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Hydrogen-Transfer-Mediated Direct β-Alkylation of Aryl-1,8-naphthyridines with Alcohols under Transition Metal Catalyst Free Conditions

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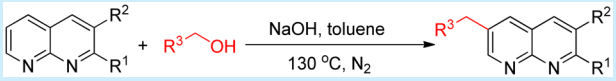
Supporting Information

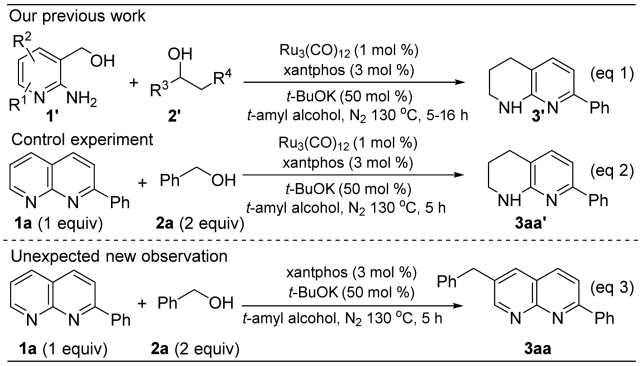
ABSTRACT: By employing abundant and sustainable alcohols as the alkylating reagents, a new and direct alkylation method has been demonstrated. This method enables the selective alkylation of the less substituted pyridyl ring at the β-site of aryl-1,8-naphthyridines, affording the desired products in moderate to excellent yields upon isolation. The method proceeds under transition-metal-free conditions in an atom- and step-economic fashion and liberates water as the sole byproduct. Mechanistic investigations suggest the reaction undergoes a hydrogen-transfer-mediated alkylation mode.



Due to the extensive applications of alkylated heteroarenes in both medicinal and material science, the alkylation of heteroaromatic C−H bonds to access such compounds has long been an attractive subject of synthetic chemistry.[1] However, due to the heteroarenes possess many C−H bonds with close dissociation energies, the control of site-selectivity has, to date, presented a challenge. Pioneered by the Friedel−Crafts alkylation,[2] great efforts have been directed toward the search for efficient approaches with alternative alkylating agents. Representative examples mainly involve the directing group-assisted C−H alkylation with alkyl halides,[3] the metal-catalyzed hydroheteroarylation of olefins,[4] carbene insertion into heteroaromatic C−H bonds,[5] radical alkylation[6] including Minisci-type reactions,[7] Catellani−Lautens-type coupling reactions[8] and ring-opening alkylation.[9] However, many of these methods require the use of prefunctionalized or less environmentally benign reagents in the presence of noble metal catalysts, which could easily result in preparation difficulties and detrimental influence on environment, and their applications to large-scale production are therefore limited. Moreover, the presence of noble metal catalysts would not only increase the procedure cost but also could constitute severe drawbacks to the methods, especially in pharmaceutical and industrial applications. Hence, the development of step- and atom-economic approaches to selectively alkylate heteroarenes even under transition metal free conditions would be highly desirable.

Prompted by the abundance and sustainability of alcohols, much attention has been focused on the utilization of such a resource for various synthetic purposes, which mainly involve the reduction of unsaturated chemical bonds with alcohols as alternative hydrogen sources,[10] the coupling reactions using the in situ formed carbonyls arising from alcohol dehydrogenation,[11] the active C−H bond alkylation, or N-alkylation by employing the hydrogen-borrowing strategy.[12] To date, the direct alkylation of heteroarenes with alcohols is generally restricted to applying the Friedel−Crafts reaction.[13] Recently, the Bruneau group has demonstrated an interesting β−C-H (sp^3) alkylation of cyclic amines with aldehydes.[14] However, the selective β-alkylation of six-membered heteroarenes with alcohols, to the best of our knowledge, is not known. As a part of our continuous research interests in converting alcohols into value-added products[15] and developing new synthetic methodologies under transition metal free conditions,[16] we recently reported a ruthenium-catalyzed straightforward synthesis of tetrahydronaphthyridines (THNADs) **3′** from *o*-aminopyridyl methanols **1′** and alcohols **2′** (Scheme 1, eq 1).[17]

Scheme 1. New Observation from a Previous Work



To gain insight into this transformation, treating intermediate naphthyridine **1a** with excess benzylic alcohol **2a** gave the transfer-hydrogenated product **3aa′** (eq 2), whereas the absence of ruthenium complex resulted in an unexpected alkylation compound **3aa** in 32% yield (eq 3). Upon a thorough investigation of this observation, we wish herein to report a new

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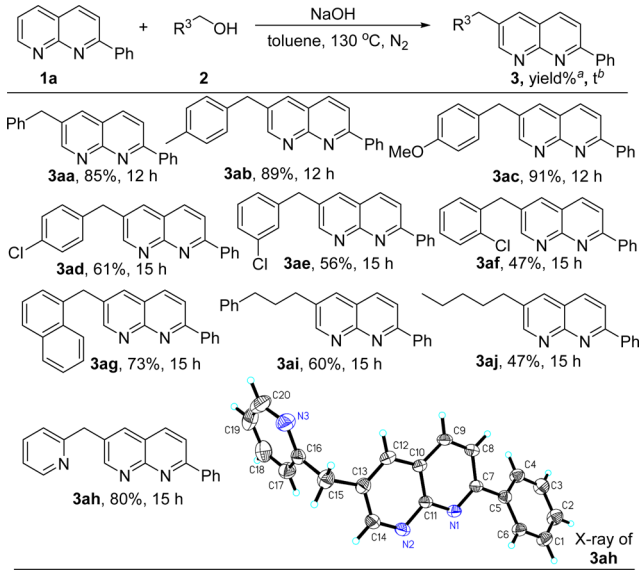
alkylation mode, which enables us to selectively functionalize the β-site of one pyridyl ring of the naphthyridines by using alcohols as the alkylating reagents. The method proceeds in a step- and atom-economic fashion, producing water as the sole byproduct.

To determine an improved reaction system, we chose the reaction of **1a** with **2a** as a model system. At the start of our work, the effect of representative bases including organic and inorganic ones, solvents, and different temperatures were evaluated (see Table S1, Supporting Information). An optimal yield of product **3aa** was obtained at 130 °C and by using 1 equiv of NaOH, along with toluene as the solvent.

With the optimized reaction conditions in hand, we examined the generality and limitations of this base-mediated synthetic protocol. First, the reactions of **1a** in combination with a wide range of aryl(heteroaryl)methanols (see the Supporting Information, Scheme S2, for the structures of substrates) were examined. As shown in Scheme 2, all of the

Scheme 2. Variation of Alcohols*

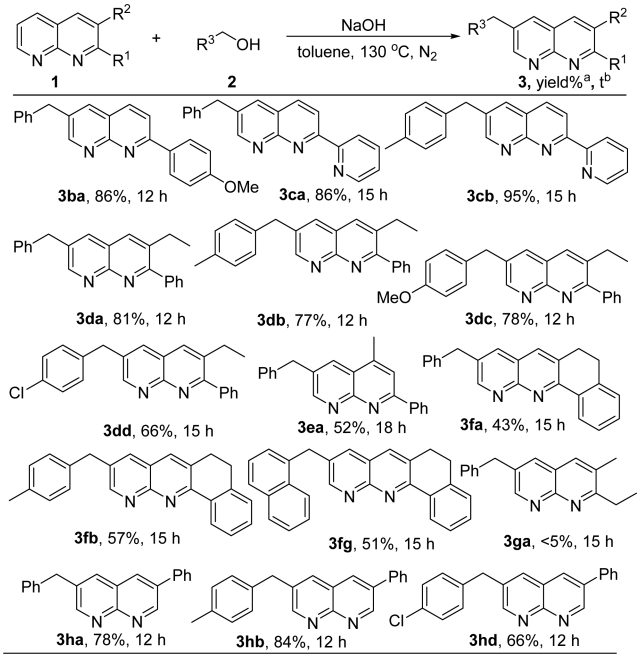


*Reaction conditions: unless otherwise stated, all reactions were carried out at 130 °C under N_2 atmosphere by using **1a** (0.5 mmol), **2** (0.6 mmol), NaOH (100 mol %), and toluene (1.5 mL). [a]Isolated yield. [b]Reaction time.

reactions proceeded smoothly, and the β-alkylation occurred selectively on the sterically less hindered pyridyl ring, affording the desired products in moderate to excellent yields upon isolation (**3aa**–**ah**). It was found that the electronic property of the substituents on the aryl ring of benzylic alcohols significantly affected the reactions. Specifically, electro-rich substitutents afforded the products (**3ab**,**ac**) in much higher yields than those of electron-withdrawing ones (**3ad**–**af**). This observation implies the reaction undergoing a nucleophilic substitution mechanism is less likely. Heteroarylmethanol **2h** demonstrated remarkable activity in affording product **3ah** (80% yield), and its structure was confirmed by X-ray diffraction. Gratifyingly, aliphatic alcohols **2i** and **2j** were also proven to be effective coupling partners, yielding the products in reasonable yields (see **3ai**,**aj**). It is noteworthy that all of the obtained products possess a benzylic position, which has the potential for further elaboration of functional ketones via direct C–H bond oxidation.[18]

Subsequently, we turned our attention to the variation of aryl-1,8-naphthyridines. Thus, the combinations of different substrates **1** with alcohols **2** were explored. Similar to the results described in Scheme 2, all of the reactions selectively furnished the β-alkylated products in moderate to excellent isolated yields (Scheme 3, **3ba**–**hd**). 2-Aryl(heteroaryl)-1,8-

Scheme 3. Variation of 1,8-Naphthyridines and Alcohols*



*Reaction conditions: same as described in Scheme 2. [a]Isolated yield. [b]Reaction time.

naphthyridines underwent very efficient coupling reactions and afforded the desired products in excellent yields (**3ba**–**cb**). Further, aryl- and alkyl-disubstituted 1,8-naphthyridines (**1d**–**f**) could afford the corresponding products in reasonable to high yields (**3da**–**dd**,**ea**,**fa**–**fb**,**fg**). However, the reaction of 2,3-dialkyl-1,8-naphthyridine **1g** with alcohol **1a** only yielded small portion of desired product, indicating substrate **1** bearing an aryl substituent is essential in affording a satisfactory yield. As expected, 3-aryl-1,8-naphthyridine **1h** demonstrated high reactivity to couple with different alcohols and produced the products in good to excellent yields (**3ha**–**hb**,**hd**).

To gain insight into the information on product formation, the model reaction was interrupted after 2 h to analyze the reaction intermediates. By means of GC–MS and NMR analyses, both product **3aa**, benzaldehyde **2a′**, and tetrahedronnaphthyridine **3aa′** were detected in 17%, 1%, and 1% yields, respectively (Scheme 4, eq 4). Then, the reaction of **3aa′** with benzaldehyde **2a′** or benzylic alcohol **2a** under standard conditions failed to yield product **3aa** (eq 5), indicating **3aa′** serving as a reaction intermediate can be ruled out. Further, naphthyridine **1a** also failed to couple with aldehyde **2a′** to give **3aa** (eq 6). However, treating **1a** with equimolar amount of 4-methoxybenzaldehyde **2c′** and benzylic alcohol **2a** gave both products **3aa** and **3ac** in close yields (eq 7), showing the alcohol plays a crucial role in activating the pyridyl ring. To further clarify this phenomenon, the reaction employing a

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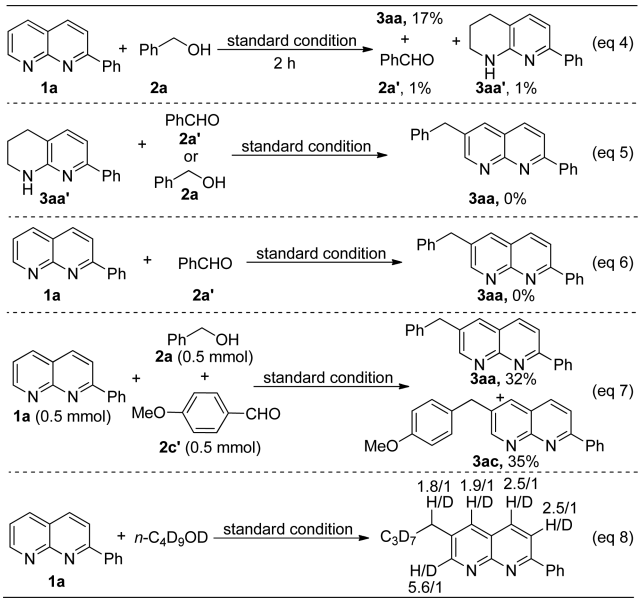
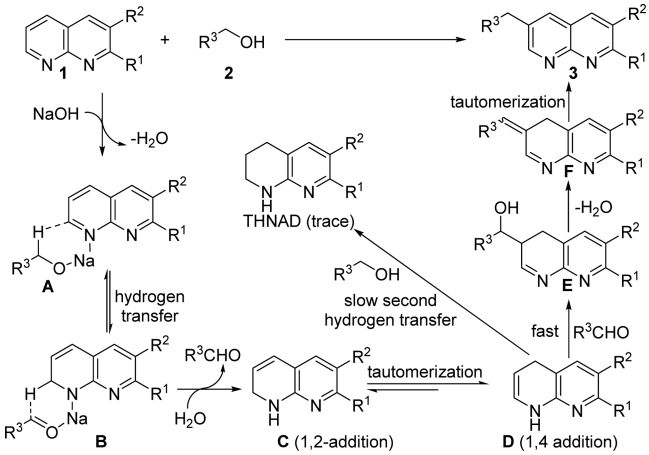
Scheme 4. Control Experiments



deuterium-labeled *n*-butanol with **1a** was tested (eq 8). Different H, D exchange ratios were found at positions 3, 4, 5, and 7 and the benzylic site, indicating the hydrogen atoms from alcohol are transferred to both pyridyl rings of naphthyridine **3aa**. Owing to the influence of substituent effect, the in situ formed aldehyde selectively couples with the sterically less hindered pyridyl ring of naphthyridine **1a**.

Although the mechanism of this β-alkylation reaction has not been fully elucidated, on the basis of the above-observed findings, a hydrogen-mediated alkylation mode is proposed in Scheme 5. The reaction initiates via a slow redox reaction of **1**

Scheme 5. Possible Pathway for the Formation of 3



and **2** in which the deprotonation of alcohol **2** by NaOH gives sodium alkoxide and H_2O and the sodium alkoxide interacts with the imine unit in **1** to form a transition state **A**. Through a reversible Meerwein–Pondorf–Verley–Oppenauer (MPV–O)-type hydrogen transfer[19] another transition state **B** is then formed. The subsequent protonation of **B** with H_2O or alcohol followed by a thermodynamically favorable tautomerization of **C** would liberate aldehyde and enamine **D**, respectively (1,2-H addition: at positions 7 and 8). Similarly, a 1,4-H addition (at positions 5 and 8) of the less substituted pyridyl ring of **1** would directly afford enamine **D**. Considering that position 5 has a higher deuterium ratio than that of position-7 (Scheme 4, see eq 5), the latter is thus believed to be a favorable hydrogen-transfer process. Further, a fast nucleophilic addition of **D** to aldehyde followed by a dehydration step gives intermediate **F**. Finally, the tautomerization of **F** would yield product **3**. It is noteworthy that a slow second transfer hydrogenation of **D** with alcohol could produce trace of tetrahydronaphthyridine (THNAD).

In summary, we have disclosed a new alkylation mode to functionalize N-heterocylces. By employing abundant and sustainable alcohols as the alkylating reagents, it enables us to directly alkylate the less substituted pyridyl ring at the β-position of 2-arylnaphthyridines, affording the alkylated products in reasonable to excellent yields upon isolation. The method proceeds under transition metal free conditions in an atom- and step-economic fashion and liberates water as the sole byproduct. Mechanistic investigations suggest the reaction undergoes a hydrogen-transfer-mediated alkylation mode. Further investigations on gaining insight into the reaction details involving DFT calculations and utilizing such a alkylation mode to functionalize other heteroarenes are ongoing in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03699.

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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