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N-heterocyclic carbene (NHC)-modulated Pd/Cu cocatalyzed three-component synthesis of 2,6-diarylquinolines†

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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 reactions. The luminescence of the resulting arylquinolines **3–30** was also investigated.

Introduction

The quinoline moiety plays 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 synthesis, 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 quite limited because phosphines and related organic ligands often degrade rapidly under oxidizing reaction conditions.[9] Recently, great progress has been made for the palladium-catalyzed oxidation using oxidatively stable ligands. These ligands often consist of nitrogen donors, such as amine and pyridine ligands.[9,10] Moreover, NHC ligands have been proven to be effective in various Pd-catalyzed processes[11] as well as in 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 synthesis.

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 synthesis 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 alcohols, aryl ketones, and arylboronic acids in air, providing a series of luminescent arylquinolines.

Results and discussion

The synthetic route to two new NHC adducts of cyclopalladated ferrocenylpyrazine complexes **1–2** is demonstrated in

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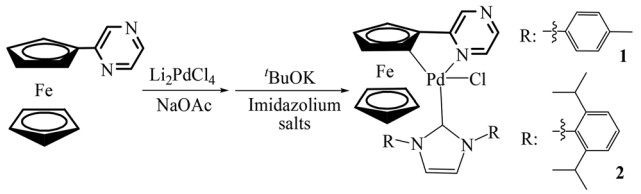
† Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR spectra for all products. The absorption and photoluminescence spectra for **3–30**. CCDC 969892–969893, 969896–969899. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob00231h



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

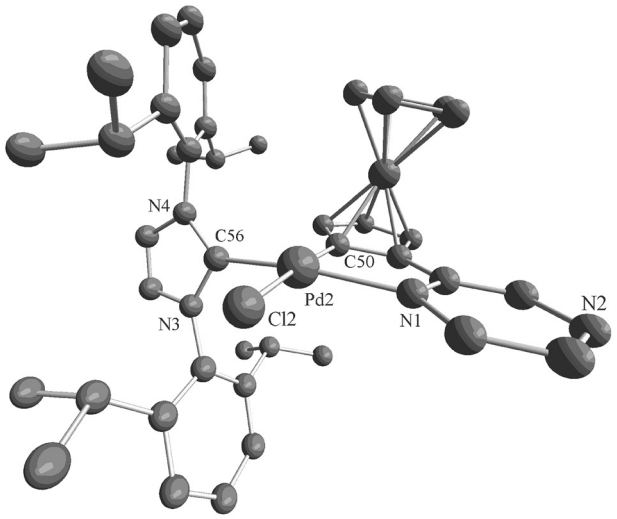


Fig. 1 Molecular structure of **2** (one of the two independent molecules).

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 a dimeric complex of palladium.[15a,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 by single crystal X-ray analysis (Fig. S1† and Fig. 1). The Pd–C_{carb} [1.991(7) and 2.010(7) Å] bond lengths of complex **2** are similar to those of the 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.

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

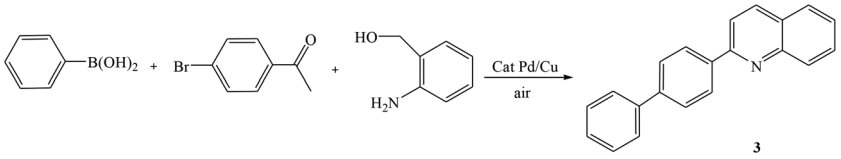
Table 1 provides information on the impact of a catalyst, a base and a solvent on the efficiency of this process. In the absence of copper salts, the desired product **3** was not observed using **2** as a catalyst and only 4-acetylbiphenyl was produced as a Suzuki coupling product. Then, different copper salts and NHC adducts of palladacycle were tested in the presence of air with K_2CO_3 as a 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 the Pd catalyst loading to 0.1 mol% led to a TON of 610 and a moderate yield (entry 15).

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 corresponding products **5–7**, the yields (89–93%) are slightly higher than the yields (76–81%) of electron-withdrawing substrates **8–10**.

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†).

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-bromoacetophenone, 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 a Pd catalyst loading of 2 mol%. In the 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 an 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 structure is not planar, the dihedral angle between the middle benzene ring and the quinoline ring is 25.4°; the benzene ring containing the methoxy group is not coplanar to the quinoline ring and the middle benzene ring (dihedral angles are 52.3° and 44.0°, respectively).

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

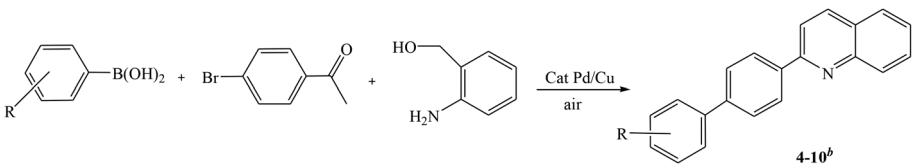


3

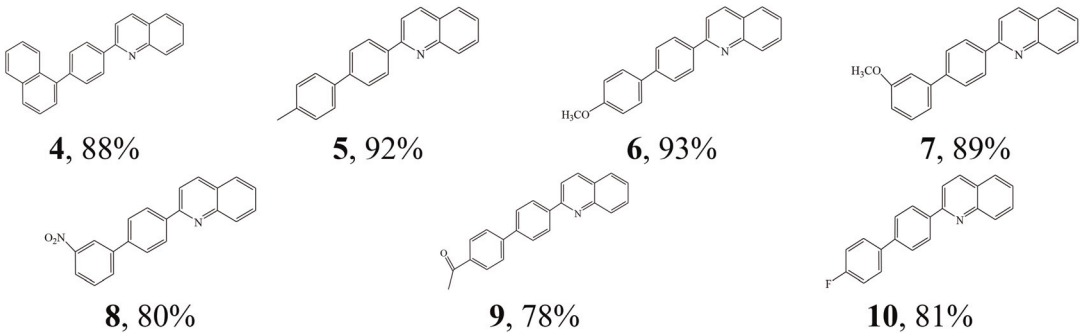
Entry	Catalyst (mol%)	Base	Solvent	Yield[b] (%)
1	**1**/$CuCl_2$ (1/6)	K_2CO_3	Dioxane	23
2	**2**/$CuCl_2$ (1/6)	K_2CO_3	Dioxane	49
3	**2**/$Cu(OAc)_2$ (1/6)	K_2CO_3	Dioxane	65
4	**2**/CuCl (1/6)	K_2CO_3	Dioxane	30
5	**2**/CuI (1/6)	K_2CO_3	Dioxane	18
6	**2**/$Cu(OAc)_2$ (1/6)	KOH	Dioxane	34
7	**2**/$Cu(OAc)_2$ (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-aminobenzyl alcohol (0.6 mmol), phenylboronic acid (0.75 mmol), base (1.5 mmol), solvent (3 mL), 110 °C, 20 h. [b] Isolated yield.

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



4-10[b]



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

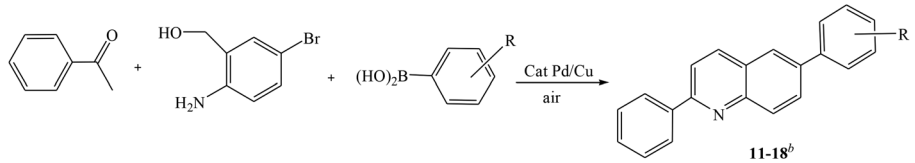
8, 80% **9**, 78% **10**, 81%

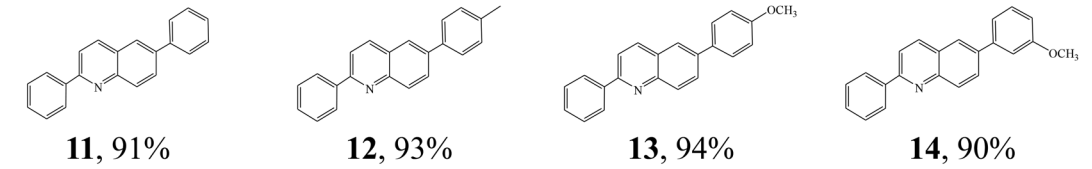
[a] Reaction conditions: **2**/$Cu(OAc)_2$ (0.005/0.03 mmol), 4-bromoacetophenone (0.5 mmol), 2-aminobenzyl alcohol (0.6 mmol), arylboronic acids (0.75 mmol), Cs_2CO_3 (1.5 mmol), dioxane (3 mL), 110 °C, 20 h. [b] Isolated yield.

The UV-Vis absorption and photoluminescence spectra of **3–27** were recorded in CH_2Cl_2 at rt, and the data are shown 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-arylquinolines. These arylquinolines show emissions ranging from the purple to the blue region. For example, the arylquinolines containing fluorine **10**, **17** and **24** exhibit major 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]

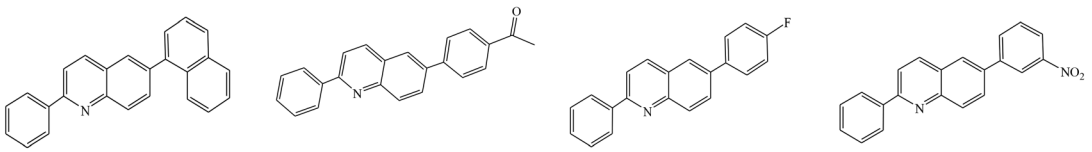
In summary, we have developed a NHC-modulated Pd/Cu cocatalyzed three-component reaction of aminobenzyl alcohols, aryl ketones, and arylboronic acids in air. This protocol provides an efficient access to a variety of 2,6-diarylquinolines

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





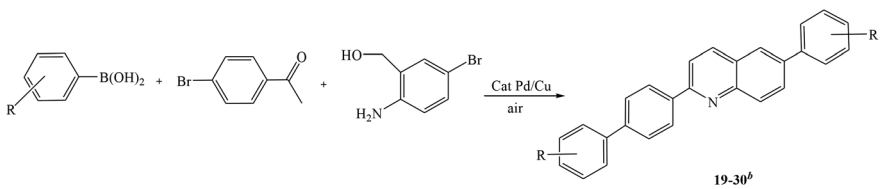
11, 91% **12**, 93% **13**, 94% **14**, 90%

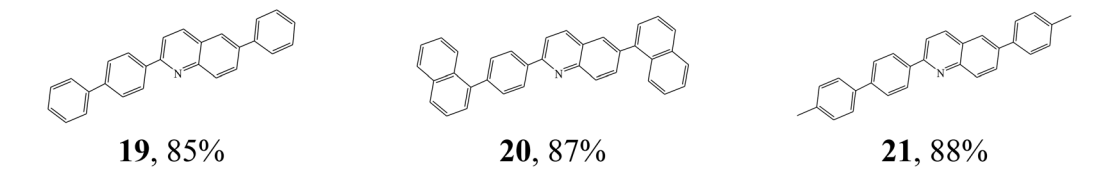


15, 87% **16**, 81% **17**, 84% **18**, 82%

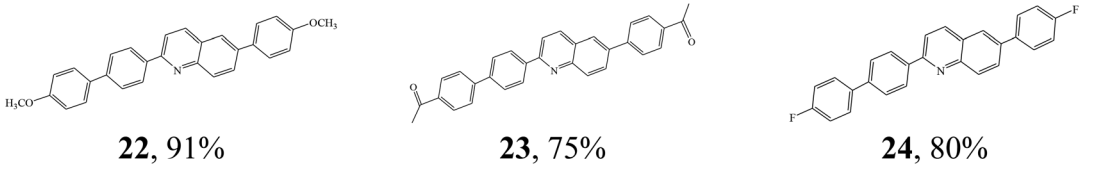
[a] Reaction conditions: **2**/$Cu(OAc)_2$ (0.005/0.03 mmol), acetophenone (0.5 mmol), (2-amino-5-bromophenyl)methanol (0.6 mmol), arylboronic acids (0.75 mmol), Cs_2CO_3 (1.5 mmol), dioxane (3 mL), 110 °C, 20 h. [b] Isolated yield.

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

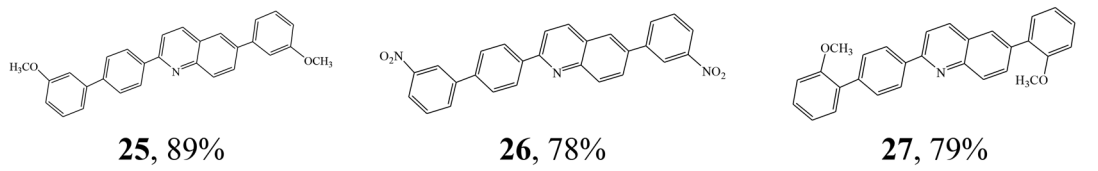




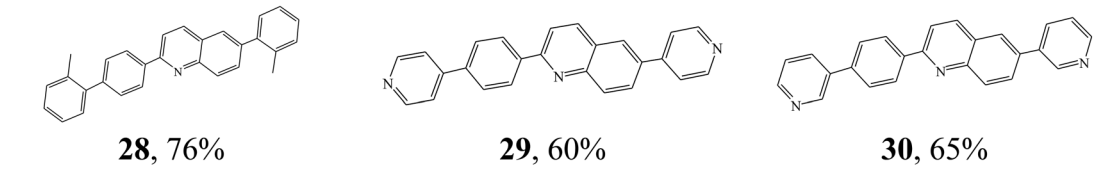
19, 85% **20**, 87% **21**, 88%



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 °C, 24 h. [b] Isolated yield.

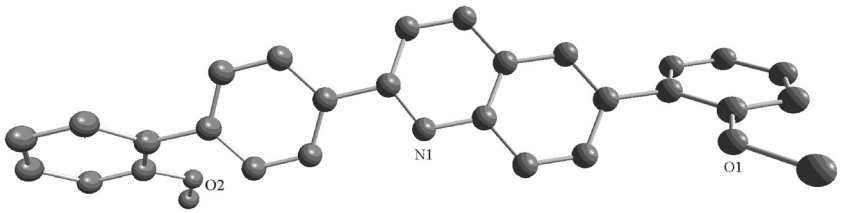


Fig. 2 Molecular structure of **27**. H atoms are omitted for clarity.

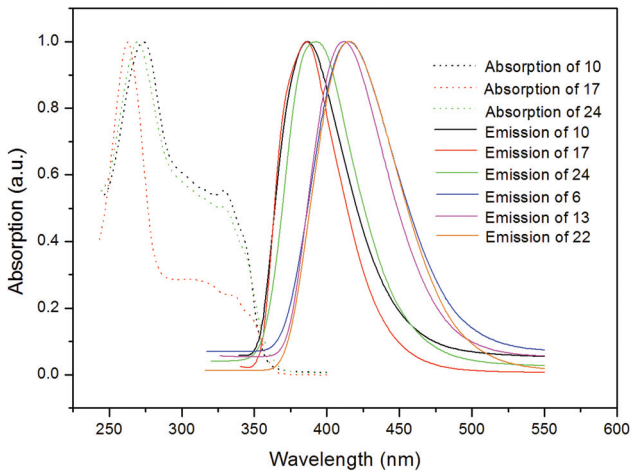


Fig. 3 Normalized absorption and emission of **10**, **17** and **24**, emission of **6**, **13** and **22** (absorption spectra are omitted for clarity) in CH_2Cl_2 at rt.

via oxidation, cyclization and Suzuki reaction. Future work will report on the photoactive complexes of these arylquinolines.

Experimental section

General methods

^1H and ^{13}C NMR spectra were recorded on a spectrometer in $CDCl_3$ at 400 and 100 MHz, respectively, with TMS as an 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 except for ferrocenylpyrazine which was prepared according to the published procedures.[21] Compounds **3**,[22] **5** (spectra not provided),[23] and **11**[19] are known compounds, while 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 an eluent, the second band was collected and afforded **1–2**. (**1**). Yield 593.3 mg, 91%; ^1H NMR (400 MHz, $CDCl_3$): δ 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), 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, $CDCl_3$): δ 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%; ^1H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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-aminobenzyl alcohol (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 °C for 20 h, then 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 an 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%; ^1H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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 (%) 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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 °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 an 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 8.16–8.23 (m, 4H), 7.96–7.98 (m, 2H), 7.87 (d, J = 8.4 Hz, 1H), 7.42–7.55 (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, $CDCl_3$): δ 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, $CDCl_3$): δ 8.20–8.29 (m, 4H), 7.88–7.96 (m, 6H), 7.45–7.58 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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,

$CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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.

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-bromoacetophenone (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 °C 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 an eluent. The third band was collected and afforded the solids **19–30**.

2-(Biaryl-4-yl)-6-phenylquinoline (19). Yield 151.8 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.4 Hz, 5H), 7.92 (d, *J* = 8.6 Hz, 2H), 7.73 (m, 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 189.5, 156.3, 148.8, 148.3, 142.3, 140.3, 139.8, 139.4, 137.1, 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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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Notes and references

1 (*a*) J. P. Michael, *Nat. Prod. Rep.*, 2008, **25**, 166; (*b*) M. Rouffet, C. A. F. Oliveira, Y. Udi, A. Agrawal, I. Sagi, J. A. McCammon and S. M. Cohen, *J. Am. Chem. Soc.*, 2010, **132**, 8232; (*c*) B. León, J. C. N. Fong, K. C. Peach, W. R. Wong, F. H. Yildiz and R. G. Linington, *Org. Lett.*, 2013, **15**, 1234.

2 (*a*) S. P. Economopoulos, C. L. Chochos, V. G. Gregorlou, J. K. Kallitsis, S. Barrau and G. Hadziioannou, *Macromolecules*, 2007, **40**, 921; (*b*) R. S. Walters, C. M. Kraml, N. Byrne, D. M. Ho, Q. Qin, F. J. Coughlin, S. Bernhard and R. A. Pascal, *J. Am. Chem. Soc.*, 2008, **130**, 16435; (*c*) R. Cinar, J. Nordmann, E. Dirksen and T. J. J. Müller, *Org. Biomol. Chem.*, 2013, **11**, 2597.

3 (*a*) Q. Zhao, C. Y. Jiang, M. Shi, F. Y. Li, T. Yi, Y. Cao and C. H. Huang, *Organometallics*, 2006, **25**, 3631; (*b*) Z. H. Ma, J. Q. Ding, B. H. Zhang, C. Y. Mei, Y. X. Cheng, Z. Y. Xie, L. X. Wang, X. B. Jing and F. S. Wang, *Adv. Funct. Mater.*, 2010, **20**, 138; (*c*) A. Wada, Q. S. Zhang, T. Yasuda, I. Takasu, S. Enomoto and C. Adachi, *Chem. Commun.*, 2012, 5340; (*d*) A. Zucca, D. Cordeschi, L. Maidich, M. I. Pilo, E. Masolo, S. Stoccoro, M. A. Cinellu and S. Galli, *Inorg. Chem.*, 2013, **52**, 7717.

4 (*a*) R. Martínez, D. J. Ramón and M. Yus, *J. Org. Chem.*, 2008, **73**, 9778; (*b*) J. Marco-Contelles, E. Pérez-Mayoral, A. Samadi, M. C. Carreiras and E. Soriano, *Chem. Rev.*, 2009, **109**, 2652; (*c*) S. V. Ryabukhin, V. S. Naumchik, A. S. Plaskon, O. O. Grygorenko and A. A. Tolmachev, *J. Org. Chem.*, 2011, **76**, 5774.

5 (*a*) C. S. Cho, B. T. Kim, T. J. Kim and S. C. Shim, *Chem. Commun.*, 2001, 2576; (*b*) C. S. Cho, B. T. Kim, H. J. Choi, T. J. Kim and S. C. Shim, *Tetrahedron*, 2003, **59**, 7997; (*c*) K. Motokura, T. Mizugaki, K. Ebitani and K. Kaneda, *Tetrahedron Lett.*, 2004, **45**, 6029; (*d*) R. Martínez, D. J. Ramón and M. Yus, *Tetrahedron*, 2006, **62**, 8988; (*e*) R. Martínez, D. J. Ramón and M. Yus, *Eur. J. Org. Chem.*, 2007, 1599.

6 (*a*) K. Taguchi, S. Sakaguchi and Y. Ishii, *Tetrahedron Lett.*, 2005, **46**, 4539; (*b*) P. J. Black, G. Cami-Kobeci, M. G. Edwards, P. A. Slatford, M. K. Whittlesey and J. M. J. Williams, *Org. Biomol. Chem.*, 2006, **4**, 116; (*c*) T. Suzuki, *Chem. Rev.*, 2011, **111**, 1825.

7 (*a*) C. S. Cho, H. J. Seok and S. C. Shim, *J. Heterocycl. Chem.*, 2005, **42**, 1219; (*b*) C. S. Cho, W. X. Ren and S. C. Shim, *Tetrahedron Lett.*, 2006, **47**, 6781; (*c*) C. S. Cho and W. X. Ren, *J. Organomet. Chem.*, 2007, **692**, 4182.

8 (*a*) R. A. Sheldon, I. W. C. E. Arends and A. Dijksman, *Catal. Today*, 2000, **57**, 157; (*b*) D. R. Jensen, J. S. Pugsley and M. S. Sigman, *J. Am. Chem. Soc.*, 2001, **123**, 7475; (*c*) A. F. Lee, J. N. Naughton, Z. Liu and K. Wilson, *ACS Catal.*, 2012, **2**, 2235.

9 B. A. Steinhoff, I. A. Guzei and S. S. Stahi, *J. Am. Chem. Soc.*, 2004, **126**, 11268.

10 (*a*) T. Nishimura, T. Onoue, K. Ohe and S. Uemura, *Tetrahedron Lett.*, 1998, **39**, 6011; (*b*) T. Nishimura, T. Onoue, K. Ohe and S. Uemura, *J. Org. Chem.*, 1999, **64**, 6750; (*c*) J. A. Mueller and M. S. Sigman, *J. Am. Chem. Soc.*, 2003, **125**, 7005; (*d*) J. A. Mueller, A. Cowell, B. D. Chandler and M. S. Sigman, *J. Am. Chem. Soc.*, 2005, **127**, 14817;

(*e*) T. S. Mei, E. W. Werner, A. J. Burckle and M. S. Sigman, *J. Am. Chem. Soc.*, 2013, **135**, 6830.

11 (*a*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (*b*) M. G. Dai, B. Liang, C. H. Wang, Z. J. You, J. Xiang, G. B. Dong, J. H. Chen and Z. Yang, *Adv. Synth. Catal.*, 2004, **346**, 1669; (*c*) S. P. Nolan, *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH, Weinheim, Germany, 2006; (*d*) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768.

12 (*a*) D. R. Jensen, M. J. Schultz, J. A. Mueller and M. S. Sigman, *Angew. Chem., Int. Ed.*, 2003, **42**, 3810; (*b*) D. R. Jensen and M. S. Sigman, *Org. Lett.*, 2003, **5**, 63; (*c*) J. A. Mueller, C. P. Goller and M. S. Sigman, *J. Am. Chem. Soc.*, 2004, **126**, 9724; (*d*) C. N. Cornell and M. S. Sigman, *J. Am. Chem. Soc.*, 2005, **127**, 2796; (*e*) C. N. Cornell and M. S. Sigman, *Inorg. Chem.*, 2007, **46**, 1903; (*f*) O. Kose and S. Saito, *Org. Biomol. Chem.*, 2010, **8**, 896; (*g*) X. L. Liu, Q. Q. Xia, Y. J. Zhang, C. Y. Chen and W. Z. Chen, *J. Org. Chem.*, 2013, **78**, 8531.

13 (*a*) *Multicomponent Reactions*, ed. J. Zhu and H. Bienaym, Wiley-VCH, Weinheim, 2005; (*b*) D. J. Ramón and M. Yus, *Angew. Chem., Int. Ed.*, 2005, **44**, 1602; (*c*) A. Dömling, *Chem. Rev.*, 2006, **106**, 17.

14 C. Xu, X. Q. Hao, Z. Q. Xiao, Z. Q. Wang, X. E. Yuan, W. J. Fu, B. M. Ji and M. P. Song, *J. Org. Chem.*, 2013, **78**, 8730.

15 (*a*) C. Xu, Z. Q. Wang, W. J. Fu, X. H. Lou, Y. F. Li, F. F. Cen, H. J. Ma and B. M. Ji, *Organometallics*, 2009, **28**, 1909; (*b*) C. Xu, Y. P. Zhang, Z. Q. Wang, W. J. Fu, X. Q. Hao, Y. Xu and B. M. Ji, *Chem. Commun.*, 2010, 6852; (*c*) J. L. Niu, X. Q. Hao, J. F. Gong and M. P. Song, *Dalton Trans.*, 2011, **40**, 5135; (*d*) C. Xu, Z. Q. Wang, Z. Li, W. Z. Wang, X. Q. Hao, W. J. Fu, J. F. Gong, B. M. Ji and M. P. Song, *Organometallics*, 2012, **31**, 798.

16 (*a*) M. S. Viciu, R. A. Kelly III, E. D. Stevens, F. Naud, M. Studer and S. P. Nolan, *Org. Lett.*, 2003, **5**, 1479; (*b*) E. A. B. Kantchev and J. Y. Ying, *Organometallics*, 2009, **28**, 289; (*c*) C. Xu, H. M. Li, Z. Q. Wang, W. J. Fu, Y. Q. Zhang and B. M. Ji, *Aust. J. Chem.*, 2012, **65**, 366.

17 (*a*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; (*b*) R. A. Altman and S. L. Buchwald, *Nat. Protocols*, 2007, **2**, 3115.

18 J. Dupont, C. S. Consorti and J. Spencer, *Chem. Rev.*, 2005, **105**, 2527.

19 M. Yao, H. Shibuya, T. Kato, H. Inoue and N. Yoshioka, *Polyhedron*, 2005, **24**, 2828.

20 (*a*) R. Ziessel, L. Bonardi and G. Ulrich, *Dalton Trans.*, 2006, 2913; (*b*) J. Massue, D. Frath, G. Ulrich, P. Retailleau and R. Ziessel, *Org. Lett.*, 2012, **14**, 230.

21 R. Horikoshi, C. Nambu and T. Mochida, *Inorg. Chem.*, 2003, **42**, 6868.

22 A. M. Berman, J. C. Lewis, R. G. Bergman and J. A. J. Ellman, *J. Am. Chem. Soc.*, 2008, **130**, 14926.

23 N. O. Buu-Hoi, N. Hoan and R. Royer, *Bull. Soc. Chim. Fr.*, 1950, 489.

