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Homogeneous Catalysis

Regiospecific Intermolecular Aminohydroxylation of Olefins by Photoredox Catalysis

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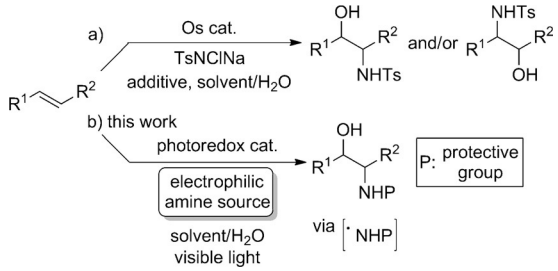
Abstract: A simple and regiospecific aminohydroxylation of olefins by photoredox catalysis has been developed. N-protected 1-aminopyridinium salts are the key compounds and serve as amidyl radical precursors by the action of Ir photocatalysts, *fac*-[Ir(ppy)$_3$] and [Ir(ppy)$_2$(dtbbpy)](PF$_6$) (ppy = 2-pyridylphenyl, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine). The present photocatalytic system allows for synthesis of vicinal aminoalcohol derivatives from olefins with various functional groups under mild reaction conditions with easy handling.

Vicinal aminoalcohol skeleton is ubiquitous in biologically active natural products and drugs.[1] Aminohydroxylation of olefin has been regarded as one of the simplest strategies to access vicinal aminoalcohols. Though various types of catalytic aminooxygenation of olefins have been reported so far,[2,3] one of the most reliable methods for intermolecular aminohydroxylation is the Os-catalyzed system, which was originally developed by Sharpless et al. (Scheme 1 a).[4,5] However, the reported methods usually use potentially toxic Os species. In addition, regioselectivity with respect to addition of the amino and hydroxyl groups to internal C=C bonds is frequently unsatisfactory. Thus, development of new methodologies for easy-to-use and selective aminohydroxylation of olefin is still highly desirable.



Scheme 1. Catalytic aminohydroxylation of olefins.

In recent years, photoredox catalysis has opened a new field in synthetic organic chemistry.[6] It can smoothly promote single-electron-transfer (SET) processes under mild reaction conditions, i.e., at room temperature and under visible light irradiation, and result in versatile radical reactions through the redox processes. The reactions involving carbon radicals are the center of research. On the other hand, more recently, several examples associated with reaction of N-centered radicals have been reported, but they are still limited.[7] We expect that photoredox catalysis can trigger generation of N-centered radicals from well-designed electrophilic amine sources following 1e reduction and lead to intermolecular aminohydoxylation of olefins through radical amination (Scheme 1 b). Herein we will first describe the development of new shelf-stable and easy-to-use amidyl radical sources derived from commercially available 1-aminopyridinium salt (**1 a**). Then, we report on photoredox-catalyzed regiospecific three-component aminohydroxylation, which is composed of olefin, the amidyl radical source, and H_2O as a novel protocol for synthesis of vicinal aminoalcohol derivatives with a range of functionalities.

First of all, we designed electrophilic amine reagents as precursors for N-centered radicals. Previously, we succeeded in development of photoredox-catalyzed trifluoromethylative difunctionalization of olefin using electrophilic Umemoto's reagent (sulfonium salt) and Togni's reagent (hypervalent iodine species) as CF_3 radical precursors.[8] These results inspired us to extend the protocol to aminative difunctionalization of olefins through N-centered radicals generated from the corresponding electron-deficient onium reagents. 1-Aminopyridinium salt (**1 a**) is a commercially available chemical, derivatives of which are usually used as building blocks for N-containing heterocycles.[9] Its primary-amine moiety can be modified and tuned through reactions with acid chloride or acid anhydride. In fact, various N-protected 1-aminopyridium salts (**1 b**–**e**)[10] were prepared from **1 a** (Scheme 2) and they turned out to be shelf-stable chemicals. During preparation of the present manuscript, the group of Studer reported similar N-radical precursors, which generate secondary-amidyl or imidyl radicals, and photoredox-catalyzed amidation and imidation of aryl compounds.[7e] On the other hand, we independently developed new N-protected 1-aminopyridium salts (**1 b**–**e**), which generate primary-amidyl radicals, and applied them to photoredox-catalyzed aminohydroxylation of olefins.[11]

With these reagents in hand, we commenced examination of photocatalytic aminohydroxylation of styrene (**2 a**) in the

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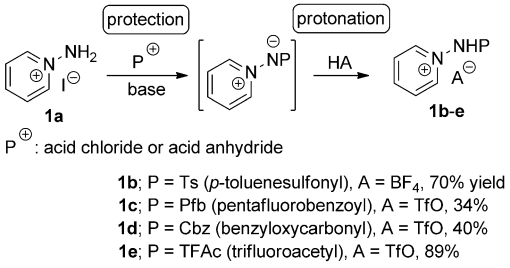
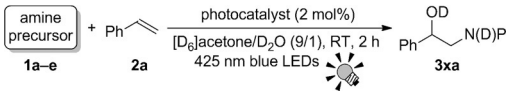
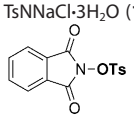


Scheme 2. Synthetic scheme for electrophilic amine reagents (**1b**–**e**).

Table 1. Optimization of the photocatalytic aminohydroxylation of styrene (**2a**).[a]



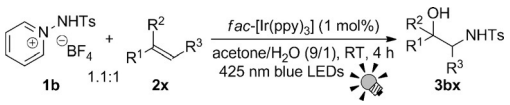
Entry	Amine source	Photocatalyst	Yield of **3xa** [%][b]
1	**1a**	*fac*-[Ir(ppy)$_3$]	0
2	**1b**	*fac*-[Ir(ppy)$_3$]	98
3[c]	**1c**	*fac*-[Ir(ppy)$_3$]	87
4[c]	**1d**	*fac*-[Ir(ppy)$_3$]	44
5[c]	**1e**	*fac*-[Ir(ppy)$_3$]	7
6[c]	TsNNaCl·3H$_2$O (**1f**)	*fac*-[Ir(ppy)$_3$]	0
7[c]	 **1g**	*fac*-[Ir(ppy)$_3$]	23
8	**1b**	[Ru(bpy)$_3$](PF$_6$)$_2$	35
9	**1b**	[Ir(ppy)$_2$(dtbbpy)](PF$_6$)	97
10	**1b**	–	0
11[d]	**1b**	*fac*-[Ir(ppy)$_3$]	0

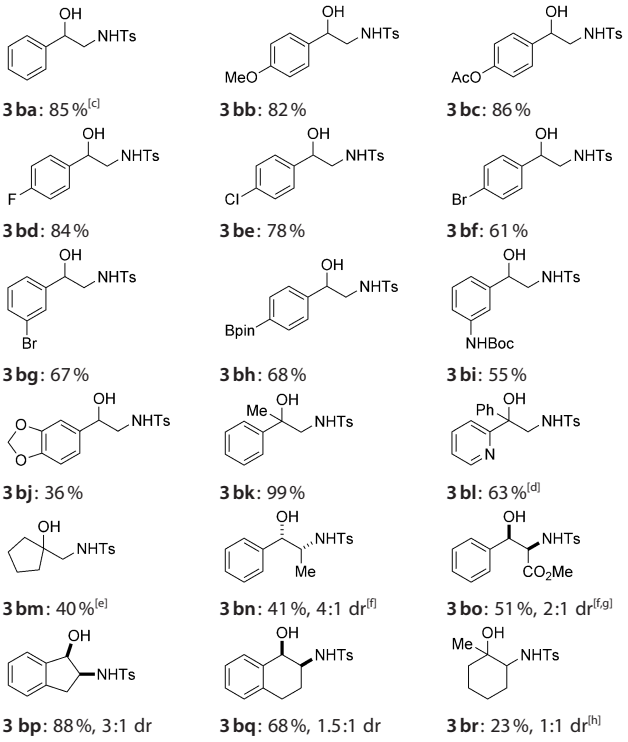
[a] For detailed reaction conditions, see the Supporting Information. [b] Yields were determined by ^{1}H NMR spectroscopy using SiEt$_4$ as an internal standard. [c] Reaction time = 24 h. [d] In the dark. ppy = 2-pyridylphenyl, bpy = 2,2′-bipyridine, dtbbpy = 4,4′-di-tert-butyl-2,2′-bipyridine, LED = light-emitting diode.

presence of 2 mol% of *fac*-[Ir(ppy)$_3$] in a mixed solvent system, [D$_6$]acetone and D$_2$O, under visible light irradiation with 425 nm blue LEDs. It is well-known that the excited species of *fac*-[Ir(ppy)$_3$] serves as a strong reductant ($E_{1/2} = -2.14$ V vs. [Cp$_2$Fe]).[12] Through elaborated exploration of amine sources (entries 1–7 in Table 1), we found *N*-Ts-protected 1-aminopyridinium salt (**1b**; Ts = *p*-toluenesulfonyl) produced 2-(*N*-Ts-amino)-1-phenylethanol (**3ba**) as a single regioisomer in an excellent yield and efficiency (98%, 2 h). Unprotected 1-aminopyridinium salt (**1a**) did not react at all (entry 1, Table 1). *N*-Pfb- (**1c**), -Cbz- (**1d**), and -TFAc- (**1e**) protected reagents were less effective (24 h) and afforded the corresponding products in low yields (**3ca**: 87%, **3da**: 44%, and **3ea**: 7%; entries 3–5, Table 1). It should be noted that classical electrophilic nitrogen sources such as chloramine-T (**1f**) and alkoxyamine derivative (**1g**) did not work well under the present photocatalytic conditions (entries 6 and 7, Table 1). The reaction with chloramine-T (**1f**) gave 1-[(4-methylphenyl)sulfonyl]-2-phenylaziridine in a 38% NMR yield as a product instead of aminoalcohol. The alkoxyamine derivative (**1g**) was less efficient. Furthermore, other photoredox catalysts, [Ru(bpy)$_3$](PF$_6$)$_2$ and [Ir(ppy)$_2$(dtbbpy)](PF$_6$), were also tested. As a result, the Ir catalyst showed high activity similar to *fac*-[Ir(ppy)$_3$], whereas the Ru catalyst turned out to be sluggish (entries 8 and 9, Table 1).[12] Finally, the present reaction did not proceed at all either in darkness or in the absence of a photocatalyst (entries 10 and 11, Table 1). These results indicated that a combination of the Ir photocatalysts, *fac*-[Ir(ppy)$_3$] and [Ir(ppy)$_2$(dtbbpy)](PF$_6$), and *N*-Ts-protected 1-aminopyridinium (**1b**) is essential for the efficient photocatalytic aminohydroxylation.

The scope of the present photocatalytic aminohydroxylation is summarized in Table 2. Styrene (**2a**) and its derivatives bearing OMe (**2b**), OAc (**2c**; Ac = acetyl), F (**2d**), Cl (**2e**), Br (**2f**,**g**), Bpin (**2h**; boronic acid pinacol ester), NHBoc (**2i**; Boc = *tert*-butoxycarbonyl), and methylenedioxy groups (**2j**) on the benzene ring produced the corresponding aminoalcohols (**3ba**–**bj**) in 36–86% yields in a regiospecific manner. Furthermore, the reaction of α-substituted styrenes, α-methylstyrene (**2k**) and α-

Table 2. Scope of the photocatalytic aminohydroxylation.[a,b]

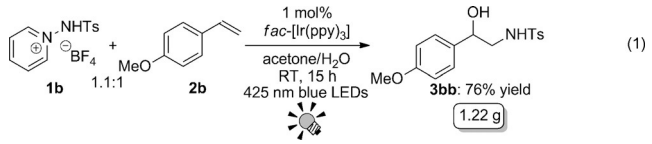




[a] For detailed reaction conditions, see the Supporting Information. Diastereomer ratios (dr) were determined by ^{1}H NMR spectra of crude reaction mixtures. [b] Yields of isolated products. [c] Reaction time = 2 h. [d] Reaction time = 10 h. [e] 1.5 equiv of **1b** with respect to olefin was used. [f] [Ir(ppy)$_2$(dtbbpy)](PF$_6$) (2 mol%) was used and reaction time was 12 h. [g] 1. 8 equiv of **1b** with respect of olefin was used. [h] Reaction time = 8 h.

pyridylstyrene (**2l**), afforded the aminoalcohols bearing tertiary alcohol moieties in good yields (**3bk**: 99%, **3bl**: 63%) exclusively. In addition, an aliphatic alkene, methylene cyclopentane (**2m**), could be also applied to the present photocatalytic system.

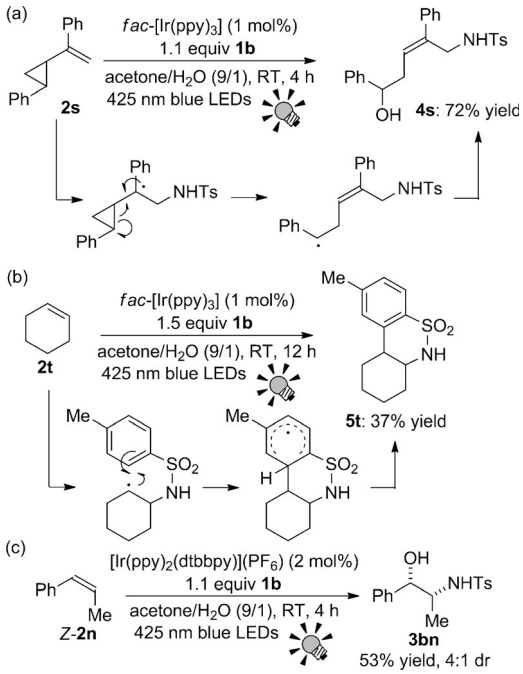
In the case of internal alkenes such as *E*-β-methylstyrene (**2n**), methyl cinnamate (**2o**), indene (**2p**), 1,2-dihydro-naphtharene (**2q**), and 1-methylcyclohexene (**2r**), the reactions also proceeded in a regiospecific manner but the products were obtained as mixtures of two diastereomers, (**3bn**: 41%, 4:1 dr, **3bo**: 51%, 2:1 dr, **3bp**: 88%, 3:1 dr, **3bq**: 68%, 1.5:1 dr,[10] **3br**: 23%, 1:1 dr). It is noteworthy that a variety of functional groups such as halogens (**2d**–**g**), ester (**2c**,**o**), boronic acid pinacol ester (**2h**), *N*-protected amine (**2i**), pyridine (**2l**), and acetal (**2j**) groups were tolerable with the present reaction. Thus, the present aminohydroxylation is a regiospecific reaction for both terminal and internal alkenes regardless of acyclic and cyclic structure.



(1)

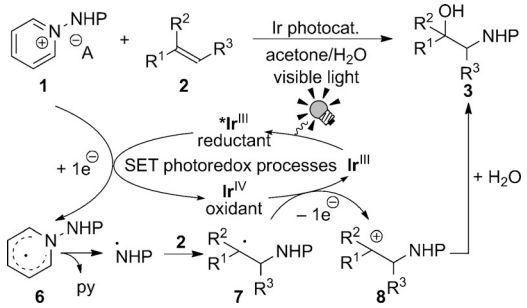
As a demonstration of scalability, aminohydroxylation of 4-methoxystyrene (**2b**) with *N*-Ts-protected 1-aminopyridinium salt (**1b**) was carried out on a gram scale. As a result, the product **3bb** was isolated in a 76% yield (1.22 g) [Eq. (1)].

To gain insight into the reaction mechanism, the photocatalytic reaction of 1-phenyl-2-(1-phenylethenyl)cyclopropane (**2s**) was examined. It turned out that the linear product **4s** was obtained in a 72% isolated yield through a ring-opening process of the cyclopropane ring (Scheme 3a).[10] In addition, the reaction of cyclohexene (**2t**) gave the cyclized product **5t** in a 37% yield.[10] This product is reminiscent of HAS (homolytic aromatic substitution) reaction involving a radical intermediate (Scheme 3b). These results strongly support that radical intermediates are involved in the present reaction. Furthermore, aminohydroxylation of *E*- and *Z*-β-methylstyrene (*E*-**2n** and *Z*-**2n**) afforded the products **3bn** with very similar diastereoselectivities (Table 2 and Scheme 3c), indicating that the present photocatalytic aminohydroxylations proceed via the same intermediate irrespective of the starting *E*- and *Z*-alkenes.



Scheme 3. Control experiments.

On the basis of these observations, as well as electrochemical and photochemical experiments (see the Supporting Information), a plausible reaction mechanism is proposed as shown in Scheme 4. First, the Ir photocatalyst $\mathbf{Ir}^{III}$ is excited by visible light to give the excited species $*\mathbf{Ir}^{III}$, which undergoes SET to aminopyridinium **1** to afford stabilized radical **6** and highly oxidizable Ir species $\mathbf{Ir}^{IV}$. Radical **6** fragments into an amidyl radical and pyridine.[13] The generated amidyl radical reacts with alkene **2** in a regiospecific manner to yield a radical intermediate **7**, which is oxidized by the strongly oxidizing Ir species $\mathbf{Ir}^{IV}$ to afford β-aminocarbocationic intermediate **8** and to regenerate the ground state Ir photocatalyst $\mathbf{Ir}^{III}$. Finally, the carbocationic intermediate **8** is susceptible to nucleophilic attack of H_2O to produce 1,2-aminoalcohol **3**.



Scheme 4. A proposed reaction mechanism.

In conclusion, we have developed a novel and simple strategy for regiospecific synthesis of 1,2-aminoalcohol derivatives by photoredox catalysis. Well-designed N-protected 1-aminopyridinium salts serve both as an electron acceptor and as an efficient amidyl radical precursor by the action of the photoexcited iridium photoredox catalysts, *fac*-[Ir(ppy)$_3$] and [Ir(ppy)$_2$(dtbbpy)](PF$_6$). The present photocatalytic system enables regiospecific intermolecular three-component aminohydroxylation of olefins bearing a wide variety of functionalities through radical processes. Further development of stereoselective aminohydroxylation by photoredox catalysis is currently underway in our laboratory.

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Keywords: amination · carbocations · electron transfer · homogeneous catalysis · photochemistry

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[10] Molecular structures of **1b**, (1*R**,2*S**)-**3bn**, (1*R**,2*S**)-**3bq**, **4s**(*trans*), and **5t** are shown in the Supporting Information. CCDC 1049306, CCDC 1052558, CCDC 1052559, CCDC 1052560 and CCDC 1049305, respectively, contain the supplementary crystallographic data, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data request/cif.

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[12] The photoexcited states of *fac*-[Ir(ppy)$_3$] and [Ir(ppy)$_2$(dtbbpy)]$^+$ are reductants ($E_{1/2} = -2.14$ V and -1.37 V vs. Cp_2Fe) stronger than the Ru photocatalyst, [Ru(bpy)$_3$]$^{2+}$ ($E_{1/2} = -1.22$ V vs. Cp_2Fe), see: a) L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura, F. Barigelletti, *Top. Curr. Chem.* **2007**, *281*, 143 – 203; b) K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, *46*, 159 – 244; c) J. D. Slinker, A. A. Gorodetsky, M. S. Lowry, J. Wang, S. Parker, R. Rohl, S. Bernhard, G. G. Malliaras, *J. Am. Chem. Soc.* **2004**, *126*, 2763 – 2767.

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