

Photoredox-Catalyzed Intermolecular Remote C-H and C-C Vinylation via Iminyl Radicals

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S Supporting Information

ABSTRACT: A unified strategy for intermolecular remote $C(sp^3)$ -H and C-C vinylation of O-acyl oximes with vinyl boronic acids has been achieved. This strategy is enabled by photoreductive generation of iminyl radicals from O-acyl oximes under irradiation by visible light. The translocated carbon-centered radicals, which are generated from the iminyl radicals through 1,5-hydrogen atom transfer or C-C cleavage, can be vinylated with vinyl boronic acids. This strategy opens up a new approach to remote functionalization via $C(sp^3)$ -H and C-C cleavage and provides an efficient and versatile solution to the synthesis of γ -vinylation of ketones and nitriles.

liphatic C-H and C-C bonds are ubiquitous in organic A liphatic C-H and C-C contact are are and and C-H molecules and are chemically inert.^{1,2} Consequently, C-H and C-C functionalization is a long sought after goal in organic synthesis, but it remains a formidable synthetic challenge due to issues of selectivity and activity.³

As pioneered by Forrester⁴ and Zard,⁵ iminyl radicals are found to be valuable intermediates for diverse chemical transformations.⁶ Oxidants, radical initiators, and transition metal catalysts are often used as promoters for the generation of iminyl radicals.⁷ Recently, visible light photoredox catalysis has emerged as a powerful method for the generation of iminyl radicals.⁸ As a result of these mild conditions, C-H and C-C functionalization mediated by iminyl radicals has become feasible.^{9–14} We reported that iminyl radicals can be generated from O-acyl oximes under photoredox catalysis and that subsequent intramolecular homolytic aromatic substitution (HAS) leads to intramolecular $C(sp^2)$ -H iminylation.⁹ It was found that the iminyl radicals can undergo 1,5-hydrogen atom transfer (HAT) followed by intramolecular HAS to achieve intramolecular C(sp³)-H arylation.^{4,10} In these two reports, iminyl radicals were produced by reductive single electron transfer (SET) through an oxidative quenching cycle of the photocatalyst. Studer¹¹ and Leonori¹² reported that photoredox-induced single-electron oxidation of α -imino-oxy acid derivatives leads to iminyl radicals. The translocated carboncentered radicals (C-radicals) generated from the iminyl radicals through 1,5-HAT can be further alkylated and halogenated, respectively. Groups led by Leonori^{12a} and Xiao¹³ described photoredox-induced C-C cleavage mediated by iminyl radicals. The resultant C-radicals could be further functionalized with Selectfluor and activated alkenes, respectively. These results show that iminyl radicals can serve as a platform for C-H and C-C functionalization. In view of the importance of remote $C(sp^3)$ -H and C-C functionalization and the ubiquity of



alkenes in pharmaceuticals and natural products, we sought to develop a unified strategy for intermolecular remote $C(sp^3)$ -H and C-C vinylation of O-acyl oximes with vinyl boronic acids promoted by visible light (Figure 1). This strategy could provide an efficient and versatile means for the synthesis of γ functionalization of ketones and nitriles.



Figure 1. Unified strategy for remote C(sp³)-H and C-C vinylation via iminyl radicals. PC = photocatalyst.

Our strategy is shown in Figure 2. For the C–H vinylation, the catalytic cycle begins with the visible-light promoted photoexcitation of a photocatalyst (Ir^{III}) to its excited state (Ir^{III}*).¹⁵ SET reductive cleavage of an acyl oxime (I) assisted by PC* produces an iminyl radical (V), an acyl anion (ArCO^{2–}), and an oxidized-state photocatalyst (Ir^{IV}) .^{9,10} 1,5-HAT¹⁵ from the distal C-H bond to the iminyl radical provides C-radical (VI), which is intermolecularly trapped by a vinyl boronic acid (II) giving the corresponding radical (VII). This radical (VII) is then oxidized by Ir^{IV}, delivering a cationic intermediate (VIII)

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Figure 2. Mechanism for intermolecular remote $C(sp^3)$ -H and C-C vinylation.

and regenerating the photocatalyst (Ir^{III}). Ultimately, deboronation¹⁶ followed by hydrolysis of **VIII** yields the remote $C(sp^3)$ -H vinylation product (**III**). Likewise, C-radical (**VI**') can be generated from iminyl radical (**V**') through C-C cleavage. C-Radical (**VI**') then follows a similar pathway as Cradical (**VI**) to give C-C vinylation product (**IV**).

Our initial investigation focused on the intermolecular remote $C(sp^3)$ -H vinylation of the *O*-acyl oxime **1a** with (*E*)-styrylboronic acid (**2a**). Investigation of the reaction parameters showed that remote C-H vinylation of **1a** by **2a** could be achieved in good isolated yield (for details, see the Supporting Information (SI)). When a mixture of **1a** (1 equiv) and **2a** (3 equiv) in 1,2-dichloroethane (DCE) was irradiated with blue LED strips in the presence of 0.5 mol % Ir(ppy)₃ as the photocatalyst at 22 °C, the desired product (**3a**) was isolated in 77% yield with a 20:1 *E/Z* ratio (Table 1, entry 1). Control experiments revealed that photocatalyst and light were necessary for the reaction to proceed (entry 2) and increased loading of the photocatalyst led to lower *E/Z* ratios (entries 3 and 4). A

Table 1. Variation of Reaction Parameters ^a			
Me 1a (1 eq (Ar = 4-Cl	OAr Ir(ppy) ₃ (0.5 mol %) H Ph B(OH) ₂ DCE, N ₂ , 22 °C, 24 blue LEDs then aqueous worku then aqueous worku uiv) 2a (3 equiv) "standard conditions" 33Ph? vinyl boronic acid	h me A" 3a remote C-H	Me vinylation
entry	deviation from standard conditions	yield (%) ^b	E/Z^{c}
1	none	77	20/1
2	w/o photocatalyst or light	0	-
3	1 mol % Ir(ppy) ₃	82	17/1
4	2 mol % Ir(ppy) ₃	75	14/1
5	$Ru(phen)_3(PF_6)_2$, instead of $Ir(ppy)_3$	trace	_
6	CH ₃ CN, instead of DCE	64	>20/1
7	CH ₂ Cl ₂ , instead of DCE	71	>20/1
8	1a/2a = 1/2	64	11/1
9	30 °C, instead of 22 °C	58	20/1

"Standard conditions A: A mixture of 1a (0.2 mmol, 1.0 equiv), 2a (0.6 mmol, 3.0 equiv), and $Ir(ppy)_3$ (0.001 mmol, 0.5 mol %) in DCE (2.0 mL) was irradiated by blue LED strips at 22 °C for 24 h, followed by aqueous workup. ^bIsolated yield. ^cDetermined by ¹H NMR analysis.

ruthenium-based photocatalyst was not suitable in this reaction (entry 5). Acetonitrile and dichloromethane were suitable as solvents but gave lower yields (entries 6 and 7). Reduced levels of boronic acid (2a) led to lower yields and reduced stereoselectivity (entry 8). The reaction is sensitive to temperature, and when it was carried out at 30 °C, the yield decreased to 58%.

We next evaluated the generality of this photoredox-catalyzed remote $C(sp^3)$ -H vinylation reaction. The scope of the reaction of O-acyl oximes with (E)-styrylboronic acid (2a) was examined (Scheme 1). O-Acyl oximes with tertiary γ -C–H bonds were well tolerated, giving the γ -vinyl ketones (3a-3f) with good yields and E/Z ratios (Scheme 1a). Unactivated secondary C–H bonds could be vinylated, but with low yields (e.g., 21% for 3g). Substrates bearing activated secondary C-H bonds (benzylic bonds or bonds adjacent to oxygen) functioned well in the reaction (3h-3j) (Scheme 1b). Primary C-H bonds remained a challenge and only moderate yields (27% for 3k and 42% for 31) could be achieved (Scheme 1c). We next varied the vinyl boronic acids using an O-acyl oxime (1a) as the substrate (Scheme 1d). Various substituted styrylboronic acids showed good reactivity, and the corresponding γ -vinyl ketones (3m-3t) were obtained in up to 78% yield. Para-substituted styrylboronic acids with electron-neutral (Me, t-Bu), -rich (MeO), and -deficient (F, Br) groups underwent the transformation smoothly (53-78% yields). Meta-substituted styrylboronic acids were also suitable, and the desired products 3r and 3s were isolated in 61% and 56% yields, respectively. Orthosubstituted styrylboronic acid gave the γ -vinyl ketone (3t) in only 34% yield. The reaction could be scaled up to the 2 mmol scale giving comparable isolated yield (77% for 0.2 mmol vs 71% for 2 mmol).

Encouraged by the successful results in the case of remote $C(sp^3)$ -H vinylation, we next sought to explore the possibility of photoredox-catalyzed remote C–C vinylation of cyclic O-acyl oximes with vinyl boronic acids. After a quick screening (for the condition optimization, see the SI), the reaction of cyclobutanone O-4-CF₃-benzoyloxime (4a) with (*E*)-styrylboronic acid (2a) was achieved with 77% isolated yield and a 20/1 *E/Z* ratio for nitrile 5a in DMSO using Ir(ppy)₃ as the photocatalyst irradiated by blue LEDs. After determining the optimized reaction conditions, the synthetic potential of this remote C–C vinylation was investigated, and the results are summarized in

Scheme 1. Scope of Remote C(sp³)-H Vinylation^{*a*}



^{*a*}Standard conditions A: A mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.6 mmol, 3.0 equiv), and $Ir(ppy)_3$ (0.001 mmol, 0.5 mol %) in DCE (2.0 mL) was irradiated by blue LED strips at 22 °C for 13–48 h, followed by aqueous workup. Isolated yield. *E/Z* ratios were determined by ¹H NMR analysis. ^{*b*}Two mmol scale (**1a**).

Scheme 2. The scope of the reaction was explored with respect to cyclic O-acyl oximes (Scheme 2a). A variety of cyclobutanone-derived O-acyl oximes bearing different functional groups at the C3-position of the cyclobutanone reacted with 2a to give the corresponding nitriles **5b**–**5f** in a range of 71–87% yields. The piperidine derivative also showed comparable reactivity and gave the product 5g in 83% yield. Furthermore, both 1-Boc-3-azetidinone and oxetan-3-one derived O-acyl oximes participated in this reaction very well to deliver products **5h** and **5i** with good yields. α -Branched cyclobutanone-derived O-acyl oximes delivered nitriles 5j and 5k in 83% and 71% yields in which C-C bond cleavage occurred selectively at the more substituted position. In addition, less-strained O-acyl oximes derived from five-membered cyclic ketones could also participate in this transformation well to give the desired products 5i and 5m in moderate yields. Notably, benzocyclobutenone derivatives worked well, forming the benzonitrile product **Sn** in 71% yield with E/Z = 14/1. To further explore the synthetic potential of this C-C vinylation reaction, a series of (E)-styrylboronic acid derivatives (2) were examined. As highlighted in Scheme 2b, para-substituted styrylboronic acids





^aStandard conditions B: A mixture of 4 (0.2 mmol, 1.0 equiv), 2a (0.6 mmol, 3.0 equiv), Na_2HPO_4 (0.4 mmol, 2.0 equiv), and $Ir(ppy)_3$ (0.001 mmol, 0.5 mol %) in DMSO (2.0 mL) was irradiated by blue LED strips at 22 °C for 9–52 h, followed by aqueous workup. Isolated yield.

on the phenyl ring were tolerated, giving the corresponding nitriles (5o-5v) in range of 43–78% yields. Meta-substituted styrylboronic acids (such as Me, Br, and Cl) also gave the desired products in 55–68% yields. *ortho*-Cl styrylboronic acid proceeded smoothly to give the target product 5z in 49% yield. Cyclopentanone and cyclohexanone-derived *O*-acyl oximes failed to give the corresponding ring opening products under our conditions.

In order to investigate the chemoselectivity of this remote C– H and C–C vinylation reaction, O-acyl oximes with several reactive sites were synthesized as the probe molecules. When the aryl ketone-derived O-acyl oxime **40** was reacted under the standard C–H vinylation conditions A, no remote C–H vinylation product (**3u**) was isolated, and instead, the intramolecular HAS product (**3u**') was obtained in 61% yield (Scheme 3a).¹⁰ This phenomenon suggests that intramolecular HAS is faster than intermolecular vinylation under our established conditions. O-Acyl oxime **4p** was then subjected

Scheme 3. Chemoselectivity Investigation^a



^{*a*}For standard conditions A and B, see footnotes of Schemes 1 and 2. Isolated yield. Ar = 4-CF₃Ph.

into C–H (conditions A) and C–C (conditions B) vinylation conditions. Only C–C vinylation product 6 was isolated under both conditions, and no C–H vinylation product 3v was observed (Scheme 3b). Furthermore, proline-derived O-acyl oxime 4q and 4r gave the same C–C cleavage product 7 (Scheme 3c). These experiments imply that C–C bond cleavage is more favorable than 1,5-HAT under our conditions, which is consistent with Leonori's observation.^{12a}

In summary, we have developed the photoredox-catalyzed intermolecular remote vinylation of *O*-acyl oximes with vinyl boronic acids. These reactions are enabled by iminyl radical-promoted 1,5-HAT and C–C bond cleavage. The reaction is applicable to a wide range of *O*-acyl oximes and vinyl boronic acid derivatives to provide the corresponding γ -vinyl ketones and nitriles under mild and redox neutral conditions. Use of this strategy will enable further discovery of remote C(sp³)–H and C–C functionalization and is currently in progress in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02540.

Experimental details, NMR spectra, and details of experiments (PDF)

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Notes

The authors declare no competing financial interest.

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