Organic LETTERS
Letter
Cite This: Org. Lett. XXXX, XXX, XXX−XXX
pubs.acs.org/OrgLett

Direct Pd(II)-Catalyzed Site-Selective C5-Arylation of 2-Pyridone Using Aryl Iodides

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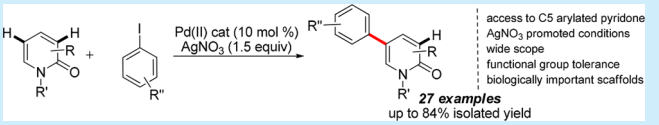
Supporting Information

ABSTRACT: A straightforward Pd(II)-catalyzed general strategy was developed for the C5-selective arylation of the 2-pyridone core with easily available aryl iodides. The transformation was highly regioselective and accomplished with a wide scope and functional group tolerance. Silver nitrate played a crucial role in this direct site-selective arylation. The method was extended to synthesize biologically active molecules.



5-Aryl-2-pyridone alkaloids represent a class of natural products with extremely rich biological profiles and pharmaceutical applications alike. They often show promising antifungal, antibacterial, and insecticidal activities against the deleterious effects of neurodegenerative diseases (Figure 1).[1,2]

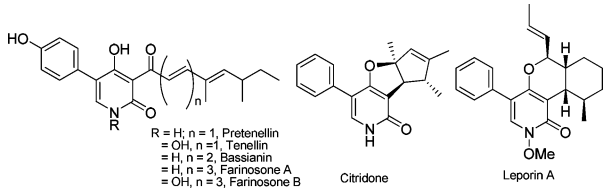
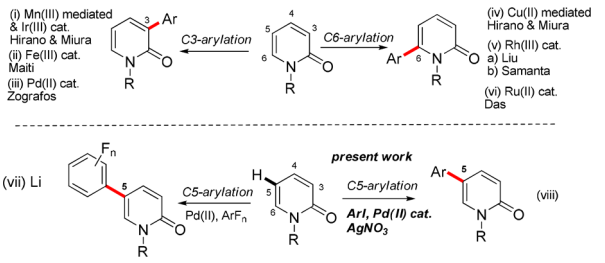


Figure 1. Biologically relevant natural products containing C5-arylated 2-pyridone scaffold.

In addition to these remarkable biological applications, the structural complexity associated with these arylated pyridones, often required the use of multiple steps for their preparation.[3] Arguably, one of the straightforward methods to construct such a scaffold is direct site-selective arylation at the C5-position via C−H functionalization. Recently, straightforward regioselective functionalizations of the 2-pyridone moiety have garnered significant attention;[4,5] arylation especially becomes an important challenge due to the omnipresence of aryl groups in various bioactive 2-pyridone scaffolds.[6,7] Recently, Hirano and Miura's group reported Mn(III) mediated C3-arylation of 2-pyridones using aryl boronic acid (Scheme 1i).[6a] Later they improved their regioselective method under visible-light-promoted Ir(III) based photoredox catalysis.[6b] Since the pioneering work by Hirano and Miura's group, Maiti and co-workers found an alternative strategy using an Fe(III) catalytic system (Scheme 1ii) for this C3-arylation.[6c] In a different approach, Zografos group showed Pd(II)-catalyzed C3-arylation of 4-hydroxy-2-pyridone scaffold utilizing its enol-like character (Scheme 1iii).[6d] In a pioneering study, the Hirano and Miura group developed a copper-mediated C6-

Scheme 1. Regioselective Direct Arylation of 2-Pyridone



selective dehydrogenative heteroarylation of 2-pyridone with 1,3-azoles (Scheme 1iv).[7a]

Following this, Liu's group and our group also showed Rh(III) catalyzed C6-arylation of the 2-pyridone scaffold using a directing group strategy (Scheme 1v).[7b,c] The method was further extended by the Das group under a Ru(II)-catalyzed oxidative arylation strategy (Scheme 1vi).[7d] Despite the elegance of the above-mentioned approaches, direct C5-arylation is quite rare.[8] In a seminal work, Li's group astutely developed a palladium-catalyzed dehydrogenative C5-arylation with highly electron-deficient polyfluoroarenes (Scheme 1vii).[8] However, direct site-selective arylation of substrates with a blocked functionalization site like cyclic enaminone,[9] quinolone scaffolds[10] is known in the literature. Nevertheless, one of the major problems behind general C5-arylation could be getting control of the C5-position over the C3-position. Often the aryl group introduces selectively at the C3-position or diarylation happens at both the C3- and C5-position of the 2-pyridone core. To overcome this challenge, some in situ generated cationic palladium catalysts especially Pd−nitrate catalytic systems[11] with enhanced electrophilicity were often used to obtain the kinetically favored C−H functionalization.[12]

Intrigued by our recent studies on direct pyridone[7c,13a−c] and other heterocycle functionalizations,[13d] we hypothesized

Received: July 5, 2018

DOI: 10.1021/acs.orglett.8b02112
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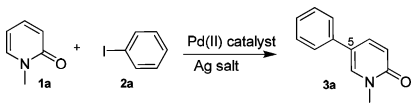
that a similar concept might lead to our desired site-selective arylation on 2-pyridone core. Herein, we report a silver nitrate promoted direct palladium-catalyzed highly site-selective C5-arylation of 2-pyridone with aryl iodide as a coupling partner (Scheme 1viii).

Our efforts began by examining a possible Pd(II)-catalyzed arylation of *N*-methyl-2-pyridone (**1a**) with iodobenzene (**2a**) as a coupling partner (Table 1). The reaction was initially

Table 1. Optimization of C5-Selective Arylation of 2-Pyridones[a]



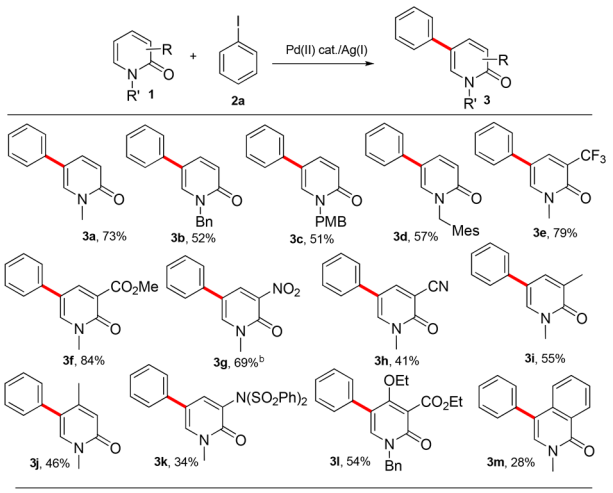
entry	catalyst	solvent	additive (equiv)	yield (%)[b]
1	$Pd(OAc)_2$	DME	–	n.d.
2	$Pd(OAc)_2$	DME	Ag_2CO_3 (1)	n.d.
3	$Pd(OAc)_2$	DME	AgOAc (1)	n.d.
4	$Pd(OAc)_2$	DME	$AgPF_6$ (1)	45
5	$Pd(OAc)_2$	DME	$AgClO_4$ (1)	50
6	$Pd(OAc)_2$	DME	$AgNO_3$ (1)	50
7	$Pd(OAc)_2$	DME	$AgNO_3$ (1.5)	63
8	$Pd(OAc)_2$	toluene	$AgNO_3$ (1.5)	30
9	$Pd(OAc)_2$	dioxane	$AgNO_3$ (1.5)	42
10	$Pd(OAc)_2$	DMF	$AgNO_3$ (1.5)	56
11	**$Pd(OAc)_2$**	**DME/DMF (5:1)**	**$AgNO_3$ (1.5)**	**73**
12	$PdCl_2$	DME	$AgNO_3$ (1.5)	17
13	$Pd(TFA)_2$	DME	$AgNO_3$ (1.5)	35
14	$Pd(PPh_3)_4$	DME	$AgNO_3$ (1.5)	n.d.
15	$Pd(OAc)_2$	DME/DMF (5:1)	$NaNO_3$ (1.5)	n.d.
16	$Pd(OAc)_2$	DME/DMF (5:1)	KNO_3 (1.5)	n.d.
17	$Pd(OAc)_2$	DME/DMF (5:1)	$[Me_4N]NO_3$ (1.5)	n.d.
18	$Pd(OAc)_2$	DME/DMF (5:1)	$AgNO_3$ (0.3)	28
19	$Pd(OAc)_2$	DME/DMF (5:1)	K_2CO_3 (1.5)	n.d.
20	$Pd(OAc)_2$	DME/DMF (5:1)	Cs_2CO_3 (1.5)	n.d.

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), Pd catalyst (10 mol %), additive (0.3 mmol), 110 °C, 0.2 M, 12 h. [b]Isolated yields. n.d. = not detected. DME = 1,2-dimethoxyethane.

screened in 1,2-dimethoxyethane (DME) with 10 mol % $Pd(OAc)_2$ catalyst and in the absence of any Ag salt or in the presence of Ag_2CO_3 or AgOAc to obtain no desired product formation (Table 1, entries 1−3). Gratifyingly, 45% of the desired product (**3a**) was isolated when the reaction was performed with the $AgPF_6$ additive (Table 1, entry 4). The isolated yield of product **3a** was marginally increased due to a change in silver salt to $AgClO_4$ (Table 1, entry 5). Unfortunately, formation of some complex mixture of products along with the desired product made this condition less effective. Furthermore, in a cleaner reaction, a comparable amount of desired product **3a** was obtained under $AgNO_3$ mediated conditions. For further improvement of reaction efficacy, the amount of $AgNO_3$ salt was increased. As expected, the yield of desired product improved to 63% (Table 1, entry 7). However, the change of solvents did not improve the desired product yields (Table 1, entries 8−10). Gladly, the efficacy of the reaction was further improved to 73% by fine-tuning the solvent mixture with DME/DMF in a 5:1 ratio (Table 1, entry 11). Next, screening of other Pd(II) and Pd(0) salts offered either a poor yield or no desired product formation (Table 1, entries 12−14). Assuming the important role of the nitrate anion,[14] other relevant nitrates were tested. But none of these nitrates were able to provide the desired product (Table 1, entries 15−17). Importantly, use of $AgNO_3$ in a substoichiometric amount (30 mol %) afforded only 28% of the desired product (Table 1, entry 18). This result indicates the stoichiometric requirement of $AgNO_3$ salt for successful transformation. In general, the examined silver salts provided C5 selective arylation with some decomposition of starting material. However, screening other additives like K_2CO_3 and Cs_2CO_3 in place of the silver salt did not provide the isolable desired product (Table 1, entries 19−20). Finally, the structure of compound **3a** with C5 phenyl group was firmly confirmed in comparison with the literature known analytical data.[15]

With the optimized conditions in hand, the scope study of 2-pyridones was carried out (Scheme 2). As expected, the

Scheme 2. Scope Using Various 2-Pyridones[a]

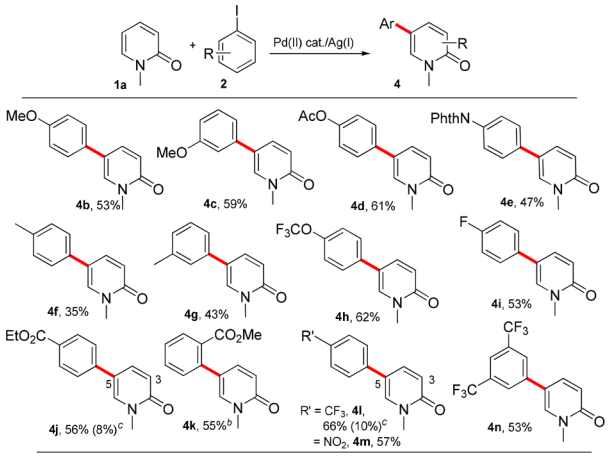


[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), $AgNO_3$ (0.3 mmol), DME/DMF (5:1; 0.2 M), 110 °C, 12 h. [b]$AgClO_4$ was used. Bn = benzyl, PMB = *p*-methoxybenzyl, Mes = mesityl.

reaction was smoothly proceeded for various *N*-alkylated 2-pyridones (Scheme 2, **3a−3d**) with good to moderate yields. Gratifyingly, electron withdrawing groups like CF_3, ester or nitro at the C3-position of 2-pyridone provided very good yields of the desired products (Scheme 2, **3e−3g**). A relatively lower yield was obtained when a CN group was tethered at the C3-position of 2-pyridone ring (Scheme 2, **3h**). Further, substrates bearing electron-donating groups at various positions worked uninterruptedly with moderate yields (Scheme 2, **3i−3k**). Moreover, this site-selective arylation was further extended with highly substituted 2-pyridone (Scheme 2, **3l**). Interestingly, our attempt to explore isoquinolone remained successful under the developed conditions, albeit in reduced yield (Scheme 2, **3m**). To our pleasure, the reaction was smoothly carried out with various aryl iodides having electronically and sterically variable functional groups (Scheme 3, **4b−4n**). Gratifyingly, electron-rich methoxy or acetoxy phenyl iodides provided satisfying yields of desired products under the optimized reaction conditions (Scheme 3, **4b−4d**). Notably, aryl iodide having *para*-amine functionality also worked uninterruptedly (Scheme 3, **4e**). Aryl iodides with a methyl group at the *para* or *meta* position gave desired products with synthetically acceptable

DOI: 10.1021/acs.orglett.8b02112
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 3. Scope Using Various Aryl Iodides[a]

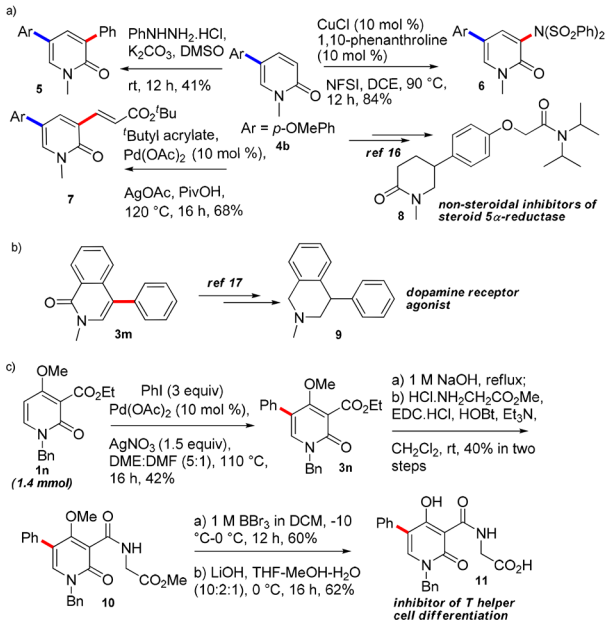


[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), $AgNO_3$ (0.3 mmol), DME/DMF (5:1; 0.2 M), 110 °C, 12 h. [b]Reaction temperature: 125 °C. [c]C3 isomer detected via crude ^1H NMR of reaction mixture.

yields (Scheme 3, **4f**–**4g**). Further, halogen-containing trifluoromethoxy or fluoro substituted aryl iodides were well survived during the transformation (Scheme 3, **4h**–**4i**). Moreover, the C5-arylation was extended with electron-deficient aryl iodides having an ester, a trifluoromethyl, or a nitro group at its different positions (Scheme 3, **4j**–**4n**).

To demonstrate the general applicability of the developed method, compound **4b** was explored with post operation modifications (Scheme 4a). Initially, it was treated with phenyl

Scheme 4. Product Modifications and Applications



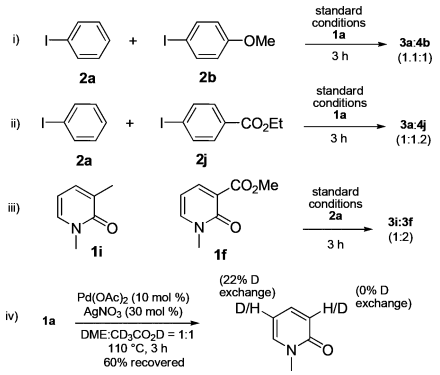
hydrazine to obtain C3 and C5 unsymmetrical diaryl substituted 2-pyridone derivative **5**.[6e] Next, C3-amidation of **4b** was done under Cu(I) catalyzed conditions to provide compound **6**.[7c] Further, **4b** was regioselectively C3-alkenylated under Pd(II)-catalyzed conditions to offer compound **7**.[8]

Importantly, a pharmaceutically active compound **8** could be obtained from compound **4b** via a literature known method.[16]

In another known procedure, 4-phenylisoquinolone derivative **3m** could be easily converted into a pharmaceutically active known compound **9** (Scheme 4b).[17] In a separate application, biologically active compound **11** was achieved from 2-pyridone derivative **1n** (Scheme 4c). Strategically, site-selective C5-arylation of **1n** followed by ester hydrolysis of **3n** and coupling with glycine methyl ester afforded compound **10**. Furthermore, cleavage of methyl ether and subsequent ester hydrolysis provided our desired compound **11** in synthetically acceptable yield.[18]

To reveal the mechanistic insight of the reaction, various control experiments were performed (Scheme 5). To under-

Scheme 5. Control Experiments

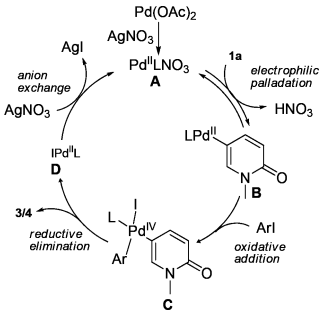


stand the preference of electronically different aryl iodides (**2b** and **2j**), they were treated separately with **2a** and **1a**. The outcome of this competition experiment illustrated that the rate of the reaction was marginally varied (Scheme 5i–ii). However, the reaction rate for electron-deficient 2-pyridone (**1f**) was strongly favored over electron-rich 2-pyridone (**1i**) under the optimized conditions (Scheme 5iii). Presumably, the electron-withdrawing group (at C3) in **1a** guided the product ratio. Next, under Pd(II)/$AgNO_3$ conditions, treatment of *N*-methyl 2-pyridone (**1a**) with CD_3CO_2D as the cosolvent in the absence of phenyl iodide offered 22% deuterium incorporation at the C5-position exclusively (Scheme 5iv). Additionally, another H/D scrambling experiment under $AgClO_4$ mediated conditions revealed 10% deuterium content at the C5-position and a trace amount of deuterium incorporation at the C3-position (see the Supporting Information). These outcomes reveal that the C–H metalation at the C5-position is reversible. Although C3-metalation is more unlikely here, the possibility of irreversible C3-metalation cannot be totally ruled out at this stage due to the observation of some amount of starting material decomposition. Based on the control experiments and previous literature,[11,12] a tentative mechanism involving a Pd(II)/Pd(IV) catalytic cycle is proposed (Scheme 6). Though the specific role of $AgNO_3$ is not fully understood, presumably it helps in the formation of an active catalyst and regenerates the active palladium catalyst via AgI formation.

Due to presence of a nitrate anion, this palladium–nitrate species is now more electrophilic and compatible for the kinetically controlled C5-metalation to generate species **B** through eletrophilic aromatic substitution (SEAr). Next, the oxidative addition of aryl iodide to the Pd(II)-intermediate **B** readily provides Pd(IV)-species **C**. Subsequently, it undergoes reductive elimination to generate compound **3** or **4** with Pd(II)-iodo species **D**. Finally, ligand exchange with the aid of

DOI: 10.1021/acs.orglett.8b02112
Org. Lett. XXXX, XXX, XXX–XXX

Scheme 6. Plausible Mechanism for C5-Arylation of 2-Pyridone



$AgNO_3$ regenerates the active Pd(II)-nitrate species **A** for continuing the catalytic cycle. Here, the possibility of a Pd(0)/Pd(II) catalytic cycle can be ruled out, as no catalytic turnover was observed under Pd(0) conditions (Table 1, entry 14). However, a concerted metalation−deprotonation (CMD) pathway cannot be ruled out at this stage, especially as this reaction worked well with electron-deficient 2-pyridones.[19]

In conclusion, we have developed unprecedented direct Pd(II)-catalyzed site-selective C5-arylation of 2-pyridones with easily available aryl iodides. The developed method exhibited a wide scope and functional group tolerance and extended to synthesize biologically important scaffolds. The admirable role of silver nitrate for the crucial site selectivity and catalytic cycle was revealed. Currently, application of this method toward the total synthesis of a related natural product is underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02112.

Experimental procedures and characterization of new compounds (^{1}H, ^{13}C, and ^{19}F NMR spectra) (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support by the SERB, India (YSS/2014/000383 and PDF/2016/000242) is acknowledged. Authors thank DST, India (SR/FST/CSII-026/2013) for 500 MHz NMR facility as well as CSIR (D.D.) and UGC (S.S.) for fellowships. We thank Dr. S. K. Patra, IIT Kharagpur for helpful mechanistic discussions and CRF, IIT Kharagpur for analytical facilities.

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DOI: 10.1021/acs.orglett.8b02112
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