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Visible-Light-Photocatalyzed C5-H Nitration of 8-Aminoquinoline Amides

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Abstract: A mild and efficient protocol for visible-light-photocatalyzed C5 nitration of 8-aminoquinoline derivatives was developed utilizing $Cu(NO_3)_2 \cdot 3H_2O$ as a nitro source. The reaction proceeded smoothly under very mild conditions, employing Acid Red 94 and a commercial household light bulb as an organic photosensitizer and a light source, respectively, making this synthetic procedure green and easy to operate. Furthermore, most products could be obtained through recrystallization, which enhanced the operational simplicity of this method.

Keywords: photocatalysis; nitration; aminoquinoline

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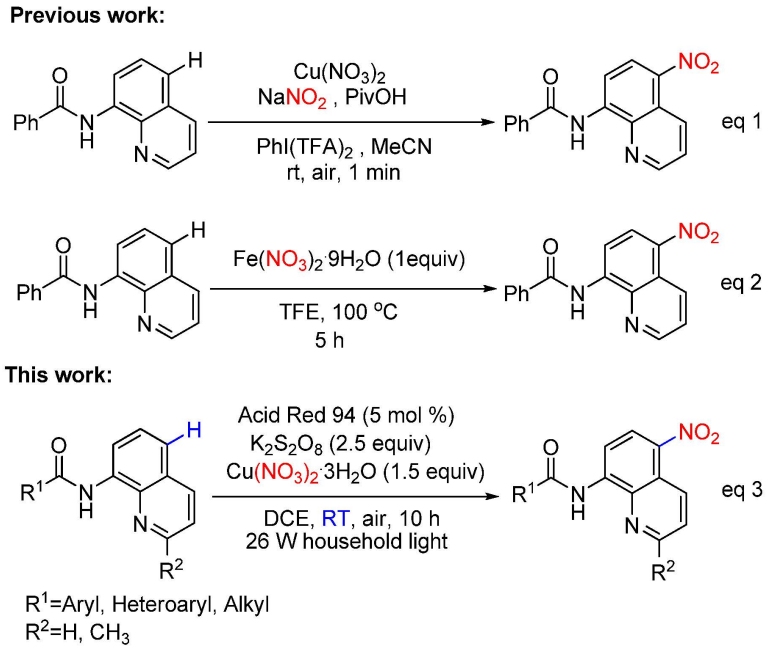
1. Introduction

Nitroarenes play an important role in the synthesis of dyes, pharmaceuticals, plastics, explosives, and perfumes [1,2]. The classical methodologies for nitration are based on a mixed acid H_2SO_4/HNO_3 protocol, but usually generate the complex mixtures of regioisomers (*o*-/*m*-/*p*- = 19:80:1 at 30 °C), thereby exhibiting from regioselectivity and functional group compatibility issues [3,4]. In order to overcome these problems, efforts have been directed towards the development of new nitration protocols. For example, nitroarenes can be readily accessed via the nitration of aryl boronic acids, aryl halides, pseudo halides, and aryl carboxylic acids, as well as the oxidation of aromatic primary amines or azides [5–11]. However, all these protocols require prefunctionalized arenes as the starting materials.

The auxiliary-assisted C–H functionalization has become a reliable and robust tool in modern organic synthesis in recent years [12–22]. Specifically, the direct functionalization of quinoline ring at the C5 position using the amide unit as a directing group has also been explored in recent years [23–34], and the nitration of C5 quinoline ring has especially received considerable attention [35–46]. Recently, the Ribas group described a mild methodology for C–H nitration of 8-aminoquinoline amides utilizing $Co(NO_3)_2 \cdot 6H_2O$ as the catalyst and *t*BuONO as the nitrating agent [38]. However, it tended to suffer from regioselectivity for quinoline rings (ratio of C5:C7 = 3:1). Subsequently, the Zhang group developed the copper-catalyzed nitration of 8-aminoquinolines at C5 position using $Cu(NO_3)_2/NaNO_2/PhI(TFA)_2$ as the nitration system (Scheme 1, eq 1) [39]. Recently, Fan also reported an alternative transformation with $Fe(NO_3)_3 \cdot 9H_2O$ as the nitro source [40], albeit this protocol should be performed at 100 °C (Scheme 1, eq 2). Despite these achievements attained in this area, these synthetic routes still require expensive oxidants, expensive metals, or a high reaction temperature. Therefore, the development of a mild and environmentally benign route to synthesize nitro compounds is highly desirable.

The recent developments on visible light photoredox catalysis provides a new possibility for modern organic synthesis due to their catalysis process with the mild, environmentally benign, operationally simple advantages and commercially available photocatalysts [47]. The research interest of our group is focused on regioselective C–H functionalization, especially that takes place at an unusual C–H site [28,29,48]. For example,

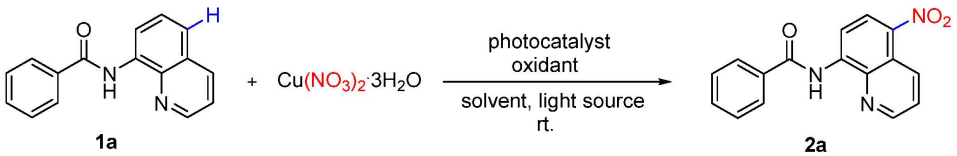
we demonstrated the C5–H sulfonylation [28] and phosphonation [29] of 8-aminoquinoline amides and developed the palladium-catalyzed picolinamide-directed C8–H amination of 1-naphthylamine derivatives with simple secondary aliphatic amines [47]. Inspired by these previous and our own reports, we envisioned achieving a mild and efficient protocol for visible-light-photocatalyzed C5 nitration on the quinoline ring (Scheme 1, eq 3).



Scheme 1. The direct nitration of C5 quinoline ring.

2. Results and Discussion

Initially, the reaction of N-(quinolin-8-yl)benzamide (**1a**) was performed as the model reaction to optimize the reaction parameters at room temperature under air as Scheme 2, and the results are displayed in Table 1. After various catalysts, solvents, and oxidants were investigated (see Supporting Information), the desired product **2a** was obtained in 68% yield in DCE using $K_2S_2O_8$, $Cu(NO_3)_2{\cdot}3H_2O$, and Eosin B as the oxidant, the nitrating agent, and the photoredox catalyst, respectively (Table 1, entry 1) [49]. Thereafter, various photocatalysts were checked, and Acid Red 94 could produce the product in a good yield of 82% (Table 1, entry 7 vs. entries 2–6). However, reducing the amount of Acid Red 94 from 5 mol % to 4 mol % resulted in a lower yield of 68% (Table 1, entry 8 vs. entry 7). Additionally, performing reaction under a nitrogen or an O_2 atmosphere did not afford better results (Table 1, entries 9 and 10 vs. entry 7). When the reaction time decreased to 8 h, a lower yield of 73% was observed (Table 1, entry 11 vs. entry 7). And the conditions in entry 7, Table 1 was selected as the optimized reaction conditions.



Scheme 2. The nitration of 1-naphthylamine derivatives.

Table 1. Screening optimal conditions [a,b].

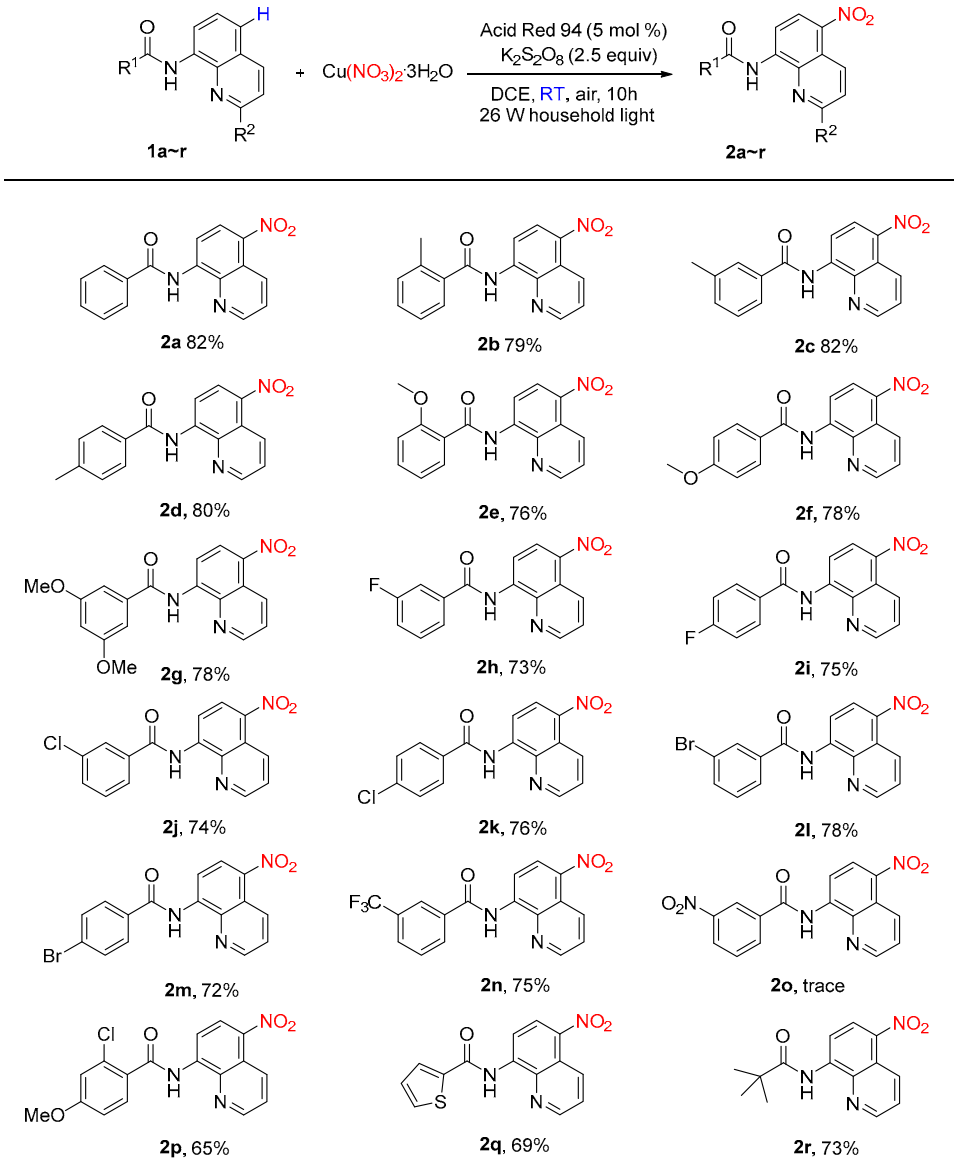
Entry	Catalyst	Oxidant	Light Source	Yield (%) [b]
1	EosinB	$K_2S_2O_8$	household light	68
2	EosinY	$K_2S_2O_8$	household light	65
3	$Ru(bpy)_3(PF_6)_2$	$K_2S_2O_8$	household light	69
4	$Ru(bpy)_3Cl_2$	$K_2S_2O_8$	household light	75
5	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	$K_2S_2O_8$	household light	76
6	Alizarin Red S	$K_2S_2O_8$	household light	72
7	**Acid Red 94**	**$K_2S_2O_8$**	**household light**	**82**
8 [c]	Acid Red 94	$K_2S_2O_8$	household light	69
9 [d]	Acid Red 94	$K_2S_2O_8$	household light	76
10 [e]	Acid Red 94	$K_2S_2O_8$	household light	68
11 [f]	Acid Red 94	$K_2S_2O_8$	household light	73
12	Acid Red 94	$K_2S_2O_8$	blue	66
13	Acid Red 94	$K_2S_2O_8$	green	62
14	Acid Red 94	$K_2S_2O_8$	red	43
15	Acid Red 94	$K_2S_2O_8$	dark	23
16	—	$K_2S_2O_8$	household light	25
17 [g]	Acid Red 94	$K_2S_2O_8$	household light	51
18 [h]	Acid Red 94	$K_2S_2O_8$	household light	NR

[a] reaction conditions: **1a** (0.20 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (1.5 equiv), photocatalyst (5 mol %), and $K_2S_2O_8$ (2.5 equiv) in DCE (1.5 mL) at room temperature under air for 10 h. [b] isolated yield of **2a**. [c] photocatalyst (4 mol %). [d] under N_2. [e] under O_2. [f] for 8 h. [g] $Cu(NO_3)_2{\cdot}3H_2O$ (1.0 equiv). [h] $AgNO_3$ (2.0 equiv) instead of $Cu(NO_3)_2{\cdot}3H_2O$ (1.5 equiv). Bold represents optimized conditions.

Finally, some other light sources were investigated (e.g., blue LED, green LED, and red LED), but they could not match the effect of household light (Table 1, entries 12–14 vs. entry 7); the yield of the target product dropped drastically in the absence of household light irradiation or photocatalysts (Table 1, entries 15 and 16). The amount of nitro source $Cu(NO_3)_2{\cdot}3H_2O$ when decreased to 1.0 equiv resulted in a lower yield of 51% (Table 1, entry 17). However, when $AgNO_3$ was utilized as the nitro source, the product was not obtained (Table 1, entry 18).

With the optimized conditions in hand, the scope of this reaction was investigated, and the results were summarized in Scheme 3. The results showed that the electronic effect is not obvious on the benzene ring of benzamides, and the desired products could be obtained in good yields. When the benzamides possessed electron-donating groups (e.g., Me and MeO), the desired products were obtained in a yield range of 76–82% (**2b**–**2g**); substrates bearing electron-withdrawing groups (e.g., F, Cl, Br, and CF_3) provided the corresponding products in yields of 72–78% (**2h**–**2n**). However, 3-nitro-*N*-(quinolin-8-yl)benzamide did not produce the corresponding nitration product (**2o**). In addition, the heterocyclic amide could produce the nitration product in a good yield of 69% (**2q**), and to our delight, aliphatic amide could also afford the corresponding product in 73% yield (**2r**).

The scope of 2-methyl-8-aminoquinoline amides was also investigated (Scheme 4). Both electron-rich and electron-poor groups on the benzene ring of benzamides were successfully tolerated in the reaction, and comparatively, substrates containing electron-donating groups could result in slightly higher yields of the coupling products than those of electron-withdrawing groups (**2a′**–**2m′**). The substrate bearing Me or MeO group on the phenyl ring could afford the nitrated products in 75–79% yield (**2b′**–**2e′**). Moreover, aromatic amides, possessing F, Cl, Br and CF_3, could afford the target compounds **2f′**–**2m′** in moderate yields (59–71%). Notably, the method was also applicable to five-membered heterocycles such as thiophene, providing the corresponding products in 72% yield (**2n′**).

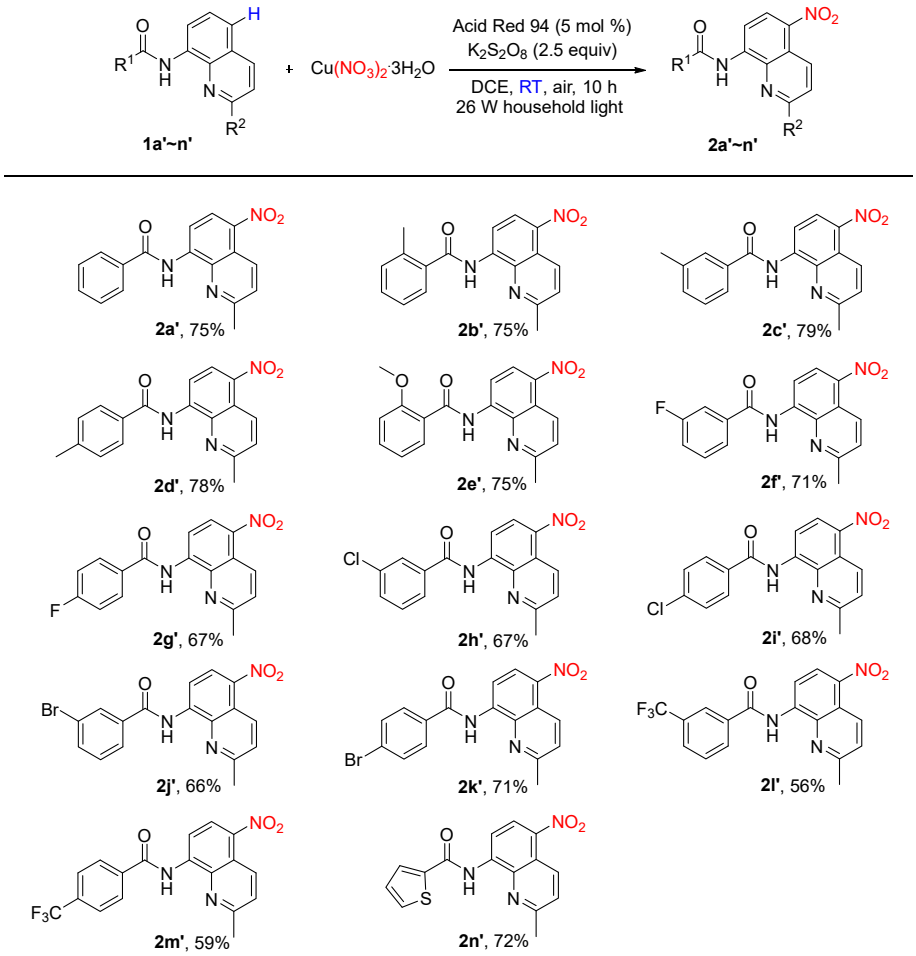


[a] reaction conditions: **1a** (0.20 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (1.5 equiv), Acid Red 94 (5 mol %), and $K_2S_2O_8$ (2.5 equiv) in DCE (1.5 mL) at room temperature under air for 10 h. [b] isolated yield.

Scheme 3. Substrate scope of 8-aminoquinoline amides [a,b].

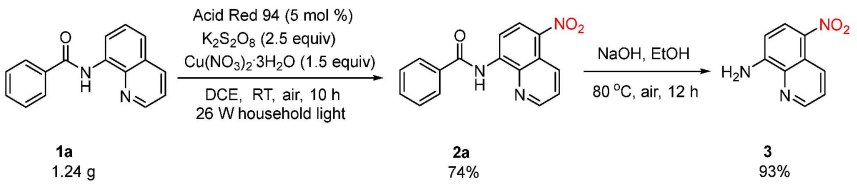
In order to prove the synthetic value of this method, we performed a gram-scale reaction (Scheme 5), and the nitrated product **2a** was isolated in 74% yield. Furthermore, the obtained product **2a** could be easily transformed into 5-nitro-8-aminoquinoline **3** in a yield of 93% via a hydrolysis process.

In order to obtain the mechanistic information about this transformation, control experiments were carried out (Scheme 6). No desired product was observed when the benzamides (**4** and **5**) and benzoate **6** participated in this reaction under the standard conditions. These results showed that the formation of a chelated complex between 8-aminoquinoline and the copper salt was crucial to the remote C–H nitration [50]. The addition of TEMPO to the reaction mixture resulted in the inhibition of the corresponding nitration products, suggesting that radical steps might be involved in this reaction. In addition, our previous report has pointed out that the C5 site on the quinoline ring has the largest p_z orbital occupancies and may be the electrophilic reactive site [28].

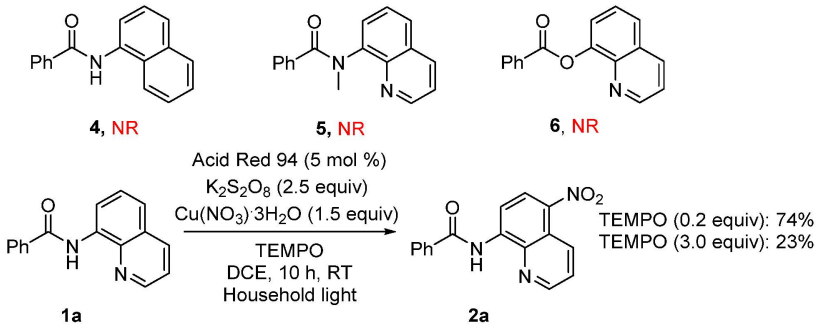


[a] reaction conditions: **1a** (0.20 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (1.5 equiv), Acid Red 94 (5 mol %), and $K_2S_2O_8$ (2.5 equiv) in DCE (1.5 mL) at room temperature under air for 10 h. [b] isolated yield.

Scheme 4. Substrate scope of 2-methyl-8-aminoquinoline amides [a,b].

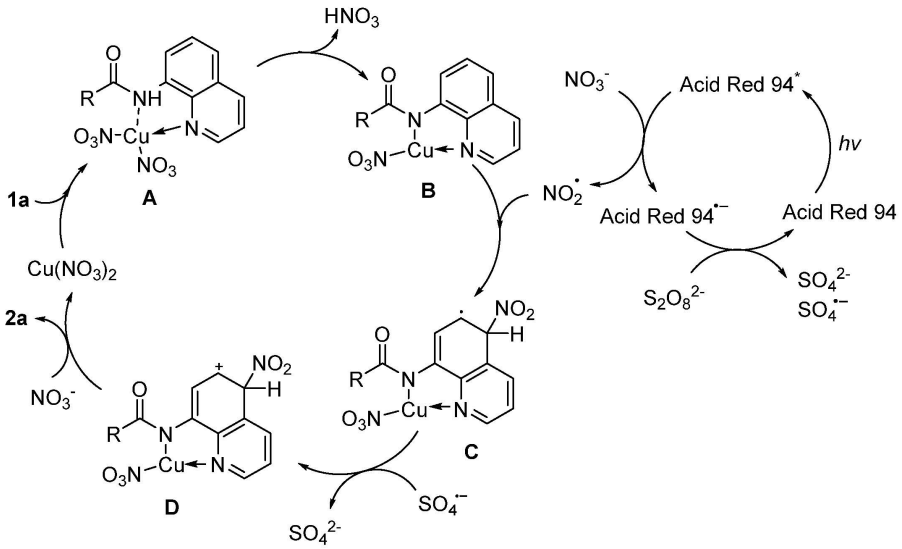


Scheme 5. A gram-scale experiment.



Scheme 6. Control experiments.

On the basis of the above experiments and previous reports, a plausible mechanism for this visible-light-promoted remote C–H nitration is proposed in Scheme 7. First, Acid Red 94 is excited by the household light, generating the excited state Acid Red 94*. Then, Acid Red 94* undergoes a reductive quenching process with $Cu(NO_3)_2$, yielding a NO_2• and Acid Red 94 radical anion. The Acid Red 94 radical anion could be oxidized by the $K_2S_2O_8$, regenerating the ground state Acid Red 94 to complete the photocatalytic cycle. On the other hand, the coordination of **1a** with $Cu(NO_3)_2$ affords the chelated intermediate **A**. Afterwards, the deprotonation of the amide group leads to the formation of the complex **B**. Then, an intermediate radical **C** is formed by the electronic attack of the nitro radical (NO_2•) at the C5 position of intermediate **B**. After that, the cationic intermediate **D** is generated through the oxidation of the intermediate radical **C** by the sulfate radical anion. Finally, a metal dissociation process of **D** occurs after the proton transfer process, providing the desired product **2a**, along with the regeneration of $Cu(NO_3)_2$ to fulfill the catalytic cycle.



Scheme 7. A plausible reaction mechanism.

3. Conclusions

We have developed a mild and green protocol for the C5 nitration on the quinoline ring of 8-aminoquinoline amides, producing the corresponding product in moderate-to-good yields. This reaction proceeded smoothly at room temperature in air under visible light photoredox catalysis. Moreover, this transformation also showed good functional group tolerance and provided a practical synthetic route for 5-nitro-8-aminoquinoline derivatives.

4. Experimental

4.1. General Information

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (Bruker BioSpin, Faellanden, Switzerland) with $CDCl_3$ as the solvent and TMS (Alfa Aesar, Shanghai, China) as an internal standard. Melting points were measured using a X-5 microscopic (Gongyi Yuhua Yiqi, Zhengzhou, China) apparatus and are uncorrected. High-resolution mass spectra were obtained with Agilent Technologies 1290-6540 UHPLC/Accurate-Mass Quadrupole Time-of-Flight LC/MS (Agilent Technologies, Wilmington, NC, USA). All solvents were used directly without further purification. Dichloromethane, ethyl acetate, and hexane were used for column chromatography. The commercials were obtained from commercial sources and used as-received without further purification unless otherwise noted. For the detailed experimental information, please see the Supplementary Materials.

4.2. Typical Procedure for Synthesizing the Catalytic C5-H Nitration of 8-Aminoquinoline Amides

(2a-2p, 2a′-2m′): To a 10 mL reaction tube, the mixture of amide (0.2 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (0.3 mmol, 1.5 equiv), Acid Red 94 (0.01 mmol, 5 mol %), $K_2S_2O_8$ (0.5 mmol, 2.5 equiv), and DCE (1.5 mL) was added. The resulting mixture was stirred under the irradiation of 26 W household light under air at room temperature for 10 h. Upon completion, the mixture was filtered through a celite pad and washed with CH_2Cl_2, the solvent was removed under reduced pressure and then followed by recrystallization to produce the corresponding product using hexane–CH_2Cl_2 as a solvent.

(2q, 2r and 2n′): To a 10 mL reaction tube, the mixture of amide (0.2 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (0.3 mmol, 1.5 equiv), Acid Red 94 (0.01 mmol, 5 mol %), $K_2S_2O_8$ (0.5 mmol, 2.5 equiv), and DCE (1.5 mL) was added. Upon completion, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography to produce the corresponding product.

***N*-(5-nitroquinolin-8-yl)benzamide (2a) [36]:** Yellow solid in 82% yield; mp 215–216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 1H), 9.30 (d, J = 8.6 Hz, 1H), 9.00 (d, J = 8.8 Hz, 1H), 8.95 (d, J = 3.3 Hz, 1H), 8.59 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 7.28 Hz, 2H), 7.75 (dd, J = 8.8, 4.1 Hz, 1H), 7.66–7.63 (m, 1H), 7.60–7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 149.1, 140.9, 138.7, 137.8, 134.1, 133.4, 132.7, 129.0, 127.9, 127.5, 124.7, 121.8, 113.7.

2-methyl-*N*-(5-nitroquinolin-8-yl)benzamide(2b) [36]: Yellow solid in 79% yield; mp 192–193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 9.30 (d, J = 8.8 Hz, 1H), 9.01 (d, J = 8.8 Hz, 1H), 8.88 (d, J = 2.8 Hz, 1H), 8.61 (d, J = 8.8 Hz, 1H), 7.74–7.69 (m, 2H), 7.74–7.69 (m, 1H), 7.38–7.34 (m, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 149.1, 141.0, 138.8, 137.6, 137.3, 135.5, 133.4, 131.7, 131.1, 127.9, 127.3 126.2, 124.7, 121.8, 113.7, 20.3.

3-methyl-*N*-(5-nitroquinolin-8-yl)benzamide (2c): Yellow solid in 82% yield; mp 201–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1H), 9.30 (d, J = 8.5 Hz, 1H), 9.01 (d, J = 8.9 Hz, 1H), 8.96 (d, J = 2.8 Hz, 1H), 8.60 (d, J = 8.8Hz, 1H), 7.88 (d, J = 11.9 Hz, 2H), 7.75 (dd, J = 9.1, 4.1 Hz, 1H), 7.49–7.45 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.94, 149.1, 141.0, 139.0, 138.6, 137.8, 134.2, 133.4, 128.9, 128.2, 127.9, 124.7, 124.4, 121.8, 113.7, 21.5; HRMS (ESI): calculated for $C_{17}H_{13}N_3O_3$: $[M + H]^+$ requires 308.1030, found 308.1031.

4-methyl-*N*-(5-nitroquinolin-8-yl)benzamide (2d) [37]: Yellow solid in 80% yield; mp 210–211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.05 (s, 1H), 9.31 (d, J = 8.7 Hz, 1H), 9.02 (d, J = 8.8 Hz, 1H), 8.96 (d, J = 3.4 Hz, 1H), 8.61 (d, J = 8.8 Hz, 1H), 7.99 (d, J = 7.8 Hz, 2H), 7.74 (dd, J = 8.9, 4.1 Hz, 1H), 7.38 (d, J = 7.9 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 149.0, 143.4, 141.0, 138.6, 137.8, 133.5, 131.4, 129.7, 128.0, 127.5, 124.7, 121.9, 113.7, 21.6; HRMS (ESI): calculated for $C_{17}H_{13}N_3O_3$: $[M + H]^+$ requires 308.1030, found 308.1033.

2-methoxy-*N*-(5-nitroquinolin-8-yl)benzamide (2e): Yellow solid in 75% yield; mp 208–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.68 (s, 1H), 9.26 (d, J = 7.9 Hz, 1H), 9.06 (d, J = 8.9 Hz, 1H), 8.93 (d, J = 2.8 Hz, 1H), 8.56 (d, J = 8.8Hz, 1H), 8.31 (d, J = 6.7, 1H), 7.69 (dd, J = 8.8, 4.1 Hz, 1H), 7.57–7.54 (m, 1H), 7.17–7.14 (m, 1H), 7.08 (d, J = 8.2 Hz, 1H), 4.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 157.9, 148.9, 142.2, 138.4, 138.2, 134.0, 133.1, 132.6, 128.1, 124.4, 121.9, 121.5, 121.4, 114.4, 111.7, 56.2; HRMS (ESI): calculated for $C_{17}H_{13}N_3O_4$: $[M + H]^+$ requires 324.0979, found 324.0977.

4-methoxy-*N*-(5-nitroquinolin-8-yl)benzamide (2f) [35]: Yellow solid in 78% yield; mp 260–261 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.03 (s, 1H), 9.34 (d, J = 8.6 Hz, 1H), 9.01 (d, J = 8.9 Hz, 1H), 8.96 (d, J = 3.6 Hz, 1H), 8.63 (d, J = 8.9 Hz, 1H), 8.07 (d, J = 8.7 Hz, 2H), 7.76 (dd, J = 8.9, 4.1 Hz, 1H), 7.07 (d, J = 8.6 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 163.2, 149.0, 141.2, 138.5, 137.8, 133.5, 129.5, 128.1, 126.4, 124.7, 121.9, 114.3, 113.5, 55.6.

3,5-dimethoxy-*N*-(5-nitroquinolin-8-yl)benzamide (2g): Yellow solid in 78% yield; mp 200–201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.00 (s, 1H), 9.30 (d, J = 8.8 Hz, 1H), 8.99–8.95 (m, 2H), 8.61 (d, J = 8.8 Hz, 1H), 7.76 (dd, J = 8.9, 4.1 Hz, 1H), 7.20 (s, 2H), 6.71 (s, 2H), 3.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 161.2, 149.2, 140.8, 138.8, 137.8, 136.3, 133.4, 127.9, 124.8, 121.8, 113.8, 105.5, 104.4, 55.7; HRMS (ESI): calculated for $C_{18}H_{15}N_3O_5$: $[M + H]^+$ requires 354.1084, found 354.1087.

3-fluoro-*N*-(5-nitroquinolin-8-yl)benzamide (2h): Yellow solid in 73% yield; mp 236–237 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 9.31 (d, J = 8.7 Hz, 1H), 9.01–8.98 (m, 2H), 8.61 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.80–7.76 (m, 2H), 7.60–7.55 (m, 1H),7.36–7.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 163.0, 149.2, 140.5, 139.0, 137.8, 136.4, 133.5, 130.8, 127.8, 124.8, 122.9, 121.8, 119.7, 114.9, 113.9; HRMS (ESI): calculated for $C_{16}H_{10}FN_3O_3$: $[M + H]^+$ requires 312.0779, found 312.0781.

4-fluoro-*N*-(5-nitroquinolin-8-yl)benzamide (2i): Yellow solid in 75% yield; mp 218–219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.03 (s, 1H), 9.31 (d, J = 8.6 Hz, 1H), 9.01–8.96 (m, 2H), 8.60 (d, J = 8.8 Hz, 1H), 8.13–8.09 (m, 2H), 7.77 (dd, J = 9.2, 4.1 Hz, 1H), 7.29–7.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 164.6, 149.1, 140.7, 138.8, 137.7, 133.5, 130.4, 130.0, 127.9, 124.8, 121.8, 116.2, 113.7; HRMS (ESI): calculated for $C_{16}H_{10}FN_3O_3$: $[M + H]^+$ requires 312.0779, found 312.0778.

3-chloro-*N*-(5-nitroquinolin-8-yl)benzamide (2j): Yellow solid in 74% yield; mp 234–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1H), 9.31 (d, J = 8.7 Hz, 1H), 8.99 (d, J = 8.8Hz, 2H), 8.62 (d, J = 8.8 Hz, 1H),8.07 (s, 1H), 7.96 (d, J = 7.5 Hz, 1H), 7.78 (dd, J = 9.1, 4.1 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.8Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 149.2, 140.5, 139.0, 137.8, 135.9, 135.3, 133.5, 132.7, 130.3, 127.9, 127.8, 125.4, 124.8, 121.8, 114.0; HRMS (ESI): calculated for $C_{16}H_{10}ClN_3O_3$: $[M + H]^+$ requires 328.0483, found 328.0483.

4-chloro-*N*-(5-nitroquinolin-8-yl)benzamide (2k) [37]: Yellow solid in 76% yield; mp 210–212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.05 (s, 1H), 9.32 (d, J = 8.1 Hz, 1H), 9.01–8.97 (m, 2H), 8.62 (d, J = 8.8 Hz, 1H), 8.04 (d, J = 8.5 Hz, 2H), 7.77 (dd, J = 9.1, 4.1 Hz, 1H), 7.56 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 149.2, 140.6, 139.1, 138.9, 137.8, 133.5, 132.5, 129.4, 128.9, 127.8, 124.8, 121.8, 113.9; HRMS (ESI): calculated for $C_{16}H_{10}ClN_3O_3$: $[M + H]^+$ requires 328.0483, found 328.0484.

3-bromo-*N*-(5-nitroquinolin-8-yl)benzamide (2l): Yellow solid in 78% yield; mp 213–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.00 (s, 1H), 9.36 (d, J = 8.8 Hz, 1H), 8.96 (d, J = 8.9 Hz, 2H), 8.61 (d, J = 8.8 Hz, 1H), 8.23 (s, 1H), 8.01 (d, J = 7.7 Hz, 1H), 7.78–7.75 (m, 2H), 7.49 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 149.2, 140.4, 139.0, 137.8, 136.1, 135.6, 133.5, 130.8, 130.5, 127.8, 125.9, 124.8, 123.3, 121.8, 114.0; HRMS (ESI): calculated for $C_{16}H_{10}BrN_3O_3$: $[M + H]^+$ requires 371.9978, found 371.9979.

4-bromo-*N*-(5-nitroquinolin-8-yl)benzamide (2m): Yellow solid in 72% yield; mp 279–280 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 9.32 (d, J = 8.2 Hz, 1H), 9.01–8.97 (m, 2H), 8.62 (d, J = 8.9 Hz, 1H),7.96 (d, J = 8.3Hz, 2H), 7.78 (dd, J = 8.9, 4.3 Hz, 1H), 7.72 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 149.2, 140.6, 138.9, 137.8, 133.5, 133.0, 132.3, 129.0, 127.8, 127.6, 124.8, 121.8, 113.9; HRMS (ESI): calculated for $C_{16}H_{10}BrN_3O_3$: $[M + H]^+$ requires 371.9978, found 371.9977.

***N*-(5-nitroquinolin-8-yl)-3-(trifluoromethyl)benzamide (2n):** Yellow solid in 75% yield; mp 181–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.08 (s, 1H), 9.30 (d, J = 8.6 Hz, 1H), 8.99–8.97 (m, 2H), 8.61 (d, J = 8.8 Hz, 1H), 8.36 (s, 1H), 8.25 (d, J = 7.6 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.79–7.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 149.3, 140.3, 139.1, 137.7, 135.0, 133.7, 133.5, 130.4, 129.7, 129.2, 127.7, 124.9, 124.7, 122.1, 114.0; HRMS (ESI): calculated for $C_{17}H_{10}F_3N_3O_3$: $[M + H]^+$ requires 362.0747, found 362.0748.

2-chloro-4-methoxy-*N*-(5-nitroquinolin-8-yl)benzamide (2p): Yellow solid in 65% yield; mp 262–263 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 9.33 (d, J = 8.8 Hz, 1H), 8.99–8.97 (m, 2H), 8.62 (d, J = 8.8 Hz, 1H), 8.14 (d, J = 1.2 Hz, 1H), 8.02 (d, J = 8.6 Hz, 1H), 7.77 (dd, J = 8.9, 4.1 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 158.5, 149.1, 140.8, 138.7, 137.8, 133.5, 129.7, 127.9, 127.7, 127.2, 124.8, 123.3, 121.9, 113.7, 111.8, 56.5; HRMS (ESI): calculated for $C_{17}H_{12}ClN_3O_4$: $[M + H]^+$ requires 358.0589, found 358.0591.

***N*-(5-nitroquinolin-8-yl)thiophene-2-carboxamide (2q) [35]:** Yellow solid in 69% yield; mp 220–221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.90 (s, 1H), 9.30 (d, J = 8.8 Hz, 1H), 8.96–8.95 (m, 1H), 8.91 (d, J = 8.8 Hz, 1H), 8.59 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 3.1 Hz, 1H), 7.76 (dd,

J = 8.9, 4.1 Hz, 1H), 7.65 (d, *J* = 4.8 Hz, 1H), 7.24–7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 149.1, 140.6, 139.0, 138.7, 137.5, 133.5, 132.2, 129.4, 128.2, 127.9, 124.8, 121.9, 113.7.

***N*-(5-nitroquinolin-8-yl)pivalamide (2r) [37]:** Yellow solid in 73% yield; mp 172–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 9.27–9.25 (m, 1H), 8.92 (d, *J* = 3.0 Hz, 1H), 8.84 (d, *J* = 8.8 Hz, 1H), 8.54 (d, *J* = 8.8 Hz, 1H), 7.71 (dd, *J* = 8.8, 4.1 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 149.0, 141.0, 138.3, 137.7, 133.3, 127.9, 124.6, 121.7, 113.4, 40.7, 27.6.

***N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2a′) [37]:** Yellow solid in 75% yield; mp 202–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.08 (s, 1H), 9.12 (d, *J* = 8.9 Hz, 1H), 8.91 (d, *J* = 8.8, 1H), 8.49 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 7.3 Hz, 2H), 7.66–7.57 (m, 4H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 158.5, 140.1, 138.7, 137.3, 134.3, 133.3, 132.6, 129.1, 127.4, 126.7, 125.6, 119.9, 113.7, 25.2; HRMS (ESI): calculated for $C_{17}H_{13}N_3O_3$: $[M + H]^+$ requires 308.1030, found 308.1035.

2-methyl-*N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2b′): Yellow solid in 75% yield; mp 209–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 9.15 (d, *J* = 8.9 Hz, 1H), 8.96 (d, *J* = 8.8, 1H), 8.51 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.48–7.44 (m, 1H), 7.39–7.35 (m, 2H), 2.75 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 158.6, 140.3, 138.9, 137.2, 137.2, 135.6, 133.3, 131.8, 131.1, 127.5, 126.7, 126.3, 125.6, 120.0, 113.7, 25.1, 20.4; HRMS (ESI): calculated for $C_{18}H_{15}N_3O_3$: $[M + H]^+$ requires 322.1186, found 322.1190.

3-methyl-*N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2c′): Yellow solid in 79% yield; mp 184–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1H), 9.15 (d, *J* = 8.9 Hz, 1H), 8.93 (d, *J* = 8.8 Hz, 1H), 8.51 (d, *J* = 8.8 Hz, 1H), 7.91 (s, 1H), 7.81 (d, *J* = 6.9 Hz, 1H), 7.59 (d, *J* = 8.9 Hz, 1H), 7.49–7.43 (m, 2H), 2.83 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 158.4, 140.2, 139.0, 138.7, 137.3, 134.3, 133.4, 133.3, 128.9, 128.3, 126.8, 125.6, 124.2, 120.0, 113.7, 25.2, 21.5; HRMS (ESI): calculated for $C_{18}H_{15}N_3O_3$: $[M + H]^+$ requires 322.1186, found 322.1190.

4-methyl-*N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2d′): Yellow solid in 78% yield; mp 206–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 9.09 (d, *J* = 8.9 Hz, 1H), 8.86 (d, *J* = 8.8 Hz, 1H), 8.44 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 2.81 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 158.4, 143.3, 140.2, 138.5, 137.2, 133.2, 131.3, 129.7, 127.4, 126.8, 125.6, 120.0, 113.5, 25.2, 21.6; HRMS (ESI): calculated for $C_{18}H_{15}N_3O_3$: $[M + H]^+$ requires 322.1186, found 322.1189.

2-methoxy-*N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2e′): Yellow solid in 75% yield; mp 258–259 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.46 (s, 1H), 9.17 (d, *J* = 8.9 Hz, 1H), 9.10 (d, *J* = 8.9 Hz, 1H), 8.51 (d, *J* = 8.9 Hz, 1H), 8.33 (d, *J* = 6.6 Hz, 1H), 7.60–7.55 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 4.23 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 157.9, 157.8, 141.6, 137.8, 134.0, 133.2, 132.8, 127.0, 125.3, 121.7, 121.6, 120.1, 114.7, 111.6, 56.2, 25.3; HRMS (ESI): calculated for $C_{18}H_{15}N_3O_4$: $[M + H]^+$ requires 338.1135, found 338.1139.

3-fluoro-*N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2f′): Yellow solid in 71% yield; mp 251–252 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 11.10 (s, 1H), 9.17 (d, *J* = 8.9 Hz, 1H), 8.94 (d, *J* = 8.8 Hz, 1H), 8.53 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 9.2 Hz, 1H), 7.63–7.55 (m, 2H), 7.36–7.32 (m, 1H), 2.84 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) *δ* 164.3, 161.8, 158.7, 139.8, 139.1, 137.4, 136.6, 133.5, 130.8, 126.7, 125.7, 122.8, 120.0, 119.6, 114.9, 113.9, 25.3; HRMS (ESI): calculated for $C_{17}H_{12}FN_3O_3$: $[M + H]^+$ requires 326.0935, found 326.0938.

4-fluoro-*N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2g′): Yellow solid in 66% yield; mp 218–219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 1H), 9.16 (d, *J* = 8.9 Hz, 1H), 8.93 (d, *J* = 8.8, 1H), 8.52 (d, *J* = 8.8 Hz, 1H), 8.11–8.08 (m, 2H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.29–7.25 (m, 2H), 2.83 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.3, 158.5, 140.0, 138.9, 137.3, 133.5, 130.5, 129.9, 126.7, 125.7, 120.0, 116.2, 113.8, 25.3; HRMS (ESI): calculated for $C_{17}H_{12}FN_3O_3$: $[M + H]^+$ requires 326.0935, found 326.0938.

3-chloro-*N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2h′): Yellow solid in 67% yield; mp 215–216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 11.08 (s, 1H), 9.15 (d, *J* = 8.9 Hz, 1H),

8.91 (d, *J* = 8.8 Hz, 1H), 8.51 (d, *J* = 8.8 Hz, 1H), 8.07 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 9.2 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 2.83 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) *δ* 164.1, 158.7, 139.7, 139.1, 137.3, 136.1, 135.4, 133.4, 132.6, 130.3, 127.9, 126.6, 125.7, 125.2, 120.0, 113.9, 25.3; HRMS (ESI): calculated for $C_{17}H_{12}ClN_3O_3$: $[M + H]^+$ requires 342.0640, found 342.0642.

4-chloro-*N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2i′) [37]: Yellow solid in 68% yield; mp 221–222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 11.08 (s, 1H), 9.16 (d, *J* = 8.9 Hz, 1H), 8.93 (d, *J* = 8.8 Hz, 1H), 8.52 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 164.5, 158.6, 139.9, 140.0, 139.0, 137.3, 133.5, 132.7, 129.4, 128.8, 126.7, 125.7, 120.0, 113.9, 25.3; HRMS (ESI): calculated for $C_{17}H_{12}ClN_3O_3$: $[M + H]^+$ requires 342.0640, found 342.0641.

3-bromo-*N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2j′): Yellow solid in 66% yield; mp 203–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 9.16 (d, *J* = 8.9 Hz, 1H), 8.91 (d, *J* = 8.8 Hz, 1H), 8.51 (d, *J* = 8.8 Hz, 1H), 8.23 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 2.88 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 158.7, 139.7, 139.1, 137.3, 136.2, 135.5, 133.4, 130.9, 130.5, 126.6, 125.7, 125.7, 123.3, 119.9, 113.9, 25.3; HRMS (ESI): calculated for $C_{17}H_{12}BrN_3O_3$: $[M + H]^+$ requires 386.0135, found 386.0136.

4-bromo-*N*-(2-methyl-5-nitroquinolin-8-yl)benzamide (2k′): Yellow solid in 71% yield; mp 249–250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 9.15 (d, *J* = 8.9 Hz, 1H), 9.17 (d, *J* = 9.0, 1H), 8.93 (d, *J* = 8.8 Hz, 1H), 8.52 (d, *J* = 8.8 Hz, 1H), 7.94(d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.9 Hz, 1H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 158.6, 139.8, 139.0, 137.3, 133.5, 133.2, 132.4, 128.9, 127.5, 126.7, 125.7, 120.0, 113.9, 25.3; HRMS (ESI): calculated for $C_{17}H_{12}BrN_3O_3$: $[M + H]^+$ requires 386.0135, found 386.0136.

***N*-(2-methyl-5-nitroquinolin-8-yl)-3-(trifluoromethyl)benzamide (2l′):** Yellow solid in 56% yield; mp 191–192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 11.19 (s, 1H), 9.15 (d, *J* = 8.9 Hz, 1H), 8.92 (d, *J* = 8.8 Hz, 1H), 8.53 (d, *J* = 8.8 Hz, 1H), 8.34 (s, 1H), 8.26 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 2.84 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) *δ* 164.0, 158.7, 139.6, 139.2, 137.3, 135.1, 133.5, 131.7, 130.5, 129.8, 129.1, 126.6, 125.8, 124.5, 123.6, 119.9, 113.9, 25.2; HRMS (ESI): calculated for $C_{18}H_{12}F_3N_3O_3$: $[M + H]^+$ requires 376.0904, found 376.0907.

***N*-(2-methyl-5-nitroquinolin-8-yl)-4-(trifluoromethyl)benzamide (2m′):** Yellow solid in 59% yield; mp 208–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.16 (s, 1H), 9.18 (d, *J* = 8.9 Hz, 1H), 8.96 (d, *J* = 8.8 Hz, 1H), 8.54 (d, *J* = 8.8 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.9 Hz, 1H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 158.7, 139.6, 139.3, 137.6, 137.4, 134.1, 133.5, 127.9, 126.6, 126.2, 125.8, 123.6, 120.0, 114.1, 25.3; HRMS (ESI): calculated for $C_{18}H_{12}F_3N_3O_3$: $[M + H]^+$ requires 376.0904, found 376.0905.

***N*-(2-methyl-5-nitroquinolin-8-yl)thiophene-2-carboxamide (2n′):** Yellow solid in 72% yield; mp 257–258 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 9.16 (d, *J* = 8.8 Hz, 1H), 8.85 (d, *J* = 8.8 Hz, 1H), 8.51 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.67 (d, *J* = 4.5 Hz, 1H), 7.61 (d, *J* = 8.9 Hz,1H), 7.23 (d, *J* = 3.9 Hz, 1H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 158.5, 139.9, 139.2, 138.8, 137.1, 133.4, 132.0, 129.3, 128.2, 126.8, 125.7, 120.0, 113.7, 25.2; HRMS (ESI): calculated for $C_{15}H_{11}N_3O_3S$: $[M + H]^+$ requires 314.0594, found 314.0596.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal14040263/s1, Table S1: Screening of reaction conditions. Copies of 1H and 13C NMR spectra for the products.

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