JOC The Journal of Organic Chemistry

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Pd-Catalyzed Ligand-Free Synthesis of Arylated Heteroaromatics by Coupling of *N*-Heteroaromatic Bromides with Iodobenzene Diacetate, Iodosobenzene, or Diphenyliodonium Salts

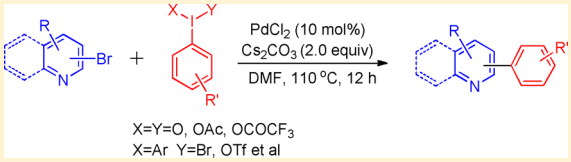
Xiajun Wang,[†] Yongqin He,[†] Mengdan Ren,[†] Shengkang Liu,[†] He Liu,[‡] and Guosheng Huang*[,†]

[†]State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Department of Chemistry, Lanzhou University, Lanzhou 730000, China

[‡]Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

Supporting Information

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] Among 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

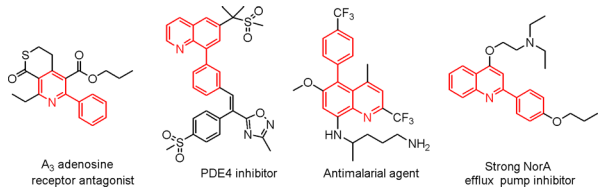
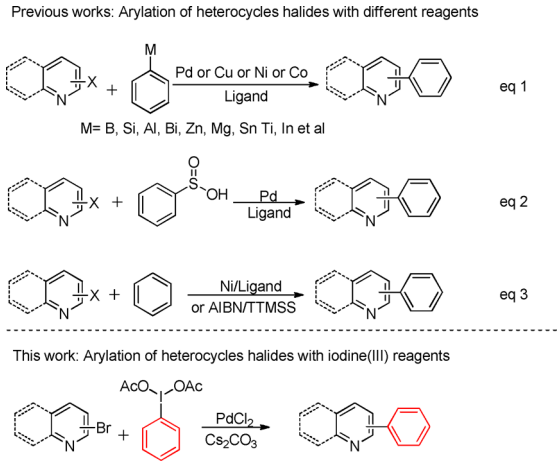


Figure 1. Selected examples of arylated pyridines and quinolines in medicine.

include an A_3 adenosine receptor antagonist,[3] a phosphodiesterase 4 (PDE4) inhibitor,[4] an antimalarial agent,[5] and a strong NorA efflux 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 toward cross-coupling of heteroaromatic halides with different arylation reagents utilizes transition metal catalysts.[7] Examples include the use of arylmetallic reagents (Scheme 1, eq 1),[8] arylsulfinates (Scheme 1, eq 2),[9] and even arenes (Scheme 1, eq 3)[10] as arylation reagents in this cross-coupling reaction. Although 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 for synthesis in this context.

Scheme 1. Arylation of *N*-Heteroaromatics



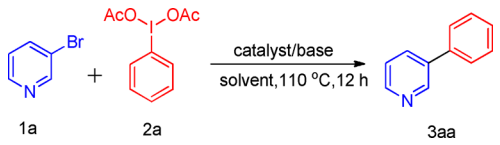
In recent years, hypervalent iodine compounds have received significant attention owing to their easy availability and nontoxic, highly stable, and low-cost features.[12] Although diaryliodonium salt was extensively studied as an arylation reagent in the past few decades, iodobenzene diacetate (PIDA), which widely serves 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 using PIDA and other hypervalent iodine compounds as arylation reagents, which has not yet been reported to our best knowledge.

Received: May 11, 2016
Published: July 26, 2016

DOI: 10.1021/acs.joc.6b01103
J. Org. Chem. 2016, 81, 7958−7962

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) and stirring under air at 110 °C for 12 h, desired product 3-phenylpyridine (**3aa**) was isolated in 69% yield (Table 1, entry 1). To standardize the reaction conditions,

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.

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 led to slightly 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 ability in this transformation (Table 1, entries 16−19). As a result, we chose entry 2 of Table 1 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 corresponding products **3aa**−**3ga** were obtained in moderate to high yields under the optimized conditions. The heteroaryl bromides containing different electronic effect substituents influenced the yields of the desired products. It is also observed that strong electron-withdrawing groups showed lower reactivity compared to that of electron-donating groups. For example, 5-bromo-2-methoxypyridine generated product **3da** easily in moderate yield of 50%, whereas 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 expected products **3ia**−**3ka** were obtained in good yields. Gratifyingly, disubstituted 3,5-dibromopyridine participated efficiently as well to give correspongding product **3la** in 70% yield. Notably, 5-, 6-, or 8-position bromo-substituted quinoline could also undergo the reaction smoothly to give products **3ma**, **3na**, and **3oa** in 56, 70, and 62% yields, respectively.

Then, our attention turned toward expanding the scope of hypervalent iodine(III) reagents (Table 3). Satisfyingly, [bis-(trifluoroacetoxy)iodo] benzene proved to be suitable as an arylation partner, which could deliver desired products **3aa** and **3ia** in 72 and 75% yields, respectively. Iodosobenzene could also give corresponding products **3aa** and **3ia** in 30 and 25% yields, respectively. Considering the wide application of quinoline derivatives in pharmaceutical chemistry, further expansion of the scope of diphenyliodonium salts was investigated with 3-bromoquinoline selected as the coupling substrate. We found that symmetric diphenyliodonium salts with different anions (Br^-, OTf^-) were smoothly converted to 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 had 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 arylated products **3if**−**3ih** in 31−60% yields. It is noteworthy that fluorine, methyl, and *tert*-butyl substituents can be converted to other valuable functional groups.

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

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.

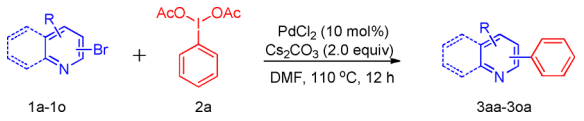
EXPERIMENTAL SECTION

General Remarks. Reagents and solvents were purchased commercially and used without further purification. Silica gel (200−300 mesh) was used for column chromatography. ^1H NMR spectra were recorded on 400 or 300 MHz in $CDCl_3$; ^{13}C NMR spectra were recorded on 101 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), and Cs_2CO_3 (130.3 mg, 0.40 mmol) were added to a test tube. Then, 1 mL of DMF was added using a syringe. The reaction was stirred at 110 °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.

DOI: 10.1021/acs.joc.6b01103
J. Org. Chem. 2016, 81, 7958−7962

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

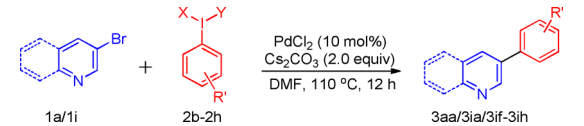


1a-1o + 2a → 3aa-3oa

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) stirred at 110 °C for 12 h. [b]Isolated yields.

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	3if	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) stirred at 110 °C for 12 h. [b]Isolated yields.

Then, the solution was diluted with ethyl acetate (10 mL), washed with brine (5 mL), and dried over Na_2SO_4. The solvent was then evaporated in vacuo, and the residues were purified by column chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give desired product **3aa**.

Analytical Data for Products. *3-Phenylpyridine (**3aa**).*[8b] Yellow oil (24 mg, 78%). ^1H 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,

DOI: 10.1021/acs.joc.6b01103
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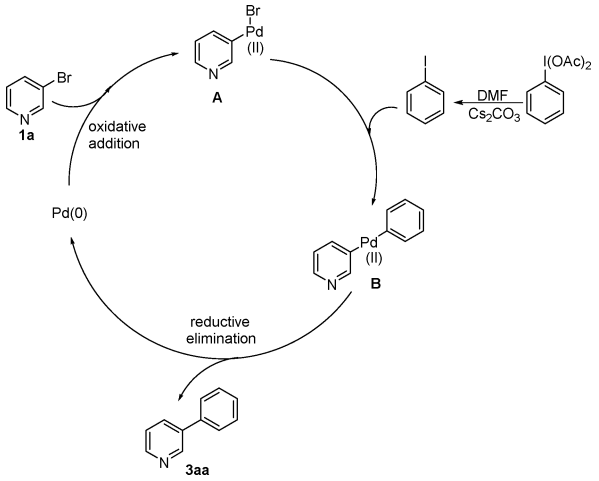
Scheme 2. Possible Mechanism



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, 4.0 Hz, 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%). Mp 103−115 °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%). Mp 115−132 °C. ^{1}H 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%). Mp 74−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 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%). Mp 99−112 °C. ^{1}H 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-Fluorophenyl)quinoline (***3if***).[8g] Yellow solid (14 mg, 31%). Mp 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%). Mp 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.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01103.

NMR spectra of all compounds (PDF)

DOI: 10.1021/acs.joc.6b01103
J. Org. Chem. 2016, 81, 7958−7962

AUTHOR INFORMATION

Corresponding Author

*Fax: +86 931 8912596. Tel: +86 931 8912586. E-mail: hgs@lzu.edu.cn.

Notes

The authors declare no competing financial interest.

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DOI: 10.1021/acs.joc.6b01103
J. Org. Chem. 2016, 81, 7958−7962