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Palladium-Catalyzed sp^3 C–H Nitration of 8-Methylquinolines

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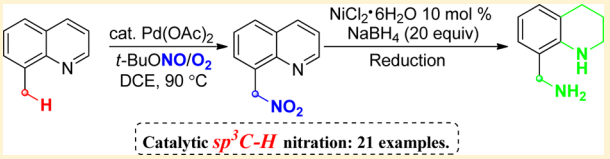
Supporting Information

ABSTRACT: Palladium-catalyzed nitration of 8-methylquinolines with *t*-BuONO to give 8-(nitromethyl)quinolines in moderate to excellent yields has been developed involving an sp^3 C–H bond activation. The resulting (nitromethyl)quinolines could be selectively reduced to (1,2,3,4-tetrahydroquinolin-8-yl)-methanamines by $NaBH_4$ in the presence of a catalytic amount of $NiCl_2{\cdot}6H_2O$.



Nitro compounds are regarded as ideal intermediates and frequently used as platform molecules in synthetic chemistry owing to the versatile transformation of the nitro group into other functional groups.[1−3] As for the preparation of nitroarenes, the traditional and predominant synthetic approach relies on electrophilic aromatic substitution by a certain nitrating agent. However, this process generally has limitations with respect to poor regio- and chemoselectivity, imperfect functional group and/or substrate tolerance, and strong orientation effects of different functional groups.[4] For regioselective issues to be overcome, several strategies[5] have been adopted including *ipso*-nitrodemetalation of organometallic reagents,[6] *ipso*-nitrodecarboxylation of aryl carboxylic acids,[7] *ipso*-oxidation of aryl amines or azides to nitroarenes,[8] and *ipso*-nitration of aryl halides catalyzed by transition metals.[9] In 2010, we initially developed,[10] extended by others,[11] an alternative *ipso*-nitration protocol directly from aromatic C–H bonds involving transition metal-catalyzed chelation-assisted C–H nitrations (Scheme 1a).

As for the preparation of nitroalkanes, the selective nitration of aliphatic C–H bonds is very challenging in comparison with the easy nitration of aromatic C–H bonds by nitrating agents. The main problem lies in the requirement of high temperatures (>200 °C) for the nitration of aliphatic hydrocarbons, which will lead to undesired C–C bond scissions and complicated products.[12] Therefore, the development of mild and selective methods for the nitration of aliphatic C–H bonds is highly desirable.[13] Encouraged by the increasing progress in transition metal-catalyzed/mediated sp^3 C–H bond functionalizations,[14] we have very recently reported the first example of transition metal-mediated ($AgNO_2$) sp^3 C–H nitration in a highly selective manner (Scheme 1b).[15] Later, we further devoted our efforts to exploring transition metal-catalyzed nitration reactions of sp^3 C–H bonds, thereby achieving an efficient and mild nitration of 8-methylquinolines via a Pd-catalyzed sp^3 C–H bond activation (Scheme 1c).[16a] Here, we present our findings and results.

In recent years, 8-methylquinolines have been served as useful substrates for the investigation of transition metal-catalyzed sp^3 C–H functionalizations.[17] We thus chose 8-methylquinoline **1a** as a model substrate for the sp^3 C–H nitration (Table 1). When **1a** was subjected to the standard reaction conditions for the aromatic sp^2 C–H nitration (10 mol % of $Pd(OAc)_2$, 2 equiv of $AgNO_2/K_2S_2O_8$, in DCE at 110 °C) according to our previous work,[10a,b] the reaction failed to give desired nitrated product **2a**; instead, the starting material was recovered (entry 1, Table 1). Switching the nitro source/oxidant to other combinations, such as $AgNO_2$/oxone, $NaNO_2/K_2S_2O_8$, and $KNO_2/K_2S_2O_8$, still gave the same result (entries 2–4, Table 1). To our delight, when *t*-BuONO was used as a nitro source, the nitration of **1a** was successfully achieved, and **2a** was obtained in 70% yield (entry 5, Table 1).

Scheme 1. Strategies for the sp^2 C–H and sp^3 C–H Bond Nitration

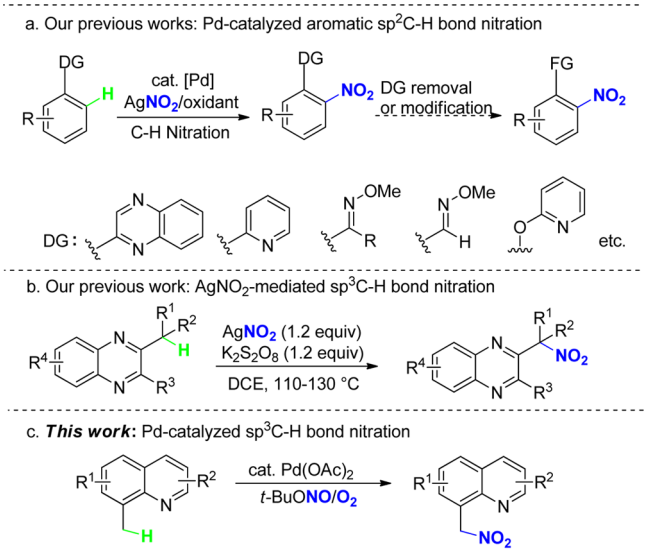


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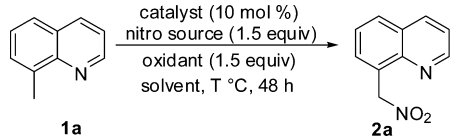
Table 1. Optimization of Reaction Conditions[a]



1a 2a

entry	catalyst	nitro source	oxidant	T (°C)	solvent	yield (%)[b]
1[c]	$Pd(OAc)_2$	$AgNO_2$	$K_2S_2O_8$	110	DCE[d]	0
2[c]	$Pd(OAc)_2$	$AgNO_2$	Oxone	110	DCE	0
3[c]	$Pd(OAc)_2$	$NaNO_2$	$K_2S_2O_8$	110	DCE	0
4[c]	$Pd(OAc)_2$	KNO_2	$K_2S_2O_8$	110	DCE	0
5	$Pd(OAc)_2$	*t*-BuONO/air		110	DCE	70
6	$Pd(CH_3CN)_2Cl_2$	*t*-BuONO/air		110	DCE	41
7	$PdCl_2$	*t*-BuONO/air		110	DCE	20
8	$Pd(PPh_3)_2Cl_2$	*t*-BuONO/air		110	DCE	17
9		*t*-BuONO/air		110	DCE	0
10	$Pd(OAc)_2$	*t*-BuONO/air		100	DCE	73
11	$Pd(OAc)_2$	*t*-BuONO/air		90	DCE	75
12	$Pd(OAc)_2$	*t*-BuONO/air		80	DCE	68
13	**$Pd(OAc)_2$**	***t*-BuONO/O_2**[e]		**90**	**DCE**	**93**
14	$Pd(OAc)_2$	*t*-BuONO/O_2		90	THF	0
15	$Pd(OAc)_2$	*t*-BuONO/O_2		90	1,4-dioxane	43
16	$Pd(OAc)_2$	*t*-BuONO/O_2		90	DMF	12
17	$Pd(OAc)_2$	*t*-BuONO/O_2		90	toluene	21
18[f]	$Pd(OAc)_2$	*t*-BuONO/O_2		90	DCE	39
19[g]	$Pd(OAc)_2$	*t*-BuONO/O_2		90	DCE	69
20[h]	$Pd(OAc)_2$	*t*-BuONO/O_2		90	DCE	41

[a]Reaction conditions: **1a** (0.3 mmol), catalyst (0.03 mmol), and *t*-BuONO (0.45 mmol) in 3 mL of solvent for 48 h unless otherwise noted. [b]GC yields using phenanthrene as an internal standard. [c]The amounts of nitro sources and oxidants are 2 equiv based on **1a**. [d]DCE: 1,2-dichloroethane. [e]O_2 pressure: 1 atm. [f]The catalyst loading is 5 mol % based on **1a**. [g]Reaction time is 36 h. [h]Reaction time is 24 h.

It was found that $Pd(CH_3CN)_2Cl_2$, $PdCl_2$, and $Pd(PPh_3)_2Cl_2$ showed low catalytic activity (entries 6−8, Table 1). Controlled experiments showed that the reaction failed to yield the desired product without a palladium catalyst instead recovering the starting material (entry 9, Table 1). Further screening of the parameter of temperature indicated that 90 °C was a more suitable temperature for the reaction (entries 10−12, Table 1). Gratifyingly, when the reaction was performed under an O_2 (1 atm) atmosphere, target product **2a** could be obtained in a higher yield of 93% (entry 13, Table 1). Investigating various solvents indicated that the reaction performed well in DCE whereas other solvents, including THF, 1,4-dioxane, DMF, and toluene, were not suitable for the reaction (entries 14−17, Table 1). Lowering the catalyst loading (5 mol % of Pd) and shortening the reaction times decreased the yield of **2a** (entries 18−20, Table 1).

With the optimized reaction conditions established, we then focused on investigating the substrate scope for the sp^3 C−H nitration (Table 2). A variety of 8-methylquinolines with different substitution patterns underwent the sp^3 C−H nitration smoothly and gave the corresponding products in moderate to excellent yields (51%−95%, **2a−u**, Table 2). Generally, the electronic properties of the substitutents (electron-withdrawing or electron-donating) have little influence on the nitrating results in terms of the yield. Substrates possessing a phenyl group at the 3-position of the 8-methylquinoline ring could deliver the desired products in good yields (**2b−d**, 81%−89%, Table 2). Note that substrates bearing substituents at the 7-position of the 8-methylquinoline scaffold could also be nitrated smoothly without being affected much by the steric hindrance of the substitutents (**2p−u**, Table 2). When 8-ethylquinoline and 8-isopropylquinoline were used, the reaction failed to give the target products.[17a] 5-Methylquinoxaline was also an inert substrate for the sp^3 C−H nitration (**2v**, Table 2). Notably, the halo (F, Cl, and Br) and nitro groups were compatible with the nitrating conditions, which may give opportunities for further chemical transformations (**2d**, **2f−I**, **2l−o**, and **2q−s**, Table 2).

To fully demonstrate the synthetic potential of the present method, we tried the nitration of **1a** at the gram-scale. To our delight, nitrated product **2a** was obtained in a satisfactory yield (81%, eq 1, Scheme 2). In addition, the selective reduction of **1a** to (1,2,3,4-tetrahydroquinolin-8-yl)methanamine **3a** was achieved. Thus, **1a** could be selectively reduced to **3a** in 92% yield by using 20 equiv of $NaBH_4$ in the presence of $NiCl_2 \cdot 6H_2O$ (10 mol %) (eq 2, Scheme 2).[18]

To gain insight into the mechanism of the sp^3 C−H nitration, we carried out several mechanistic experiments (Scheme 3). First, an intermolecular competition experiment between electron-rich substrate **1e** and electron-deficient substrate **1h** (both substituted at the 5-position) showed that the molar ratio of products **2e** and **2h** was 42:58 (eq 1, Scheme 3), whereas electron-rich substrate **1p** and electron-deficient substrate **1u** (both substituted at the 7-position) showed that the molar ratio of products **2p** and **2u** was 69:31 (eq 2, Scheme 3). These results showed that both the electronic nature of substituents and the substituted position have a certain effect on the reactivity of the substrates. Next, palladacycle intermediate **A** was prepared through a stoichiometric reaction of $Pd(OAc)_2$ with 8-methylquinoline **1a** in AcOH according to reported literature (eq 3, Scheme 3).[19] Employing **A** (5 mol %) as a catalyst, the nitration of **1a** also occurred smoothly to give

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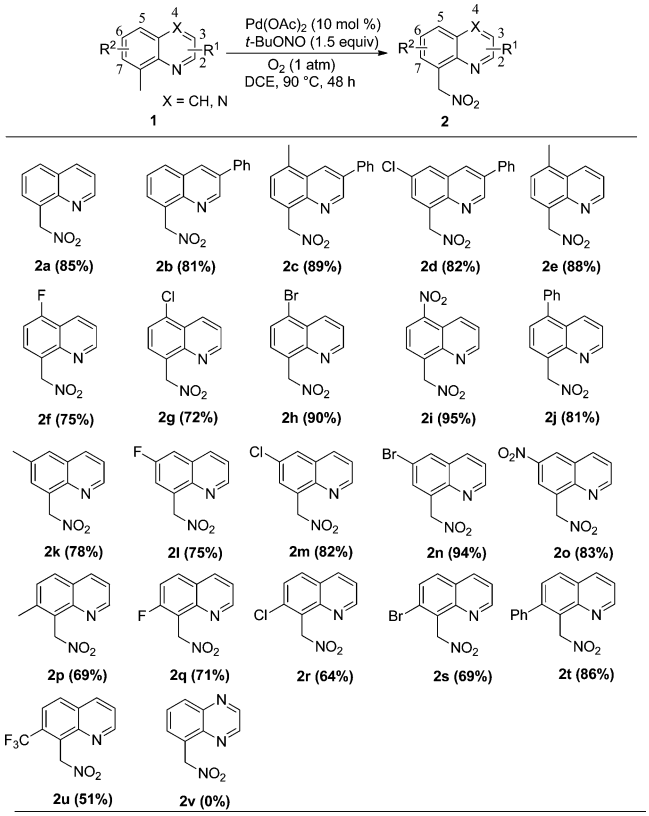
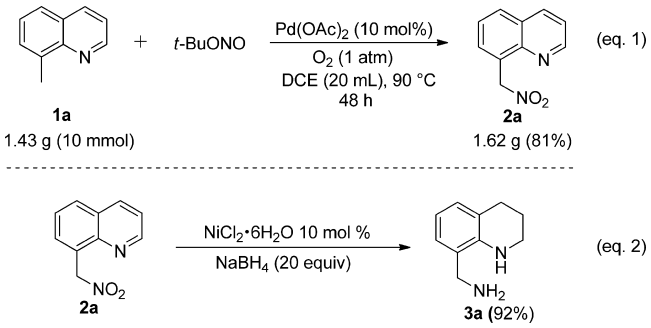
Table 2. Palladium-Catalyzed Nitration of 8-Methylquinolines 1 for the Synthesis of 2 via sp^3 C−H Bond Activation[a]



[a]Reaction conditions: **1** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol), and *t*-BuONO (0.45 mmol), in 3.0 mL of DCE under an O_2 atmosphere (1 atm) at 90 °C for 48 h.

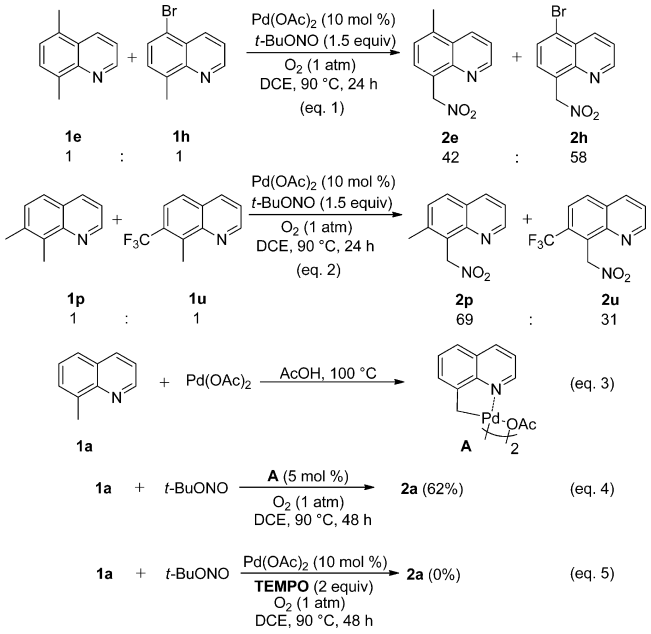
Scheme 2. Gram-Scale Nitration of 1a and the Selective Reduction of 1a to 3a



2a in 62% yield (eq 4, Scheme 3). Finally, it was found that the addition of TEMPO, a radical scavenger,[20] to the reactants significantly suppressed the nitrating reaction, suggesting a radical process might be involved (eq 5, Scheme 3).[10,11d,16]

On the basis of these preliminary results and related literature,[10,11d,16] a possible mechanism for palladium-catalyzed sp^3 C−H nitration of 8-methylquinoline **1a** is proposed (Scheme 4). Initially, binuclear palladacycle species **A** was produced from **1a** and $Pd(OAc)_2$,[19] and the NO radical generated from *tert*-butyl nitrite was converted to the NO_2 radical under aerobic conditions.[11d,16] Then the addition of NO_2 radicals to the palladium center of **A** delivered Pd(III)−Pd(III) species **B**[10,21] and/or Pd(IV)−Pd(II) species **C**.[10,22,23]

Scheme 3. Mechanistic Experiments



The reductive elimination of **B** and/or **C** in the presence of another molecule of **1a** could deliver **2a** and regenerate **A**.[10,21−23]

CONCLUSION

In summary, we have developed a palladium(II)-catalyzed sp^3 C−H nitration of 8-methylquinolines to give 8-(nitromethyl)-quinolines in moderate to excellent yields under relatively mild conditions. Notably, the nitration could be conducted on a gram-scale and applied to the synthesis of (1,2,3,4-tetrahydroquinolin-8-yl)methanamines based on selective reductions.

EXPERIMENTAL SECTION

General Information. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a spectrometer at 25 °C in $CDCl_3$ at 500 and 125 MHz, respectively, with TMS as the internal standard. Chemical shifts (δ) are expressed in ppm, and coupling constants (J) are given in Hz. The IR spectra were recorded on an FT-IR spectrometer. GC-MS experiments were performed with an EI source, and high resolution mass spectra (HRMS) were obtained on a TOF MS instrument with an EI source. 8-Methylquinolines (**1a−t**) were prepared according to reported literature.[19,24]

General Procedure for the Synthesis of 8-(Nitromethyl)quinolines (2) from 8-Methylquinolines (1). A mixture of 8-methylquinolines **1** (0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), *t*-BuONO (46.4 mg, 0.45 mmol), and anhydrous DCE (3.0 mL) was sealed in a 15 mL Schlenk flask under 1 atm O_2. Then, the flask was stirred at 90 °C for 48 h. After being cooled to room temperature, the mixture was filtered with Celite, and the filtrate was evaporated in a vacuum. The residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to give pure **2**.

8-(Nitromethyl)quinoline (2a). Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (48.0 mg, 85%); mp 64−65 °C; IR (KBr) ν 1518 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.98 (dd, J_1 = 4.5, J_2 = 2.0 Hz, 1H), 8.20 (dd, J_1 = 8.5, J_2 = 2.0 Hz, 1H), 7.89 (dd, J_1 = 8.5 Hz, J_2 = 1.0 Hz, 1H), 7.81 (d, J = 7.0 Hz, 1H), 7.57 (t, J = 8.5 Hz, 1H), 7.48 (dd, J_1 = 8.0 Hz, J_2 = 4.5 Hz, 1H), 6.22 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.3, 146.2, 136.3, 130.6, 129.9, 129.5, 128.3, 126.1, 121.7, 71.1; HRMS (EI) for $C_{10}H_8N_2O_2$ $[M]^+$ calcd 188.0586, found 188.0594.

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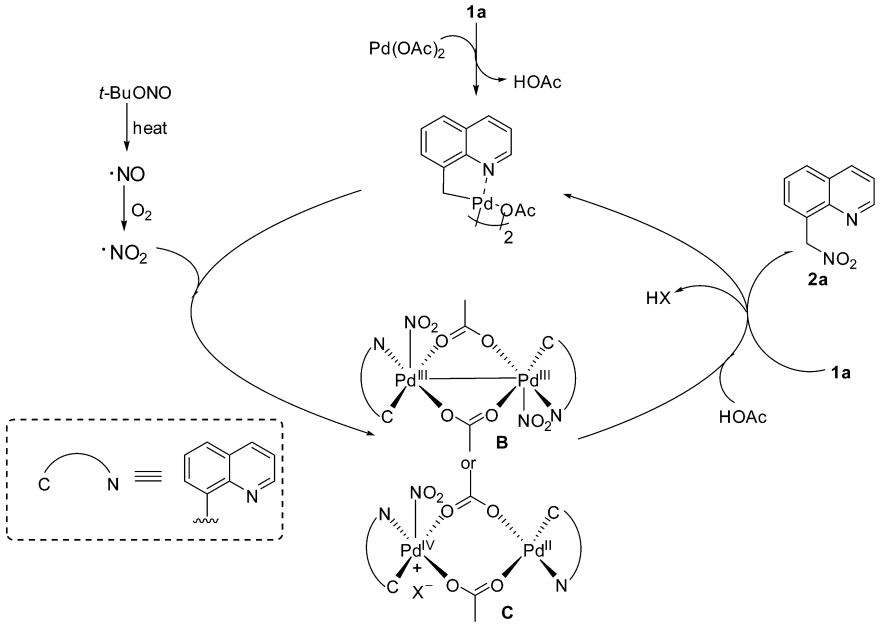
Scheme 4. Proposed Mechanism



*8-(Nitromethyl)-3-phenylquinoline (**2b**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a yellow oil (64.2 mg, 81%); IR (neat) ν 1518 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.24 (d, J = 2.5 Hz, 1H), 8.34 (d, J = 2.5 Hz, 1H), 7.95 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.80−7.48 (m, 8H), 6.25 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 149.8, 145.1, 138.5, 137.5, 134.5, 133.4, 130.5, 129.8, 129.6, 129.3, 128.3, 127.4, 126.6, 71.1; HRMS (EI) for $C_{16}H_{12}N_2O_2$ $[M]^+$ calcd 264.0899, found 264.0891.

*5-Methyl-8-(nitromethyl)-3-phenylquinoline (**2c**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a yellow oil (74.3 mg, 89%); IR (neat) ν 1517 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.26 (d, J = 2.0 Hz, 1H), 8.52 (s, 1H), 7.74−7.72 (m, 3H), 7.59−7.45 (m, 5H), 6.22 (s, 2H), 2.79 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 149.1, 137.8, 137.0, 134.2, 130.6, 130.3, 129.3, 128.4, 127.9, 127.6, 127.5, 127.22, 127.20, 71.4, 18.9; HRMS (EI) for $C_{17}H_{14}N_2O_2$ $[M]^+$ calcd 278.1055, found 278.1048.

*6-Chloro-8-(nitromethyl)-3-phenylquinoline (**2d**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a yellow oil (73.5 mg, 82%); IR (neat) ν 1518 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.21 (d, J = 2.0 Hz, 1H), 8.23 (d, J = 2.5 Hz, 1H), 7.90 (d, J = 2.0 Hz, 1H), 7.74−7.47 (m, 6H), 6.20 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.0, 143.4, 137.1, 135.4, 132.8, 132.4, 132.3, 129.9, 129.3, 128.9, 128.6, 127.8, 127.4, 70.1; HRMS (EI) for $C_{16}H_{11}ClN_2O_2$ $[M]^+$ calcd 298.0509, found 298.0501.

*5-Methyl-8-(nitromethyl)quinoline (**2e**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (53.4 mg, 88%); mp 82−84 °C; IR (neat) ν 1515 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.98 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 1H), 8.38 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.50 (dd, J_1 = 8.5 Hz, J_2 = 4.0 Hz, 1H), 7.40 (d, J = 7.0 Hz, 1H), 6.17 (s, 2H), 2.72 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 149.8, 146.3, 136.8, 132.9, 130.2, 128.4, 127.7, 126.6, 121.2, 71.5, 18.7; HRMS (EI) for $C_{11}H_{10}N_2O_2$ $[M]^+$ calcd 202.0742, found 202.0748.

*5-Fluoro-8-(nitromethyl)quinoline (**2f**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (46.4 mg, 75%); mp 51−53 °C; IR (KBr) ν 1519 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.02 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 1H), 8.47 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.77 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 7.54 (dd, J_1 = 8.5 Hz, J_2 = 4.0 Hz, 1H), 7.24 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 6.15 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 158.6 (d, J = 257.5 Hz), 151.2, 146.9 (d, J = 2.5 Hz), 130.2 (d, J = 10 Hz), 129.5 (d, J = 5 Hz), 126.7 (d, J = 3.8 Hz), 121.7 (d, J = 2.5 Hz), 119.2 (d, J = 16.3 Hz), 109.7 (d, J = 20 Hz), 70.7; HRMS (EI) for $C_{10}H_7FN_2O_2$ $[M]^+$ calcd 206.0492, found 206.0498.

*5-Chloro-8-(nitromethyl)quinoline (**2g**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (48.1 mg, 72%); mp 49−51 °C; IR (KBr) ν 1519 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.00 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 8.60 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 4.0 Hz, 1H), 6.16 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.9, 146.6, 133.1, 132.9, 130.1, 129.5, 126.4, 126.2, 122.4, 70.7; HRMS (EI) for $C_{10}H_7ClN_2O_2$ $[M]^+$ calcd 222.0196, found 222.0191.

*5-Bromo-8-(nitromethyl)quinoline (**2h**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (72.1 mg, 90%); mp 47−48 °C; IR (KBr) ν 1520 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.99 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 1H), 8.59 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 4.5 Hz, 1H), 6.17 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 151.0, 146.7, 135.9, 130.9, 130.0, 129.9, 127.8, 123.6, 122.8, 70.7; HRMS (EI) for $C_{10}H_7BrN_2O_2$ $[M]^+$ calcd 265.9691, found 265.9685.

*5-Nitro-8-(nitromethyl)quinoline (**2i**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (66.5 mg, 95%); mp 68−70 °C; IR (KBr) ν 1519 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.08−9.04 (m, 2H), 8.40 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.73 (dd, J_1 = 9.0 Hz, J_2 = 4.5 Hz, 1H), 6.28 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 151.2, 145.9, 145.6, 138.7, 132.4, 126.2, 124.4, 124.1, 121.3, 70.2; HRMS (EI) for $C_{10}H_7N_3O_4$ $[M]^+$ calcd 233.0437, found 233.0445.

*8-(Nitromethyl)-5-phenylquinoline (**2j**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (64.2 mg, 81%); mp 88−90 °C; IR (KBr) ν 1518 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.97 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 8.24 (d, J = 1.5 Hz, 1H), 8.06 (dd, J_1 = 9.5 Hz, J_2 = 2.0 Hz, 1H), 7.72 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.54−7.45 (m, 4H), 6.27 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.2, 145.5, 139.8, 139.1, 136.5, 131.2, 129.7, 129.1, 128.6, 128.1, 127.5, 126.9, 122.0, 71.1; HRMS (EI) for $C_{16}H_{12}N_2O_2$ $[M]^+$ calcd 264.0899, found 264.0892.

*6-Methyl-8-(nitromethyl)quinoline (**2k**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (47.3 mg, 78%); mp 62−64 °C; IR (KBr) ν 1517 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.90 (d, J = 2.5 Hz, 1H), 8.11 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.64 (s, 2H), 7.44 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.18 (s, 2H), 2.56 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ

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149.5, 144.8, 136.1, 135.6, 132.2, 130.2, 128.4, 128.2, 71.2, 21.6; HRMS (EI) for $C_{11}H_{10}N_2O_2$ $[M]^+$ calcd 202.0742, found 202.0748.

*6-Fluoro-8-(nitromethyl)quinoline (**2l**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (46.4 mg, 75%); mp 74−76 °C; IR (KBr) ν 1519 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.92 (dd, J_1 = 9.0 Hz, J_2 = 1.5 Hz, 1H), 8.15 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.59 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 7.51−7.47 (m, 2H), 6.21 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 159.8 (d, J = 247.5 Hz), 149.5, 143.1, 135.7 (d, J = 6.3 Hz), 134.1 (d, J = 8.8 Hz), 129.2 (d, J = 10 Hz), 12.4, 119.4 (d, J = 27.5 Hz), 118.8 (d, J = 21.3 Hz), 70.2; HRMS (EI) for $C_{10}H_7FN_2O_2$ $[M]^+$ calcd 206.0492, found 206.0498.

*6-Chloro-8-(nitromethyl)quinoline (**2m**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (54.8 mg, 82%); mp 52−54 °C; IR (KBr) ν 1520 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.95 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 8.13 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.86 (d, J = 2.5 Hz, 1H), 7.75 (d, J = 2.5 Hz, 1H), 7.51 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.18 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.4, 144.5, 135.4, 133.1, 132.0, 130.1, 129.0, 127.7, 122.5, 70.1; HRMS (EI) for $C_{10}H_7ClN_2O_2$ $[M]^+$ calcd 222.0196, found 222.0189.

*6-Bromo-8-(nitromethyl)quinoline (**2n**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (75.3 mg, 94%); mp 64−66 °C; IR (KBr) ν 1521 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.96 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 8.10 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 8.02 (d, J = 2.0 Hz, 1H), 7.86 (d, J = 2.0 Hz, 1H), 7.49 (dd, J_1 = 8.5, Hz, J_2 = 4.0 Hz, 1H), 6.17 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.5, 144.6, 135.3, 133.0, 132.6, 131.1, 129.4, 122.5, 119.9, 70.1; HRMS (EI) for $C_{10}H_7BrN_2O_2$ $[M]^+$ calcd 265.9691, found 265.9687.

*6-Nitro-8-(nitromethyl)quinoline (**2o**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (58.1 mg, 83%); mp 105−107 °C; IR (KBr) ν 1523 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.14 (dd, J_1 = 4.5 Hz, J_2 = 2.0 Hz, 1H), 8.84 (d, J = 2.5 Hz, 1H), 8.56 (d, J = 2.5 Hz, 1H), 8.42 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.67 (dd, J_1 = 8.5 Hz, J_2 = 4.5 Hz, 1H), 6.24 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 153.6, 147.8, 145.0, 138.2, 133.7, 127.2, 125.5, 123.5, 122.4, 69.8; HRMS (EI) for $C_{10}H_7N_3O_4$ $[M]^+$ calcd 233.0437, found 233.0431.

*7-Methyl-8-(nitromethyl)quinoline (**2p**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (41.9 mg, 69%); mp 112−114 °C; IR (KBr) ν 1518 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.95 (dd, J_1 = 4.5 Hz, J_2 = 2.0 Hz, 1H), 8.14 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.46−7.40 (m, 2H), 6.35 (s, 2H), 2.66 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.4, 147.2, 141.2, 136.1, 129.6, 129.5, 126.6, 120.8, 68.0; HRMS (EI) for $C_{11}H_{10}N_2O_2$ $[M]^+$ calcd 202.0742, found 202.0735.

*7-Fluoro-8-(nitromethyl)quinoline (**2q**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (43.9 mg, 71%); mp 86−88 °C; IR (KBr) ν 1524 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.00 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 8.20 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.93 (dd, J_1 = 9.0 Hz, J_2 = 6.0 Hz, 1H), 7.48−7.39 (m, 2H), 6.24 (d, J = 1.5 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 162.3 (d, J = 253.8 Hz), 151.5, 147.4 (d, J = 7.5 Hz), 136.3, 131.9 (d, J = 10 Hz), 125.3, 121.0, 116.8 (d, J = 25 Hz), 114.5 (d, J = 13.8 Hz), 64.2; HRMS (EI) for $C_{10}H_7FN_2O_2$ $[M]^+$ calcd 206.0492, found 206.0486.

*7-Chloro-8-(nitromethyl)quinoline (**2r**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (42.7 mg, 64%); mp 106−108 °C; IR (KBr) ν 1520 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.99 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.48 (dd, J_1 = 8.5 Hz, J_2 = 4.5 Hz, 1H), 6.39 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 151.4, 147.4, 138.0, 136.2, 128.1, 127.2, 126.8, 121.7, 67.6; HRMS (EI) for $C_{10}H_7ClN_2O_2$ $[M]^+$ calcd 222.0196, found 222.0189.

*7-Bromo-8-(nitromethyl)quinolone (**2s**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (55.3 mg, 69%); mp 108−110 °C; IR (KBr) ν 1523 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.97 (dd, J_1 = 4.5 Hz, J_2 = 2.0 Hz, 1H), 8.17 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.77 (t, J = 9.0 Hz, 1H), 7.50 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.40 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 151.3, 147.5, 136.3, 130.9, 130.8, 129.4, 128.5, 127.2, 121.8, 70.1; HRMS (EI) for $C_{10}H_7BrN_2O_2$ $[M]^+$ calcd 265.9691, found 265.9699.

*8-(Nitromethyl)-7-phenylquinoline (**2t**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a white solid (68.2 mg, 86%); mp 92−94 °C; IR (KBr) ν 1517 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.97 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 8.24 (d, J = 1.5 Hz, 1H), 8.06 (dd, J_1 = 9.5 Hz, J_2 = 1.5 Hz, 2H), 7.72 (d, J = 7.5 Hz, 2H), 7.55−7.45 (m, 4H), 6.27 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.2, 145.5, 139.7, 139.1, 136.4, 131.2, 129.7, 128.6, 128.1, 127.5, 126.9, 122.0, 71.1; HRMS (EI) for $C_{16}H_{12}N_2O_2$ $[M]^+$ calcd 264.0899, found 264.0892.

*8-(Nitromethyl)-7-(trifluoromethyl)quinoline (**2u**).* Purified by column chromatography (petroleum ether/EtOAc, 10/1) as a yellow oil (39.2 mg, 51%); IR (KBr) ν 1520 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.05 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H), 8.23 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.57 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.42 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 151.8, 146.5, 136.2, 131.7 (q, J = 31.2 Hz), 130.7, 129.6, 128.9, 123.8 (q, J = 275 Hz), 123.4, 122.4 (q, J = 5 Hz), 66.1; HRMS (EI) for $C_{11}H_7F_3N_2O_2$ $[M]^+$ calcd 256.0460, found 256.0468.

*Selective Reduction of 8-(Nitromethyl)quinoline **2a** to (1,2,3,4-Tetrahydroquinolin-8-yl)methanamine **3a** using $NaBH_4$ in the Presence of $NiCl_2{\cdot}6H_2O$.* **2a** (0.50 mmol) and $NiCl_6{\cdot}H_2O$ (10 mol %) were dissolved in MeOH (4 mL), $NaBH_4$ (20 mmol) was added in portions with stirring under 0 °C for 0.5 h; then, the stirring was continued for another 2 h. The mixture was filtered with Celite, and the filtrate was evaporated in a vacuum. The residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to give pure **3a** (74.6 mg, 92%).

*(1,2,3,4-Tetrahydroquinolin-8-yl)methanamine (**3a**).* Purified by column chromatography (petroleum ether/EtOAc, 6/1) as a yellow oil; IR (neat) ν 3396 (NH) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.96 (d, J = 7.5 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 6.58 (t, J = 7.5 Hz, 1H), 4.83 (s, 2H), 3.38 (t, J = 5.5 Hz, 2H), 3.15 (br s, 3H), 2.81 (t, J = 6.0 Hz, 2H), 1.98−1.93 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 143.9, 129.7, 126.9, 123.7, 122.0, 116.0, 64.5, 42.0, 27.3, 21.8; HRMS (EI) for $C_{10}H_{14}N_2$ $[M]^+$ calcd 162.1157, found 162.1164.

Mechanistic Studies. *Intermolecular Competition Experiment on **1e** and **1h**.* A mixture of **1e** (0.15 mmol), **1h** (0.15 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), *t*-BuONO (46.4 mg, 0.45 mmol), and anhydrous DCE (3.0 mL) was sealed in a 15 mL Schlenk flask under 1 atm O_2. Then, the flask was stirred at 90 °C for 24 h. After being cooled to room temperature, the mixture was filtered with Celite, and the filtrate was evaporated in vacuum; the residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to give a mixture of **2e** and **2h** with a molar ratio of 42:58.

*Intermolecular Competition Experiment on **1p** and **1u**.* The procedure is the same as the procedure for **1e** and **1h**. The molar ratio of nitrated products **2p** and **2u** was calculated as 69:31 based on NMR spectra analysis.

*Nitration of **1a** Catalyzed by Complex **A**.* Complex **A** was prepared according to a literature procedure.[19] The procedure for using **A** as a catalyst for the nitration of **1a**: **1a** (0.3 mmol), **A** (0.015 mmol), *t*-BuONO (0.45 mmol), and anhydrous DCE (3.0 mL) was sealed in a 15 mL Schlenk flask under 1 atm O_2. Then, the flask was stirred at 90 °C for 48 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. A sample was taken for GC analysis, and 62% yield of **2a** was found.

Effect of Radical Scavenger TEMPO on Nitration. A mixture of 8-methylquinoline **1a** (0.30 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), *t*-BuONO (46.4 mg, 0.45 mmol), TEMPO (0.6 mmol), and anhydrous DCE (3.0 mL) was sealed in a 15 mL Schlenk flask under 1 atm O_2. Then, the flask was stirred at 90 °C for 48 h. Upon completion, the resulting mixture was analyzed by GC. No desired product was detected.

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■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR spectra of the products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00735.

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Notes

The authors declare no competing financial interest.

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