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Visible-Light-Induced Direct Oxidative C−H Amidation of Heteroarenes with Sulfonamides**

Kun Tong,[a] Xiaodong Liu,[a] Yan Zhang,*[a] and Shouyun Yu *[a]

Abstract: *A direct oxidative C−H amidation of heteroarenes with sulfonamides via nitrogen-centered radicals has been achieved. Nitrogen-centered radicals are directly generated from oxidative cleavage of N–H bonds under visible-light photoredox catalysis. Sulfonamides, which are easily accessed, are used as tunable nitrogen sources and bleach (aqueous NaClO solution) is used as the oxidant. A variety of heteroarenes, including indoles, pyrroles and benzofurans, can undergo this amidation with high yields (up to 92%). These reactions are highly regioselective, and all the products are isolated as single regioisomer.*

The installation of nitrogen atom into organic molecules has been of intensive research interest in synthetic, material and medicinal chemistry.[1] As important structural fragments, these aminated products often exhibit significant biological properties.[2] The most classic method for C–N bond formation is copper-promoted Ullman coupling of aryl halides with amines.[3] Palladium-catalyzed Buchwald−Hartwig amination/amidation of aryl or vinyl (pseudo)halides with amines (amides) have recently emerged as valuable synthetic tools for C−N bond formation.[4] Copper-catalyzed and ligand-accelerated variations have also been achieved, which are good alternatives for the synthesis of vinyl or aryl amines.[5] However, these procedures usually need elevated temperature, pre-functionalized substrates, e. g. halides or pseudohalides and also provide stoichiometric halide salts as by-products requiring stoichiometric base to facilitate the reaction. The most desirable but challenging C–N bond formation strategy is direct oxidative C–H amination of hydrocarbons with amines.[6] Although some significant contributions have been reported,[7] this attractive strategy still suffers from some disadvantages, including harsh reaction conditions, stoichiometric oxidants, and directing groups. Therefore, the development of efficient and practical direct C−H amination/amidation is still highly desirable and valuable.

Nitrogen-centered radicals (NCRs) has aroused increasing concern in synthetic community.[8] Visible-light-induced C–H amidation of (hetero)arenes via NCRs has emerged as an attractive strategy for C–N bond formation (Figure 1a).[9-12] One of disadvantages of these known methods is that photolabile handles are preinstalled on the precurssors of NCRs, such as hydroxyamine derivatives,[9] acyl azides,[10] *N*-haloamides,[11] and *N*-aminopyridiniums.[12] Nicewicz[13a] and Xia[13b] reported visible-light-induced oxidative C–H amination of (hetero)arenes via arene cation radicals using nonactivated *N*-heterocyles as nucleophiles (Figure 1b). Very recently, Knowles[14] and Xiao[15] reported that direct cleavage of strong N–H bond to generate of NCRs by oxidative proton-coupled electron transfer (PCET) or oxidative deprotonation electron transfer (ODET), which allowed radical cascade reactions for *N*-heterocycle synthesis. Inspired by these work, as well as our research interests on visible-light-mediated NCR chemistry,[16-17] we sought to develop a direct oxidative C–H amidation of (hetero)arenes with nonactivated sulfonamides under photoredox catalysis[18] (Figure 1c).

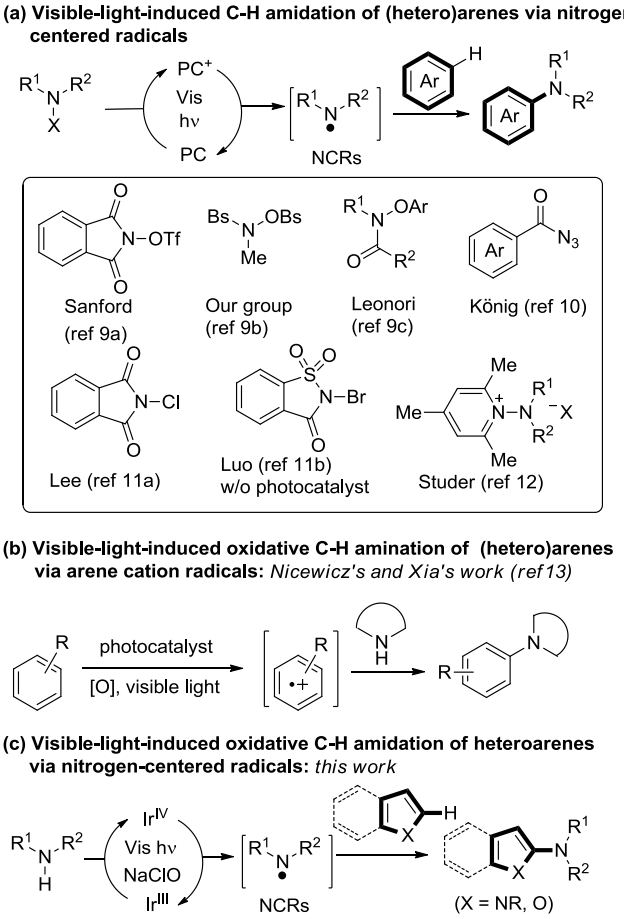

Figure 1. Visible-light-induced C-H amidation of (hetero)arenes.

Our initial efforts toward this goal focused on the use of *N*-methylindole (**1a**) and *N*-methyl-*para*-toluenesulfonamide (**2a**) as coupling partners. The photocatalyst $Ir(ppy)_2(dtbbpy)PF_6$ (**I**) and bleach (aqueous NaClO solution) were chosen as the catalyst and oxidant respectively. When a solution of **1a** and **2a** in CH_3CN was irradiated by white LED strips in the presence of $Ir(ppy)_2(dtbbpy)PF_6$ (**I**) and bleach for 30 min, the desired 2-amidated indole **3a** was isolated in 62% yield as single regioisomer (Table 1, entry 1). Other photocatalysts, such as $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (**II**), *fac*-$Ir(ppy)_3$ (**III**), $Ru(bpy)_3Cl_2$ (**IV**), $Ru(bpy)_3(PF_6)_2$ (**V**), and $Ru(phen)_3(PF_6)_2$ (**VI**), could not give

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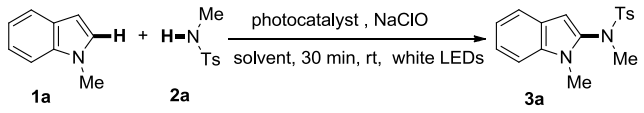
improved results (entries 2−6). A variety of solvents were then tested (entries 7−16). To our delight, a 81% yield was achieved when 1,4-dioxane was used as the solvent (entry 16). Control experiments verified the necessity of irradiation, and photocatalyst (entries 17−18).

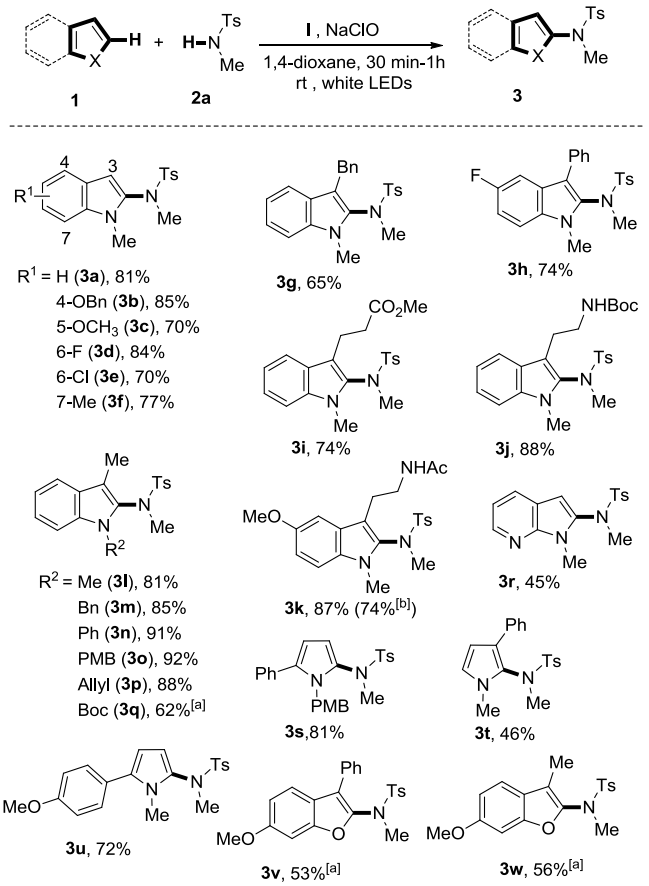
Table 1. Optimization of reaction conditions.[a]



Entry	Photocatalyst	Solvent	Yield (%)[b]
1	**I**	CH_3CN	62
2	**II**	CH_3CN	40
3	**III**	CH_3CN	51
4	**IV**	CH_3CN	51
5	**V**	CH_3CN	54
6	**VI**	CH_3CN	50
7	**I**	MeOH	23
8	**I**	DMF	46
9	**I**	THF	62
10	**I**	DMSO	NR
11	**I**	acetone	NR
12	**I**	*t*-BuOH	57
13	**I**	DCE	38
14	**I**	THP	44
15	**I**	MTBE	41
16	**I**	**1,4-dioxane**	**81**
17	none	1,4-dioxane	trace
18[c]	**I**	1,4-dioxane	trace

[a] Reaction conditions: A solution of **1a** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), NaClO (aq., 0.3 mmol, 3.0 equiv), and photocatalyst (0.002 mmol, 2 mol %) in 1,4-dioxane (2.0 mL) was irradiated with 5 W white LEDs for 30 min. [b] Isolated yield. [c] No irradiation. NR = no reaction.

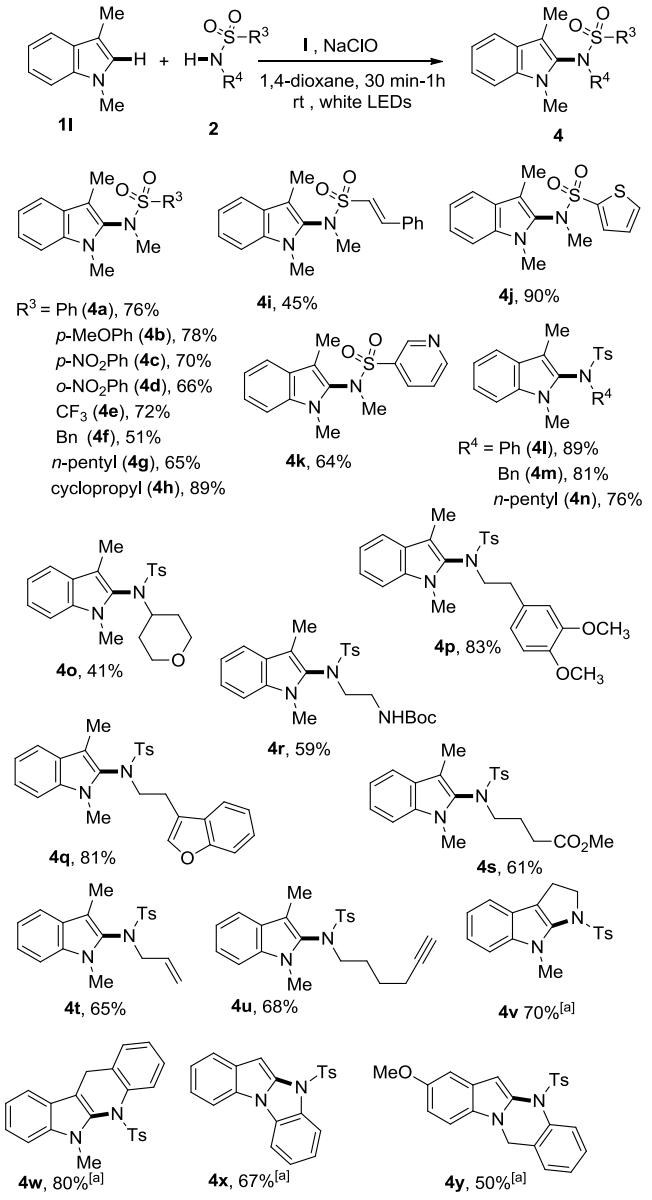
In order to explore the scope of this transformation under the established optimized conditions, a variety of heteroarenes were amidated with *N*-methyl-*p*-toluenesulfonamide (**2a**) (Scheme 1). It was found that indoles bearing various substituents at the C4−C7 positions gave 2-amidated indole derivatives **3a−f** with satisfactory yields (70−85%). C3-substituted indoles could undergo this transformation smoothly. 3-Benzyl and 3-phenyl indole derivatives could give 2-amidated indoles **3g** and **3h** in reanonable yields (65% and 74% respectively). More biologically important indole derivatives, such as indole propanoic acid, tryptamine and melatonin derivatives, could also be amidated under the identical conditions to give the corresponding amidated indoles **3i−k** with 74−88% yields. The substituents at the N1 position were also explored. *N*-Methyl (Me), benzyl (Bn), phenyl (Ph), *para*-methoxyphenyl (PMB), and allyl indoles worked quite well to give the desired products **3l−p** in decent yields (81−92%). *N*-Boc indole could be also amidated with slightly lower yields (62% for **3q**). 7-Azaindole derivative was compatible in this transformation (45% for **3r**). Amidated pyrrole and benzofuran derivatives were also accessible by means of this method to give the corresponding amidated pyrroles **3s−u** and benzofurans **3v−w** with acceptable yields (46−81%). To demonstrate the practicability of this method, we subsequently conducted this intramolecular amidation on a gram scale. When 1.23 g of melatonin-derived indole **1k** was subjected to standard conditions, a comparative isolated yield of amidated melatonin derivative **3k** (74%, 1.59 g) was achieved. It is worth noting that all the amidated products were isolated in single regioisomer.



Scheme 1. C−H amidation of different heteroarenes. Reaction conditions: A solution of **1** (0.1 mmol, 1.0 equiv), **2a** (0.2 mmol, 2.0 equiv), NaClO (aq., 0.3 mmol, 3.0 equiv), and photocatalyst **I** (0.002 mmol, 2 mol %) in 1,4-dioxane (2.0 mL) was irradiated with 5 W white LEDs for 1 h. The yields are for the isolated products. [a] 4.0 equivs of **2a** were used for 4 h. [b] The reaction was run in 5.0 mmol scale.

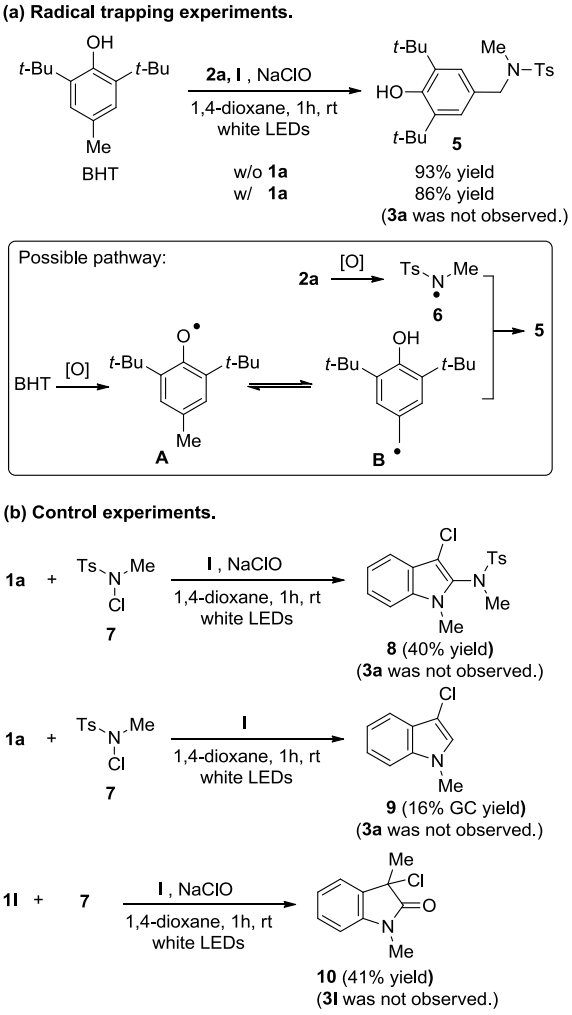
We next sought to establish the scope of the sulfonamide coupling partners with indole **1l** in this reaction (Scheme 2). We were pleased find that these mild photoxidative conditions accommodated a wide range of sulfonamides. Different aromatic sulfonamides can serve as coupling partners to give the corresponding amidated indoles **4a-4d** with 66−78% yields. Aliphatic sulfonamides, such as trifluoromethyl (CF_3), benzyl (Bn), *n*-pentyl, cyclopropyl, and even styryl groups, could also undergo this transformation in 45−89% yields (**4e-4i**). Heterocyclic sulfonyl groups (furan and pyridine) could also give amidation products **4j** (90% yield) and **4k** (64% yield) respectively. *N*-alkyl substituents on sulfonamides were next

explored. *N*-phenyl, *N*-benzyl and *N*-pentyl sulfonamides worked quite well to give the desired products **4l-4n** in decent yields (76-89% yields). Functionalized *N*-alkyl groups, such as ether, carbomate, phenol ether, benzofuran, ester, olefin and alkyne, were also worked well to furnish the amidation products **4n-4u** in 41-83% yields. Moreover, several heterocycle-fused 2-amidated indole derivatives, typified by tetrahydropyrrolo[2,3-*b*]indole **4v**, dihydroindolo[2,3-*b*]quinolines **4w**, enzo-[4,5]imidazo[1,2-*a*]indole **4x**, and dihydroindolo[2,1-*b*]quinazoline **4y**, could been constructed in 50-80% yields by intramolecular C2-amidative cyclization of indoles.



Scheme 2. C−H amidation with different sulfonamides. Reaction condition: A solution of **1l** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv), NaClO (aq., 0.3 mmol, 3.0 equiv), and photocatalyst **I** (0.002 mmol, 2 mol %) in 1,4-dioxane (2.0 mL) was irradiated with 5 W white LEDs for 30min. The yields are for the isolated products. [a] 2.0 equivs of NaClO (0.2 mmol) were used.

To better understand the mechanism of this transforamtion, a series of control reactions were conducted, as shown in Scheme 3. First, NCR **6** could be trapped by 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Scheme 3a). When a mixture of sulfonamide **2a** and BHT was subjected to the standard photoxidative conditions, trapping product **5** was isolated in very good yield no matter that indole **1a** was present or not. Given that benzyl radical **B** can be fromed from oxygen-centered radical **A** through an intramolecular radical transfer,[19] it is envisaged that trapping product **5** was generated by the coupling of NCR **6** with radical **B**. It is known that treatment of sulfonamide **2a** with NaClO can give *N*-chlorosulfonamide **7**,[20] which can served as the precurssor of NCR.[11] A series of control reactions were designed to explore this possibility. As shown in Scheme 3b, when preformed *N*-chlorosulfonamide **7** was subjected to the standard conditions instead of sulfonamide **2a**, no amidation product **3a** was observed. Instead, chloroamidation product **8** was isolated in 40% yield. And chlorination product **9** was obtained in 16% GC yield if NaClO was absent. Furthermore, coupling of indole **1l** with *N*-chlorosulfonamide **7** under the standard photooxidative



Scheme 3. Mechanism Studies. The yields are for the isolated products.

conditions gave oxidative chlorination product **10** in 41% yield. No amidation product **3l** was observed. These phenomena suggest that *N*-centred radical **6** is not generated from *N*-chlorosulfonamide **7**.

In order to determine the quencher of the excited photocatalyst, the fluorescence quenching [1]experiments and Stern-Volmer analysis were performed (Figure 2a). It was observed that the fluorescence intensity of $Ir(ppy)_2(dtbbpy)PF_6$ (**I**) decreased with increasing concentration of NaClO (Figure 2a) while the fluorescence intensity kept unchanged with increasing concentration of **2a** (Figure 2b). A linear relationship between I_0/I and the concentration of NaClO was observed at low concentrations (I_0 and I are the fluorescence intensities before and after the addition of NaClO, Figure 2d). These results strongly suggest that the photoexcited catalyst **I** was quenched by NaClO.

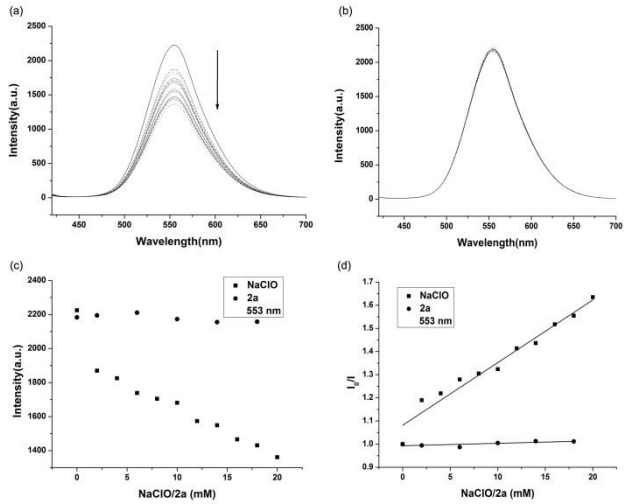


Figure 2. (a) Emission spectra of 5×10^{-5} M $Ir(ppy)_2(dtbbpy)PF_6$ at λ_{ex} = 400 nm showing the quenching effect of increasing of NaClO. (b) Emission spectra of 5×10^{-5} M $Ir(ppy)_2(dtbbpy)PF_6$ at λ_{ex} = 400 nm showing the quenching effect of increasing of **2a**. (c) The maximum emission wavelength (λ_{em}) for $Ir(ppy)_2(dtbbpy)PF_6$ was about 553 nm. (d) The linear relationship over the increasing concentration of NaClO and **2a**.

Based on these observations, a possible mechanism for this transformation is proposed. As shown in Figure 3, the photocatalyst $Ir(ppy)_2(dtbbpy)PF_6$ (**I**) is excited by visible light to generate excited photocatalyst $Ir(ppy)_2(dtbbpy)PF_6$*. It is then oxidatively quenched by NaClO to give $Ir(ppy)_2(dtbbpy)PF_6^+$. *N*-methyl-*p*-toluenesulfonamide (**2a**) was oxidized by $Ir(ppy)_2(dtbbpy)PF_6^+$ with the assistance of base to give NCR **6**[14-15] and regenerate $Ir(ppy)_2(dtbbpy)PF_6$. Radical **6** adds onto *N*-methylindole **1a** to afford intermediate **11**, which is oxidized, most likely by NaClO，to form cation intermediate **12**. Ultimately, 2-amidated indole **3a** is produced after deprotonation.

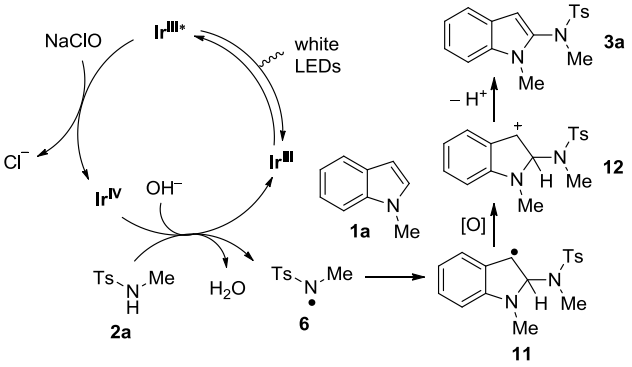


Figure 3. Proposed reaction mechanism.

In summary, we have reported a visible-light-promoted direct oxidative C−H amidation of heteroarenes. Nitrogen-centered radicals directly generated from sulfonamides were proved to be the key intermediates. All reactions proceeded at room temperature under visible light irradiation. Bleach (aqueous NaClO solution), which is clean and economic, was used as the solely oxidant. A series of heteroarenes, including indoles, pyrroles, and benzofurans, could undergo this amidation with high yields (up to 92%). All the amidated products were isolated in single regioisomer. Further explorations on the chemistry of nitrogen-centered radicals are underway in our laboratory.

Keywords: photochemistry • visible light • C–H amidation • nitrogen-centered radical • heterocycle

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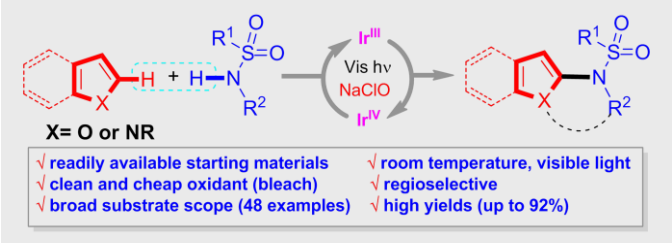

A direct oxidative C−H amidation of heteroarenes with sulfonamdes via nitrogen-centered radical under photoredox catalysis has been achieved.

*Kun Tong, Xiaodong Liu, Yan Zhang * and Shouyun Yu **

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Visible-Light-Induced Direct Oxidative C−H Amidation of Heteroarenes with Sulfonamides