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## Introduction

Cyclometalation has become one of the most popular organometallic reactions, providing a straightforward entry to cyclometalated complexes that feature a metal–carbon bond.<sup>1</sup> Among them, cyclometalated palladium( $\pi$ ),<sup>2</sup> iridium( $\pi$ )<sup>3</sup> complexes have been successfully developed as highly active precatalysts for coupling reactions. For example, Buchwald<sup>4</sup> and Ishii<sup>5</sup> groups have reported the use of dialkylbiaryl phosphinepalladacycle complexes and [Ir(cod)Cl]<sub>2</sub>/PPh<sub>3</sub> as efficient catalysts for the Suzuki reaction of unactivated aryl chlorides and the  $\alpha$ -alkylation of alcohols. As an alternative, NHCs have proved to be excellent ligands in transition-metal-catalyzed coupling reactions.<sup>6</sup> Especially the NHC-palladacycles reported by the groups of Nolan,<sup>7</sup> Herrmann<sup>8</sup> have successfully been

## Cyclometalated Pd(II) and Ir(III) 2-(4-bromophenyl)pyridine complexes with N-heterocyclic carbenes (NHCs) and acetylacetonate (acac): synthesis, structures, luminescent properties and application in one-pot oxidation/Suzuki coupling of aryl chlorides containing hydroxymethyl<sup>†</sup>

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A series of cyclopalladated 2-(4-bromophenyl)pyridine (bpp) complexes [Pd(bpp)(NHC)Cl] **1–3**, [Pd(bpp)-(acac)] **4**, cyclometalated iridium(III) complexes [Ir(bpp)<sub>2</sub>Cl]<sub>2</sub> **5** and [Ir(bpp)<sub>2</sub>(acac)] **6** have been synthesized and characterized. Their detailed structures have been determined by X-ray diffraction and many intermolecular C–H···X (Cl, Br,  $\pi$ ) and  $\pi$ ··· $\pi$  interactions were found in their crystals. Cyclometalated complexes **1–4** and **6** exhibit luminescence with emission peaks of 390–543 nm in dichloromethane solution under UV irradiation. Their application to coupling reactions of aryl chlorides containing hydroxymethyl was also investigated. An efficient **3**/Cu cocatalyzed oxidation/Suzuki reaction for the synthesis of biarylaldehydes from chloro-phenylmethanol and arylboronic acids in air has been developed. In addition, a **6/3**-cocatalyzed one-pot reaction of acetylferrocene, (2-amino-5-chlorophenyl)methanol, and arylboronic acids provided 6-aryl-2-ferrocenylquinolines in moderate to good yields.

applied to the coupling reactions of aryl chlorides. However, aryl halides containing hydroxymethyl as substrates have been relatively less reported.9 Alcohols are of great importance as cheap and readily available materials for the preparation of pharmaceutical products and fine chemicals. In addition, palladium-catalyzed aerobic alcohol oxidation to carbonyl compounds is one of the most common classes of oxidation reactions in organic chemistry.<sup>10</sup> Great progress has made recently in palladium-catalyzed oxidation by using NHC ligands reported by the group of Sigman.<sup>11</sup> We have also developed NHC-palladacycles/Cu12 and cyclometallated Ir/Pd13 cocatalyzed a-alkylation/Suzuki reaction for the synthesis of 2,6-diarylquinolines from (2-amino-5-bromophenyl)methanol. To the best of our knowledge, there are no reports concerning reactions involving oxidation and the Suzuki reaction for the synthesis of biarylaldehydes from aryl chlorides containing hydroxymethyl and arylboronic acids.

On the other hand, cyclometalated iridium complexes have attracted a great deal of attention due to their possible applications as organic light-emitting diodes (OLEDs).<sup>14</sup> In these studies, acetylacetonate (acac) is one of the most widely used ancillary ligands providing additional possibilities for tuning the electro-optical properties. Furthermore, the use of NHCs as ancillary ligands has opened up new routes for the design of



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 $<sup>\</sup>dagger$  CCDC 981473–981478 for 1-6 and 992168 for 9h. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00833b



Scheme 1 Synthesis of palladacycles 1–4 and cyclometalated iridium complexes 5–6.

phosphorescent materials, because of their high stability and excellent color purity.<sup>15</sup> However, the luminescence of NHCpalladacycles has not been reported to date. As a continuation of our interest in the application of cyclometalated complexes,<sup>16</sup> we prepared four new palladacycles **1–4** and two cyclometalated Ir complexes **5–6** (Scheme 1) and examined their luminescent properties and catalytic activity. Here, we also reported that the **3**/Cu(OAc)<sub>2</sub> and **6**/3-cocatalyzed one-pot reaction of aryl chlorides containing hydroxymethyl, provides a series of biarylaldehydes and 6-aryl-2-ferrocenylquinolines.

### **Results and discussion**

### Synthesis and characterization of the complexes 1-6

The preparation of six new cyclometalated palladium, iridium complexes **1–6** is as follows (Scheme 1). The cyclopalladation reaction was carried out with bpp and 1 equivalent of  $\text{Li}_2\text{PdCl}_4$  and NaOAc in methanol at rt for 12 h. The formed yellow solids were collected by filtration, and can be assigned as a chloride-bridged palladacyclic dimer.<sup>16a,b</sup> Because of its poor solubility in all common organic solvents, it was not characterized and directly subjected to bridge-splitting reaction. Three NHC adducts of palladacycles **1–3** have been easily prepared *in situ* from the reaction of the above dimer and 1,3-bis(4-methylphenyl) imidazolium chloride (ITolHCl), 1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride (IMeOHCl) or 1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride (IMeSHCl) in THF at rt under N<sub>2</sub>. The chloride-bridged dimer [Ir(bpp)<sub>2</sub>Cl]<sub>2</sub> **5** was synthesized according to the reported procedure.<sup>17</sup> Then,

the Pd(II), Ir(III) dimers were directly subjected to bridge-splitting reactions with acac to produce the mononuclear cyclometalated Pd(II), Ir(III) acac complexes 4 and 6.

These complexes were characterized by elemental analysis, IR, ESI-MS, and <sup>1</sup>H NMR. The <sup>1</sup>H NMR spectra of these complexes were consistent with the proposed structures. The lowest field resonance appear as a doublet at  $\delta$  8.43–9.24 ppm, and was assigned to the proton *ortho* to the nitrogen in the pyridyl ring. NHC-palladacycles **1–3** all exhibit singlets for the methyl groups of the NHCs at  $\delta$  2.31, 3.57 and 2.43, 2.29, 2.26 ppm, respectively. In the mass spectra of **1–3**, the most intense peak was attributed to  $[M - Cl]^+$ . The acac *CH* proton is observed as a sharp singlet at  $\delta$  5.41 and 5.30 ppm for complexes **4** and **6**, respectively. Furthermore, the X-ray molecular structures of all complexes were determined.

### X-ray molecular structures of palladacycles

Single crystal structure analyses reveal that **1–4** are mononuclear and the palladium centers feature a square planar coordination geometry. The molecules are shown in Fig. 1–4. The bicyclic system formed by the palladacycle and the pyridyl ring is approximately coplanar (dihedral angles of 5.7°, 0.6°, 3.8° and 1.5°, 0.9° for complexes **1–4**, respectively). The Pd– C<sub>bpp</sub> and Pd–N<sub>bpp</sub> bond lengths are elongated to 1.990(2) and 2.071(2) Å in **1**, 1.992(3) and 2.070(2) Å in **2**, 1.984(4) and 2.083(3) Å in **3**, due to the stronger electron-withdrawing ability of the chloride anion. The Pd–C<sub>carb</sub> [1.998(3) Å] bond length of **3** is similar to those of related carbene adducts [1.992–1.998 Å],<sup>18</sup> while it is longer than those of **1–2** [1.976(2)



Fig. 1 The molecular structure of 1 with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bonds distances (Å): Pd(1)-C(1) 1.976(2), Pd(1)-C(24) 1.990(2), Pd(1)-N(3), 2.071(2), Pd(1)-Cl(1), 2.4205(7).



Fig. 2 The molecular structure of 2 with displacement ellipsoids drawn at the 50% probability level. H atoms and  $CH_2Cl_2$  are omitted for clarity. Selected bonds distances (Å): Pd(1)-C(19) 1.981(3), Pd(1)-C(7) 1.992(3), Pd(1)-N(1) 2.070(2), Pd(1)-Cl(1) 2.4255(10).



Fig. 3 The molecular structure of 3 with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bonds distances (Å): Pd(1)-C(7) 1.984(4), Pd(1)-C(21) 1.998(3), Pd(1)-N(1) 2.083(3), Pd(1)-Cl(1) 2.4061(11).



Fig. 4 The molecular structure of 4 with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bonds distances (Å): Pd(1)-C(1) 1.958(7), Pd(1)-N(1) 2.006(6), Pd(1)-O(1) 2.010(5), Pd(1)-O(2) 2.088(5), Pd(2)-C(18) 1.955(9), Pd(2)-O(4) 2.015(7), Pd(2)-N(2) 2.031(7), Pd(2)-O(3) 2.072(7).

and 1.981(3) Å] possibly due to the steric bulk of the IMes ligand.

For 4, it crystallizes in the triclinic  $P\bar{1}$  space group with two mononuclear molecules [Pd(bpp)(acac)] in each asymmetric unit. The two crystallographic independent Pd(II) ions have the same coordination mode which is chelated by one acac ligand and one bpp ligand, yielding one five-membered ring (NCCCPd) and one six-membered ring (OCCCOPd) around the Pd(II) center (Fig. 4). The Pd–C<sub>bpp</sub> and Pd–N<sub>bpp</sub> bond lengths were found to be in the range of 1.958(7)–1.955(9) and 2.006(6)– 2.031(7) Å, respectively, which are comparable to those of other reported cyclopalladated diketonate complexes.<sup>19</sup> In addition, the bpp and acac ligands are almost coplanar in 4, whereas for 1–3 the imidazole rings of the NHC ligands are almost perpendicular to the bpp plane [76.64(7)° for 1, 87.40(9)° for 2, and 73.08(13)° for 3] for the sake of steric hindrance.

Conventional and unconventional hydrogen interactions are very interesting in crystal engineering and supramolecular chemistry.<sup>20</sup> In **1–3**, there are a plenty of C–H···Cl and C–H···Br interactions with the D···A distances and DHA angles varying from 3.273(5) to 3.821(4) Å, and 123.2 to 166.4°, respectively. Besides C–H···Cl and C–H···Br interactions, there are also some  $\pi$ ··· $\pi$  interactions between the metal-involved rings and aromatic groups of bpp and NHC ligands (Table 1). A closer look at the structures reveals the presence of C–H··· $\pi$  interactions in **1–2**, and **4** (Table 2).

For 1 and 2, both bpp and NHC ligands can serve as H-donors or acceptors of C–H··· $\pi$  interactions (Fig. 5). In the case of 4, the C–H··· $\pi$  interactions are formed between the methyl groups of the acac ligands and pyridine or the benzene ring of the bpp ligands with the H···centroid (aromatic ring) and C···centroid distances falling in the range of 2.8593(5)–3.0388(5) and 3.5836(5)–3.9482(5) Å, respectively. The H···centroid distances of 4 are longer than those of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-stabilized benzene–ammonia and benzene water compounds, but

4

**Table 1** Geometric parameters of the  $\pi \cdots \pi$  interactions in **1–4** 

Complex	$\pi \cdots \pi$	$Cg^{a}$ ···Cg (Å)	$\alpha^b$	$\beta^{c}$	Cg…plane (Cg <sup>2</sup> ) (Å)	Symm. op. on $Cg^2$
1	C18→N3…C18→N3	3.577(1)	0	76.49(1)	3.478(1)	-x, -y, -z
2	$N1 \rightarrow C5 \cdots C6 \rightarrow C11$	3.747(3)	1.07(2)	73.42(2)	3.591(3)	1 - x, 1 - y, 1 - z
3	$C1 \rightarrow N1 \cdots C1 \rightarrow N1$	3.463(1)	0	82.7(1)	3.435(1)	1.5 - x, 0.5 - y, 1 - z
4	$Pd2 \rightarrow O4 \cdots Pd2 \rightarrow N2$	3.644(3)	5.74(3)	69.69(1)	3.417(3)	1 - x, -y, 1 - z

 ${}^{a}$  Cg = centre of gravity of the interacting ring.  ${}^{b}\alpha$  = angle between the planes of the two interacting rings.  ${}^{c}\beta$  = angle between the Cg...Cg line and the plane of the first interacting ring.

Table 2	Geometric parameters	of the $C-H\cdots\pi$	interactions in 1-2 and
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#### Complex H…centroid (Å) C…centroid (Å) C-H--centroid (°) 1 2.962(1)3.775(1)143.32(1)2.664(1)3.557(2)161.09(1)3.069(7) 3.97(1)165.8(3)2 2.8944(4)3.7597(5)150.49(2)4 3.0012(4) 3.9482(5) 169.15(2) 2.8593(5) 133.01(2) 3.5836(5)3.0388(5)3.9385(6)156.63(2)

shorter than that of Cu( $\pi$ )-carboxylate.<sup>21</sup> But in **3**, no obvious C-H··· $\pi$  interactions can be found. These unconventional hydrogen interactions work together and assemble the respective mononuclear molecules into 3D supramolecular structures (Fig. 6).

X-ray molecular structures of cyclometalated iridium complexes

Although many structures of mononuclear cyclometalated iridium complexes have been determined,<sup>3</sup> there are very limited reports on the structures of dinuclear Cl-bridged dimers.<sup>11b,22</sup> The dimer 5 adopts the *racemate* form, rather than the *meso* form. Each iridium atom locates at a distorted octahedral environment with *cis*-C–C and *trans*-N–N chelate dispositions. A two-fold axis passes through both chlorine atoms, thus, the asymmetric unit consists of half of the molecule (Fig. 7). The central iridium atom in **6** is surrounded by two bbp and one acac with *cis*-C–C, *trans*-N–N and *cis*-O–O chelate dispositions (Fig. 8). The Ir–C, Ir–N and Ir–O bond lengths are similar to the reported values of cyclometalated 2-phenylpyridine (ppy) iridium complex (ppy)<sub>2</sub>Ir(acac).<sup>23</sup> The crystal structure of **6** is also similar to that of (ppy)<sub>2</sub>Ir(acac) by



Fig. 5 C-H... $\pi$  interactions found in complexes 1 (a), 2 (b) and 4 (c).



Fig. 6 Three-dimensional packing diagrams of 1 (a), 2 (b), 3 (c) and 4 (d). The  $\pi$ --- $\pi$  interactions are shown as dotted lines.



Fig. 7 The molecular structure of 5 with displacement ellipsoids drawn at the 50% probability level. H atoms and  $CH_2Cl_2$  are omitted for clarity. Selected bonds distances (Å): Ir(1)-N(1) 2.070(6), Ir(1)-N(2) 2.077(6), Ir(1)-C(1) 1.998(12), Ir(1)-C(12) 1.989(10), Ir(1) -Cl(1) 2.494(3), Ir(1)-Cl(2) 2.530(3).

the existence of  $\pi \cdots \pi$  interaction with a *ca*. 3.838 Å face–face separation between the adjacent ring planes.

### Luminescent properties

The UV-Vis absorption and photoluminescence (PL) spectra of these complexes in  $CH_2Cl_2$  at rt are shown in Fig. 9 and 10 and Table 3. The absorption spectra of **1–3** have similar features. Two intense absorption peaks appear at 220 nm and 295 nm, and weaker absorptions were also observed between 295 nm



Fig. 8 The molecular structure of 6 with displacement ellipsoids drawn at the 50% probability level. H atoms and  $CH_2Cl_2$  are omitted for clarity. Selected bonds distances (Å): Ir(1)-C(7) 1.994(11), Ir(1)-C(18) 1.996(12), Ir(1)-N(1) 2.049(10), Ir(1)-N(2) 2.014(11), Ir(1)-O(1) 2.158(8), Ir(1)-O(2) 2.140(8).

and 375 nm, respectively. These absorption bands can all be assigned to the ligand localized  $\pi$ - $\pi$ \* transitions. Three NHCpalladacycles all exhibit luminescence in CH<sub>2</sub>Cl<sub>2</sub> at rt. **1** and **3** display emission peaks at 390 nm and 394 nm suggesting that steric factors have less influence on the luminescence. However, the emission peak (414 nm) of **2** containing –OCH<sub>3</sub> is obviously higher than those of **1** and **3** containing –CH<sub>3</sub>,





indicating that the inductive effect of the substituents on the NHC ligand have more effect on the luminescence. The absorption spectra of cyclometalated acac complexes **4** and **6** are very different to each other. Complex **4** shows three intense absorption bands from ligands below 375 nm, in contrast, complex **6** exhibits obvious metal-to-ligand charge transition (MLCT) absorption bands between 407 nm and 510 nm. Thus, the emission ( $\lambda_{\text{max}} = 543$  nm) of complex **6** should be phosphorescence, the emission ( $\lambda_{\text{max}} = 391$  nm) of complex **4** is fluorescence. Similar to the luminescence of (ppy)<sub>2</sub>Ir(acac),<sup>23</sup> **6** shows a yellow phosphorescence, which implies that it not only can be used as





Fig. 11 The cyclic voltammetry spectra of 6.

an emitting material in yellow OLEDs, but in the fabrication of white OLEDs combined with blue emitters.

Moreover, the electrochemical property of **6** was investigated by cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M tetrabutylammonium hexafluorophosphate with a 0.05 V s<sup>-1</sup> scan rate. The cyclic voltammogram shows a reversible oxidation wave due to iridium(III/IV) with  $E_{1/2}^{ox}$  of 1.04 V vs. Ag/AgCl (Fig. 11). The highest occupied molecular orbital (HOMO) energy level was calculated to be -5.36 eV relative to the value of -4.8 eV for ferrocene (Fc) with respect to the zero vacuum level.<sup>24</sup> The lowest unoccupied molecular orbital (LUMO) energy level was estimated to be -2.88 eV according to the HOMO energy level value in combination with the band gap derived from the absorption band edge.

### Pd/Cu cocatalyzed oxidation/Suzuki reaction

Palladium-catalyzed Suzuki coupling is well-known as being one of the most versatile and utilized reactions for the construction of a C–C bond, in particular for the formation of biaryls.<sup>2,4</sup> Generally, Suzuki coupling of aryl halides containing hydroxymethyl produced the corresponding biarylalcohols.<sup>25</sup> Initially, we examined the catalytic activity of palladacycles **1–4** for the Suzuki reaction of (4-bromophenyl) methanol with phenylboronic acid. Based on our previous experiments in palladacyclic precatalysts for Suzuki coupling,<sup>20b,d</sup> the reaction was performed under a nitrogen atmosphere in dioxane in the presence of Cs<sub>2</sub>CO<sub>3</sub> as base at 110 °C for 18 h. 3 was the most efficient among these palladacycles **1–4** and produced the

Table 3Photophysical data for 1-4 and 6

Complex	$\lambda_{\rm abs}/{ m nm}~(\varepsilon  imes 10^{-3}/{ m M}^{-1}~{ m cm}^{-1})^a$	$\lambda_{\rm em}(\lambda_{\rm ex})/{\rm nm}$	Stokes shift/nm	$\Phi^{b}\left(\% ight)$
1	233 (2.08), 270 (1.13), 317 (0.19), 339 (0.22), 353 (0.16)	390 (353)	37	2.4
2	235 (2.57), 268 (1.49), 318 (0.34), 339 (0.41), 353 (0.38)	414 (353)	51	3.6
3	235 (2.25), 270 (1.31), 318 (0.27), 339 (0.29), 353 (0.20)	394 (353)	41	1.7
4	229 (0.45), 265 (0.27), 316 (0.133), 359 (0.08)	391 (359)	32	1.8
6	268 (0.96), 337 (0.21), 361 (0.14), 407 (0.10), 454 (0.06), 488 (0.01)	543 (407)	136	6.3

<sup>*a*</sup> Measured in  $CH_2Cl_2$  (10 × 10<sup>-5</sup> M). <sup>*b*</sup> Measured in  $CH_2Cl_2$  used 9,10-diphenylanthracene and *fac*-Ir(ppy)<sub>3</sub> as the reference standard for 1–4 and 6, respectively.

 Table 4
 Suzuki coupling of aryl halides containing hydroxymethyl with phenyl boronic acid catalyzed by palladacycles<sup>a</sup>

	но х	+ $(HO)_2B$ + $OHC$ + $OHC$ + $7a$ 7b		
Entry	X	Catalyst (mol%)	7 <b>a</b> Yield <sup><math>b</math></sup> (%)	7 <b>b</b> Yield <sup><math>b</math></sup> (%)
1	Br	1(1)	51	0
2	Br	2(1)	58	0
3	Br	3 (1)	93	0
4	Br	4 (1)	16	0
5	Cl	1 (1)	Trace	0
6	Cl	2 (1)	Trace	0
7	Cl	3 (1)	82	0
8 <sup>c</sup>	Cl	1 (1)	Trace	24
9 <sup>c</sup>	Cl	2 (1)	Trace	29
$10^{c}$	Cl	3 (1)	47	45

<sup>*a*</sup> Reaction conditions: aryl halides containing hydroxymethyl (0.5 mmol), phenylboronic acid (0.75 mmol), Cs2CO3 (1.0 mmol), dioxane (3 mL), 110 °C, 18 h, nitrogen atmosphere. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> In air.

expected coupled product 7a in 93% with a catalyst loading of 1 mol% (Table 4, entries 1–4). In the case of (4-chlorophenyl)methanol, 1 and 2 were almost inactive under the same reaction conditions, however, 3 generated 7a in a good yield (82%, entry 7). Then, the coupling of (4-chlorophenyl)methanol was performed in air. It is interesting that an unexpected coupled product 7b was obtained besides 7a (entries 8–10). The results indicated that palladacycles can also catalyze aerobic alcohol oxidation in the above reaction.

On the basis of this finding, we were interested to see whether the palladacycles could efficiently catalyze the reactions involving oxidation and the Suzuki reaction for the synthesis of biarylaldehydes. The results from this study are summarized in Table 5. Under the same reaction conditions ( $Cs_2CO_3$ , dioxane, air), the yield was improved by the addition of copper salts (entries 1–3) suggesting that copper participated in the catalytic cycles. The 3/CuCl<sub>2</sub> system was obviously

Table 5	5 0	ntimization	of the	reaction	conditions <sup>a</sup>
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Entry	Catalyst (mol%)	Base	Solvent	Yield <sup><math>b</math></sup> (%)		
1	$1/CuCl_2(1/5)$	$Cs_2CO_3$	Dioxane	53		
2	$2/CuCl_2(1/5)$	$Cs_2CO_3$	Dioxane	60		
3	$3/CuCl_2(1/5)$	$Cs_2CO_3$	Dioxane	81		
4	3/CuCl (1/5)	$Cs_2CO_3$	Dioxane	72		
5	3/CuI (1/5)	$Cs_2CO_3$	Dioxane	64		
6	$3/Cu(OAc)_2$ (1/5)	$Cs_2CO_3$	Dioxane	92		
7	$3/Cu(OAc)_2(1/5)$	$K_2CO_3$	Dioxane	85		
8	$3/Cu(OAc)_2(1/5)$	$Na_2CO_3$	Dioxane	67		
9	$3/Cu(OAc)_2(1/5)$	$K_3PO_4$	Dioxane	56		
10	$3/Cu(OAc)_2(1/5)$	$Cs_2CO_3$	Toluene	88		
11	$3/Cu(OAc)_2(1/5)$	$Cs_2CO_3$	THF	55		
12	$3/Cu(OAc)_2(1/5)$	$Cs_2CO_3$	DMF	62		

<sup>*a*</sup> Reaction conditions: (4-chlorophenyl)methanol (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.0 mmol), solvent (3 mL), 110 °C, 18 h, air atmosphere. <sup>*b*</sup> Isolated yield. more active than the other two systems. Different copper salts/ palladacycle **3** were then tested (entries 4–6). The results indicated that  $3/Cu(OAc)_2$  was among the best of these tested catalysts (92%, entry 6). Other reaction conditions (entries 7–12) such as  $K_2CO_3$  in dioxane and  $Cs_2CO_3$  in toluene also afforded good yields (85% and 88%, respectively).

To test this procedure, the coupling reactions of (4-chlorophenyl)methanol with a variety of electronically and structurally diverse arylboronic acids were investigated (Table 6). Electron-donating substrates reacted to give the corresponding products **7c** and **7d**, the yields (93% and 95%) are higher than the yields of electron-withdrawing substrates containing –CO– and –NO<sub>2</sub> groups. A slight decrease in the yields (86% and 82%) of *meta*-substitution products **7e** and **7f** was observed. The method proved to be effective for pyridinylboronic acids bearing functional groups, including esters (**7j**) and amines (**7k**).

This newly developed coupling protocol was also successfully applied to the synthesis of 2-biarylcarboxaldehydes *via* oxidation and the Suzuki reaction of (2-chlorophenyl)methanol (Table 7). Similar to the results of (4-chlorophenyl)methanol, the corresponding 2-biaryl-carboxaldehydes **8a–8c** were also obtained with good yields (86–91%). On the basis of the success of this approach, we were interested to see whether  $3/Cu(OAc)_2$  could efficiently cocatalyze double oxidation and the Suzuki reaction of hydroxymethylphenylboronic acids. The desired products biphenyldialdehydes **8d–8f** were isolated in moderate yields (53–76%). Compared with the yields of **7i–7k**, the yields of **8g–8i** starting from the same arylboronic acid were slightly decreased possibly due to steric hindrance.

#### Ir/Pd cocatalyzed α-alkylation and the Suzuki reaction

In recent years, there has been significant interest in the metal-catalyzed hydrogen autotransfer process by alcohols as a more benign alternative to potentially genotoxic halides.<sup>26</sup> Although iridium complexes serve as efficient catalysts for the hydrogen transfer process,<sup>3</sup> cyclometalated iridium acac complexes-catalyzed  $\alpha$ -alkylation of alcohols has not been explored





<sup>*a*</sup> Reaction conditions: (4-chlorophenyl)methanol (0.5 mmol), arylboronic acid (0.75 mmol), 3/Cu(OAc)<sub>2</sub> (0.005/0.025 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.0 mmol), dioxane (3 mL), 110 °C, 18 h, air atmosphere. <sup>*b*</sup> Isolated yield.





<sup>*a*</sup> Reaction conditions: (2-chlorophenyl)methanol (0.5 mmol), arylboronic acid (0.75 mmol), 3/Cu(OAc)<sub>2</sub> (0.005/0.025 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.0 mmol), dioxane (3 mL), 110 °C, 18 h, air atmosphere. <sup>*b*</sup> Isolated yield.

until now. Considering that cyclometalated iridium complexes are active catalysts for  $\alpha$ -alkylation of alcohols,<sup>13,16d</sup> we hypothesized that the cyclometalated iridium acac complex **6** should catalyze the  $\alpha$ -alkylation of acetylferrocene with benzyl alcohol. Thus, the reaction of (4-bromophenyl)methanol with acetylferrocene was performed under a nitrogen atmosphere in dioxane in the presence of 2 mol [Ir]% of 5 or **6** as catalyst and KOH as base at 110 °C for 12 h (Scheme 2). To our delight, **6** 



**Scheme 2**  $\alpha$ -alkylation of acetylferrocene catalyzed by **5** and **6**.



<sup>*a*</sup> Reaction conditions: acetylferrocene (0.5 mmol), (2-amino-5-halophenyl)methanol (0.6 mmol), phenylboronic acid (0.75 mmol), KOH–Cs<sub>2</sub>CO<sub>3</sub> (0.5 mmol/1 mmol), dioxane (3 mL), 110 °C, nitrogen atmosphere. <sup>*b*</sup> Isolated yield.

displayed high catalytic activity producing the desired product in an excellent yield (91%). However, the dimer 5 generated the product only in 40% yield. Furthermore, we also investigated the one-pot synthesis of 6-aryl-2-ferrocenylquinolines *via* Ir/Pd-cocatalyzed  $\alpha$ -alkylation/Suzuki reaction, using the present cyclometalated complexes **1–6** as catalysts.

We have previously shown that PPh3-cyclometallated iridium hydride is an efficient catalyst for the one-pot synthesis of 6-aryl-2-ferrocenylquinolines with 3 mol% Pd(OAc)2.<sup>13</sup> Under the same conditions, acetylferrocene, (2-amino-5-bromophenyl) methanol and phenylboronic acid were efficiently converted to the 6-phenyl-2-ferrocenylquinoline in high yields (82-94%) with a catalytic loading as low as 1 mol% palladacycles 1-3, respectively (Table 8, entries 1-3). For cheaper and more readily available (2-amino-5-chlorophenyl)methanol, Pd(OAc)<sub>2</sub>, 1 and 2 were almost inactive (entries 4-6), but 3 displayed high efficiency (87%, entry 7). The scope of the procedure was further investigated by varying the arylboronic acids (Table 9). The corresponding 6-aryl-2-ferrocenylquinolines 9a-9g were isolated in good yields (81-93%). The hindered arylboronic acids provided the products 9h and 9i in moderate yields (72% and 60%, respectively). The detailed structure of 9h was confirmed by single-crystal X-ray crystallography (Fig. 12).

## Conclusion

In summary, a series of cyclometallated complexes have been synthesized and characterized. X-ray diffraction analysis confirms that there are a variety of intermolecular C–H···X (Cl, Br,  $\pi$ ) and  $\pi$ ··· $\pi$  interactions in their crystals. These cyclometallated complexes show emissions ranging from the purple to the yellow region. Their catalytic activity was evaluated in the coupling reactions of aryl chlorides containing hydroxymethyl. We have developed an efficient NHC-palladacycle/Cu(OAc)<sub>2</sub> cocata-

lyzed oxidation and Suzuki reaction for the synthesis of biarylaldehydes in air. Cyclometalated Ir acac complex **6** was an efficient catalyst for the  $\alpha$ -alkylation of acetylferrocene. It was also successfully applied to the one-pot synthesis of 6-aryl-2ferrocenylquinolines from (2-amino-5-chlorophenyl)methanol using palladacycle **3** as cocatalyst.

## Experimental

#### **General information**

Solvents were dried and freshly distilled prior to use. All reagents and substrates were commercially available. (2-Amino-5-chlorophenyl)methanol was synthesized according to the reported procedure.<sup>27</sup> IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. Elemental analyses were determined with a Carlo Erba 1160 Elemental Analyzer. <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra were recorded on a Bruker DPX-400 spectrometer in CDCl<sub>3</sub> with TMS as an internal standard. Mass spectra were measured on a LC-MSD-Trap-XCT instrument. The absorption and photoluminescence spectra were recorded on a Hitachi U-3010 UV-Vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer in CH<sub>2</sub>Cl<sub>2</sub> at rt, respectively. Cyclic voltammetry was performed on a CHI620C electrochemical analyzer. The electrolytic cell was a conventional three-electrode cell consisting of a Pt bottom working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode.

#### Preparation of complexes 1-3

A mixture of 2-(4-bromophenyl)pyridine (bpp) (1 mmol),  $Li_2PdCl_4$  (1 mmol) and NaOAc (1.1 mmol) in 10 mL of dry methanol was stirred for 12 h at rt. The yellow solids (0.694 g, 93%) were collected by filtration and washed several times with methanol. A Schlenk tube was charged with the above

Table 9 One-pot synthesis of 6-aryl-2-ferrocenylquinolines<sup>a</sup>



<sup>*a*</sup> Reaction conditions: acetylferrocene (0.5 mmol), (2-amino-5-chlorophenyl)methanol (0.6 mmol), arylboronic acids (0.75 mmol), 6/3 (2 mol %/1 mol%), KOH–Cs<sub>2</sub>CO<sub>3</sub> (0.5 mmol/1 mmol), dioxane (3 mL), 110 °C, nitrogen atmosphere. <sup>*b*</sup> Isolated yield.



Fig. 12 The molecular structure of 9h with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

palladacyclic dimer (0.5 mmol), the corresponding imidazolium salts (1.25 mmol) and KO<sup>t</sup>Bu (2.5 mmol) under nitrogen. Dry THF was added by a cannula and stirred at rt for 3 h. The product was separated by passing through a short silica gel column with  $CH_2Cl_2$  as eluent, the second band was collected and afforded the corresponding carbene adducts **1–3**.

[**Pd(bpp)(Itol)Cl**] (1). Yield: 0.559 g, 90%. IR (KBr, cm<sup>-1</sup>): 3073, 2987, 2859, 1697, 1605, 1506, 1454, 1401, 1270, 1109, 1046, 1017, 895, 786, 740, 688, 654. <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>):  $\delta$  9.22 (d, J = 5.2 Hz, 1H), 7.89 (d, J = 8.0 Hz, 4H), 7.68 (t, J = 7.6 Hz, 1H), 7.42–7.45 (m, 3H), 7.26 (s, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.11–7.16 (m, 2H), 7.03 (d, J = 8.0 Hz, 1H), 6.22 (s, 1H), 2.31 (s, 6H). MS (EI) m/z = 586.0 (M – Cl)<sup>+</sup>. Elemental analysis calcd (%) for C<sub>28</sub>H<sub>23</sub>BrClN<sub>3</sub>Pd: C 53.96, H 3.72, N 6.74. Found: C 54.18, H 3.61, N 6.85.

[**Pd(bpp)(IMeO)Cl**] (2). Yield: 0.601 g, 92%. IR (KBr, cm<sup>-1</sup>): 3567, 3213, 2949, 1840, 1652, 1521, 1427, 1362, 1284, 1202, 1145, 1025, 948, 920, 855, 801, 737, 703. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.13 (d, *J* = 5.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (s, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 6.4 Hz, 1H), 6.74–6.85 (m, 6H), 6.15 (s, 1H), 3.57 (s, 6H). MS (EI) *m*/*z* = 618.0 (M − Cl)<sup>+</sup>. Elemental analysis calcd (%) for  $C_{28}H_{23}BrClN_3O_2Pd$ : C 51.32, H 3.54, N 6.41. Found: C 51.45, H 3.43, N 6.47.

[Pd(bpp)(IMes)Cl] (3). Yield: 0.582 g, 86%. IR (KBr, cm<sup>-1</sup>): 2921, 2852, 1693, 1603, 1567, 1510, 1484, 1418, 1328, 1252, 925, 908, 848, 751, 735, 704, 690, 657. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.24 (d, J = 5.2 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.67–7.73 (m, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.25 (s, 1H), 7.02 (d, J = 8.2 Hz, 2H), 6.93 (s, 2H), 6.79 (d, J = 8.0 Hz, 2H), 6.31 (s, 1H), 2.43 (s, 6H), 2.29 (s, 6H), 2.26 (s, 6H). MS (EI)  $m/z = 642.1 (M - Cl)^+$ . Elemental analysis calcd (%) for  $C_{32}H_{31}BrClN_3Pd$ : C 56.57, H 4.60, N 6.19. Found: C 56.51, H 4.52, N 6.35.

[Pd(bpp)(acac)] (4). The above palladacyclic dimer (0.5 mmol), acac (0.25 mmol), K<sub>2</sub>CO<sub>3</sub> (0.5 mmol), and ethanol (10 mL) were added into a three-necked flask. The mixture was refluxed under nitrogen for 12 h and then cooled to room temperature. A yellow precipitate was filtered and washed with water and ethanol several times. The resulting yellow solid was purified by passing through a short silica gel column with  $CH_2Cl_2$  as eluent to give 4. Yield: 0.371 g, 85%. IR (KBr, cm<sup>-1</sup>): 2971, 2440, 1604, 1511, 1388, 1370, 1260, 1017, 1007, 890, 822, 719, 704, 695, 655. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.75 (d, J = 5.2 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.66 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.25 (s, 2H), 7.18 (t, J = 6.4 Hz, 1H), 5.41 (s, 1H), 2.12 (s, 3H), 2.06 (s, 3H). MS (EI)  $m/z = 437.9 (M + H)^+$ . Elemental analysis calcd (%) for C<sub>16</sub>H<sub>14</sub>BrNO<sub>2</sub>Pd: C 43.81, H 3.22, N 3.19. Found: C 43.89, H 3.05, N 3.23.

### Preparation of complexes 5-6

Iridium trichloride (0.5 mmol), bpp (1.5 mmol), 2-ethoxyethanol (15 mL), and water (5 mL) were added into a three-necked flask. The mixture was refluxed under nitrogen for 24 h and then cooled to rt. A yellow precipitate was filtered and washed with water and ethanol several times. The resulting yellow solid was purified by passing through a short silica gel column with  $CH_2Cl_2$ -ethyl acetate (3 : 1) as eluent to give solid 5. Then, the complex 5 (0.1 mmol), acac (0.22 mmol),  $K_2CO_3$  (0.4 mmol), and 2-ethoxyethanol (10 mL) were added into a three-necked flask. The mixture was refluxed under nitrogen for 12 h and then cooled to rt. A yellow precipitate was filtered and washed with water and ethanol several times. The resulting yellow solid was purified by passing through a short silica gel column with  $CH_2Cl_2$  as eluent to give solid 6.

**[Ir(bpp)**<sub>2</sub>**Cl]**<sub>2</sub> (5). Yield: 0.609 g, 88%. IR (KBr, cm<sup>-1</sup>): 2768, 1605, 1564, 1530, 1471, 1418, 1369, 1298, 1160, 1005, 883, 868, 766, 749, 719, 711, 644. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.11 (d, J = 5.2 Hz, 4H), 7.87(d, J = 8.0 Hz, 4H), 7.81(d, J = 8.0 Hz, 4H), 7.58 (d, J = 7.2 Hz, 4H), 7.48 (t, J = 7.2 Hz, 4H), 6.96 (d, J = 8.0 Hz, 4H), 6.83 (s, 4H). MS (EI) m/z = 1383.8 (M<sup>+</sup>). Elemental analysis calcd (%) for C<sub>44</sub>H<sub>28</sub>Br<sub>4</sub>Cl<sub>2</sub>Ir<sub>2</sub>N<sub>4</sub>: C 38.08, H 2.03, N 4.04. Found: C 38.15, H 1.98, N 4.01.

**[Ir(bpp)<sub>2</sub>(acac)]** (6). Yield: 0.643 g, 85%. IR (KBr, cm<sup>-1</sup>): 2993, 1816, 1582, 1510, 1474, 1367, 1252, 1228, 1056, 1004, 879, 868, 788, 766, 748, 722, 714, 693. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.43 (d, J = 5.2 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.77 (t, J = 7.8 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.19 (t, J = 6.4 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.29 (s, 2H), 5.30 (s, 1H), 1.79 (s, 6H). MS (EI) m/z = 757.0 (M + H)<sup>+</sup>. Elemental analysis calcd (%) for C<sub>27</sub>H<sub>21</sub>Br<sub>2</sub>IrN<sub>2</sub>O<sub>2</sub>: C 42.81, H 2.79, N 3.70. Found: C 42.89, H 2.71, N 3.77.

### Single-crystal structure determination

Single crystal X-ray diffraction measurements of **1**, **2**, **4–6** and **9h** were carried out on a Bruker SMART APEX II CCD diffractometer (Mo K $\alpha$  radiation,  $\lambda$  = 71.073 pm) at rt. Crystallographic

data for **3** was measured on a Xcalibur, Eos, Gemini diffractometer. Crystal structures were solved by direct methods using SHELXS, subsequent difference Fourier analyses and least squares refinement with SHELXL-97<sup>28</sup> allowed for the location of the atom positions. All non-hydrogen atoms were refined anisotropically. In the final step of the crystal structure refinement hydrogen atoms of idealized  $-CH_2$  and  $-CH_3$  groups were added and treated with the riding atom mode, their isotropic displacement factor was chosen as 1.2 and 1.5 times the preceding carbon atom, respectively. One  $CH_2Cl_2$  molecule (Cl3, Cl4, C29) in **2** is disordered over two positions with an occupancy of 0.5, it is also refined isotropically. C23 to C27 in 4 were refined isotropically because of their higher thermal parameters.

#### General procedure for synthesis of biarylaldehydes

A 10 mL round-bottomed flask was charged with the prescribed amount of catalyst Pd/Cu, aryl halides containing hydroxymethyl (0.5 mmol), arylboronic acid (0.75 mmol), the selected base (1.0 mmol) and solvent (3 mL) in air. The reaction mixture was then placed in an oil bath and heated at 110 °C for 18 h. After removal of the solvent, the resulting residue was purified by flash chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>–petroleum ether (1/1) as eluent. The products 7a,<sup>9b</sup> 7b,<sup>29a</sup> 7c,<sup>29b</sup> 7d,<sup>29c</sup> 7e–g,<sup>29d</sup> 7h,<sup>29a</sup> 7i<sup>29e</sup> and 8a–c,<sup>30a</sup> 8d,<sup>30b</sup> 8e–f,<sup>30c</sup> 8g<sup>29e</sup> are known compounds except for 7j–k and 8h–i.

4-(5-Ethoxycarbonylpyridin-3-yl)benzaldehyde (7j). Yield: 0.194 g, 76%. IR (KBr, cm<sup>-1</sup>): 2818, 1721, 1701, 1607, 1565, 1452, 1362, 1307, 1251, 1216, 1173, 1110, 1022, 915, 829, 762, 702. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.10 (s, 1H), 9.26 (s, 1H), 9.05 (s, 1H), 8.54 (s, 1H), 8.04 (d, J = 6.8 Hz, 2H), 7.82 (d, J =8.0 Hz, 2H), 4.48 (q, 2H), 1.46 (t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 191.6, 165.0, 151.7, 150.3, 142.5, 136.1, 135.4, 135.1, 130.5, 127.8, 126.5, 61.8, 14.3. MS (EI) m/z = 254.1 (M<sup>+</sup>). Elemental analysis calcd (%) for C<sub>15</sub>H<sub>13</sub>NO<sub>3</sub>: C 70.58, H 5.13, N 5.49. Found: C 70.65, H 5.02, N 5.56.

**4-(4-Dimethylaminopyridin-3-yl)benzaldehyde** (7k). Yield: 0.192 g, 85%. IR (KBr, cm<sup>-1</sup>): 2853, 1690, 1592, 1523, 1503, 1388, 1282, 1213, 1170, 1067, 1030, 958, 832, 807, 778, 690. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.99 (s, 1H), 8.50 (s, 1H), 7.90 (d, J =7.2 Hz, 2H), 7.73 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 8.8 Hz, 1H), 3.20 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 191.8, 159.0, 146.7, 144.4, 135.7, 134.3, 130.5, 128.2, 126.0, 122.5, 105.8, 38.1. MS (EI) m/z = 225.1 (M<sup>+</sup>). Elemental analysis calcd (%) for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O: C 74.31, H 6.24, N 12.38. Found: C 74.37, H 6.13, N 12.42.

**2-(5-Ethoxycarbonylpyridin-3-yl)benzaldehyde** (8h). Yield: 0.181 g, 71%. IR (KBr, cm<sup>-1</sup>): 2874, 1719, 1596, 1445, 1364, 1294, 1267, 1248, 1198, 1109, 1019, 974, 823, 782, 759, 711. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.98 (s, 1H), 9.29 (s, 1H), 8.80 (s, 1H), 8.34 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.71–7.75 (m, 1H), 7.62 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 4.46 (q, 2H), 1.43 (t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  190.8, 164.9, 153.4, 150.2, 140.5, 137.7, 134.0, 133.7, 131.2, 129.2, 125.9, 61.7, 14.3. MS (EI) *m*/*z* = 254.1 (M<sup>+</sup>). Elemental analysis calcd (%) for C<sub>15</sub>H<sub>13</sub>NO<sub>3</sub>: C 70.58, H 5.13, N 5.49. Found: C 70.63, H 5.06, N 5.54. **2-(4-Dimethylaminopyridin-3-yl)benzaldehyde** (8i). Yield: 0.174 g, 77%. IR (KBr, cm<sup>-1</sup>): 2850, 1687, 1601, 1547, 1515, 1479, 1439, 1386, 1320, 1192, 1152, 1063, 957, 828, 812, 768, 733. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.05 (s, 1H), 8.19 (s, 1H), 8.00 (d, J = 7.2 Hz, 1H), 7.59–7.62 (m, 1H), 7.39–7.49 (m, 3H), 6.60 (d, J = 8.8 Hz, 1H), 3.15 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  192.3, 158.8, 148.6, 143.2, 138.6, 133.8, 130.7, 128.0, 127.3, 120.7, 105.2, 38.1. MS (EI) m/z = 225.1 (M<sup>+</sup>). Elemental analysis calcd (%) for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O: C 74.31, H 6.24, N 12.38. Found: C 74.40, H 6.15, N 12.47.

### General procedure for synthesis of 6-aryl-2-ferrocenylquinolines

In a Schlenk tube, a mixture of the acetylferrocene (0.5 mmol), (2-amino-5-chlorophenyl) methanol (0.6 mmol), KOH (0.5 mmol), and **6** (0.01 mmol) in dioxane (3 mL) was evacuated and charged with nitrogen. The mixture was heated at 110 °C for 12 h then allowed to cool to rt. The vessel was opened, and arylboronic acids (0.75 mmol),  $Cs_2CO_3$ (1.0 mmol), and **3** (0.005 mmol) were added to it under nitrogen. The mixture was heated at 110 °C for another 12 h. After removal of the solvent, the resulting residue was purified by column chromatography on silica gel using  $CH_2Cl_2$  as eluent. The products 6-aryl-2-ferrocenyl quinolines **9c–i**<sup>13</sup> are known compounds except for **9a–b**.

**2-Ferrocenyl-6-(3-methylphenyl)quinoline** (9a). Yield: 0.179 g, 89%. IR (KBr, cm<sup>-1</sup>): 2922, 1593, 1478, 1378, 1337, 1287, 1180, 1135, 1104, 1012, 905, 894, 837. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.12 (m, 2H), 7.97 (s, 2H), 7.56–7.64 (m, 3H), 7.43 (t, 1H), 7.26 (d, J = 7.6 Hz, 2H), 5.13 (s, 2H), 4.53 (s, 2H), 4.12 (s, 5H), 2.51 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.5, 140.6, 138.6, 138.3, 135.7, 129.3, 129.2, 128.9, 128.3, 128.1, 125.3, 124.5, 119.9, 83.9, 70.5, 69.7, 68.0, 21.6. MS (EI, 70 eV) m/z = 404.1 (M + H)<sup>+</sup>. Elemental analysis calcd (%) for C<sub>26</sub>H<sub>21</sub>FeN: C 77.43, H 5.25, N 3.47. Found: C 77.57, H 5.10, N 3.59.

**2-Ferrocenyl-6-(4-ethylphenyl)quinoline (9b).** Yield: 0.190 g, 91%. IR (KBr, cm<sup>-1</sup>): 2966, 1594, 1566, 1499, 1460, 1337, 1279, 1133, 1104, 1029, 1014, 900, 826, 733. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.07–8.26 (m, 2H), 7.83–7.93 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 2H), 4.47 (s, 2H), 4.05 (s, 5H), 2.71 (q, 2H), 1.29 (t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  159.4, 147.6, 143.7, 138.1, 138.0, 136.6, 129.3, 128.5, 128.3, 127.3, 127.0, 125.0, 119.9, 84.0, 70.5, 69.7, 68.0, 29.8, 15.7. MS (EI) *m*/*z* = 418.1 (M + H)<sup>+</sup>. Elemental analysis calcd (%) for C<sub>27</sub>H<sub>23</sub>FeN: C 77.71, H 5.56, N 3.36. Found: C 77.79, H 5.43, N 3.43.

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