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Graphical Abstract

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Visible-light-induced 1,2-alkylarylation of alkenes with *a*-C(sp^3)–H bonds of acetonitriles involving neophyl rearrangement under transition-metal-free conditions

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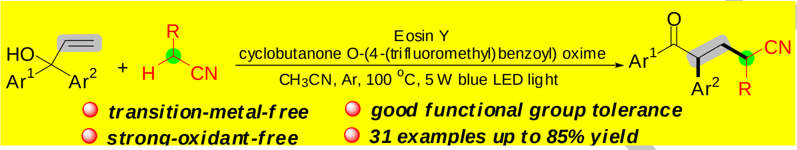

- transition-metal-free
- strong-oxidant-free
- good functional group tolerance
- 31 examples up to 85% yield

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Visible-light-induced 1,2-alkylarylation of alkenes with *α*-C(sp^3)–H bonds of acetonitriles involving neophyl rearrangement under transition-metal-free conditions

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ABSTRACT

An efficient visible-light-induced difunctionalization of alkenes with *α*-C(sp^3)–H bonds of nitriles is described for the constructing of diverse 5-*oxo*-pentanenitriles under transition-metal-free conditions. This protocol proceeds *via* the functionalization of C(sp^3)−H bond and radical addition/intramolecular 1,2-aryl migration processes, which features a wide scope of substituted *α*,*α*-diaryl allylic alcohols. The results of kinetic isotope experiments show that the cleavage of C(sp^3)–H bond of acetonitriles is a rate-limiting step.

1. Introduction

Recently, the direct C–H functionalization for the constructing of carbon-carbon bonds or carbon-hetero bonds has been even more attractive strategy for its playing an important role in building complex molecules.[1] As a result, many chemists pay their attention to the development of new strategy for radical C(sp^3)–H functionalization.[2,3] Especially, significant advances have been made in selective activation of C(sp^3)–H bond in alcohols, ethers, alkanes, amines and other activated compounds.[4] However, it is a more taxing target for functionalization of C(sp^3)–H in simple nitriles under mild conditions.

Nitriles, commonly exist in bioactive molecules and natural products, are important synthetic intermediates in organic synthesis, agricultural and pharmaceutical chemistry, as well as polymers and materials science.[5] Thus, the preparation and utilization of organonitriles have become one of the most popular and interesting topics in organic and biological chemistry.[6]

The difunctionalization of alkenes has become a class of powerful and efficient chemical transformation in organic synthesis, by that two functional groups can be contemporaneous introduced into a double bond.[7] In recent years, aryl allylic alcohols were proved to be practicable substrates for difuctionalization of alkenes,[8–16] which deliver a series of *α*-aryl-*β*-substituted ketones *via* 1,2-migration. Through this method, a series of radicals such as alkyl,[9] acyl,[10] CF$_3$,[11] N$_3$,[12] S,[13] P,[14] Si,[15] Se-contained[16] radicals, were introduced to the radical-mediated difunctionalization of aryl allylic alcohols (Scheme 1, a). The alkyl radicals mainly generated from cleavage of C–X, C–C or C(sp^3)–H bonds. However, 1,2-alkylarylation of *α*,*α*-diaryl allylic alcohol with C(sp^3)–H bonds in alcohols, ethers, alkanes, nitriles, amines have made great progress. In 2016, Cheng's group developed the peroxide facilitated [3+2] cyclization of *α*,*α*-diaryl allylic alcohols with *sec*-alcohols *via* neophyl rearrangements under transition-metal-free conditions.[9c] Ji's group presented the novel and straightforward strategy for the synthesis of *α*-aryl-*β*-alkylated ketones by peroxide initiated difunctionalization of aryl allylic alcohols with ethers (open-chain and cyclic ethers) without any metal catalyst, which formed two new carbon–carbon bonds in one step.[9d] In 2014, Tu and co-workers described the Ni-mediated difunctionalization of inactive alkenes with the *α*-C(sp^3)–H bonds of *N*, *N*-substituted amides for the building of *α*-aryl-*γ*-amine ketones.[9g] Li and Ji groups reported the oxidative difunctionalization of allylic alcohols with the C(sp^3)–H bonds of acetonitriles,[9a,9b] ketones[9e] or alkanes[9f]. Unfortunately, most of these conversions exist the defects of harsh reaction conditions, such as expensive catalysts, high temperatures, strong oxidants or limitation to the start materials. Hence, a simple and economic, environmentally benign method for difunctionalization of *α*,*α*-diaryl allylic alcohols with C(sp^3)–H bonds is lacking.

Recently, organic chemists have paid close attention to the visible-light photoredox catalysis for the view of economy and environment-friendliness.[17] Particularly, organic photosensitizers, usually organic small molecular dyes, which have been widely used as photocatalysts in pharmaceutical and organic synthesis.[18] Eosin Y, a common photocatalyst, can avoid metal remain in the

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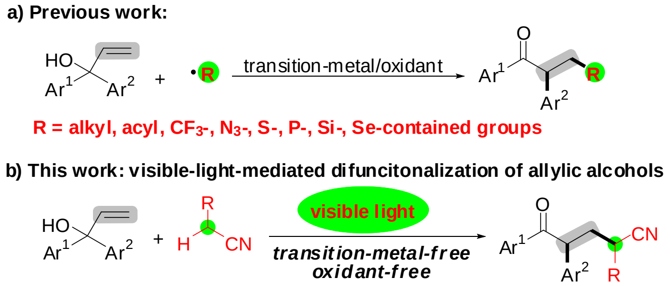
final products. Additionally, eosin Y is greener than the transition-metal based photocatalysts.[18d–k] According to the previous researches on α,α-diaryl allylic alcohols and our works on the development of visible-light phororedox catalysis,[19] we also present the first visible-light-induced difunctionalization of α,α-diaryl allylic alcohols with α-C(sp^3)–H bonds of nitriles for the building of 5-*oxo*-pentanenitriles under transition-metal-free and oxidant-free conditions with high efficiency and selectivity.



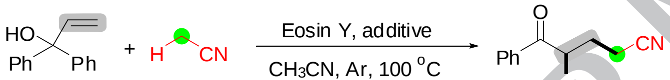
Scheme 1. Oxidative radical functionalization of allylic alcohols.

2. Results and Discussion

Based on the visible-light photoredox catalysis strategy, we initially chose 1,1-diphenylprop-2-en-1-ol (**1a**) and acetonitrile (**2a**) as the model substrates to optimize the reaction conditions (Table 1). Firstly, the α,α-diaryl allylic alcohol **1a** (0.2 mmol) reacted with acetonitrile **2a** (2 mL) in presence of cyclobutanone *O*-(4-(trifluoromethyl)-benzoyl) oxime (additive **I**, 1.5 equiv) as additive and Eosin Y (5 mol%) as photocatalyst, under an argon atmosphere at 100 °C by irradiation with a 5 W blue LED light for 24 h, afforded the target α-aryl-γ-cyano ketone **3aa** in 78% yield (entry 1). Firstly, we examined the effect of additives, a series of additives such as cyclobutanone *O*-(4-nitrobenzoyl) oxime (additive **II**), cyclobutanone *O*-benzoyl oxime (additive **III**), and 4-MeOC$_6$H$_4$N$_2$BF$_4$ (additive **IV**)[19a,c,d] were conducted (entries 2–4). The results indicated that all of the additives could afford the desired product **3aa**, albeit with lower yields (entries 2–4). However, the 4-MeOC$_6$H$_4$N$_2$BF$_4$, an excellent radical initiator, could not improve the yield of this 1,2-alkylarylation process (entry 4). Remarkably, the reaction could not occur without additional additive (entry 5). Next, the transition-metal photocatalysts Ir(ppy)$_3$ or Ru(bpy)$_2$Cl$_2$ were also tested, the results revealed that they were failed in improving the reaction yield (entries 6–7 vs entry 1). Additionally, the transformation could not occur without photocatalyst or visible-light irradiation (entries 8–9). The amount of Eosin Y also effected the reaction and 5 mol% was the best choice according to the reaction yields (entries 10–11 vs. entry 1). Other solvents (toluene, THF, dichloromethane) were also tested in presence of MeCN (5 equiv) as the reactant, and using THF as solvent could afford the target product in 68% yield (entries 12–14). Unfortunately, other light sources such as 3 W blue LED light, 36 W compact fluorescent light or sunlight showed less efficient than 5 W blue LED light (entries 15–17 vs. entry 1). The reaction performed at 80 °C or 120 °C only afforded target product **3aa** in 63% or 65% yield respectively (entries 18–19). Furthermore, the presented transformation was easily scaled up to 1 gram in moderate yield (entry 20).

Table 1

Optimization of the reaction conditions [a]



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

Entry	Variation from the standard conditions	Yield %
1	None	78
2[b]	Additive **II** instead of additive **I**	52
3[c]	Additive **III** instead of additive **I**	43
4[d]	Additive **IV** instead of additive **I**	18
5	Without additive	0
6	Ir(ppy)$_3$ instead of Esoin Y	71
7	Ru(bpy)$_2$Cl$_2$ instead of Eosin Y	63
8[c]	Without Eosin Y	0
9[d]	Without additional light	0
10	Eosin Y (2 mol %)	67
11	Eosin Y (10 mol %)	77
12[e]	Toluene instead of MeCN	28
13[e]	THF instead of MeCN	68
14[e]	DCM instead of MeCN	23
15[f]	None	70
16[g]	None	64
17[h]	None	52
18	At 80 °C	63
19	At 120 °C	65
20[i]	None	72

[a] Reaction conditions: **1a** (0.2 mmol), MeCN **2a** (2 mL), Eosin Y (5 mol %), cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime (additive **I**, 1.5 equiv) at 100 °C under an argon atmosphere and 5 W blue LED light for 24 h.

[b] additive **II**: cyclobutanone *O*-(4-nitrobenzoyl) oxime.

[c] additive **III**: cyclobutanone *O*-benzoyl oxime.

[d] additive **IV**: 4-MeOC$_6$H$_4$N$_2$BF$_4$.

[e] MeCN (5 equiv, 1 mmol).

[f] 3 W blue LED light instead of 5 W blue LED light.

[g] 36 W compact fluorescent light instead of 5 W blue LED light.

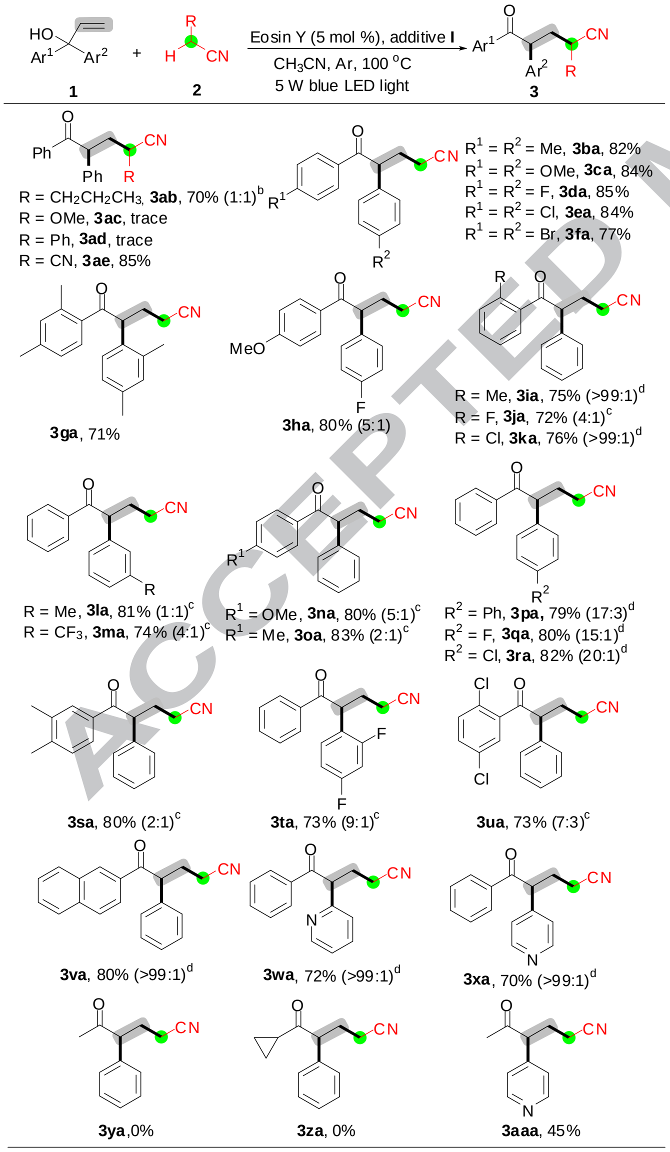
[h] sunlight instead of 5 W blue LED light.

i **1a** (1.0 g, 4.76 mmol) and MeCN **2a** (10 mL) for 48 h.

With these established conditions, we set out to research the substrates scope of allylic alcohols (**1**) and nitriles (**2**) (Table 2). Firstly, a series of nitriles, including pentanenitrile (**2b**), 2-methoxyacetonitrile (**2c**), phenylacetonitrile (**2d**) or malononitrile (**2e**), were examed by using 1,1-diphenylprop-2-en-1-ol (**1a**), cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime (additive **I**) and Eosin Y (products **3ab**–**ae**). To our delighted, pentanenitrile (**2b**) was suitable for this transformation, affording the target product **3ab** in 70% yield. However, utilizing 2-methoxyacetonitrile (**2c**) or 2-phenylacetonitrile (**2d**) in the 1,2-alkylarylation failed to construct 5-*oxo*-pentanenitriles **3** (**3ac** and **3ad**), due to the hydrogen abstraction of **2c** and **2d** was difficult. Furthermore, malononitrile (**2e**) could delivered the desired product **3ae** in good yield under the optimal conditions (**3ae**).

Next, a range of symmetric α,α-diaryl allylic alcohol **1** with acetonitrile **2a** were tested under the optimal conditions. Allylic alcohols (**1b**–**g**), with the same aryl groups on the α position, such as aryl rings with electron-donating groups (Me or OMe) or electron-withdrawing groups (F, Cl or Br) all transformed smoothly to generate the desired products **3** in moderate to excellent yields (**3ba**–**ga**). On the other hand, allylic alcohols with two different aryl rings were proved suitable for this difunctionalization and afforded the desired corresponding products **3** in moderate to good yields (**3ha**–**xa**). The results showed that the migration activities of aryl groups depended on the electronic effects and sterical hindrance properties of substituents on the aryl groups: according to the electronic effect, the electron-deficient aryl groups were more easily proceed migration than electron-rich ones, and according to the steric hindrance property, the migration reactivity order of aryl groups is *para* > *meta* > *ortho*. Actually, the electronic effects and sterical hindrance properties of substituents on the aryl groups worked together. Interestingly, when utilizing 1-(4-fluorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-ol **1h** in this transformation gave two isomers **3ha** and **3ha'** (5 : 1) and the isomers could be easily isolated by silica column chromatography. Alcohols **1i**–**k** have an unsubstituted aryl ring and a 2-substituted ary ring on the *α* position, gave the unsubstituted aryl ring migrating *α*-aryl-*γ*-cyano ketones **3ia**–**ka** as the major products. In these transformation, the steric effects overruled the electronic effects due to the steric hinderance in the formation of spiro intermediate and always afforded the migration product with the unsubstituted-Ar groups. However, allylic alcohol **1l** with an unsubstituted aryl ring and a *m*-Me-substituted aryl ring on the *α* position underwent the 1,2-alkylarylation providing the Ph-migration product (**3la**) and *m*-Me-Ph-migration product (**3la'**) in 1 : 1, and the total yield was 81%, which combined the effects of the electronic effects and sterical hindrance acting together. Alcohol **1m** with an unsubstituted aryl ring and a *m*-CF_3-substituted aryl ring on the *α* position took place the *m*-CF_3-Ph group migration as the major process, affording the target product **3ma** in 74% yield. A similar rearrangement was suitable for allylic alcohols **1n**–**r**, which with an unsubstituted *α*-aryl ring and a 4-substituted *α*-aryl ring, the electronic effects were more important than the steric effects so that the electron-withdrawing and relatively neutral Ar groups migrated while electron-donating groups (OMe or Me) did not migrate (**3na**–**ra**).

Table 2 Reaction Scope of alkenes (**1**) with nitriles (**2**).[a]



[a] Reaction conditions: **1** (0.2 mmol), **2** (2 mL), Eosin Y (5 mol%), cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime (additive **I**, 1.5 equiv) at 100 °C under an argon atmosphere and 5 W blue LED light for 24 h.

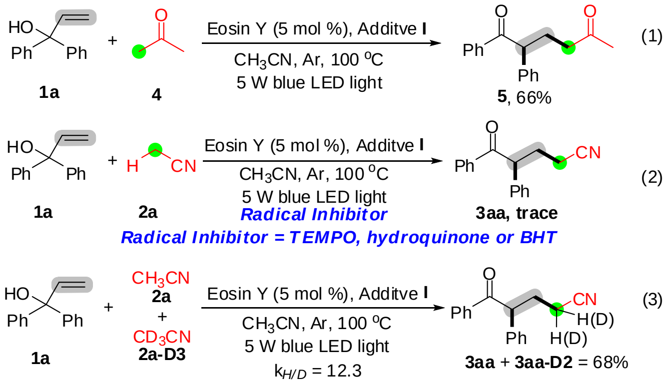
[b] The d.r. value ratio of product **3ab** was detected by GC-MS analysis of the crude product.

[c] The ratio of **3** and its isomer was determined by ^1H NMR analysis of the isolated product, only major product was shown.

[d] The ratio of **3** and its isomer was determined by GC-MS analysis of the crude product, only major product was shown.

However, allylic alcohols **1s**–**u** with two substituents on one aryl group, could go through the 1,2-alkylarylation and selectively furnished the major products **3sa**–**ua** in good yields. As for allylic alcohols **1s,** the electronic effects and sterical hindrance properties of the two Me groups worked together so that this reaction afforded the unsubstituted-Ar groups migrated product as the major product (**3sa**). As for allylic alcohols **1t,** the electronic effects overruled the steric effects and afforded the migration product with the difluro-substituted-Ar groups (**3ta**). As for allylic alcohols **1u,** the steric effects were more important than the electronic effects, provided the Ph-migration product as the major product (**3ua**). Furthermore, substrate **1v** was viable in the construction of 5-*oxo*-pentanenitriles, giving the phenyl group migrated product **3va** in 80% yield. To our surprise, substrates **1w** and **1x** could go through the 1,2-migration process and give the solely targeted products **3wa** and **3xa**, respectively, due to the relative lower aromaticity of pyridinyl groups. However, the allylic alcohols **1y**–**z** with an *α*-Ph and an *α*-alkyl group were not compatible for this reaction system (**3ya**–**za**). Notably, the 1,2-migration process was suitable for 2-(pyridin-4-yl)but-3-en-2-ol (**1aa**), proceed *via* the migration of pyridin-4-yl group and afforded the sole product **3aaa** in 45% yield, due to the nitrogen atom of pyridine could afford a more stable intermediate in these transformations.

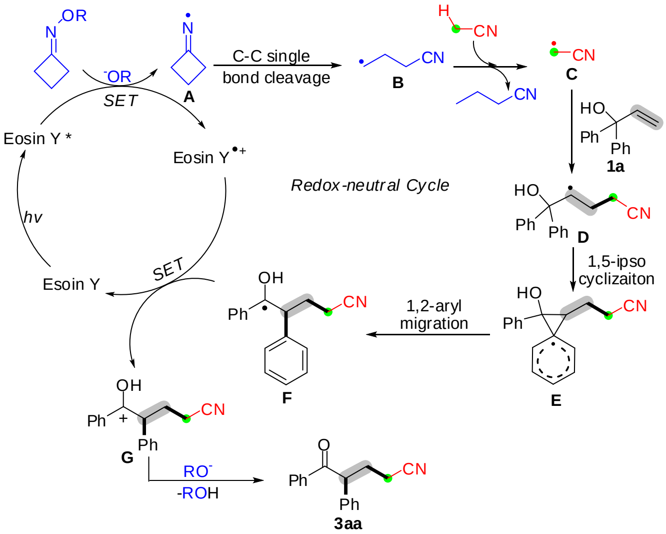
Control experiments was conducted by using acetone **4** instead of nitrile **2** to react with allylic alcohols **1a** under the standard conditions. We were pleased to find that the corresponding products **5** were obtained in moderate yields (eq 1, Scheme 2). Previously studies showed that this transformation went through a radical process.[9a,b,19a,d,e,20] Several control experiments were proceeded to demonstrate the reaction pathway. The allylic alcohol **1a** reacted with nitrile **2a** under the standard conditions in the presence of TEMPO, hydroquinone or BHT (2,6-di-*tert*-butyl-4- methylphenol), and the reaction was almost completely suppressed (eq 2, Scheme 2). The results indicated that this difunctionalization may proceed *via* a radical pathway. From the result of kinetic isotope effect ($kH/kD = 12.3$), it is believed that the cleavage of $C(sp^3)$–H bonds in acetonitriles is a rate-limiting step, by using **1a** reacted with **2a** and **2a**-D3 (eq 3, Scheme 2).[9e]



Scheme 2. Control experiments.

According to the experiment results and literature reports,[8–20] a plausible mechanism is presented in Scheme 3. Photocatalyst

Eosin Y is being photoexcited by blue LED light, and converts into strong reductant Eosin Y*.[18] Then, this Eosin Y* undergoes reductive quenching by *O*-(4-(trifluoromethyl)benzoyl) oxime to give the iminyl radical **A** and Eosin Y$^{\bullet+}$ radical cation *via* single electron transfer (*SET*).



Scheme 3. Proposed mechanism.

The iminyl radical **A** undergoes a ring-opening homolytic C–C single bond cleavage, and generates a unstable cyanoalkyl radical **B**.[20] Then, hydrogen abstraction of **2a** by unstable cyanoalkyl radical **B** produces a more stable cyanomethyl radical **C**. Therefore, the concentration of cyanomethyl radical **C** is much higher than that of cyanoalkyl radical **B** probably due to their stability. Next, radical addition of cyanomethyl radical **C** to the carbon–carbon double bond of allylic alcohols furnishes a new alkyl radical intermediate **D**. Within intermediate **D**, intramolecular 5-*ispo* cyclization provides spiro[2,5]octadienyl radical **E**, follows by 1,2-aryl migration to give benzyl radical intermediate **F**. Subsequently, radical **F** is oxidized by the oxidizing Eosin Y$^{\bullet+}$ species to afford the carbocation intermediate **G** with regeneration of Eosin Y, closing the photocatalytic cycle. Finally, a base-mediated deprotonation of the carbocation intermediate **G** by RO$^-$, which resulted from the fragmentation of *O*-(4-(trifluoromethyl)benzoyl) oxime, gives the 5-*oxo*-pentanenitrile **3aa** and ROH.

3. Conclusion

In conclusion, we have described the first visible-light-mediated difunctionalization of *α*,*α*-aryl allylic alcohols with the *α*-C(sp^3)–H bonds of nitriles under transition-metal-free and oxidant-free conditions, during which two new carbon-carbon bonds were formed in this transformation *via* a C(sp^3)–H bond functionalization and 1,2-aryl migration process. This difunctionalization of alkenes avoids limitations commonly associated with transition-metal and strong oxidant mediated C(sp^3)–H bond activation. The further applications of the developed method in synthesis of bioactive compounds and natural products are underwaying in our laboratory.

4. Experimental section

4.1 General information and materials.

All reactions were carried out with magnetic stirring and in dried glassware. Standard syringe techniques were applied for transfer of dry solvents. All reagents and solvents were commercially available and used without any further purification unless specified. Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

4.2 General procedure.

To a Schlenk tube were added **1** (0.2 mmol), **2** (1.5 eqiuv, 0.3 mmol), Eosin Y (5 mol%, 0.004 mmol), additive **I** (cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime, 1.5 equiv, 0.3 mmol), CH_3CN (2 mL). Then the mixture was stirred at 100 ^{o}C (oil bath temperature) in argon atmosphere (1 atm) under 5 W blue LED light for 24 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 5 : 1 to 3 : 1) to afford the desired products **3**.

Acknowledgments

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Supplementary Material

Supplementary data associated with this article can be found in the online version.

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Highlight

- The 1,2-alkylarylation occurs under transition-metal-free and oxidant-free conditions.
- A variety of improtant 5-*oxo*-pentanenitriles were obtained.
- The results proved that the cleavage of C(sp^3)–H bond of acetonitrile is a rate-limiting step.

Graphical Abstract

Visible-light-induced 1,2-alkylarylation of alkenes with *a*-C(sp^3)–H bonds of acetonitriles involving neophyl rearrangement under transition-metal-free conditions

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