

"One-Pot" Approach to 8-Acylated 2-Quinolinones via Palladium-Catalyzed Regioselective Acylation of Quinoline *N*-Oxides

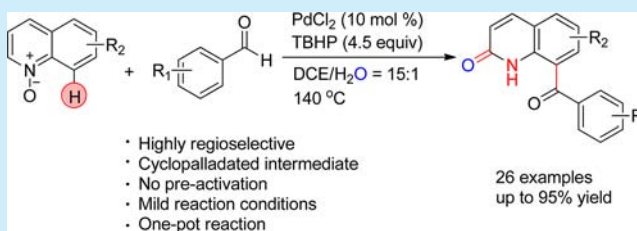
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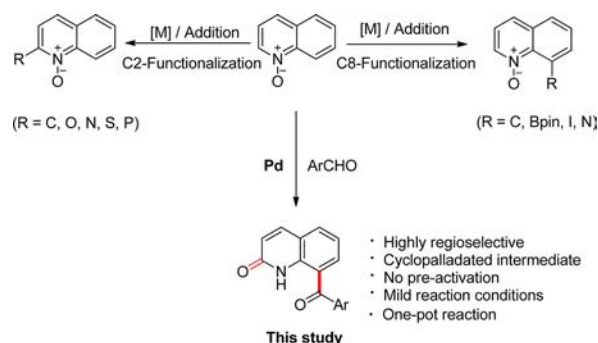
S Supporting Information

ABSTRACT: A "one-pot" facile and efficient protocol for 8-acylated 2-quinolinones has been developed through palladium-catalyzed acylation of quinoline *N*-oxides, which proceeds with high selectivity at the C8-position. The desired products were isolated in up to 95% yield and good functional group tolerance. A palladacycle was isolated from the catalytic process and proposed as a key intermediate.



Transition-metal-catalyzed direct C–H bond functionalization has emerged as an ideal strategy in organic transformations, owing to its atomic economy, its short synthetic route, and the utilization of readily available, cheap and environmentally benign starting materials. It has been successfully used as a powerful tool for the modular, facile synthesis of structurally diversified organic molecules as well as complicated natural products.¹ The challenge still remains with regioselective C–H bond functionalization since multiple C–H bonds are present in most organic molecules. Therefore, a variety of directing groups (DGs) have been intensively investigated and used to achieve the desired regioselective control.² *N*-Oxide as a directing group has recently attracted great attention owing to its advantages, such as (1) its use as an internal oxidant, avoiding external oxidant and deprotection step; (2) its use as a polar chemical bond, accelerating C–H activation; and (3) its ability to undergo O atom transfer to construct various C–C, C–O, and C–N bonds. Various heterocycles containing an N atom, such as quinolines, pyridines,³ and triazoles,⁴ were synthesized through transition-metal-catalyzed selective C–H bond functionalization directed by *N*-oxide. Regarding quinolines, the C2-substituted derivatives are easily accessed through metal-catalyzed C–H functionalization such as olefination,⁵ sulfonylation,⁶ alkylation,⁷ acetoxylation,⁸ phosphonation,⁹ arylation,¹⁰ and amination¹¹ developed by the groups of Fagnou, Li, and Larionov and our group (Scheme 1). The procedure for C8-substituted quinolines is rarely reported.¹² Chang and co-workers reported their elegant works on 8-iodinated and 8-aminated quinolines using rhodium and iridium catalytic systems.^{12a} Rh- and Co-catalyzed redox-neutral coupling with alkynes at C8 of quinoline *N*-oxides was disclosed by the groups of Li, Chang, and Sundararaju.^{12b–d} To the best of our knowledge, there are only two reports from the Larionov group on the palladium-

Scheme 1. Selectivity C–H Functionalization of Quinoline *N*-Oxides



catalyzed C8 arylation of quinoline *N*-oxides.^{12g,h} On the other hand, 2-quinolinone is a naturally occurring class of compounds, which exhibit a broad spectrum of pharmacological activity, including antibiotic, anticancer, antiviral, antihypertensive, and other bioactivities.¹³ Herein, we describe the first one pot procedure to 8-acylated 2-quinolinones starting from quinoline *N*-oxides and aldehydes catalyzed by palladium. The mechanistic investigations indicate that the high regioselectivity was achieved through the smooth formation of *N*-oxide-chelated palladacycle.

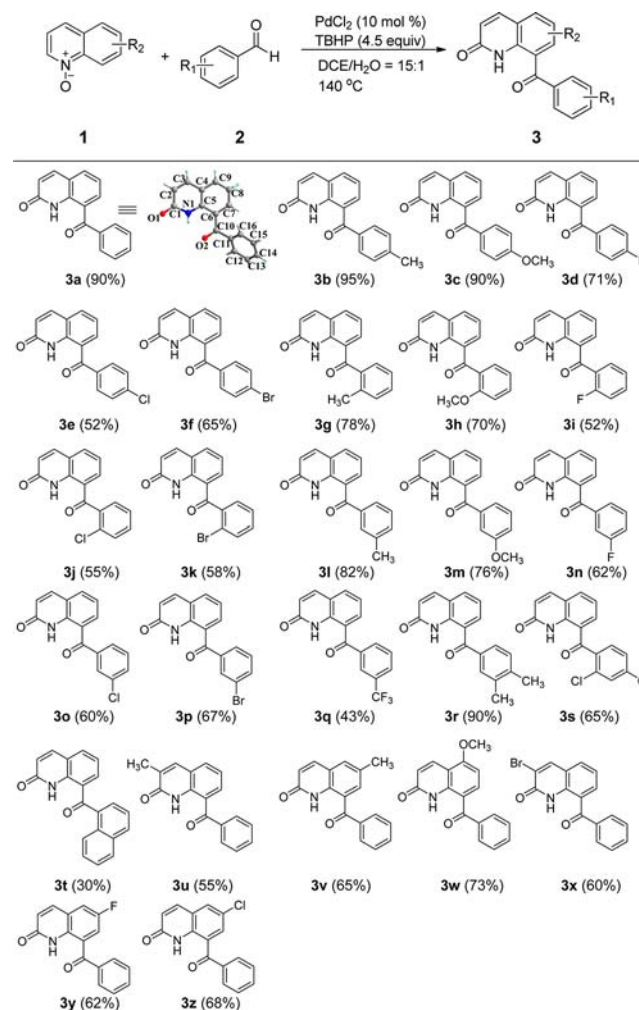
We initiated our investigation on the model reaction of quinoline *N*-oxide (1a) with benzaldehyde (2a) to optimize various reaction parameters. The results are summarized in Table S1. The desired product 3a was obtained in a yield of 52%, as well as the product 4a in 45% yield in 1,2-

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dichloroethane (DCE) using PdCl_2 as a catalyst, and 70% *tert*-butyl hydroperoxide (TBHP) in water as an oxidant (entry 1). The molecular structures of products **3a** and **4a** were confirmed by NMR spectra and single-crystal X-ray diffraction analysis. However, $\text{Pd}(\text{OAc})_2$ and $\text{Pd}(\text{TFA})_2$ gave a trace amount of the desired product **3a** as a main product (entries 2 and 3), and no acylated product was observed with CuI and CuCl_2 (entries 4 and 5). Other oxidants, such as $\text{K}_2\text{S}_2\text{O}_8$, AgOAc , benzoquinone (BQ), and di-*tert*-butylperoxide (DTBP), did not favor the formation of **3a** (entries 6–9). Moreover, only **4a** was obtained when *tert*-butyl hydroperoxide (TBHP) in decane was used as an oxidant (entry 10). To our delight, addition of water to the reaction system could efficiently support the formation of **3a** (entry 11). The yield of **3a** could be improved to 90% when the temperature of the oil bath was increased to 140 °C (entry 14). When the reaction was protected by nitrogen, the desired C8-acylated product **3a** was obtained in 85% yield (entry 15), which indicated that the oxygen molecule from air was tolerated. Finally, the optimized reaction conditions were identified as follows: 10 mol % of PdCl_2 as the catalyst, TBHP in decane as the oxidant, water as the additive in DCE in 140 °C oil bath under air atmosphere for 24 h.

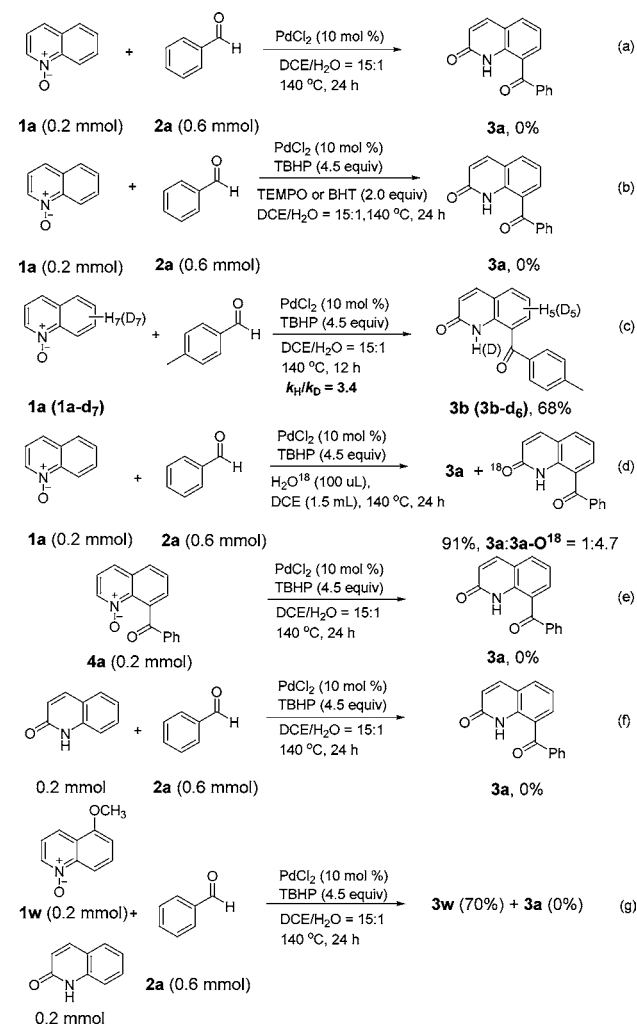
With the optimal reaction conditions in hand, we turned our attention to the generality and scope of the substrates for this transformation. A wide range of benzaldehydes were first evaluated in the reaction with quinoline *N*-oxide (**1a**) (Scheme 2, **3a–t**). Benzaldehydes with electron-donating and weak electron-withdrawing substituents (such as Me, MeO, F, Cl, and Br) at the *para*-position of the benzene ring gave the desired products (**3a–f**) in good to excellent yields. Generally, benzaldehydes with electron-donating groups gave higher yields than electron-withdrawing groups (**3a–c** vs **3d–f**). The efficiency of the acylation was slightly affected by steric hindrance. For instance, *p*-methylbenzaldehyde gave a slightly higher yield relative to *o*- and *m*-methyl-substituted benzaldehydes (**3b** vs **3g** and **3l**). A similar trend was observed for MeO- and halogen-substituted benzaldehydes (**3c–p**). In particular, halogen could work well to give the desired products in moderate to good yields, which makes this reaction particularly attractive for further transformation by transition-metal-catalyzed coupling reactions. Furthermore, the presence of the strong electron-withdrawing group, such as 3-(trifluoromethyl)benzaldehyde (**2q**), generated the product **3q** in 43% yield. It is worth noting that disubstituted benzaldehydes **2r** and **2s** exhibited good reactivity and provided the desired products in 90% (**3r**) and 65% (**3s**) yields, respectively. 1-Naphthaldehyde **2t** also could afford the desired product **3t**, though it exhibited low efficiency in this transformation. To expand the scope of this method, some quinoline *N*-oxides were evaluated in reaction with benzaldehyde (**2a**). The reaction efficiency was not significantly affected by the electronic variation of substrates (**3u–z**). The position of alkyl substituents did not interfere with the formation of the desired products, as shown with methylated substrates (**3u**, **3v**). Electron-donating groups, for example, 5-methoxyquinoline *N*-oxide, reacted smoothly under the optimal conditions to afford **3w** in 73% yield. Similar yields were observed with electron-withdrawing groups, such as halogenated quinoline *N*-oxides (**3x–z**), significantly expanding the synthetic utility of the current acylation protocol. While, this catalytic system was not applied to aliphatic aldehydes. When caproaldehyde and cyclohexanecarboxaldehyde were used as the substrates, the corresponding products were not obtained.

Scheme 2. Scope of Substrates^{a,b}

^aReaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), PdCl_2 (10 mol %), TBHP (0.9 mmol, 5–6 M in decane), H_2O (100 μL), and DCE (1.5 mL), under air, 140 °C, 24 h. ^bIsolated yield.

To clarify the reaction mechanism, some control experiments were carried out (Scheme 3). When the palladium-catalyzed acylation of **1a** with **2a** was carried out in the absence of TBHP (Scheme 3, a), no acylated product **3a** was detected. Moreover, addition of a radical scavenger 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) or butylated hydroxytoluene (BHT) to the reaction mixture under the standard reaction conditions made this acylation suppressed, suggesting the possibility of a radical process (Scheme 3, b). Parallel competition reactions between **1a** and its deuterated analogue **1a-d₇** were performed under the standard reaction conditions and revealed a notable kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 3.4$, Scheme 3, c), indicating that the C–H bond cleavage would be rate-limiting in the overall process. To explore the source of O atom in the product, the coupling reaction between **1a** and **2a** was conducted in the presence of H_2O^{18} (Scheme 3, d), the corresponding product (**3a-O¹⁸**) was obtained with incorporation of the ¹⁸O atom detected by HRMS analysis. Therefore, water might be involved in the reaction and provided the O atom. To further understand whether **4a** leads to an isomerization,¹⁴ so **4a** was subjected to the optimal reaction conditions (Scheme 3, e). Essentially no conversion **3a** was observed. Therefore, the intermediacy of **4a** can be ruled out. To establish the

Scheme 3. Control Experiments

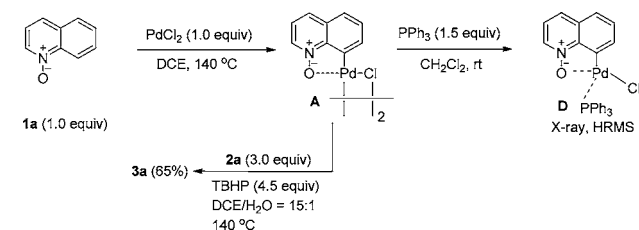


sequencing of the oxygen transposition¹⁵ and the C–H activation, the reaction of 2-quinolinone with benzaldehyde **2a** was carried out, the desired product **3a** was not detected (Scheme 3, f). The mixture of 1:1 5-methoxy quinoline *N*-oxide **1w** and 2-quinolinone was added to the reaction system charged with 2.0 equiv of **3a** under the optimized reaction conditions (Scheme 3, g). The product **3w** was obtained in 70% yield, while no product from 2-quinolinone was observed. These results suggested that *N*-oxide might play a crucial role in this transformation and 2-quinolinone could not be initiated at first process.

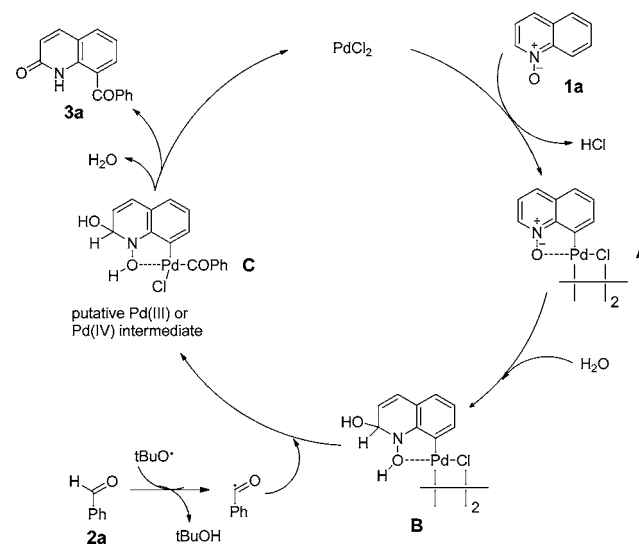
Furthermore, the reaction of quinoline *N*-oxide with stoichiometric PdCl₂ gave the chloride-bridged palladacycle dimer **A**, which produced the corresponding triphenylphosphine (PPh₃) adduct **D** by treatment with triphenylphosphine (PPh₃) in dichloromethane at room temperature (Scheme 4). The structure was confirmed by single-crystal X-ray diffraction (CCDC 1441432) (Figure S1). The reaction of complex **A** with benzaldehyde (**2a**) afforded the desired product **3a** in 65% yield, which implied the possible intermediacy of a five-membered complex in the catalytic cycle.

On the basis of the results obtained above and the literature,¹⁶ the reaction mechanism was proposed and is shown in Scheme 5. First, the palladacycle¹⁷ dimer intermediate **A** was formed via coordination of the palladium with O atom

Scheme 4. Reaction Mechanistic Studies



Scheme 5. Proposed Reaction Mechanism



from the *N*-oxide and subsequent electrophilic attack at the C8. Next, the complex **A** could convert into intermediate **B** through nucleophilic addition of H₂O at C2 of quinoline. Meanwhile, an acyl radical was generated from benzaldehyde (**2a**) by treatment with TBHP. Then, the intermediate **B** would react with the acyl radical, affording the oxidative addition intermediate as a palladium(III) or palladium(IV) **C**. Finally, the reductive elimination of intermediate **C** gave the product **3a** and regenerated Pd(II) for the next cycle.

In summary, we have for the first time successfully synthesized 8-acylated 2-quinolinones in a one-pot manner through palladium-catalyzed selective C8-H activation of quinoline *N*-oxides with aldehydes. In this approach, *N*-oxide was utilized as a stepping stone for the remote C–H functionalization. This protocol is a convergent one-pot cascade sequence rather than one which often requires multiple steps. This reaction proceeds with high regioselectivity at the C8 position of quinolines with good tolerance of various functional groups. The reaction mechanistic studies indicate that water played an important role as a source of oxygen atom in the reaction and a palladacycle intermediate has been isolated from the catalytic conditions. Further exploration of the synthetic potential of this regioselective C–H bond functionalization platform is underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00923.

¹H NMR and ¹³C NMR spectra of compounds **3a–z**, **4a**, and **D** (PDF)
X-ray data for **3a** (CIF)
X-ray data for **4a** (CIF)
X-ray data for **D** (CIF)

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Notes

The authors declare no competing financial interest.

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