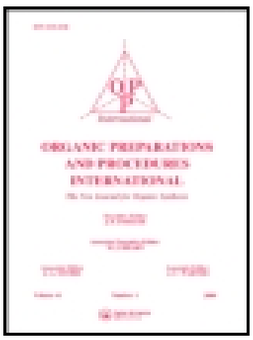

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A Novel, Multi-component Method of Preparation of Quinolines Using Recyclable CeO_2-TiO_2 Nanocomposite Catalyst under Solvent-free Conditions

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In view of our ongoing interest in nanocatalysis, multicomponent reactions (MCR) and solvent free synthesis, we have developed a new procedure for the preparation of quinolines. The procedure involves substituted aromatic anilines, aldehydes and acetophenone and is catalyzed by CeO_2-TiO_2 under solvent-free conditions (*Scheme 1*). We now present a study on the substrate scope and the effect of temperature, solvent, and catalyst concentration for this environmentally friendly protocol.

Aniline **(1)**, benzaldehyde **(2)** and acetophenone **(3)** were selected as model substrates to optimize the reaction conditions. The reaction was carried out in several solvents including DMF, toluene, ethanol, 1,4-dioxane and solvent free as summarized in *Table 1*. Reaction in solvents took longer, and gave lower yields, when compared to the solvent-free reaction. We view this as a fortunate combination of efficiency and green characteristics.

In order to investigate the effect of temperature on the reaction, the concentration of catalyst was kept constant at 2 wt.% and a mixture of the substrates was heated at temperatures ranging from 30–80°C. The reaction was monitored by TLC under solvent free conditions. After stirring for 360 min, no reaction occurred at room temperature. Increasing the reaction temperature to 70°C (*Table 2*, entry 5) resulted in a better yield and shorter reaction time. Further increases in the temperature did not show any material improvement in the yield or reaction time. Therefore, 70°C was chosen as the reaction temperature for all further reactions.

We studied the effect of catalyst concentration on the reaction by varying the amounts of catalyst (0.5, 1, 2, and 5 wt. %) at 70°C under solvent-free conditions. According to the results presented in *Table 3*, in the absence of the CeO_2-TiO_2, the reaction did not produce any products after refluxing for 70°C for 360 min (*Table 3*, entry 1). The best results were obtained using 1 wt. % of CeO_2-TiO_2 (*Table 3*, entry 3)

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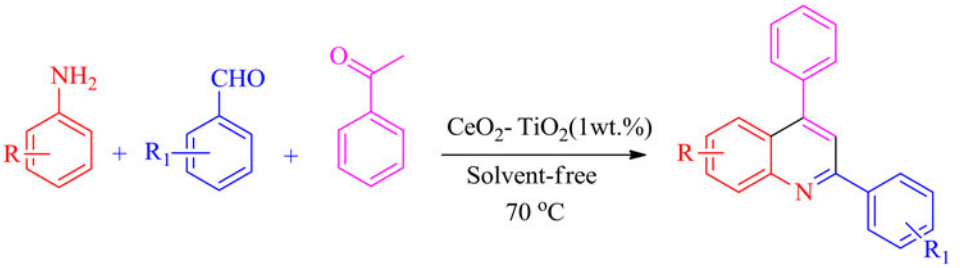


Scheme 1. One-pot synthesis of 2,4-disubstituted quinolines using CeO_2-TiO_2 under solvent-free conditions.

Table 1
CeO_2-TiO_2 Catalyzed One-pot Synthesis of 4-Diphenylquinoline[a] **(4a)** with and without Solvent

Entry	Solvent	Time (min)[b]	Yield (%)[c]
1	DMF	150	75
2	Toluene	150	68
3	Ethanol	120	78
4	Dioxane	180	81
5	**Solvent free**	**90**	**95**

[a]Reaction conditions: Aniline (1 mmol), benzaldehyde (1 mmol), and acetophenone (1 mmol), solvent (5 mL) or no solvents 80°C using 2 wt. % of CeO_2-TiO_2 catalyst.
[b]Reaction time is monitored by TLC.
[c]Isolated yields.

Table 2
Temperature Optimization for the Synthesis 2,4-Diphenylquinoline[a] **(4a)** under Solvent free Conditions using CeO_2-TiO_2 Catalyst

Entry	Temperature (°C)	Time (min)[b]	Yield (%)[c]
1	r.t	360	—
2	40	240	65
3	50	240	68
4	60	160	76
5	**70**	**90**	**95**
6	80	90	95
7	90	90	94

[a]Reaction conditions: Aniline (1 mmol), benzaldehyde (1 mmol), and acetophenone (1 mmol), at various temperatures under solvent-free conditions using 2 wt.% of CeO_2-TiO_2 catalyst.
[b]Reaction time monitored by TLC.
[c]Isolated yields.

and the data suggest that the catalyst shows excellent activity at lower concentration, in terms of duration and yield. Use of higher amounts of catalyst improved neither the yield nor the reaction time.

Summarizing, the best result was obtained when the CeO_2-TiO_2 catalyst was at 1 wt. %, while the reaction was performed at 70°C under solvent-free conditions. Under

Table 3
Effect of Catalyst Concentration on the Synthesis of 2,4-Diphenylquinoline[a] **(4a)**

Entry	Catalyst concentration (wt. %)	Time (min)[b]	Yield (%)[c]
1	—	360	—
2	0.5	180	77
3	**1**	**90**	**94**
4	2	90	93
5	5	90	90

[a]Reaction conditions: Aniline (1 mmol), benzaldehyde (1 mmol), and acetophenone (1 mmol), at 70°C under solvent-free conditions at various catalyst concentrations.
[b]Reaction time monitored by TLC.
[c]Isolated yields.

the optimized conditions, the model reaction gave a 95% yield of 2,4-diphenylquinoline **(4a)** after 90 min. With the optimized reaction conditions in hand, we performed the reaction with different substituted anilines and aldehydes (*Scheme 2*).

We have compared our method using CeO_2-TiO_2 with reported catalysts such as TiO_2, $Yb(Pfb)_3$ and silver catalyst using **4a** as a representative example (*Table 4*). The results clearly reveal that the present protocol could serve as a better method than some previously reported (*Table 4*).

The reusability and recyclability of the CeO_2-TiO_2 catalyst was examined in the reaction of aniline, benzaldehyde, and acetophenone under solvent-free conditions. After completion, ethyl alcohol was added to the reaction mixture, which was stirred and then boiled for a few minutes to dissolve the product. The insoluble catalyst was filtered, and the filtrate was evaporated *in vacuo* to dryness to get the product. The recovered catalyst was reused for successive experiments. At the end of five cycles, the yield had only diminished a few percent to 89%

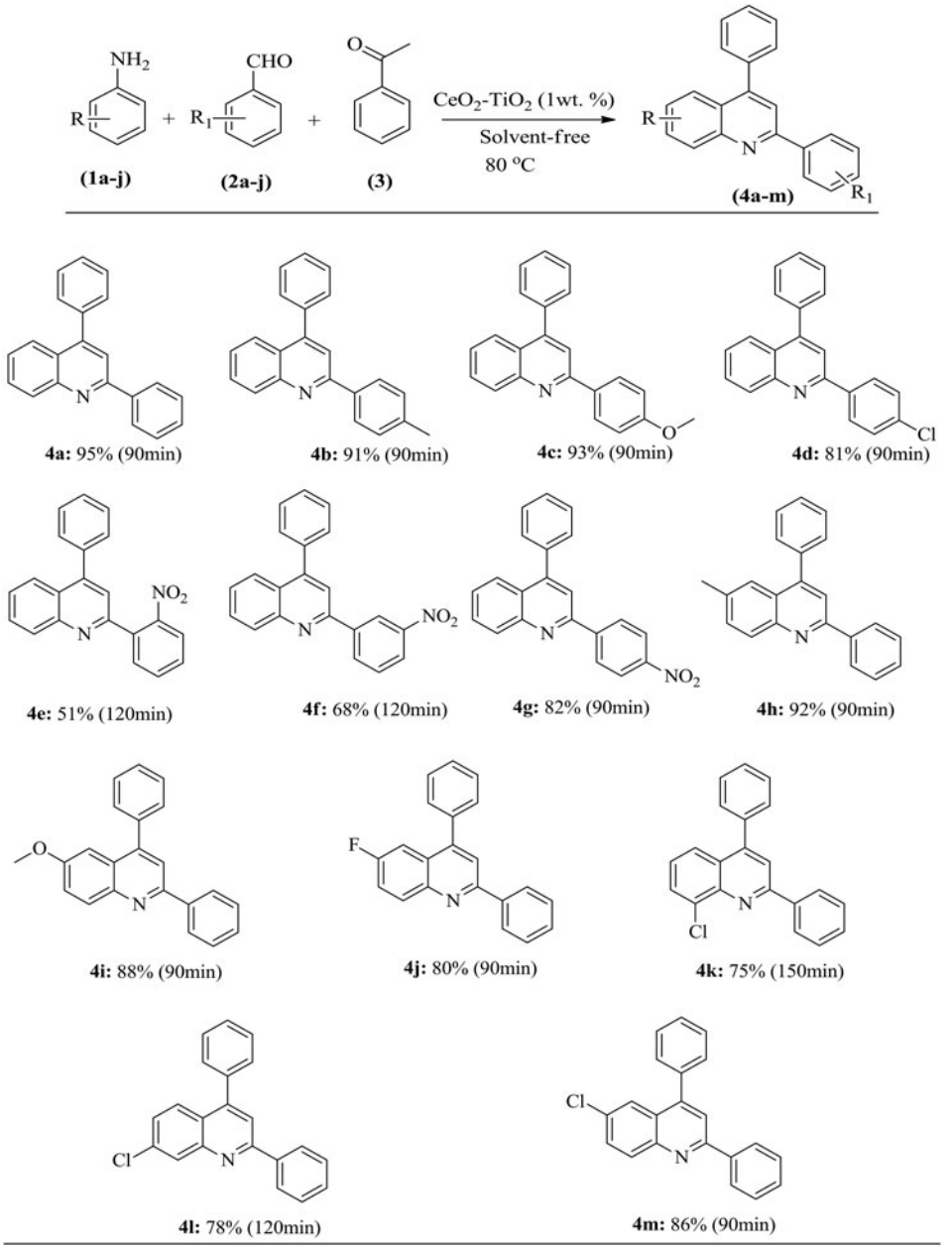
In summary, we have successfully developed a facile, efficient, environmentally benign, multicomponent synthesis of 2,4-disubstituted quinolines using 1 wt.% CeO_2-TiO_2 catalyst, prepared by the wet-impregnation method, under solvent-free conditions. Reactions of substituted anilines, and aldehydes with acetophenone resulted in good yields of the corresponding products, and the reaction conditions were optimized. Considering the commercial availability of the starting materials and the ease of preparation of the catalyst, as well as the low cost, we hope that this method will find numerous applications. Further investigations on the scope of the reaction and its applications in organic synthesis and drug discovery are ongoing in our laboratory.

Experimental Section

Catalyst Preparation

Materials

Titanium(IV) chloride (Lobachemie), and cerous nitrate hexahydrate (SD Fine Chem. Ltd.) were purchased and used without further purification. Analytical grade reagents were purchased from Sigma-Aldrich, Fluka and Acros. Solvents and were dried according to standard methods.[1]



Scheme 2. Examples of 2,4-disubstituted quinoline derivatives. Reaction conditions: Aniline (1 mmol), benzaldehyde (1 mmol), and acetophenone (1 mmol), at 70°C under solvent-free conditions at 1 wt.% of CeO_2-TiO_2 catalyst. Yields of isolated products are reported.

Synthesis of Single Oxides by Precipitation Method

TiO_2 and CeO_2 single oxides were synthesized by a simple precipitation method by taking ammonium hydroxide as precipitating agent. In a typical experiment, the required quantities of $TiCl_4$ or $Ce(NO_3)_3{\cdot}6H_2O$ were dissolved in deionized water to which dilute aqueous ammonia (1M) was added dropwise with vigorous stirring until the

Table 4
Comparison of Efficiency of Catalysts for Synthesis of 4-Diphenylquinoline[a] **(4a)**

Entry	Catalysts	Reaction time (min)	Yield (%)[b]
1	TiO_2	300	53
2	CeO_2	900	32
3	$Yb(Pfb)_3$	120	86
4	AgoTf, HoTf	600	85
5	**CeO_2-TiO_2**	**90**	**95**

[a]Reaction conditions: Aniline (1 mmol), benzaldehyde (1 mmol), and acetophenone (1 mmol), at 70°C under solvent-free conditions (similar protocols for all reactions).
[b]Isolated yields.

precipitation was complete (pH = 9.5). The resultant precipitates were aged at room temperature under stirring for 12h, filtered and washed with deionized water until free from impurities. The obtained cake was oven dried at 120°C for 12h and finally calcined at 500°C for 4h in static air with a ramping rate of 3°C min^{-1}.

Synthesis of Mixed Oxides by Impregnation Method

For the synthesis of 5 wt.% CeO_2-TiO_2, the required amount of $Ce(NO_3)_2{\cdot}H_2O$ was dissolved in deionized water and wet impregnated on TiO_2 under constant stirring. The resultant powder was dried at 100°C for 12h and then finally calcined in static air at 600°C for 4h with a ramping rate of 3°C min^{-1}. The catalyst was fully characterized, and all data supported the catalyst as herein reported. Complete data including adsorption and desorption isotherms of nitrogen, dextral properties, X-ray diffraction patterns, scanning electron micrographs and element mapping, were submitted for review by the editors and are available from the corresponding author upon request.

Quinoline Characterization Techniques

The ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE III spectrometers at 300 and 75 MHz, respectively. Chemical shifts (δ) are reported in ppm from the standard internal reference tetramethylsilane (TMS). Mass spectra were recorded on Micromass Quattro II instrument using the electrospray ionization (ESI) technique, showing the (M + H) peak as a prominent base peak. The homogeneity of the compounds was determined by TLC (silica gel 60 F254 (Merck) detected by UV light (254 nm) and iodine vapors; (DCM: MeOH (10:1)). The melting points of the products were determined by open capillaries and are uncorrected.

General Procedure for the Synthesis of 2,4–Disubstituted Quinoline Derivatives (4a-m)

A mixture of aniline (1mmol), benzaldehyde (1mmol), and acetophenone (1mmol) and CeO_2-TiO_2 (1 wt. %) was refluxed within an oil bath at 70°C under stirring for the appropriate time shown in *Scheme 2*. After completion of the reaction as monitored by TLC, ethanol (10 mL) was added, and the catalyst was recovered by filtration. The mixture was evaporated under reduced pressure and yielded high purity products. All the synthesized products are known compounds and were characterized using ATR-IR, ^1H NMR, ^{13}C NMR and mass spectral techniques. Each compound had a satisfactory

elemental analysis. The mp and spectral data of the reported compounds matched reported data. Similar protocols were followed in our laboratory for the comparison studies shown in *Table 4*.

Characterization Data for the Synthesized Quinolines

2,4-Diphenylquinoline (4a). Aniline **(1a)**, benzaldehyde **(2a)** and acetophenone **(3)** afforded the pure title product; mp. 121-123°C, lit mp 120°C[2]; IR υ_{max} (KBr, cm^{-1}): 1621 (-C = N stretching), 1575 (-C = C stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.31 (d, *J*=8.3Hz, 1H), 8.20 (d, *J*=7.1Hz, 2H), 7.88 (d, *J*=8.3Hz, 1H), 7.82 (s, 1H), 7.73 (t, *J*=7.2Hz, 1H), 7.62–7.41 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 156.8, 150.4, 146.5, 139.5, 138.8, 132.0, 129.9, 129.7, 129.4, 129.2, 129.0, 128.4, 128.0, 127.8, 127.6, 127.5, 127.3, 127.0, 124.3, 116.8, 101.2; MS-ESI (m/z): 281 (M^+), 282 $(M + 1)^+$.

Anal. Calcd. for $C_{21}H_{15}N$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.77; H, 5.42; N, 4.78.

4-Phenyl-2-(p-tolyl)quinoline (4b). Aniline **(1a)**, *p*-methyl-benzaldehyde **(2b)** and acetophenone **(3)** afforded the pure title product; mp. 104–106°C, lit mp 105°C[2]; IR υ_{max} (KBr, cm^{-1}): 1616 (-C = N stretching), 1566 (-C = C stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.20-8.11 (m, 3H), 7.79 (s, 1H), 7.65 (s, 1H), 7.41–7.29 (m, 9H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 157.0, 150.7, 146.0, 139.2, 137.0, 131.5, 130.2, 129.9, 129.7(2C), 129.4 (3C), 127.8, 127.5, 127.2, 125.2, 123.3, 123.0, 117.1, 102.1, 21.7; MS-ESI (m/z): 295 (M^+), 296 $(M + 1)^+$.

Anal. Calcd. for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.61; H, 5.66; N, 4.79.

2-(4-Methoxyphenyl)-4-phenylquinoline (4c). Aniline **(1a)**, *p*-methoxy-benzaldehyde **(2c)** and acetophenone **(3)** afforded the pure title product; mp. 132–134°C, lit mp 134°C[2]; IR υ_{max} (KBr, cm^{-1}): 1623 (-C = N stretching), 1571 (-C = C stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.19-8.10 (m, 3H), 7.80 (s, 1H), 7.58–7.40 (m, 9H), 7.18 (d, *J*=2.2Hz, 1H), 2.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 159.8, 156.4, 150.5, 146.2, 139.3, 132.2, 131.5, 130.2, 129.4 (3C), 128.2 (2C), 127.7, 127.3, 127.0, 124.9, 118.5, 115.1, 114.5, 102.5, 56.1; MS-ESI (m/z): 311 (M^+), 312 $(M + 1)^+$.

Anal. Calcd. for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 85.03; H, 5.41; N, 4.62.

2-(4-Chlorophenyl)-4-phenylquinoline (4d). Aniline **(1a)**, *p*-chloro-benzaldehyde **(2d)** and acetophenone **(3)** afforded the pure title product; mp. 104–106°C, lit mp 105°C[2]; IR υ_{max} (KBr, cm^{-1}): 1616 (-C = N stretching), 1560 (-C = C stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.21-8.11 (m, 3H), 7.95 (d, *J*=2.2Hz, 1H), 7.82 (s, 1H), 7.64 (dd, *J*=9.1,2.2Hz, 1H), 7.61–7.43 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 156.1, 150.1, 145.5, 139.0, 137.5, 132.5, 131.2, 129.5, 129.2 (3C), 129.0 (2C), 128.5, 128.2, 127.7, 127.3, 127.0, 124.2, 116.7, 102.8; MS-ESI (m/z): 316 (M^+), 317 $(M + 1)^+$.

Anal. Calcd. for $C_{21}H_{14}ClN$: C, 79.87; H, 4.47; N, 4.44. Found: C, 79.65; H, 4.62; N, 4.52.

2-(2-Nitrophenyl)-4-phenylquinoline (4e). Aniline **(1a)**, *o*-nitro-benzaldehyde **(2e)** and acetophenone **(3)** afforded the pure title product; mp. 140–143°C; IR υ_{max} (KBr, cm^{-1}): 1632 (-C = N stretching), 1539 (-C = C stretching), 1462 ($-NO_2$ stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.25 (d, *J*=7.8Hz, 1H), 8.09–7.95 (m, 4H), 7.90-7.73 (m, 4H), 7.64–7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 156.5, 150.4, 147.5,

145.6, 139.4, 134.9, 132.9, 131.7, 129.9, 129.4 (3C), 129.2 (2C), 128.4, 128.0, 127.4, 127.1, 125.6, 124.7, 117.7, 102.1; MS-ESI (m/z): 326 (M^+), 327 $(M + 1)^+$.

Anal. Calcd. for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58. Found: C, 77.35; H, 4.52; N, 8.29.

2-(3-Nitrophenyl)-4-phenylquinoline (4f). Aniline **(1a)**, *m*-nitro-benzaldehyde **(2f)** and acetophenone **(3)** afforded the pure title product; mp. 134–136°C; IR υ_{max} (KBr, cm^{-1}): 1636 (-C = N stretching), 1542 (-C = C stretching), 1460 ($-NO_2$ stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.94 (s, 1H), 8.62 (dd, J=7.8, 1.5Hz, 1H), 8.62 (d, J=7.5 Hz, 1H), 8.23 (d, J=7.5 Hz, 1H), 8.09-7.92 (m, 2H), 7.80–7.75 (m, 4H), 7.61–7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 156.1, 150.2, 148.1, 145.3, 139.1, 134.2, 133.1, 132.0, 130.1, 129.7 (3C), 129.1 (2C), 127.8, 123.3, 122.9, 117.7, 104.1, 102.1; MS-ESI (m/z): 326 (M^+), 327 $(M + 1)^+$.

Anal. Calcd. for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58. Found: C, 77.20; H, 4.48; N, 8.32.

2-(4-Nitrophenyl)-4-phenylquinoline (4g). Aniline **(1a)**, *p*-nitro-benzaldehyde **(2g)** and acetophenone **(3)** afforded the pure title product; mp. 147–148°C; IR υ_{max} (KBr, cm^{-1}): 1651 (-C = N stretching), 1562 (-C = C stretching), 1472 ($-NO_2$ stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.45–8.32 (m, 4H), 8.28 (d, J=8.4Hz, 1H), 8.00 (d, J=7.5Hz, 2H), 7.79 (s, 1H), 7.71-7.59 (m, 2H), 7.55–7.41 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 156.7, 150.8, 148.8, 145.1, 139.7, 134.2, 133.4, 131.7, 129.9, 129.3 (3C), 129.0 (2C), 127.4, 124.4, 123.1, 122.7, 117.2, 102.7; MS-ESI (m/z): 326 (M^+), 327 $(M + 1)^+$.

Anal. Calcd. for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58. Found: C, 77.41; H, 4.43; N, 8.53.

6-Methyl-2,4-diphenylquinoline (4h). *p*-Methyl-aniline **(1b)**, benzaldehyde **(2a)** and acetophenone **(3)** afforded the pure title product; mp. 123–124°C, lit mp 126°C[2]; IR υ_{max} (KBr, cm^{-1}): 1629 (-C = N stretching), 1572 (-C = C stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.19–8.10 (m, 3H), 7.72 (s, 1H), 7.62 (s, 1H), 7.59-7.49 (m, 4H), 7.44–7.30 (m, 5H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 155.2, 150.1, 144.1, 139.4, 138.9, 132.3, 131.4, 129.7, 129.4, 129.2, 129.0, 128.7, 128.4, 127.6, 127.5, 127.3, 127.0, 126.4, 124.3, 117.4, 102.0, 22.5; MS-ESI (m/z): 295 (M^+), 296 $(M + 1)^+$.

Anal. Calcd. for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74; Found: C, 89.71; H, 5.62; N, 4.89.

6-Methoxy-2,4-diphenylquinoline (4i). *p*-Methoxy-aniline **(1c)**, benzaldehyde **(2a)** and acetophenone **(3)** afforded the pure title product; mp. 116-117°C, lit mp 118°C[2]; IR υ_{max} (KBr, cm^{-1}): 1635 (-C = N stretching), 1566 (-C = C stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.17-8.12 (m, 3H), 7.74 (s, 1H), 7.62–7.54 (m, 4H), 7.47–7.35 (m, 5H), 7.18 (d, J=2.4Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 155.7, 152.2, 146.5, 139.7, 138.1, 132.7, 131.3, 130.7, 130.2, 129.7, 129.2, 128.9, 128.3, 128.0, 127.8, 127.4, 126.8, 125.1, 123.2, 115.1, 101.8, 55.4; MS-ESI (m/z): 311 (M^+), 312 $(M + 1)^+$.

Anal. Calcd. for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.75; H, 5.41; N, 4.64.

6-Fluoro-2,4-diphenylquinoline (4j). *p*-Fluoro-aniline **(1c)**, benzaldehyde **(2a)** and acetophenone **(3)** afforded the pure title product; mp. 128–130°C; IR υ_{max} (KBr, cm^{-1}): 1630 (-C = N stretching), 1552 (-C = C stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ

ppm): 8.20 (dd, *J*=8.7, 5.3Hz, 1H), 8.15-8.11 (m, 2H), 7.81 (s, 1H), 7.74–7.63 (m, 5H), 7.61–7.43 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 157.5, 155.2, 149.2, 142.7, 139.1, 130.3, 130.0, 129.7, 129.0, 128.7, 128.3, 128.0, 127.5, 127.2, 126.7, 125.4, 125.0, 122.1, 121.2, 108.7, 103.1; MS-ESI (m/z): 299 (M^+), 300 $(M + 1)^+$.

Anal. Calcd. for $C_{22}H_{14}FN$: C, 84.26; H, 4.71; N, 4.68. Found: C, 84.02; H, 4.92; N, 4.58.

8-Chloro-2,4-diphenylquinoline (4k). *o*-Chloro-aniline **(1d)**, benzaldehyde **(2a)** and acetophenone **(3)** afforded the pure title product; mp. 112–114°C, lit mp 114°C[2]; IR υ_{max} (KBr, cm^{-1}): 1638 (-C = N stretching), 1545 (-C = C stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.29 (d, *J*=2.2Hz, 1H), 8.17–8.10 (m, 2H), 7.80 (d, *J*=8.6Hz, 1H), 7.76 (s, 1H), 7.60-7.51 (m, 4H), 7.48–7.43 (m, 4H), 7.36 (dd, *J*=2.2,9.0Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 157.0, 150.2, 140.8, 139.2, 138.2, 133.7, 130.5, 129.8, 129.5, 129.2, 128.5, 128.1, 127.9, 127.4, 127.0, 126.5, 125.6, 124.1, 122.1, 121.7, 103.1; MS-ESI (m/z): 316 (M^+), 317 $(M + 1)^+$.

Anal. Calcd. for $C_{21}H_{14}ClN$: C, 79.87; H, 4.47; N, 4.44. Found: C, 79.65; H, 4.55; N, 4.62.

7-Chloro-2,4-diphenylquinoline (4l). *m*-Chloro-aniline **(1e)**, benzaldehyde **(2a)** and acetophenone **(3)** afforded the pure title product; mp. 118–120°C, lit mp 118°C[2]; IR υ_{max} (KBr, cm^{-1}): 1622 (-C = N stretching), 1530 (-C = C stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.40–8.32 (m, 2H), 7.94 (s, 1H), 7.83 (dd, *J*=7.6,1.2Hz, 1H), 7.76 (dd, *J*=7.6, 1.2Hz, 1H), 7.66–7.54 (m, 4H), 7.50–7.36 (m, 4H), 7.36 (dd, *J*=8.4,7.0Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 156.6, 149.1, 145.8, 139.7, 139.0, 134.5, 130.2, 130.0, 129.6, 129.3, 128.4, 128.0, 127.7, 127.2, 126.9, 126.0, 125.1, 123.4, 120.2, 115.5, 102.7; MS-ESI (m/z): 316 (M^+), 317 $(M + 1)^+$.

Anal. Calcd. for $C_{21}H_{14}ClN$: C, 79.87; H, 4.47; N, 4.44 . Found: C, 79.93; H, 4.62; N, 4.30.

6-Chloro-2,4-diphenylquinoline (4m). *p*-Chloro-aniline **(1e)**, benzaldehyde **(2a)** and acetophenone **(3)** afforded the pure title product; mp. 121–123°C, lit mp 125°C[2]; IR υ_{max} (KBr, cm^{-1}): 1625 (-C = N stretching), 1526 (-C = C stretching); ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.42–8.32 (m, 3H), 7.84 (d, *J*=2.4Hz, 1H), 7.84 (s, 1H), 7.74 (dd, *J*=9.2, 2.2Hz, 1H), 7.69-7.57 (m, 4H), 7.52–7.39 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 156.0, 150.1, 143.2, 139.3, 138.2, 132.1, 131.5, 130.0, 129.8, 129.5, 129.1, 128.7, 127.8, 127.0, 126.4, 125.5, 125.0, 123.4, 120.5, 114.4, 103.1; MS-ESI (m/z): 316 (M^+), 317 $(M + 1)^+$.

Anal. Calcd. for $C_{21}H_{14}ClN$: C, 79.87; H, 4.47; N, 4.44. Found: C, 79.77; H, 4.77; N, 4.56.

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