Palladium-Catalyzed Chelation-Assisted C–H Bond Halogenation: Selective Chlorination of 2-Arylpyridines with Acid Chlorides

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Abstract: Palladium-catalyzed chelation-assisted C–H bond halogenation of arenes using acid chlorides as chlorinating agents is reported. This method provides a monoselective, straightforward, and clean route for the construction of aryl chlorides as privileged motifs in organic transformations.

Key words: aroyl chlorides, C–H activation, chlorination, palladium, 2-phenylpyridine

Halogenated compounds are a crucial class of materials because of their vital applications in many synthetic routes. They also serve as key intermediates for the construction of several biologically active molecules, natural products, pharmaceuticals, and agrochemicals.[1] Furthermore, aryl chlorides are employed as precursors of organolithium[2] and Grignard reagents,[3] and they are also among the most versatile sources of aryl motifs in transition-metal-catalyzed cross-coupling reactions.[4,5] In this context, metal-catalyzed site selective direct halogenation of C–H bonds of arenes bearing directing groups has attracted much attention in the last few years.[6]

The pioneering work of Fahey in 1970 demonstrated the viability of the direct conversion of C–H bonds into C–halogen bonds by palladium-catalyzed chlorination of azobenzene using chlorine as an oxidant.[7] However, it resulted in a mixture of mono-, di-, tri-, and tetrachlorinated adducts and the use of chlorine as a toxic halogen source limited its wide application. Related elegant studies on chelation-assisted C–H bond halogenations were further developed by the groups of Sanford,[8] Yu,[9] Bedford,[10] Shi,[11] Kakiuchi,[12] Fabis,[13] and Xu.[14] Among the various halogenating agents investigated, *N*-halosuccinimides have received widespread research attention, and it use has been extended to a wide variety of directing groups, including oxime ethers,[8e,f,13] isoquinolines,[8e] pyridine derivatives,[8b,e,f,10b,15a] ketones[15a], amides,[8e,f,10a,b,15a] carbamates,[8e,15a,b] isoxazolines,[8b,e,f,10a,b,13,15] esters,[16] and nitriles.[17]

Although selective *ortho*-halogenation of 2-arylpyridines is broadly useful in organic synthesis and medicinal chemistry, there are few examples of the monoselective chlorination of these scaffolds. A significant advance in this area was reported by Sandford who demonstrated that 2-arylpyridines could be *ortho*-chlorinated using palladium(II) acetate as the catalyst and *N*-chlorosuccinimide as the halide source and terminal oxidant.[8] However, the yields were moderate and di-*ortho*-halogenated products were typically observed unless a steric bias was introduced into the substrates. Elegant work from the groups of Yu[9] and Kakiuchi[12] on metal-catalyzed *ortho* C–H chlorination of 2-arylpyridines using 1,1,2,2-tetrachloroethane and aqueous hydrogen chloride as chlorinating agents, was also accompanied by regioselectivity issues. Dong[18] also highlighted the use of arylsulfonyl chlorides as chlorinating agents for the chlorination of sterically encumbered 2-arylpyridines. Furthermore, recently Chen and Cheng communicated a copper-catalyzed *ortho*-benzoxylation of 2-arylpyridine C–H bonds and extend it to an *ortho*-chlorination reaction with benzoyl chloride.[19] Despite the importance of this communication, the reactions required the use of overstoichiometric amounts of lithium carbonate as the base and the use of 2-arylpyridines with a blocked *ortho*-position or increased steric hindrance, either on the aryl or pyridinyl ring, to circumvent overhalogenation.

Thus, the need for new methodology for the selective monohalogenation of certain C–H bonds remains an important challenge in organic synthesis. Herein, we report the monoselective *ortho*-chlorination of 2-arylpyridines under mild base and oxygen-free reaction conditions using a palladium catalytic system and readily available, inexpensive, and versatile acid chloride agents.

Initially we examined the feasibility of the monoselective *ortho*-chlorination of 2-phenylpyridine (**1a**) with benzoyl chloride (**2a**) using reaction conditions similar to those of Dong and co-workers:[18] $PdCl_2(PhCN)_2$ (10 mol%), $CuCl_2$ (10 mol%), and 4 Å molecular sieves in *N*,*N*-dimethylformamide at 140 °C for 24 hours (Table 1, entry 1), however, the desired adduct **3a** was obtained in <5% yield. Varying the palladium source did not improve the yield further (entries 2–4). Next we examined the use of various solvents and found that the use of 1,4-dioxane led to the formation of the monochlorinated 2-phenylpyridine **3a** in 71% yield (entries 4–7). Varying the oxidant showed palladium(II) chloride/copper(II) chloride to be the most effective catalytic system (entries 7–11). A control reaction also showed the crucial role of copper(II) chloride in the formation of chloroarenes in the palladium(II)-catalyzed reaction of 2-phenylpyridine derivatives with aroyl chlorides (entries 12). Further optimization showed that lowering the amount of the aroyl chloride to two equivalents

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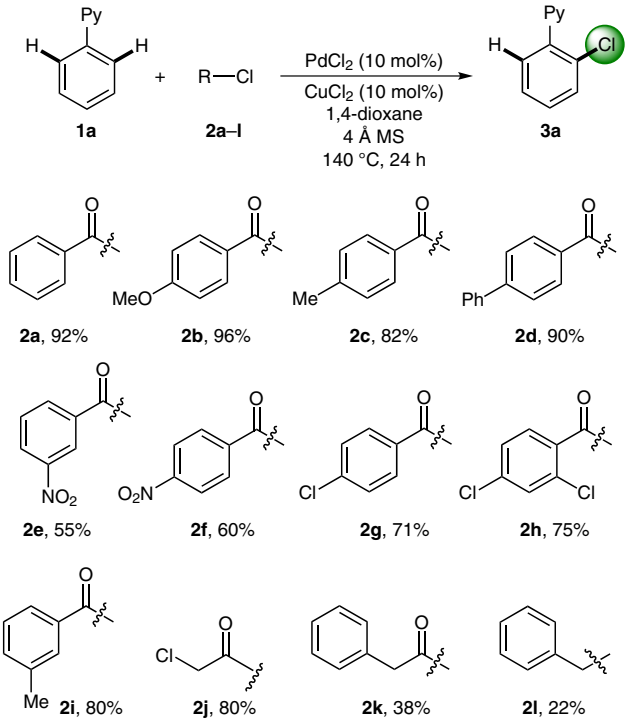
substantially increased the yield of **3a** (entry 13); however lowering the reaction temperature or running the reaction without palladium decreased the yield remarkably (entries 15 and 16). The optimized conditions, 2-phenylpyridine (**1a**), benzoyl (2 equiv), palladium(II) acetate and copper(II) chloride in 1,4-dioxane at 140 °C for 24 hours, generate the chlorinated 2-phenylpyridine **3a** in 92% yield with excellent regioselectivity. To the best of our knowledge, this transformation represents the first successful palladium-catalyzed monoselective *ortho*-C–H chlorination of 2-arylpyridines. Furthermore, aroyl chlorides are less toxic and they are readily available chlorinating agents that may provide a valuable starting point in the sp^2 C–H chlorination of arenes. Although the use of benzoyl chloride detracts from the atom economy of this process, their cost, stability, and availability makes this an interesting source of electrophilic chloride.

Table 1 Screening Reaction Conditions for the C–H Chlorination of 2-Phenylpyridine (**1a**)[a]

Entry	Catalyst	Oxidant	Solvent	Yield[b] (%)
1	$PdCl_2(PhCN)_2$	$CuCl_2$	DMF	<5
2	$Pd_2(dba)_3$	$CuCl_2$	DMF	<5
3	$Pd(acac)_2$	$CuCl_2$	DMF	<5
4	$PdCl_2$	$CuCl_2$	DMF	10
5	$PdCl_2$	$CuCl_2$	DMSO	10
6	$PdCl_2$	$CuCl_2$	1,4-dioxane	71
7	$PdCl_2$	$CuCl_2$	MeCN	20
8	$PdCl_2$	$Cu(OAc)_2 \cdot 2\,H_2O$	1,4-dioxane	30
9[c]	$PdCl_2$	$ZnCl_2$	1,4-dioxane	<5
10	$PdCl_2$	O_2	1,4-dioxane	<5
11[c]	$PdCl_2$	NCS	1,4-dioxane	45
12	$PdCl_2$	–	1,4-dioxane	0
13[d]	$PdCl_2$	$CuCl_2$	1,4-dioxane	92
14[e]	$PdCl_2$	$CuCl_2$	1,4-dioxane	41
15[f]	$PdCl_2$	$CuCl_2$	1,4-dioxane	33
16	–	$CuCl_2$	1,4-dioxane	18

[a] Reaction conditions: 2-phenylpyridine (**1a**, 0.1 mmol, 1.0 equiv), benzoyl chloride (**2a**, 3.0 equiv), palladium catalyst (10 mol%), oxidant (10 mol%), 4 Å MS, solvent (0.1 M), 140 °C, 24 h.
[b] Isolated yields.
[c] 20 mol% of oxidant was added.
[d] Benzoyl chloride (2.0 equiv).
[e] 12 h.
[f] 120 °C.

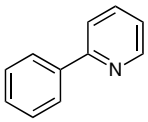
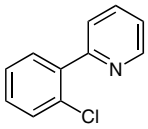
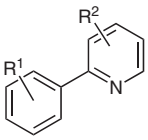
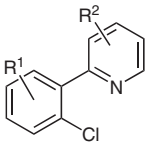
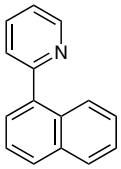
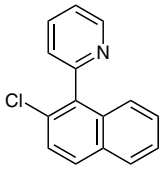
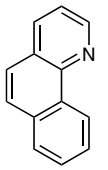
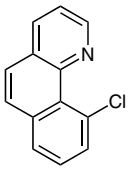
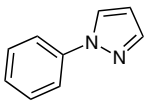
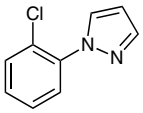
We next used the optimal reaction condition to examine the scope of the *ortho*-C–H chlorination using a range of aroyl chlorides. 2-(2-Chlorophenyl)pyridine (**3a**) was obtained regioselectively when various aroyl chlorides were employed (Scheme 1). Electron-rich aroyl chlorides **2b**–**d**,**i** reacted smoothly with **1a** to afford **3a** in high to excellent yields. The use of 4-methoxybenzoyl chloride (**2b**) was the most effective, resulting in the formation of **3a** in almost quantitative yield. Electron-deficient aroyl chlorides with nitro and chloro substituents **2e**–**h**, were also tolerated under the reaction conditions and successfully afforded **3a**, albeit in lower yields. Next we examined the use of aliphatic acid chlorides and intriguingly found that highly monoselective chlorination of 2-phenylpyridine (**1a**) was achieved in 80% yield using 2-chloroacetyl chloride (**2j**) as the chlorinating agent. 2-Phenylacetyl chloride (**2k**) also afforded the desired adduct **3a** in 38% yield, but benzyl chloride (**2l**) gave **3a** in only 22% yield.



Scheme 1 Scope of the chlorinating agents. *Reagents and conditions*: 2-Arylpyridine (0.1 mmol, 1.0 equiv), acid chloride **2** (2.0 equiv), $PdCl_2$ (10 mol%), $CuCl_2$ (10 mol%), 4 Å MS, 1,4-dioxane (0.1 M), 140 °C, 24 h.

As summarized in Table 2, *ortho*-C–H chlorination of 2-phenylpyridine using aroyl chlorides was extended to a range of 2-arylpyridines. Chlorination took place smoothly with *ortho*-blocked 2-phenylpyridine, or substrates with increased hindrance on either the phenyl or pyridinyl rings (entries 2–5 and 8). 2-Aryl-5-methylpyridines also afforded monochlorinated arenes in good yields (entries 6 and 7). With 4-methylphenyl-substituted pyridine however, a competitive di-*ortho*-halogenation reaction resulted in a mixture of mono- and dichloroarylpyridines (entry 4). The *ortho*-chlorination reaction also worked well with a benzoquinoline substrate and afforded the desired product in 65% yield (entry 9). We were delighted to see that 1-phenylpyrazole also reacted under the optimized reaction

Table 2 Scope of the Chlorination Reaction of 2-Arylpyridines[a]

Entry	Substrate	Aroyl chloride	Product		Yield (%)
1		**2a**		**3a**	92
2		**2b**		**3b**: R^1 = 6-Me, R^2 = H	68
3		**2a**		**3c**: R^1 = 5-Me, R^2 = H	55
4		**2f**		**3d**: R^1 = 4-Me, R^2 = H	82[b]
5		**2a**		**3e**: R^1 = H, R^2 = 3-Me	48
6		**2a**		**3f**: R^1 = H, R^2 = 5-Me	68
7		**2a**		**3g**: R^1 = 4-Me, R^2 = 5-Me	61
8		**2b**		**3h**	61
9		**2a**		**3i**	65
10		**2a**		**3j**	63

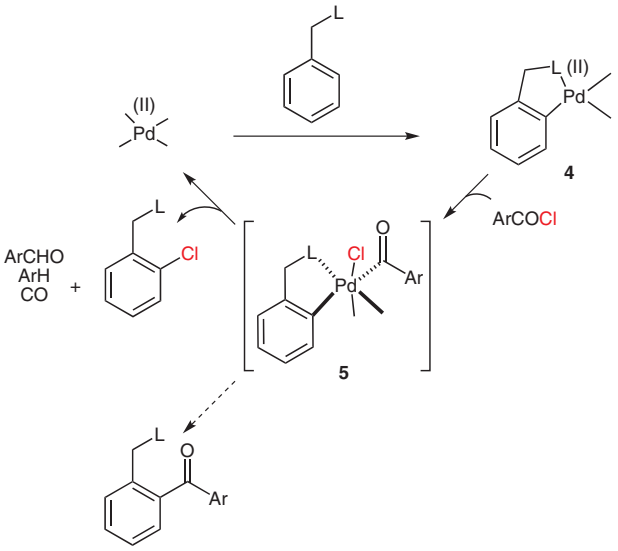
[a] Reaction conditions: 2-arylpyridine (0.1 mmol, 1.0 equiv), aroyl chloride (2.0 equiv), $PdCl_2$ (10 mol%), $CuCl_2$ (10 mol%), 4 Å MS, 1,4-dioxane (0.1 M), 140 °C, 24 h.
[b] A mixture of mono and dichloroarylpyridines (1:1) was obtained.

conditions to give the desired monochlorinated adduct **3j** in 63% isolated yield (entry 10).

A plausible mechanism for this transformation may involve the initial formation of palladium(II) species **4** that undergoes an oxidative addition to the aroyl chloride to form the palladium(IV) species **5**. Carbon–halogen bond-forming reductive elimination from this species affords the chlorinated product. It is interesting that C–Cl reductive elimination occurs in preference to C–C reductive elimination (the acylated product was not observed in the reaction mixture) (Scheme 2).

In summary, the palladium-catalyzed regioselective C–H monochlorination of 2-phenylpyridine with acid chlorides as a safe and available halogen source under mild reaction conditions was developed. Importantly, both aroyl chlorides and aliphatic acid chlorides could be utilized in this halogenation reaction. It is noteworthy that under the optimized reaction conditions, overhalogenation was precluded, which is not feasible in similar copper-catalyzed chlorination approaches. Furthermore, the protocol could be readily extended to the monohalogenation of 2-phenylpyrazole. Broadening the scope of the reaction to the halogenation of simple arenes as a crucial class of materials is currently under investigation.

All reagents and metal catalysts were commercially available and used as received. All reactions were carried out in an oil bath using Microwave Vials (2–5 mL). NMR spectra were recorded at r.t. on 500, 400, and 300 MHz spectrometers using $CDCl_3$ as the NMR solvent.



Scheme 2 Possible mechanistic route to chlorinated pyridines

2-(2-Chlorophenyl)pyridine (3a);[9d] Typical Procedure
A vial equipped with a stirrer bar was charged with 2-phenylpyridine (0.2 mmol, 1.0 equiv), benzoyl chloride (2.0 equiv), $PdCl_2$ (10 mol%), $CuCl_2$ (10 mol%), and 4 Å MS. Then anhyd 1,4-dioxane (0.1 M) was added, and the vial was capped. The resulting mixture was heated in an oil bath at 140 °C for 24 h, cooled, and then filtered through a short plug of silica. Removal of the solvent gave a crude mixture that was purified by flash column chromatography (hexanes–EtOAc gradient) to give a colorless oil; yield: 17 mg (92%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.73 (br s, 1 H), 7.77 (t, *J* = 7.2 Hz, 1 H), 7.65 (d, *J* = 7.5 Hz, 1 H), 7.60 (d, *J* = 6.7 Hz, 1 H), 7.48 (d, *J* = 7.1 Hz, 1 H), 7.38–7.34 (m, 2 H), 7.30 (d, *J* = 7.6 Hz, 1 H).

Anal. Calcd for $C_{11}H_8ClN$: C, 69.67; H, 4.25; N, 7.39. Found: C, 69.92; H, 4.37; N, 7.53.

2-(2-Chloro-6-methylphenyl)pyridine (3b)[9d]
Colorless oil; yield: 14 mg (68%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 4.5 Hz, 1 H), 7.70 (t, *J* = 7.2 Hz, 1 H), 7.33–7.29 (m, 3 H), 7.26–7.17 (m, 2 H), 2.10 (s, 3 H, Me).

Anal. Calcd for $C_{12}H_{10}ClN$: C, 70.77; H, 4.95; N, 6.88. Found: C, 71.01; H, 5.06; N, 7.02.

2-(2-Chloro-5-methylphenyl)pyridine (3c)[16]
Colorless oil; yield: 11 mg (55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 4.2 Hz, 1 H), 7.74 (t, *J* = 7.3 Hz, 1 H), 7.65 (d, *J* = 7.5 Hz, 1 H), 7.42 (br s, 1 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.24–7.30 (m, 1 H), 7.1 (d, *J* = 7.8 Hz, 1 H), 2.37 (s, 3 H, Me).

Anal. Calcd for $C_{12}H_{10}ClN$: C, 70.77; H, 4.95; N, 6.88. Found: C, 71.06; H, 5.09; N, 7.04.

2-(2-Chloro-4-methylphenyl)pyridine (3d)[6c]
Colorless oil; yield: 17 mg (82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 4.3 Hz, 1 H); 7.74 (t, *J* = 7.6 Hz, 1 H), 7.64 (d, *J* = 7.6 Hz, 1 H), 7.49 (d, *J* = 7.1 Hz, 1 H), 7.26–7.31 (m, 2 H), 7.16 (d, *J* = 7.6 Hz, 1 H), 2.38 (s, 3 H, Me).

Anal. Calcd for $C_{12}H_{10}ClN$: C, 70.77; H, 4.95; N, 6.88. Found: C, 70.98; H, 5.05; N, 7.00.

2-(2-Chlorophenyl)-3-methylpyridine (3e)[9d]
Colorless oil; yield: 10 mg (48%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 4.2 Hz, 1 H), 7.59 (d, *J* = 6.4 Hz, 1 H), 7.48–7.46 (m, 1 H), 7.36–7.31 (m, 3 H), 7.24 (d, *J* = 7.3 Hz, 1 H), 2.18 (s, 3 H, Me).

Anal. Calcd for $C_{12}H_{10}ClN$: C, 70.77; H, 4.95; N, 6.88. Found: C, 70.51; H, 4.84; N, 6.70.

2-(2-Chlorophenyl)-5-methylpyridine (3f)
Yellow oil; yield: 14 mg (68%).

IR (neat): 1693, 2853, 2923 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (br s, 1 H), 7.57–7.60 (m, 3 H), 7.48 (d, *J* = 6.3 Hz, 1 H), 7.28–7.39 (m, 2 H), 2.42 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.0, 149.9, 139.0, 136.6, 132.1, 131.6, 130.1, 129.5, 127.1, 124.4, 21.0, 18.3.

MS (EI, 70 eV): *m*/*z* = 203 [M^+].

Anal. Calcd for $C_{12}H_{10}ClN$: C, 70.77; H, 4.95; N, 6.88. Found: C, 71.13; H, 5.11; N, 7.12.

2-(2-Chloro-4-methylphenyl)-5-methylpyridine (3g)
Yellow oil; yield: 13 mg (61%).

IR (neat): 1699, 2923 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (br s, 1 H), 7.56 (s, 2 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.29 (s, 1 H), 7.17 (d, *J* = 8.7 Hz, 1 H).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 154.1, 149.8, 139.7, 136.5, 136.2, 131.8, 131.3, 130.5, 129.6, 127.9, 125.8, 124.4.

MS (EI, 70 eV): *m*/*z* = 217 [M^+].

Anal. Calcd for $C_{13}H_{12}ClN$: C, 71.72; H, 5.56; N, 6.43. Found: C, 72.03; H, 5.70; N, 6.65.

2-(2-Chloronaphthalen-1-yl)pyridine (3h)
Yellow solid; mp 86–87 °C (Lit.[8e] 85.7–86.4 °C); yield: 15 mg (61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79–8.80 (m, 1 H), 7.95–8.03 (m, 3 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.48–7.58 (m, 3 H), 7.43 (d, *J* = 7.6 Hz, 1 H), 7.25 (d, *J* = 7.9 Hz, 1 H).

Anal. Calcd for $C_{15}H_{10}ClN$: C, 75.16; H, 4.21; N, 5.84. Found: C, 74.92; H, 4.09; N, 5.67.

10-Chlorobenzo[*h*]quinoline (3i)
Yellow solid; yield: 14 mg (65%); mp 79–80 °C (Lit.[9d] 81–82 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.12 (d, *J* = 4.1, 1 H), 8.17 (d, *J* = 7.8 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 2 H), 7.77 (d, *J* = 8.2 Hz, 1 H), 7.69 (d, *J* = 8.2 Hz, 1 H), 7.54 (t, *J* = 7.0 Hz, 2 H).

Anal. Calcd for $C_{13}H_8ClN$: C, 73.08; H, 3.77; N, 6.56. Found: C, 72.84; H, 3.65; N, 6.40.

1-(2-Chlorophenyl)-1*H*-pyrazole (3j)[8e]
Colorless oil; yield: 11 mg (63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 1.8 Hz, 1 H), 7.76 (d, *J* = 1.2 Hz, 1 H), 7.57–7.61 (m, 1 H), 7.51–7.54 (m, 1 H), 7.31–7.40 (m, 2 H), 6.47–6.48 (m, 1 H).

Anal. Calcd for $C_9H_7ClN_2$: C, 60.52; H, 3.95; N, 15.68. Found: C, 60.78; H, 4.09; N, 15.85.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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