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# *N*-Heterocyclic carbene (NHC)-modulated Pd/Cu cocatalyzed three-component synthesis of 2,6-diarylquinolines

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**Abstract:** Two new NHC adducts of cyclopalladated ferrocenylpyrazine complexes **1**–**2** have been prepared and characterized. An efficient NHC-modulated Pd/Cu cocatalyzed three-component coupling reaction for the synthesis of 2,6-diarylquinolines from aminobenzyl alcohols, aryl ketones, and arylboronic acids in air is described. The reaction involves oxidation, cyclization and Suzuki reaction. The luminescence of resultant arylquinolines **3**–**30** was also investigated.

## Introduction

The quinoline moiety play a vital role as an intermediate for the design of many biologically active compounds.[1] Moreover, quinolines also found wide utility as synthons for formation of conjugated molecules[2] or ligands for the preparation of phosphorescent complexes.[3] Among several routes to quinoline syntheses, the metal-catalyzed modified Friedländer reaction[4] is one of the simplest methods, where 2-aminobenzyl alcohol, which is cheaper and more stable than 2-aminobenzaldehyde, is allowed to react with carbonyl compounds to form quinoline derivatives. Several groups have reported the use of Ru,[5] Ir[6] and other metal catalysts[7] for the synthesis of quinolines from amino alcohols and ketones via oxidation and cyclization. The first step of the reaction is metal-catalyzed oxidation of alcohols. Among metal salts and complexes, those of palladium have been widely used in alcohol oxidation.[8] This reaction traditionally requires catalytic Pd(II) and stoichiometric Cu salts under aerobic conditions. However, palladium complexes compatible with these reaction conditions are

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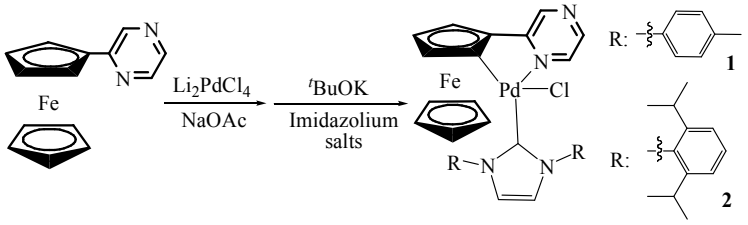
quite limited because phosphines and related organic ligands often degrade rapidly under oxidizing reaction conditions.[9] Great recent progress has been obtained for the palladium-catalyzed oxidation by using oxidatively stable ligands. These ligands often consist of nitrogen donors, such as amine and pyridine ligands.[9,10] Moreover, NHC ligands have proven effective in various Pd-catalyzed processes[11] as well as alcohol oxidation.[12] Considering the unique activity of NHC ligand-modulated Pd catalysts, we were interested in developing a NHC-modulated Pd-catalyzed modified Friedländer reaction for the quinoline syntheses.

On the other hand, multicomponent reactions (MCRs) are ideal synthetic tools to generate multiple molecular scaffolds from readily available starting materials in a single synthetic operation without the need for isolation of intermediates.[13] Very recently we have developed a $PPh_3$-cyclometallated iridium(III) hydride/$Pd(OAc)_2$ cocatalyzed reaction of acetylferrocene, bromoarylmethanols, and arylboronic acids under nitrogen.[14] This method was successfully applied to one-pot synthesis of 6-aryl-2-ferrocenylquinolines. However, the metals (Ir/Pd) involved are certainly expensive, the synthesis of ferrocenylquinolines was not a multicomponent reaction but a sequential process. Therefore, the development of a more convenient and inexpensive catalyst system that can be used for the quinoline syntheses is desired. As a continuation of our interest in the synthesis and application of cyclometalated complexes,[15] we prepared new adducts of cyclopalladated ferrocenylpyrazine complexes and described the first NHC-modulated Pd/Cu cocatalyzed three-component reaction of aminobenzyl alcohol, aryl ketone, and arylboronic acids in air, providing a series of luminescent arylquinolines.




**Scheme 1** Preparation of adducts of cyclopalladated ferrocenylpyrazine complexes **1–2**.

## Results and discussion

The synthetic route of two new NHC adducts of cyclopalladated ferrocenylpyrazine



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complexes **1**–**2** is demonstrated in Scheme 1. The cyclopalladation reaction was carried out with ferrocenylpyrazine and 1 equivalent of $Li_2PdCl_4$ and NaOAc in methanol at room temperature for 24 h. The formed red solids were collected by filtration, and can be assigned to be a dimeric complex of palladium.[15*a-b*] Because of its poor solubility in all common organic solvents, it was not characterized and directly subjected to bridge-splitting reaction. The complexes **1**–**2** are air and moisture stable both in the solid state and in solution. Their structures were fully characterized by NMR and MS as well as single crystal X-ray analysis (Fig S1 and 1). The Pd-$C_{carb}$ [1.991(7) and 2.010(7) Å] bond lengths of complex **2** are similar to those of related carbene adducts (1.991–1.998 Å),[16] while they are longer than that of complex **1** [1.984(4) Å] possibly due to the steric bulk of the IPr [*N*, *N*′-bis(2,6-diisopropylphenyl)-imidazole-2-ylidene] ligand.

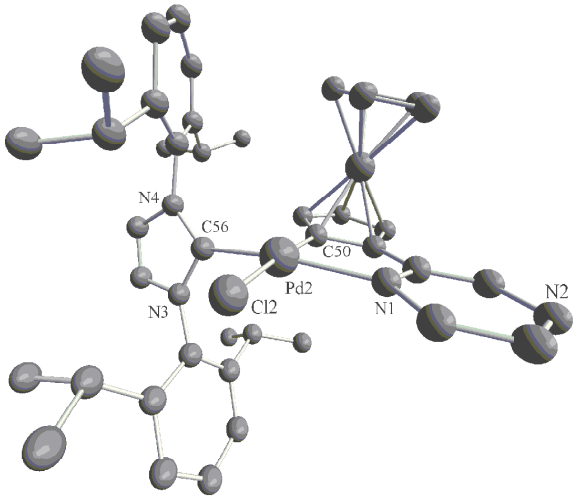


**Fig 1** Molecular structure of **2** (one of the two independent molecules).

Suzuki reaction was an extremely practical method in organic synthesis. These reactions were generally carried out under the protection of inert gas.[17] Under ambient atmosphere, NHC-modulated Pd-catalyzed Suzuki reaction and alcohol oxidation have been relatively less reported.[11*b*,12*a*] Considering that palladacycles are one of the most active catalysts for coupling reactions,[18] we hypothesized that NHC adduct of palladacycle in combination with copper additive can cocatalyze one-pot oxidation/Suzuki reaction. Thus, the three-component reaction of 4-bromoacetophenone, 2-aminobenzylalcohol, and phenylboronic acid in air was chosen as the model reaction.



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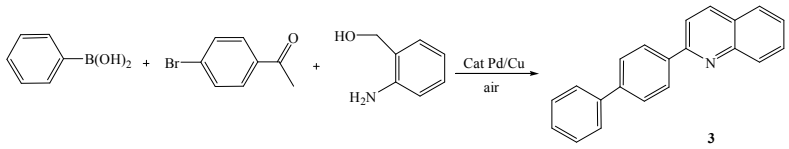
**Table 1** Optimization of the three-component reaction conditions[a]




| Entry | Catalyst (mol %) | Base | Solvent | Yield (%)[b] |
|---|---|---|---|---|
| 1 | **1**/$CuCl_2$ (1/6) | $K_2CO_3$ | dioxane | 23 |
| 2 | **2**/$CuCl_2$ (1/6) | $K_2CO_3$ | dioxane | 49 |
| 3 | **2**/$Cu(OAc)_2$ (1/6) | $K_2CO_3$ | dioxane | 65 |
| 4 | **2**/CuCl (1/6) | $K_2CO_3$ | dioxane | 30 |
| 5 | **2**/CuI (1/6) | $K_2CO_3$ | dioxane | 18 |
| 6 | **2**/$Cu(OAc)_2$ (1/6) | KOH | dioxane | 34 |
| 7 | **2**/$Cu(OAc)_2$ (1/6) | $Na_2CO_3$ | dioxane | 51 |
| 8 | **2**/$Cu(OAc)_2$ (1/6) | $Cs_2CO_3$ | dioxane | 90 |
| 9 | **2**/$Cu(OAc)_2$ (1/6) | $K_3PO_4$ | dioxane | 58 |
| 10 | **2**/$Cu(OAc)_2$ (1/6) | KOAc | dioxane | 37 |
| 11 | **2**/$Cu(OAc)_2$ (1/6) | $Cs_2CO_3$ | THF | 45 |
| 12 | **2**/$Cu(OAc)_2$ (1/6) | $Cs_2CO_3$ | toluene | 72 |
| 13 | **2**/$Cu(OAc)_2$ (1/6) | $Cs_2CO_3$ | xylene | 67 |
| 14 | **2**/$Cu(OAc)_2$ (1/6) | $Cs_2CO_3$ | DMF | 42 |
| 15 | **2**/$Cu(OAc)_2$ (0.1/6) | $Cs_2CO_3$ | dioxane | 61 |

[a] Reaction conditions: 4-bromoacetophenone (0.5 mmol), 2-aminobenzylalcohol (0.6 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), solvent (3 mL), 110 °C, 20 h. [b] Isolated yield.

Table 1 provides information on the impact of catalyst, base and solvent on the efficiency of this process. In the absence of copper salts, the desired product **3** was not observed using **2** as catalyst and only 4-acetylbiphenyl was produced as a Suzuki coupling product. Then, different copper salts and NHC adducts of palladacycle were tested in the presence of air with $K_2CO_3$ as base in dioxane (entries 1–5). The results indicated that **2**/$Cu(OAc)_2$ was the best among these tested catalysts (65%, entry 3). The effect of bases and solvents was further investigated under the above conditions (entries 6–14). We were delighted to find that the use of $Cs_2CO_3$ and dioxane leads to an improvement in performance of this MCR, and **3** was isolated in a 90% yield (entry 8), showing that this MCR is viable. Decreasing Pd catalyst loading to 0.1 mol% led to a TON of 610 and a moderate yield (entry 15).

**Table 2** Three-component reaction for the synthesis of 2-(1,1'-biaryl-4-yl)quinolines[a]

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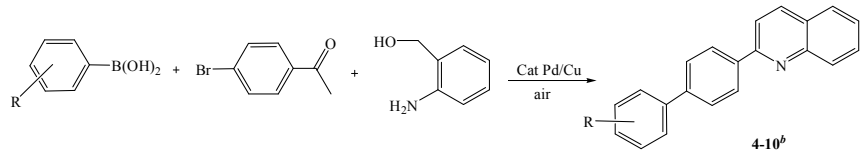
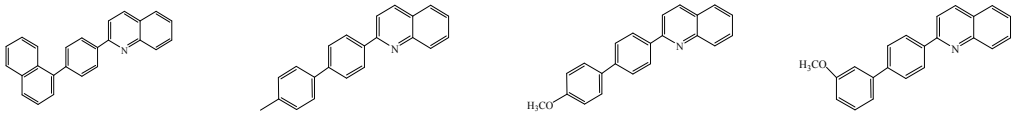
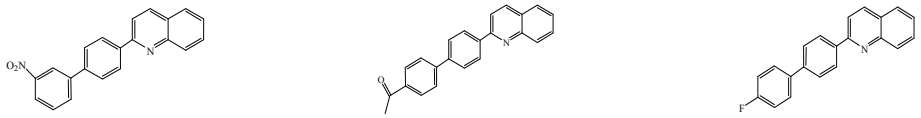


**4**, 88% **5**, 92% **6**, 93% **7**, 89%

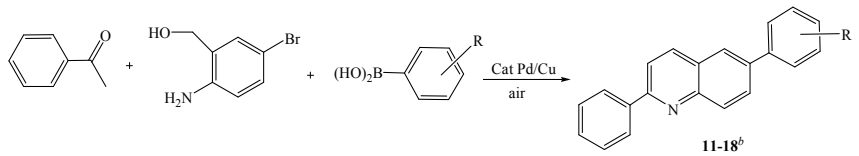


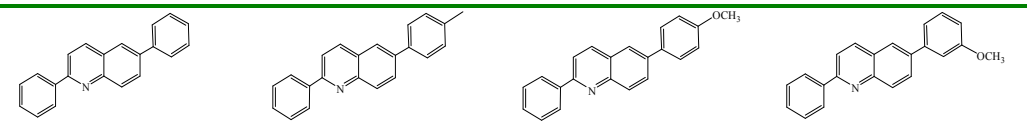
**8**, 80% **9**, 78% **10**, 81%

[a] Reaction conditions: **2**/$Cu(OAc)_2$ (0.005/0.03 mmol), 4-bromoacetophenone (0.5 mmol), 2-aminobenzylalcohol (0.6 mmol), arylboronic acids (0.75 mmol), $Cs_2CO_3$ (1.5 mmol), dioxane (3 mL), 110 °C, 20 h. [b] Isolated yield.

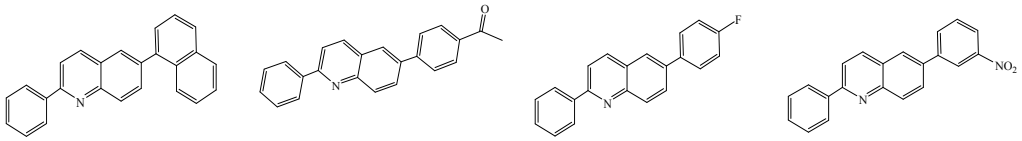
With the optimized conditions in hand, the scope of the reaction was investigated with various arylboronic acids (Table 2). Similar to the result of phenylboronic acid, a good yield (88%) was obtained in the case of 1-naphthylboronic acid. The electronic nature of the substituents on the arylboronic acids did have an effect on the reaction. Electron-donating substrates reacted to give the correponding products **5**–**7**, the yields (89–93%) are slightly higher than the yields (76–81%) of electron-withdrawing substrates **8**–**10**.

**Table 3** Three-component reaction for the synthesis of 6-aryl-2-phenylquinolines[a]



**11**, 91% **12**, 93% **13**, 94% **14**, 90%



**15**, 87% **16**, 81% **17**, 84% **18**, 82%

[a] Reaction conditions: **2**/$Cu(OAc)_2$ (0.005/0.03 mmol), acetophenone (0.5 mmol), (2-amino-5-bromophenyl)methanol (0.6 mmol), arylboronic acids (0.75 mmol), $Cs_2CO_3$ (1.5 mmol), dioxane (3 mL), 110 °C, 20 h. [b] Isolated yield.

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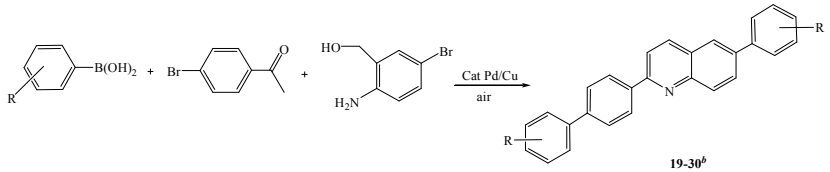
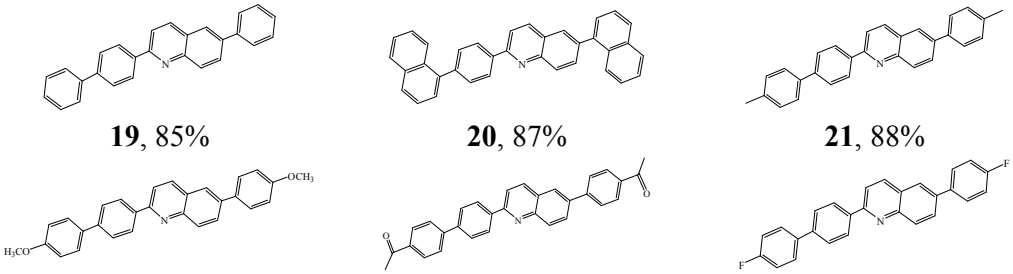
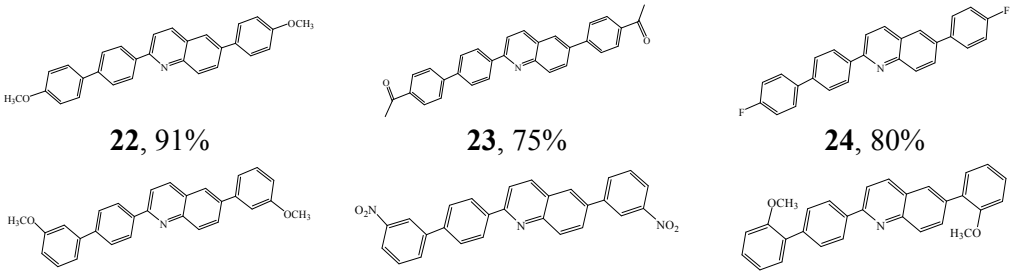
In contrast to 2-arylquinolines, only one example of 2,6-diarylquinoline has been reported.[19] To broaden the substrate scope, we further investigated this MCR under the same reaction conditions using (2-amino-5-bromophenyl)methanol instead of 2-aminobenzyl-alcohol. Gratifyingly, as depicted in Table 3, the corresponding 6-aryl-2-phenylquinolines **11–18** were also obtained with good yields (79–94%). Moreover, arylquinolines **13**, **15** and **17** were confirmed by X-ray diffraction (Fig S2–4).

**Table 4** Synthesis of 6-aryl-2-(1,1'-biaryl-4-yl)quinolines[a]

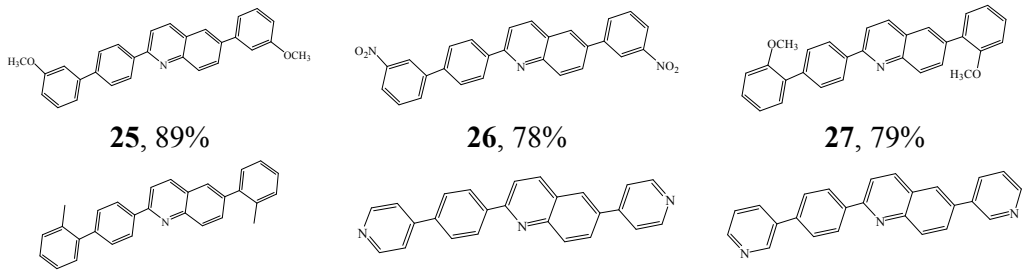


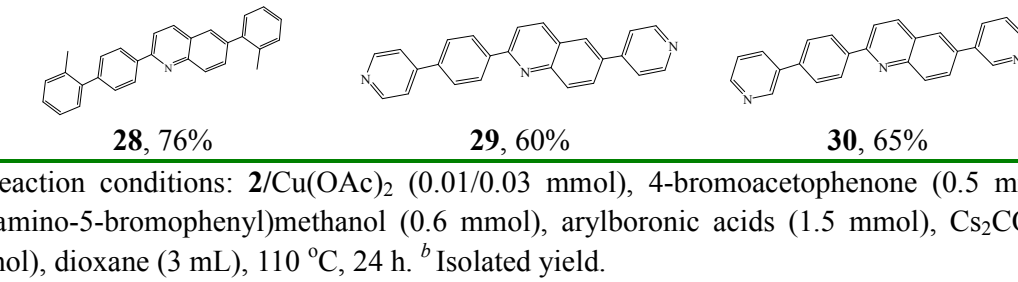
**19**, 85% **20**, 87% **21**, 88%



**22**, 91% **23**, 75% **24**, 80%



**25**, 89% **26**, 78% **27**, 79%



**28**, 76% **29**, 60% **30**, 65%

[a] Reaction conditions: **2**/$Cu(OAc)_2$ (0.01/0.03 mmol), 4-bromoacetophenone (0.5 mmol), (2-amino-5-bromophenyl)methanol (0.6 mmol), arylboronic acids (1.5 mmol), $Cs_2CO_3$ (3 mmol), dioxane (3 mL), 110 $^oC$, 24 h. [b] Isolated yield.

Finally, this newly developed coupling protocol was applied to the synthesis of larger conjugated 6-aryl-2-((1,1'-biaryl)-4-yl)quinolines via oxidation/double Suzuki coupling of arylboronic acids, 4-bromoaceto-phenone, and (2-amino-5-bromophenyl) methanol. As shown in Table 4, the desired 2,6-diarylquinolines **19**–**25** were isolated in good yields (75–91%) by using 3 equiv of arylboronic acids and Pd catalyst loading of 2 mol %. In the

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same manner, switching the methyl or methoxy group from the *para*-position to the *ortho*-position on the benzene ring does influence the yields (76 and 79%) of **26** and **27**, demonstrating that steric factors have influence on the Suzuki reaction. This protocol was found also to proceed successfully with pyridinylboronic acid, furnishing moderate yields (60 and 65%) of **29** and **30**. Additionally, the molecular structure of **27** is depicted in Fig 2. The whole molecular is not planar, the dihedral angle between the middle benzene ring and quinoline ring is 25.4°, the benzene ring containing methoxy group are not coplanar to the quinoline ring and middle benzene ring (dihedral angles are 52.3° and 44.0°, respectively).

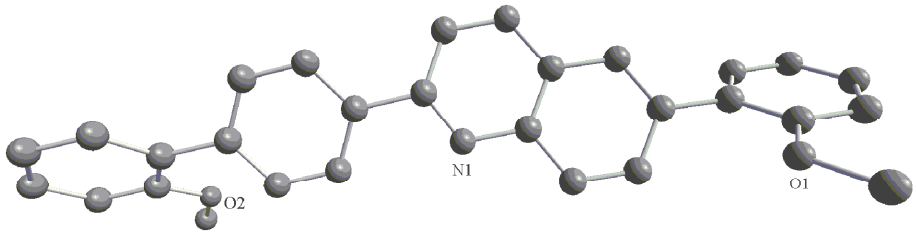


**Fig 2** Molecular structure of **27**. H atoms are omitted for clarity.

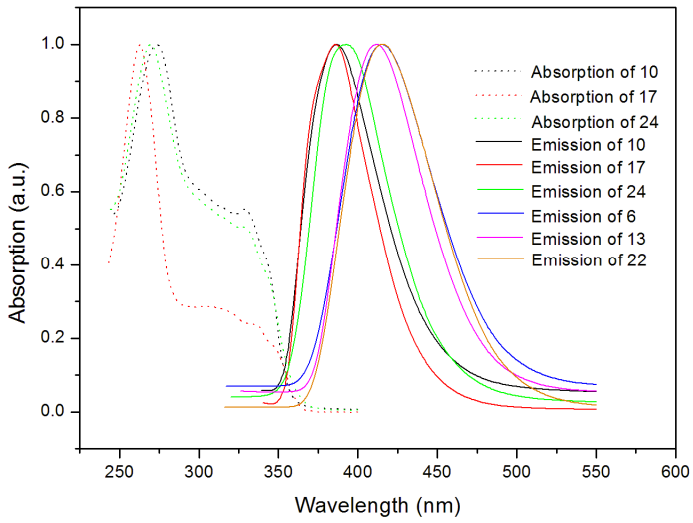


**Fig 3** Normalized absorption and emission of **10**, **17** and **24**, emission of **6**, **13** and **22** (absorption spectra are omitted for clarity) in $CH_2Cl_2$ at rt.

The UV-Vis absorption and photoluminescence spectra of **3**–**27** were recorded in $CH_2Cl_2$ at rt, and the data were collected in ESI. Briefly, the structures of absorption and emission spectra of the 2, 6-diarylquinolines are similar to those of the same substituent-containing 2-aryl-quinolines. These arylquinolines show emissions ranging from the purple to the blue region. For example, the arylquinolines containing fluorine **10**, **17** and **24** exhibit major



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absorption and emission bands at 263–274 nm and 385–395 nm (Fig 3), whereas the $\lambda_{max,em}$ (411–417 nm) of arylquinolines bearing a electron-donating methoxy group **6**, **13** and **22** show a red shift versus the above arylquinolines. In strong contrast, for **8, 18** and **26** the fluorescence is heavily quenched, likely by a photoinduced electron transfer process with the nitro group.[20]

In summary, we have developed a NHC-modulated Pd/Cu cocatalyzed three-component reaction of aminobenzyl alcohols, aryl ketones, and arylboronic acids in air. This protocol provides an efficient access to a variety of 2,6-diarylquinolines via oxidation, cyclization and Suzuki reaction. Future work will report the photoactive complexes of these arylquinolines.

## Experimental section

### General methods

$^1$H and $^{13}$C NMR spectra were recorded on a spectrometer in $CDCl_3$ at 400 and 100 MHz, respectively, with TMS as internal standard. MS experiments were performed with EI source. All new compounds were further characterized by elemental analysis. The absorption and photoluminescence spectra were recorded on a UV-Vis and a fluorescence spectrophotometer in $CH_2Cl_2$ at rt, respectively. Solvents were dried and freshly distilled prior to use. All other chemicals were commercially available expect for ferrocenylpyrazine which was prepared according to the published procedures.[21] Compounds **3**,[22] **5** (not provided spectra),[23] and **11**[19] are known compounds, other compounds are new compounds.

### Preparation of complexes 1–2

A mixture of ferrocenylpyrazine (1 mmol), $Li_2PdCl_4$ (1.1 mmol) and NaOAc (1 mmol) in 20 mL of dry methanol was stirred for 24 h at room temperature. The red solids (yield: 91%) were collected by filtration and washed several times with methanol. A Schlenk tube was charged with the above red solids (0.5 mmol), the corresponding imidazolium salts (1.25 mmol) and $^t$BuOK (2.5 mmol) under nitrogen. Dry THF was added by a cannula and stirred at room temperature for 3 hours. 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 **1**–**2**. **(1)**. Yield 593.3 mg, 91%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.99 (d, 1H), 8.38 (s, 1H), 8.27–8.32 (m, 3H), 7.76 (d, $J$ = 8.2 Hz, 2H), 7.38–7.46 (m, 4H), 7.13 (d, $J$ = 8.1 Hz, 2H), 4.49 (s, 1H),



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4.19 (s, 1H), 3.45 (s, 5H), 3.41 (s, 1H), 2.37 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 169.9, 161.6, 143.3, 140.5, 139.9, 138.7, 138.3, 138.1, 130.3, 129.7, 125.7, 125.2, 123.4, 122.8, 95.6, 85.1, 73.9, 70.2, 69.5, 63.0, 21.4; MS (EI, 70 eV) *m*/*z* = 617.1 $(M–Cl)^+$; Elemental analysis calcd (%) for $C_{31}H_{27}ClFeN_4Pd$: C 56.99, H 4.17, N 8.58. Found: C 57.05, H 4.02, N 8.77; **(2)**. Yield 697.1 mg, 88%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.05 (s, 1H), 8.34 (s, 1H), 8.11 (d, 1H), 7.46–7.50 (m, 3H), 7.30–7.35 (m, 3H), 7.19–7.21 (m, 3H), 7.05 (d, 1H), 4.55 (s, 1H), 4.32 (s, 1H), 3.92 (s, 1H), 3.39 (s, 5H), 3.12–3.27 (m, 2H), 2.88–2.94 (m, 2H), 1.53–1.62 (m, 9H), 1.42 (d, 3H), 1.12–1.22 (m, 3H), 0.98 (d, 3H), 0.86 (d, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 173.8, 161.4, 148.1, 147.1, 145.5, 144.7, 143.6, 140.3, 139.1, 136.6, 136.3, 130.4, 130.1, 125.5, 125.1, 124.9, 124.7, 124.5, 123.3, 96.8, 84.9, 70.5, 69.6, 62.9, 29.8, 29.2, 29.1, 28.6, 28.0, 27.4, 25.6, 25.2, 23.8, 23.5, 23.4, 21.8; MS (EI, 70 eV) *m*/*z* = 757.2 $(M–Cl)^+$; Elemental analysis calcd (%) for $C_{41}H_{47}ClFeN_4Pd$: C 62.05, H 5.97, N 7.06. Found: C 62.11, H 5.79, N 7.13.

**General procedure for synthesis of 2-(1,1'-biaryl-4-yl)quinolines 3–10**

A 10 mL round–bottom flask was charged with the prescribed amount of catalyst, 4-bromoacetophenone (0.5 mmol), 2-aminobenzylalcohol (0.6 mmol), arylboronic acids (0.75 mmol), the selected base (1.5 mmol) and solvent (3 mL). The reaction mixture was then placed in an oil bath and heated at 110 $^o$C for 20 h, cooled and quenched with water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate, then the combined organic layers were washed with water, dried over $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator. The resulting residue was purified by flash chromatography on silica gel using $CH_2Cl_2$/petroleum ether (1/1) as eluent. The third band was collected and afforded the solids **3–10**.

**2-(1'-Naphthyl-1-phenyl-4-yl)quinoline (4)**. Yield 109.7 mg, 88%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.23–8.30 (m, 4H), 7.82–8.03 (m, 5H), 7.73–7.80 (m, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.42–7.55 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 157.2, 148.4, 141.9, 139.8, 138.7, 136.9, 131.6, 130.7, 129.8, 128.4, 127.9, 127.6, 127.3, 127.0, 126.4, 126.2, 126.0, 125.9, 125.5, 119.1; MS (EI, 70 eV) *m*/*z* = 332.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{25}H_{17}N$: C 90.60, H 5.17, N 4.23. Found: C 90.69, H 5.06, N 4.28.

**2-(4'-Methylbiphenyl-4-yl)quinoline (5)**. Yield 119.2 mg, 92%; $^1$H NMR (400 MHz,



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$CDCl_3$): $\delta$ 8.20–8.24 (m, 4H), 7.90 (d, $J$ = 4.6 Hz, 1H), 7.84 (d, $J$ = 4.6 Hz, 1H), 7.73–7.75 (m, 3H), 7.51–7.57 (m, 3H), 7.28 (d, $J$ = 7.9 Hz, 2H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 157.0, 148.3, 142.0, 138.3, 137.7, 137.5, 136.8, 129.7, 129.6, 128.0, 127.5, 127.4, 127.2, 127.0, 126.3, 119.0, 21.2; MS (EI, 70 eV) $m/z$ = 296.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{22}H_{17}N$: C 89.46, H 5.80, N 4.74. Found: C 89.52, H 5.89, N 4.57.

**2-(4'-Methoxybiphenyl-4-yl)quinoline (6)**. Yield 149.7 mg, 93%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.24 (d, $J$ = 8.4 Hz, 3H), 8.21 (d, $J$ = 8.4 Hz, 1H), 7.93 (d, $J$ = 8.6 Hz, 1H), 7.83 (d, $J$ = 8.0 Hz, 1H), 7.73 (m, 3H), 7.62 (m, 2H), 7.55 (m, 1H), 7.02 (d, $J$ = 8.8 Hz, 2H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 159.4, 148.4, 141.7, 136.8, 133.1, 129.7, 129.6, 128.2, 127.9, 127.5, 127.1, 126.2, 118.9, 114.3, 55.4; MS (EI, 70 eV) $m/z$ = 312.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{22}H_{17}NO$: C 84.86, H 5.50, N 4.50. Found: C 84.80, H 5.43, N 4.64.

**2-(3'-Methoxybiphenyl-4-yl)quinoline (7)**. Yield 138.5 mg, 89%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.17–8.25 (m, 4H), 7.89 (d, $J$ = 8.6 Hz, 1H), 7.81 (d, $J$ = 8.1 Hz, 1H), 7.70–7.76 (m, 3H), 7.51–7.53 (m, 1H), 7.36–7.40 (m, 1H), 7.20–7.27 (m, 2H), 6.91–6.94 (m, 1H), 3.87 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 160.0, 156.9, 148.4, 142.1, 141.9, 138.7, 136.9, 129.9, 129.8, 129.7, 128.0, 127.6, 127.5, 127.3, 126.4, 119.7, 118.9, 113.0, 112.9, 55.4; MS (EI, 70 eV) $m/z$ = 312.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{22}H_{17}NO$: C 84.86, H 5.50, N 4.50. Found: C 84.77, H 5.45, N 4.61.

**2-(3'-Nitrobiphenyl-4-yl)quinoline (8)**. Yield 130.5 mg, 80%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.51 (s, 1H), 8.19–8.24 (m, 5H), 7.92–8.00 (m, 2H), 7.54–7.86 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.4, 148.8, 148.3, 142.3, 139.8, 139.4, 137.0, 133.1, 129.9, 129.8, 128.3, 127.6, 127.5, 127.3, 126.6, 122.3, 121.9, 118.9; MS (EI, 70 eV) $m/z$ = 327.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{21}H_{14}N_2O_2$: C 77.29, H 4.32, N 8.58. Found: C 77.22, H 4.27, N 8.66.

**2-(4'-Acetylbiphenyl-4-yl)quinoline (9)**. Yield 126.5 mg, 78%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.18–8.30 (m, 3H), 8.05 (m, 3H), 7.93 (d, $J$ = 8.6 Hz, 1H), 7.70–7.85 (m, 6H), 7.55 (t, 1H), 2.65 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 197.8, 156.6, 148.4, 145.1, 144.4, 140.6, 139.5, 136.9, 136.6, 136.1, 129.8, 129.7, 129.0, 128.1, 127.7, 127.5, 127.4, 127.3, 127.2, 126.5, 118.9, 26.7; MS (EI, 70 eV) $m/z$ = 324.1 $(M + H)^+$; Elemental analysis calcd



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(%) for $C_{23}H_{17}NO$: C 85.42, H 5.30, N 4.33. Found: C 85.49, H 5.25, N 4.26.

**2-(4'-Fluorobiphenyl-4-yl)quinoline (10)**. Yield 121.2 mg, 81%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.17–8.25 (m, 4H), 7.50–7.90 (m, 8H), 7.24–7.31 (m, 1H), 7.12–7.17 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 157.2, 156.8, 148.4, 143.1, 141.5, 141.1, 138.6, 136.9, 136.7, 136.6, 135.5, 131.6, 130.5, 130.0, 129.8, 129.7, 128.8, 128.7, 128.0, 127.7, 127.6, 127.5, 127.4, 127.3, 126.4, 126.0, 125.9, 119.0, 118.8, 115.9, 115.7; MS (EI, 70 eV) *m*/*z* = 300.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{21}H_{14}FN$: C 84.26, H 4.71, N 4.68. Found: C 84.21, H 4.64, N 4.86.

**General procedure for synthesis of 6-aryl-2-phenylquinolines 11–18**

A 10 mL round–bottom flask was charged with **2**/$Cu(OAc)_2$ (0.005/0.03 mmol), acetophenone (0.5 mmol), (2-amino-5-bromophenyl)methanol (0.6 mmol), arylboronic acids (0.75 mmol), $Cs_2CO_3$ (1.5 mmol) and dioxane (3 mL). The reaction mixture was then placed in an oil bath and heated at 110 $^o$C for 20 h. After removal of the solvent, the resulting residue was purified by flash chromatography on silica gel using $CH_2Cl_2$/petroleum ether (1/1) as eluent. The third band was collected and afforded the solids **11–18**.

**6-(4-Methylphenyl)-2-phenylquinoline (12)**. Yield 137.2 mg, 93%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.16–8.24 (m, 4H), 7.98 (m, 2H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.46–7.55 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 157.2, 147.6, 139.7, 138.9, 138.3, 137.6, 137.5, 136.9, 136.8, 136.7, 130.1, 129.7, 129.5, 129.4, 129.3, 128.9, 127.6, 127.2, 126.8, 124.8, 119.4, 21.2; MS (EI, 70 eV) *m*/*z* = 296.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{22}H_{17}N$: C 89.46, H 5.80, N 4.74. Found: C 89.55, H 5.72, N 4.67.

**6-(4-Methoxyphenyl)-2-phenylquinoline (13)**. Yield 146.2 mg, 94%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.17–8.26 (m, 4H), 7.97 (t, 2H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.47–7.54 (m, 3H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 159.5, 147.4, 138.6, 136.8, 132.9, 130.1, 129.3, 129.2, 128.9, 128.4, 127.5, 127.4, 124.3, 119.3, 114.4, 55.4; MS (EI, 70 eV) *m*/*z* = 312.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{22}H_{17}NO$: C 84.86, H 5.50, N 4.50. Found: C 84.74, H 5.42, N 4.67.

**6-(3-Methoxyphenyl)-2-phenylquinoline (14)**. Yield 140.0 mg, 90%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.16–8.23 (m, 4H), 7.96–7.98 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.42–7.55



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(m, 3H), 7.38–7.40 (m, 1H), 7.32 (m, 1H), 7.25 (m, 1H), 6.93 (m, 1H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 160.1, 157.3, 147.7, 141.9, 139.6, 138.8, 136.9, 130.1, 129.9, 129.3, 128.9, 127.5, 127.3, 125.2, 119.9, 119.4, 113.1, 113.0, 55.3; MS (EI, 70 eV) *m*/*z* = 312.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{22}H_{17}NO$: C 84.86, H 5.50, N 4.50. Found: C 84.95, H 5.44, N 4.58.

**6-(1-Naphthyl)-2-phenylquinolines (15)**. Yield 144.1 mg, 87%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.20–8.29 (m, 4H), 7.88–7.96 (m, 6H), 7.45–7.58 (m, 7H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 157.5, 147.6, 139.7, 139.5, 138.8, 136.9, 136.5, 133.8, 132.3, 131.6, 129.4, 129.3, 128.9, 128.8, 128.4, 128.2, 128.0, 127.6, 127.3, 127.1, 126.3, 125.9, 125.8, 125.4, 119.4; MS (EI, 70 eV) *m*/*z* = 332.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{25}H_{17}N$: C 90.60, H 5.17, N 4.23. Found: C 90.71, H 5.08, N 4.34.

**6-(4-Acetylphenyl)-2-phenylquinoline (16)**. Yield 130.9 mg, 81%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.27 (m, 2H), 8.19 (m, 2H), 8.02–8.10 (m, 5H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.65 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 197.8, 157.8, 148.0, 144.9, 144.3, 139.4, 137.6, 137.1, 136.6, 136.1, 130.5, 129.6, 129.1, 129.0, 128.9, 127.6, 127.5, 127.4, 127.3, 125.8, 119.6, 26.8; MS (EI, 70 eV) *m*/*z* = 324.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{23}H_{17}NO$: C 85.42, H 5.30, N 4.33. Found: C 85.48, H 5.26, N 4.24.

**6-(4-Fluorophenyl)-2-phenylquinoline (17)**. Yield 125.6 mg, 84%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.16–8.21 (m, 4H), 7.88–7.94 (m, 3H), 7.66–7.70 (m, 2H), 7.47–7.55 (m, 3H), 7.16–7.20 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 163.9, 161.5, 157.4, 147.6, 139.6, 138.0, 136.9, 136.6, 136.5, 130.3, 129.4, 129.2, 129.1, 129.0, 128.9, 127.6, 127.4, 125.0, 119.5, 116.0, 115.8; MS (EI, 70 eV) *m*/*z* = 300.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{21}H_{14}FN$: C 84.26, H 4.71, N 4.68. Found: C 84.32, H 4.61, N 4.77.

**6-(3-Nitrophenyl)-2-phenylquinoline (18)**. Yield 133.7 mg, 82%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.49 (t, 1H), 8.30 (m, 1H), 8.16–8.23 (m, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.82–7.84 (m, 2H), 7.67–7.75 (m, 3H), 7.44–7.55 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 157.4, 148.3, 140.3, 139.7, 136.8, 133.1, 130.3, 129.8, 129.7, 129.3, 128.9, 127.6, 127.5, 127.2, 126.3, 123.3, 122.1, 119.1; MS (EI, 70 eV) *m*/*z* = 327.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{21}H_{14}N_2O_2$: C 77.29, H 4.32, N 8.58. Found: C 77.21, H 4.24, N 8.69.



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**General procedure for synthesis of 6-aryl-2-(1,1'-biaryl-4-yl)quinolines 19–30**

A 10 mL round–bottom flask was charged with **2**/$Cu(OAc)_2$ (0.01/0.03 mmol), 4-bromo-acetophenone (0.5 mmol), (2-amino-5-bromophenyl)methanol (0.6 mmol), arylboronic acids (1.5 mmol), $Cs_2CO_3$ (3.0 mmol) and dioxane (3 mL). The reaction mixture was then placed in an oil bath and heated at 110 $^oC$ for 24 h. After removal of the solvent, the resulting residue was purified by flash chromatography on silica gel using $CH_2Cl_2$/petroleum ether (1/1) as eluent. The third band was collected and afforded the solids **19–30**.

**2-(Biaryl-4-yl)-6-phenylquinoline (19)**. Yield 151.8 mg, 85%; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.17–8.26 (m, 5H), 8.00 (t, 1H), 7.90–7.93 (m, 1H), 7.83 (d, $J$ = 8.6 Hz, 1H), 7.67–7.77 (m, 5H), 7.46–7.53 (m, 5H), 7.39 (t, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 157.3, 148.4, 142.1, 140.6, 140.4, 139.7, 139.0, 138.6, 137.0, 136.8, 130.2, 129.7, 129.4, 129.0, 128.9, 128.0, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 126.3, 125.2, 119.4; MS (EI, 70 eV) $m/z$ = 358.2 $(M + H)^+$; Elemental analysis calcd (%) for $C_{27}H_{19}N$: C 90.72, H 5.36, N 3.92. Found: C 90.78, H 5.25, N 3.97.

**2-(1'-Naphthyl-1-phenyl-4-yl)-6-(1-naphthyl)quinoline (20)**. Yield 198.9 mg, 87%; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.31–8.38 (m, 4H), 7.95–8.05 (m, 9H), 7.72 (d, $J$ = 7.8 Hz, 2H), 7.49–7.61 (m, 8H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 147.7, 141.9, 138.9, 138.7, 137.0, 133.9, 132.4, 131.6, 130.7, 129.5, 128.5, 128.4, 128.3, 128.1, 127.9, 127.6, 127.4, 127.2, 126.9, 126.4, 126.2, 126.0, 125.9, 125.5, 119.5; MS (EI, 70 eV) $m/z$ = 458.2 $(M + H)^+$; Elemental analysis calcd (%) for $C_{35}H_{23}N$: C 91.87, H 5.07, N 3.06. Found: C 91.96, H 5.01, N 3.13.

**2-(4'-Methylbiphenyl-4-yl)-6-(4-methylphenyl)quinoline (21)**. Yield 169.5 mg, 88%; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.21–8.25 (m, 5H), 7.98 (s, 1H), 7.91 (d, $J$ = 8.8 Hz, 2H), 7.74 (d, $J$ = 8.4 Hz, 3H), 7.52–7.59 (m, 4H), 7.28 (d, $J$ = 8.0 Hz, 2H), 2.41 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 160.0, 148.4, 142.0, 138.3, 137.7, 137.6, 137.5, 136.9, 136.8, 130.1, 129.7, 129.6, 129.3, 128.9, 127.9, 127.6, 127.5, 127.4, 127.2, 127.0, 126.3, 124.8, 119.4, 118.9, 21.2; MS (EI, 70 eV) $m/z$ = 386.2 $(M + H)^+$; Elemental analysis calcd (%) for $C_{29}H_{23}N$: C 90.35, H 6.01, N 3.63. Found: C 90.46, H 5.92, N 3.55.

**2-(4'-Methoxybiphenyl-4-yl)-6-(4-methoxyphenyl)quinoline (22)**. Yield 189.8 mg, 91%; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.23 (d, $J$ = 8.4 Hz, 5H), 7.92 (d, $J$ = 8.6 Hz, 2H), 7.73 (m,



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2H), 7.63 (d, $J$ = 8.8 Hz, 3H), 7.53–7.55 (m, 2H), 7.02 (d, $J$ = 8.8 Hz, 3H), 3.87 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 159.4, 157.0, 148.4, 141.7, 137.9, 136.8, 133.1, 129.7, 129.6, 128.2, 127.9, 127.5, 127.2, 127.1, 126.3, 118.9, 114.3, 55.4; MS (EI, 70 eV) $m/z$ = 418.2 (M + H)$^+$; Elemental analysis calcd (%) for $C_{29}H_{23}NO_2$: C 83.43, H 5.55, N 3.35. Found: C 83.32, H 5.61, N 3.48.

**2-(4'-Acetylbiphenyl-4-yl)-6-(4-acetylphenyl)quinoline (23)**. Yield 165.5 mg, 75%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.25–8.31 (m, 2H), 8.19 (d, $J$ = 7.6 Hz, 1H), 8.05–8.09 (m, 5H), 7.94 (d, $J$ = 8.6 Hz, 1H), 7.71–7.82 (m, 7H), 7.55 (m, 1H), 2.66 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 197.7, 169.0, 166.5, 156.6, 148.2, 144.4, 136.6, 129.8, 129.7, 129.0, 128.1, 127.7, 127.5, 127.4, 127.2, 126.5, 118.9, 26.8; MS (EI, 70 eV) $m/z$ = 442.2 (M + H)$^+$; Elemental analysis calcd (%) for $C_{31}H_{23}NO_2$: C 84.33, H 5.25, N 3.17. Found: C 84.44, H 5.32, N 3.05.

**2-(4'-Fluorobiphenyl-4-yl)-6-(4-fluorophenyl)quinoline (24)**. Yield 157.2 mg, 80%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.18–8.23 (m, 4H), 7.91–7.96 (m, 2H), 7.84 (d, $J$ = 8.2 Hz, 1H), 7.68–7.76 (m, 3H), 7.62–7.65 (m, 2H), 7.48–7.56 (m, 2H), 7.15–7.22 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.9, 148.5, 141.2, 138.7, 138.2, 137.0, 136.9, 130.5, 129.9, 129.8, 129.2, 129.1, 129.0, 128.9, 128.8, 128.2, 127.7, 127.6, 127.5, 126.5, 125.2, 119.6, 118.9, 116.1, 116.0, 115.9, 115.8; MS (EI, 70 eV) $m/z$ = 394.1 (M + H)$^+$; Elemental analysis calcd (%) for $C_{27}H_{17}F_2N$: C 82.43, H 4.36, N 3.56. Found: C 82.27, H 4.26, N 3.75.

**2-(3'-Methoxybiphenyl-4-yl)-6-(3-methoxyphenyl)quinoline (25)**. Yield 185.7 mg, 89%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.22–8.27 (m, 4H), 7.98 (m, 2H), 7.93 (d, $J$ = 8.6 Hz, 1H), 7.76 (d, $J$ = 8.4 Hz, 2H), 7.37–7.44 (m, 2H), 7.32 (d, $J$ = 8.0 Hz, 1H), 7.21–7.28 (m, 3H), 6.92–6.97 (m, 2H), 3.90 (s, 3H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 160.1, 160.0, 156.8, 147.8, 142.1, 141.9, 141.8, 138.8, 138.6, 137.0, 130.1, 130.0, 129.9, 129.4, 127.9, 127.6, 127.3, 125.2, 119.9, 119.7, 119.2, 113.1, 113.0, 112.9, 55.4, 55.3; MS (EI, 70 eV) $m/z$ = 418.2 (M + H)$^+$; Elemental analysis calcd (%) for $C_{29}H_{23}NO_2$: C 83.43, H 5.55, N 3.35. Found: C 83.61, H 5.43, N 3.46.

**2-(3'-Nitrobiphenyl-4-yl)-6-(3-nitrophenyl)quinoline (26)**. Yield 174.4 mg, 78%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.54 (m, 1H), 8.50 (m, 1H), 8.18–8.33 (m, 5H), 8.07–8.09 (m, 1H), 7.93–8.01 (m, 3H), 7.86 (d, $J$ = 8.2 Hz, 1H), 7.58–7.81 (m, 4H), 7.54–7.58 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 189.5, 156.3, 148.8, 148.3, 142.3, 140.3, 139.8, 139.4, 137.1,



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136.9, 133.2, 133.1, 133.0, 129.8, 128.9, 128.3, 127.6, 127.5, 126.5, 123.3, 122.9, 122.3, 122.2, 122.1, 121.9, 119.8, 118.8; MS (EI, 70 eV) $m/z$ = 448.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{27}H_{17}N_3O_4$: C 72.48, H 3.83, N 9.39. Found: C 72.63, H 3.70, N 9.28.

**2-(2'-Methoxybiphenyl-4-yl)-6-(2-methoxyphenyl)quinoline (27)**. Yield 164.8 mg, 79%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.18–8.26 (m, 4H), 7.92–7.95 (m, 3H), 7.71 (d, $J$ = 8.4 Hz, 2H), 7.37–7.47 (m, 4H), 7.01–7.11 (m, 4H), 3.86 (s, 3H), 3.85 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 157.1, 156.7, 156.6, 147.6, 139.6, 138.3, 136.9, 136.7, 131.9, 130.8, 130.2, 130.1, 129.1, 129.0, 128.9, 127.6, 127.2, 127.1, 121.0, 120.9, 119.1, 111.3, 55.6; MS (EI, 70 eV) $m/z$ = 418.2 $(M + H)^+$; Elemental analysis calcd (%) for $C_{29}H_{23}NO_2$: C 83.43, H 5.55, N 3.35. Found: C 83.26, H 5.49, N 3.54.

**2-(2'-Methylbiphenyl-4-yl)-6-(2-methylphenyl)quinoline (28)**. Yield 146.4 mg, 76%; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.20–8.26 (m, 4H), 7.95 (d, $J$ = 8.6 Hz, 1H), 7.72–7.77 (m, 2H), 7.48–7.52 (m, 3H), 7.29–7.32 (m, 7H), 2.35 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 157.2, 147.4, 143.1, 141.5, 141.2, 140.1, 138.3, 136.9, 135.6, 135.5, 131.6, 130.5, 130.0, 129.8, 129.3, 127.7, 127.5, 127.3, 127.2, 127.0, 126.3, 126.0, 119.3, 119.0, 20.6; MS (EI, 70 eV) $m/z$ = 386.2 $(M + H)^+$; Elemental analysis calcd (%) for $C_{29}H_{23}N$: C 90.35, H 6.01, N 3.63. Found: C 90.48, H 6.13, N 3.84.

**2-(4-Phenylpyridine-4-yl)-6-pyridin-4-ylquinoline (29)**. Yield 107.7 mg, 60%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.75 (br, 7H), 8.29–8.35 (m, 1H), 8.00–8.13 (m, 1H), 7.83 (d, $J$ = 8.4 Hz, 1H), 7.54–7.68 (m, 7H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 150.7, 150.5, 150.4, 147.6, 145.5, 137.4, 130.8, 128.6, 128.3, 127.5, 127.4, 126.0, 121.5, 119.6; MS (EI, 70 eV) $m/z$ = 360.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{25}H_{17}N_3$: C 83.54, H 4.77, N 11.69. Found: C 83.65, H 4.68, N 11.74.

**2-(4-Phenylpyridine-3-yl)-6-pyridin-3-ylquinoline (30)**. Yield 116.7 mg, 65%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.86 (br, 3H), 8.66 (br, 4H), 8.31–8.34 (m, 1H), 8.00–8.05 (m, 1H), 7.89 (d, $J$ = 8.0 Hz, 3H), 7.78 (d, $J$ = 8.4 Hz, 1H), 7.41–7.44 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.9, 149.3, 148.8, 148.2, 147.9, 139.1, 137.1, 135.6, 134.6, 134.3, 133.5, 131.9, 130.7, 129.0, 128.3, 127.6, 127.4, 126.8, 125.6, 123.8, 123.0, 119.5; MS (EI, 70 eV) $m/z$ = 360.1 $(M + H)^+$; Elemental analysis calcd (%) for $C_{25}H_{17}N_3$: C 83.54, H 4.77, N 11.69. Found: C 83.61, H 4.83, N 11.58.



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Electronic supplementary information (ESI) available: $^{1}H$ and $^{13}C$ NMR spectra for all products. The absorption and photoluminescence spectra for **3–30**. CCDC 969892-969893, 969896–969899. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/.

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