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Visible-Light-Driven Direct Oxidative Coupling Reaction Leading to Alkyl Aryl Ketones Catalyzed by Nano Pd/ZnO

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Abstract: Direct alkyl sp^3 C-H activation to form new C-C bonds is one of the major challenges. Here, for the first time, we represent a new way using nano Pd/ZnO which plays both as photoredox and transition-metal catalyst for C-C bond formations. By using this catalyst, we have accomplished an oxidative coupling reaction between aryl halides and tertiary amines to yield the corresponding naturally occurring alkyl aryl ketones by using visible light irradiation**.** Furthermore, the carbonylation process was carried out on 10 gram scale, with visible light and thermally condition, and it was proved to be scalable, efficient and economical.

Introduction

Over the past decade, palladium-catalyzed carbonylation reactions have become one of the most important reactions to construct carbon-carbon and carbon-heteroatom bonds formation such as ketones, esters, aldehydes, amides, carboxylic acids and their derivatives.[1] Among these carbonyl compounds, the synthesis of alkyl aryl ketones have attracted significant interest because of their widespread use in fragrance, pharmaceutical, agrochemical, dye, functional material industries and in organic synthesis (Scheme 1a).[2] So, considerable efforts have been made to extend capable methods for alkyl aryl ketone synthesis. Traditionally, Friedel-Crafts acylation employing acid halides or acid anhydrides have been used for the synthesis of alkyl aryl ketones.[1-3] Low regioselectivity, releasing large amounts of waste, harsh reaction conditions, incompatibility with electron-deficient functional groups (specially nitro aromatic compounds), and the need for stoichiometric amounts of catalyst make this process undesirable on large scale. Hence, the synthesis of alkyl aryl ketones have been mainly based on the oxidation of alkylbenzenes,[4] in the industrial processes. Synthesis of pharmaceuticals and fine chemicals, stoichiometric oxidants such as permanganate and dichromate were used. Strongly exothermic reaction is the serious problem by using these oxidants.

Also thermodynamically oxidation is highly favorable, the reaction is kinetically hindered so that the oxidations have been often performed at high temperatures (175−225 °C).[5] Therefore, these processes are undesirable in large scale. To overcome the difficulties of traditional methods, palladium catalyzed carbonylation reactions are virtually attractive. For the these transformations, carbon monoxide (CO) has been mostly used as the source of the carbonyl group.[6] It is a highly poisonous and flammable gas.[7] Due to the improvement of safer and more suitable sources of carbonyl group, metal carbonyl complexes such as $Mo(CO)_6$, $Co_2(CO)_8$, have been were used. However, the main problem is, their high cost, toxicity and un-stability.[8] In the last two decades, cheaper organic carbonyl compounds such as dimethylformamide, formates, acid halides, formic anhydride, chloroform, aldehydes, and formic acid derivatives have been also reported in carbonylative reactions.[9] In 2011, Li and co-workers reported a new procedure by using palladium which catalyzed oxidative coupling of aryl iodides and trialkylamines for the synthesis of alkyl aryl ketones. It was the first and the only report in the literature, using trialkylamines in water as carbonyl sources (Scheme 1b).[2a] The literature studies have revealed that there is no report of using a photoredox catalysis in visible light for the synthesis of alkyl aryl ketones by using a trialkylamine as carbonyl source. Tertiary amines which have highly stable C-N bond, the activation of this bond is an important challenge in organic synthesis. So, to the best of our knowledge, use of stable tertiary amines as the carbonyl source for this transformation by using a photocatalyst is unprecedented (Scheme 1c).

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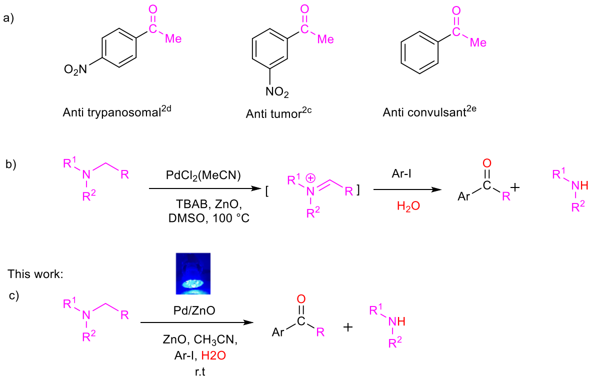


Scheme 1. (a) Selective bioactive molecules bearing carbonyl group. (b-c) Synthesis of alkyl aryl ketones.

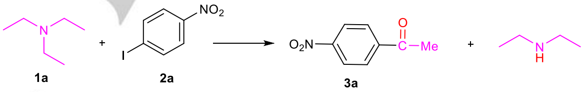
Zinc oxide (ZnO), has possessed significant attention for a long time as a kind of capable photocatalyst. Only 3-7% of the total solar light reaching Earth's surface is UV light, and particularly photocatalytic processes using visible light by ZnO photocatalyts in behalf of broad band gap and great excitation binding energy is difficult.[10] Hence, research groups have focused on the improvement of ZnO as photocatalysts. One approach for achieving these goals is, to load noble metals (such as Au, Pd, Pt) nanoparticles on the surface of ZnO nanostructures.[11] Noble metals exhibit strong visible-light absorption characteristics because of localized surface plasmon resonance (LSPR) which are located on semiconductor-based photocatalysts.[12] A new nano sized Pd doped on ZnO as a catalyst for the C-C and C-N bonds formation, under thermally condition have been reported by us.[13] We also reported its photocatalytic activity in Suzuki reaction.[14] So, considering that nano Pd/ZnO showed excellent results as photocatalyst, it encouraged us to use it for the synthesis of alkyl aryl ketons. Notably, this is the first example for the synthesis of alkyl aryl ketones using trialkylamines as carbonyl source under visible light irradiation at ambient temperatures. Herein, we report an efficient and scalable process for the formation of alkyl aryl ketons.

Results and Discussion

Initially, we focused on the reaction between triethylamine (**1a**) and 1-iodo-4-nitrobenzene (**2a**) as a model compound. A solution of (**1a**) and (**2a**) in DMSO was irradiated by 11 W white LED in the attendance of nano Pd/ZnO as photocatalyst and TBAB for 24 h at room temperature. Then the reaction mixture was worked up by H_2O and the desired ketone (**3a**) was obtained in 60% yield (Table 1, entry1). This promising result inspired us to improve the reaction. So, we changed a lot of factors, including solvent, photocatalyst loading, additive, light source, atmosphere, and also reaction time (Tables S1-S4).

Solvents are important in photocatalysis reactions, so we used some commonly solvents while other reaction conditions were maintained unchanged. The solvents such as DMF, CH_3CN, dioxane and EtOH were used for 24 h, and then the reaction mixture was worked up with H_2O and the desired ketone (**3a**) was obtained (Table S1, entries 1-6). To improve the reaction condition, we decided to remove aqueous work up and instead use water as solvent. In the presence of water as sole solvent the yield of (**3a**) decreased (Table S1, entry 5) but we found that a mixture of CH_3CN and water improved the reaction (Table 1, entry 2 and Table S1, entries 7-13). Afterwards, selection of some additives, were further investigated (Table S2). The results showed that the excess amount of ZnO or mixture of both TBAB and ZnO were more effective and the yield of (**3a**) was increased sharply to 71% (Table 1, entries 3, 4 and Table S2, entries 8, 13). So excess amount of ZnO (4 mmol) for further investigations was chosen. It is noteworthy that the yield was sharply reduced when reaction was investigated under argon atmosphere, whereas under air and O_2 the yield was increased up to 76%, which demonstrated that O_2 was necessary for this transformation (Table 1, entry5 and Table S3, entries 5, 6).

Table 1. Selected optimization data for synthesis of alkyl aryl ketones under visible-ligh irradiation.[a]



Entry	Additive (mmol)	Solvent (mL)	Yield[b] (%)
1	TBAB (1)	DMSO	60
2	TBAB (1)	CH_3CN/H_2O (2:1)	66
3	TBAB (1)/ZnO (1)	CH_3CN/H_2O (2:1)	71
4	ZnO (1)	CH_3CN/H_2O (2:1)	71
5[c]	ZnO (1)	CH_3CN/H_2O (2:1)	76
6[d]	TBAB (1)	CH_3CN/H_2O (2:1)	0

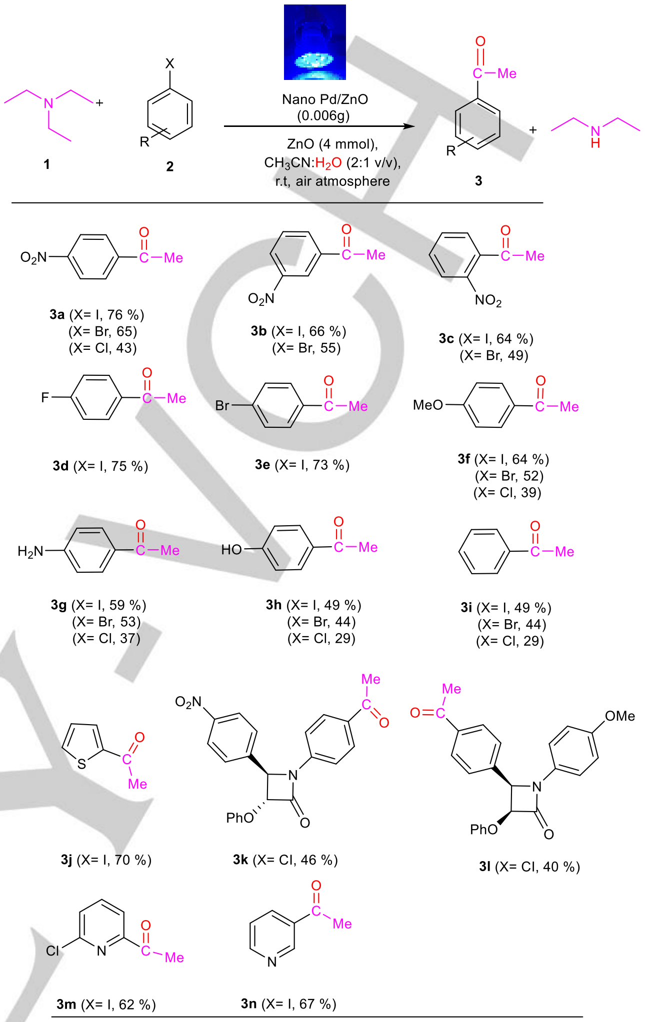
[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), nano Pd/ZnO (0.006g), solvent (3 mL) at room temperature, 11 W white LED (wavelength in the range 450-750 nm), 24 h. [b] isolated product. [c] O_2 atmosphere. [d] Dark condition.

To better understand the enhancement of the catalytic performance that occurs through light irradiation of the Pd/ZnO NPs, the dependence of the catalyzed reaction on the light's wavelength and intensity were investigated. As shown in Figure S1a, increasing the light intensity white LED resulted in an almost linear increase in the conversion of the carbonylation coupling reaction catalyzed by the Pd/ZnO NPs. It can be seen that the higher the light intensity, the greater the contribution due to light irradiation to the overall conversion rate.

We also used different wavelengths including red (620-750 nm), green (495-570 nm) and blue (450-495 nm). The yield improved to78% when the reaction was under irradiation by 11 W blue LED instead of white LED, Figure S1b. All the light intensities were strictly the same (0.4 W/cm^2) in every wavelength region. The dependence of photocatalytic activity on light intensity and wavelength indicates that energetic electrons excited by light absorption are responsible for the observed photocatalytic activity. Since the reaction rate is expected to depend on the population of electrons with sufficient energy to initiate the reaction of the reactant molecules, one can increase the number of energetic electrons by applying higher light intensity. Tuning the irradiation wavelength can also increase the number of energetic electrons and may also assist us to understand the mechanism of the reactions.

Outdoor proficiency under sunlight was also investigated. This was executed on a winter day, in January, in Shiraz with the sun at 68.5° zenith angles and temperature 10-15 $^\circ$C ranges. This result shows that the nano Pd/ZnO catalyst has excellent sunlight applicability (Figure S2). In order, to find the recycling ability of nano Pd/ZnO photocatalyst it was used for five runs without any remarkable loss of yield or increase of the reaction time (Figure S3). After optimization of the reaction conditions, the substrate scope was examined (Table 2). All the reactions were carried out in air atmospheres using $CH_3CN:H_2O$ (2:1) as solvent, nano Pd/ZnO (0.006 g) as photocatalyst and ZnO (4 mmol) as additive at room temperature by using blue LED. The yield of the carbonylation reaction depends on the type of the aryl halide. The results disclosed that both electron-donating and electron-withdrawing groups of aryl iodides were suitable for the reaction, but aryl chlorides and bromides showed little reactivity and lower conversion in comparison with the similar iodides. Interestingly, when two different halides are presented in a substrate, chemoselectivity between these halo groups was observed (entry **3d**, **3e**). Furthermore, when using the substrates supporting an ortho-group on the aryl halides, the yield was decreased, this can be explained by the steric effect. Surprisingly, free NH_2 and OH groups on the substrate did not cause affected serious problem and the desired product was obtained in moderate yield. However, to comparison with other substrates the yields were decreased. Moreover, nitrogen and sulfur containing heteroarenes, such as pyridines (**3k**-**3n**), and thiophene (**3j**), were amenable to this carbonylation reaction, affording a satisfying outcome. The synthesis of some new biologically active β-lactams (**3k-3l**), were treated and the desired alkyl aryl ketones were obtained.[15]

Table 2. Visible-light photoredox carbonylation of aryl halids (**2**) with triethylamine (**1a**) using nano Pd/ZnO.[a, b]



3a (X= I, 76 %) (X= Br, 65) (X= Cl, 43)
3b (X= I, 66 %) (X= Br, 55)
3c (X= I, 64 %) (X= Br, 49)
3d (X= I, 75 %)
3e (X= I, 73 %)
3f (X= I, 64 %) (X= Br, 52) (X= Cl, 39)
3g (X= I, 59 %) (X= Br, 53) (X= Cl, 37)
3h (X= I, 49 %) (X= Br, 44) (X= Cl, 29)
3i (X= I, 49 %) (X= Br, 44) (X= Cl, 29)
3j (X= I, 70 %)
3k (X= Cl, 46 %)
3l (X= Cl, 40 %)
3m (X= I, 62 %)
3n (X= I, 67 %)

[a] Reaction conditions: **2** (1 mmol), **1** (1 mmol), ZnO (4 mmol), CH_3CN (2 mL), water (1 mL), nano Pd/ZnO (0.006g), 11 W blue LED irradiation, room temperature, air atmosphere, 24 h. [b] Isolated product.

Nitroaromatic compounds are one of the important group of industrial chemicals in use today. Many pharmaceuticals are emanating from nitroaromatic compounds. For example, many substituted nitroaromatic compounds are used to synthesize various indole derivatives which are bioactive member of many drugs and agrochemicals. Among these, nitroacetophenones have been commonly used in the synthesis of chemical and pharmaceutical compounds. 4-Nitroacetophenone is recently identified as a class of anti-trypanosomal drug candidates.[2d] 2-Nitroacetophenone is used as an intermediate for the synthesis of cinoxacin that is prescribed medication in adults for urinary tract infections.[2c] 3-Nitroacetophenone is used as intermediate for flurbiprofen synthesis which is managed for the treatment of inflammation and arthritis pain. Chalcones which are important compounds with pharmacological activity (anti-inflammatory, anti-ulcerative, antibacterial, antifungal and antimalarial) are synthesized from 3-nitroacetophenone as an intermediate

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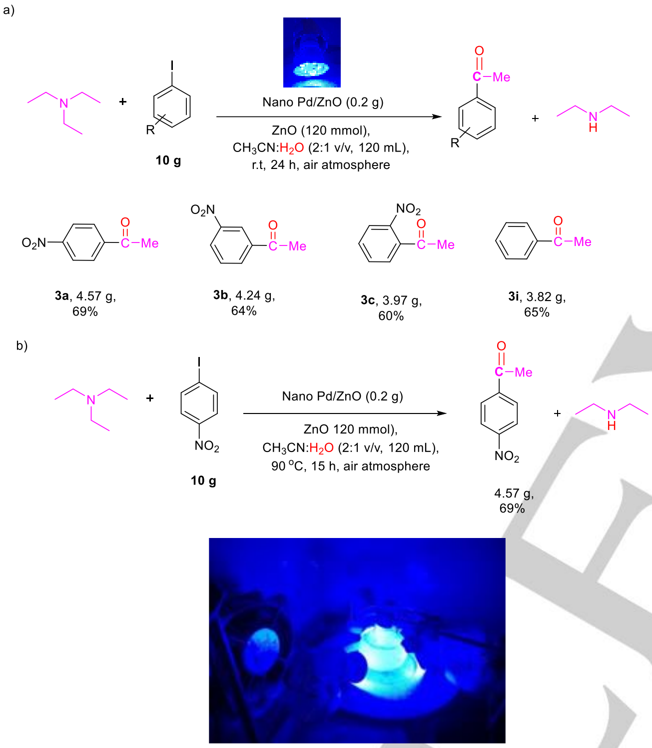
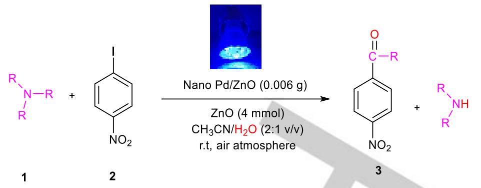
compound.[2] Due to the low price of the reagents and low amount of catalyst loadings, we started up to accredit the viability of our procedure on gram scale (Scheme 2). A preparative scale reaction on 10 g of 1-iodo-4-nitrobenzene, 1-iodo-3-nitrobenzene iodobenzene, 1-iodo-2-nitrobenzene and iodobenzene afforded the Products **3a-3c** and **3i** in good yields of 69%, 64%, 60% and 65%, respectively (Scheme 2a). The results exhibited that the conversion was similar to those observed in the corresponding bench scale experiments. Also, the reaction could be started thermally by heating to 90 °C for 15 hours in the absence of light, again providing similar yield (69%) (Scheme 2b). These results show that the method is potentially suitable to large-scale production.

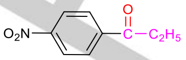
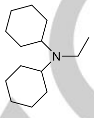
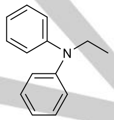
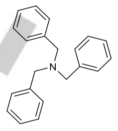
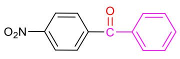


Scheme 2. Gram-scale carbonylation.

In the next step, efforts were made to use other trialkylamines (Table 3). The results indicated that tripropylamine (**1b**) successfully underwent the carbonylation reaction with 1-iodo-4-nitrobenzene (**2a**) in excellent yield (entry 1). Also, the steric effect seemed to be important to the reaction, because when *N*-cyclohexyl-*N*-ethylcyclohexanamine (**1c**) and *N*-ethyl-*N*-phenylaniline (**1d**) were used instead of triethylamine, lower yields were obtained (entries 2, 3). Notably, other symmetric tertiary amines, such as tribenzylamine (**1e**) did not afford the desired product (entry 4).

Table 3. Visible-light photoredox carbonylation of aryl halids with trialkylamines using nano Pd/ZnO. [a]



Entry	Amine	Product	Yield[b](%)
1	(n-Pr)$_3$N **1b**	 **3o**	62
2	 **1c**	**3a**	17
3	 **1d**	**3a**	34
4	 **1e**	 **3p**	Trace

[a] Reaction conditions: **2** (1 mmol), **1** (1 mmol), ZnO (4 mmol), CH_3CN (2 mL), water (1 mL), nano Pd/ZnO (0.006g), 11 W blue LED irradiation, room temperature, air atmosphere, 24 h. [b] Isolated product.

To attain deeper knowledge into a possible mechanism, a set of control reactions were managed. Addition of triethanolamine and ammonium oxalate (hole scavengers) gave only trace and 12% of product **3a,** respectively, denoting the participation of holes. Addition of *t*-BuOH ($OH^{\bullet}$ radical scavenger) did not change the yield of product **3a**, indicating that $OH^{\bullet}$ radical was not presented in the photocatalytic process. And finally addition of TEMPO ($O_2^{\bullet-}$, radical scavenger) or NaN_3 (singlet $^1O_2$ scavenger) gave product **3a** in trace and 10% yield, respectively. The deficiency of any reaction in the dark declared that the alkyl aryl ketones formation activated and deactivated by visible light. To find this "On-Off" visible light irradiation experiment was operated. These preparative result only show that radical-chain propagation in this transformation is not a key step (Figure S4). So, according to control experiments a detailed depiction of our proposed mechanism is defined in Figure 1. We assumed that irradiation of nano Pd/ZnO photocatalyst by visible light, electrons in Pd nanoparticle according to LSPR are excited and then transferred to the CB of ZnO. So an electron/hole (e^-/h^+) generated.[12] Triethylamine (E^{ox}= -0.88 V vs) is oxidized to the corresponding radical cation by a single-electron transfer to the hole generated in Pd nanoparticles.[14] The iminium ion **II** has been formed by a hydrogen ($H^{\bullet}$) abstraction of **I** by superoxide anion ($O^{\bullet-}$) [16] which was formed by electron transfer in CB of ZnO to $O_2^{\bullet}$. Contemporaneously with e^-/h^+ generated, nano Pd/ZnO could play another role in this mechanism. We believed that oxidation addition of the Pd (0) in nano Pd/ZnO photocatalyst into aryl halide would generate the intermediate **III** (in a Pd catalytic cycle),[13] the iminum ion **II** reacted with ArPdI from Pd catalytic cycle to afford intermediate **IV**. Abstraction of a proton (H^+) from intermediate **IV** generated intermediate **V**, which was hydrolyzed to produce the desired product. The production of H_2O_2 during the reaction was indicated by test strip and ^{1}HNMR (see SI).

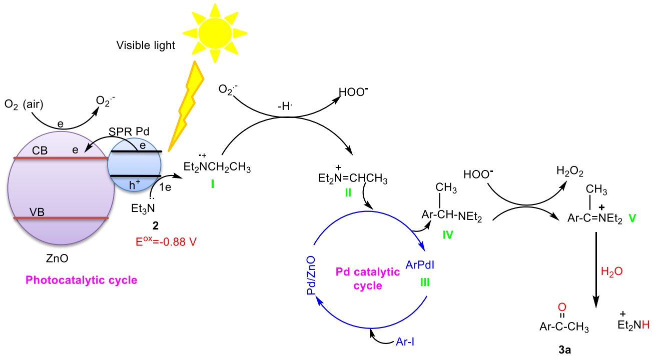


Figure 1. Proposed mechanism.

Conclusions

In this work, we have shown the capability of nano Pd/ZnO as a dual catalyst (both in absorption visible light irradiation as photoredox and also in catalytic cycle for C-C bond formation). To the best of our knowledge this is the first example that a catalyst plays two roles and we believe that it would open up a new way. In this method, it does not implicate the use of any ligands to stabilize the metal catalyst. Notably, in this method tertiary amines (which are commercial accessible) were used as the carbonyl sources, so, makes it more marvelous for organic transformations and industry synthesis. In addition, this transformation is easily, simple, green and eliminate any harsh conditions (high temperature, strong oxidant, etc). Finally, the carbonylation process was conducted on 10 gram scale, both with visible light and thermal initiation, proving that this method is scalable and efficient. In conclusion, the improved process is a good candidate for the industrial preparation and pharmaceutical development of **3a-3c** and **3i** from the perspective of efficiency, economy and scalability. This study will help researchers to design similar photocatalysts and improve many protocols in organic synthesis.

Experimental Section

The general procedure for the carbonylation of aryl halids. In a typical reaction, the mixture of arylhalide (**2**, 1 mmol), trialkylamine (**1**, 1 mmol) or one of its derivatives, ZnO (4 mmol), deionized water (1 mL), CH_3CN (2 mL) and 0.006 g of nano Pd/ZnO catalyst were put into a Pyrex glass in which a 11 W LED was used as a light source and the reactant mixture was carried out under air atmosphere at room temperature. After the reaction was complete, it was centrifuged to remove the catalyst andthe mixture purified by column chromatography on silicagel (Petroleumether:Ethyl acetate 10:2 v/v) to give the desired product. The products were characterized with IR, ^{1}H NMR and ^{13}C NMR.

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Keywords: alkyl aryl ketones • carbonylation • aldehydes • lactams • nano Pd/ZnO

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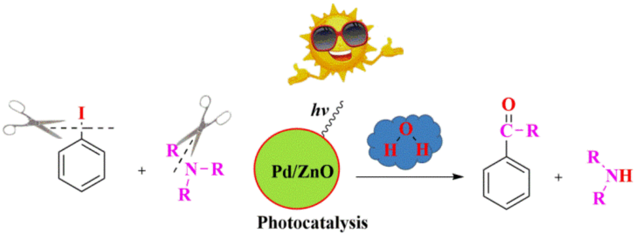
COMMUNICATION

We have been show the capability of nano Pd/ZnO as a dual catalyst. This method is the first example using a metal doped metal oxides, as a dual photoredox and transition-metal catalyst. By employing this heterogeneous photocatalyst, carbonylation reaction can proceed under visible light.



Photoredox

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Visible-Light-Driven Direct Oxidative Coupling Reaction Leading Alkyl Aryl Ketones Catalyzed by Nano Pd/ZnO