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# Synthesis of 2,4-Diarylquinoline Derivatives via Chloranil-Promoted Oxidative Annulation and One-Pot Reaction

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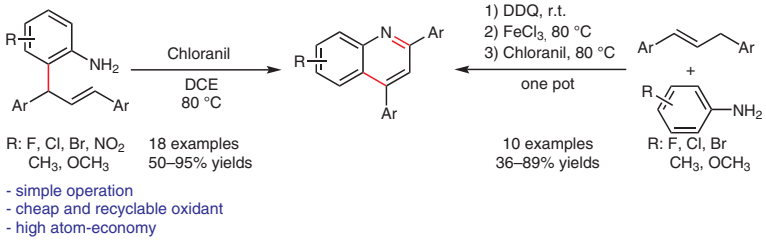


Received: 24.12.2019
Accepted after revision: 06.02.2020
Published online: 24.02.2020
DOI: 10.1055/s-0039-1691740; Art ID: ss-2019-f0706-op

**Abstract** An oxidative annulation for the synthesis of 2,4-diarylquinolines from *o*-allylanilines is disclosed that uses recyclable reagent Chloranil as the oxidant. The corresponding products are obtained in moderate to excellent yields. Furthermore, a one-pot access to 2,4-diarylquinolines from easily available anilines and 1,3-diarylpropenes is described as a highly atom-efficient protocol that involves oxidative coupling, rearrangement, and oxidative annulation.

**Key words** oxidative annulation, one-pot reaction, chloranil, 2,4-diarylqunoline

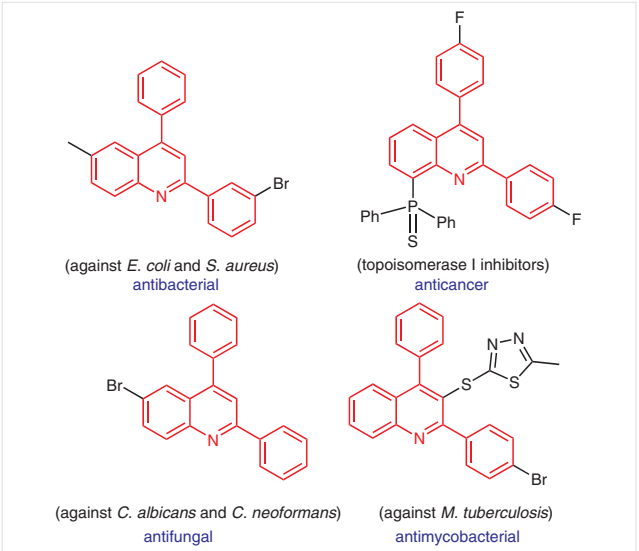


**Figure 1** Bioactive 2,4-diarylquinoline skeleton

The quinoline nucleus is an important structure unit that exists widely in natural products and pharmaceuticals such as antibacterial,[1] antimalarial,[2] antioxidant,[3] anti-inflammatory,[4] and insecticidal agents.[5] Quinolines are also applied as crucial ligands in the synthesis of phosphorescent materials, fluorsensors, and asymmetric catalysts.[6] Given their outstanding characteristics, various quinoline derivatives containing different substituents at specific positions have been designed and synthesized.[7] Among them, 2,4-diarylquinolines have been proven to be especially important because of their potential biological activities, as shown in Figure 1.[3,8] As a result, a large number of synthetic protocols have been developed for the preparation of 2,4-diarylquinolines.[9]

The traditional routes for synthesizing 2,4-diarylquinolines include the Combes reaction of anilines and 1,3-diaryl-1,3-diketones,[10] the Friedländer reaction of 2-aminobenzophenone and acetophenones/benzylalcohols,[11] the Povarov reaction of anilines, arylaldehydes, and arylacetylenes/arylethylenes,[12] and the transition-metal- or acid-catalyzed cyclization of *N*-benzylanilines and arylacetylenes/arylethylenes.[13] However, these methods usually suffer from the drawbacks of prolonged reaction time and undesired self-condensation of the starting materials. Recently, a strategy based on the cyclization of *o*-functionalized anilines has emerged as an efficient alternative for constructing 2,4-diarylquinolines.[14] For example, the Ghorai group developed the KO$^t$Bu-mediated oxidative cycloisomerization of *o*-cinnamylanilines with DMSO as an oxidant (Scheme 1, a).[15] The Alabugin group reported the DDQ/$FeCl_3$-mediated intramolecular oxidative amination of *o*-substituted anilines (Scheme 1, b).[16] Considering the importance of 2,4-diarylquinolines, it is still desirable to develop new, concise and efficient routes for the preparation of such structures under mild conditions. Recently, our group has explored the use of metal-free tandem annulations for constructing heterocycles with potential biological

 
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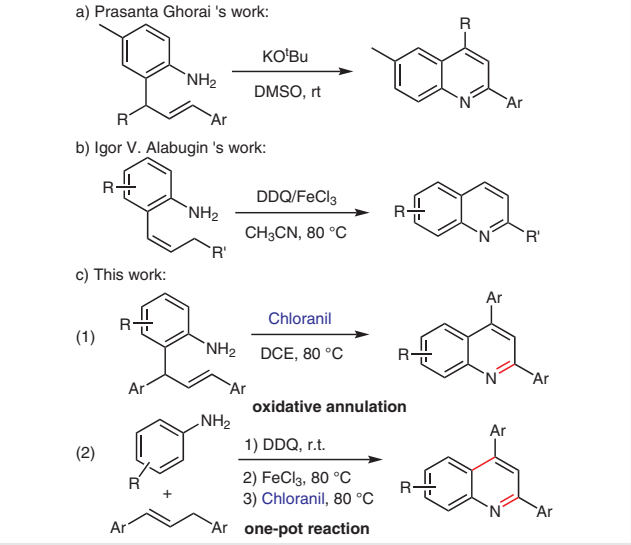
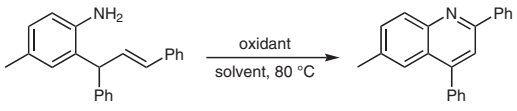
activities.[17] With our ongoing interest in this research area, herein, we disclose an oxidative annulation for the synthesis of 2,4-diarylquinolines from *o*-allylanilines mediated by Chloranil. Quinones as good oxidants have been widely applied in organic synthesis.[18] Although Chloranil is a cheap and recyclable reagent, an extensive review of the literature revealed that the application of Chloranil in oxidative coupling/annulation reactions is not common.[19] Based on our previous report,[20] a one-pot access to 2,4-diarylquinolines from easily available anilines and 1,3-diarylpropenes is also developed in this paper. The approach affords a highly atom-efficient protocol, with the loss of only six hydrogen atoms, which involves oxidative coupling, rearrangement, and oxidative annulation.




**Scheme 1** Previous and present strategies via oxidative annulation

Considering the similarity of *o*-allylaniline **1a** to Alabugin's substrate, the standard reaction conditions of Alabugin's method were tried (Table 1, entry 1).[16] That is, the cyclization of **1a** was performed in $CH_3CN$ at 80 °C in the presence of DDQ/$FeCl_3$. Unfortunately, the desired product 2,4-diphenylquinoline could be isolated in only 39% yield. To optimize the reaction conditions, other quinones such as benzoquinone (BQ, $E_{red}$ = –0.50 V vs. SCE) and Chloranil (CA, $E_{red}$ = 0.01 V vs. SCE) were used instead of DDQ ($E_{red}$ = 0.51 V vs. SCE) (entries 2 and 3).[21] The reaction did not proceed when benzoquinone was used as an oxidant. It was found that $FeCl_3$ did not promote the reaction and the product was obtained in 66% yield only in the presence of Chloranil (entries 3 and 4). Encouraged by the result, several solvents, such as 1,4-dioxane, $CH_3NO_2$, 1,2-$ClCH_2CH_2Cl$ (DCE), DMSO, and DMF were screened (entries 6–10). The reaction was found to proceed in all the examined solvents, but DCE was optimal. Decreasing the temperature to 60 °C reduced the yield (entry 11). Furthermore, the amount of Chloranil was examined and the results indicated that 2.1 equivalents Chloranil was best suited for the reaction (entries 12–14). After the reaction, the tetrachlorohydroquinone formed could be recycled to Chloranil by aerobic oxidation (see the Supporting Information for recyclability experiments).[22] The reaction proceeded well and the product was obtained in 88% yield when recycled Chloranil was used.

**Table 1** Screening of the Optimal Conditions[a]




**1a** **2a**

| Entry | Oxidant | Solvent | Temp (°C) | Yield (%)[b] |
|---|---|---|---|---|
| 1[c] | DDQ/$FeCl_3$ | $CH_3CN$ | 80 | 39 |
| 2[c] | BQ/$FeCl_3$ | $CH_3CN$ | 80 | – |
| 3[c] | Chloranil/$FeCl_3$ | $CH_3CN$ | 80 | 60 |
| 4 | Chloranil | $CH_3CN$ | 80 | 66 |
| 5 | DDQ | $CH_3CN$ | 80 | 48 |
| 6 | Chloranil | 1,4-dioxane | 80 | 73 |
| 7 | Chloranil | $CH_3NO_2$ | 80 | 76 |
| 8 | Chloranil | DCE | 80 | 88 |
| 9 | Chloranil | DMSO | 80 | 41 |
| 10 | Chloranil | DMF | 80 | 64 |
| 11 | Chloranil | DCE | 60 | 76 |
| 12[d] | Chloranil | DCE | 80 | 93 |
| 13[e] | Chloranil | DCE | 80 | 81 |
| 14[f] | Chloranil | DCE | 80 | 82 |
| 15 | Chloranil[g] | DCE | 80 | 88 |

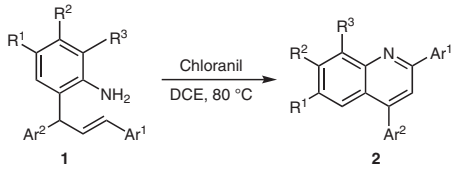
[a] Reaction conditions: **1a** (0.2 mmol), oxidant (2.2 equiv), solvent (3 mL), 2 h.
[b] Isolated yield.
[c] $FeCl_3$ (20 mol%).
[d] Chloranil (2.1 equiv).
[e] Chloranil (2.0 equiv).
[f] Chloranil (2.3 equiv).
[g] Recycled Chloranil was used.

With the optimized conditions in hand, *o*-allylanilines with different substituents on the aniline moiety were first investigated. Aniline moieties containing electron-donating or electron-withdrawing substituents were good candidates for the reaction and afforded the corresponding products **2b–i** in 68–93% yields (Table 2, entries 2–9). Notably, *o*-allylaniline, with a nitro group on the aniline moiety, reacted smoothly and provided the product **2f** in 76% yield (entry 6). The desired products **2g–h** were obtained in 86–93% yield when the *ortho*-position of the aniline moiety was substituted with a methyl or methoxyl group, regardless of their steric hindrance effect (entries 7 and 8). Secondly, various symmetrical 1′,3′-diarylallyl groups of *o*-allylanilines were examined (entries 10–16). The products were obtained in 90–91% yields when methyl group was

attached at the *para*- and *meta*- position of 1′,3′-diarylallyls (entries 10 and 11). Only 61% yield was obtained when a methyl group was attached to the *ortho*-position, likely due to its steric bulk (entry 12). The yields were slightly lower when the *para*- and *meta*-position of 1′,3′-diarylallyls contained electron-withdrawing substituents such as F, Cl, or Br (entries 13–16). Finally, isomerized *o*-allylanilines with an unsymmetrical 1′,3′-diarylallyl group were examined, giving the isomerized products with excellent yields (entries 17 and 18).

**Table 2** Substrate Scope[a]

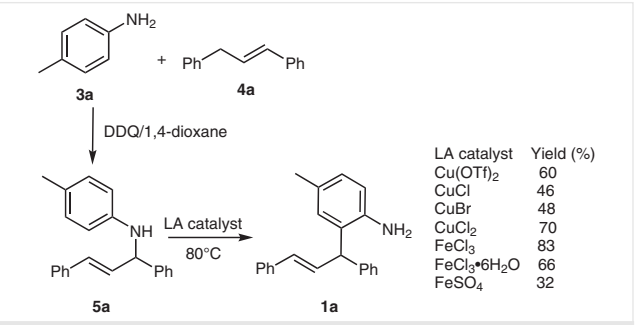



1 2

| Entry | $R^1$ | $R^2$ | $R^3$ | $Ar^1$ | $Ar^2$ | Product | Yield (%)[b] |
|---|---|---|---|---|---|---|---|
| 1 | $CH_3$ | H | H | $C_6H_5$ | $C_6H_5$ | **2a** | 93 |
| 2 | $CH_3O$ | H | H | $C_6H_5$ | $C_6H_5$ | **2b** | 80 |
| 3 | F | H | H | $C_6H_5$ | $C_6H_5$ | **2c** | 88 |
| 4 | Cl | H | H | $C_6H_5$ | $C_6H_5$ | **2d** | 76 |
| 5 | Br | H | H | $C_6H_5$ | $C_6H_5$ | **2e** | 90 |
| 6 | $NO_2$ | H | H | $C_6H_5$ | $C_6H_5$ | **2f** | 76 |
| 7 | $CH_3$ | H | $CH_3$ | $C_6H_5$ | $C_6H_5$ | **2g** | 86 |
| 8 | $CH_3O$ | H | $CH_3O$ | $C_6H_5$ | $C_6H_5$ | **2h** | 93 |
| 9 | $CH_3O$ | $CH_3O$ | H | $C_6H_5$ | $C_6H_5$ | **2i** | 68 |
| 10 | $CH_3$ | H | H | 4-$CH_3C_6H_4$ | 4-$CH_3C_6H_4$ | **2j** | 90 |
| 11 | $CH_3$ | H | H | 3-$CH_3C_6H_4$ | 3-$CH_3C_6H_4$ | **2k** | 91 |
| 12 | $CH_3$ | H | H | 2-$CH_3C_6H_4$ | 2-$CH_3C_6H_4$ | **2l** | 61 |
| 13 | $CH_3$ | H | H | 4-$FC_6H_4$ | 4-$FC_6H_4$ | **2m** | 80 |
| 14 | $CH_3$ | H | H | 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | **2n** | 56 |
| 15 | $CH_3$ | H | H | 4-$BrC_6H_4$ | 4-$BrC_6H_4$ | **2o** | 50 |
| 16 | $CH_3$ | H | H | 3-$ClC_6H_4$ | 3-$ClC_6H_4$ | **2p** | 70 |
| 17 | $CH_3$ | H | H | $C_6H_5$ | 4-$ClC_6H_4$ | **2q** | 95 |
| 18 | $CH_3$ | H | H | $C_6H_5$ | 4-$CH_3C_6H_4$ | **2r** | 90 |

[a] Reaction conditions: **1** (0.5 mmol), Chloranil (1.05 mmol), DCE (3 mL), 80 °C, 1–2 h.
[b] Isolated yield.

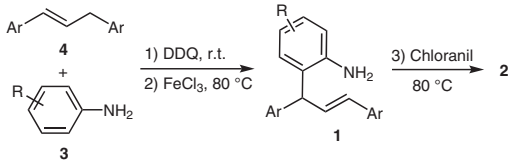
In 2012, our group reported the DDQ-mediated oxidative coupling of anilines and 1,3-diarylpropenes, which provided an efficient and convenient method for preparing *N*-allylanilines.[20] To obtain *o*-allylaniline **1a**, the rearrangement of the coupling product *N*-allylaniline **5a** was tried. Lewis acid $Cu(OTf)_2$ (5 mol%) was subsequently added to the reaction mixture after the oxidative coupling of 4-methylaniline **3a** and 1,3-diphenylpropene **4a** (Scheme 2). To our delight, the desired 2-allylaniline **1a** was isolated in 60% yield when the reaction was stirred at 80 °C for 1 h. Screening other Lewis acids such as $FeCl_3$, $FeCl_3{\cdot}6H_2O$, $CuCl_2$, CuCl, CuBr, and $FeSO_4$ indicated that $FeCl_3$ was the best catalyst.




**Scheme 2** The conversion of *N*-allylaniline **5a** into *o*-allylaniline **1a**

Based on the above experiments, a one-pot cascade approach to 2,4-diarylquinolines from easily available anilines and 1,3-diarylpropenes was explored (Table 3). The tandem reaction of 4-methylaniline **3a** and 1,3-diphenylpropene **4a** was carried out in 1,4-dioxane, which gave the final product 2,4-diphenylquinoline in 77% yield (entry 1). Examining a selection of solvents revealed that the yield could be increased to 87% when DCE was used (entry 2). Several corresponding products **2** were obtained from anilines **4** and symmetrical 1,3-arylpropenes **3** in moderate to good yields (entries 3–11).

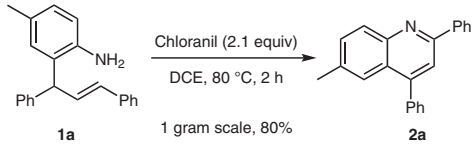
**Table 3** One-Pot Synthesis of 2,4-Diarylquinolines[a]




| Entry | Ar | R | Product | Yield (%)[b] |
|---|---|---|---|---|
| 1 | $C_6H_5$ | 4-$CH_3$ | **2a** | 77[c] |
| 2 | $C_6H_5$ | 4-$CH_3$ | **2a** | 87 |
| 3 | $C_6H_5$ | 4-$CH_3O$ | **2b** | 61 |
| 4 | $C_6H_5$ | 4-F | **2c** | 74 |
| 5 | $C_6H_5$ | 4-Cl | **2d** | 65 |
| 6 | $C_6H_5$ | 4-Br | **2e** | 70 |
| 7 | $C_6H_5$ | 2,4-$(CH_3)_2$ | **2g** | 89 |
| 8 | 4-$CH_3C_6H_4$ | 4-$CH_3$ | **2j** | 67 |
| 9 | 3-$CH_3C_6H_4$ | 4-$CH_3$ | **2k** | 66 |
| 10 | 2-$CH_3C_6H_4$ | 4-$CH_3$ | **2l** | 36 |
| 11 | 4-$FC_6H_4$ | 4-$CH_3$ | **2m** | 67 |

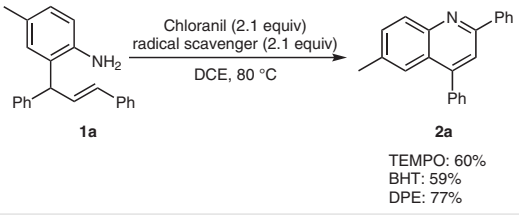
[a] Reaction conditions: **3** (0.55 mmol), **4** (0.5 mmol), DDQ (0.55 mmol), DCE (3 mL), r.t., 10 min; $FeCl_3$ (0.025 mmol), 80 °C, 1 h; Chloranil (1.05 mmol), 80 °C, 1–2 h.
[b] Isolated yield.
[c] 1,4-Dioxane (3 mL) as solvent.

Further, gram-scale oxidative annulation of **1a** under similar reaction conditions provided the desired product **2a** in good yield (80% isolated yield) (Scheme 3).

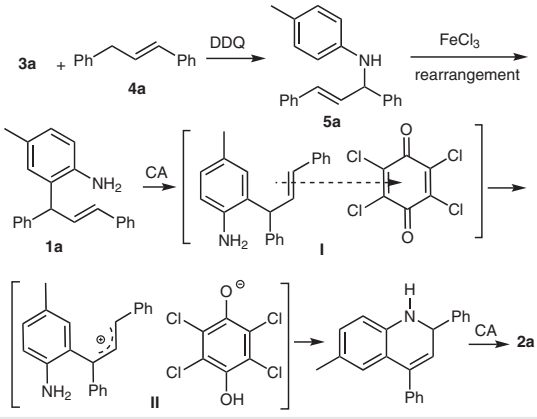



**Scheme 3** Gram-scale synthesis

To establish the mechanism of reaction, a series of control experiments were conducted (Scheme 4). The desired product **2a** was obtained in good yield when 2.1 equivalents of radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), butylated hydroxytoluene (BHT), or 1,1-diphenylethene (DPE) was added to the reaction mixture, which indicated that a radical process was disfavored in the oxidative annulation. Based on our previous work and on the above results, a plausible mechanism is proposed in Scheme 5. Firstly, 4-methylaniline **3a** reacts with 1,3-diphenylpropene **4a** in the presence of DDQ to give **5a**, which then rearranges to give *o*-allylaniline **1a**. The latter reacts with Chloranil to afford the ion pair **II** via charge-transfer complex **I** and subsequent hydride transfer.[23] Finally, attack of the amino group on the allylic cation occurs, followed by oxidative dehydro-aromatization to generate the product **2a**.




**Scheme 4** Control experiments




**Scheme 5** Proposed mechanism

In summary, an efficient method for the synthesis of 2,4-diarylquinolines from *o*-allylanilines that uses recyclable Chloranil as the oxidant has been developed. The corresponding products are obtained in moderate to excellent yields. Additionally, a one-pot protocol is extended to the synthesis of 2,4-diarylquinolines from easily available anilines and 1,3-diarylpropenes through a three-step tandem reaction, which involves oxidative coupling, rearrangement, and oxidative annulation.

Column chromatography was carried out on silica gel (200–300 mesh). $^1$H NMR spectra were recorded with a 500 MHz spectrometer (Bruker AVANCE III 500MHz NMR spectrometer) or 600 MHz spectrometer (Bruker Ascend™ 600MHz superconducting NMR spectrometer). $^{13}$C NMR spectra were recorded with a 125 MHz spectrometer (Bruker AVANCE III 500MHz NMR spectrometer) or 150 MHz spectrometer (Bruker Ascend™ 600MHz superconducting NMR spectrometer). Chemical shifts are reported in parts per million (δ) relative to the internal standard TMS (0 ppm) for $CDCl_3$ or DMSO. The coupling constants, *J*, are reported in hertz (Hz). High-resolution mass spectra (HRMS) were recorded with a ESI-TOF (Agilent 6210 TOF LC/MS). Melting points were measured with a SGW X-4. The reagents were purchased from commercial chemical reagent companies and used without further purification unless otherwise stated. *o*-Allylaniline **1** was prepared according to reported procedures.[24]

### Synthesis of 2 through Oxidative Annulation; General Procedure

In a 10 mL round-bottomed flask *o*-allylaniline **1** (0.5 mmol) was dissolved in DCE (3 mL), then Chloranil (1.05 mmol, 0.2582 g) was added. The reaction mixture was stirred at 80 °C for 2 h. After the reaction, chloroform (10 mL) was added and the organic layer was washed with 2 N NaOH solution to remove tetrachlorohydroquinone completely, then with brine, dried over $Na_2SO_4$, and filtered. The solution was concentrated to dryness under reduced pressure and the crude product was purified by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (10:1–80:1) as eluent to give the pure product **2**.

### Synthesis of 2 through One-Pot Reaction; General Procedure

A solution of 1,3-diarylpropene **4** (0.5 mmol) and DDQ (0.55 mmol, 0.1249 g) in DCE (3 mL) was stirred at r.t. for 5 minutes. Aniline **3** (0.55 mmol) was added and the solution was stirred for 10 minutes, then $FeCl_3$ (0.025 mmol, 0.0041 g) was added and the reaction mixture was stirred at 80 °C for 1 h. Finally, Chloranil (1.05 mmol, 0.2582 g) was added and the mixture was stirred at 80 °C for another 2 h. After completion of the reaction, the solution was concentrated under reduced pressure and the product was purified by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (10:1–60:1) as eluent to give the pure product **2**.

For the recyclability of Chloranil and its use in the one-pot synthesis of 2,4-diarylquinones, see the Supporting Information.

### 6-Methyl-2,4-diphenylquinoline (2a)

Reaction time: 1 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (15:1) as eluent.

Yield: 0.1374 g (93%); yellow solid; mp 127–129 °C (lit.[25] 130–131 °C).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.23–8.18 (m, 3 H), 7.82 (s, 1 H), 7.69 (s, 1 H), 7.61–7.53 (m, 8 H), 7.50–7.47 (m, 1 H), 2.51 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 156.0, 148.5, 147.4, 139.8, 138.7, 136.2, 131.7, 129.9, 129.5, 129.1, 128.8, 128.6, 128.3, 127.5, 125.7, 124.4, 119.4, 21.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{18}N$: 296.1434; found: 296.1435.

### 6-Methoxy-2,4-diphenylquinoline (2b)

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (10:1) as eluent.

Yield: 0.1246 g (80%); yellow solid; mp 296–298 °C.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.20–8.18 (m, 3 H), 7.80 (s, 1 H), 7.62–7.52 (m, 7 H), 7.48–7.45 (m, 1 H), 7.43 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.22 (d, *J* = 2.8 Hz, 1 H), 3.82 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 157.8, 154.6, 147.8, 144.9, 139.7, 138.8, 131.6, 129.4, 129.0, 128.8, 128.7, 128.4, 127.3, 126.7, 121.8, 119.7, 103.7, 55.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{18}NO$: 312.1383; found: 312.1378.

### 6-Fluoro-2,4-diphenylquinoline (2c)

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (40:1) as eluent.

Yield: 0.1317 g (88%); light-yellow solid; mp 98–100 °C.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.27 (dd, *J* = 9.1, 5.6 Hz, 1 H), 8.21–8.20 (m, 2 H), 7.86 (s, 1 H), 7.60–7.48 (m, 10 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 161.8 (d, *J* = 245.8 Hz), 156.3 (d, *J* = 2.7 Hz), 148.8, 148.7, 145.9, 139.3, 138.0, 132.5 (d, *J* = 9.0 Hz), 129.43, 129.36, 128.9, 128.8, 128.7, 127.5, 126.5 (d, *J* = 9.6 Hz), 119.9, 119.7 (d, *J* = 25.6 Hz), 109.1 (d, *J* = 23.0 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{15}FN$: 300.1183; found: 300.1174.

### 6-Chloro-2,4-diphenylquinoline (2d)

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (60:1) as eluent.

Yield: 0.1200 g (76%); white solid; mp 97–99 °C (lit.[15] 92–95 °C).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.22–8.19 (m, 3 H), 7.89 (d, *J* = 2.1 Hz, 1 H), 7.86 (s, 1 H), 7.69 (dd, *J* = 9.0, 2.2 Hz, 1 H), 7.61–7.54 (m, 7 H), 7.51–7.48 (m, 1 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 157.0, 148.5, 147.2, 139.2, 137.8, 132.2, 131.7, 130.5, 129.6, 129.4, 128.9, 128.8, 128.7, 127.5, 126.5, 124.5, 120.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{15}ClN$: 316.0888; found: 316.0885.

### 6-Bromo-2,4-diphenylquinoline (2e)

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (60:1) as eluent.

Yield: 0.1621 g (90%); pale-yellow solid; mp 150–152 °C (lit.[26] 152–154 °C).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.2 Hz, 2 H), 8.14 (d, *J* = 8.9 Hz, 1 H), 8.06 (d, *J* = 1.8 Hz, 1 H), 7.85 (s, 1 H), 7.82 (dd, *J* = 9.0, 2.1 Hz, 1 H), 7.61–7.53 (m, 7 H), 7.51–7.48 (m, 1 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 157.2, 148.5, 147.4, 139.1, 137.7, 133.1, 131.8, 129.7, 129.5, 128.9, 128.84, 128.75, 127.8, 127.6, 127.0, 120.5, 120.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{15}BrN$: 360.0382; found: 360.0379.

### 6-Nitro-2,4-diphenylquinoline (2f)

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (10:1) as eluent.

Yield: 0.1240 g (76%); white solid; mp 204–206 °C (lit.[15] 197–200 °C).

$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 8.71 (d, *J* = 2.4 Hz, 1 H), 8.53 (dd, *J* = 9.2, 2.5 Hz, 1 H), 8.44–8.42 (m, 2 H), 8.36 (d, *J* = 9.2 Hz, 1 H), 8.29 (s, 1 H), 7.76–7.59 (m, 8 H).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{15}N_2O_2$: 327.1128; found: 327.1141.

### 6,8-Dimethyl-2,4-diphenylquinoline (2g)

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (40:1) as eluent.

Yield: 0.1330 g (86%); white solid; mp 124–126 °C.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.35–8.33 (m, 2 H), 7.86 (s, 1 H), 7.60–7.55 (m, 8 H), 7.51–7.49 (m, 2 H), 2.99 (s, 3 H), 2.48 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 154.0, 148.6, 146.3, 139.9, 139.2, 137.6, 135.7, 131.9, 129.6, 129.1, 128.7, 128.5, 128.1, 127.4, 125.7, 122.3, 118.7, 21.8, 18.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{20}N$: 310.159; found: 310.1582.

### 6,8-Dimethoxy-2,4-diphenylquinoline (2h)

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (15:1) as eluent.

Yield: 0.1588 g (93%); white solid; mp 147–149 °C (lit.[25] 145–148 °C).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.16–8.15 (m, 2 H), 7.69 (s, 1 H), 7.62–7.55 (m, 5 H), 7.54–7.51 (m, 3 H), 7.46–7.43 (m, 1 H), 7.19 (s, 1 H), 4.10 (s, 3 H), 3.87 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 155.1, 152.5, 149.8, 147.5, 146.0, 139.9, 139.0, 129.3, 128.9, 128.8, 128.7, 128.3, 127.3, 121.1, 117.9, 108.7, 103.4, 56.2, 55.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{20}NO_2$: 342.1489; found: 342.1489.

### 6,7-Dimethoxy-2,4-diphenylquinoline (2i)

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (20:1) as eluent.

Yield: 0.1161 g (68%); white solid; mp 164–165 °C (lit.[15] 160–162 °C).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.21–8.20 (m, 2 H), 7.81 (s, 1 H), 7.60–7.55 (m, 4 H), 7.53–7.49 (m, 3 H), 7.44–7.41 (m, 1 H), 6.77 (s, 2 H), 4.11 (s, 3 H), 3.79 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 158.1, 156.8, 153.4, 147.8, 139.8, 139.1, 137.4, 129.3, 128.8, 128.7, 128.6, 128.3, 127.5, 127.4, 120.4, 101.2, 95.3, 56.3, 55.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{20}NO_2$: 342.1489; found: 342.1486.

**6-Methyl-2,4-di-*p*-tolylquinoline (2j)**

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (30:1) as eluent.

Yield: 0.1455 g (90%); light-yellow solid; mp 105–107 °C (lit.[25] 105–106 °C).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.6 Hz, 1 H), 8.13 (d, *J* = 8.2 Hz, 2 H), 7.79 (s, 1 H), 7.71 (s, 1 H), 7.58 (dd, *J* = 8.6, 1.8 Hz, 1 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.40 (d, *J* = 7.8 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 2.51 (2 s, 2 × $CH_3$, 6 H), 2.47 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 156.0, 148.4, 147.4, 139.1, 138.1, 137.0, 135.9, 135.8, 131.6, 129.8, 129.51, 129.46, 129.26, 127.33, 125.7, 124.4, 119.2, 21.8, 21.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{22}N$: 324.1747; found: 324.1757.

**6-Methyl-2,4-di-*m*-tolylquinoline (2k)**

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (40:1) as eluent.

Yield: 0.1472 g (91%); light-yellow solid; mp 93–95 °C.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 10.0 Hz, 1 H), 8.09 (s, 1 H), 8.01 (d, *J* = 7.8 Hz, 1 H), 7.82 (s, 1 H), 7.72 (s, 1 H), 7.61 (dd, *J* = 8.6, 1.9 Hz, 1 H), 7.50–7.36 (m, 5 H), 7.31 (d, *J* = 5.0 Hz, 1 H), 2.52 (2 s, 3 × $CH_3$, 9 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 156.2, 148.7, 147.2, 139.6, 138.6, 138.5, 138.4, 136.2, 131.8, 130.2, 120.0, 129.7, 129.0, 128.7, 128.4, 128.2, 126.7, 125.8, 124.7, 124.5, 119.5, 21.8, 21.6, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{22}N$: 324.1747; found: 324.1751.

**6-Methyl-2,4-di-*o*-tolylquinoline (2l)**

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (20:1) as eluent.

Yield: 0.0986 g (61%); light-yellow oil.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.6 Hz, 1 H), 7.61–7.58 (m, 2 H), 7.43–7.41 (m, 3 H), 7.36–7.30 (m, 6 H), 2.48 (2 s, 2 × $CH_3$, 6 H), 2.15 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 158.8, 147.7, 146.7, 140.7, 137.9, 136.4, 136.1, 136.0, 131.8, 130.8, 130.2, 129.8, 129.7, 129.6, 128.4, 128.3, 126.0, 125.79, 125.76, 124.5, 122.8, 21.7, 20.4, 20.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{22}N$: 324.1747; found: 324.1736.

**2,4-Bis(4-fluorophenyl)-6-methylquinoline (2m)**

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (60:1) as eluent.

Yield: 0.1325 g (80%); white solid; mp 138–140 °C.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.20–8.14 (m, 3 H), 7.70 (s, 1 H), 7.62 (s, 1 H), 7.58 (dd, *J* = 8.6, 1.8 Hz, 1 H), 7.54–7.52 (m, 2 H), 7.29–7.25 (m, 2 H), 7.22–7.18 (m, 2 H), 2.50 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 164.7, 163.8, 162.7, 161.9, 154.8, 147.5, 147.3, 136.5, 135.69, 135.66, 134.44, 134.42, 131.9, 131.2, 131.1, 129.8, 129.3, 129.2, 125.6, 124.1, 118.9, 115.74, 115.70, 115.6, 115.5, 21.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{16}F_2N$: 332.1245; found: 332.1249.

**2,4-Bis(4-chlorophenyl)-6-methylquinoline (2n)**

Reaction time: 5 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (80:1) as eluent.

Yield: 0.1020 g (56%); white solid; mp 183–184 °C (lit.[15] 182–185 °C).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.16–8.12 (m, 3 H), 7.70 (s, 1 H), 7.60 (d, *J* = 7.0 Hz, 2 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 8.4 Hz, 4 H), 2.50 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 154.6, 147.5, 147.2, 137.8, 136.9, 136.8, 135.5, 134.6, 132.2, 130.8, 129.8, 129.0, 128.9, 128.7, 125.5, 124.1, 118.8, 21.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd. for $C_{22}H_{16}Cl_2N$: 364.0654; found: 364.0643.

**2,4-Bis(4-bromophenyl)-6-methylquinoline (2o)**

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (80:1) as eluent.

Yield: 0.1133 g (50%); yellow solid; mp 182–184 °C (lit.[15] 188–190 °C).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.4 Hz, 1 H), 8.08–8.06 (m, 2 H), 7.73–7.70 (m, 3 H), 7.67–7.64 (m, 2 H), 7.61–7.59 (m, 2 H), 7.45–7.42 (m, 2 H), 2.50 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 154.7, 147.6, 147.3, 138.3, 137.3, 136.9, 132.2, 132.0, 131.9, 131.1, 129.8, 129.0, 125.5, 124.1, 123.9, 122.8, 118.7, 21.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{16}Br_2N$: 451.9644; found: 451.9651.

**2,4-Bis(3-chlorophenyl)-6-methylquinoline (2p)**

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (40:1) as eluent.

Yield: 0.1275 g (70%); white solid; mp 124–125 °C.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 1.9 Hz, 1 H), 8.16 (d, *J* = 8.4 Hz, 1 H), 8.07–8.05 (m, 1 H), 7.72 (s, 1 H), 7.62–7.43 (m, 8 H), 2.51 (s, 3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 154.3, 140.7, 140.2, 137.2, 135.0, 134.7, 132.3, 130.1, 129.9, 129.5, 129.3, 128.6, 127.8, 127.6, 125.61, 125.55, 124.1, 119.0, 21.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{16}Cl_2N$: 364.0654; found: 364.0661.

**Mixture of 4-(4-Chlorophenyl)-6-methyl-2-phenylquinoline and 2-(4-Chlorophenyl)-6-methyl-4-phenylquinoline as 3:4 (2q)**

Reaction time: 1 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (80:1) as eluent.

Yield: 0.1567 g (95%); white solid.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.20–8.18 (m, 1 H), 8.16–8.14 (m, 3/7×5 H), 7.75 (d, *J* = 4.2 Hz, 1 H), 7.67 (s, 1 H), 7.60–7.48 (m, 5+4/7×5 H), 2.50 (s, 3/7×3 H), 2.50 (s, 4/7×3 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 156.0, 154.6, 148.7, 147.3, 139.5, 138.5, 138.1, 137.0, 136.6, 135.4, 134.5, 131.98, 131.96, 130.9, 129.9, 129.8, 129.5, 129.3, 129.0, 128.87, 128.85, 128.7, 128.6, 128.4, 127.5, 125.8, 125.5, 124.4, 124.1, 119.3, 119.0, 21.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{17}ClN$: 330.1044; found: 330.1054.



**Mixture of 6-Methyl-4-phenyl-2-(*p*-tolyl)quinoline and 6-Methyl-2-phenyl-4-(*p*-tolyl)quinoline as 3:1 (2r)**

Reaction time: 2 h; purification by column chromatography on silica gel (200–300 mesh) with petroleum ether and EtOAc (25:1) as eluent.

Yield: 0.1392 g (90%); white solid.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.24–8.19 (m, 1+3/4×2 H), 8.14 (d, *J* = 8.2 Hz, 1/4×2 H), 7.81 (d, 1 H), 7.74 (s, 3/4×1 H), 7.69 (s, 1/4×1 H), 7.61–7.55 (m, 4 H), 7.51–7.49 (m, 2 H), 7.40 (d, *J* = 7.9 Hz, 3/4×2 H), 7.37 (d, *J* = 8.0 Hz, 1/4×2 H), 2.53–2.47 (m, 6 H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ = 156.0, 148.5, 147.4, 139.8, 139.2, 138.7, 138.2, 136.9, 136.1, 136.0, 135.7, 131.7, 129.8, 129.7, 129.52, 129.49, 129.4, 129.3, 129.1, 128.8, 128.5, 128.2, 127.5, 127.3, 125.8, 125.6, 124.44, 124.35, 119.3, 119.2, 21.8, 21.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{20}N$: 310.159; found: 310.1577.

## Funding Information

The authors are grateful to the Natural Science Foundation of China (21602197) and the Natural Science Foundation of Zhejiang Province (LY18B020018).

## Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1691740.

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