Nd@g-C3N4 Dual-Functional Photocatalysis Enabled Fluoroalkylative Heteroarylation of Alkenes with RfSO2Cl as Both the Fuoroalkyl Radical and Chloride Radical Source

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February 13, 2025

Abstract

Semiconductor dual-functional photocatalysis composed of selective organic oxidation and reduction has attracted increasing attention owing to the green and environmental advantages. Herein, the Nd@g-C_3N_4 dual-functional photocatalysis enabled fluoroalkylative heteroarylation of alkenes with R_fSO_2Cl under visible-light and ultrasound conditions was firstly reported. The photogenerated electron-driven reductive production of fluoroalkyl radical paired with photogenerated hole-driven oxidative production of chloride radical resulted in the full utilization of photogenerated carrier for bond formation. The use of sono-photocatalysis enhances both energy efficiency and the rate of chemical reactions. A wide range of *N*-heteroarenes, alkenes and R_fSO_2Cl, were well compatible for this reaction to access valuable fluoroalkylated *N*-heteroarenes with diverse structural features. We anticipate that this report will provide a sustainable synthetic protocol for fluoroalkylated *N*-heteroarenes but also develop the photoinduced chloride radical-mediated reaction and the dual-functional photocatalysis.

Cite this paper: *Chin. J. Chem.* **2022** ,*40* , XXX—XXX. **DOI: 10.1002/cjoc.202200XXX**

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Comprehensive Summary

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Keywords

Dual-functional photocatalysis | Dual role | Quinoxalin-2(1*H*)-one | Fluoroalkylation | Fluoroalkyl sulfonyl chloride

Background and Originality Content Heterogeneous photocatalysis with recyclable semiconductor photocatalyst is identified as an ideal organic synthetic method, which utilizes visible light to promote carbon-carbon/heteroatom bond formation under environmentally friendly and mild conditions.[1]However, sacrificial electron donor/acceptor reagents are widely applied for increasing the photogenerated carrier separation and migration efficiency by driving redox half reactions, resulting in rising environmental and economic cost as well as wasting the redox capacity of photogenerated carrier. The dual-functional photocatalysis composed of organic oxidation and reduction is considered as one of the most promising solutions to the limitation, because it can take full advantage of both photogenerated holes and electrons for producing value-added products.[2]Visible-light photoredox-catalyzed chloride radical (Cl.)-mediated reaction has contributed significantly to the synthesis of value-added compounds during the past decades.[3] Although much progress has been made, most of these reactions rely on the usage of exogenous HCl/chloride salts as the Cl. source, which compromises the atom economy and increases the production cost. Fluoroalkyl sulfonyl chloride ($\mathrm{R_fSO_2Cl}$) is a low cost and readily available fluoroalkylation reagent that has been widely used as the $\mathrm{R_f}$ radical source for the visible-light photoinduced fluoroalkylation reaction.[4] In 2015, Zhang and Liu developed the UV-light photocatalyzed Cl.-mediated trifluoromethylation with $\mathrm{CF_3SO_2Cl}$ as both the $\mathrm{CF_3}$ radical and Cl. source via the homolysis of $\mathrm{CF_3SO_2Cl}$ under alkaline condition.[5] However, the use of harmful UV radiation (300 W Xe arclamp) restricts its practical application. The visible-light photo-oxidation of Cl anion into Cl. via single electron transfer (SET) is generally challenging, because the oxidation potential of Cl- is much higher ($\mathrm{E_{ox}}$(Cl-/Cl.) = + 2.03 V vs. SCE in MeCN)[6] than the excited-state oxidation potentials of commonly used homogeneous photocatalysts.[7] To the best of our knowledge, visible-light photocatalyzed Cl.-mediated fluoroalkylation reaction with $\mathrm{R_fSO_2Cl}$ as both the $\mathrm{CF_3}$ radical and Cl. source remain elusive. Recently, our group developed the Ce@g-$\mathrm{C_3N_4}$ dual-functional photocatalysis of cooperative Cl.-mediated alkylation of *N* -heteroarenes and hydrogen evolution with ^{n} $\mathrm{Bu_4NCl}$ as the Cl. source.[8] Inspired by this work, we anticipate that semiconductor dual-functional photocatalysis can enable Cl-mediated fluoroalkylation with $\mathrm{R_fSO_2Cl}$ as both the $\mathrm{CF_3}$. and Cl. source. Fluoroalkylated *N* -heterocycles are important*N* -heterocyclic derivatives encountered in numerous biologically active molecules, pharmaceuticals and organic materials.[9] Recently, the visible-light induced fluoroalkylative heteroarylation of alkenes with various fluoroalkylation reagents has emerged as a powerful tool for the homogeneous synthesis of fluoroalkylated*N* -heterocycles.[10] In 2023, Dolbier Jr reported the visible-light induced $\mathrm{Ru(bpy)_3Cl_2{\cdot}6H_2O}$-photocatalyzed fluoroalkylative heteroarylation of alkenes and $\mathrm{R_fSO_2Cl}$ with $\mathrm{K_2HPO_4}$ as the base additive (Scheme 1a).[11] Despite this success, the use of non-recyclable ruthenium-based photocatalyst and stoichiometric amounts of base additive eroded their overall appeal.**Scheme 1** Visible-light Photoredox-Catalyzed Fluoroalkylative Heteroarylation of Alkenes with $\mathrm{R_fSO_2Cl}$ Sono-photocatalysis, which is characterized by the merits of combination of ultrasonic catalysis and photocatalysis, shows interesting advantages at the kinetic level and energy consumption. [12]However, sono-photocatalysis enabled organic bond formation reaction is extremely rare in the literature.[13] With our ongoing studies on photocatalysis,[14] herein, we wish to report the Nd@g-$\mathrm{C_3N_4}$ dual-functional photocatalysis enabled fluoroalkylative heteroarylation of alkenes with $\mathrm{R_fSO_2Cl}$ under visible light (or sunlight) and ultrasound irradiation conditions (Scheme 1b). $\mathrm{R_fSO_2Cl}$ acted as both the fuoroalkyl radical and Cl radical source, thus avoiding the usage of exogenous HCl/chloride salts. A broad range of fuoroalkylated*N* -heteroarenes could be obtained in good to excellent yields under base additive-, chemical redox regent- and sacrificial reagent-free conditions. Results and Discussion**Table 1** Optimization of the reaction conditions^{a,b}

Entry
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[a]Conditions: 1a (0.2 mmol), 2a (0.3 mmol), 3a (0.3 mmol), catalyst (5 mg or 5 mol%), EtOH (2 mL), N_2, Blue LED (7 W)

To explore the appropriate reaction conditions, 1-methylquinoxalin-2(1*H*)-one (**1a**), styrene (**2a**) and CF_3SO_2Cl (**3a**) were treated with the association of 7 W blue LED with Nd@g-C_3N_4 as the heterogeneous photocatalyst and 22 kHz/30 W US for 4 h in EtOH under nitrogen atmosphere at room temperature. To our delight, the desired product**4aaa** was generated in 96% GC yield (entry 1). In contrast, the intrinsic g-C_3N_4 produced **4aaa** in 41% GC yield and the single Nd$(NO_3)_3$showed no reactivity in this reaction while no better performance was observed with mixing the g-C_3N_4 and Nd$(NO_3)_3$ physically (entries 2 - 4). These results suggested that the catalytic activity of the composite photocatalyst were tremendously improved by dropping the Nd into intrinsic g-C_3N_4. Replacing Nd with K, Fe, Cu, Zn, Ag or Ce in the composite photocatalyst led to a lower yield (entries 5 - 10). Compared to Nd@g-C_3N_4,yields of 21% -42% were obtained with homogeneous noble metal photocatalysts [(*fac*-**Ir(pp** y)$_3$ and Ru(bpy)$_3$Cl$_2$. 6H$_2$O] and organic photocatalysts (Rhodamine B and 4CzIPN) (entries 11-12). The product **4aaa** was obtained only in 19% yield without photocatalyst (entry 13). Using sunlight instead of blue light led to the formation of **4aaa** in 84% yield (entry 14). Carrying out this reaction with conventional stirring for 24 hours delivered**4aaa** in 85% yield (entry 15). No reaction occurred under the air atmosphere, suggesting that the presence of oxygen molecule suppressed this transformation (entry 16). Performing the template reaction in darkness gave no product (entry 17).

Table 2 Reaction Scope[a, b]

[a] Conditions: **1** (0.2 mmol), **2** (0.3 mmol), **3a** (0.3 mmol), Nd@g-C_3N_4 (5 mg), EtOH (2 mL), N_2, Blue LED (7 W), US (22 kHz/30 W), r.t..[b] Isolated yields.

Having established the optimum reaction conditions, we began to probe the generalizability of this reaction (Table 2). Firstly, quinoxalin-2(1*H*)-ones bearing a series of aliphatic groups at*N* -position such as methyl, ethyl, *n* -pentyl, cyclopropylmethyl, ester, cyano, benzyloxycarbonyl (Cbz), benzyl (Bn),*p* -methoxybenzyl (PMB) reacted efficiently in this system to furnish the target products **4aaa** -**4kaa** in high yields and excellent regioselectivity. Notably, easily oxidizable allyl or propargyl group could survive in the reaction. To our delight, unprotected quinoxalin-2(1*H*)-one was also well tolerated under standard conditions, yielding the product **4laa** in 86%. Next, electron-donating (OMe) or electron-withdrawing groups (F, Cl, Br, CF_3 or NO_2) at the phenyl part of the*substrates* **1** had no effect on the reaction efficiencies and the desired products **4maa** - **4saa** were obtained in good yields. Di-substituted (Me or Cl) quinoxalin-2(1*H*)-ones underwent this transformation well to afford the corresponding products**4taa** and **4uaa** in 90% and 84%, respectively. Pleasingly, a range of *N* -heteroarenes, including 1-methylbenzo[*g*]quinoxalin-2(1*H*)-one, quinoxaline, 1-

methyl-1,2-dihydroquinoxaline, quinazoline were suitable substrates and generated the desired products **4vaa - 4yaa** in moderate to good yields.

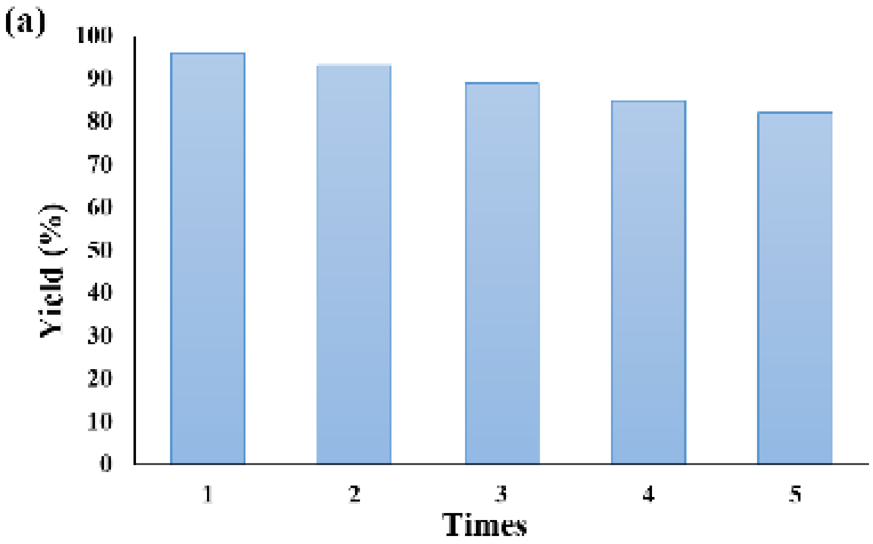
Table 3 Reaction Scope[a, b]

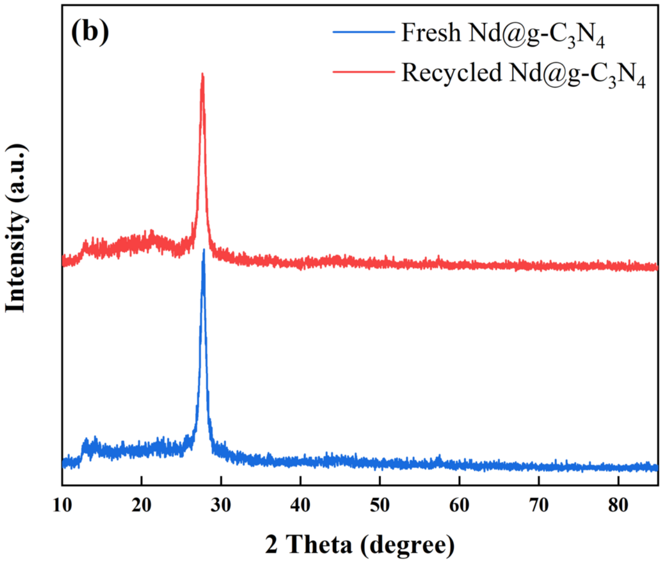
[a] Conditions: **1a** (0.2 mmol), **2** (0.3 mmol), **3** (0.3 mmol), Nd@g-C_3N_4 (5 mg), EtOH (2 mL), N_2, Blue LED (7 W), US (22 kHz/30 W), r.t..[b] Isolated yields.

Next, the substrate scope with respect to alkenes (**2**) was examined (Table 3). The methyl group at C2 or C3-position of styrenes could participate well in this reaction to provide the desired products**4aba** and **4aca** in 85% and 81% isolated yields, respectively. Styrenes modified with electron-neutral (Ph), electron-donating (Me or ^{t} Bu) or electron-withdrawing groups (F, Cl, Br, CF_3, Ac or CN) were well-compatible in the present transformation, affording the target compounds **4ada - 4ala** in good yields. These results indicated that neither steric hindrance nor electronic effect of styrenes significantly influence the reaction efficiency. Moreover, 2-vinylnaphthalene also proceeded smoothly to give the product**4ama** in 88% yield. Subsequently, various aliphatic alkenes were explored. It was gratifying to find that a variety of alkenes, including acyclic terminal ones (3-methylbutene, allylbenzene, ethyl acrylate and 2-phenylpropylene), acyclic internal ones (1-phenylpropylene and ethyl cinnamate) and cyclic ones (cyclohexene and norbornene) could deliver the corresponding products **4ana -4ara** in high yields. Gratifyingly, the reaction with phenylethyne gave product **4ava** in good yield. To further investigate the reaction scope, various fluoroalkylation reagents were investigated. Both CHF_2SO_2Cl and perfluoroalkylsulfonyl chlorides ($C_4F_9SO_2Cl$ and $C_6F_{13}SO_2Cl$) were readily converted into their corresponding products **4aab -4aad** in good yields.

Scheme 3 Large-scale synthesis of **4aaa**

Figure 1 (a) The Reusability of Nd@g-C_3N_4; (b) XRD patterns of fresh Nd@g-C_3N_4 and recycled Nd@g-C_3N_4





To demonstrate the synthetic utility of the present reaction, both the gram-scale synthesis and photocatalyst cycling experiments were performed. As shown in Scheme 3, carrying out the scaled-up template reaction (5 mmol) gave **4aaa** in 83% yield (1.37 g). To our delight, reducing almost quarter of the loading of Nd@g-C_3N_4 also led to a good yield of**4aaa** (Scheme 3). Afterwards, photocatalyst recycling experiments were conducted in five consecutive reaction-separation processes in which Nd@g-C_3N_4 could be easily recovered from and reused for next use only via centrifugation without an obvious loss of catalytic activity (Figure 1a). The nearly indistinguishable X-ray diffraction suggested that the basic structure of the recovered photocatalysts remained unchanged before and after experiments (Figure 1b).

Scheme 4 Control experiments.

To elucidate reaction mechanism of the dual-functional photocatalytic reaction, a series of mechanistic studies were conducted. First, this photochemical reaction was markedly inhibited in the presence of radical scavenger (TEMPO and 1,1-diphenylethylene), and TEMPO-CF_3 adduct **5aa** , diphenylethene-CF_3 **5ab** and diphenylethene-Cl**5ac** adduct were detected by GC-MS (Scheme 3a-b), demonstrating that both the CF_3 radical and Cl radical intermediates might be involved in the catalytic cycle. With photogenerated hole scavenger Na_2S or photogenerated electron scavenger CCl_4 as the additive, the heterogeneous bond formation was entirely suppressed, indicating that both h^+ and e^-were necessary for this photocatalytic process (Scheme 3c-d). The addition of SET inhibitor $CuCl_2$ to the reaction mixture did not result in any reaction, suggesting a SET process was involved in this transformation (Scheme 3e). The turn-on/off blue-light experimental results suggested that the continuous light irradiation is indispensable for the reaction to proceed. This observation and the quantum yield ($\Phi = 6.08\%$, see the ESI+ for details) of this transformation ruled out the possibility of a radical chain process.

Scheme 4 Proposed reaction mechanism

A plausible reaction mechanism was proposed based on the above-mentioned experimental results and relevant reports[5, 10g, 11, 15] (Scheme 4). First, the irradiation of Nd@g-C_3N_4 by blue LED generates e- in the conduction band (CB) and h^+ in the valence band (VB). The special shell structure of Nd^{3+} with unfilled 4f electron orbitals can trap e- to form the reduction state Nd^{2+}, which then reduces R_fSO_2Cl into R_f radical via a heterogeneous SET along with the extrusion of Cl- and SO_2. Subsequently, the R_f radical can be trapped by the anti-Markovnikov addition of alkene **2** to produce the alkyl radical **IM1** , which attacked the C=N bond of quinoxalin-2(1*H*)-one **1** to yield the N-center radical**IM2** , followed by a 1,2-H shift process to provide the C-center radical **IM3** . A heterogeneous SET process from the dissociative Cl- to h^+ give the Cl., which then abstracts a hydrogen atom from **IM3** to deliver the target product**4** .

Conclusions

In conclusion, we for the first time demonstrated the Nd@g-C_3N_4 dual-functional photocatalysis enabled fluoroalkylative heteroarylation of alkenes with R_fSO_2Cl under visible-light and ultrasound irradiation conditions. The photogenerated electron-driven reduction of R_fSO_2Cl into fluoroalkyl radical paired with photogenerated hole-driven oxidation chloride anion into chloride radical led to the full utilization of photogenerated carriers for bond formation. The dropping Nd into intrinsic g-C_3N_4 largely improved the photocatalytic performance of Nd@g-C_3N_4. A broad range of *N* -heteroarene, alkenes and R_fSO_2Cl were well compatible for this reaction to access valuable fluoroalkylated *N* -heteroarenes with diverse structural features. R_fSO_2Cl served as both the R_f radical and Cl radical source, thus simplifying this reaction system. The Nd@g-C_3N_4 was also validated in both gram-scale synthesis, sunlight-induced photocatalysis and catalyst cycling experiment. Importantly, this strategy does not require any exogenous Cl anion reagents, chemical redox reagents or sacrificial reagents, which can proceed efficiently under sustainable and mild reaction conditions. We anticipate that this report will provide an efficient and green synthetic protocol for fluoroalkylated*N* -heteroarenes but also develop the photoinduced Cl radical-mediated reaction and the dual-functional photocatalysis.

Experimental

The mixture of 4-amino coumarin **1** (1.0 equiv., 0.2 mmol), N-fluorobenzenesulfonimide (2.0 equiv., 0.40 mmol), and H_2O (5.0 equiv., 1.0 mmol, about 1 drop) in dimethyl carbonate (2.0 mL) was open to the air and stirred at room temperature under the irradiation of 10 W LED (455 nm) for about 12 h. After completion of the reaction, the resulting mixture was extracted with CH_2Cl_2 (5 mL × 3) and the organic phase was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA = 6/1-3/1) to give the desired α,α-difluoro-β-ketoamide products **3** .

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2021xxxxx.

Acknowledgement

We are grateful for financial support from University of South China and Postgraduate Scientific Research Innovation Project of Hunan Province (No. CX20230949).

References

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1) (a) Savateev, A.; Antonietti, M. Heterogeneous Organocatalysis for Photoredox Chemistry. *ACS Catal.* **2018** , *8* , 9790-9808; (b) Verma, S. K.; Verma, R.; Girish, Y. R.; Xue, F.; Yan, L.; Verma, S.; Singh, M.; Vaishnav, Y.; Shaik, A. B.; Bhandare, R. R.; Rakesh, K. P.; Sharath Kumar, K. S.; Rangappa, K. S. Heterogeneous graphitic carbon nitrides in visible-light-initiated organic transformations. *Green Chem.* **2022** , *24* , 438-479; (c) Hou, J.-C.; Cai, W.; Ji, H.-T.; Ou, L.-J.; He, W.-M. Recent advances in semi-heterogenous photocatalysis in organic synthesis. *Chin. Chem. Lett.* **2025** , *36* , 110469; (d) Ruban, S. M.; Ramadass, K.; Singh, G.; Talapaneni, S. N.; Kamalakar, G.; Gadipelly, C. R.; Mannepalli, L. K.; Sugi, Y.; Vinu, A. Organocatalysis with carbon nitrides. *Sci. Technol. Adv. Mat.* **2023** , *24* , 2188879.(2) (a) Kampouri, S.; Stylianou, K. C. Dual-Functional Photocatalysis for Simultaneous Hydrogen Production and Oxidation of Organic Substances. *ACS Catal.* **2019** , *9* , 4247-4270; (b) Shang, W.; Li, Y.; Huang, H.; Lai, F.; Roeffaers, M. B. J.; Weng, B. Synergistic Redox Reaction for Value-Added Organic Transformation via Dual-Functional Photocatalytic Systems. *ACS Catal.* **2021** , *11* , 4613-4632.(3) (a) Bonciolini, S.; Noël, T.; Capaldo, L.

Synthetic Applications of Photocatalyzed Halogen-Radical Mediated Hydrogen Atom Transfer for C-H Bond Functionalization. *Eur. J. Org. Chem.* **2022** , *2022* , e202200417; (b) Itabashi, Y.; Asahara, H.; Ohkubo, K. Chlorine-radical-mediated C–H oxygenation reaction under light irradiation. *Chem. Commun.* **2023** , *59* , 7506-7517; (c) Sadeghi, M. C(sp3)-H Functionalization Using Chlorine Radicals.*Adv. Synth. Catal.* **2024** , *366* , 2898-2918; (d) Yuan, X.-Y.; Wang, C.-C.; Yu, B. Recent advances in FeCl$_3$-photocatalyzed organic reactions via hydrogen-atom transfer. *Chin. Chem. Lett.* **2024** , *35* , 109517.(4) (a) Xiao, H.; Zhang, Z.; Fang, Y.; Zhu, L.; Li, C. Radical trifluoromethylation. *Chem. Soc. Rev.* **2021** , *50* , 6308-6319; (b) Shaw, R.; Sihag, N.; Bhartiya, H.; Yadav, M. R. Harnessing photocatalytic and electrochemical approaches for C–H bond trifluoromethylation and fluoroalkylation. *Org. Chem. Front.* **2024** , *11* , 954-1014; (c) Liu, J.; Cui, Z.; Bi, J.; He, X.; Ding, Q.; Zhu, H.; Ma, C. Photocatalytic fluoroalkylation by ligand-to-metal charge transfer. *Front. Chem.* **2024** ,*12* , 1481342.(5) Tang, X.; Song, S.; Liu, C.; Zhu, R.; Zhang, B. Light triggered addition/annulation of 2-isocyanobiphenyls toward 6-trifluoromethyl-phenanthridines under photocatalyst-free conditions.*RSC Adv.* **2015** , *5* , 76363-76367.(6) Isse, A. A.; Lin, C. Y.; Coote, M. L.; Gennaro, A. Estimation of Standard Reduction Potentials of Halogen Atoms and Alkyl Halides. *J. Phys. Chem. B* **2011** , *115* , 678-684.(7) Shields, B. J.; Doyle, A. G. Direct C(sp$_3$)-H Cross Coupling Enabled by Catalytic Generation of Chlorine Radicals. *J. Am. Chem. Soc.* **2016** ,*138* , 12719-12722.(8) Ji, H.-T.; Tang, Y.-Q.; Wang, Y.-H.; Wang, J.-S.; Xu, Y.-D.; Zeng, Y.-Y.; Li, T.; Gong, S.-F.; He, W.-M. Dual Ce@g-C$_3$N$_4$-Photoredox/Chlorine Catalysis: Cross-Dehydrogenative Coupling of N-Heteroarenes and Alkanes/Ethers with H$_2$ Evolution. *Org. Lett.* **2024** ,*26* , 9822-9827.(9) (a) Johnson, B. M.; Shu, Y.-Z.; Zhuo, X.; Meanwell, N. A. Metabolic and Pharmaceutical Aspects of Fluorinated Compounds. *J. Med. Chem.* **2020** , *63* , 6315-6386; (b) He, J.; Li, Z.; Dhawan, G.; Zhang, W.; Sorochinsky, A. E.; Butler, G.; Soloshonok, V. A.; Han, J. Fluorine-containing drugs approved by the FDA in 2021. *Chin. Chem. Lett.* **2023** , *34* , 107578; (c) Wang, C.-Q.; Feng, C. Applications of Nucleophilic Fluorine Sources in the Selective Fluorofunctionalization of Unsaturated Carbon-Carbon Bonds. *Acat Chim. Sinica* **2024** , *82* , 160-170; (d) Henary, E.; Casa, S.; Dost, T. L.; Sloop, J. C.; Henary, M. The Role of Small Molecules Containing Fluorine Atoms in Medicine and Imaging Applications. *Pharmaceuticals* **2024** , *17* , 281.(10) (a) Zheng, D.; Studer, A. Photoinitiated Three-Component α-Perfluoroalkyl-β-heteroarylation of Unactivated Alkenes via Electron Catalysis. *Org. Lett.* **2019** , *21* , 325-329; (b) Meng, N.; Wang, L.; Liu, Q.; Li, Q.; Lv, Y.; Yue, H.; Wang, X.; Wei, W. Metal-Free Trifluoroalkylation of Quinoxalin-2(1H)-ones with Unactivated Alkenes and Langlois' Reagent. *J. Org. Chem.* **2020** ,*85* , 6888-6896; (c) Shao, Z.; Zhang, S.; Chen, Y.; Liu, Y.-L.; Tang, R.-Y.; Li, Z. Transition-metal-free, three-component trifluoromethylative heteroarylation of unactivated alkenes: Efficient access to β-trifluoromethylated quinoxalinones and preliminary antifungal evaluation against Magnaporthe grisea. *Tetrahedron* **2020** , *76* , 131199; (d) Meng, N.; Lv, Y.; Liu, Q.; Liu, R.; Zhao, X.; Wei, W. Visible-light-induced three-component reaction of quinoxalin-2(1*H*)-ones, alkenes and CF$_3$SO$_2$Na leading to 3-trifluoroalkylated quinoxalin-2(1*H*)-ones. *Chin. Chem. Lett.* **2021** ,*32* , 258-262; (e) Yang, X.; Meng, W.-D.; Xu, X.-H.; Huang, Y. Photoredox-catalyzed 2,2,2-trifluoroethylation and 2,2-difluoroethylation of alkenes with concomitant introduction of a quinoxalin-2(1H)-one moiety. *Org. Chem. Front.* **2021** ,*8* , 6597-6602; (f) Wang, H.; Li, S.; Cui, Y.; Liu, M.; Bu, X.; Tian, H.; Yang, X. A covalent organic framework-catalyzed visible-light-induced three-component cascade synthesis of trifluoroalkyl and trifluoroalkenyl quinoxalin-2(1H)-one derivatives.*New J. Chem.* **2022** , *46* , 20412-20418; (g) Zhou, N.; Liu, R.; Zhang, C.; Wang, K.; Feng, J.; Zhao, X.; Lu, K. Photoinduced Three-Component Difluoroalkylation of Quinoxalinones with Alkenes via Difluoroiodane(III) Reagents. *Org. Lett.* **2022** ,*24* , 3576-3581; (h) Shen, L.; Yuan, J.-W.; Zhang, B.; Song, S.-Y.; Yang, L.-R.; Xiao, Y.-M.; Zhang, S.-R.; Qu, L.-B. Photoredox-catalyzed three-component difluorobenzylation of quinoxalin-2(1H)-ones with unactivated vinylarenes and BrCF2CO2Et/HCF2CO2H. *Z. Naturforsch. B.* **2023** , *78* , 245-260; (i) Wang, W.; Zhu, T.; Wu, J. Direct C(sp2)–H fluoroalkylation of quinoxalin-2(1H)-ones with (fluoroalkyl)triphenylphosphonium salts and alkenes. *Org. Chem. Front.* **2023** , *10* , 5375-5382.(11) Li, X.; Dolbier Jr, W. R. Visible-Light-Induced Three-Component Tetrafluoroethyl-heteroarylation of Alkenes with 1,1,2,2-Tetrafluoroethanesulfonyl Chloride and Quinoxalin-2(1H)-ones.*Chem - Eur. J.* **2023** , *29* , e202301814.(12) (a) Joseph, C. G.; Li Puma, G.; Bono, A.; Krishnaiah, D. Sonophotocatalysis in advanced oxidation process: A short review. *Ultrason. Sonochem.* **2009** , *16* , 583-589; (b) Ahmed, M. A.; Mohamed, A. A. Advances in ultrasound-assisted synthesis of photocatalysts and sonophotocatalytic processes: A review. *iScience* **2024** ,*27* , 108583; (c) Paustian, D.; Franke, M.; Stelter, M.; Braeutigam, P. Sonophotocatalysis-Limits and Possibilities for Synergistic Effects. *Catalysts* **2022** , *12* , 754.(13) Ouyang, W.-T.; Jiang, J.; Jiang, Y.-F.; Li, T.; Liu, Y.-Y.; Ji, H.-T.; Ou, L.-J.; He, W.-M. Sono-photocatalytic amination of quinoxalin-2(1*H*)-ones with aliphatic amines. *Chin. Chem. Lett.* **2024** , *35* , 110038.(14) (a) Lu, Y.-H.; Wu, C.; Hou, J.-C.; Wu, Z.-L.; Zhou, M.-H.; Huang, X.-J.; He, W.-M. Ferrocene-Mediated Photocatalytic Annulation of *N* -Sulfonyl Ketimines on a Polycrystalline WSe$_2$ Semiconductor Photocatalyst. *ACS Catal.* **2023** , *13* , 13071-13076; (b) Ji, H.-T.; Peng, Q.-H.; Wang, J.-S.; Lu, Y.-H.; Dai, H.; Luo, Q.-X.; He, W.-M. Decatungstate-photocatalyzed tandem acylation/cyclization/self-hydrogenation of isocyanides with aldehydes to hydroxyalkylated N-heteroarenes via multiple hydrogen atom transfer.*Green Chem.* **2024** , *26* , 12084-12089; (c) Xin, C.; Jiang, J.; Deng, Z.-W.; Ou, L.-J.; He, W.-M. Photoinduced FeCl$_3$-catalyzed Cross-Dehydrogenative Alkylation of Benzoxazin-2-ones with Alkanes. *Acat Chim. Sinica* **2024** ,*82* , 1109-1113; (d) Huang, X.-J.; Ji, H.-T.; Li, X.; Luo, Q.-X.; Li, T.; Ou, L.-J.; He, W.-M. NPh$_3$-Mediated WO$_3$-Photocatalyzed Semiheterogeneous Hydroxylation of Aryl and Alkyl Boronic Acids. *J. Org. Chem.* **2024** ,*89* , 10654-10659; (e) Ji, H.-T.; Lu, Y.-H.; Liu, Y.-T.; Huang, Y.-L.; Tian, J.-F.; Liu, F.; Zeng, Y.-Y.; Yang, H.-Y.; Zhang, Y.-H.; He, W.-M. Nd@C$_3$N$_4$-photoredox/chlorine dual catalyzed synthesis and evaluation of antitumor activities of 4-alkylated sulfonyl ketimines. *Chin. Chem. Lett.* **2025** ,*36* , 110568.(15) (a) Muralirajan, K.; Kancherla, R.; Bau, J. A.; Taksande, M. R.; Qureshi, M.; Takanabe, K.; Rueping, M. Exploring the Structure and Performance of Cd–Chalcogenide Photocatalysts in Selective Trifluoromethylation. *ACS Catal.* **2021** ,*11* , 14772-14780; (b) Liu, Q.-H.; Kang, S.-L.; Cui, Z.-S.; Liu, Y.-H.; Zhang, M.; Zhang, Z.-H. Visible light-driven C–H arylation of heteroarenes with aryl diazonium salts in water catalyzed by a Z-scheme CuInS2/K-C3N4 heterojunction. *Green Chem.* **2024** ,*26* , 4803-4810.

(The following will be filled in by the editorial staff)
Manuscript received: XXXX, 2022 Manuscript revised: XXXX, 2022 Manuscript accepted: XXXX, 2022 Accepted manuscr

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Nd@g-C$_3$N$_4$ Dual-Functional Photocatalysis Enabled Fluoroalkylative Heteroarylation of Alkenes with R$_\mathrm{f}$S