JOC The Journal of Organic Chemistry

Note

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b01103 • Publication Date (Web): 26 Jul 2016

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Pd-catalyzed Ligand-Free Synthesis of Arylated heteroaromatics by Coupling of *N*-heteroaromatic Bromides with Iodobenzene diacetate, Iodosobenzene or Diphenyliodonium salts

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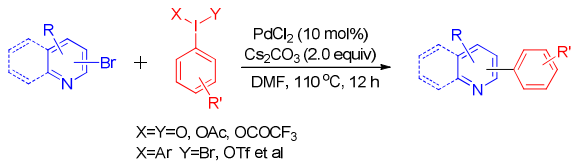
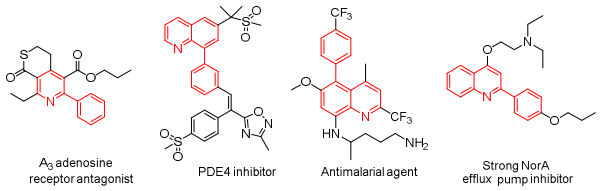


Abstract: An efficient method for synthesizing arylated heteroaromatics has been reported via Pd-catalyzed ligand-free cross-coupling of *N*-heteroaromatic bromides with iodine (III) reagents under mild conditions. Iodobenzene diacetate, iodosobenzene and diphenyliodonium salts act as ideal arylated sources in this reaction, producing bioactive aromatic substituted pyridines and quinolines in moderate to high yields.

Nitrogen-containing heteroaromatics are a class of significant building blocks used in the construction of a wide range of compounds, including natural products, pharmaceuticals, agrochemicals, ligands, and advanced materials.[1] Amongst them, arylated pyridines and quinolines,

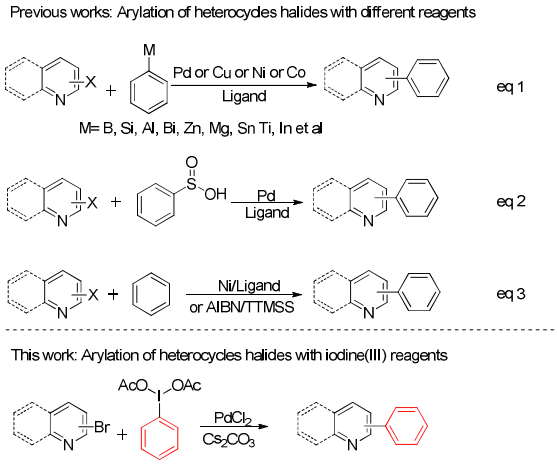
two important skeleton motifs of heterocycles, are frequently used in the preparation of diverse medicinal intermediates (Figure 1).[2] Examples of which include an A_3 adenosine receptor antagonist,[3] a phosophodiesterase 4 (PDE4) inhibitor,[4] an antimalarial agent,[5] and a strong NorA efflux

Figure 1. Selected Examples of Arylated Pyridines and Quinolines on Medicine



pump inhibitor.[6] Consequently, the synthesis of arylated pyridines and quinolines have received considerable attention over the past few decades and significant efforts have been devoted to seeking more efficient preparation methods. With regard to the arylation of pyridines and quinolines, one of the most prevalent strategies towards cross-coupling of heteroaromatic halides with different arylation reagents is done by using transition metal catalysts.[7] Examples include the use of arylmetallic reagents (Scheme 1, eq 1),[8] arylsulfinates (Scheme 1, eq 2),[9] even arenes (Scheme 1, eq 3)[10] as arylation reagents

Scheme 1. Arylation of *N*-heteroaromatics



in this cross-coupling reaction. While prevalent, the requirement of

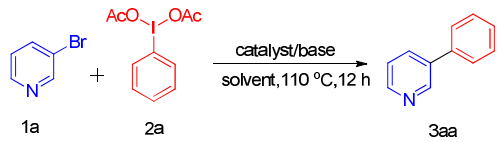
unstable arylation reagents and suitable ligands, poor functional group compatibility, and a somewhat limited substrate scope reduce the attractiveness of this method.[11] Thus, it is meaningful to develop a direct and efficient arylation approach in the synthesis of this context.

In recent years, hypervalent iodine compounds have received significant attention owing to their easily available, non-toxic, highly stable and low-cost features.[12] Although diaryliodonium salt was extensively studied as an arylation reagent in the past few decades, iodobenzene diacetate (PIDA), which is widely served as an oxidant or acetoxylation reagent in organic synthesis,[13] was less applied in the arylation of heterocyclic derivatives. Herein we present a novel Pd-catalyzed ligand-free method for the synthesis of arylated *N*-heteroaromatics by using PIDA and other hypervalent iodine compounds as arylation reagents. To our best knowledge, this has not been reported so far.

We began our investigation with a model reaction using 3-bromopyridine (**1a**) and PIDA (**2a**). In the presence of $Pd(OAc)_2$ (10 mol%, 0.02 mmol) as catalyst and Cs_2CO_3 (2.0 equiv, 0.40 mmol) as base in *N*,*N*-dimethylformamide (DMF) (1 mL) stirring under air at 110 ^oC for 12 h, the desired product 3-phenylpyridine (**3aa**) was isolated in 69% yield (Table 1, entry 1). To standardize the reaction conditions, we conducted a series of experiments with variation of the reaction parameters. Palladium and other transition metal catalysts were tested first, and $PdCl_2$ gave the best result of 78% yield (Table 1, entries 1-7). Subsequently, different bases were examined and the results showed that Cs_2CO_3 offered higher yield (Table 1, entries 8-13). Reducing the amount of Cs_2CO_3 slightly led to lower yield of 68%, but reactivity was not

increased when excess Cs_2CO_3 was applied (Table 1, entries 14 and 15). Further screening of solvents demonstrated that DMF displayed the best

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3aa

Entry	Catalyst(10 mol %)	Base(equiv)	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$	Cs_2CO_3(2.0)	DMF	69
2	**$PdCl_2$**	**Cs_2CO_3(2.0)**	**DMF**	**78**
3	$Pd(PPh_3)_4$	Cs_2CO_3(2.0)	DMF	64
4	$Pd(OCOCF_3)_2$	Cs_2CO_3(2.0)	DMF	69
5	$Pd_2(dba)_3$	Cs_2CO_3(2.0)	DMF	71
6	CuI	Cs_2CO_3(2.0)	DMF	0
7	$FeCl_3$	Cs_2CO_3(2.0)	DMF	0
8	$PdCl_2$	K_3PO_4(2.0)	DMF	64
9	$PdCl_2$	K_2CO_3(2.0)	DMF	70
10	$PdCl_2$	Na_2CO_3(2.0)	DMF	67
11	$PdCl_2$	NaOH(2.0)	DMF	50
12	$PdCl_2$	*t*-BuOK(2.0)	DMF	75
13	$PdCl_2$	Et_3N(2.0)	DMF	59
14	$PdCl_2$	Cs_2CO_3(1.0)	DMF	68
15	$PdCl_2$	Cs_2CO_3(4.0)	DMF	78
16	$PdCl_2$	Cs_2CO_3(2.0)	DMA	70
17	$PdCl_2$	Cs_2CO_3(2.0)	NMP	74
18	$PdCl_2$	Cs_2CO_3(2.0)	DMSO	trace
19	$PdCl_2$	Cs_2CO_3(2.0)	xylene	0

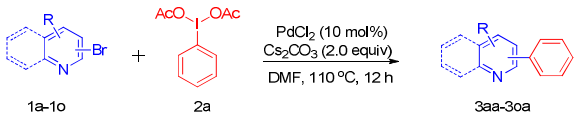
[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), catalyst (10 mol%, 0.02 mmol) and base in solvent (1 mL) at 110 °C for 12 h.
[b] Isolated yields

ability in this transformation (Table 1, entries 16-19). As a result, we chose Table 1, entry 2 as the optimized reaction conditions.

With the optimized reaction conditions established, we proceeded to examine the scope of heteroaryl bromides (Table 2). As expected, we found that a wide array of heteroaryl bromides bearing different functional groups (methyl, methoxy, ester) all exhibited good compatibility in this transformation and the corresponding products

3aa-3ga were obtained in moderate to high yields under the optimized conditions. The heteroaryl bromides containing different electronic effect

Table 2. Synthesis of Arylated Heteroaromatics from Substituted Heteroaryl Bromides and PIDA[a]



1a-1o 2a 3aa-3oa

Entry	Heteroaryl bromides	Products	Yield[b] (%)	Entry	Heteroaryl bromides	Products	Yield[b] (%)
1	1a	3aa	78	9	1i	3ia	72
2	1b	3ba	41	10	1j	3ja	69
3	1c	3ca	60	11	1k	3ka	71
4	1d	3da	50	12	1l	3la	70
5	1e	3ea	65	13	1m	3ma	56
6	1f	3fa	80	14	1n	3na	70
7	1g	3ga	43	15	1o	3oa	62
8	1h	3ha	0				

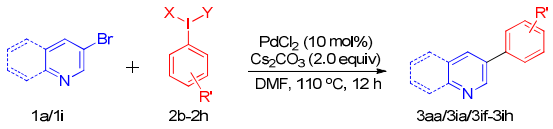
[a] Reaction conditions: heteroaryl halides (0.20 mmol), PIDA (0.40 mmol), $PdCl_2$ (10 mol%, 0.02 mmol) and Cs_2CO_3 (0.40 mmol) in DMF (1 mL). The reaction was stirred at 110 °C for 12 h.
[b] Isolated yield

substituents influenced the yields of the desired products. It is also observed that strong electron-withdrawing groups showed lower reactivity compared to electron-donating groups. For example, 5-bromo-2-methoxypyridine generated the product **3da** easily in moderate yield of 50%, while no reaction occurred when 5-bromo-2-nitropyridine was employed in this reaction. To further extend the scope of this reaction, we next investigated several other nitrogen-containing heterocycles and the expected products **3ia-3ka** were

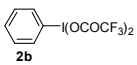
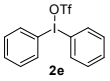
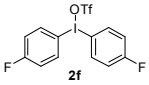
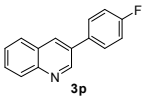
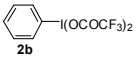
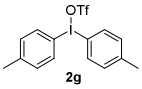
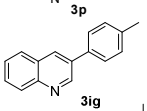
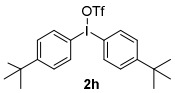
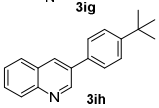
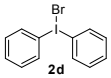
obtained in good yields. Gratifyingly, disubstituted 3,5-dibromopyridine participated efficiently as well to give the correspongding product **3la** in 70% yield. Notably, 5-, 6- or 8- position bromo-substituted quinoline could also undergo the reaction smoothly to give the products **3ma, 3na,** and **3oa** in 56%, 70% and 62% yields, respectively.

Then our attention turned towards expanding the scope of hypervalent iodine (III) reagents (Table 3). Satisfyingly, [bis(trifluoroacetoxy)iodo] benzene was proved to be suitable as an arylation partner which could deliver the desired products **3aa** and **3ia** in 72% and 75% yields. Iodosobenzene could also give the corresponding products **3aa** and **3ia** in 30% and 25% yields, respectively. Considering the wide application of quinoline derivatives in pharmaceutical

Table 3. Synthesis of Arylated Heteroaromatics from Substituted Heteroaryl Bromides and Other Iodine (III) Reagents[a]



1a/1i 2b-2h 3aa/3ia/3if-3ih

Entry	Heteroaryl bromides	Iodine (III) reagents	Products	Yield[b] (%)	Entry	Heteroaryl bromides	Iodine (III) reagents	Products	Yield[b] (%)
1	**1a**	 **2b**	**3aa**	72	6	**1i**	 **2e**	**3ia**	53
2	**1a**	 **2c**	**3aa**	30	7	**1i**	 **2f**	 **3p**	31
3	**1i**	 **2b**	**3ia**	75	8	**1i**	 **2g**	 **3ig**	60
4	**1i**	 **2c**	**3ia**	25	9	**1i**	 **2h**	 **3ih**	40
5	**1i**	 **2d**	**3ia**	30					

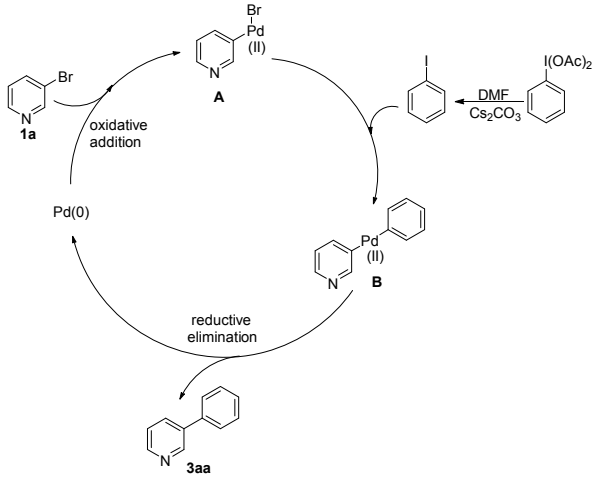
[a] Reaction conditions: heteroaryl bromides (0.20 mmol), iodine(III) reagents (0.40 mmol), $PdCl_2$ (10 mol%, 0.02 mmol) and Cs_2CO_3 (0.40 mmol) in DMF (1 mL). The reaction was stirred at 110 °C for 12 h.
[b] Isolated yield

chemistry, further expansion of the scope of diphenyliodonium salts were investigated, with 3-bromoquinoline selected as the coupling substrate.

We found that symmetric diphenyliodonium salts with different anion (Br^-, OTf^-) were smoothly converted into the corresponding products **3ia** in moderate yields (Table 3, entries 5 and 6). Subsequently, we noticed that the introduction of an electron-donating/-withdrawing group on the diphenyliodonium salts has little impact on the success of this transformation, albeit with lower yield. Fluorine, methyl and *tert*-butyl groups on phenyl rings were well tolerated, affording the arylated products **3if-3ih** in 31-60% yields. It is noteworthy that fluorine, methyl and *tert*-butyl substituents can be converted into other valuable functional groups.

Based on the observations above, we proposed a plausible mechanism for this reaction in Scheme 2. Step i: oxidative addition of 3-bromopyridine (**1a**) to Pd(0) to form the aryl-Pd(II)-Br species **A**.[14a,14b] Step ii: PIDA degrades to iodobenzene with the aid of base in DMF under 110 ^oC.[12d] Step iii: iodobenzene, which is obtained from step ii, reacts with aryl-Pd(II)-Br species **A**, affording intermediate **B**.[14c,14d] Step iv: reductive elimination of **B** would produce the product **3aa** and regenerate the Pd(0) species for next catalytic cycle.[14e]

Scheme 2. Possible Mechanism



In summary, we have developed a novel and convenient protocol for the synthesis of arylated nitrogen-containing heteroaromatics using

heteroaryl bromides, hypervalent iodine(III) reagents and a Pd-based catalyst. This method shows good functional compatibility. It uses iodine(III) compounds as a promising direct arylation reagent and generates the corresponding products in moderate to high yields.

Experimental Section

General Remarks: Reagents and solvents were purchased commercially and used without further purification. Silica gel (200-300 mesh) was used for column chromatography. ^{1}H NMR spectra were recorded on 400MHz or 300MHz in $CDCl_3$; ^{13}C NMR spectra were recorded on 101 MHz or 75 MHz in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. The high-resolution mass spectra (HRMS) was recorded on an FT-ICR mass spectrometer using electrospray ionization (ESI). All melting points were determined without correction.

General Procedure for the Synthesis of 3 (3aa as an example).

3-bromopyridine (**1a**) (31.6 mg, 0.20 mmol), PIDA (**2a**) (128.8 mg, 0.40 mmol), $PdCl_2$ (3.5 mg, 0.02 mmol), Cs_2CO_3 (130.3 mg, 0.40 mmol) were added to a test tube. Then 1 mL DMF was added using a syringe. The reaction was stirred at 110 ^{o}C for 12 h under air atmosphere. After completion of the reaction (monitored by TLC), the test tube was allowed to cool to room temperature. After that, the solution was diluted with ethyl acetate (10 mL), washed with brine (5 mL) and dried over Na_2SO_4. Then the solvent was evaporated in vacuo, the residues were purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the desired product **3aa**.

Analytical Data for Products.

3-Phenylpyridine (**3aa**).[8b] Yellow oil (24 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (d, *J* = 2.2 Hz, 1H), 8.60 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.88 (dt, *J* = 8.8, 3.2 Hz, 1H), 7.62-7.55 (m, 2H), 7.52-7.34 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 148.2, 137.7, 136.6, 134.4, 129.0, 128.1, 127.1, 123.5. **HRMS(ESI)*m/z* calcd for** $C_{11}H_9N$ $[M+H]^+$ 156.0808, **found** 156.0806 .

2-Methyl-3-phenylpyridine **(3ba)**.[15] Yellow oil (14 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.45-7.42 (m, 2H), 7.40-7.34 (m, 1H), 7.34-7.29 (m, 2H), 7.17 (dd, *J* = 7.6, 4.9 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 147.8, 139.9, 137.1, 136.9, 128.9, 128.3, 127.4, 120.9, 23.3. **HRMS(ESI)*m/z* calcd for** $C_{12}H_{11}N$ $[M+H]^+$ 170.0964, **found** 170.0966 .

2-Methyl-5-phenylpyridine **(3ca)**.[15] Yellow oil (20 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 2.0 Hz, 1H), 7.77 (dd, *J* = 8.0, 4.0Hz, 1H), 7.59-7.54 (m, 2H), 7.48-7.44 (m, 2H), 7.40-7.36 (m, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 147.5, 137.9, 134.7, 133.7, 129.0, 127.8, 126.9, 123.1, 24.0. **HRMS(ESI)*m/z* calcd for** $C_{12}H_{11}N$ $[M+H]^+$ 170.0964, **found** 170.0966 .

2-Methoxy-5-phenylpyridine **(3da)**.[8b] Yellow oil (18 mg, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 2.5, 0.7 Hz, 1H), 7.79 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.56-7.49 (m, 2H), 7.48-7.41 (m, 2H), 7.39-7.31 (m, 1H), 6.82 (dd, *J* = 8.6, 0.7 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 144.9, 137.8, 137.4, 130.0, 128.9, 127.3, 126.6, 110.8, 53.5. **HRMS(ESI)*m/z* calcd for** $C_{12}H_{11}NO$ $[M+H]^+$ 186.0914, **found** 186.0915

3-Methoxy-5-phenylpyridine **(3ea)**.[16] Yellow oil (24 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.31 (s, 1H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.43-7.38 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 137.6, 136.0, 129.0, 128.2, 127.2, 119.1, 55.6, 29.7. **HRMS(ESI)*m/z* calcd for** $C_{12}H_{11}NO$ $[M+H]^+$ 186.0914, **found** 186.0915

2-Methoxy-6-phenylpyridine **(3fa)**.[17] White solid (30 mg, 80%), m. p. 103-115 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.4 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 8.1, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37-7.33 (m, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 4.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 153.3, 141.2, 139.2, 128.7, 127.2, 127.1, 113.6, 110.8, 53.2. **HRMS(ESI)*m/z* calcd for** $C_{12}H_{11}NO$ $[M+H]^+$ 186.0914, **found** 186.0915 .

Methyl-5-phenylpicolinate **(3ga)**.[18] Yellow oil (18 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 9.01 (s, 1H), 8.50 (t, *J* = 2.0 Hz, 1H), 7.66-7.59 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 151.8, 149.4, 135.2, 129.2, 128.6, 127.2, 52.5. **HRMS(ESI)*m/z* calcd for** $C_{13}H_{11}NO_2$ $[M+H]^+$ 214.0863, **found** 214.0861.

3-Phenylquinoline (**3ia**).[9] Yellow oil (29 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.19 (d, *J* = 2.2 Hz, 1H), 8.30 (d, *J* = 2.2 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.76-7.68 (m, 3H), 7.61-7.39 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 147.3, 137.8, 133.8, 133.2, 129.4, 129.2, 129.1, 128.1, 128.0, 127.4, 127.0. **HRMS(ESI)*m/z* calcd for** $C_{15}H_{11}N$ $[M+H]^+$ 206.0964, **found** 206.0966.

4-Phenylisoquinoline **(3ja)**.[9] Yellow oil (28 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.50 (s, 1H), 8.09-8.00 (m, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.73-7.59 (m, 2H), 7.58-7.43 (m, 5H). ^{13}C NMR (101 MHz, MHz, $CDCl_3$) δ 151.9, 142.7, 136.9, 134.2, 133.3, 130.5, 130.1, 128.6, 127.9, 127.8, 127.1, 124.8. **HRMS(ESI)*m/z* calcd for** $C_{15}H_{11}N$ $[M+H]^+$ 206.0964, **found** 206.0966.

5-Phenylpyrimidine **(3ka)**.[9] Yellow oil (22 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.97 (s, 2H), 7.64-7.43 (m, 5H). ^{13}C NMR

(75 MHz, $CDCl_3$) δ 157.4, 154.9, 134.3, 134.2, 129.4, 129.0, 127.0. **HRMS(ESI)*m/z* calcd for** $C_{10}H_8N_2$ $[M+H]^+$ 157.0760, **found** 157.0763.

3,5-Diphenylpyridine **(3la)**.[19] White solid (33 mg, 70%), m. p. 115-132 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 2H), 8.05 (t, *J* = 2.1 Hz, 1H), 7.66-7.64 (m, 4H), 7.53-7.47 (m, 4H), 7.45-7.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 137.8, 132.9, 129.1, 128.2, 127.3. **HRMS(ESI)*m/z* calcd for** $C_{17}H_{13}N$ $[M+H]^+$ 232.1121, **found** 232.1122 .

5-Phenylquinoline (**3ma**).[8d] White solid (23 mg, 56%), m. p. 74-78 ^oC. ^1H NMR (400MHz, $CDCl_3$) δ 8.96-8.90 (m, 1H), 8.26-8.21 (m, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.54-7.42 (m, 6H), 7.35 (dd, *J* = 8.6, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 148.5, 140.5, 139.4, 134.3, 130.0, 128.9, 128.9, 128.4, 127.6, 127.2, 126.7, 121.0. **HRMS(ESI)*m/z* calcd for** $C_{15}H_{11}N$ $[M+H]^+$ 206.0964, **found** 206.0966.

6-Phenylquinoline **(3na)**.[8d] White solid (28 mg, 70%), m. p. 99-112 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 8.92 (d, *J* = 2.8 Hz, 1H), 8.25-8.14 (m, 2H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.44-7.38 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 147.6, 140.3, 139.3, 136.2, 129.9, 129.2, 128.9, 128.5, 127.7, 127.4, 125.5, 121.4. **HRMS(ESI)*m/z* calcd for** $C_{15}H_{11}N$ $[M+H]^+$ 206.0964, **found** 206.0966.

8-Phenylquinoline **(3oa)**.[8d] Yellow oil (25 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.20 (dd, *J* = 8.1, 3.7, 1H), 7.82 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.75-7.67 (m, 3H), 7.60 (t , *J* = 7.9, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.44-7.37 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.1, 140.9, 139.5, 136.2, 130.6, 130.3, 128.7, 128.0, 127.5, 127.3, 126.2, 120.9. **HRMS(ESI)*m/z* calcd for** $C_{15}H_{11}N$ $[M+H]^+$ 206.0964, **found** 206.0966.

3-(4-Flourophenyl)quinoline **(3if)**.[8g] Yellow solid (14 mg, 31%), m. p. 83-89 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (d, *J* = 2.3 Hz, 1H), 8.25 (d, *J* = 2.3 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.77-7.63 (m, 3H), 7.62-7.54 (m, 1H), 7.27-7.16 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9 (d, *J* = 246.7 Hz), 149.7, 147.3, 134.0, 133.1, 132.9, 129.5, 129.2, 129.1, 129.0, 127.9, 127.1, 116.1 (d, *J* = 21.7 Hz). **HRMS(ESI)*m/z* calcd for** $C_{15}H_{10}FN$ $[M+H]^+$ 224.0870, **found** 224.0873.

3-(*p*-Tolyl)quinoline **(3ig)**.[8g] Yellow solid (26 mg, 60%), m. p. 82-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, *J* = 2.3 Hz, 1H), 8.24 (d, *J* = 2.1 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.70-7.66 (m, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.56-7.51 (m, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 147.2, 138.0, 134.9, 133.7, 132.7, 129.8, 129.2, 129.1, 128.0, 127.9, 127.2, 126.8, 21.1. **HRMS(ESI)*m/z* calcd for** $C_{16}H_{13}N$ $[M+H]^+$ 220.1121, **found** 220.1120.

3-((4-*tert*-Butyl)phenyl)quinoline **(3ih)**.[11g] Yellow oil (21 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.29 (d, J = 2.1 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.74-7.65 (m, 3H), 7.59-7.55 (m, 3H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 150.0, 147.2, 134.9, 133.7, 132.9, 129.2, 128.1, 127.9, 127.1, 126.9, 126.2, 34.7, 31.3. **HRMS(ESI)*m/z* calcd for** $C_{19}H_{19}N$ $[M+H]^+$ 262.1590, **found** 262.1591.

Supporting Information

NMR spectra of all compounds. The materials is available free of charge on the ACS Publications website.

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