

Photocatalytic Decarboxylative Minisci Reaction Catalyzed by Palladium-Loaded Gallium Nitride

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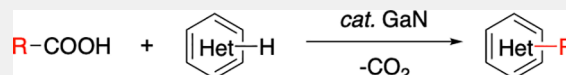
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ABSTRACT: The decarboxylative Minisci reaction is a versatile tool for the direct C–H alkylation of heteroarenes, where stoichiometric amounts of oxidants or expensive, precious metal reagents are commonly used. Herein, we reported a photodriven decarboxylative Minisci reaction enabled by a gallium nitride-based heterogeneous photocatalyst under mild conditions. This method can be effectively applied to a broad substrate scope of acids, including primary, secondary, and tertiary carboxylic acids and *N*-heteroarenes effectively. The practicability and robustness of the approach are demonstrated for the functionalization of biologically active compounds.

KEYWORDS: *Heterogeneous catalysis, Minisci reaction, Photocatalytic decarboxylation, N-heteroarenes, C–H alkylation, Gallium nitride*



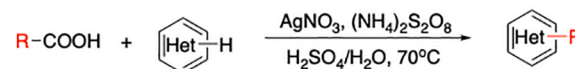
- ✓ Heterogeneous catalysis
- ✓ Photocatalytic decarboxylation
- ✓ Broad substrate scope
- ✓ Gram-scale synthesis

INTRODUCTION

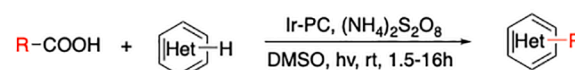
The pursuit of direct C–H alkylation of *N*-heteroarenes under mild conditions has gained much attention owing to the ubiquitous presence of *N*-heteroaryl motifs in functional materials, pharmaceuticals, and biological systems.^{1–3} For this endeavor, the Minisci-type reaction serves as a useful synthetic tool for heteroarene functionalization, which involves the alkyl radical addition to the protonated heteroarene under oxidative conditions.^{4,5} Compared with the common alkyl radical precursors like alkyl peroxides, alkyl halides, boronic acids, and sulfonates, the usage of aliphatic carboxylic acid stands out due to its ease of storage, low cost, natural abundance, and easy accessibility.^{6,7} Previously, some examples of direct C–H alkylation of *N*-heteroarenes using aliphatic carboxylic acid were reported with metal catalysts like silver, copper, or iron catalysts with persulfate additive or radical initiators such as *tert*-butyl peroxide under high temperatures (Scheme 1a).^{8–13} While effective, the harsh reaction conditions usually compromised synthetic application. Recently, photoredox catalysis has opened new opportunities in synthetic organic chemistry for rapid and efficient assembly of complex molecules.^{14–16} Within this domain, the Glorius group in 2017 demonstrated a mild method of direct alkylation of *N*-heteroarenes using an iridium photocatalyst (Ir-PC) and ammonium persulfate under blue LEDs (Scheme 1b).¹⁷ In 2020, Xu's group reported a novel electro-photocatalytic decarboxylative C–H functionalization of heteroarenes using cerium salts (Scheme 1c).¹⁸ Both strategies possess high functional group tolerance as well as a broad substrate scope due to their milder reaction conditions. Installing an activation group like *N*-(acyloxy)-phthalimide on carboxylic acid is another effective strategy of the decarboxylative Minisci

Scheme 1. Methods for Decarboxylative Minisci C–H Alkylation of *N*-Heteroarenes

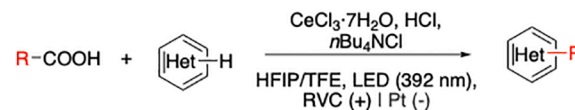
a. Perchinnmo's work



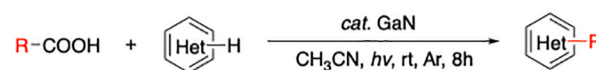
b. Glorius's work



c. Xu's work



d. This work

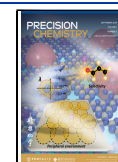


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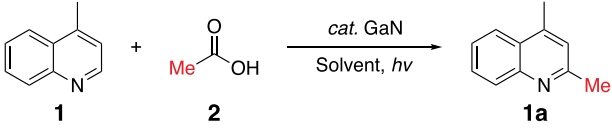
reaction combined with photoredox and Brønsted catalysis, achieving a broad range of substrates and enantioselective alkylation of *N*-heterocycles.^{19–21} Despite current advancements, the use of iridium or cerium catalysts leaves room for improvement as they are either expensive or hazardous and difficult to isolate or reuse in the eyes of overall reaction sustainability. Furthermore, the involvement of hazardous solvents like DMSO or HFIP also raises additional environmental concerns. Therefore, to fully utilize the potential of the photodriven decarboxylative Minisci reaction as well as to develop greener reaction protocols, it is highly desirable to promote an affordable and reusable photocatalyst with high energy efficiency and recyclability.

In particular, the advancement of semiconductors as photocatalysts has provided some of the most promising alternative strategies for addressing the environmental and energy issues while maintaining high catalytic performance with the harness of solar energy.^{22,23} Under light irradiation, the photogenerated electrons will travel from the valence band (VB) to the conduction band (CB) while generating an equivalent number of electron holes (h^+). The electron–hole pairs can further migrate to the surface of the semiconductor and ultimately participate in redox reactions. Among the common semiconductor photocatalysts, gallium nitride (GaN), a wide band gap, III–V semiconductor, has superior intrinsic properties due to its high electromigration rate, excellent breakdown voltage, tunable wide band gap, and unique ionicity structure leading to high reactivity, long-term stability, and unprecedented chemical reactions.^{24,25} Notably, GaN possesses a valence band at -3.2 eV (with respect to vacuum level) and a wide band gap (3.4 eV), showing its excellent oxidizing ability.^{26,27} Since the generation of an alkyl radical from oxidative decarboxylation is critical in the Minisci reaction, this significant oxidizing power makes GaN a potential photocatalyst candidate for direct C–H alkylation of *N*-heteroarenes. Previously, alkyl radicals including methyl radicals have been produced via semiconductor photocatalyst-catalyzed decarboxylation for hydromethylation, hydroalkylation, dimerization, deuteration, and C(sp³)–F bond formation.^{28–31} These works demonstrate the feasibility and significance of using semiconductor photocatalysts for decarboxylative transformations. Inspired by previous literature, herein, we reported a GaN-based photocatalysis for the decarboxylative Minisci reaction under ambient conditions (Scheme 1d). The method includes the utilization of acetic acid for methylation as well as other easily accessible carboxylic acids for the alkylation of heteroarenes.

RESULT AND DISCUSSION

To initiate our research, we first examined the methylation of heteroarenes reaction between lepidine (**1**) and 2 equiv of acetic acid (**2**) in acetonitrile at room temperature under an argon atmosphere for 6 h. A broad-spectrum xenon lamp served as the light source, and commercial GaN powders were used as the catalyst. To our delight, 21% of the desired product (**1a**) was observed (Table 1, entry 1). Examination of solvents (entries 2–5) showed that acetonitrile gave the highest reactivity among common solvents (entries 2–5). For further optimization, we explored the deposition of metal as a cocatalyst on the semiconductor surface to significantly improve the catalytic performance. For example, previous works have shown that the loading of metallic palladium and platinum on TiO₂ significantly enhanced photocatalytic fatty

Table 1. Reaction Condition Optimization^a

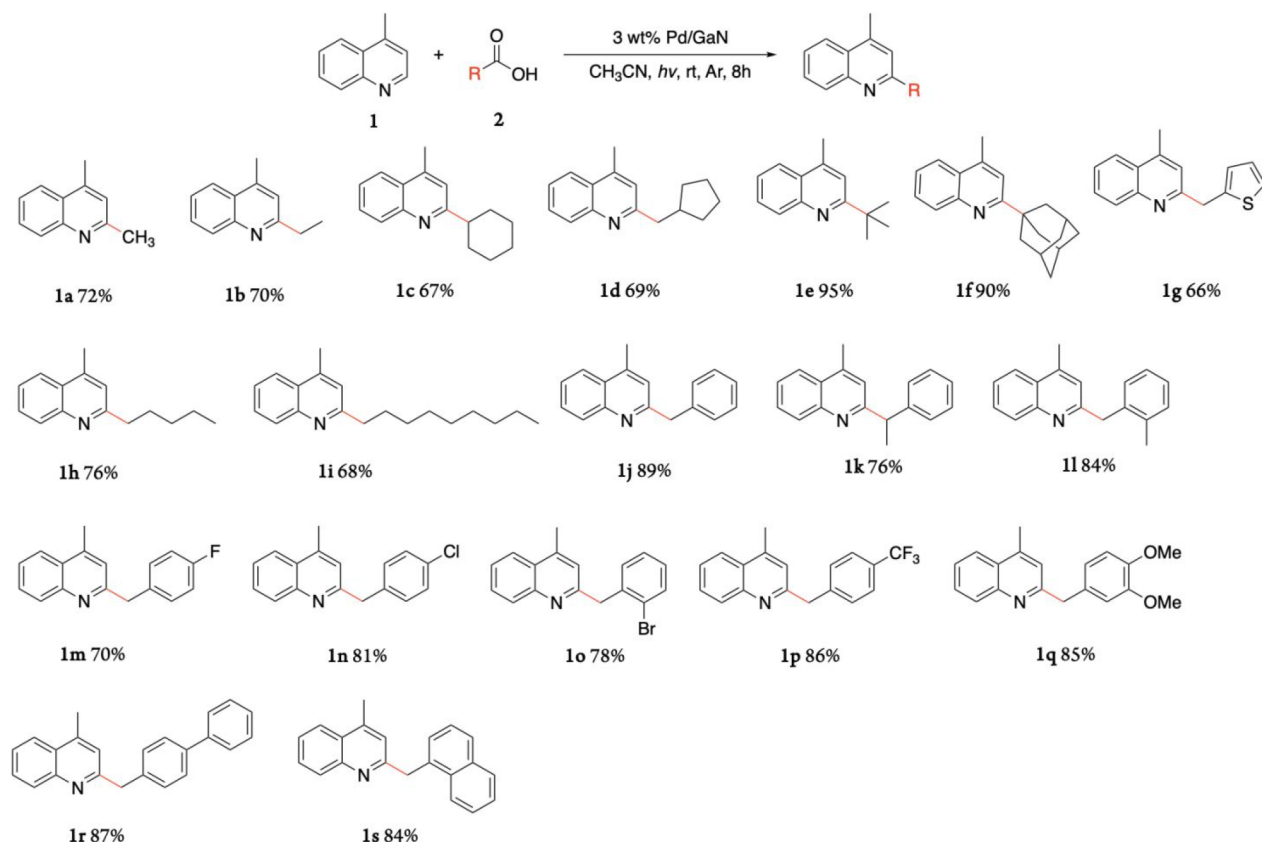
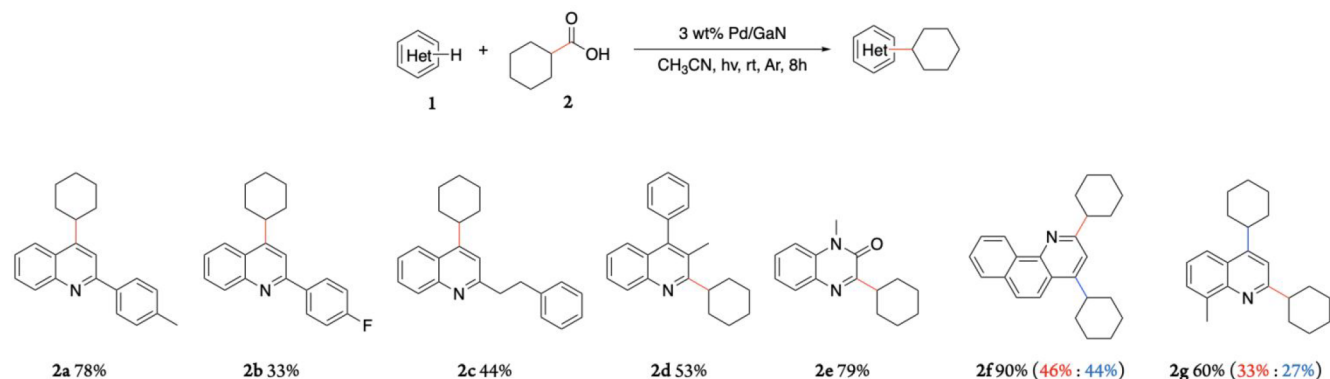
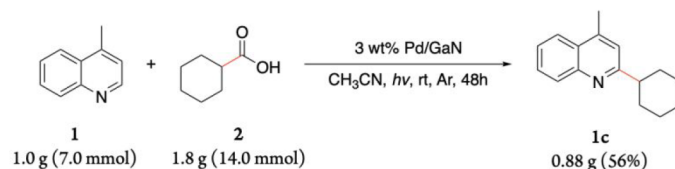


entry	solvent (1 mL)	catalyst	yield, %
1	CH ₃ CN	GaN	21
2	MeOH	GaN	13
3	THF	GaN	4
4	H ₂ O	GaN	6
5	hexane	GaN	14
6	CH ₃ CN	3.0 wt % Cu/GaN	15
7	CH ₃ CN	3.0 wt % Pt/GaN	46
8	CH ₃ CN	3.0 wt % Pd/GaN	66
9 ^b	CH ₃ CN	3.0 wt % Pd/GaN	72
10 ^c	CH ₃ CN	3.0 wt % Pd/GaN	70
11 ^d	CH ₃ CN	3.0 wt % Pd/GaN	27
12	CH ₃ CN	N/A	n.d.
13 ^e	CH ₃ CN	3.0 wt % Pd/GaN	n.d.

^aReaction conditions: All reactions were run at a 0.1 mmol scale of **1** with 5 mg of catalyst under Xe lamp irradiation at room temperature and under an inert atmosphere for 6 h. ^bReaction time: 8 h. ^cReaction time: 10 h. ^dUnder air atmosphere. ^eUnder darkness.

acid decarboxylation.^{32,33} Encouraged by such a design, various metals were photodeposited on GaN powders. Interestingly, the deposition of copper had little effect on the catalyst's activity, while the deposition of platinum and palladium showed a positive influence (entries 6–8). Additional optimization revealed 3 wt % Pd/GaN to be the most efficient catalyst, affording 66% yield of the desired product (Table S1). With the optimal reaction time, we were able to increase the yield to 72% (entry 9). Control experiments showed that the argon atmosphere was crucial for this reaction, and both light and catalyst are necessary for this reaction (entries 11–13).

With the optimized conditions in hand, we proceeded to investigate the substrate scope of the carboxylic acid reactant, as shown in Table 2. Simple aliphatic acids, including primary (**1a**, **1b**, and **1d**), secondary (**1c**), and tertiary (**1e** and **1f**) carboxylic acids, worked smoothly in the reaction, giving moderate to high yields. The heterocyclic derivative 2-thiopheneacetic acid (**1g**) gave a good yield of 66%. Short-chain aliphatic acids such as hexanoic and decanoic acids (**1h** and **1i**) can be well tolerated, affording the corresponding products in 76% and 68% yields, respectively. This validates the feasibility of using easily accessible fatty acids as effective coupling partners by this method. Moreover, benzylic analogues, such as phenylacetic, 2-phenylpropanoic, and *o*-tolylacetic acids (**1j**, **1k**, and **1l**) worked well in this transformation, giving the corresponding products in good yields. Under the same conditions, the fluoro, chloro, and bromo (**1m**, **1n**, and **1o**) substituted substrates performed in good yields. The strong electron-withdrawing compound (**1p**) also performed well in this reaction, albeit with a slightly lower yield than that of the electron-donating substrate (**1q**). Steric hindrance did not influence the reactivity, as the desired product could be obtained from the bulky substrates (**1r**, **1s**) with high yields. Additionally, gram-scale synthesis was performed between lepidine and cyclohexane carboxylic acid, which shows the potential for industrial large-scale applications.

Table 2. Substrate Scope of Photocatalytic Decarboxylative Minisci Reaction by GaN-Based Photocatalysis^aGram-scale reaction^b

^aReaction conditions: 1 (0.1 mmol), 2 (0.2 mmol, 2.0 equiv), and 3 wt % Pd/GaN (5 mg) in CH₃CN (1.0 mL) were stirred under Xe light irradiation at room temperature for 8 h under Ar atmosphere. ^bReaction conditions: 1 (1.0 g, 0.93 mL, 7.0 mmol), 2 (1.8 g, 14.0 mmol, 2.0 equiv), and 3 wt % Pd/GaN (100 mg) in CH₃CN (10.0 mL) were stirred under Xe light irradiation at room temperature for 48 h under Ar atmosphere.

Next, the substrate scope of heteroarenes was examined. Various quinoline moieties can be successfully converted into the corresponding alkylated products with up to 78% yield (2a–2d and 2g). However, lower conversions observed with

bulky substrates are likely due to weak contact with the catalyst surface. Other heterocycles such as quinoxalinone and benzoquinoline (2e and 2f) were also compatible with this method. To explore the stability of the heterogeneous catalyst,

we performed a recycling test with the model methylation reaction. The same catalyst was isolated and reused repeatedly for a total of six reactions without significantly lowering the yield (Figure S1), demonstrating its long-term stability.

Transmission electron microscopy (TEM) characterization was done to gain insight into the catalyst. The images showed that the metallic Pd nanoparticles were successfully deposited with good distribution on the surface of GaN (Figures S2 and S3). Previous reports have shown that the deposition of high work function metal Pd on GaN could form the Schottky junction, which is critical for charge transfer.^{34,35} These metal–semiconductor interfaces can significantly increase the lifetime of electron–hole pairs, enhancing the catalytic activity.^{36–38} Figure 1a displays the photoluminescence spectra of

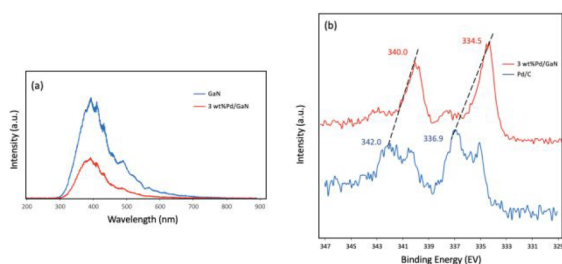


Figure 1. (a) Photoluminescence spectra of GaN and 3 wt % Pd/GaN. (b) Pd 3d spectra of Pd/C and 3 wt % Pd/GaN.

commercial GaN and the designed 3 wt % Pd/GaN. The intensity of the photoluminescence emission decreases as Pd nanoparticles are deposited on the surface of GaN. This phenomenon suggests that the electron transfer from GaN to Pd nanoparticles has occurred, leading to improvement of charge separations. To further investigate this electron transfer, X-ray photoelectron spectroscopy (XPS) analysis was performed. Figure 1b illustrates the Pd 3d peaks of Pd/C and 3 wt % Pd/GaN. The Pd 3d peaks of 3 wt % Pd/GaN appear at 334.5 and 340.0 eV, which is a shift toward lower binding energy as compared to Pd 3d peaks of Pd/C (336.9 and 342.0 eV) and confirms the electron transfer from the semiconducting GaN to Pd nanoparticles.

To investigate the mechanism of the reported photocatalytic alkylation via decarboxylation, 2 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to inhibit the reaction under the standard conditions (Figure 2a). The cyclohexyl-TEMPO product was achieved in 60% yield with a significant decrease in the generation of the desired alkylated product. The TEMPO adduct was detected by mass spectroscopy (MS) (Figure S4). The result suggests that the reaction goes through a radical based mechanism. Furthermore, electro-paramagnetic resonance (EPR) studies were conducted to corroborate a possible radical mechanism. With the presence of Pd/GaN catalyst, the obvious EPR signal of cyclohexyl-DMPO component could be obtained (Figure 2b). The detected signal agreed with the reported literature.³⁹ This result supports the production of an alkyl radical species via the semiconductor catalyzed decarboxylation. As for the isotopic study (Figure 2c), d_4 -acetic acid was applied for the methylation of lepidine. Deuterated dimethylquinoline, 12%, was obtained (Figure S5), demonstrating that the methyl group originated from acetic acid.

Based on prior research and the mechanistic investigations described above, a tentative mechanism was proposed, as

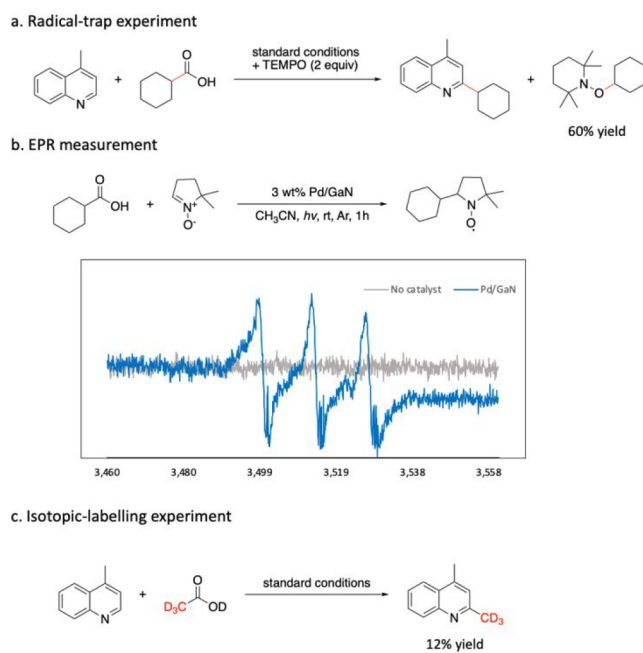


Figure 2. Mechanistic studies for photocatalytic decarboxylative Minisci reaction by GaN-based photocatalysis. (a) Radical-trap experiment with TEMPO. (b) EPR analysis. (c) Isotopic-labelling experiment with d_4 -acetic acid.

shown in Figure 3. Upon photoexcitation, the carboxylic acid will be oxidized to a radical anion by the photogenerated hole

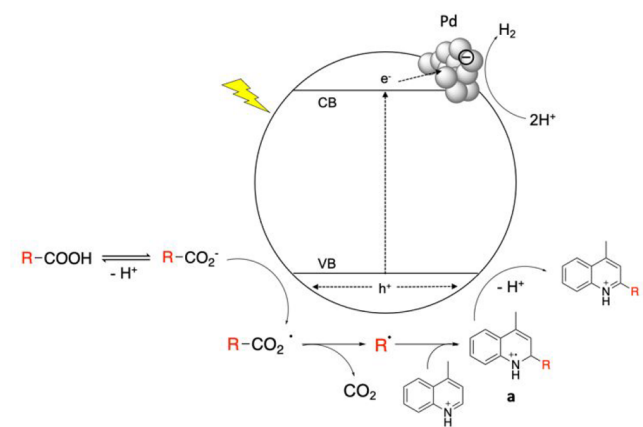


Figure 3. Proposed mechanism for the decarboxylative Minisci reaction.

at the surface of GaN. After the loss of a proton, the anion intermediate would become an acyloxy radical, which would readily turn into an alkyl radical via the release of CO_2 . Then, the alkyl radical would rapidly add to the electron-deficient heteroarenes, generating intermediate **a**. The adduct radical can be further oxidized by the catalyst following deprotonation to obtain the desired alkylated product. The photogenerated electrons eventually reduce protons to H_2 . The generation of H_2 was verified by GC-TCD (gas chromatography-thermal conductivity detector).

CONCLUSION

In conclusion, we demonstrated the direct C–H alkylation of N-heteroarenes via a photodriven decarboxylative Minisci

reaction. The method is enabled by the heterogeneous Pd/GaN catalyst. Broad scopes of carboxylic acids and heteroarenes were functionalized with high efficiency. The recycling test and gram-scale synthesis showed the possibility of applications for the sustainable and efficient synthesis of complex organic molecules.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/prechem.3c00054>.

Experimental procedures, catalyst characterization, details of the catalytic activity measurement results (PDF)

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Author Contributions

[§]L.-D.T., H.K., and M.-X.L. contributed equally. C.-J.L. proposed the research idea and supervised the project. L.-D.T. designed and prepared catalyst, characterized samples, and performed catalytic measurements. L.-D.T., H.K., and M.-X.L. wrote the manuscript. H.S. and J.-T.H. revised the manuscript and participated in critical discussions. All authors interpreted the results and contributed to the development of the manuscript.

Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Dennis Curran for his contribution to radical chemistry on the occasion of his 70th birthday.

■ REFERENCES

- (1) Zhang, J.-R.; Xu, L.; Liao, Y.-Y.; Deng, J.-C.; Tang, R.-Y. Advances in Radical Oxidative C–H Alkylation of N-Heteroarenes. *Chin. J. Chem.* **2017**, *35* (3), 271–279.
- (2) Li, G.-X.; Morales-Rivera, C. A.; Wang, Y.; Gao, F.; He, G.; Liu, P.; Chen, G. Photoredox-Mediated Minisci C–H Alkylation of N-Heteroarenes Using Boronic Acids and Hypervalent Iodine. *Chem. Sci.* **2016**, *7* (10), 6407–6412.
- (3) Bera, A.; Kabadwal, L. M.; Bera, S.; Banerjee, D. Recent Advances on Non-Precious Metal-Catalyzed C–H Functionalization of N-Heteroarenes. *Chem. Commun.* **2021**, *58* (1), 10–28.
- (4) Proctor, R. S. J.; Phipps, R. J. Recent Advances in Minisci-Type Reactions. *Angew. Chem., Int. Ed.* **2019**, *58* (39), 13666–13699.
- (5) Dong, J.; Lyu, X.; Wang, Z.; Wang, X.; Song, H.; Liu, Y.; Wang, Q. Visible-Light-Mediated Minisci C–H Alkylation of Heteroarenes with Unactivated Alkyl Halides Using O₂ as an Oxidant. *Chem. Sci.* **2019**, *10* (4), 976–982.
- (6) Rodríguez, N.; Goossen, L. J. Decarboxylative Coupling Reactions: A Modern Strategy for C–C-Bond Formation. *Chem. Soc. Rev.* **2011**, *40* (10), 5030–5048.
- (7) Schwarz, J.; König, B. Decarboxylative Reactions with and without Light - a Comparison. *Green Chem.* **2018**, *20* (2), 323–361.
- (8) Minisci, F.; Bernardi, R.; Bertini, F.; Galli, R.; Perchinummo, M. Nucleophilic Character of Alkyl Radicals—VI: A New Convenient Selective Alkylation of Heteroaromatic Bases. *Tetrahedron* **1971**, *27* (15), 3575–3579.
- (9) Mai, D. N.; Baxter, R. D. Unprotected Amino Acids as Stable Radical Precursors for Heterocycle C–H Functionalization. *Org. Lett.* **2016**, *18* (15), 3738–3741.
- (10) Xia, X.-F.; Zhu, S.-L.; Gu, Z.; Wang, H. Copper-Catalyzed C–H Alkylation of 8-Aminoquinolines via 8-Amide Chelation Assistance. *RSC Adv.* **2015**, *5* (37), 28892–28895.
- (11) Bi, H.-P.; Chen, W.-W.; Liang, Y.-M.; Li, C.-J. A Novel Iron-Catalyzed Decarboxylative Csp³-Csp² Coupling of Proline Derivatives and Naphthol. *Org. Lett.* **2009**, *11* (15), 3246–3249.
- (12) Bi, H.-P.; Zhao, L.; Liang, Y.-M.; Li, C.-J. The Copper-Catalyzed Decarboxylative Coupling of the Sp³-Hybridized Carbon Atoms of α -Amino Acids. *Angew. Chem., Int. Ed.* **2009**, *48* (4), 792–795.
- (13) Shang, R.; Liu, L. Transition Metal-Catalyzed Decarboxylative Cross-Coupling Reactions. *Sci. China Chem.* **2011**, *54* (11), 1670–1687.
- (14) Schultz, D. M.; Yoon, T. P. Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* **2014**, *343* (6174), 1239176.
- (15) Xuan, J.; Xiao, W.-J. Visible-Light Photoredox Catalysis. *Angew. Chem., Int. Ed.* **2012**, *51* (28), 6828–6838.
- (16) Yoon, T. P.; Ischay, M. A.; Du, J. Visible Light Photocatalysis as a Greener Approach to Photochemical Synthesis. *Nat. Chem.* **2010**, *2* (7), 527–532.
- (17) Garza-Sanchez, R. A.; Tlahuext-Aca, A.; Tavakoli, G.; Glorius, F. Visible Light-Mediated Direct Decarboxylative C–H Functionalization of Heteroarenes. *ACS Catal.* **2017**, *7* (6), 4057–4061.

- (18) Lai, X.-L.; Shu, X.-M.; Song, J.; Xu, H.-C. Electrophotocatalytic Decarboxylative C-H Functionalization of Heteroarenes. *Angew. Chem., Int. Ed.* **2020**, *59* (26), 10626–10632.
- (19) Cheng, W.-M.; Shang, R.; Fu, Y. Photoredox/Bronsted Acid Co-Catalysis Enabling Decarboxylative Coupling of Amino Acid and Peptide Redox-Active Esters with N-Heteroarenes. *ACS Catal.* **2017**, *7* (1), 907–911.
- (20) Cheng, W.-M.; Shang, R.; Fu, M.-C.; Fu, Y. Photoredox-Catalysed Decarboxylative Alkylation of N-Heteroarenes with N-(Acyloxy) Phthalimides. *Chem. - Eur. J.* **2017**, *23* (11), 2537–2541.
- (21) Fu, M.-C.; Shang, R.; Zhao, B.; Wang, B.; Fu, Y. Photocatalytic Decarboxylative Alkylations Mediated by Triphenylphosphine and Sodium Iodide. *Science* **2019**, *363* (6434), 1429–1434.
- (22) Tong, H.; Ouyang, S.; Bi, Y.; Umezawa, N.; Oshikiri, M.; Ye, J. Nano-Photocatalytic Materials: Possibilities and Challenges. *Adv. Mater.* **2012**, *24* (2), 229–251.
- (23) Zhang, F.; Wang, X.; Liu, H.; Liu, C.; Wan, Y.; Long, Y.; Cai, Z. Recent Advances and Applications of Semiconductor Photocatalytic Technology. *Appl. Sci.* **2019**, *9* (12), 2489.
- (24) Kibria, M. G.; Mi, Z. Artificial Photosynthesis Using Metal/Nonmetal-Nitride Semiconductors: Current Status, Prospects, and Challenges. *J. Mater. Chem. A* **2016**, *4* (8), 2801–2820.
- (25) Liu, M.; Tan, L.; Zhou, B.; Li, L.; Mi, Z.; Li, C.-J. Group-III Nitrides Catalyzed Transformations of Organic Molecules. *Chem.* **2021**, *7* (1), 64–92.
- (26) Wu, J. When Group-III Nitrides Go Infrared: New Properties and Perspectives. *J. Appl. Phys.* **2009**, *106* (1), 011101.
- (27) Arafin, S.; Liu, X.; Mi, Z. Review of Recent Progress of III-Nitride Nanowire Lasers. *J. Nanophotonics* **2013**, *7* (1), 074599.
- (28) Zhu, Q.; Nocera, D. G. Photocatalytic Hydromethylation and Hydroalkylation of Olefins Enabled by Titanium Dioxide Mediated Decarboxylation. *J. Am. Chem. Soc.* **2020**, *142* (42), 17913–17918.
- (29) Manley, D. W.; McBurney, R. T.; Miller, P.; Howe, R. F.; Rhydderch, S.; Walton, J. C. Unconventional Titania Photocatalysis: Direct Deployment of Carboxylic Acids in Alkylations and Annulations. *J. Am. Chem. Soc.* **2012**, *134* (33), 13580–13583.
- (30) Shi, J.; Yuan, T.; Zheng, M.; Wang, X. Metal-Free Heterogeneous Semiconductor for Visible-Light Photocatalytic Decarboxylation of Carboxylic Acids. *ACS Catal.* **2021**, *11* (5), 3040–3047.
- (31) Tarantino, G.; Hammond, C. Catalytic Formation of C(Sp³)-F Bonds via Heterogeneous Photocatalysis. *ACS Catal.* **2018**, *8* (11), 10321–10330.
- (32) Huang, Z.; Zhao, Z.; Zhang, C.; Lu, J.; Liu, H.; Luo, N.; Zhang, J.; Wang, F. Enhanced Photocatalytic Alkane Production from Fatty Acid Decarboxylation via Inhibition of Radical Oligomerization. *Nat. Catal.* **2020**, *3* (2), 170–178.
- (33) Kuwana, D.; Komori, Y.; Nagatomo, M.; Inoue, M. Photo-induced Decarboxylative Radical Coupling Reaction of Multiply Oxygenated Structures by Catalysis of Pt-Doped TiO₂. *J. Org. Chem.* **2022**, *87* (1), 730–736.
- (34) Grodzicki, M.; Mazur, P.; Zuber, S.; Pers, J.; Ciszewski, A. Pd/GaN(0001) Interface Properties. *Mater. Sci.-Polym.* **2014**, *32* (2), 252–256.
- (35) Li, Z.; Zhang, F.; Han, J.; Zhu, J.; Li, M.; Zhang, B.; Fan, W.; Lu, J.; Li, C. Using Pd as a Cocatalyst on GaN-ZnO Solid Solution for Visible-Light-Driven Overall Water Splitting. *Catal. Lett.* **2018**, *148* (3), 933–939.
- (36) Xu, D.; Zhang, S.-N.; Chen, J.-S.; Li, X.-H. Design of the Synergistic Rectifying Interfaces in Mott-Schottky Catalysts. *Chem. Rev.* **2023**, *123* (1), 1–30.
- (37) Wenderich, K.; Mul, G. Methods, Mechanism, and Applications of Photodeposition in Photocatalysis: A Review. *Chem. Rev.* **2016**, *116* (23), 14587–14619.
- (38) Yang, X.; Wang, D. Photocatalysis: From Fundamental Principles to Materials and Applications. *ACS Appl. Energy Mater.* **2018**, *1* (12), 6657–6693.
- (39) Kvasovs, N.; Iziuchenko, V.; Palchykov, V.; Gevorgyan, V. Visible Light-Induced Pd-Catalyzed Alkyl-Heck Reaction of Oximes. *ACS Catal.* **2021**, *11* (6), 3749–3754.