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Scope of Successive C−H Functionalizations of the Methyl Group in 3-Picolines: Intramolecular Carbonylation of Arenes to the Metal-Free Synthesis of 4-Azafluorenones

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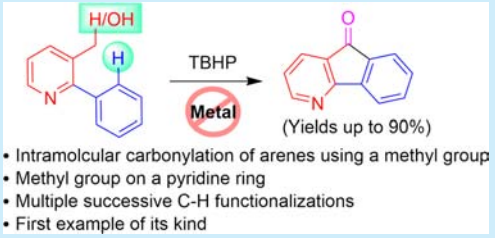
Supporting Information

ABSTRACT: A transition-metal-free, *t*-BuOOH mediated intramolecular carbonylation of arenes in 2-aryl-3-picolines via oxidative C−H functionalizations of the methyl group has been developed, providing an expedient synthesis of 4-azafluorenones. Distinct from the current literature wherein methylarenes have been used as acylating agents, 2-aryl-3-picolines in this study are transformed into aldehydes, which give 4-azafluorenones upon rapid intramolecular acylation. The study demonstrates the first example of intramolecular carbonylation of arenes utilizing a methyl group as latent carbonyl functionality.



Carbon−carbon (C−C) bond formation between two C−H bonds (sp, sp^2 or sp^3 C−H), traditionally known as oxidative or cross-dehydrogenative coupling, has become the central focus in C−C bond forming reactions obviating the use of prefunctionalized substrates and alleviating the generation of salt waste, thereby rendering superior sustainability and environmental compatibility.[1] The growing dependence on these direct oxidative C−H functionalizations that feature higher atom economy and sustainability has witnessed a hefty evolution over the past two decades, which signifies the importance of and emergent interest in this synthetic technology. However, a fundamental challenge intrinsic to these oxidative C−H functionalizations lies in achieving high regioselectivity.[2] The challenge is further exacerbated by the requirement of achieving regioselective oxidative functionalizations of an unactivated sp^3 C−H bond, especially under transition-metal-free conditions. Nevertheless, successful realizations of multiple regioselective C(sp^3)−H functionalizations are among the various reaction tools celebrated in organic chemistry.[3]

Oxidation of methylarenes to aryl methanols, aldehydes, and carboxylic acids merits extensive discussion.[4] Remarkably, methylarenes have served as acylating agents for the carbonylation of hetero(arenes) via successive oxidative C−H functionalizations of the methyl group.[5] While there has been much effort devoted toward the catalytic oxidation of picolines to pyridine carboxylic acids,[6] oxidations of picolines followed by in situ trapping of the aldehydes with amines or thiols yielding pyridine carboxamides,[7] cyanopyridines,[8] or thiolesters[9] are especially noteworthy. Perhaps most importantly, picolines have not been demonstrated to serve as acylating agent for the direct acylation of arenes. Moreover, an intramolecular carbonylation of arenes or heteroarenes via successive C−H functionalizations of a methyl group, a widely sought yet elusive transformation, remains unrealized.

4-Azafluorenones, a privileged molecular scaffold ubiquitously found in natural products, display various biological activities including antimicrobial, antimalarial, and DNA-damaging activities (Figure 1).[10] 4-Azafluorenone derivatives

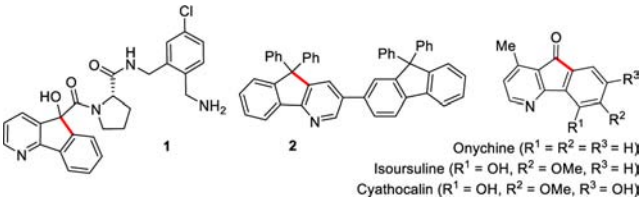


Figure 1. Compounds containing a 4-azafluorenone skeleton.

have found various other applications, for example, compound **1** as a thrombin inhibitor[11] and **2** as an electron-transporting host material capable of being fabricated into efficient organic light-emitting devices (LED).[12] Despite these diverse applications, the chemistry of 4-azafluorenones has been least investigated.[13]

The strategies reported for the synthesis of 4-azafluorenones fall in three categories: intramolecular Friedel−Crafts acylation on 2-arylpyridines containing a carboxylic acid[11,14] or an ester group[14a,15] appropriately placed on one of the two rings (Paths A and B), biaryl linkage formation by intramolecular Heck reactions on 3-aroylpyridines (Path C),[10a,16] and a three-component reaction (Path D, Scheme 1).[17] Remarkably, Sneickus et al. reported a more general approach to the

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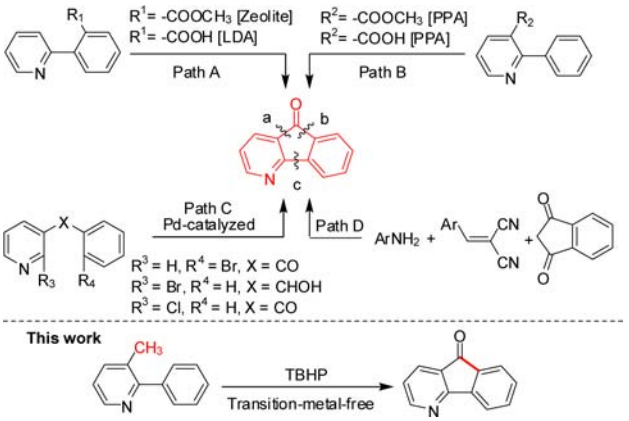
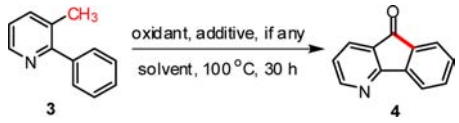
Scheme 1. Synthetic Approaches to 4-Azafluorenones



synthesis of azafluorenones from arylpyridines containing an *N*,*N*-dialkylamide group in the presence of LDA.[18] However, synthesis of 4-azafluorenones has not been demonstrated in this report. While several of these methods are elegant and appear to be appealing, they suffer from limitations such as harsh reaction conditions, use of elaborated synthetic precursors, requiring multiple steps, and frequent use of transition metals. Despite significant advances realized in 4-azafluorenone synthesis largely using classical chemistry, important questions still remain: (a) whether a methyl group on 2-aryl-3-picolines could be used as a latent carbonyl functionality, (b) whether a transition-metal-free as opposed to a transition-metal-catalyzed oxidative approach could be developed, and (c) whether a single, nontoxic oxidant that is compatible with environmental safety could execute successive C−H functionalizations of a methyl group. Nevertheless, a defined objective considering these questions collectively would be a daunting challenge. Remarkably, Glorius et al. and Studer et al. independently reported the intramolecular carbonylation of arenes via C−H functionalization of the aldehyde group present in 2-arylbenzaldehydes yielding flurenones in good to excellent yields.[19] Inspired by their work, and based on our recent experiences on sp^2 C−H oxidative couplings in the synthesis of biaryl sultams,[20] heterobiaryl sultams,[21] and carbazoles as well as α-carbolines,[22] we surmised that an intramolecular carbonylation of arenes in 2-aryl-3-picolines via successive oxidative C−H functionalizations of the methyl group, while an ambitious objective, would be a distinct, straightforward gateway to 4-azafluorenones. Herein, we describe a first report on the intramolecular carbonylation of arenes via successive C−H functionalization of a methyl group present in 2-aryl-3-picolines. The successive C−H functionalization of a methyl group present on a pyridine ring, a strategy previously unexplored, is now unveiled. The optimized conditions in our study are quite resourceful, warranting broad applications to the synthesis of 4-azafluorenones.

We commenced our study with the C−H functionalizations of readily available 2-phenyl-3-picoline (**3**) aiming at the synthesis of azafluorenone **4**. Initial efforts to effect annulations using many oxidants that are generally used for methyl C−H functionalizations are ineffective in this study (Table 1, entry 1). However, 4 equiv of TBHP in DCE were able to transform **3** to **4** in 35% yield (entry 2). Similarly, 2 equiv of $K_2S_2O_8$ in acetonitrile resulted in conversion of **3** to **4** with a comparable yield (30%, entry 3). Greater conversion of **3** to **4** was apparent using higher stoichiometries of TBHP (entries 4−5). However,

Table 1. Optimization Study[a]



entry	oxidant[b]	additive[b]	solvent	yield (%)[c]
1[d]	oxidants		DCE	0
2	TBHP (4)		DCE	35
3	$K_2S_2O_8$ (2)		MeCN	30
4	TBHP (6)		DCE	58
5[e]	TBHP (8)		DCE	**70**
6[e]	TBHP (1 mL)		DCE	63
7	TBHP (8)	TBAI (0.5)	DCE	trace
8	TBHP (8)	base[f]	DCE	40−45
9	TBHP (8)			20
10	TBHP (8)		DMSO	40
11	TBHP (8)		MeCN/THF	trace
12	TBHP (8)		DCB[g]	70
13[e]	TBHP[h]		DCE	60
14[e,i]	TBHP (8)		DCE	48
15[e,j]	TBHP (8)		DCB[g]	55
16	TBHP (8)	TEMPO (10)	DCE	0

[a]**3** (0.15 mmol), oxidants (2 equiv to large excess), additive (if any, 10 mol % to 150 mol %), DCE (1 mL), 100 °C, 30 h. [b]Number of equivalents in parentheses. [c]Isolated yields. [d]Oxidants used [oxygen, DTBP (4 equiv), TBPB (4 equiv), $(NH_4)S_2O_8$ (2 equiv), Oxone (2 equiv), DDQ (2 equiv), or $PhI(OAc)_2$ (2 equiv)]. [e]DCE (0.5 mL). [f]KOBu-*t* (1.5 equiv) or Li_2CO_3 (0.1 equiv). [g]1,2-Dichlorobenzene. [h]0.25 mL of 70% aqueous TBHP solution. [i]80 °C. [j]130 °C.

a large excess of TBHP was detrimental (entry 6). Thus, heating a solution of **3** in DCE (200 mM) with 8 equiv of TBHP gave **4** in 70% isolated yield. However, TBHP in combination with TBAI, largely used for C−H functionalizations,[23] was ineffective in our study (entry 7). In addition, TBHP in the presence of a base resulted in reduced conversion of **3** to **4** yielding a 40−45% yield of **4** (entry 8). Solventless conditions or a different solvent gave varying yields of **4** (entries 9−12). TBHP in water gave a slightly reduced yield (entry 13). Conversion of **3** to **4** is affected by lowering the temperature or heating at higher temperature (entries 14−15). Exposure of **3** to the standard conditions in the presence of 10 equiv of TEMPO, a radical trapping agent, could markedly suppress the formation of **4**, suggesting a free-radical intermediate was involved in this reaction (entry 16).

We further investigated the scope of substrates that could participate in the intramolecular carbonylation. The starting materials (**5**−**19**) were easily prepared by Suzuki coupling of 2-bromo-3-picoline with commercially available aryl boronic acids or aryl pinacolboranes, prepared from aryl bromides (see Supporting Information).[24]

2-Aryl-3-picoline **5** containing an electron-donating *para*-OMe group on the phenyl ring worked well, yielding azafluorenone **20** in 70% yield (Scheme 2, entry 1). However, compound **6** containing a *para*-OCF_3 group reacted less effectively yielding azafluorenone **21** in reduced yield (24%) together with **22** containing an aldehyde group (entry 2). Evidently, the methyl group in **6** is oxidized to aldehyde, which upon subsequent acylation, similar to that reported,[19] could give **21**. However, unlike literature,[19] an arene is acylated intramolecularly with an aldehyde group present on a pyridine ring. While a *tert*-butyl group produced an inferior result

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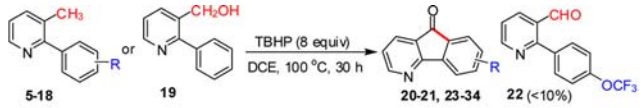
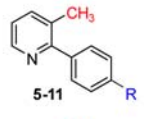
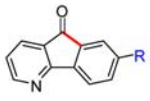
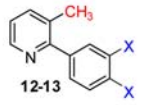
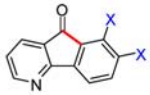
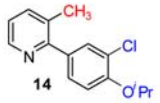
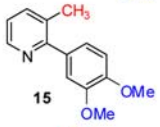
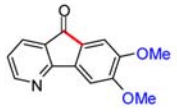
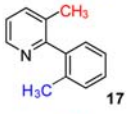
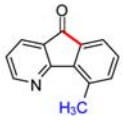
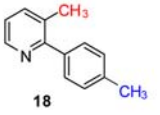
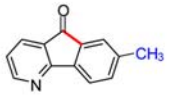
Scheme 2. Substrates Scope for the 4-Azafluorenones Synthesis



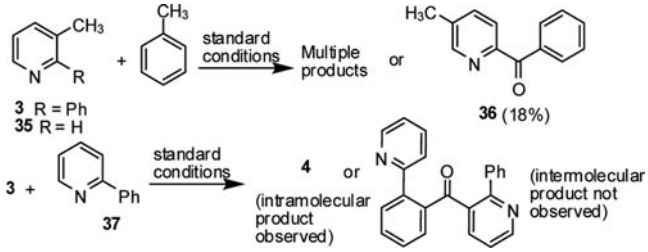
entry	substrate	product	yield
1 2 3 4 5 6 7			20 R = OMe (70%) 21 R = OCF_3 (24%)[a] 23 R = *t*-Bu (55%) 24 R = Ph (78%) 25 R = Cl (60%) 26 R = F (46%) 27 R = CF_3 (43%)
8 9			28 X = Cl (58%)[b] 29 X = F (47%)[b]
10			30 66%
11			31 68%
12			32 62%
13			33 53%[c]
14			34 0%
15	19	4	90%

[a]42 h. [b]36 h. [c]24 h.

producing azafluorenone **23** in 55% yield, a phenyl group restored the yield (78%) (entries 3–4). A *para*-chloro group is somewhat better than *tert*-butyl yielding azafluorenone **25** in 60% yield (entry 5). An electron-withdrawing group F or CF_3 exerts a diminishing effect producing azafluorenone **26** or **27** in reduced yields (43–46%) (entries 6–7). Dichloro- or fluorophenyl-3-picoline **12** and **13** reciprocated the same reactivity as that of monosubstituted derivatives **9** and **10**, respectively, affording azafluorenones **28** and **29** in comparable yields (entries 8–9). 3-Picolines **14**–**15** having two electron-donating groups, the same or different, were also viable substrates yielding disubstituted azafluorenones **30**–**31** in 66–68% yields (entries 10–11). Furthermore, 3-picoline **16** containing a highly substituted aryl group at the 2-position furnished a trisubstituted azafluorenone **32** in 62% yield suggesting that the intramolecular carbonylation may occur irrespective of steric effects (entry 12). Under the standard conditions, 2-arylpyridines containing two methyl groups, one at the 3-position of the pyridine ring and another on the benzene ring, for example **17**, gave 4-azafluorenone **33** in 53% yield (entry 13). In contrast, **18** produced a complex mixture of products (entry 14). This dissimilarity could be explained by the anomalous reactivity of two methyl groups present on the phenyl ring. It is important to realize that the formation of **33** from **17** was pertinent to successive C–H functionalizations occurring exclusively at the methyl group present on the pyridine ring. Second, the intramolecular carbonylation occurred exclusively on the sp^2 C–H bond rather than the sp^3 C–H bond of the methyl group in the phenyl ring. Pivotal to this study was the finding that a hydroxymethyl group at the 3-position of the pyridine ring gave an excellent yield (90%) of azafluorenone **4** under the standard conditions. The relative ease of intramolecular carbonylation with a hydroxymethyl compared to a methyl group is particularly noteworthy (entry 15). Therefore, a hydroxymethyl group on the pyridine ring could be a starting platform for heteroaroylation of arenes. More importantly, carbonylation of arenes via transition-metal-free oxidative C–H functionalizations of a hydroxymethyl group present on pyridine is currently unavailable in the literature.

To gain further insight into the mechanism, we performed additional experiments. The results of these experiments were quite informative in formulating a plausible mechanism. While compound **3** alone forms **4** under standard conditions, the product **4** was not observed in the presence of excess (20 equiv) toluene (Scheme 3). A competitive C–H functionaliza-

Scheme 3. Control Experiments



tion of both methyl groups could explain, however, the formation of multiple products in the reaction of **3** and excess toluene. More interestingly, 3-picoline (**35**) itself that does not have a 2-aryl group remained largely unreacted in the presence of excess toluene. Only an intermolecular acylated product **36** was isolated albeit in low yield. Further optimization could result in a new protocol for the direct C-2 aroylation of pyridines, which remains unexplored in the literature. Nevertheless, this experiment implies that an aryl group at the 2-position could facilitate C–H functionalization of the methyl group on the pyridine ring. A crossover experiment involving **3** and 2-phenylpyridine (**37**) gave azafluorenone **4** under the standard conditions. However, no crossover product that could result from intermolecular reaction of **3** and **37** was observed. This experiment suggests that the *ortho*-hydrogen of the phenyl ring in **3** is vulnerable for direct acylation with aldehyde.

Based on these studies, a plausible mechanism is depicted in Scheme 4. The formation of a radical from TBHP may be initiated upon heating. Initially, hydrogen abstraction from the methyl group could form a 3-picoline radical, which upon subsequent proton abstraction could form a primary alcohol. Oxidation of the primary alcohol could generate an aldehyde. The aldehyde could form an aryl carbonyl radical by reaction with TBHP, which upon subsequent acylation with arene would deliver **4**.

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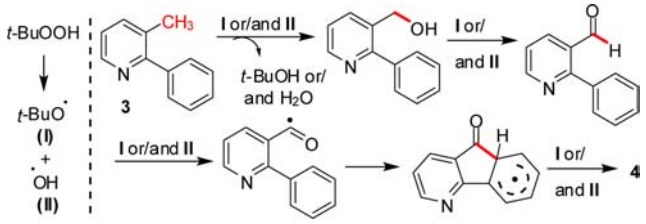
Scheme 4. Plausible Mechanism of Successive C−H Functionalizations of Methyl Group



In conclusion, an intramolecular carbonylation of arenes via oxidative C−H functionalizations of a methyl group present in 2-aryl-3-picolines has been developed, providing an expedient access to 4-azafluorenones. The current study complements the literature protocol, wherein a carboxylic ester or acid group is converted to the carbonyl group using classical chemistry. The protocol unveils a new strategy for the intramolecular oxidative heteroaroylation of arenes via successive C−H functionalizations of a methyl or hydroxymethyl group present on pyridine.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03071.

Experimental procedures, characterization data of new compounds, and copies of ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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