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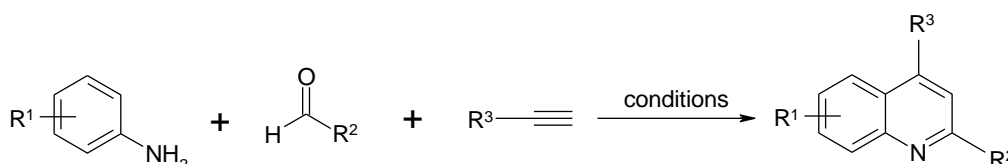
## A GREEN, SOLVENT-FREE ONE-POT SYNTHESIS OF DISUBSTITUTED QUINOLINES VIA A<sup>3</sup>-COUPLING USING 1 MOL% FeCl<sub>3</sub>

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**Abstract** – A simple and green route towards disubstituted quinolines via A<sup>3</sup>-coupling using 1 mol% FeCl<sub>3</sub> is described. Using this approach, the above-mentioned derivatives were synthesized in moderate to good yields (45-95%) under solvent-free, microwave conditions. Preliminary investigations have indicated that a further decrease in catalyst amount is possible with a satisfactory yield still observed.

The advancement of new resourceful procedures that allow for the formation of C–C bonds with high selectivity, operational simplicity, functional group tolerance and environmentally friendly properties from easily obtainable reagents is an important topic in synthetic organic chemistry.<sup>1</sup> Within this context, A<sup>3</sup>-coupling has proven to be an exciting and innovative method for the formation of C–C bonds.<sup>2</sup> The coupling reaction of an aldehyde, amine and alkyne (hence A<sup>3</sup>-coupling) has been shown to be a convenient process for the formation of propargylamines and this methodology has been well documented in the literature.<sup>3</sup> In addition to the well-studied propargylamine synthesis, the A<sup>3</sup>-coupling can also produce quinolines under the appropriate reaction conditions. (**Scheme 1**).<sup>2</sup>



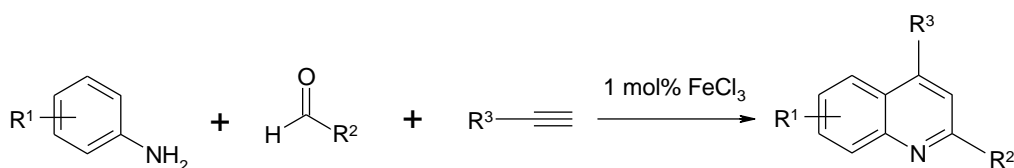
**Scheme 1.** Synthesis of disubstituted quinolines via A<sup>3</sup>-coupling

Quinolines, in particular, have generated considerable interest due to their broad range of biological activity against Alzheimer's disease,<sup>4</sup> neovascular eye diseases<sup>5</sup> and protein kinase, DYRK1A, which is a vital

intercellular regulator which fuels neurological alterations found in persons with Down syndrome<sup>6</sup> to name but a few.

In 2002, the first synthesis of quinolines via A<sup>3</sup>-coupling was reported using 30 mol% CuCl as a catalyst, however, in this case, the yields were low (34-48%), due to side products such as the reduced imine and uncyclized propargylamine.<sup>7</sup> In 2003, Yadav and co-workers<sup>8</sup> and, in 2004, Zhang and co-workers,<sup>9</sup> both used 30 mol% CuBr doped Montmorillonite K-10 as a catalyst. While both these papers report the synthesis of quinolines in good to excellent yields via A<sup>3</sup>-coupling, they must be judged with caution, as these reactions were carried out with multimode commercial microwaves (“kitchen” microwave ovens), which are incompatible with currently employed, temperature and pressure controlled single mode scientific reactors.<sup>10</sup> In 2010, Török and co-workers used unmodified Montmorillonite K-10 towards the synthesis of substituted quinolines and good to excellent yields were obtained, however, a large amount of catalyst was required (0.50 g).<sup>11</sup> In 2009, FeCl<sub>3</sub> was applied to A<sup>3</sup>-coupled quinoline synthesis due to its low cost and environmentally friendly properties.<sup>12</sup> This reaction, however, was characterized by good to excellent yields (56-95%) in long reaction times (24 h).<sup>13</sup> In an attempt to address these issues, Wang and co-workers changed the solvent from toluene to dichloroethane and a slight improvement in reaction time (12 h) was observed, although the desired products were formed in excellent yields (81-93%).<sup>14</sup> In addition, it has been argued that in both of the systems above, the FeCl<sub>3</sub> catalyst loading of 10 mol% was unsatisfactory.<sup>15</sup> Recently, the scientific community has moved away from the use of metal chlorides, due to the above-mentioned disadvantages, and has directed their research, in A<sup>3</sup>-coupled quinoline synthesis, towards metal triflates such as the use of 5 mol% Cu(OTf)<sub>2</sub><sup>16</sup> and 5 mol% Fe(OTf)<sub>3</sub>.<sup>17</sup> The use of metal triflates produced the disubstituted quinolines in excellent yields, however, these catalysts are expensive and a tedious, time-consuming catalyst recover and reuse study must be undertaken.<sup>17</sup>

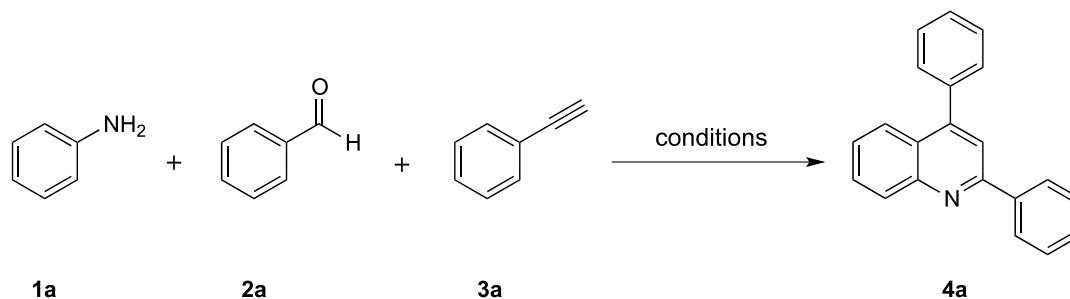
We believe that metal chlorides are preferable over metal triflates if the above-mentioned challenges can be overcome. Herein, we propose an advancement of previously reported syntheses through the development of a green, solvent-free method for synthesizing 2,4-disubstituted quinolines via an A<sup>3</sup>-coupled approach, using just 1 mol% FeCl<sub>3</sub> (**Scheme 2**). We envisaged that a low catalyst loading coupled with the inexpensive nature of FeCl<sub>3</sub> will generate a powerful catalytic system and proceeded to test this hypothesis by attempting the synthesis of quinolines via A<sup>3</sup>-coupling.



**Scheme 2.** Current work to synthesize 2,4-diphenylquinolines via A<sup>3</sup>-coupling

Our studies commenced with a test reaction using aniline (**1a**), benzaldehyde (**2a**) and phenylacetylene (**3a**) under various conditions such as sonication and conventional heating, but the desired product was formed in disappointing yields (**Table 1, entries 1 and 2**). We then focused our attention towards microwave-assisted organic synthesis (MAOS), as these conditions have shown to greatly reduce reaction times and improve yields when compared to conventional heating.<sup>18</sup> The use of solvents such as dichloromethane, water, and toluene under microwave irradiation, was then evaluated (**Table 1, entries 3-5**) and again disappointing yields were observed (trace-40%). This prompted us to test the effect of solvent-free reactions as microwave-assisted organic synthesis is known to benefit under these conditions.<sup>19</sup> The reaction was attempted under open and closed-vessel microwave irradiation as the choice of these conditions has a pronounced effect on the reaction yield.<sup>20</sup> Under closed-vessel microwave conditions (**Table 1, entry 6**) the desired product was formed in a moderate yield (51%). Next, the reaction was performed under open-vessel conditions, (**Table 1, entry 7**) and, to our delight; the desired compound was formed in a 91% isolated yield. To highlight the importance of FeCl<sub>3</sub>, the reaction was attempted in the absence of a catalyst and, as expected, no product was detected under these conditions (**Table 1, entry 8**).

**Table 1.** Optimization of reaction conditions for the synthesis of 2,4-diphenylquinoline **4a** via A<sup>3</sup>-coupling<sup>a</sup>



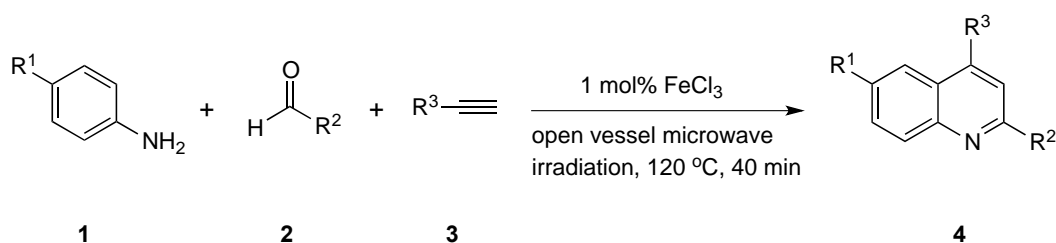
Entry	Catalyst (1 mol%)	Solvent	Conditions	Temp. (°C)	Time	Yield (%) <sup>b</sup>
1	FeCl <sub>3</sub>	–	sonication	room temperature	3 h	trace
2	FeCl <sub>3</sub>	–	conventional heating	120	3 h	26
3	FeCl <sub>3</sub>	dichloromethane	MW <sup>c</sup>	35	40 min	trace
4	FeCl <sub>3</sub>	water	MW	100	40 min	15
5	FeCl <sub>3</sub>	toluene	MW	110	40 min	40
6	FeCl <sub>3</sub>	–	MW (closed-vessel)	120	40 min	51
7	FeCl <sub>3</sub>	–	MW (open-vessel)	120	40 min	91

8	–	–	MW (open-vessel)	120	40 min	0
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<sup>a</sup> Optimization study for the synthesis of 2,4-diphenylquinoline via A<sup>3</sup>-coupling: aniline (**1a**) (1 mmol), benzaldehyde (**2a**) (1 mmol) and phenylacetylene (**3a**) (1 mmol). <sup>b</sup> Isolated yield. <sup>c</sup> MW = Microwave.

With the optimized conditions in hand, we turned our attention to evaluating the scope and limitations of the devised system. A variety of aldehydes and anilines were used to synthesize various disubstituted quinolines and the results are summarized in **Table 2**. Aldehydes bearing a range of functional groups (**Table 2, entries 2-4**), displayed good to excellent yields (55-93%) while substituted anilines (**Table 2, entries 5-7**), also displayed excellent results (71-90%). To further investigate our procedure, substituted benzaldehydes, anilines and phenylacetylenes were evaluated (**Table 2, entries 8-10**) and under these reaction conditions, the desired quinolines were formed in excellent yields (83-95%). Next, we expanded our substrate scope to alkyl aldehydes and alkyl alkynes as alkyl substrates are rarely investigated in A<sup>3</sup>-coupled quinoline synthesis<sup>17</sup> and when they are, the yields are often low,<sup>13</sup> even when scientific microwave reactors were used.<sup>11a</sup> In our first study; we investigated the coupling of cyclohexanecarboxaldehyde, *p*-anisidine, and phenylacetylene in the presence of 1 mol% FeCl<sub>3</sub>. The reaction mixture was purified by column chromatography and we were delighted to isolate the desired product **4k** (**Table 2, entry 11**) albeit in a moderate yield of 45%. To further test the robustness of the 1 mol% FeCl<sub>3</sub> system, we sought to test the effect of an alkyl alkyne on the devised system and the reaction of benzaldehyde, aniline and 3-butyn-1-ol was examined (**Table 2, entry 12**). The reaction mixture was analyzed using <sup>1</sup>H NMR spectroscopy and only starting materials were present with a trace amount of product detected. The 1 mol% FeCl<sub>3</sub> system was extremely efficient on aryl substrates but the synthesis of alkyl substituted quinolines continues to be a challenge for synthetic organic chemists.<sup>21</sup>

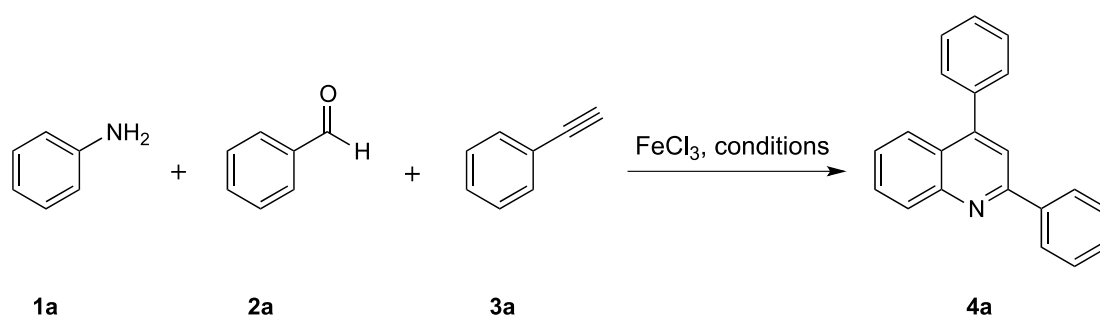
**Table 2.** Quinoline derivatives synthesized using 1 mol% FeCl<sub>3</sub> via A<sup>3</sup>-coupling



Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Product (%)
1	H	Ph	Ph	<b>4a</b> (91)
2	H	4-BrC <sub>6</sub> H <sub>4</sub>	Ph	<b>4b</b> (80)
3	H	4-MeC <sub>6</sub> H <sub>4</sub>	Ph	<b>4c</b> (93)
4	H	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Ph	<b>4d</b> (55)

5	Cl	Ph	Ph	<b>4e</b> (90)
6	Et	Ph	Ph	<b>4f</b> (71)
7	OMe	Ph	Ph	<b>4g</b> (71)
8	Cl	Ph	4-MeC <sub>6</sub> H <sub>4</sub>	<b>4h</b> (86)
9	Br	4-BrC <sub>6</sub> H <sub>4</sub>	Ph	<b>4i</b> (95)
10	OMe	4-BrC <sub>6</sub> H <sub>4</sub>	Ph	<b>4j</b> (83)
11	OMe	cyclohexyl	Ph	<b>4k</b> (45)
12	H	Ph	(CH <sub>2</sub> ) <sub>2</sub> OH	<b>4j</b> (trace)

To complement our studies above, we attempted to further decrease the catalyst amount to 0.5 and 0.1 mol% (**Scheme 3, entries 1 and 2**), using our optimized test reaction (**Table 1, entry 7**), however, in these cases, only trace amounts of the product were observed. The use of microwave chemistry has a number of advantages such as high yields and short reaction times and the benefits of this approach have been well documented in the literature.<sup>18</sup> There are, however, limitations to microwave chemistry such as; scale-up applicability and consequently, scientific microwave reactors cannot be run for hours on end and these factors must be considered when choosing reaction conditions.<sup>22</sup> Due to the limitations of microwave chemistry highlighted above, we chose to exploit our earlier observation in which 26% of the desired quinoline was formed in 3 hours under conventional heating (**Table 1, entry 2**). The optimized reaction was repeated in the presence of 0.5 and 0.1 mol% FeCl<sub>3</sub> under conventional heating for 7 days. When the catalyst loading was decreased to 0.1 mol%, only trace amounts of the product was observed (**Scheme 3, entry 4**). However, when the catalyst loading was decreased to just 0.5 mol% FeCl<sub>3</sub> (**Scheme 3, entry 3**), an excellent isolated yield of 73% was obtained. These results indicate that with sufficient time, the catalyst loading can be further decreased and still produce the desired compound in a satisfactory yield.



- 1.) 0.5 mol% FeCl<sub>3</sub>, 40 min, 120 °C, open-vessel microwave irradiation, trace
- 2.) 0.1 mol% FeCl<sub>3</sub>, 40 min, 120 °C, open-vessel microwave irradiation, trace
- 3.) 0.5 mol% FeCl<sub>3</sub>, 7 days, 120 °C, conventional heating, 73%**
- 4.) 0.1 mol% FeCl<sub>3</sub>, 7 days, 120 °C, conventional heating, trace

**Scheme 3.** Synthesis of 2,4-diphenylquinoline using decreased amounts of FeCl<sub>3</sub> under microwave and conventional heating

In summary, we have developed a convenient and green method towards disubstituted quinolines using an  $A^3$ -coupling approach. A series of 2,4-disubstituted quinolines were synthesized in moderate to good yields, from a variety of readily available aldehydes, amines, and alkynes, under solvent-free, microwave conditions using just 1 mol%  $FeCl_3$ . The catalyst loading was further decreased to 0.5 mol% and the desired product was still obtained in a satisfactory yield of 73%. The application of very low catalyst loadings coupled with the inexpensive nature of  $FeCl_3$  make this a very attractive route towards quinolines and will be a valuable addition to synthetic organic chemistry. Further studies are underway to expand this catalytic system to other challenging substrates, using the above-mentioned protocol and will be reported in due course.

## EXPERIMENTAL

All starting reagents were purchased from Sigma-Aldrich and used without further purification. The silica gel (130–270 mesh) was used for column chromatography. All microwave synthesis was carried out on a CEM Focused Microwave<sup>TM</sup> which uses an infrared sensor located below the microwave cavity floor to measure temperature. The  $^1H$  and  $^{13}C$  NMR spectra were obtained on a Bruker Avance III 400 or Bruker Avance III 500 spectrometer operating at 400 MHz or 100 MHz. NMR spectra were referenced against the residual  $CDCl_3$  present in  $\delta_H$  7.26 ppm or the  $\delta_C$  77.0 ppm. The mass spectrometric identification of the products has been carried out using a Perkin Elmer Spectra One. IR spectra were recorded on a Smiths IdentifyIR<sup>®</sup> Spectrometer. All melting points were determined using a Kofler hot-stage melting apparatus and are uncorrected.

### General procedure for the synthesis of quinolines

Aldehyde (1 mmol), amine (1 mmol), alkyne (1 mmol) and  $FeCl_3$  (1 mol%) was added to a cylindrical microwave reaction vessel and irradiated for 40 min at 120 °C. The reaction mixture was cooled to room temperature, filtered through a short silica plug and the solid residues washed well with EtOAc. The solvent was removed *in vacuo* and the product purified by column chromatography to produce the title compounds.

**2,4-Diphenylquinoline (Table 2, 4a):** a yellow solid; mp 110–111 °C; IR (neat,  $cm^{-1}$ ): 2932, 1458, 1276;  $^1H$  NMR  $\delta$  (ppm) 8.30–8.27 (d,  $J = 8.62$ , 1H), 8.23–8.20 (m, 2H), 7.93–7.90 (d,  $J = 8.33$ , 1H), 7.83 (s, 1H), 7.77–7.72 (m, 1H), 7.58–7.46 (m, 9H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) 156.9, 149.3, 148.7, 139.6, 138.4, 130.1, 129.6, 129.4, 129.3, 128.9, 128.6, 128.5, 127.5, 126.4, 125.8, 127.7, 119.3;  $m/z$  (%) = 282 (29), 281 ( $M^+$ ) (100), 280 (100), 278 (15). Data in agreement with literature.<sup>13,23</sup>

**2-(4-Bromophenyl)-4-phenylquinoline (Table 2, 4b):** a white solid; mp 113-114 °C; IR (neat,  $\text{cm}^{-1}$ ): 1458, 1276, 1054, 758;  $^1\text{H}$  NMR  $\delta$  (ppm) 8.25 (d,  $J = 8.52$ , 1H), 8.10 (d,  $J = 8.73$ , 2H), 7.91 (d,  $J = 8.51$ , 1H), 7.77-7.53 (m, 10H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 155.8, 152.5, 150.2, 148.8, 138.5, 132.4, 130.3, 130.2, 129.6, 129.4, 129.1, 129.0, 127.1, 126.2, 124.5, 124.2, 119.3;  $m/z$  (%) = 360 (100), 359 ( $\text{M}^+$ ) (82), 278 (41), 139 (41). Data in agreement with literature.[24,25](#)

**2-(4-Methylphenyl)-4-phenylquinoline (Table 2, 4c):** a yellow solid; mp 115-116 °C; IR (neat,  $\text{cm}^{-1}$ ): 2932, 2932, 1738, 1622, 1458;  $^1\text{H}$  NMR  $\delta$  (ppm) 8.29 (d,  $J = 8.32$ , 1H), 8.11 (d,  $J = 8.32$ , 2H), 7.91 (d,  $J = 8.46$ , 1H), 7.81 (s, 1H), 7.77-7.72 (m, 1H), 7.58-7.50 (m, 5H), 7.50-7.45 (m, 1H), 7.35 (d,  $J = 8.21$ , 2H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 157.2, 149.6, 149.0, 139.9, 138.8, 137.0, 130.3, 129.9, 129.8, 128.9, 128.7, 127.9, 126.5, 126.1, 126.0, 119.6, 21.7;  $m/z$  (%) = 295 ( $\text{M}^+$ ) (100), 294 (100), 202 (35). Data in agreement with literature.[23,26](#)

**2-(4-Nitrophenyl)-4-phenylquinoline (Table 2, 4d):** a yellow solid; mp 155-156 °C; IR (neat,  $\text{cm}^{-1}$ ): 2850, 1738, 1622;  $^1\text{H}$  NMR  $\delta$  (ppm) 8.41-8.36 (m, 4H), 8.28 (d,  $J = 8.59$ , 1H), 7.94 (d,  $J = 8.63$ , 1H), 7.86 (s, 1H), 7.79 (t,  $J = 8.14$ , 1H), 7.58-7.53 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 154.4, 150.4, 149.0, 148.8, 145.7, 138.2, 130.6, 130.5, 129.9, 129.1, 128.7, 127.7, 126.6, 126.2, 124.3, 119.4;  $m/z$  (%) = 326 ( $\text{M}^+$ ) (100), 280 (44), 279 (38), 139 (29). Data in agreement with literature.[24,27,15](#)

**6-Chloro-2,4-diphenylquinoline (Table 2, 4e):** a yellow solid; mp 129-130 °C; IR (neat,  $\text{cm}^{-1}$ ): 2932, 1738, 1054;  $^1\text{H}$  NMR  $\delta$  (ppm) 8.20-8.18 (m, 3H), 7.87 (d,  $J = 2.09$ , 1H), 7.84 (s, 1H), 7.66-7.67 (m, 1H), 7.60-7.48 (m, 8H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 157.4, 149.0, 147.4, 139.4, 138.1, 132.6, 132.0, 130.9, 130.0, 129.8, 129.3, 129.2, 129.1, 127.9, 126.9, 124.9, 120.4;  $m/z$  (%) = 317 (33), 316 (60), 315 ( $\text{M}^+$ ) (100), 314 (100). Data in agreement with literature.[23,28](#)

**6-Ethyl-2,4-diphenylquinoline (Table 2, 4f):** a brown oil; IR (neat,  $\text{cm}^{-1}$ ): 2964, 1574, 1276, 1255;  $^1\text{H}$  NMR  $\delta$  (ppm) 8.20 (d,  $J = 7.40$ , 2H), 7.80 (s, 1H), 7.69 (s, 1H), 7.55 (m, 10H), 2.79 (q,  $J = 7.40$ , 2H), 1.29 (t,  $J = 7.52$ , 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 156.4, 149.1, 147.9, 142.9, 140.1, 139.0, 131.0, 130.3, 130.0, 129.5, 129.2, 128.9, 128.7, 127.9, 126.1, 123.6, 119.8, 29.5, 15.9;  $m/z$  (%) = 309 ( $\text{M}^+$ ) (100), 294 (89), 280 (71), 139 (19). Data in agreement with literature.[11a](#)

**6-Methoxy-2,4-diphenylquinoline (Table 2, 4g):** a brown oil; IR (neat,  $\text{cm}^{-1}$ ): 2932, 1738, 1622, 1054, 1022, 758;  $^1\text{H}$  NMR  $\delta$  (ppm) 8.18-8.17 (m, 3H), 7.78 (s, 1H), 7.58-7.47 (m, 7H), 7.45-7.40 (m, 2H), 7.20 (d,  $J = 2.75$ , 1H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 158.1, 154.9, 148.1, 145.2, 140.0,

139.1, 131.9, 129.7, 129.3, 129.1, 129.0, 128.7, 127.6, 127.0, 122.1, 119.9, 104.0, 55.7;  $m/z$  (%) = 312 (20), 311 ( $M^+$ ) (100), 310 (27). Data in agreement with literature.<sup>29</sup>

**6-Chloro-2-phenyl-4-p-tolylquinoline (Table 2, 4h):** a yellow oil; IR (neat,  $\text{cm}^{-1}$ ): 2850, 2432, 1738, 1622, 1244;  $^1\text{H}$  NMR  $\delta$  (ppm) 8.19 (m, 3H), 7.90 (d, 1H,  $J = 2.19$ ), 7.83 (s, 1H), 7.67 (dd,  $J = 9.00$ , 2.38 Hz, 1H), 7.46 (m, 7H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 157.4, 148.9, 147.5, 139.6, 139.0, 135.2, 132.5, 132.0, 130.7, 129.9, 129.7, 129.3, 127.9, 127.0, 126.4, 124.9, 120.4, 21.6;  $m/z$  (%) = 330 (38), 329 ( $M^+$ ) (100), 328 (52). Data in agreement with literature.<sup>11a</sup>

**6-Bromo-2-(4-bromophenyl)-4-phenylquinoline (Table 2, 4i):** a yellow oil; IR (neat,  $\text{cm}^{-1}$ ): 2932, 2850, 1738, 1628, 1244;  $^1\text{H}$  NMR  $\delta$  (ppm) 8.14-8.08 (d, 3H), 8.04-8.03 (d, 1H), 7.82 (s, 2H), 7.67-7.60 (d, 2H), 7.59-7.52 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 156.2, 137.9, 133.7, 132.5, 132.0, 129.8, 129.5, 129.3, 128.3, 127.4, 124.7, 121.2, 119.9;  $m/z$  (%) = 439 ( $M^+$ ) (100), 358 (29), 278 (41), 139 (64). Data in agreement with literature.<sup>30</sup>

**2-(4-Bromophenyl)-6-methoxy-4-phenylquinoline (Table 2, 4j):** a yellow solid; mp 134-136 °C, IR (neat,  $\text{cm}^{-1}$ ): 2932, 2850, 1738, 1622, 1054, 1022;  $^1\text{H}$  NMR  $\delta$  (ppm) 8.16 (d,  $J = 9.14$ , 1H), 8.06 (d,  $J = 8.60$ , 2H), 7.73 (s, 1H), 7.64 (d,  $J = 8.48$ , 2H), 7.56-7.52 (m, 5H), 7.42 (q,  $J = 6.49$ , 1H), 7.19 (d,  $J = 2.68$ , 1H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 158.5, 153.5, 148.9, 144.8, 138.8, 132.4, 131.6, 129.7, 129.4, 129.2, 128.9, 127.3, 126.8, 124.2, 122.7, 119.6, 104.2, 55.9;  $m/z$  (%) = 390 (41), 389 ( $M^+$ ) (100), 388 (18). Data in agreement with literature.<sup>29</sup>

**2-Cyclohexyl-6-methoxy-4-phenylquinoline (Table 2, 4k):** a yellow oil; IR (neat,  $\text{cm}^{-1}$ ): 2924, 2853, 1618, 1593, 1493, 1473, 1440;  $^1\text{H}$  NMR  $\delta$  (ppm) 8.06 (d,  $J = 9.13$  Hz, 1H), 7.56-7.48 (m, 5H), 7.35 (dd,  $J = 9.1$ , 2.7 Hz, 1H), 7.22 (s, 1H), 7.16 (d,  $J = 2.7$  Hz, 1H), 3.77 (s, 3H), 2.95 (tt,  $J = 11.8$ , 3.1 Hz, 1H), 2.07 (d,  $J = 11.7$  Hz, 2H), 1.89 (d,  $J = 12.8$  Hz, 2H), 1.78 (d,  $J = 12.7$  Hz, 1H), 1.65 (ddd,  $J = 24.80$ , 12.50, 2.60 Hz, 2H), 1.48 (ddd,  $J = 15.60$ , 11.20, 3.10 Hz, 2H), 1.38-1.28 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 164.0, 157.5, 147.7, 144.0, 139.0, 130.6, 129.4, 128.6, 128.3, 126.3, 121.4, 120.2, 103.9, 55.5, 47.2, 33.0, 26.6, 26.1;  $m/z$  (%) = 317 ( $M^+$ ) (5), 316 (13), 290 (37), 235 (24). Data in agreement with literature.<sup>16</sup>

## ACKNOWLEDGEMENTS

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