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Synthetic Methods

Redox-Neutral α-Allylation of Amines by Combining Palladium Catalysis and Visible-Light Photoredox Catalysis**

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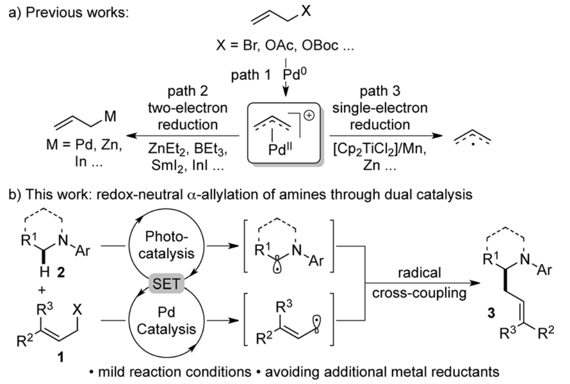
Abstract: *An unprecedented α-allylation of amines was achieved by combining palladium catalysis and visible-light photoredox catalysis. In this dual catalysis process, the catalytic generation of allyl radical from the corresponding π-allylpalladium intermediate was achieved without additional metal reducing reagents (redox-neutral). Various allylation products of amines were obtained in high yields through radical cross-coupling under mild reaction conditions. Moreover, the transformation was applied to the formal synthesis of 8-oxoprotoberberine derivatives which show potential anticancer properties.*

Palladium-catalyzed allylation reactions are among the most important methods for creating new chemical bonds.[1–4] Critical to the success of this chemistry is the formation of key π-allylpalladium intermediates from allylic esters or their analogues (Scheme 1 a, path 1), which can be utilized as efficient electrophilic components to react with diverse carbon or heteroatom nucleophiles.[1,2] In contrast, reversal of reactivity of the π-allylpalladium complex can be realized through two-electron[3] or single-electron reduction[4] (Scheme 1 a, paths 2 and 3) in the presence of stoichiometric amounts of reducing reagents (e.g., Et_3B, Et_2Zn, InI, SmI_2, or Mn powder). The resultant allylic metal complex (η^1-type) or allylic radical enables the nucleophilic addition to aldehydes, ketones, and imines,[3] as well as radical homocoupling[4a,d] and intramolecular radical addition reactions.[4b–d] Despite the advances, the catalytic generation of an allylic radical from a π-allylpalladium complex without additional reductants remains a challenge. Furthermore, developing novel transformations and expending the substrate scope of this chemistry is highly desirable.



Scheme 1. Palladium-catalyzed allylation reactions. Cp = cyclopentadiene.

Recently, visible-light-induced photoredox catalysis has become an important platform for the design and development of a variety of radical reactions under remarkably mild reaction conditions.[5] More intriguingly, dual catalysis combining photocatalysis with transition-metal catalysis[6,7] can accomplish many new chemical transformations which are impossible or not easily accessible for a single catalytic cycle. For instance, the group of Sanford successfully achieved photoredox Pd/Ru-catalyzed C–H arylation reactions using aryldiazonium and diaryliodonium salts as the radical source.[7b,c] The key to these reactions was the oxidation of Ar–Pd^{III} to Ar–Pd^{IV} in with the high-valent Ru^{III} or Ir^{IV} species, which was generated by the oxidative quenching of the visible-light excited $Ru^{II}*$ or $Ir^{III}*$ complex. In contrast, we questioned whether the π-allylpalladium complex could be reduced to a neutral π-allyl radical and Pd^0 species using the low-valent species, generated from the excited state of the photocatalyst, through reductive quenching. As part of our ongoing efforts to develop novel photocatalytic reactions,[8] we herein disclose an unprecedented redox-neutral α-allylation of amines (Scheme 1 b)[9] through radical cross-coupling by combining palladium catalysis (to generate π-allylic radical) and photoredox catalysis (to generate α-amino radical).

Initially, cinnamyl acetate (**1a**) and *N*-phenyltetrahydroisoquinoline (**2a**) were selected as model substrates to

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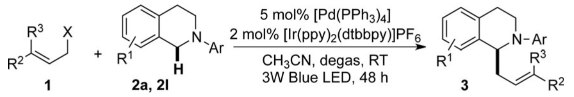
examine the feasibility of the designed process. Fortunately, optimization of the reaction conditions showed that the proposed α-allylation reaction of amines did indeed occur with an 81 % yield in the presence of 5 mol % [Pd(PPh$_3$)$_4$] and 2 mol % [Ir(ppy)$_2$(dtbbpy)]PF$_6$ in degassed CH$_3$CN under irradiation with a 3 W blue LED for 48 hours (for details of the optimization, see the Supporting Information). Control experiments indicated that the photosensitizer, palladium catalyst, visible-light irradiation, and degassing procedure are all crucial for this dual catalytic α-allylation reaction of amines (see Table S7 in the Supporting Information).

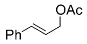
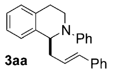
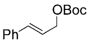
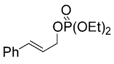
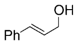
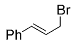
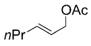
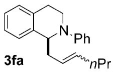
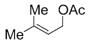
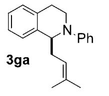
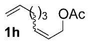
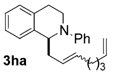
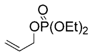
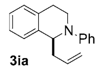
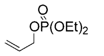
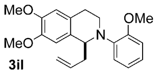
Under the optimal reaction conditions, we evaluated the generality of this photoredox Pd/Ir dual catalytic allylation reaction. As highlighted in Table 1, a wide range of allylic compounds were applicable and generally moderate to good yields were achieved. With cinnamyl alcohol as an example, not only its acetate (**1a**) but also *tert*-butoxy carbonate (**1b**) and diethyl phosphate (**1c**) proved successful for this reaction (Table 1, entries 1–3). Notably, the direct employment of allylic alcohol **1d** itself as the allyl radical precursor was also feasible with the assistance of formic acid (entry 4). When cinnamyl bromide (**1e**) was used under best reaction conditions, the allylation product **3aa** was obtained in 45 % yield. A control experiment revealed that the absence of the palladium catalyst did not affect the reaction efficiency and a similar yield of isolated **3aa** was obtained (entry 5), presumably because **1e** can directly undergo a visible-light-induced reductive dehalogenation process to give the key allylic radical intermediate. Other substituted allylic reagents were also surveyed to explore the potential of this methodology. The results in entries 6–8 revealed that alkyl- (**1f** and **1g**) and ω-vinyl- (**1h**) substituted substrates were well tolerated under this dual catalytic system and moderate to good yields of corresponding products were obtained (**3fa**–**3ha**: 57-69 % yields). Notably, simple allylic esters could be employed in the reaction. With **2a** and its electron-rich analogue **2l** as the example, the Pd/Ir-catalyzed α-allylation of amines with **1i** proceeded well, thus affording desired products in good yields upon isolation (entries 8 and 9).

The experiments investigating the scope of the amine component are described in Table 2. The reaction appears to be general with a variety of N-aryl tetrahydroisoquinolines. For example, the substitutes on the benzene ring of tetrahydroisoquinoline can be varied, thus delivering the allylation products in satisfactory yields (**3cb**: 81 % yield and **3cc**: 62 % yield). Moreover, both electron-withdrawing groups (i.e., F, Cl, and ester) and electron-donating groups (i.e., Me and OMe) can be successfully introduced to the *para*, *meta*, and *ortho* positions of the benzene ring on the nitrogen atom, thus giving the corresponding allylation products (**3cd**–**3ci**) in good yields. It is important to note that the substrate **2j**, with a sensitive vinyloxy functional group, can participate in this transformation, thus giving the desired product in 51 % yield. Additionally, the N-alkyl substituted tetrahydroisoquinoline **2k** is suitable for this dual catalytic process, albeit with relatively low yield of the corresponding allylation product (**3ck**, 15 % yield).

The success of this dual catalysis system could be also significantly extended to the allylation reaction of secondary amines. For instance, the α-amino methyl ester **4a** and ethyl ester derivatives **4b** and **4c** can facilely react with cinnamyl diethyl phosphate **1c**, and the resulting allylation products were obtained in moderate yields (Table 3). Additionally, we

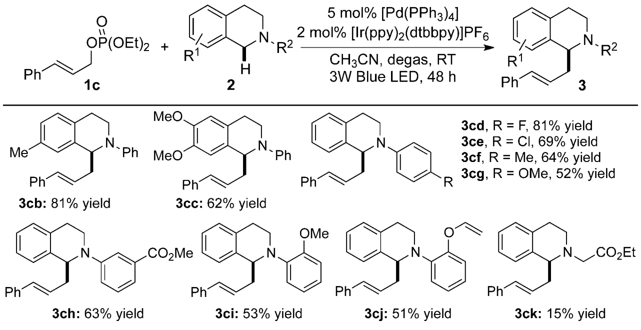
Table 1: Substrate scope of allylic esters.[a]



Entry	Substrate	Product	Yield [%][b]
1	 **1a**	 **3aa**	81
2	 **1b**		70
3	 **1c**		83
4[c]	 **1d**		42
5	 **1e**		45 (41)[d]
6	 **1f**	 **3fa**	60[e]
7	 **1g**	 **3ga**	57
8[f]	 **1h**	 **3ha**	69[e]
9	 **1i**	 **3ia**	73
10	 **1i**	 **3il**	76

[a] Reaction conditions: **1** (0.3 mmol), **2a** or **2l** (0.36 mmol), [Pd(PPh$_3$)$_4$] (5 mol %), [Ir(ppy)$_2$(dtbbpy)]PF$_6$ (2 mol %), and CH$_3$CN (3 mL) at RT for 48 h under irradiation with a 3 W blue LED. [b] Yield of the isolated product. [c] Adding 1.0 equiv of HCO$_2$H. [d] Without the addition of [Pd(PPh$_3$)$_4$]. [e] 3:1 *E*/*Z* of products. [f] 6:1 *E*/*Z* of substrate **1g**. Ac = acetyl, Boc = *tert*-butoxycarbonyl, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, ppy = 2-phenylpyridine.

Table 2: Substrate scope of tetrahydroisoquinolines.[a]



[a] Reaction conditions: **1c** (0.3 mmol), **2** (0.36 mmol), [Pd(PPh$_3$)$_4$] (5 mol %), [Ir(ppy)$_2$(dtbbpy)]PF$_6$ (2 mol %), and CH$_3$CN (3 mL) at RT for 48 h under irradiation with a 3 W blue LED. Yield is that of the isolated product.

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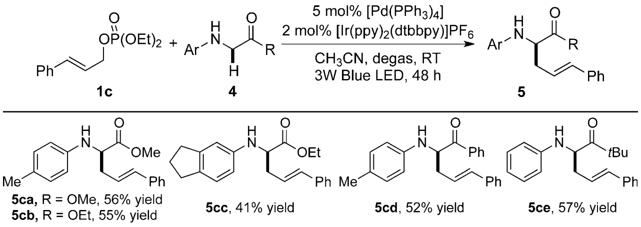
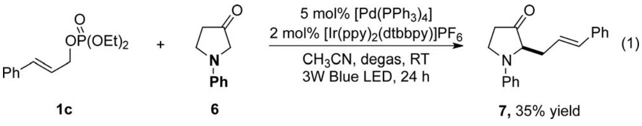
Table 3: Substrate scope of secondary amines.[a]



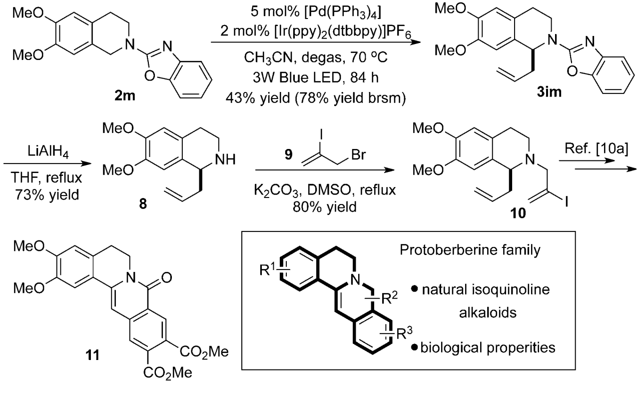
[a] Reaction conditions: **1b** (0.3 mmol), **2** (0.36 mmol), [Pd(PPh$_3$)$_4$] (5 mol%), [Ir(ppy)$_2$(dtbbpy)]PF$_6$ (2 mol%), and CH$_3$CN (3 mL) at RT for 48 h under irradiation with a 3 W blue LED. Yield is that of the isolated product.

demonstrated that α-amino ketones, such as aryl- and alkyl-derived systems, are amenable to this allylation process using this dual palladium/photoredox catalysis (**5 cd**: 52% yield and **5ce**: 57% yield).

Moreover, to our delight, 1-phenylpyrrolidin-3-one (**6**) was also suitable for this transformation. The allylation reaction occurred selectively at the C–H bond between the carbonyl group and nitrogen atom, thus delivering the corresponding product **7** in moderate yield [Eq. (1)]. Other types of amines (i.e., N-Boc-protected tetrahydroisoquinoline, *N*-phenylpyrrolidine, and triethylamine) were also tested under optimal reaction conditions, and no reaction or only 1,5-diene was obtained as a major product in most cases (see the Supporting Information for details).



Remarkably, this reaction can be further applied to the formal synthesis of the 8-oxoprotoberberine derivative **11**, a member of natural isoquinoline alkaloids in the protoberberine family, which holds potential anticancer properties (Scheme 2).[10] As shown, the heteroaryl-substituted tetrahydroisoquinoline **2m** was successfully incorporated into this dual catalytic allylation reaction, thus giving the corresponding product **3im** in good yield based on recovering starting material. It is noteworthy that a higher reaction temperature is needed for the process, presumably because of the steric hindrance of the benzoxazole moiety. Subsequently, the benzoxazole moiety can be easily removed under reductive conditions with LiAlH$_4$ in refluxing THF.[11] A S$_N$2 substitution reaction of **8** with 3-bromo-2-iodoprop-1-ene (**9**) gave a good yield of the product **10**, which is the key synthetic intermediate to the target molecule **11**.[10a]



Scheme 2. Formal synthesis of the 8-oxoprotoberberine derivative **11**. DMSO = dimethylsulfoxide, THF = tetrahydrofuran.

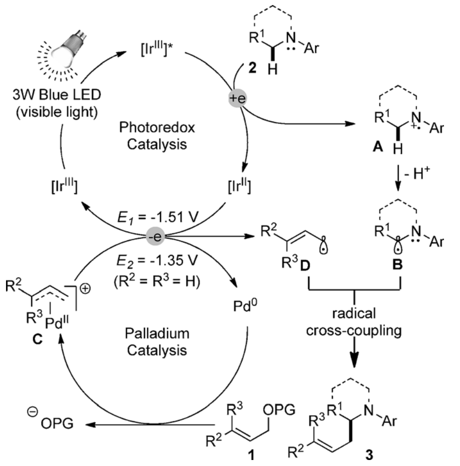


Figure 1. Plausible reaction mechanism.

A plausible reaction mechanism was proposed (Figure 1) based on the several mechanism studies (see Section S7). The reductive quenching process of the visible-light excited Ir^{III}* by amine substrates **2** initially generated a low-valent Ir^{II} complex and simultaneously delivered the radical cation **A**, the deprotonation of which afforded the α-amino alkyl radical **B**.[12] In contrast, the palladium catalytic cycle started from the formation of the π-allylpalladium complex **C**, which was subsequently reduced by Ir^{II} to afford the allyl radical **D** and regeneration of the Pd^0 catalyst as well as ground-state Ir^{III} photocatalyst to complete both catalytic cycles. The proposed redox process was consistent with the redox potentials of key intermediates (i.e., Ir^{II} as reductant: $E_1 = -1.51$ V vs SCE;[3d,13a] **C** as oxidant: when R^2 = R^3 = H, $E_2 = -1.35$ V vs SCE[13b]). Finally, the radical cross-coupling of **B** and **D** delivered the desired allylation product.[14] As evidence, the homocoupling adducts of **D** were observed in certain cases. It is worthy to note that in 2012, the group of Reiser reported an addition reaction of Michael acceptors with α-amino radical derived from N-aryltetrahydroisoquinoline.[12a] In this elegant work, they isolated and confirmed the radical self-coupling product in the absence of Michael acceptors. The yield of the reaction is 10% after one week, and indicates that this type of α-amino radical might be stable and self-coupling does not proceed easily, probably because it is quite bulky. In contrast, the allylic radical generated from the reduction reaction of π-allylic palladium complex was relatively reactive. At low concentration, this radical tends to react with the α-amino radical to form the desired cross-coupling product. Another reaction pathway involving the addition of α-amino radical **B** to π-allylpalladium species might be possible and cannot be totally ruled out at the current stage (see Section S7.5). However, the fact that no enantioselectivity was observed when chiral ligands were used in the reaction, made radical cross-coupling more favorable.[15]

In conclusion, we have developed the catalytic generation of an allyl radical from a π-allylpalladium complex by combining visible-light-induced photoredox catalysis and palladium catalysis. The α-amino radical derived from the same catalytic cycle can react with the allyl radical through a cross-coupling process to afford various α-allylation products of amines in high yields. In contrast to prior reduction methods using stoichiometric amounts of additional reductants, this strategy utilized the bifunctional property of the photoredox catalyst: oxidizing amines to α-amino radical and reducing π-allylpalladium complex to allyl radical. Notably, this reaction has been successfully applied to the formal synthesis of the 8-oxoprotoberberine derivative **11**, which has potential anticancer activities. Moreover, a plausible reaction mechanism was proposed based on a series of control experiments and EPR studies.

Experimental Section

Representative procedure: **1a** (0.3 mmol), **2a** (0.36 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (0.006 mmol), $[Pd(PPh_3)_4]$ (0.015 mmol) and dry CH_3CN (3.0 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar was added. The resulting mixture was degassed by using a freeze–pump–thaw procedure (3 times). The solution was then stirred at a distance of ca. 5 cm from a 3 W blue LED at room temperature for 48 h. Then, the solvent was removed by vacuum and the crude reaction mixture was purified by flash chromatography on silica gel (silica: 200 to 300; eluent: petroleum ether/CH_2Cl_2 (5:1 to 3:1) to provide pure product **3aa** as a light yellow oil in 81 % yield.

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[15] For details on a chiral ligand screening, please see the Supporting Information.

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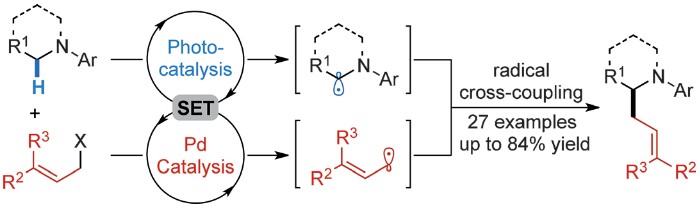
These are not the final page numbers!

Communications

Synthetic Methods

J. Xuan, T.-T. Zeng, Z.-J. Feng, Q.-H. Deng, J.-R. Chen, L.-Q. Lu,* W.-J. Xiao,* H. Alper ______ ▮▮▮▮–▮▮▮▮

Redox-Neutral α-Allylation of Amines by Combining Palladium Catalysis and Visible-Light Photoredox Catalysis



Double up: The title reaction was accomplished by merging palladium catalysis and visible-light photoredox catalysis. The catalytic generation of an allyl radical from the corresponding π-allyl-palladium intermediate was realized without additional metal reducing reagents for the first time. Various α-allylation products of amines were achieved in high yields by radical cross-coupling under mild reaction conditions. SET = single-electron transfer.

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