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Visible Light Irradiation of Acyl Oxime Esters and Styrenes Efficiently Constructs β-Carbonyl Imides by a Scission and Four-Component Reassembly Process

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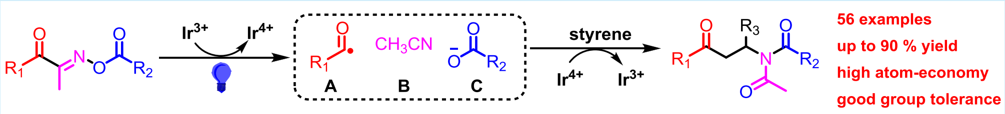
Supporting Information



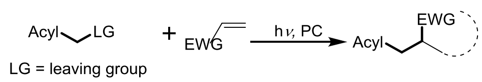
56 examples
up to 90 % yield
high atom-economy
good group tolerance

ABSTRACT: Acyl radical triggered difunctionalizations of aryl olefins have been realized using oxime ester as the acyl precursor for the first time. Irradiation of *fac*-Ir(ppy)$_3$ and oxime ester by visible light caused scission into three components, which recombined with olefins to yield significant β-carbonyl imides showing good functional group tolerance and high atom economy. Control experiments as well as spectroscopic and electrochemical studies revealed the efficient intermolecular reorganization of oxime ester into styrene with the aid of solvent exchange.

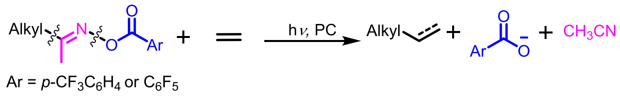
Difunctionalization of a double bond is a significant strategy to obtain diverse structure-complex and value-added compounds.[1,2] In recent years, the advancement in visible light catalysis[3] facilitated its development, especially in carbon radical triggered difunctionalization, for example, alkyl[4] and aryl radical[5] species, providing a facile way to construct valuable molecules. However, the use of an acyl radical[6] as a highly active species on the difunctionalization of a double bond is mostly limited to an electron-withdrawing double bond (i.e., acrylate derivatives) and merely yielded C−C/C−C bond (Scheme 1a).[7] For an electron-donating double bond such as in an aryl olefin, only hydrogenation[8] or a double-bond intact product[9] was obtained, leading to the acyl radical triggered difuntionalization being locked.

Scheme 1. Acyl-imidization of Aryl Olefins via Visible Light Catalysis

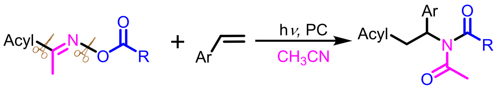
a) Acyl radical triggered difunctionalization of withdrawing C=C bond



b) Application of oxime with release of ester anion and nitrile subunits



This work: Acyl radical triggered difunctionalization of aryl C=C bond



Here we report an acyl radical triggered difuntionalization of aryl olefin for the first time. In our design, well-designed oxime ester[9] was utilized as an acyl radical precursor to react with aryl olefins for β-carbonyl imides (C−C/C−N bond) formation. Under visible light irradiation of simple *fac*-Ir(ppy)$_3$, different substitutions including electron-withdrawing and -donating groups in both oxime ester and styrene were well tolerated. This method could further extend to cyclic oxime species to smoothly produce alkyl imides with good yields. In contrast to the previous utilization of oxime ester[6e,10−12] which always wasted almost half of its molecular weight by losing an ester, even an additional nitrile fragment (Scheme 1b), in our reaction the acryl, nitrile, and ester subunits of oxime substrate generated in situ can reassemble with a double bond to yield β-carbonyl imides in CH$_3$CN. This rearrangement addition of oxime ester to olefin not only realizes a high-economic application of oxime ester in an intermolecular way but also provides an intriguing complementary approach for acyl-triggered difunctionalization of olefins.

Initially, easily prepared oxime ester **1** and styrene **2** were selected as substrate to explore the feasibility of our design. When the CH$_3$CN solution of these two reagents and *fac*-Ir(ppy)$_3$ (1 mol %) was irradiated under blue LEDs for 12 h, imide **3** with a 65% yield was obtained, which was confirmed via ^{1}H, ^{13}C NMR and high resolution mass spectra (HRMS) (Table 1, entry 1). Encouraged by this result, optimization of

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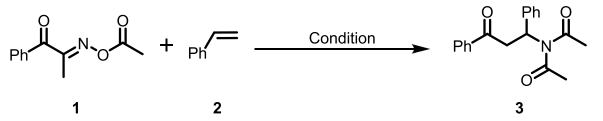
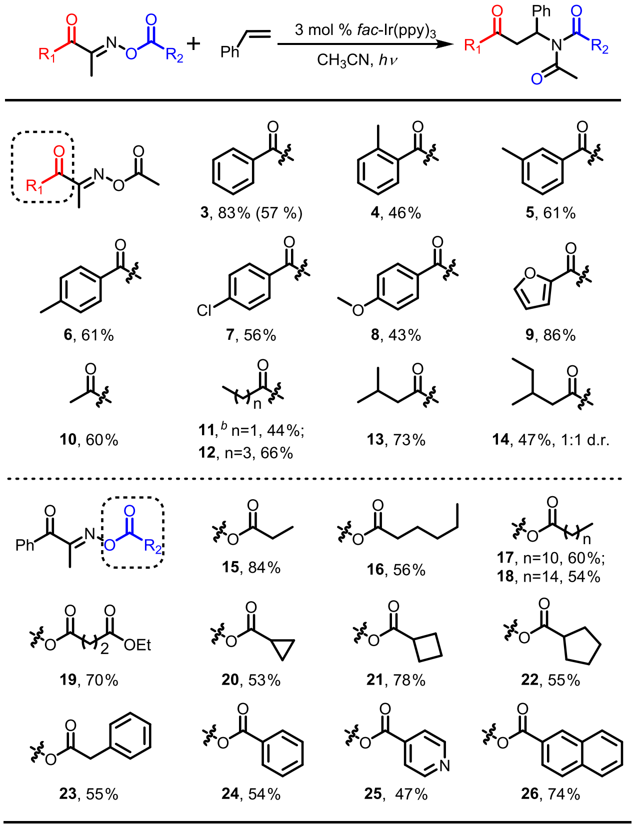
Table 1. Optimization of Reaction Conditions[a,b]



entry	photocatalyst	solvent	yield (%)
1	*fac*-Ir(ppy)$_3$	CH_3CN	65
2	$[Ir(dtbbpy)(ppy)_2]PF_6$	CH_3CN	20
3	$Ru(bpy)_3(BF_4)_2$	CH_3CN	0
4	Eosin Y	CH_3CN	0
5	*fac*-Ir(ppy)$_3$	EtOH	0
6	*fac*-Ir(ppy)$_3$	DMF	0
7	*fac*-Ir(ppy)$_3$	1,4-Dioxane	0
8	*fac*-Ir(ppy)$_3$	DCE	<5
9[c]	*fac*-Ir(ppy)$_3$	CH_3CN/DMF	0
10[d]	*fac*-Ir(ppy)$_3$	CH_3CN	70
11[d,e]	*fac*-Ir(ppy)$_3$	CH_3CN	86
12[d,e,f]	*fac*-Ir(ppy)$_3$	CH_3CN	57

[a] Reaction Condition: oxime ester **1** (0.2 mmol), styrene **2** (5 equiv, 1.0 mmol), and photocatalyst (1 mmol %) in CH_3CN (2.0 mL) under 460 nm LEDs irradiation for 12 h at rt. [b] ^1H NMR yield with 2,2-diphenylacetonitrile as internal standard. [c] Volume ratio was 1:1. [d] 24 h. [e] 3 mol % *fac*-Ir(ppy)$_3$. [f] In air.

Scheme 2. Scope of Oxime Ester[a]



[a] Reaction condition: oxime ester (0.2 mmol), styrene (5 equiv, 1.0 mmol), *fac*-Ir(ppy)$_3$ (3 mmol %) in CH_3CN (2.0 mL) under 460 nm LEDs irradiation for 24 h at rt. [b] (*E*)-4-(Acetoxyimino) hexan-3-one as the substrate.

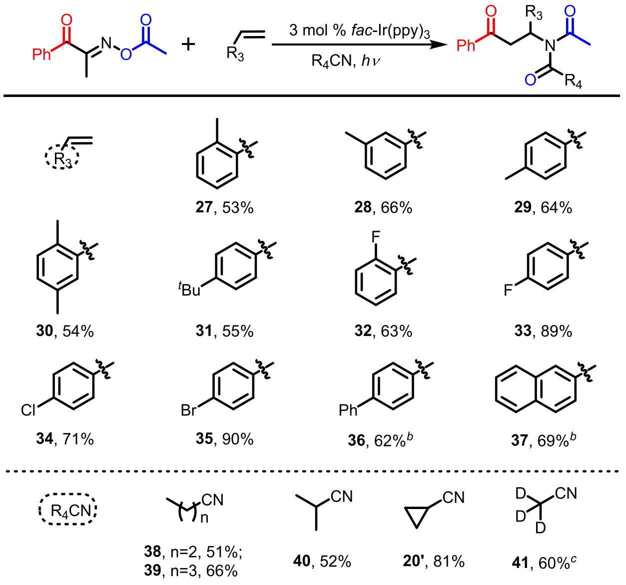
the reaction conditions was carried out. As shown in Table 1, variations on other different photocatalysts including $[Ir(dtbbpy)(ppy)_2]PF_6$, $Ru(bpy)_3(BF_4)_2$, and Eosin Y showed that only $[Ir(dtbbpy)(ppy)_2]PF_6$ gave a 20% yield of product and no outcomes at all for others (Table 1, entries 2−4). Screening solvents revealed that CH_3CN as solvent was essential to realize this unique transformation. EtOH, DMF, 1,4-dioxane, DCE, or a mixture of CH_3CN/DMF (1/1) as reaction media gave trace products (Table 1, entries 5−9). Doubling the reaction time could promote the reaction yield up to 70% (Table 1, entry 10), and subsequently, increasing the dosage of *fac*-Ir(ppy)$_3$ to 3 mol % gained the highest 86% yield (Table 1, entry 11). It should be noted that this reaction worked smoothly in air and provided the target imide **3** in 57% yield (Table 1, entry 12). Control experiments confirmed that no reaction occurred in the absence of light or photocatalyst, confirming the nature of visible light catalysis (Table S1). On the basis of these results, optimized reaction conditions, which consist of 0.2 mmol of oxime ester, 5 equiv of styrene, 3 mol % *fac*-Ir(ppy)$_3$ in 2 mL of CH_3CN under irradiation by blue LEDs for 24 h, were achieved.

With the optimized reaction condition in hand, the generality of this unique photochemical transformation was examined. As shown in Scheme 2, diverse oxime esters showed good reactivity to reassemble into styrene, leading to the following observations: (a) As for the acyl subunit on oxime ester, the electron property and steric effect on aryl substitutions (**3**−**8**), length, and configuration difference on alkyl ones (**10**−**14**) were all well tolerated. A heteroaryl acyl group like furan was also compatible to give an 86% yield of imide (**9**). (b) In terms of ester moiety on oxime ester, an alkyl ester with three (**15**), six (**16**), 12 (**17**), and 16 (**18**) linear carbons, or cyclopropane (**20**), cyclobutane (**21**), cyclopentane (**22**), and 2-phenylacetate (**23**) substitutions, worked smoothly to provide relative products in 47%−84% yields. Interestingly, ethyl succinate containing two ester groups was eligible to give product **19** in 70% yield. Similarly, aryl ester groups including benzoate (**24**), isonicotinate (**25**), and 1-naphthoate (**26**) were successfully reorganized into corresponding imides. (d) To further document the potential of our method, a scale-up experiment of oxime ester **1** (4.8 mmol) gave rise to a 57% yield under irradiation of 460 nm LEDs for 24 h, demonstrating its possible applications in organic synthesis.

For aryl olefins (Scheme 3), styrene with *o*-, *m*-, *p*-, 2,5-dimethyl and steric *p*-^{t}Bu groups were all competent to react with oxime ester **1**, affording 53−66% yields of products (**27**−**31**). Incorporation of halogens (2-F, 4-F, 4-Cl, 4-Br) showed a relatively higher reactivity (**32**−**35**, 63−90%). Besides, the extended conjugated 4-vinyl-1,1′-biphenyl (**36**) and 2-vinylnaphthalene (**37**) were viable reactants to provide relative nonsymmetric imides. Considering the possible solvent exchange effect, several other nitriles including butyronitrile, pentanenitrile, isobutyronitrile, and cyclopropanecarbonitrile as media have been tested for the reaction between oxime ester **1** and styrene **2**. Consequently, relative butyl-, pentane-, isobutyl-, and cyclopropane-carbonyl groups were found to insert into the imides with good yields (**20′**, **38**−**40**, 51−81%). More interestingly, a D-labeled product with a 60% yield was obtained when the reaction was performed in CD_3CN (**41**).

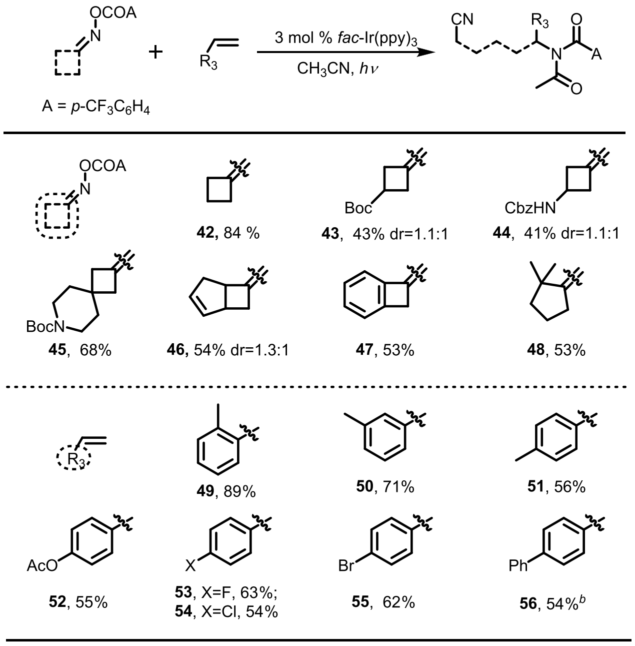
The synthetic application of this high atom-economic reaction was further documented by alkyl-imidazation of styrene from cyclic alkyl oxime ester. As shown in Scheme 4, diverse cyclic oxime esters were found to smoothly provide remote cyano imides via ring opening/internal rearrangement with olefins successfully (**42**−**56**). Tested cyclobutanone

Scheme 3. Scope of Aryl olefins and Solvent Exchange Effect[a]



[a] Reaction condition: oxime ester (0.2 mmol), styrene (5 equiv, 1.0 mmol), *fac*-Ir(ppy)$_3$ (3 mmol %) in CH$_3$CN (2.0 mL) under 460 nm LEDs irradiation for 24 h at rt. [b] Oxime ester (2 equiv, 0.4 mmol), styrene (0.2 mmol); isolated yield based on styrene. [c] ^{1}H NMR yield with 2,2-diphenylacetonitrile as internal standard.

Scheme 4. Further Synthetic Application to Cyclic Oxime Ester[a]



[a] Reaction conditions: oxime ester (0.2 mmol), styrene (5 equiv, 1.0 mmol), *fac*-Ir(ppy)$_3$ (3 mmol %) in CH$_3$CN (2.0 mL) under 460 nm LEDs irradiation for 24 h at rt. [b] Oxime ester (2 equiv, 0.4 mmol), styrene (0.2 mmol); isolated yield based on styrene.

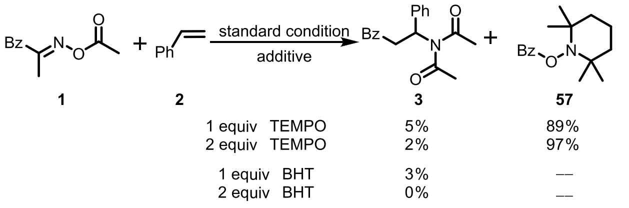
derived substrates containing an ester (**43**), a Cbz protected-amine (**44**), and a spiro ring (**45**) were well tolerant to yield structural-complex imides with moderate efficiency. Besides, the conversion of bicyclo[3.2.0]hept-2-en-6-one and benzocyclobutenone derived substrates to the target products were also observed with a 54% (**46**) and 53% yields (**47**). The same good result was obtained for more ring-stable cyclopentanone derivatives (**48**), and selectively occurred in a multisubstituted site, providing a *regio*-specific conversion into a single product. Herein, aryl olefins as reaction partner with electron-donating (*o*-Me, *m*-Me, *p*-Me, *p*-OAc), electron-withdrawing (*p*-F, *p*-Cl, *p*-Br), or extended conjugated (*p*-Ph) groups were all compatible (**49**−**56**).

To figure out the details on the reaction mechanism, spectroscopic and electrochemical data were provided to identify the interaction between photocatalyst *fac*-Ir(ppy)$_3$ and substrates. UV−vis absorption spectra showed that only *fac*-Ir(ppy)$_3$ strongly responded to visible light and no absorption for **1** and **2** in >400 nm region (Figures S1, S2). Further excitation of *fac*-Ir(ppy)$_3$ with visible light resulted in an intense luminescence at 550 nm, which was subsequently quenched by **1** (Figures S3, S4). This result indicated a strong interaction between oxime ester and the excited photocatalyst. Electrochemical data established the oxidative potential $E^{IV/*III}$ of excited *fac*-Ir(ppy)$_3$ to be −1.73 V vs SCE,[13] which was enough to reduce oxime ester **1** (E_1^{red} = −1.42 V vs SCE) (Figure S5). By combining these results, it is therefore reasonable to consider that a single electron transfer (SET) from the excited photocatalyst to oxime ester was thermodynamically feasible to trigger the whole reaction circle. An additional radical capture experiment with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and butylated hydroxytoluene (BHT) seriously suppressed the conversion efficiency (Scheme 5a) accompanied by an isolated coupling product of the benzoyl (Bz) group and TEMPO (Scheme 5a, **57**, 89% for 1 equiv and 97% for 2 equiv), clearly suggesting the existence of a benzoyl radical in this process.

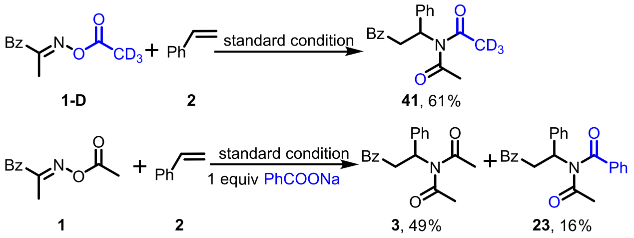
Furthermore, deuterated substrate **1-D** was synthesized to react with styrene **2** to trace the migration behavior of the ester subunit in oxime ester. The final product with the *N*-

Scheme 5. Mechanistic Study

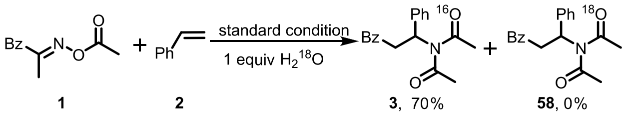
a) Radical capture of benzoyl subunit in oxime by TEMPO and BHT



b) Scission and reassembly of ester group

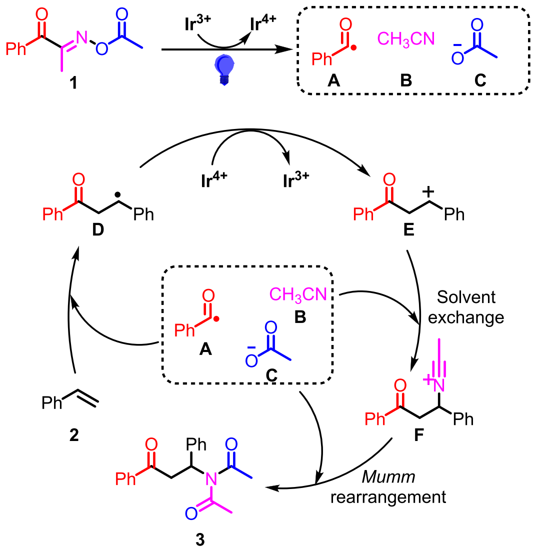


c) ^{18}O-labeled reaction for the reaction possibility of water



deuterated acetyl group was obtained in 61% yield (Scheme 5b), and a 16% yield of benzoyl product was detected when sodium benzoate was added as an exotic competing carboxyl source. When 1 equiv of $H_2{}^{18}O$ was used as an additive, no ^{18}O labeled product was detected, ruling out the possibility of water in the oxygen atom transfer of this reaction (Scheme 5c). On the basis of the above experimental results, a plausible mechanism was outlined in Scheme 6. Upon visible light irradiation, *fac*-Ir(ppy)$_3$ (Ir^{3+}) is excited to its triplet state and then transfers a single electron to oxime ester **1**, to afford *fac*-Ir(ppy)$_3^+$ (Ir^{4+}) and a radical anion of **1**. Further fragmentation of the latter species forms triple units of acyl radical **A**, acetonitrile **B**, and carboxylate anion **C**. Highly active acyl radical **A** selectively adds to terminal styrene **2** and was subsequently oxidized by *fac*-Ir(ppy)$_3^+$ (Ir^{4+}) to afford benzyl cation intermediate **E** and ground-state *fac*-Ir(ppy)$_3$ (Ir^{3+}). The generated species **E** is attacked by acetonitrile via solvent exchange to yield the cation **F** and then undergoes *Mumm* rearrangement[12i,14] with carboxylic fragment **C** to give the final product **3**. As for cyclic oxime ester, an alkyl group triggers the generation of a benzyl cation, which further captures one solvent molecule and proceeds in the following carboxylate anion rearrangement to provide the remote cyano substituted imide.

Scheme 6. Proposed Mechanism



In conclusion, we report a facile, efficient, and atom-economic acyl-triggered difunctionalization of both electron-donating and -withdrawing aryl olefins by using oxime ester as a precursor. In our system, the subunits of oxime ester, which was always wasted in previous reports, successfully reassemble into diverse styrene with good functional group tolerance and high atom economy to produce a well-functionalized and complex nonasymmetric acyl imide (C−C/C−N bond formation). The features of good scope generality and high atom utilization provide a straightforward and efficient strategy for acyl-imidization of aryl olefins, which makes up the utilization of an acyl radical in the difunctionalization of a double bond.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b03409.

> Materials and methods; condition optimization and general experimental procedures; scale-up reaction; optical spectroscopic and electrochemical data; control experiments; characterization data of all products; ^1H, ^{13}C, and ^{19}F spectra of all products; references (PDF)

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Notes

The authors declare no competing financial interest.

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