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Visible-light-induced radical 1,2-aryl migration in diaryl allyl alcohols for efficient synthesis of 1,5-dicarbonyl compounds†

Lijuan Li, Ping Jiang and Keyume Ablajan *

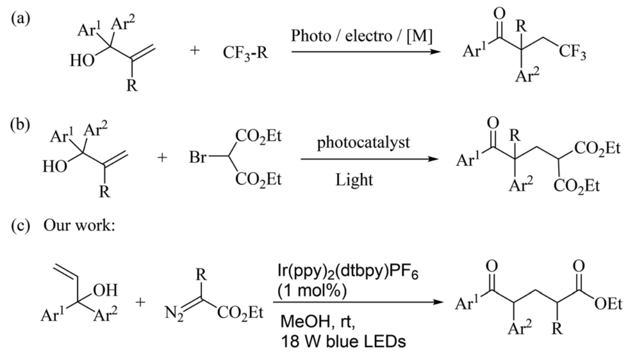
Herein, we developed a protocol for Ir(III)-photocatalyzed, visible-light-driven radical 1,2-aryl migration in diaryl allyl alcohols, leading to the formation of 1,5-dicarbonyl compounds under additive-free conditions, with broad substrate tolerance. Electron-deficient aryl groups exhibit enhanced migration efficiency compared to electron-rich or *ortho*-substituted analogs. Mechanistic studies implicated the formation of alkyl ester radical intermediates. This is a sustainable method that can be performed under mild conditions.

Allylic alcohols are versatile synthons in organic chemistry due to their dual functionalization capacity, which enables allylic nucleophilic substitutions.[1–3] Recent advances in aryl migration chemistry have demonstrated its power in constructing medicinally privileged architectures, exemplified by copper-catalyzed heteroarylethylamine synthesis *via* radical migration pathways[4] and catalytic asymmetric 1,4-aryl migrations, which enable the stereoselective assembly of chiral benzannulated seven-membered rings.[5]

The 1,2-aryl migration of diarylallyl alcohols has emerged as a powerful strategy for accessing α-aryl-β-substituted carbonyl compounds.[6] Significant progress has been achieved through diverse approaches to facilitate the 1,2-migration reaction, reflecting a paradigm shift toward sustainable and atom-economical strategies. Notably, recent advances in radical 1,2-aryl migration of α,α-diarylallylic alcohols enabled the synthesis of β-silyl carbonyl compounds in the presence of a copper catalyst[7] and direct access to β-polychloromethylated ketones mediated by visible light.[8]

The synergistic use of photoredox catalysis with hypervalent iodine reagents has been developed to produce γ-sulfinyl ketones and 1,2-dicarbonyl compounds *via* 1,2-aryl migration.[9,10] The versatility of this migration mechanism is further highlighted by its application in synthesizing ketone derivatives through phosphonylation,[11] oxidative acylation,[12] selenation,[13] and amination reactions.[14] Additionally, the reductive radical-polar crossover strategy for 1,2-C migration in 2-azido allyl alcohols has proven to be useful, where the azidyl group simultaneously serves as a radical initiator and leaving group to enable *n* + 1 ring expansion.[15] The CO_2-promoted photocatalytic synthesis of tetra- and tri-substituted alkenyl amides through unusual radical 1,4-aryl migration,[16] and electrochemically mediated synthesis of γ-keto sulfone *via* 1,2-migration provides another green strategy for ketone synthesis.[17]

Due to the importance of α-aryl-β-trifluoromethyl ketones, recent reports describe the trifluoromethylation of α,α-diaryl allyl alcohols using cost-effective reagents and electrochemical methods (Scheme 1a).[18–21] Similarly, δ-ketonitrile synthesis—critical for pharmaceutical and materials science—has been achieved *via* a copper-catalyzed 1,2-migration route using TBPB or DTBP as oxidants.[22–25] Recently, a four-component radical difunctionalization of alkenes, aldehydes, and TBHP to construct 1,5-dicarbonyl scaffolds was reported.[26] In contrast, visible-light-driven 1,2-aryl migration offers distinct advantages by eliminating metal catalysts and harsh conditions, thereby enhancing sustainability and reducing costs. Other approaches enable the direct α-aryl-β-alkylation of allyl alcohols to afford 1,5-diketones, showcasing the potential of photoredox catalysis (Scheme 1b).[27,28]



Scheme 1 Aryl migration reaction produced from diaryl allyl alcohol.

State Key Laboratory of Chemistry and Utilization of Carbon-Based Energy Resources, College of Chemistry, Xinjiang University, Urumqi, 830017, P. R. China. E-mail: ablajan209@hotmail.com

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Previous research on allyl alcohol functionalization was often limited by demands for substrate pre-activation and harsh conditions. To overcome these limitations, we present a visible light-induced alkylation of diaryl allyl alcohols using an iridium(III) photocatalyst under additive-free conditions, enabling efficient 1,2-aryl migration to access 1,5-dicarbonyl compounds (Scheme 1c). This strategy offers a broad substrate scope, mild reaction conditions, and operational simplicity, while eliminating the need for pre-activated substrates. Our work combines photoredox catalysis with atom-economical transformations, offering a sustainable and practical approach to synthesizing structurally complex ketones.

Using unsubstituted α,α-diaryl allyl alcohol **1a** and ethyl diazoacetate **2a** as model substrates, we systematically optimized the reaction conditions for the synthesis of diphenyl 5-oxo-pentanoate **3a** by evaluating various photocatalysts, solvents, light sources, and reaction times (Table 1; see ESI† for detailed optimization data). The standard conditions (Table 1, entry 1) employed Ir(ppy)$_2$(dtbpy)PF$_6$ as the photocatalyst, MeCN as the solvent, and irradiation with an 18 W blue LED (λ = 455–460 nm) for 24 hours under air, yielding **3a** at 43%. Replacing Ir(ppy)$_2$(dtbpy)PF$_6$ with other photocatalysts significantly impacted the yield. Ru(bpy)$_3$Cl$_2$ (Table 1, entry 2) and Ir(ppy)$_3$ (Table 1, entry 3) resulted in no reaction and trace yields, respectively, but in contrast, *fac*-Ir(ppy)$_3$ generated 13% yield of **3a** (Table 1, entry 4). Notably, the organic photocatalyst 4CzIPN (Table 1, entry 5) performed comparably to the standard (38% yield), whereas eosin Y was ineffective (Table 1, entry 6). These results highlight the superior efficiency of Ir(ppy)$_2$(dtbpy)PF$_6$ for this transformation.

The solvent played a crucial role in the reaction outcome. MeOH and a MeCN : MeOH (1 : 1) mixture (Table 1, entries 7 and 8) gave higher yields of 65% and 62%, respectively, suggesting that protic solvents may enhance the reactivity. In contrast, EtOH was ineffective, yielding only a trace amount (Table 1, entry 9), while DCM provided a yield similar to that of the standard (47%) (Table 1, entry 10). The use of DMF/H$_2$O resulted in no reaction, likely due to incompatibility issues (Table 1, entry 11). In addition, varying the light source and intensity revealed that the standard 18 W blue LED was optimal (Table 1, entry 12). Reducing the power to 5 W decreased the yield to 39% (Table 1, entry 13), while irradiation at 390–395 nm resulted in no reaction (Table 1, entry 14).

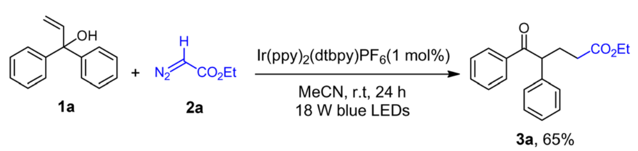
White light (Table 1, entry 15) also afforded a lower yield (39%), underscoring the importance of the 455–460 nm wavelength for efficient photocatalysis. Furthermore, decreasing the reaction time to 12 h resulted in a satisfactory yield of 53% (Table 1, entry 16), indicating that the reaction proceeds efficiently within a shorter timeframe. However, extending the time to 18 hours further increased the yield to 65%, suggesting that prolonged irradiation may enhance conversion. Finally, the optimal conditions for synthesizing product **3** involve Ir(ppy)$_2$(dtbpy)PF$_6$ as the photocatalyst, MeOH as the solvent, and irradiation with an 18 W blue LED (λ = 455–460 nm) for 18 hours.

Having established the optimal reaction conditions, we subsequently investigated the substrate scope of diaryl allyl alcohols. Initial studies revealed that substrates bearing electron-donating methyl (Me) groups exhibited lower reactivity compared to their electron-withdrawing counterparts. Symmetrical diaryl allyl alcohols containing fluorine, chlorine, or bromine substituents at α-position underwent efficient reaction with ethyl diazoacetate, furnishing 5-oxo-pentanoates **3b–3e** in 63–83% yields. Notably, substrates bearing electron-withdrawing groups consistently demonstrated yields superior to those with electron-donating substituents. When *tert*-butyl diazoacetate was employed under identical conditions with a symmetrical allyl alcohol substrate, the corresponding product **3f** was obtained in diminished yield (56%).

Expanding our investigation to asymmetrical diaryl allyl alcohols as substrates revealed them to be competent partners for the 1,2-aryl migration process. The migratory aptitude of aryl groups showed significant dependence on electronic and steric factors. Substrates containing *para*-substituted electron-withdrawing groups (F, Cl, Br) on both aromatic rings preferentially underwent migration of the α-4-substituted phenyl group, delivering products **3b–3f** in 66–78% yields. This trend extended to a *para*-CF$_3$-substituted substrate, which provided product **3j** in 61% yield through migration of the CF$_3$-bearing aryl group. Products **3k** and **3l** were obtained in 63% and 59% yields, respectively, with isomer ratios of 1.6 : 1 (**3k** : **3k′**) and 1.2 : 1 (**3l** : **3l′**).

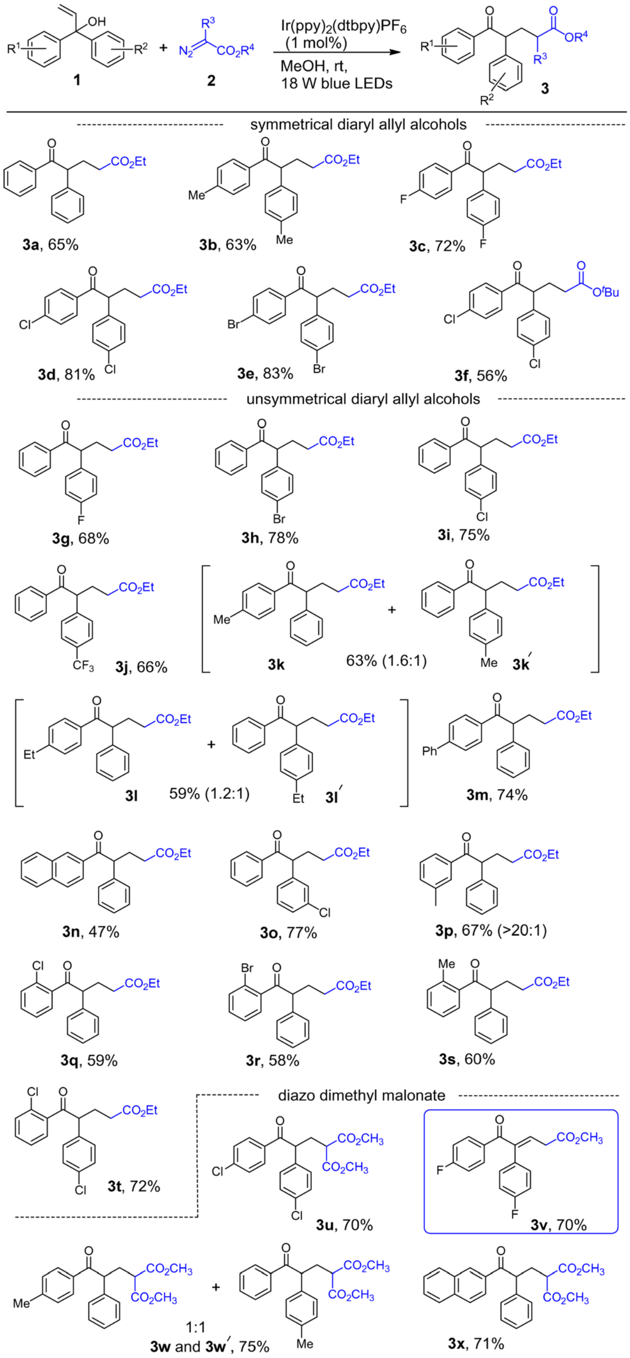
Notably, substrates featuring extended aromatic systems proved amenable to the reaction conditions. Allyl alcohols containing *para*-substituted benzene rings or 2-naphthyl groups underwent efficient 1,2-phenyl migration, yielding products **3m** (74%) and **3n** (47%), respectively. *meta*-Substitution patterns were also well-tolerated, with a 3-chlorophenyl-substituted substrate producing **3o** in 77% yield through migration of the chlorinated aryl group. A *meta*-methyl-

Table 1 Optimization of the reaction conditions[a]



Entry	Variations from standard conditions	Yield[b] (%)
1	None	43
2	Ru(bpy)$_3$Cl$_2$ instead of Ir(ppy)$_2$(dtbpy)PF$_6$	n.r.
3	Ir(ppy)$_3$ instead of Ir(ppy)$_2$(dtbpy)PF$_6$	Trace
4	*fac*-Ir(ppy)$_3$ instead of Ir(ppy)$_2$(dtbpy)PF$_6$	13
5	4CzIPN instead of Ir(ppy)$_2$(dtbpy)PF$_6$	38
6	Eosin Y instead of Ir(ppy)$_2$(dtbpy)PF$_6$	Trace
7	MeOH instead of MeCN	65
8	MeCN : MeOH (1 : 1) instead of MeCN	62
9	EtOH instead of MeCN	Trace
10	DCM instead of MeCN	47
11	DMF/H$_2$O instead of MeCN	n.r.
12	Irradiated at 455–460 nm (15 W)	47
13	Irradiated at 455–460 nm (5 W)	39
14	Irradiated at 390–395 nm (18 W)	n.r.
15	White light	39
16	18 h/12 h	65/53[c]

n.r. = no reaction. [a] Reaction conditions: (0.3 mmol), **2a** (0.6 mmol) and Ir(ppy)$_2$(dtbpy)PF$_6$ (1 mol%) in solvent (2 mL) at room temperature for 24 h under air, 18 W blue LED (λ = 455–460 nm). [b] Isolated yields. [c] Reaction time 12 h.



Scheme 2 Investigation of substrate scopes.

substituted analogue afforded product **3p** as the major isomer in 67% yield with excellent selectivity (>20 : 1) (Scheme 2).

To further probe the limitations of this transformation, we examined α-*ortho*-substituted diaryl allyl alcohols. Interestingly, *ortho*-substituted aryl groups demonstrated significantly reduced migratory aptitude, likely due to steric constraints. When *ortho*-chloro, -bromo, or -methyl substituents were present, preferential migration of the α-phenyl group occurred, yielding products **3q–3s** in moderate yields. This steric effect was particularly pronounced in dichloro-substituted substrates, where the *para*-chlorophenyl group exhibited an enhanced migratory tendency, leading to product **3t** in good yield.

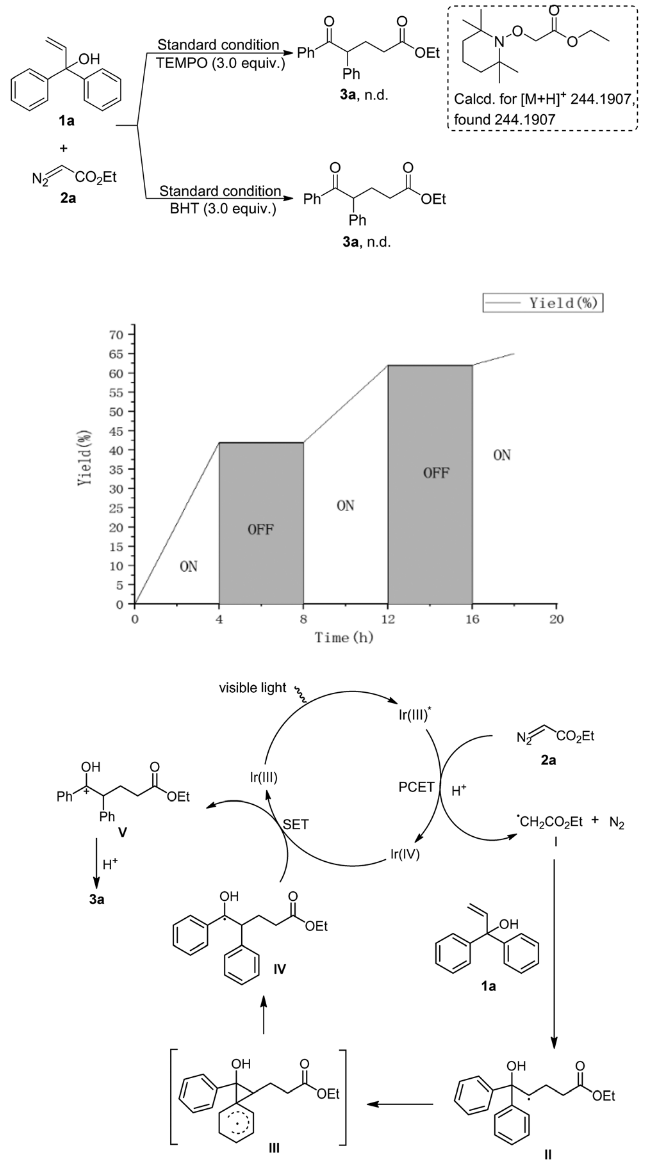
To further demonstrate the versatility of this transformation, we examined reactions between diazodimethylmalonate and various aryl allyl alcohols under standard conditions. Symmetrical allyl alcohols bearing chlorine substituents on both aromatic rings afforded product **3u** in 70% yield. However, symmetrical difluoronated allylic alcohol **1d** generated condensed product **3v** rather than a malonate product. In contrast, an asymmetrical substrate containing a *para*-methyl group yielded a 1 : 1 mixture of migration products **3w** and **3w′** in a total yield of 75%, demonstrating comparable migratory aptitudes for both aryl groups. Notably, naphthyl-containing substrates exhibited exclusive phenyl group migration, delivering the corresponding product **3x** in 71% yield.

Mechanistic investigations were conducted to elucidate the reaction pathway. Initial control experiments addressed a potential radical pathway, and it was observed that the addition of stoichiometric radical scavengers (TEMPO or BHT, 3.0 equiv. each) completely suppressed product formation. Subsequent HR-MS analysis of the TEMPO-containing reaction mixture revealed a trapped alkyl radical adduct, unambiguously confirming the radical intermediate and excluding ionic pathways. Light dependency was established through intermittent irradiation experiments, where the reaction progress immediately ceased upon deactivation of the light source, whereas continuous illumination enabled progressive yield enhancement.

These findings support the mechanistic proposal outlined in Scheme 3. The catalytic cycle initiates with visible light excitation of the Ir(III) photocatalyst to its photoactive Ir(III)* state. Single-electron transfer from the excited catalyst to diazo compound **2a** facilitates N_2 extrusion, generating a reactive α-carbonyl radical intermediate (**I**). This radical species undergoes conjugate addition to the allylic alcohol **1a**, forming intermediate **II**. Subsequent 5-*exo*-trig cyclization produces bicyclic radical **III**, which undergoes neophyl-type rearrangement to establish the quaternary carbon center in intermediate **IV**. Finally, oxidation of **IV** by the Ir(IV) species regenerates the ground-state catalyst, while forming a carbocation that undergoes deprotonation to yield the observed α-aryl-β-alkyl ester product **3a**.

In conclusion, the aryl migration of carbonyl compounds has been innovatively achieved through 1,2-aryl migration in α,α-diaryl allyl alcohols in the presence of an iridium catalyst under visible light irradiation. A series of 1,5-dicarbonyl compounds was efficiently synthesized without the addition of other additives. The substrates involved in this reaction showed satisfactory tolerance. The electronic effect and spatial configuration of substituents were found to significantly influence the migration reaction. There was a higher migration tendency for electron-deficient aryl groups in asymmetric diaryl allyl alcohols. *ortho*-Substituted aryl rings exhibited lower migration efficiency, regardless of whether the substituent was electron-withdrawing or electron-donating.

Verification experiments were performed to ascertain a possible reaction mechanism, which is shown in Scheme 3. This method provides mild conditions and convenient



Scheme 3 Proposed reaction mechanism.

operation, thereby enriching green and straightforward methods for the synthesis of 1,5-dicarbonyl compounds.

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Conflicts of interest

There are no conflicts of interest.

Data availability

The data supporting this article have been included as part of the ESI.†

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