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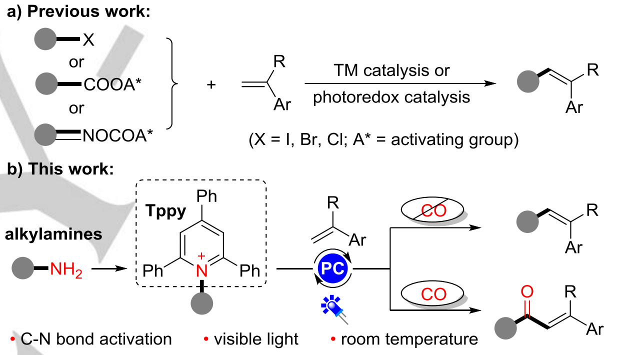
Deaminative (Carbonylative) Alkyl-Heck-type Reactions Enabled by Photocatalytic C-N Bond Activation

Xuan Jiang,[a] Mao-Mao Zhang,[a] Wei Xiong,[a] Liang-Qiu Lu,*,[a] and Wen-Jing Xiao*,[a,b]

Abstract: The Pd-catalyzed Heck reaction is a well-known, Nobel Prize-awarded transformation for producing alkenes. Unlike the state-of-the-art alkenyl- and aryl-Heck reaction, the alkyl-Heck reaction is still underdeveloped due to the competitive side reactions of alkyl-Pd species. In this work, a deaminative alkyl-Heck-type reaction was developed through C-N bond activation by visible-light photoredox catalysis. A variety of aliphatic primary amines together with alkenes were determined to be efficient feedstock for this new protocol, affording alkene products in good yields under mild conditions. Moreover, this strategy can be successfully extended to deaminative carbonylative alkyl-Heck-type reactions.

The delivery of new protocols complementary to state-of-the-art transformations is a central goal of modern chemical synthesis. In 2010, the Heck reaction, which was pioneered by Heck and Mizoroki in approximately 1970,[1] was awarded the Nobel Prize in Chemistry together with other two Pd-catalyzed coupling reactions because these reactions revolutionized organic chemistry and related pharmaceutical and materials science fields.[2] Despite the revolutionary advances of nearly half a century and compared with the Heck reaction of unsaturated halide (or triflate) substrates, alkyl-Heck reactions are still underdeveloped due to the inherent instability of alkyl palladium species (i.e., the preference for the competing β-hydrogen elimination over the insertion reaction with alkene).[3] Until recently, significant breakthroughs have been made in this field by replacing traditional two-electron pathways with single-electron-transfer (SET) processes.[4-7] In these studies, redox-reactive substrates such as activated alkyl halides and carboxylic acids have been commonly applied as efficient alkyl radical sources in alkyl-Heck-type reactions.[5-7] Despite this impressive achievement, efforts toward expanding the range of alkyl radical sources are still important for the synthetic community because new protocols would streamline alkene synthesis and realizes novel functional group transformations.

Alkylamines are fundamental compounds that are widely found in natural products and synthetic chemicals.[8] However, their potential as effective carbon sources in organic synthesis is still underexploited, possibly due to the high bond energy of the sp^3 C-N bonds.[9] In approximately 1980, Katritzky found that converting primary alkylamines into pyridinium salts (namely, Katritzky's salts) can efficiently activate inert C-N bonds; however, high temperatures are still required for further transformations.[10] In 2017, Watson reported a Ni-catalyzed deaminative C-C coupling reaction of Katritzky salts with boronic acids at room temperature.[11] Soon after, Glorius developed a visible-light photocatalytic deaminative alkylation of heteroarenes by using Katritzky salts.[12] Both of these mild-condition transformations were built heavily on the single electron reduction (SER) of Katritzky salts to reactive alkyl radicals. Inspired by these advances and following our interest in organic photochemical synthesis,[13] we envisioned that this concept could be used for the deaminative alkyl-Heck-type reaction and carbonylative alkyl-Heck-type reaction of alkylamines through visible-light photoredox catalysis (PC). Clearly, this study represents a complementary protocol to the previously developed Heck reactions described above, featuring mild reaction conditions and readily available starting materials.



Scheme 1. Reaction design: deaminative (carbonylative) Heck-type reactions.

We began this study by choosing a Katritzky salt **1a** and 1,1-diphenyl ethylene **2a** as the model substrates, an iridium complex **[Ir]-1** as the photocatalyst and DABCO as the base under irradiation by 2 x 3 W blue LEDs in CH_3CN (Table 1). To our delight, the reaction proceeded very well under the initial conditions, leading to the formation of product **3aa** in 86% NMR yield (entry 1). A variation of photocatalysts, including $Ru(bpy)_3Cl_2•6H_2O$ and other Ir-based photocatalysts, did not provide improved yields (entries 2-4). The replacement of DABCO with other bases resulted in worse yields (entries 5 and 6), while a lower DABCO concentration slightly improved the reaction yield (entry 7, 93% yield). Control experiments implied that both visible light and a photocatalyst are necessary for the present transformation and that the absence of DABCO resulted in a slightly lower yield (entries 8-10).

Under the optimum reaction conditions, we observed a broad scope of Katritzky salts that were prepared from primary alkylamines. As highlighted in Table 2, both cyclic and acyclic amine substrates were efficiently converted to alkenylation products in good yields (**3aa**-**3ia**: 65-97% yields). In particular, fluorine-containing carbocyclic and *O*- or *N*-heterocyclic substrates also participated well in this transformation (**3fa**-**3ia**, 65%-93%). Other Katritzky salts prepared from functionalized alkylamines, such as benzyl amine, α-amino acetonitrile and amino acid esters, were tolerant of the photocatalysis system,

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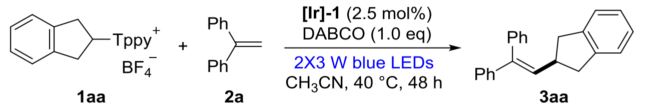
Table 1. Condition optimization for the deaminative Heck-type reaction.[a]



1aa **2a** **3aa**

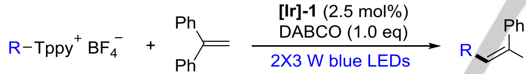
Entry	Variation of initial reaction conditions	Yield[b]
1	No variation	86%
2	Replace **[Ir]-1** with **[Ru]**	73%
3	Replace **[Ir]-1** with **[Ir]-2**	83%
4	Replace **[Ir]-1** with **[Ir]-3**	77%
5	Replace DABCO with DIPEA	35%
6	Replace DABCO with K_2HPO_4	72%
7	Performed at 0.08 M	93% (91%)[c]
8	Performed in dark at 0.08 M	0%
9	Performed without **[Ir]-1** at 0.08 M	3%
10	Performed without DABCO at 0.08 M	84%

[a] Initial reaction conditions: **1a** (0.2 mmol), **2a** (0.32 mmol), **[Ir]-1** (2.5 mol%), DABCO (0.2 mmol), in CH_3CN (2.5 mL) at 40 °C under an argon atmosphere and irradiation by 2x3 W blue LEDs. [b] Determined by ^1H NMR analysis using 3,5-dimethyltoluene as the internal standard. [c] Isolated yield in parentheses. DABCO: 1,4-diazabicyclo [2.2.2]octane; **[Ir]-1**: $Ir(4\text{-}Fppy)_2(bpy)PF_6$; **[Ir]-2**: $Ir(ppy)_2(dtbbpy)PF_6$; **[Ir]-3**: $Ir(2,4\text{-}dFppy)_2(bpy)PF_6$; **[Ru]**: $Ru(bpy)_3Cl_2{\cdot}6H_2O$.

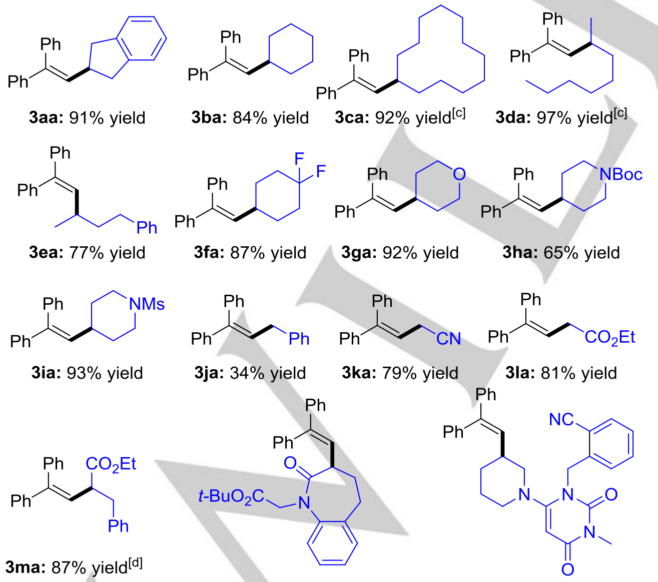
and the corresponding products were produced in moderate to good yields (**3ja**-**3ma**: 34%-87% yields). To demonstrate the utility of this methodology, a gram-scale reaction with an aniline acid-derived substrate was performed with reduced photocatalyst loading. As a result, the reaction still proceeded very well to generate the alkene product **3ma** in 81% yield. Furthermore, a commercially available dipeptide and an *anti*-diabetic drug, Alogliptin,[14a] were chosen as two platform molecules to demonstrate the potential of this deaminative Heck-type reaction. Indeed, these two transformations produced the deaminative alkenylation derivatives in moderate and high yields, respectively (Table 2, **3na**: 61% yield; **3oa**: 92% yield). Notably, the diversification of commercial drug molecules is well-accepted to be a fruitful approach to pharmaceutical candidate discovery.[14b]

Subsequently, we continued to probe the scope of the alkene partner under the optimum conditions. As summarized in Table 3, the electronic properties of the diarylalkenes were examined in the deaminative alkyl-Heck-type reaction. Substrates with weakly electron-withdrawing groups (F-, Cl-) or electron-donating group (Me-) at the 4-position of the benzene ring exhibited higher reaction efficiency than those with electron-rich substrates (MeO-, Me_2N-) and the 4-phenyl-substitued substrate. This might be the result of higher reactivity of electro-deficient diaryl alkenes to nucleophilic alkyl radicals.[6c,7c] Overall, all the reactions proceeded well under the standard photocatalytic conditions (**4ib-4ig**, 68% to 95% yields). Delightedly, this success was extended to cyclic arylalkenes and cinnamylic acid, delivering the corresponding products (**4ih**, 60% yields; **4ai**, 66% yields). Moreover, we found that α-aryl, α-heteroaryl silyl enol ethers or amide-derived enamines could be used as effective coupling partners, affording ketone products or a new enamine in moderate to high yields (**5ib-5id**, **5ke**, **5af**: 40% to 93% yields).

Table 2. Scope of Katritzky salts for the deaminative Heck-type reaction.[a,b]



1 **2a** **3**



3aa: 91% yield **3ba**: 84% yield **3ca**: 92% yield[c] **3da**: 97% yield[c]

3ea: 77% yield **3fa**: 87% yield **3ga**: 92% yield **3ha**: 65% yield

3ia: 93% yield **3ja**: 34% yield **3ka**: 79% yield **3la**: 81% yield

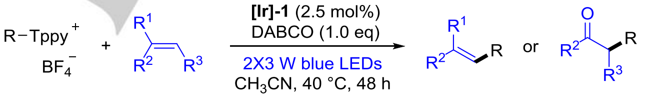
3ma: 87% yield[d]
81% yield[e]

3na: 61% yield[d]

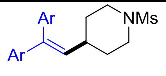
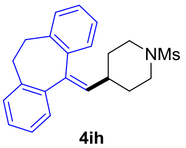
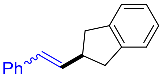
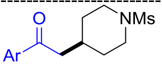
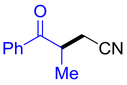
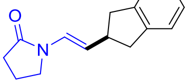
3oa: 92% yield

[a] Reaction conditions 1: see entry 7 in Table 1. [b] Isolated yield. [c] 1 (0.24 mmol), **2a** (0.2 mmol). [d] Without DABCO. [e] Gram-scale reaction: **1m** (2.29 g, 4.0 mmol), **2a** (1.12 ml, 6.4 mmol), **[Ir]-1** (1.5 mol%) in CH_3CN (25 mL) at 40°C under an argon atmosphere and irradiation by 2x3 W blue LEDs for 48 h.

Table 3. Scope of alkenes for the deaminative Heck-type reaction.[a]



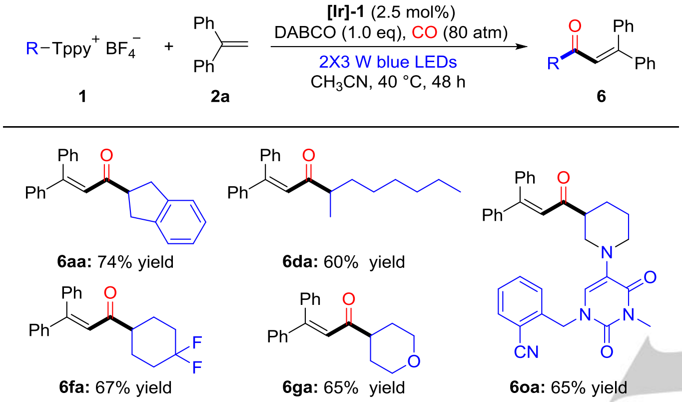
1i or 1k **2** or **3** (**3:** R^1 = OTMS or 2-pyrrolidone) **4** **5**

Entry	Product **4** or **5**		Yield[b]
1	 **4ib-4ig**	**4ib:** Ar = $4\text{-}FC_6H_4$	90%
2		**4ic:** Ar = $4\text{-}ClC_6H_4$	89%
3		**4id:** Ar = $4\text{-}MeC_6H_4$	95%
4	 **4ih**	**4ie:** Ar = $4\text{-}MeOC_6H_4$	78%
5		**4if:** Ar = $4\text{-}Me_2NC_6H_4$	71%
6		**4ig:** Ar = $4\text{-}PhC_6H_4$	68%
7	 **4ai**	**4ih**	60%
8		**4ai**	66%[c]
9	 **5ia-5id**	**5ia:** Ar = Ph	93%
10		**5ib:** Ar = $4\text{-}ClC_6H_4$	71%
11	 **5ke**	**5ic:** Ar = $4\text{-}MeOC_6H_4$	77%
12		**5id:** Ar = 2-Thiophenyl	56%
13		**5ke**	65%
14	 **5af**	**5af**	40%

[a] Reaction conditions 1: see entry 7 in Table 1. [b] Isolated yield. [c] Using *trans*-cinnamylic acid; E/Z ratio = 8:1.

The carbonylative Heck reaction is an important method for synthesizing α,β-unsaturated ketones.[15] However, this reaction was limited to aryl or vinyl electrophilic reagents, with few examples of carbonylative alkyl-Heck reactions.[16] Based on our experience in photocatalytic radical carbonylation,[17] the optimum conditions for the deaminative carbonylative Heck-type reaction were quickly established. As shown in Table 4, representative Katritzky salts prepared from primary alkylamines, including linear and cyclic amines, successfully participated in the designed reaction, affording the corresponding enone products in 65-74% yields (Table 4). To our delight, the Alogliptin-derived substrate was also successful for this deaminative carbonyl Heck-type reaction with a good yield (Table 4, **6oa**: 65% yield).

Table 4. Representative examples of the deaminative carboxylative Heck-type reaction.[a,b]

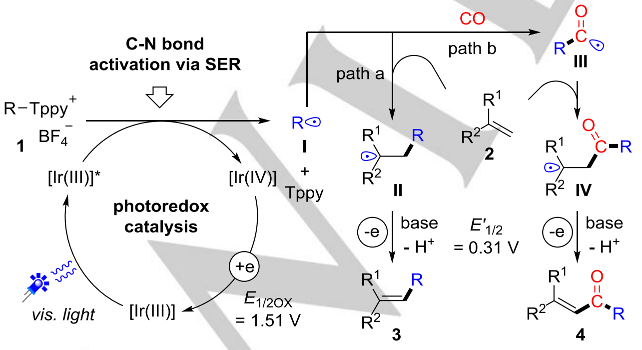


1 **2a** **6**

6aa: 74% yield **6da:** 60% yield **6fa:** 67% yield **6ga:** 65% yield **6oa:** 65% yield

[a] Reaction condition 2: the same as entry 7 in Table 1 except argon was replaced with CO (80 atm). [b] Isolated yield.

We then proposed a possible reaction mechanism for the deaminative Heck-type reaction and its carboxylative variant based on previous work[5-7,12a] and our preliminary mechanistic investigations. As simply illustrated in Scheme 2, the [Ir(III)] photocatalyst reaches an excited state ([Ir(III)]*) under the illumination of blue LEDs and is then subsequently quenched by the oxidative Katritzky salt **1** via a SER pathway. This process was strongly supported by the results of the Stern-Volmer fluorescence quenching experiment.[18] For the alkyl-Heck-type reaction, the resultant unstable heteroaryl radical immediately undergoes a C-N bond cleavage to form a stable pyridine species (Tppy) and a reactive alkyl radical **I**. The addition of radical **I** to alkene substrate **2** produces a new, more stable carbon radical **II**. Finally, the single electron oxidation of **II** (Ar = Ar' = Ph, $E'_{1/2}$ = 0.31 V vs. SCE)[19a] by the oxidation state of the photocatalyst ($E_{1/2\mathrm{OX}}$ = 1.51 V vs. SCE)[19b] and the subsequent deprotonation process produces the desired alkenylation product **3**. For the carbonylative alkyl-Heck-type reaction, the alkyl radical **I** is first captured by the carbon oxide; then, the generated acyl radical **III** reacts with the alkene to form a relatively stable radical **IV**. The same oxidation/deprotonation process affords the final enone product **4**.



Scheme 2. A proposed mechanism.

In summary, we have developed the first deaminative alkyl-Heck-type reaction and deaminative carbonylative alkyl-Heck-type reaction of primary alkylamines. The described protocol represents a significant complement to the Pd-catalyzed, state-of-the-art Heck reaction. A variety of alkene products were obtained from readily available feedstock at room temperature under visible light irradiation. The conversion of primary alkylamines to Katritzky salts and the subsequent C-N activation through a photocatalytic SER process were crucial to the success of this approach. Furthermore, these two efficient deaminative transformations successfully proved their synthetic potential for structure modification of dipeptide or drug molecules.

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Keywords: Heck reaction • carbonylative Heck reaction • deaminative transformation • visible light photocatalysis

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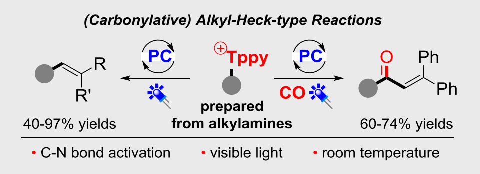
Entry for the Table of Contents (Please choose one layout)

COMMUNICATION

This work describes the first example of deaminative alkyl-Heck-type reaction and its carbonylative variant through photocatalytic C-N bond activation. This new protocol represents a significant complement to the classic Pd-catalyzed Heck reactions, featuring easily available feedstock, good reaction efficiency and mild reaction conditions.



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Deaminative (Carbonylative) Alkyl-Heck-type Reactions Enabled by Photocatalytic C-N Bond Activation