituent behaved better than tolyl bromides; however, a selectivity higher than 99% was always observed.



Scheme 30. Visible-light-mediated cobalt-catalyzed alkoxy carbonylation of aryl bromides.

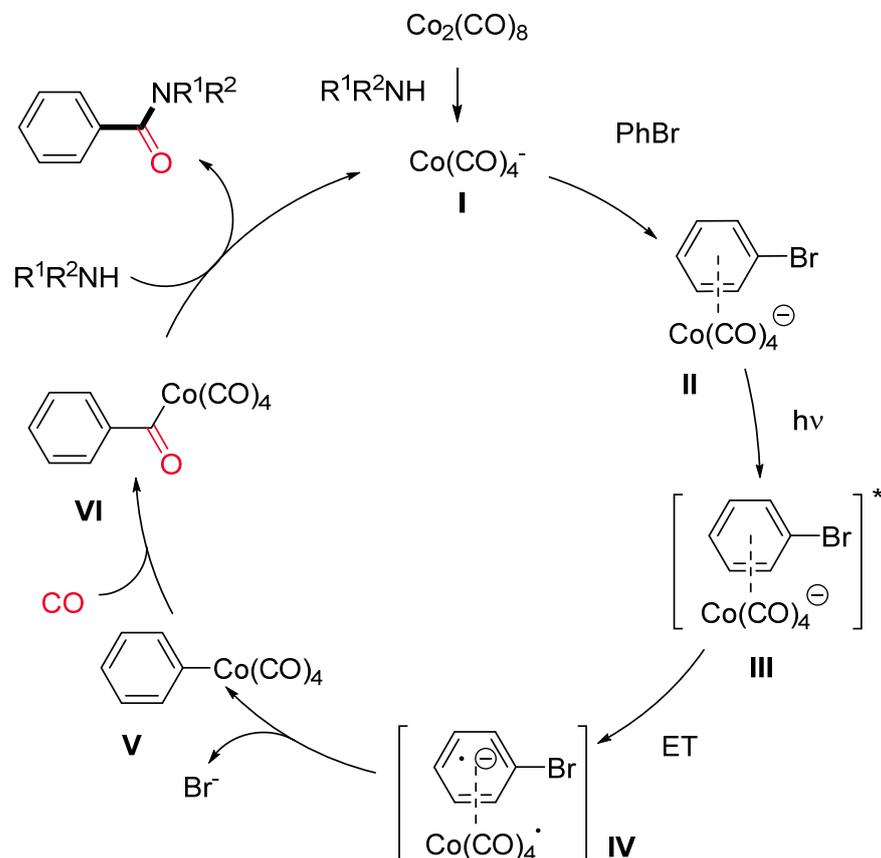
Recently, Alexanian et al. reported the visible-light-promoted aminocarbonylation of (hetero) aryl/vinyl bromides and chlorides using an inexpensive cobalt catalyst ($\text{Co}_2(\text{CO})_8$) in conjunction with tetramethylpiperidine (TMP) (Scheme 31) [62].



Scheme 31. Visible-light-mediated cobalt-catalyzed aminocarbonylation of bromo and chloroaryls.

Aryl bromides having both electron-rich and electron-deficient groups, as well as vinyl bromides, were well tolerated. In addition, bromo heteroaryls, such as pyridines, furans, quinolines and indoles, also performed nicely in this reaction. Aryl chlorides with electron-deficient groups gave the expected amides in satisfactory to good yields. A wide variety of primary and secondary aliphatic amines, including amino acids, gave the corresponding amides in moderate to high yields. Preliminary mechanistic investigations were consistent with the first formation of a cobaltate anion $[\text{Co}(\text{CO})_4]^-$ (I) as an active catalyst and the subsequent generation of an electron donor–acceptor complex (EDA) II

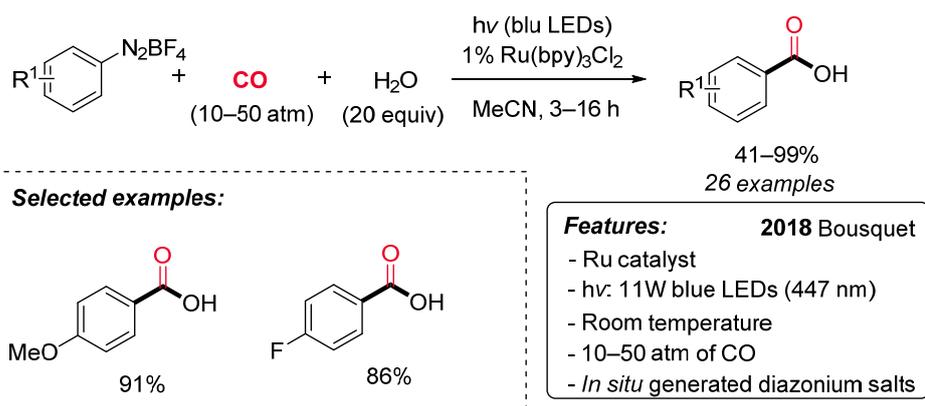
(Scheme 32). The intermediacy of the visible light leads to the corresponding excited species **III**. Then, a single-electron transfer produces two radical species (**IV**), which recombines, leading to a (hetero)aryl or vinyl cobalt species **V**. Finally, migratory insertion of CO affords intermediate **VI**, which undergoes displacement of the amine delivering the amide and the active catalyst.



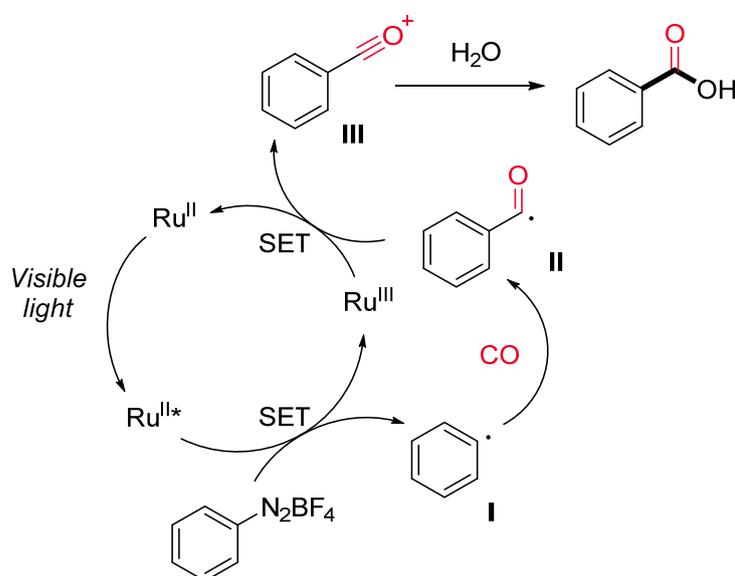
Scheme 32. The proposed reaction pathway.

1.4. Visible-Light-Promoted Ruthenium-Catalyzed Carbonylations

Carboxylic acids are ubiquitous in a wide range of bioactive molecules and industrially relevant compounds and represent a versatile, functional group in organic synthesis. Bousquet et al. have recently reported a ruthenium-catalyzed visible-light-promoted synthesis of benzoic acids starting from aryl diazonium salts, carbon monoxide (10–50 atm) and water under mild conditions (Scheme 33) [63]. The reaction displays a good functional group tolerance and generality. Notably, satisfactory results were achieved directly starting from anilines through the in situ generation of aryl diazonium salts, avoiding in this way their isolation. The proposed reaction pathway starts with the generation of an aryl radical (**I**) by SET with the excited $\text{Ru}(\text{II})^*$ (Scheme 34). Next, the insertion of CO on the aryl radical gives rise to an acyl radical (**II**), which is oxidized by the $\text{Ru}(\text{III})$ species to an acylium ion **III**. The $\text{Ru}(\text{II})$ is regenerated, and the acylium ion reacts with water delivering the desired carboxylic acid.



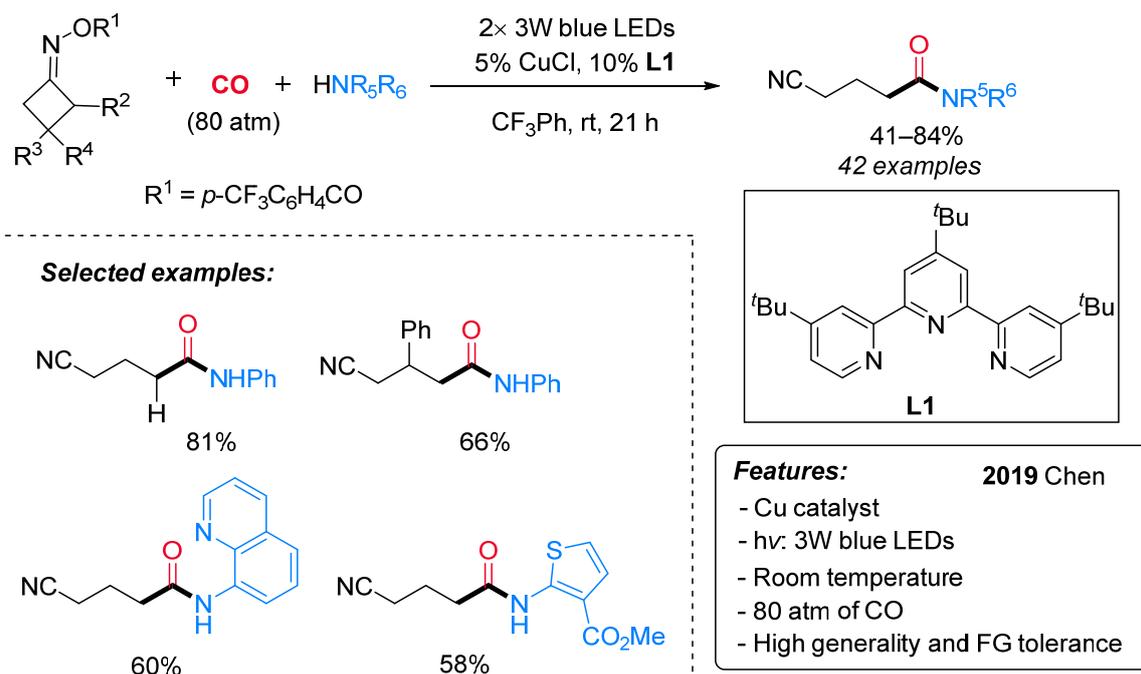
Scheme 33. The Ru-catalyzed synthesis of carboxylic acids via hydroxycarbonylation of aryl diazonium salts under irradiation conditions.



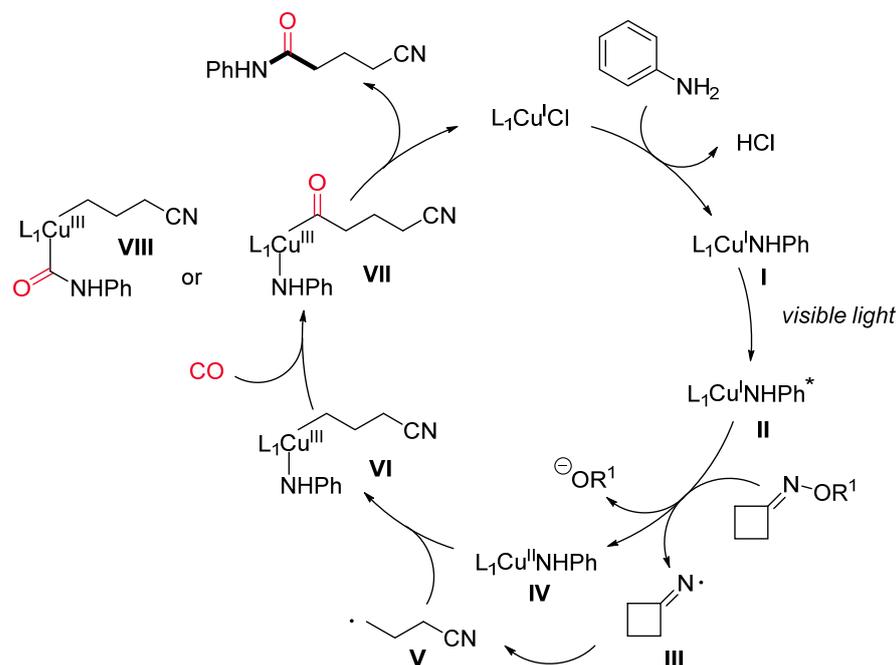
Scheme 34. The proposed reaction mechanism for the hydroxycarbonylation reaction.

1.5. Visible-Light-Promoted Copper-Catalyzed Carbonylations

To the best of our knowledge, the first and only example of copper-catalyzed photoinduced carbonylation reaction has been recently reported by Chen and co-workers [64] and is aimed at the synthesis of cyano-tethered amides by aminocarbonylation of oxime esters with amines and CO under mild conditions (Scheme 35). A number of cycloketone oxime esters and alkyl/aryl amines were evaluated, and a high level of functional group tolerance was found. Larger than four-membered rings, such as cyclopentanone and cyclohexanone oxime esters, did not lead to the expected products. For this aminocarbonylation reaction, the authors proposed a visible light-mediated Cu(I)/Cu(II)/Cu(III)-based catalytic cycle (Scheme 36). The first step is a single-electron transfer between the photoexcited $L_nCu(I)-NHPH$ complex (II)* or, alternatively, the ground state $L_nCu(I)-NHPH$ species (I) and the oxime, leading to an iminyl radical III and the oxidized $L_nCu(II)-NHPH$ complex (IV). Then, III undergoes a selective β -C–C bond cleavage to form the alkyl radical V, which can react with Cu(II)-complex IV producing a Cu(III) organometallic species VI. The latter, after sequential coordination and insertion of CO, leads to an acyl copper intermediate (VII or VIII), providing the final amide by reductive elimination and regenerating the active Cu(I) catalyst.



Scheme 35. The Cu-catalyzed synthesis of amides via aminocarbonylation of oximes under visible-light irradiation.



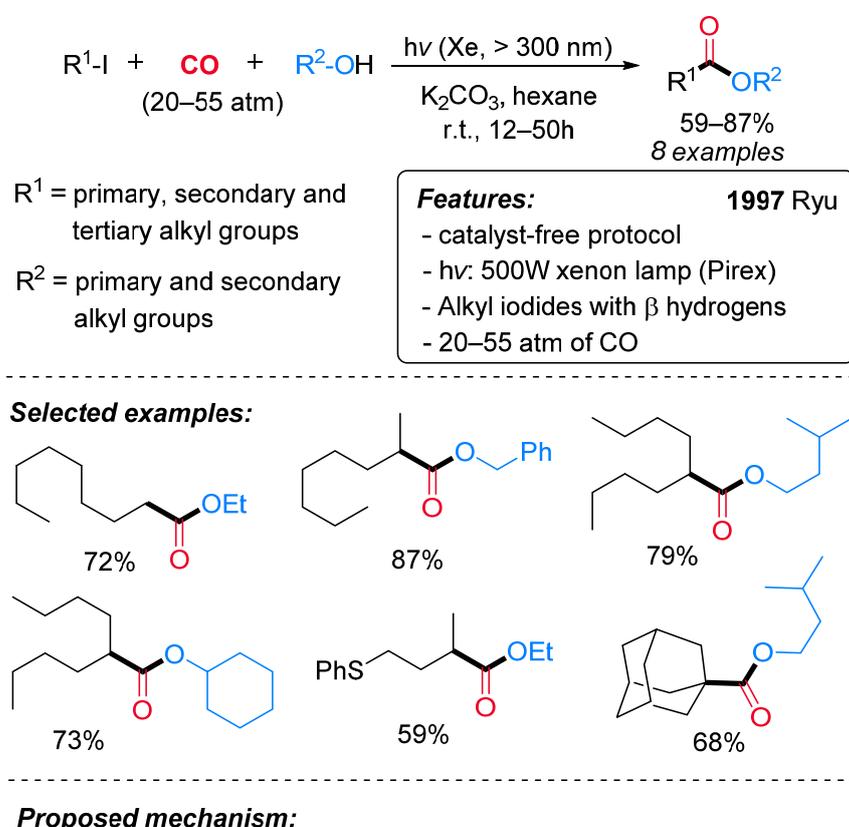
Scheme 36. The proposed reaction pathway.

1.6. Visible-Light-Promoted Metal-Free Carbonylations

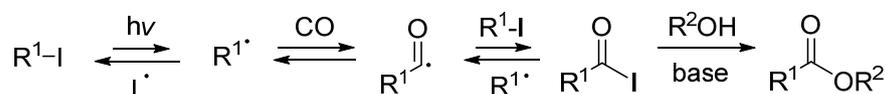
The major achievements in visible-light-mediated carbonylation reactions were obtained under transition-metal catalysis. The requirement of transition-metal catalysts often in connection with organic ligands is undoubtedly expensive, and the removal of their traces from the final products is necessary, particularly in the synthesis of pharmaceutical compounds. Metal-free photocatalytic protocols can overcome the above-mentioned drawbacks and may represent attractive greener and more sustainable alternatives.

In 1997, the efficient conversion of alkyl iodides to the corresponding esters was achieved under photoirradiation conditions in the absence of catalysts (Scheme 37) [29].

The presence of hydrogens in the β position on the alkyl iodides results in the formation of positional isomers via the β -elimination pathway under conventional transition metal-catalyzed carbonylation conditions [65]. This radical protocol allows the selective alkoxy carbonylation at the carbon attached to the halogen, and, for this reason, a wide range of aliphatic iodides, including tertiary ones, can be efficiently employed (Scheme 37, *selected examples*). High pressure of CO (from 20 to 55 atm) and the presence of an organic (triethylamine) or inorganic base (K_2CO_3 , KOH) were essential to the reaction outcome. Mechanistically, by irradiation, the homolytic cleavage of the C–I bond produces an alkyl radical species that reacts with the carbon monoxide, providing an acyl radical intermediate. In the presence of another molecule of alkyl iodide, an acyl iodide is then generated, and, after reaction with R^2OH , the corresponding ester is produced (Scheme 37, *proposed mechanism*). Remarkably, the reaction can be extended to the synthesis of amides using amines in place of alcohols [28].



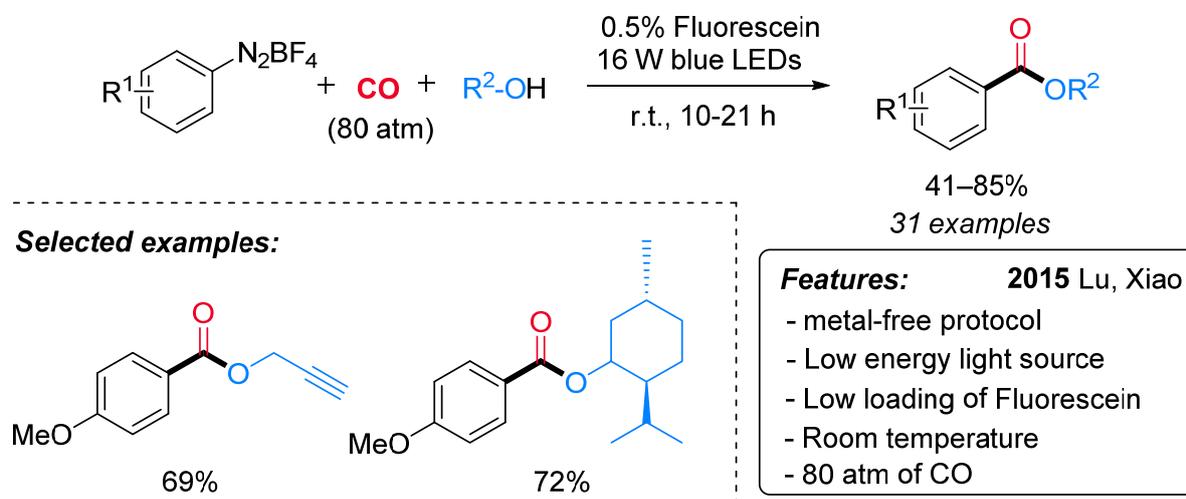
Proposed mechanism:



Scheme 37. The catalyst-free synthesis of esters via radical alkoxy carbonylation of alkyl iodides under irradiation conditions.

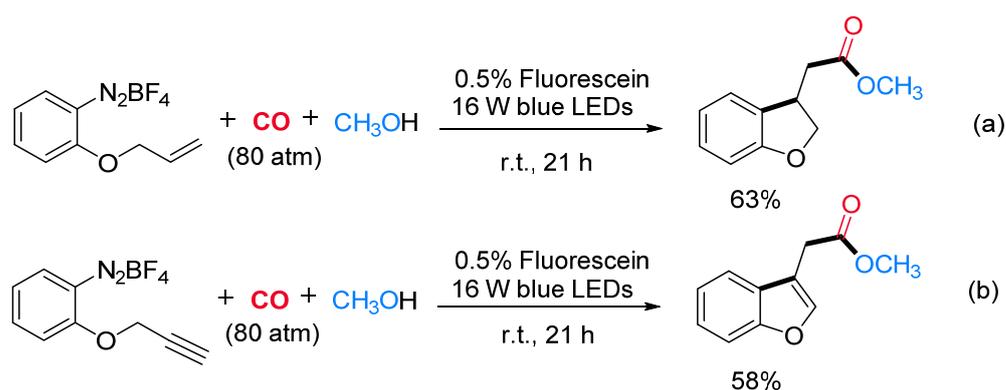
The first example of radical alkoxy carbonylation of aryl diazonium salts using CO gas through visible-light-induced photoredox catalysis has been reported in 2015 by the Xiao research group (Scheme 38) [66]. A wide variety of aryl carboxylic acid esters, bearing both electron-donating and electron-withdrawing groups, were obtained in good to excellent yields at room temperature. The generality of the alcohol coupling partner, including the use of chiral alcohols, was also demonstrated. Notably, terminal alkynes, which are known to be good acceptors in radical reactions, remained untouched. Sensitive functional groups (such as iodo, bromo) in traditional transition metal-catalyzed alkoxy carbonylation reactions were compatible in this process, thus allowing further synthetic manipulations.

Remarkably, a low loading of an organic dye (fluorescein) is employed as a photocatalyst, and a low energy visible light (16 W blue LEDs) is enough to promote the reaction. However, high pressure of CO (80 atm) proved to be crucial for the success of the reaction.

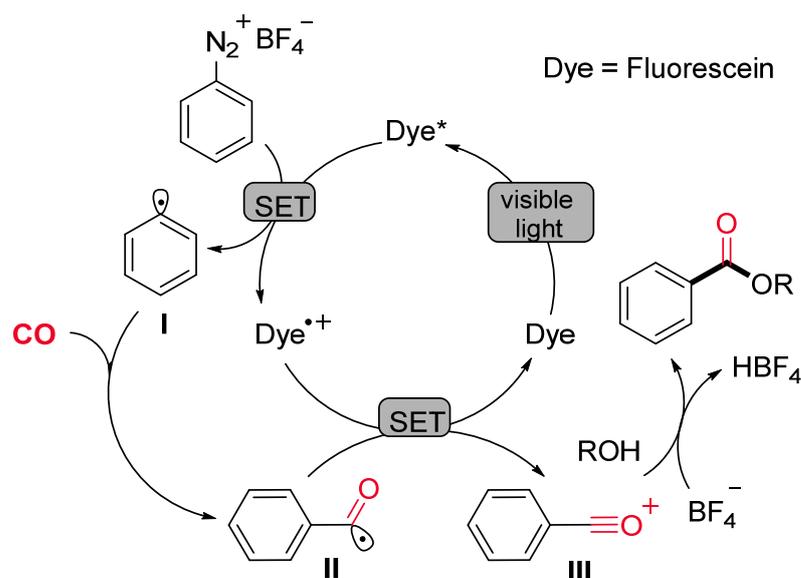


Scheme 38. Visible light-induced fluorescein-catalyzed alkoxylation of aryldiazonium salts.

This radical alkoxylation protocol was applicable to other radical carboxylation cascade reactions. For example, when benzenediazonium salts, bearing the allyl or the propargyl function at the *ortho* position, were caused to react under standard reaction conditions, the corresponding methyl 2-(2,3-dihydrobenzofuran-3-yl)acetate (Scheme 39a) and methyl 2-(benzofuran-3-yl)acetate (Scheme 39b) were obtained in satisfactory yields. Mechanistic studies suggested that the reaction might proceed via carbon radical intermediates **I** formed by single-electron reduction of the substrate with the fluorescein photocatalyst in its excited state. The reactive intermediate **I** might be able to trap the CO molecule delivering the benzoyl radical **II**, which is oxidized by the dye radical cation (Dye^{•+}) with concomitant restoring of the active photocatalyst. The resulting cation **III** could be directly trapped by various alcohols leading to a wide range of alkyl benzoates (Scheme 40).

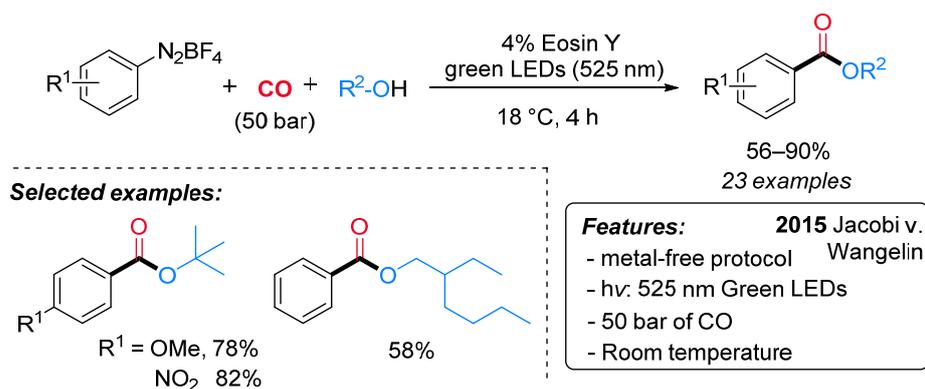


Scheme 39. Fluorescein-catalyzed radical addition/alkoxylation reaction sequences from alkene (a) and alkyne (b) derivatives.



Scheme 40. The proposed mechanism for the fluorescein-catalyzed visible light-induced alkoxy-carboxylation of aryldiazonium salts.

A very similar approach was developed in the same period by Jacobi von Wangelin's group. Alkyl benzoates were efficiently obtained from arene diazonium salts, carbon monoxide and alcohols under visible-light irradiation and in the presence of eosin Y as the catalyst (Scheme 41) [67]. Under metal and base-free conditions, a variety of functionalities were well tolerated both on the substrates and on various functionalized additives. Interestingly, tertiary esters, which are difficult to obtain by conventional esterification procedures due to their steric hindrance, can also be prepared in excellent yields. Moreover, the industrially relevant intermediate, 2-ethylhexyl benzoate, has been obtained in 58% yield from PhN_2BF_4 , 2-ethylhexanol and CO under standard conditions.

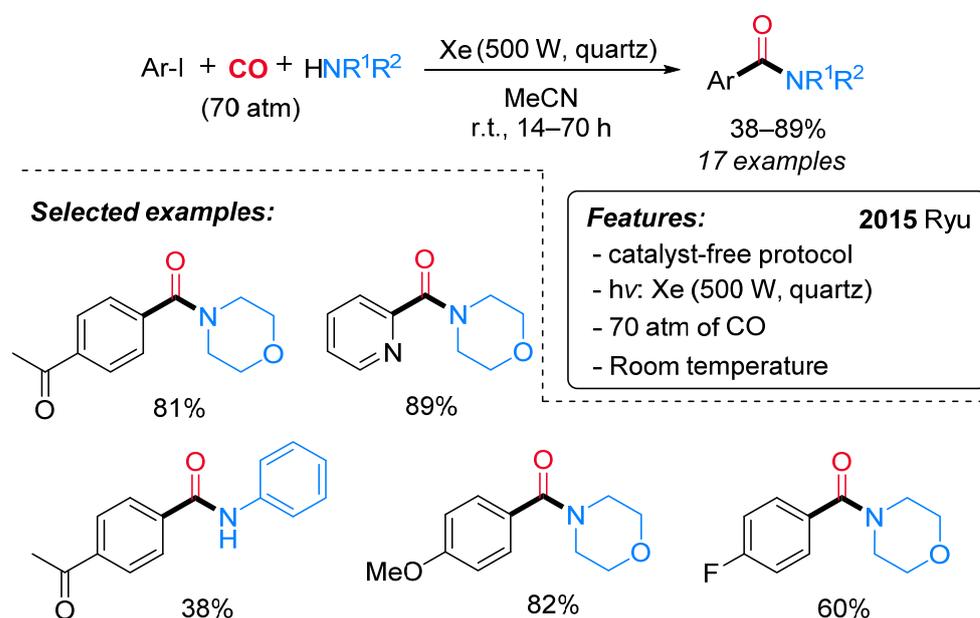


Scheme 41. The synthesis of benzoates through visible light-driven eosin Y-catalyzed alkoxy-carboxylation of arene diazonium salts.

The mechanistic investigations, including the observation of benzoyl-TEMPO adduct, support the sequential reduction (SET), carbonylation, and oxidation (SET) to arylium cations, which undergo rapid addition to alcohols (Scheme 40, Dye = Eosin Y).

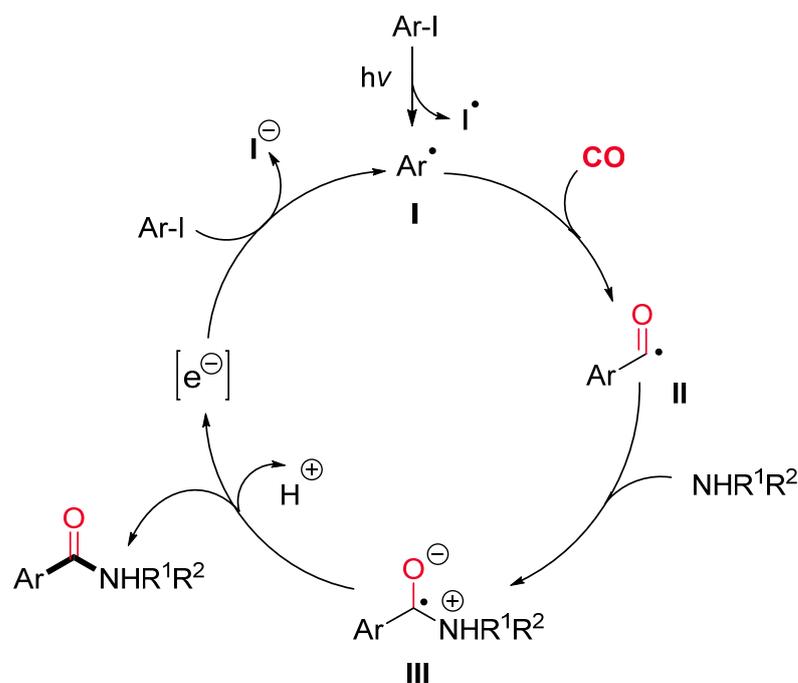
From the pioneering work of Heck on palladium-catalyzed aminocarbonylation of aryl iodides [68], several efforts have been accomplished for the synthesis of aromatic amides [69,70] through radical carbonylative pathways as well [66,67,71]. Recently, the first example of catalyst-free photo-induced aminocarbonylation of aryl iodides with CO and amines has been reported by Ryu and co-workers [72]. A wide variety of amides, including

hetero aromatic amides, has been obtained in good yields under mild reaction conditions (Scheme 42).



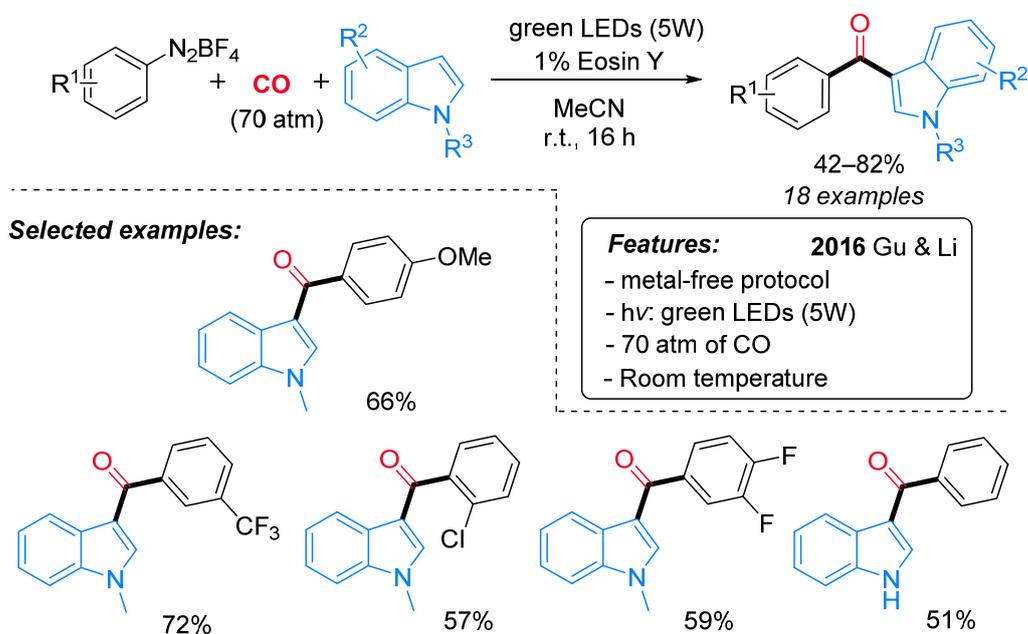
Scheme 42. Photo-induced aminocarbonylation of aryl iodides with primary and secondary amines.

The aryl radical **I**, generated by a photo-induced cleavage of the starting aryl iodide, might react with CO leading to the corresponding acyl radical **II** (Scheme 43). The nucleophilic addition of an amine to the latter gives a zwitterionic radical intermediate **III**. Finally, electron transfer to the aryl iodide would provide the aryl radical **I** and the expected amide.



Scheme 43. The proposed mechanistic pathway for the catalyst-free photo-induced aminocarbonylation of aryl iodides.

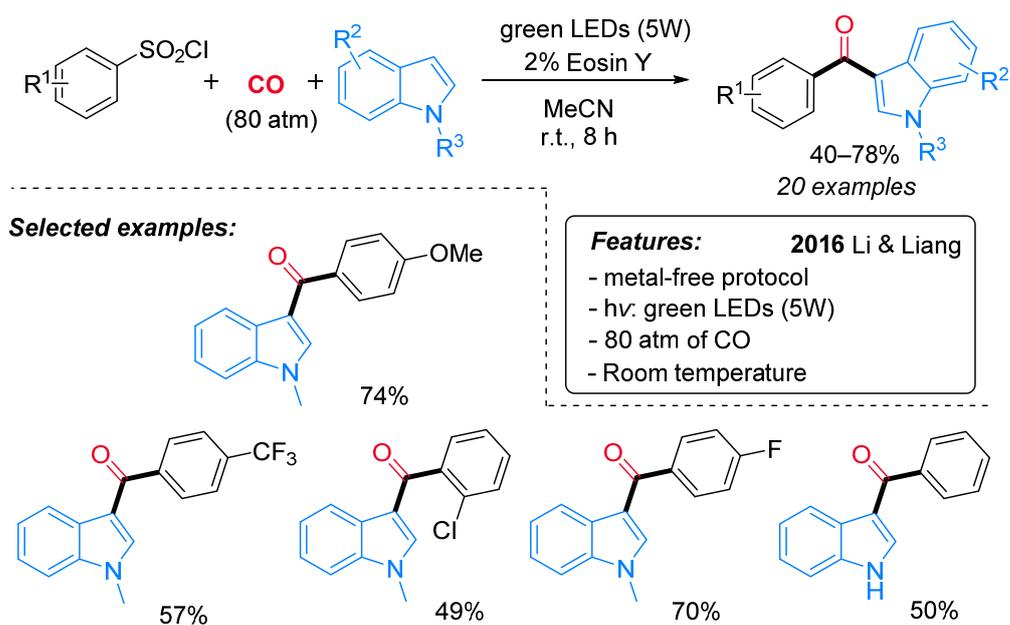
Inspired by Xiao [66] and Wangelin [67] independent reports, the Eosin-Y-catalyzed synthesis of indol-3-yl aryl ketones from indoles, CO and aryldiazonium salts has been recently reported by Gu and Li (Scheme 44) [73]. This protocol features high versatility, high functional group tolerance and mild reaction conditions except for the high pressure of CO required (70 atm).



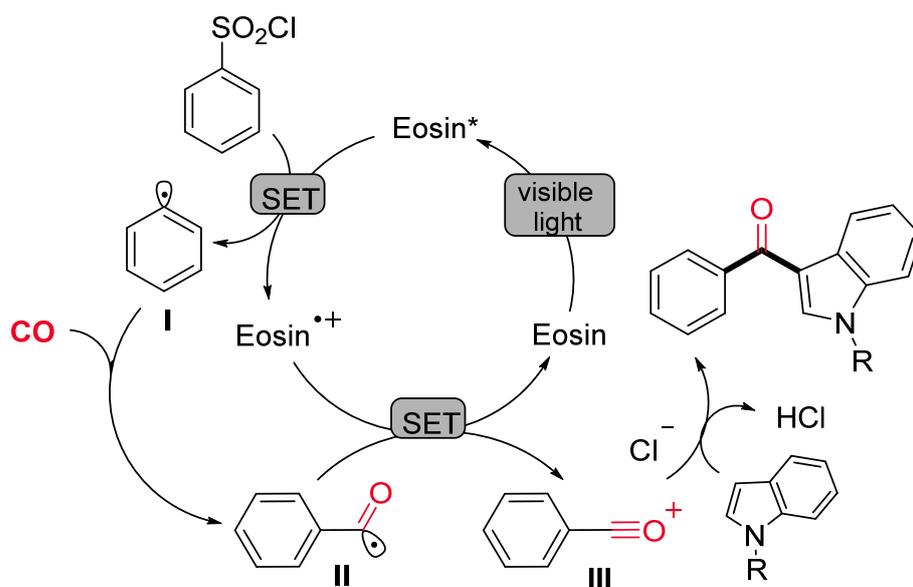
Scheme 44. The photo-induced synthesis of indol-3-yl aryl ketones from indoles, CO and aryldiazonium salts.

The synthesis of indol-3-yl aryl ketones was achieved also by Li, Liang and colleagues, starting from arylsulfonyl chlorides in place of aryldiazonium salts under very similar photocatalytic conditions (Scheme 45) [74]. Notably, the methodology demonstrated wide applicability with both electron-rich and electron-deficient functional groups at reduced reaction time if compared with Gu and Li's protocol [73]. The proposed pathway starts with the reduction of the arylsulfonyl chloride by a single-electron transfer process (SET) to produce an aryl radical **I** and the Eosin radical cation [Eosin^{•+}] (Scheme 46). Then, the aryl radical **I** reacts with CO, delivering an acyl radical **II**, which is oxidized to an acylium intermediate **III** by the Eosin radical cation [Eosin^{•+}]. The active photocatalytic species is indeed regenerated while the acylium ion undergoes nucleophilic attack by the indolyl species, leading to the final product.

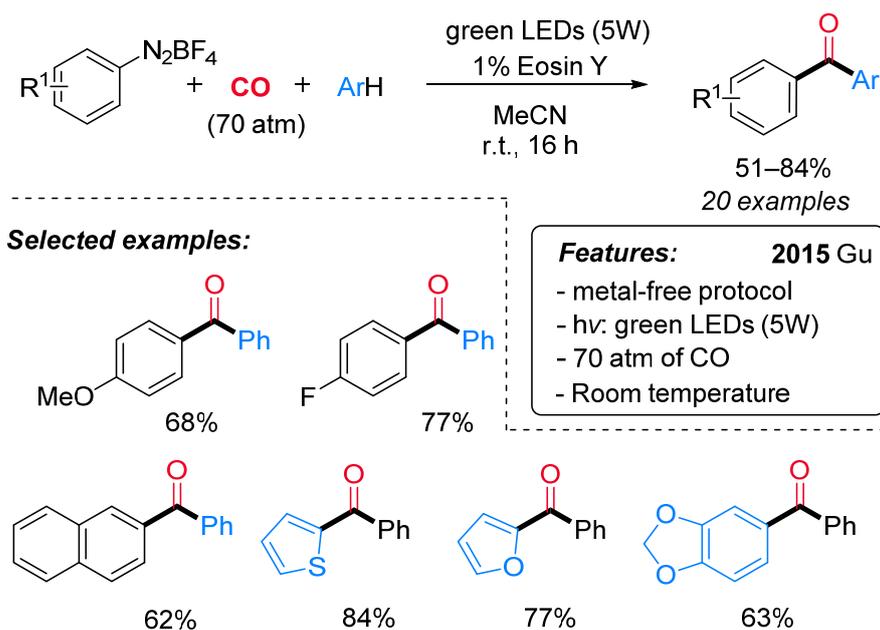
It has been demonstrated that not only indoles but also (hetero)arenes might serve as a platform to trap benzyldyneoxonium cations [75]. Under very similar reaction conditions [67,73], a wide variety of unsymmetrical aryl and heteroaryl ketones were successfully obtained from (hetero)arenes, CO and aryldiazonium salts in the presence of Eosin Y and green LEDs (Scheme 47). Interestingly, the electronic nature of the diazonium salt has little influence on the reaction, while electron-rich (hetero)arenes gave the best results. Based on control experiments and in agreement with the previous reports [67], the proposed mechanism is shown in Scheme 48. Under irradiation conditions, the excited photocatalyst (Eosin Y^{*}) is generated. Then, the electron-deficient phenyl diazonium salt is reduced to **I** by Eosin Y^{*} through a single-electron transfer (SET). The aryl radical species **I** react with CO, providing the acyl radical **II**, which is oxidized by Eosin Y^{•+} to cationic intermediate **III**. Finally, benzyldyneoxonium **III** is trapped by the arene (or heteroarene) derivative, delivering the desired ketone.



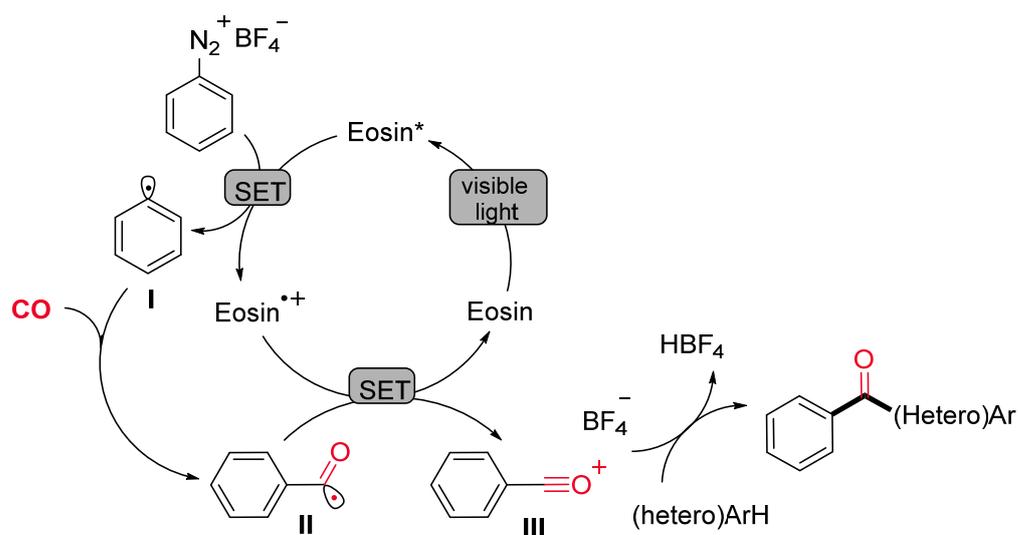
Scheme 45. The photo-induced synthesis of indol-3-yl aryl ketones from indoles, CO and aryl sulfonyl chlorides.



Scheme 46. The proposed mechanism for the Eosin-catalyzed visible-light-promoted indolylcarboxylation of aryl sulfonyl chlorides.

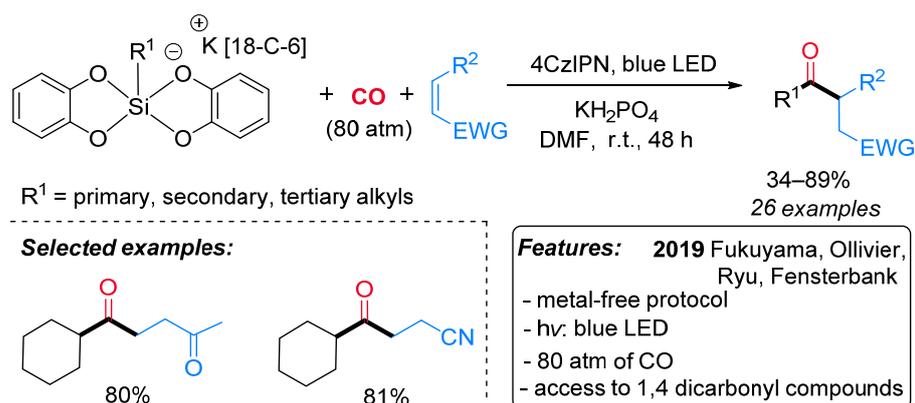


Scheme 47. The photo-induced synthesis of unsymmetrical aryl ketones from (hetero)arenes, CO and aryldiazonium salts.



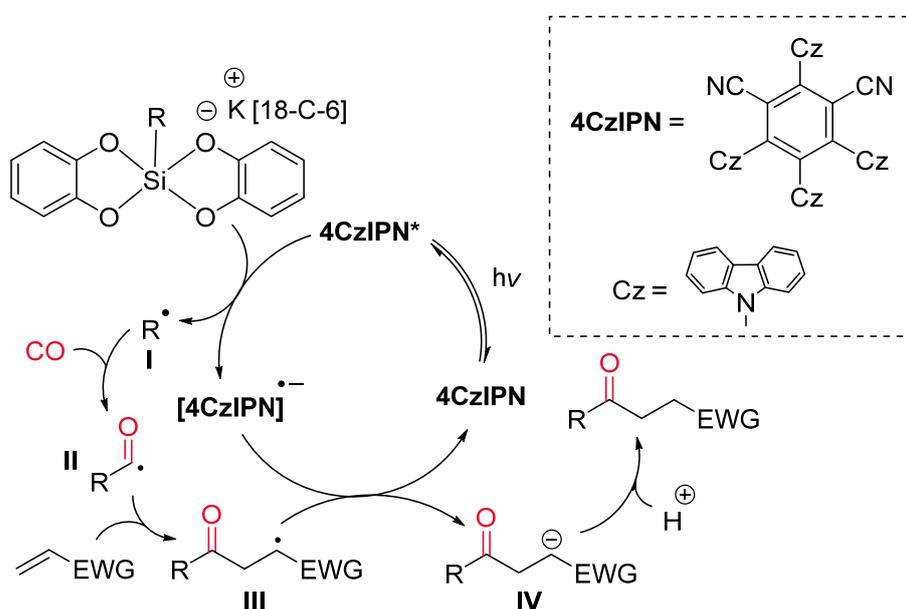
Scheme 48. The proposed mechanism for the photo-induced synthesis of indol-3-yl aryl ketones from indoles, CO and aryldiazonium salts.

Recently, the first example of photocatalyzed oxidative carbonylation of organosilicates to unsymmetrical ketones has been reported by Fukuyama, Ollivier, Ryu, Fensterbank and co-workers [76]. This metal-free procedure is based on the use of an inexpensive organic dye, 4CzIPN, which, in combination with the blue led, is able to catalyze the reaction of alkyl bis(catecholato)silicates, CO (80 atm) and activated olefins to produce a wide range of ketones (Scheme 49). Notably, primary, secondary and tertiary alkyl radicals generated by the photocatalyzed oxidation of organosilicates underwent efficient carbonylation with CO under standard conditions. Interestingly, 1,4-dicarbonyl compounds were efficiently accessed through this protocol, while allyl sulfones were successfully employed as radical acceptors in this three-component reaction.



Scheme 49. The synthesis of unsymmetrical ketones via 4CzIPN-catalyzed radical carbonylations.

Mechanistic studies reveal that, initially, the photocatalyst is excited under visible-light irradiation. Then, the alkyl bis(catecholato)silicate undergoes oxidation by the excited 4CzIPN* through a single-electron-transfer (SET) process, leading to the formation of the alkyl radical species **I** and the reduced organocatalyst [4CzIPN]^{•−}. The alkyl radical **I** reacts with CO to generate the acyl radical **II**, which, in turn, adds to the activated alkene affording the radical intermediate **III**. Catalyst [4CzIPN]^{•−} converts **III** into the carbanionic species **IV** by reduction (SET), and, in this way, the photocatalyst is able to restart a new catalytic cycle. Finally, the base (KH₂PO₄) provides the proton for the formation of the final product (Scheme 50).



Scheme 50. Proposed mechanism for the 4CzIPN-catalyzed carbonylative synthesis of ketones from organosilicates, CO and activated alkenes.

More recently, the same authors have developed a visible-light-driven photocatalyzed aminocarbonylation of alkyl bis(catecholato)silicates with amines under similar reaction conditions [77]. In this approach, the CCl₄ was used as a mediator in order to promote the formation of acyl chloride, which is intermediate in the formation of the corresponding amides.

2. Conclusions

In this review, the major advances in the field of visible-light-induced catalyzed and un-catalyzed carbon monoxide-based carbonylation reactions have been described. The use of visible light in carbonylation chemistry has led to valuable and more sustainable alternatives for the synthesis of carbonyl-containing compounds. Mild reaction conditions, such as room temperature, are routinely applied. However, the use of low CO pressure is less frequent, and many improvements are expected from this point of view. The employment of greener reaction media and the application of continuous flow conditions can be beneficial to this chemistry. The use of CO surrogates, so attractive in conventional carbonylation reactions, can lead to several advantages in photocatalytic carbonylation reactions. The research in this field should be focused on discovering more efficient photocatalysts, possibly in combination with co-catalysts or additives, in order to increase both turnover number and turnover frequency (TON and TOF) and to improve the industrial attractiveness of these carbonylative methodologies. Heterogeneous systems, although sometimes hardly compatible, should be considered to improve the sustainability of these processes.

Despite the increasing number of high-impact publications in the field, this is, undoubtedly, an underdeveloped area, and the real potential of this highly sustainable carbonylation strategy still needs to be discovered. We hope that this contribution might help other researchers in developing even more attractive visible-light-driven carbonylation protocols in the coming years.

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