SUPPORTING INFORMATION

Base-Controlled Chemoselectivity Reaction of Vinylanilines with Isothiocyanates for Synthesis of Quinolino-2-thione and 2-Aminoquinoline derivatives

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Experimental

1.1. General information

$^1$H NMR and $^{13}$C NMR data analyses were performed with a Varian Mercury plus-400 and Agilent 600 MHz DD2 instruments unless otherwise specified. CDCl$_3$ and DMSO-$d_6$ as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the $^1$H NMR spectrum as 0.00 ppm. The data of $^1$H NMR was reported as follows: chemical shift, multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $m$ = multiplet and $br$ = broad), coupling constant ($J$ values) in Hz and integration. Chemical shift for $^{13}$C NMR spectra were recorded in ppm from TMS using the central peak of CDCl$_3$ (77.0 ppm) as the internal standard. $^{19}$F NMR spectra were recorded on a Varian Mercury 400 plus instrument. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Melting points were measured with an XT-4 apparatus. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and Orbitrap Elite mass spectrometer. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC analyses were conducted on silica gel GF254 plates. All reagents were directly used from purchased without any further purification unless otherwise specified.

1.2 Scheme S-1. Roads to quinoline derivatives from arylisothiocyanates and alkynes/alkenes.

**Previous work**, cyclization of isothiocyanates with alkynes

$$
\text{(a)} \quad \begin{array}{c}
\text{ArNH}_2 \\
\text{N} \\
\end{array} + \begin{array}{c}
\text{CS}_2 \\
\text{Ph} \\
\end{array} \rightarrow \begin{array}{c}
\text{ArH(\text{Ar-SH})} \\
\text{N=C=S} \\
\text{in or THF} \\
\text{Ar} \\
\text{N} \\
\end{array}
$$

**Our previous work**, base-catalyzed cyclization of 2-(1-arylvinyl)anilines with CS$_2$

$$
\text{(c)} \quad \begin{array}{c}
\text{ArNH}_2 \\
\text{Ph} \\
\end{array} + \begin{array}{c}
\text{RNC} \\
\text{PhCON-C=S} \\
\text{or} \\
\text{Ag}_2\text{CO}_3 \\
\text{or} \\
\text{Cs}_2\text{CO}_3 \\
\end{array} \rightarrow \begin{array}{c}
\text{ArH(\text{Ph})} \\
\text{N} \\
\text{R} \\
\text{Ph} \\
\text{N} \\
\end{array}
$$

**Present work**, cyclization of 2-(1-arylvinyl)anilines with isothiocyanates

$$
\text{(e)} \quad \begin{array}{c}
\text{Ar} \\
\text{PhNCS} \\
\text{dioxane} \\
\text{K}_3\text{PO}_4 \\
\text{NH}_2 \\
\text{Ph} \\
\end{array} \rightarrow \begin{array}{c}
\text{Ar} \\
\text{N} \\
\text{S} \\
\text{Ph} \\
\text{N} \\
\end{array}
$$

metal-free; bases controlled chemoselectivity
**Scheme S-1.** Roads to quinoline derivatives from arylisothiocyanates and alkynes/alkenes.

1.3 Optimization of thio-lactamization of 2-(1-arylvinyl)anilines with CS$_2$

We first explored the solvent effects in the cyclization thio-lactamization of 2-(1-arylvinyl)aniline (1a) with phenyl isothiocyanate (2a) employing catalytic amount of Et$_3$N as base-catalyst (Supporting Informations, Table S-1, entries 1-6). The desired product 3a was obtained with excellent selective in 94% and 93% yield in DMSO and dioxane, respectively (entries 1 and 2). The use of THF and DMF lowered selectivity, along with forming aminoquinoline (4a) and trace amount of thiourea (5a). Surprisingly, the regioselectivity and conversion were terribly deduced when MeCN and EtOH were employed as solvents, without offering the product 3a (entries 5 and 6). In addition, selective production of 3a was also obtained in the case of using other bases such as DBU and t-BuONa; nevertheless, formation of 4a and slightly low yield was observed (entries 7 and 8). The use of Cs$_2$CO$_3$ as base resulted in a clear drop in yield (entry 9). In contrast, use of excess amounts of bases favoured the formation of 4a (entries 11-14 vs entries 1-9).

We found that the chemoselectivity was completely reversed when 2 equivalents of K$_3$PO$_4$ were employed as base in dioxane for 12 h, solely offering the product 4a in 84% yield with excellent chemo-selectivity (entry 13). Evaluation of alternative solvents or bases gave a visible effect, and both of lower selectivity and lower yield were observed (entries 14-18). The reaction stopped completely when it was carried out in EtOH solvent (entry 18).

**Table S-1.** Optimization of thio-lactamization of 2-(1-arylvinyl)anilines with CS$_2$

<table>
<thead>
<tr>
<th>entry</th>
<th>Catalyst (eq.)/ pKa (in water)</th>
<th>Solvent</th>
<th>Solvent pKa</th>
<th>Temp. (°C)</th>
<th>3a/Yield ( (%)$^b$)</th>
<th>4a/Yield (%)$^b$</th>
<th>5a/Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NEt$_3$ (0.4)/11</td>
<td>DMSO</td>
<td>35</td>
<td>140</td>
<td>94 trace</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>NEt$_3$ (0.4)/11</td>
<td>dioxane</td>
<td>10 (18% H$_2$O)</td>
<td>110</td>
<td>93 trace</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>NEt$_3$ (0.4)/11</td>
<td>THF</td>
<td>-</td>
<td>65</td>
<td>84 9</td>
<td>16</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>NEt$_3$ (0.4)/11</td>
<td>DMF</td>
<td>30</td>
<td>140</td>
<td>77 16</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>NEt$_3$ (0.4)/11</td>
<td>CH$_3$CN</td>
<td>25</td>
<td>80</td>
<td>ND 17</td>
<td>11</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>NEt$_3$ (0.4)/11</td>
<td>EtOH</td>
<td>16</td>
<td>80</td>
<td>ND 18</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>DBU (0.4)/12</td>
<td>DMF</td>
<td>30</td>
<td>140</td>
<td>88 5</td>
<td>6</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>t-BuONa (0.4)/20</td>
<td>DMF</td>
<td>30</td>
<td>100</td>
<td>65 12</td>
<td>6</td>
<td>trace</td>
</tr>
<tr>
<td>9</td>
<td>Cs$_2$CO$_3$ (0.4)/12</td>
<td>DMF</td>
<td>30</td>
<td>140</td>
<td>ND 10</td>
<td>15</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>K$_3$PO$_4$ (0.4)/13</td>
<td>dioxane</td>
<td>10 (18% H$_2$O)</td>
<td>100</td>
<td>45 35</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>11</td>
<td>NEt$_3$ (2.0)/11</td>
<td>dioxane</td>
<td>10 (18% H$_2$O)</td>
<td>100</td>
<td>53 18</td>
<td>15</td>
<td>8</td>
</tr>
<tr>
<td>12</td>
<td>Cs$_2$CO$_3$ (2.0)/12</td>
<td>dioxane</td>
<td>10 (18% H$_2$O)</td>
<td>100</td>
<td>11 48</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>13</td>
<td>K$_3$PO$_4$ (2.0)/13</td>
<td>dioxane</td>
<td>10 (18% H$_2$O)</td>
<td>100</td>
<td>trace 84</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>14</td>
<td>t-BuONa (2.0)/20</td>
<td>dioxane</td>
<td>10 (18% H$_2$O)</td>
<td>100</td>
<td>trace 62</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td></td>
<td>K$_3$PO$_4$ (2,0)/13</td>
<td>Solvent</td>
<td>T</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>---</td>
<td>------------------</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>15</td>
<td>THF</td>
<td></td>
<td>-</td>
<td>100</td>
<td>30</td>
<td>53</td>
<td>12</td>
</tr>
<tr>
<td>16</td>
<td>CH$_3$CN</td>
<td></td>
<td>25</td>
<td>100</td>
<td>15</td>
<td>56</td>
<td>12</td>
</tr>
<tr>
<td>17</td>
<td>toluene</td>
<td></td>
<td>41</td>
<td>100</td>
<td>36</td>
<td>55</td>
<td>10</td>
</tr>
<tr>
<td>18</td>
<td>EtOH</td>
<td></td>
<td>16</td>
<td>100</td>
<td>N.R.</td>
<td>N.R.</td>
<td>N.R.</td>
</tr>
</tbody>
</table>

*a* Performed with 1a (0.5 mmol) and phenyl isothiocyanate 2a (0.9 mmol), in solvent (3.0 mL), 12 h.  

**1.4 Controlled experiments**

To test whether the products are formed from thiourea product via addition of vinylaniline into isothiocyanate, the addition product 5a was synthesized and tested under the optimized conditions. As expected, quinolino-2-thione (3a) formed in 85% yield by losing one molecular phenylamine catalyzed by Et$_3$N (Scheme S-2b), meanwhile, in the presence of K$_3$PO$_4$, desulfurization is more favorable to give 4a in 87% yield (Scheme S-2c). The fact that formation of desired product was observed suggests that the reaction through cyclization of phenylamino-1,2-dihydroquinoline-2-thiol or 2-vinylphenylcarbodiimide derived from thiourea is more likely. When N-($t$-butyloxycarbonyl) substituted vinylaniline derivatives 1A was used as substrate reacting with 2a in the presence of 2 equivalents of K$_3$PO$_4$, the deprotected product 3a and 4a was obtained (Scheme S-2d). No reaction occurred when N-methyl protected 2-(1-arylvinyl)aniline (1B) was used, while addition reaction proceeded to afford a thiourea 5B in 34% yield (Scheme S-2e).
1.5 General procedure for the synthesis of 2-(1-arylvinyI)aniline 1. Starting materials 1 was prepared according to the reported procedures.1 1.0 g of montmorillonites K10 was added to a solution of phenylacetylene (1.0 g, 10.0 mmol) and para-tolldidine (1.1 g, 10.0 mmol) in the xylene (10.0 mL). The mixture was heated at the 140 °C under stirring for 5 hours. After cooling to room temperature, filtration, washing with diethyl ether and distillation of the solvents. The volatiles were removed in vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:5) to give the corresponding products.

1.6 General procedure for the synthesis of 4-phenylquinoline-2(1H)-thione 3. Under an atmosphere of air, 2-(1-phenylvinyl) aniline 1a (0.5 mmol, 0.104 g), PhNCS 2a (1.2 eq. 0.6 mmol, 0.081 g), Et3N (40 mol%, 0.040 g) were added to a tube. Dixoane (3.0 mL) was added by dropper and the mixture was stirred for 12 h at 110 °C and the reaction was monitored by TLC analysis. Then, 2.0 mL ammonium chloride were added to the mixture to quench the reaction and extracted with ethyl acetate (3× 25 mL). The combined organic layers were washed with aqueous NaHCO3 and brine, dried over MgSO4, filtered, and the volatiles were removed in vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:5) to give the corresponding products. All of the products 3b-u were synthesized according to above described procedure.

6-Methyl-4-phenylquinoline-2(1H)-thione (3a). Yellow solid (93%, 0.117 g): mp 215-217 °C. IR (KBr) 3435, 1713, 1649, 1362, 1035, 1007, 825 cm⁻¹; ¹H NMR (600 MHz, DMSO-d6) δ: 13.68 (s, 1H), 7.60 (d, J = 2.4 Hz, 1H), 7.54 - 7.51 (m, 3H), 7.48-7.46 (m, 3H), 7.25 (s, 1H), 7.08 (s, 1H), 2.27 (s, 3H).

4-Phenylquinoline-2(1H)-thione (3b). Yellow solid (87%, 0.103 g): mp 187-188 °C. IR (KBr) 3055, 1745, 1651, 1116, 1045, 823 cm⁻¹; ¹H NMR (600 MHz, CDCl3) δ: 7.97 (d, J = 9.0 Hz, 1H), 7.79 (d, J = 2.4 Hz, 1H), 7.75 (s, 1H), 7.63 (dd, J = 9.0, 1.8 Hz, 1H), 7.49 (dd, J = 4.8, 1.8 Hz, 3H), 7.40 - 7.38 (m, 2H). ¹³C NMR (150 MHz, CDCl3) δ: 158.93, 149.16, 146.84, 136.76, 132.34, 131.04, 130.32, 129.33, 128.96, 128.80, 125.98, 124.82, 118.21. HRMS (ESI⁺) m/z: Calcd for C₁₅H₁₂NS 238.0685 [M+H]⁺, Found 238.0684.

7-Methyl-4-phenylquinoline-2(1H)-thione (3c). Yellow solid (85%, 0.106 g): mp 252-254 °C. ¹H NMR (600 MHz, DMSO-d₆) δ: 13.52 (s, 1H), 7.52 (d, J = 7.2 Hz, 3H), 7.46 (dd, J = 7.8, 1.8 Hz, 2H), 7.39 (d, J = 9.0
Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 6.97 (s, 1H), 6.93 (dd, J = 9.0, 2.4 Hz, 1H), 3.82 (s, 3H). 13C NMR (150 MHz, DMSO-d6) δ: 180.55, 161.93, 146.59, 141.96, 136.58, 129.48, 129.23, 129.19, 128.72, 127.98, 116.05, 114.28, 99.23, 56.05. HRMS (ESI+) m/z: Calcd for C16H14NS 252.0841 [M+H]+, Found 252.0842.

8-Methyl-4-phenylquinoline-2(1H)-thione (3d). Yellow solid (84%, 0.105 g): mp 185-187 ºC.

1H NMR (600 MHz, CDCl3) δ: 13.01 (s, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.53 - 7.47 (m, 6H), 7.27 - 7.23 (m, 1H), 7.03 (d, J = 3.0 Hz, 1H), 3.73 (s, 3H). 13C NMR (150 MHz, CDCl3) δ: 177.34, 156.63, 147.48, 136.37, 131.39, 129.25, 129.16, 128.81, 128.80, 128.64, 121.15, 117.94, 107.50, 55.59. HRMS (ESI+) m/z: Calcd for C16H14NS 252.0841 [M+H]+, Found 252.0842.

6-Methoxy-4-phenylquinoline-2(1H)-thione (3e). Yellow solid (90%, 0.120 g): mp 181-182 ºC.

IR (KBr) 1725, 1676, 1296, 1035, 1028, 822 cm⁻¹; 1H NMR (400 MHz, DMSO-d6) δ: 13.75 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 4.0 Hz, 5H), 7.36 (dd, J = 12, 4.0 Hz, 1H), 7.15 (s, 1H), 6.92 (d, J = 2.8 Hz, 1H), 3.70 (s, 3H). 13C NMR (150 MHz, DMSO-d6) δ: 178.38, 156.09, 145.83, 136.42, 135.23, 131.70, 129.57, 129.32, 129.18, 122.54, 121.16, 118.72, 107.34, 55.76. HRMS (ESI+) m/z: Calcd for C16H14NOS 268.0791 [M+H]+, Found 268.0793.

7-Methoxy-4-phenylquinoline-2(1H)-thione (3f). Yellow solid (85%, 0.113 g): mp 256-258 ºC. 1H NMR (400 MHz, DMSO-d6) δ: 12.10 (s, 1H), 7.57 - 7.50 (m, 5H), 7.30 - 7.28 (m, 2H), 7.19 (s, 1H), 7.08 (dd, J = 7.2, 2.4 Hz, 1H), 4.00 (s, 3H). 13C NMR (150 MHz, DMSO-d6) δ: 180.20, 146.42, 146.32, 136.42, 135.23, 131.70, 129.57, 129.32, 129.18, 122.54, 121.16, 118.72, 117.94, 116.00, 112.00, 56.89. HRMS (ESI+) m/z: Calcd for C16H14NOS 268.0791 [M+H]+, Found 268.0790.

8-Methoxy-4-phenylquinoline-2(1H)-thione (3g). Yellow solid (83%, 0.110 g): mp 216-218 ºC. 1H NMR (400 MHz, CDCl3) δ: 10.96 (s, 1H), 7.51 - 7.44 (m, 6H), 7.20 (d, J = 6.8 Hz, 2H), 7.04 (dd, J = 6.8, 2.4 Hz, 1H), 4.04 (s, 3H). 13C NMR (150 MHz, CDCl3) δ: 180.04, 147.14, 136.29, 131.97, 130.00, 130.39, 129.57, 129.25, 129.21, 124.84, 122.30, 118.00, 112.00, 56.89. HRMS (ESI+) m/z: Calcd for C16H14NOS 268.0791 [M+H]+, Found 268.0794.
6-Ethoxy-4-phenylquinoline-2(1H)-thione (3h). Yellow solid (78%, 0.109 g): mp 159-162 °C. 
\(^1\)H NMR (600 MHz, DMSO-d6) \(\delta\): 13.68 (s, 1H), 7.65 (d, \(J = 6.0\) Hz, 1H), 7.54 - 7.49 (m, 5H), 7.31 (dd, \(J = 6.0, 6.0\) Hz, 1H), 7.10 (s, 1H), 6.85 (d, \(J = 3.0\) Hz, 1H), 3.89 (q, \(J = 6.6\) Hz, 2H), 1.25 (t, \(J = 6.6\) Hz, 3H). 
\(^{13}\)C NMR (150 MHz, DMSO-d6) \(\delta\): 178.35, 155.37, 145.84, 136.43, 135.13, 131.63, 129.56, 129.32, 122.58, 121.41, 118.69, 108.03, 63.87, 14.87. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{17}\)H\(_{16}\)NOS 282.0947 [M+H]\(^+\), Found 282.0943.

6-Chloro-4-phenylquinoline-2(1H)-thione (3i). Yellow solid (79%, 0.107 g): mp 213-215 °C. 
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.97 (d, \(J = 8.0\) Hz, 1H), 7.79 (d, \(J = 4.0\) Hz, 1H), 7.76 (s, 1H), 7.63 (dd, \(J = 8.0, 4.0\) Hz, 2H). 
\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 158.94, 149.14, 146.86, 136.77, 132.33, 131.03, 130.33, 129.33, 128.96, 128.80, 125.98, 124.81, 118.21. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{15}\)H\(_{11}\)ClNS 272.0295 [M+H]\(^+\), Found 272.0292.

7-Chloro-4-phenylquinoline-2(1H)-thione (3j). Yellow solid (86%, 0.116 g): mp 243-245 °C. 
\(^1\)H NMR (400 MHz, DMSO-d6) \(\delta\): 13.96 (s, 1H), 7.73 (dd, \(J = 8.4, 1.2\) Hz, 1H), 7.60 (t, \(J = 7.6\) Hz, 1H), 7.45 - 7.43 (m, 3H), 7.35 - 7.32 (m, 3H), 7.05 (s, 1H). 
\(^{13}\)C NMR (150 MHz, DMSO-d6) \(\delta\): 158.94, 149.14, 146.86, 136.77, 131.92, 131.44, 128.57, 128.54, 128.33, 127.49, 119.10, 116.76. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{15}\)H\(_{11}\)ClINS 272.0295 [M+H]\(^+\), Found 272.0297.

8-Chloro-4-phenylquinoline-2(1H)-thione (3k). Yellow solid (77%, 0.104 g): mp 187-188 °C. 
\(^1\)H NMR (600 MHz, DMSO-d6) \(\delta\): 13.73 (s, 1H), 7.68 (d, \(J = 2.4\) Hz, 1H), 7.54 - 7.51 (m, 3H), 7.48 - 7.45 (m, 3H), 7.30 (dd, \(J = 1.8, 8.4\) Hz, 1H), 7.10 (d, \(J = 1.2\) Hz, 1H). 
\(^{13}\)C NMR (150 MHz, DMSO-d6) \(\delta\): 186.36, 150.52, 145.49, 140.98, 140.64, 136.39, 134.43, 134.03 (d, \(J = 8.6\) Hz), 133.16, 129.56, 125.25, 120.93. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{15}\)H\(_{11}\)ClINS 272.0295 [M+H]\(^+\), Found 272.0297.
4-(4-Methoxyphenyl)-6-methylquinoline-2(1H)-thione (3l). Yellow solid (78%, 0.127 g): mp 192-194 °C. 1H NMR (600 MHz, CDCl3) δ: 7.91 (d, J = 9.0 Hz, 1H), 7.52 - 7.46 (m, 8H), 7.14 (s, 1H), 2.72 (s, 3H), 2.42 (s, 3H). 13C NMR (150 MHz, CDCl3) δ: 179.69, 146.16, 143.90, 138.44, 134.00, 133.76, 133.07, 131.27, 129.17 (d, J = 10.1 Hz), 125.69, 121.66, 117.07, 35.34, 21.27. HRMS (ESI+) m/z: Calcd for C17H16NOS 282.0947 [M+H]+, Found 282.0950.

6-Methyl-4-(p-tolyl)quinoline-2(1H)-thione (3m). Yellow solid (85%, 0.112 g): mp 194-196 °C. IR (KBr) 2924, 1722, 1646, 1367, 1120, 833 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ: 7.93 (d, J = 8.4 Hz, 1H), 7.72 (s, 1H), 7.60 (d, J = 1.6 Hz, 1H), 7.51 (dd, J = 8.4, 2.0 Hz, 1H), 7.31 - 7.27 (m, 4H), 2.42 (d, J = 1.6 Hz, 6H). 13C NMR (150 MHz, CDCl3) δ: 157.74, 149.39, 147.03, 138.47, 136.21, 134.74, 132.22, 129.39, 129.25, 128.42, 125.23, 124.80, 117.36, 21.74, 21.28. HRMS (ESI+) m/z: Calcd for C17H16NS 266.0998 [M+H]+, Found 266.100.

6-Methyl-4-(m-tolyl)quinoline-2(1H)-thione (3n). Yellow solid (88%, 0.116 g): mp 242-244 °C. IR (KBr) 3207, 3004, 1691, 1593, 1535, 1495, 1315, 1028, 823 cm⁻¹; 1H NMR (600 MHz, CDCl3) δ: 13.34 (s, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.48 (s, 1H), 7.46 (s, 1H), 7.11 (t, J = 8.4 Hz, 3H), 2.37 (s, 3H), 1.40 (s, 9H). 13C NMR (150 MHz, CDCl3) δ: 178.62, 148.02, 138.54, 137.77, 136.36, 134.67, 132.83, 131.00, 129.78, 129.56, 128.49, 126.10 (d, J = 2.7 Hz), 122.49, 116.41, 21.40. HRMS (ESI+) m/z: Calcd for C17H16NS 266.0998 [M+H]+, Found 266.0996.

4-(4-(Tert-butyl)phenyl)-6-methylquinoline-2(1H)-thione (3o). Yellow solid (85%, 0.130 g): mp 253-255 °C. 1H NMR (600 MHz, CDCl3) δ: 13.34 (s, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.48 (s, 1H), 7.46 (s, 1H), 7.11 (t, J = 8.4 Hz, 3H), 2.37 (s, 3H). 13C NMR (150 MHz, CDCl3) δ: 178.34, 152.30, 147.91, 137.91, 134.62, 133.43, 132.78, 130.97, 128.80, 126.11, 125.66, 122.47, 116.54, 34.81, 31.31, 21.35. HRMS (ESI+) m/z: Calcd for C20H22NS 322.1624 [M+H]+, Found 322.1626.
6-Methyl-4-(4-pentylphenyl)quinoline-2(1H)-thione (3p). Yellow solid (89%, 0.143 g): mp 215-217 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 13.0 (s, 1H), 7.64 - 7.61 (m, 1H), 7.45 (d, $J = 10.2$ Hz, 2H), 7.40 (m, 3H), 7.32 (d, $J = 7.8$ Hz, 2H), 2.78 - 2.61 (m, 1H), 2.36 (s, 2H), 1.79 - 1.65 (m, 1H), 1.38 (dd, $J = 7.4$, 3.6 Hz, 2H), 0.97 - 0.86 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 178.55, 147.97, 144.19, 137.80, 134.62, 133.63, 132.78, 130.97, 128.93, 128.72, 126.15, 122.48, 116.42, 35.77, 31.58, 31.01, 22.54, 21.33, 14.03. HRMS (ESI$^+$) m/z: Calcd for C$_{21}$H$_{24}$NS 322.1624 [M+H]$^+$, Found 322.1627.

4-(4-Chlorophenyl)-6-methylquinoline-2(1H)-thione (3q). Yellow solid (88%, 0.125 g): mp 240-243 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 13.16 (s, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.46 - 7.32 (m, 4H), 7.35 (s, 1H), 7.22 (t, $J = 8.4$ Hz, 2H), 2.36 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 178.55, 164.03, 162.37, 146.76, 137.81, 134.90, 133.00, 132.33 (d, $J = 3.4$ Hz), 131.18, 130.79 (d, $J = 8.4$ Hz), 125.78, 122.37, 116.52, 115.97, 115.82, 21.35. HRMS (ESI$^+$) m/z: Calcd for C$_{16}$H$_{13}$ClNS 286.0452 [M+H]$^+$, Found 286.0455.

4-(4-Fluorophenyl)-6-methylquinoline-2(1H)-thione (3r). Yellow solid (78%, 0.104 g): mp 230-233 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 11.86 (s, 1H), 7.51-7.34 (m, 8H), 2.38 (s, 3H). $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 179.73, 144.93, 135.27, 134.28 (d, $J = 66.0$ Hz), 133.23, 131.46, 131.17, 129.30, 125.49, 121.48, 117.08, 21.23. $^{19}$F NMR (CDCl$_3$, 376.5 MHz) $\delta$: -112.22 - (-112.27 (m). HRMS (ESI$^+$) m/z: Calcd for C$_{16}$H$_3$FNS 270.0747 [M+H]$^+$, Found 270.0745.

4-Phenylbenzo[h]quinoline-2(1H)-thione (3s). Yellow solid (90%, 0.129 g): mp 180-184 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 9.24 (d, $J = 12.0$ Hz, 1H), 7.90 (s, 1H), 7.84 (d, $J = 11.6$ Hz, 1H), 7.17 - 7.56 (m, 5H), 7.44 (s, 5H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 157.37, 149.56, 146.89, 137.96, 133.59, 130.90, 129.58, 128.53, 128.48, 128.42, 127.40, 127.16, 127.02, 125.21, 122.73 (d, $J = 30.0$ Hz), 118.73. HRMS (ESI$^+$) m/z: Calcd for C$_{19}$H$_{14}$NS 288.0841 [M+H]$^+$, Found 288.0843.
4-Phenylbenzo[g]quinoline-2(1H)-thione (3t). Yellow solid (80%, 0.115 g): mp 244-246 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\): 14.07 (s, 1H), 8.16 (d, \(J = 8.8\) Hz, 1H), 7.96 (d, \(J = 7.6\) Hz, 1H), 7.86 (d, \(J = 9.2\) Hz, 1H), 7.58 - 7.57 (m, 3H), 7.47 - 7.40 (m, 3H), 7.25 (d, \(J = 8.4\) Hz, 1H), 7.17 (d, \(J = 8.4\) Hz, 2H). \(^13\)C NMR (150 MHz, DMSO-\(d_6\)) \(\delta\): 178.13, 147.36, 141.06 (d, \(J = 1.5\) Hz), 134.19, 134.00, 131.23, 129.70 (d, \(J = 3.0\) Hz), 129.11 (d, \(J = 11.0\) Hz), 127.99, 127.07, 126.11, 125.85, 117.32, 116.64. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{19}\)H\(_{14}\)NS 288.0841 [M+H]\(^+\), Found 288.0833.

6-Methyl-4-((thiophen-3-yl)quinoline-2(1H)-thione (3u). Yellow solid (73%, 0.094 g): mp 333-335 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\): 10.91 (s, 1H), 7.93 (d, \(J = 6.0\) Hz, 1H), 7.79 (s, 1H), 7.73 (s, 1H), 7.54 (d, \(J = 6.0\) Hz, 1H), 7.52 (d, \(J = 0.6\) Hz, 1H), 7.45 - 7.42 (m, 2H), 7.23 (dd, \(J = 1.2, 1.2\) Hz, 1H), 2.46 (s, 3H). \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 157.81, 147.11, 144.00, 138.10, 136.44, 132.33, 128.78, 128.53, 126.21, 125.21, 125.16, 124.57, 117.19, 21.78. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{14}\)H\(_{12}\)NS 258.0406 [M+H]\(^+\), Found 258.0408.

1.7 General procedure for the synthesis of 2-aminoquinoline 4. Under an atmosphere of air, 2-(1-phenylvinyl) aniline 1a (0.5 mmol, 0.104 g), PhNCS (1.8 eq. 0.9 mmol, 0.121 g), K\(_3\)PO\(_4\) (2 eq, 0.212 g) were added to a tube. Dixoane (3.0 mL) was added by dropper and the mixture was stirred for 12 h at 100 °C and the reaction was monitored by TLC analysis. Then, 2.0 mL ammonium chloride were added to the mixture to quench the reaction and extracted with ethyl acetate (3×25 mL). The combined organic layers were washed with aqueous NaHCO\(_3\) and brine, dried over MgSO\(_4\), filtered, and the volatiles were removed in vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:5) to give the corresponding products. All of the products 4b-4a were synthesized according to above described procedure.

6-Methyl-N,4-diphenylquinolin-2-amine (4a). Oil (84 %, 0.130 g). IR (KBr) 3408, 3018, 2943, 1739, 1618, 1362, 1216, 1093 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\): 7.91 (dd, \(J = 2.4, 2.4\) Hz, 1H), 7.68 - 7.65 (m, 2H), 7.57 (s, 1H), 7.56 - 7.45 (m, 7H), 7.42 - 7.38 (m, 2H), 7.13 - 7.10 (m, 1H), 6.95 (s, 1H), 2.46 (s, 3H). \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 153.75, 149.64, 146.74, 140.67, 138.57, 132.73, 131.77, 129.44, 129.28, 128.54, 128.28, 127.06, 124.86.
123.11, 122.81, 120.42, 21.55. HRMS (ESI+) m/z: Calcd for C_{22}H_{19}N_{3} 311.1543 [M+H]^+, Found: 311.1551.

**Methyl-4-phenyl-N-(p-tolyl)quinolin-2-amine (4b).** Solid (80 %, 0.1296 g): mp 153-155 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 7.72 (d, $J$ = 8.4 Hz, 1H), 7.50 - 7.38 (m, 9H), 7.14 (d, $J$ = 7.2 Hz, 2H), 6.87 (s, 1H), 6.85 (s, 1H), 2.38 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 153.91, 149.61, 146.62, 138.53, 137.64, 132.82, 132.48, 131.67, 129.80, 129.32, 128.41, 128.15, 126.69, 124.75, 122.91, 121.15, 111.21, 21.44, 20.84. HRMS (ESI+) m/z: Calcd for C$_{23}$H$_{21}$N$_3$ 325.1699 [M+H]$^+$, Found: 325.1703.

The crystal structure of compound 4b (CCDC 1823828).

**N-(4-Fluorophenyl)-6-methyl-4-phenylquinolin-2-amine (4c).** Oil (75 %, 0.123 g). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.74 (d, $J$ = 8.0 Hz, 1H), 7.56 - 7.41 (m, 10H), 7.07 - 7.02 (m, 2H), 6.78 (d, $J$ = 2.0 Hz, 1H), 2.39 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 153.48, 149.89, 138.33, 132.80, 131.80, 129.26, 128.46, 128.25, 126.67, 124.76, 122.93, 122.50, 122.44, 115.91, 115.76, 111.28, 21.42. HRMS (ESI+) m/z: Calcd for C$_{23}$H$_{18}$FN$_2$ 329.1449 [M+H]$^+$,
6-Methoxy-N,4-diphenylquinolin-2-amine (4d). Oil (88 %, 0.143 g). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\): 7.78 (d, \(J = 9.0\) Hz, 1H), 7.54 (d, \(J = 7.8\) Hz, 2H), 7.50 (dd, \(J = 0.6, 6.6\) Hz, 4H), 7.34 (t, \(J = 9.6\) Hz, 2H), 7.29 (d, \(J = 3.0\) Hz, 1H), 7.27 (d, \(J = 3.0\) Hz, 1H), 7.07 - 7.03 (m, 2H), 6.93 (s, 1H), 6.80 (s, 1H), 3.75 (s, 3H). \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 155.63, 152.73, 149.03, 145.18, 143.87, 140.80, 138.55, 129.40, 129.25, 128.63, 128.33, 123.59, 122.51, 120.92, 119.96, 112.29, 105.25, 55.48. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{22}\)H\(_{19}\)N\(_2\)O 327.1492 [M+H]\(^+\), Found: 327.1486.

6-Methoxy-4-phenyl-N-(p-toly)quinolin-2-amine (4e). Oil (82 %, 0.139 g). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\): 7.78 (d, \(J = 9.6\) Hz, 1H), 7.51 – 7.44 (m, 5H), 7.42 – 7.39 (m, 2H), 7.28 (dd, \(J = 3.0, 3.0\) Hz, 1H), 7.15 (d, \(J = 7.8\) Hz, 2H), 7.07 (d, \(J = 2.4\) Hz, 1H), 6.90 (s, 2H), 3.75 (s, 3H). \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 155.45, 153.14, 149.04, 143.92, 138.57, 137.91, 132.51, 129.78, 129.18, 128.53, 128.40, 128.22, 123.44, 120.86, 120.83, 111.67, 105.20, 55.44, 20.83. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{23}\)H\(_{21}\)N\(_2\)O 341.1648 [M+H]\(^+\), Found: 341.1641.

N-(4-Fluorophenyl)-6-methoxy-4-phenylquinolin-2-amine (4f). Oil (78 %, 0.134 g). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\): 7.78 (d, \(J = 9.0\) Hz, 1H), 7.54 - 7.47 (m, 7H), 7.28 (dd, \(J = 3.0, 3.0\) Hz, 1H), 7.07 (d, \(J = 3.0\) Hz, 1H), 7.03 (t, \(J = 17.4\) Hz, 2H), 6.91 (s, 1H), 6.79 (s, 1H), 3.74 (s, 3H). \(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 159.47, 157.87, 155.59, 152.80, 149.22, 143.65, 138.39, 129.13, 128.58, 128.44, 122.07, 120.94, 115.84, 115.69, 111.83, 105.22, 55.44. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{22}\)H\(_{18}\)FN\(_2\)O 345.1398 [M+H]\(^+\), Found: 345.1401.

6-Methoxy-N-(naphthalen-1-yl)-4-phenylquinolin-2-amine (4g). Solid (73 %, 0.137 g): mp 161-163 °C. IR (KBr) 3406, 3020, 2923, 1740, 1606, 1513, 1368, 1217, 1118 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\): 8.14.
(d, J = 7.2 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 9.6 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.53 - 7.41 (m, 8H), 7.30 (dd, J = 3.0, 2.4 Hz, 1H), 7.08 (d, J = 3.0 Hz, 1H), 6.86 (s, 1H), 4.16 (s, 1H), 3.75 (s, 3H).

$^1$C NMR (150 MHz, CDCl$_3$) $\delta$: 155.54, 154.42, 149.26, 144.02, 138.52, 135.97, 134.67, 129.16, 128.49, 128.21, 126.30, 126.19, 125.93, 125.14, 124.83, 123.61, 122.10, 121.12, 120.12, 111.17, 109.66, 105.24, 55.47. HRMS (ESI+) m/z: Calcd for C$_{26}$H$_{21}$N$_2$O 377.1648 [M+H]$^+$, Found: 377.1641.

6-Chloro-N,4-diphenylquinolin-2-amine (4h). Oil (70 %, 0.115 g). IR (KBr) 3433, 3006, 2925, 1739, 1618, 1566, 1218, 1114 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 7.78 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 1.8 Hz, 1H), 7.58 (dd, J = 1.2, 1.2 Hz, 2H), 7.53 - 7.48 (m, 4H), 7.45 - 7.35 (m, 2H), 7.38 - 7.35 (m, 2H), 7.20 (s, 1H), 7.12 - 7.09 (m, 1H), 6.91 (s, 1H). $^1$C NMR (150 MHz, CDCl$_3$) $\delta$: 154.22, 149.42, 146.74, 139.92, 137.56, 130.32, 129.30, 128.70, 128.61, 128.58, 128.55, 124.64, 123.82, 123.35, 120.69, 112.43. HRMS (ESI+) m/z: Calcd for C$_{21}$H$_{16}$ClN$_2$ 311.0997 [M+H]$^+$, Found: 311.1012.

6-Chloro-4-phenyl-N-(p-tolyl)quinolin-2-amine (4i). Solid (75 %, 0.129 g): mp 152-154 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 7.74 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.52 - 7.47 (m, 4H), 7.44 - 7.40 (m, 4H), 7.17 (d, J = 8.4 Hz, 2H), 6.89 (s, 1H), 6.79 (s, 1H), 2.34 (s, 3H). $^1$C NMR (150 MHz, CDCl$_3$) $\delta$: 154.48, 149.43, 137.62, 137.03, 133.42, 130.30, 129.86, 129.17, 128.64, 128.54, 128.38, 128.35, 124.62, 123.72, 121.43, 111.92, 20.85. HRMS (ESI+) m/z: Calcd for C$_{22}$H$_{18}$ClN$_2$ 345.1153 [M+H]$^+$, Found: 345.1148.

8-Methyl-N-(naphthalen-1-yl)-4-(m-tolyl)quinolin-2-amine (4j). Oil (78 %, 0.145 g). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 8.03 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 7.2 Hz, 1H), 7.79 (d, J = 1.8 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.43 - 7.38 (m, 2H), 7.25 (t, J = 15.0 Hz, 1H), 7.15 (d, J = 7.8 Hz, 3H), 7.09 (t, J = 15.6 Hz, 1H), 6.80 (d, J = 3.0 Hz, 1H), 2.77 (s, 3H), 2.32 (s, 3H). $^1$C NMR (150 MHz, CDCl$_3$) $\delta$: 154.47, 150.75, 147.47, 138.83, 138.07, 135.93, 134.78, 134.67, 130.12, 130.04, 128.90, 128.66, 128.58, 128.30, 126.59, 126.23, 126.09, 126.06, 124.76, 123.99, 123.18, 122.64, 121.94, 119.56, 110.88, 21.53, 18.68. HRMS (ESI+) m/z: Calcd for C$_{27}$H$_{23}$N$_2$ 375.1856 [M+H]$^+$,

S13
Found: 375.1860.

**N-isopropyl-6-methyl-4-phenylquinolin-2-amine (4k).** Oil (72 %, 0.099 g). $^1$H NMR (600 MHz, CDCl$_3$) δ: 7.63 (d, $J = 9.0$ Hz, 1H), 7.52 - 7.45 (m, 4H), 7.36 (d, $J = 9.6$ Hz, 2H), 6.53 (s, 1H), 4.69 (s, 1H), 4.22 - 4.15 (m, 1H), 2.35 (s, 3H), 1.29 (d, $J = 6.0$ Hz, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 155.55, 149.22, 146.89, 138.82, 131.39, 131.30, 129.28, 128.36, 128.01, 126.11, 124.74, 122.10, 110.96, 42.96, 23.25, 21.31. HRMS (ESI+) m/z: Calcd for C$_{19}$H$_{21}$N$_2$ 277.1699 [M+H$^+$], Found: 277.1703.

**N-isopropyl-6-methyl-4-(4-pentylphenyl)quinolin-2-amine (4l).** Oil (65 %, 0.112 g). $^1$H NMR (600 MHz, CDCl$_3$) δ: 7.62 (d, $J = 8.4$ Hz, 1H), 7.41 (s, 1H), 7.39 - 7.33 (m, 3H), 7.31 (d, $J = 7.8$ Hz, 2H), 6.53 (s, 1H), 4.69 (s, 1H), 4.18 - 4.13 (m, 1H), 2.72 - 2.68 (m, 2H), 2.36 (s, 3H), 1.73 - 1.68 (m, 2H), 1.40 - 1.38 (m, 4H), 1.29 (d, $J = 6.6$ Hz, 6H), 0.96 - 0.91 (m, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ: 142.97, 136.00, 131.37, 129.36, 129.17, 128.66, 128.51, 128.39, 124.85, 115.74, 110.82, 43.01, 35.75, 31.62, 31.13, 29.68, 23.25, 22.56, 21.31, 14.04. HRMS (ESI+) m/z: Calcd for C$_{24}$H$_{31}$N$_2$ 347.2482 [M+H$^+$], Found: 347.2486.

**N-butyl-6-chloro-4-phenylquinolin-2-amine (4m).** Oil (72 %, 0.111 g). IR (KBr) 3448, 2921, 1647, 1367, 1217, 1051 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) δ: 7.65 (d, $J = 8.4$ Hz, 1H), 7.56 (d, $J = 2.4$ Hz, 1H), 7.52 - 7.42 (m, 6H), 6.56 (s, 1H), 4.78 (s, 1H), 3.49 (q, $J = 6.6$ Hz, 2H), 1.68 - 1.63 (m, 2H), 1.49 - 1.43 (m, 2H), 0.97 (t, $J = 15.6$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 156.75, 148.81, 147.25, 137.91, 129.95, 129.15, 128.59, 128.39, 127.96, 127.11, 124.59, 123.08, 111.77, 41.51, 31.86, 20.20, 13.87. HRMS (ESI+) m/z: Calcd for C$_{19}$H$_{20}$ClN$_2$ 311.1310 [M+H$^+$], Found: 311.1312.

**6-Chloro-N-heptyl-4-phenylquinolin-2-amine (4n).** Oil (65 %, 0.114 g). IR (KBr) 3395, 2920, 2843, 1739, 1709, 1645, 1366, 1220, 1055 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) δ: 7.65 (d, $J = 9.0$ Hz, 1H), 7.56 (d, $J = 2.4$ Hz, 1H), 7.52 - 7.45 (m, 4H), 7.44 - 7.42 (m, 2H), 6.56 (s, 1H), 4.77 (s, 1H), 3.49 - 3.45 (m, 2H), 1.69 - 1.64 (m, 2H), 1.45 - 1.39 (m, 2H), 1.38 - 1.27 (m, 6H), 0.89 (t, $J = 13.8$ Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 156.74, 148.81, 147.26, 137.92, 129.95, 129.15, 128.58, 128.39, 127.96, 127.11, 124.58, 123.07, 111.74, 41.82, 31.77, 29.75, 29.05.
N-butyl-8-methyl-4-(m-tolyl)quinolin-2-amine (4o). Oil (62%, 0.094 g). ¹H NMR (600 MHz, CDCl₃) δ: 7.50 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 7.38 (t, J = 15.0 Hz, 1H), 7.30 - 7.26 (m, 3H), 7.06 (t, J = 21.0, 1H), 6.54 (s, 1H), 4.71 (s, 1H), 3.55 (q, J = 8.0 Hz, 2H), 2.73 (s, 3H), 2.45 (s, 3H), 1.73 - 1.68 (m, 2H), 1.52 - 1.46(m, 2H), 1.01 (t, J = 14.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 155.68, 149.89, 147.46, 139.09, 137.95, 134.24, 130.02, 129.51, 128.65, 128.17, 126.47, 123.71, 122.11, 121.21, 110.77, 41.49, 31.87, 21.48, 20.33, 18.32, 13.96. HRMS (ESI+) m/z: Calcd for C₂₂H₂₆ClN₂ 353.1779 [M+H]⁺, Found: 353.1783.

N-benzyl-4-(4-fluorophenyl)-6-methylquinolin-2-amine (4p). Oil (61%, 0.104 g). ¹H NMR (400 MHz, CDCl₃) δ: 7.69 (d, J = 13.2 Hz, 1H), 7.43 - 7.37 (m, 6H), 7.34 (d, J = 6.6 Hz, 3H), 7.21 - 7.12 (m, 6H), 6.52 (d, J = 1.8 Hz, 1H), 5.03 (s, 1H), 4.74 (d, J = 7.8 Hz, 2H), 2.37 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 163.50, 155.71, 139.35, 134.50, 131.81, 131.56, 130.94, 130.88, 128.62, 127.77, 127.29, 126.40, 124.53, 122.35, 115.49, 115.34, 111.27, 45.91, 21.35. HRMS (ESI+) m/z: Calcd for C₂₃H₂₀FN₂ 343.1605 [M+H]⁺, Found: 343.1610.

8-Methyl-N-phenethyl-4-phenylquinolin-2-amine (4q). Oil (65%, 0.110 g). ¹H NMR (600 MHz, CDCl₃) δ: 7.52 - 7.45 (m, 6H), 7.36 (t, J = 15.6 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.28 - 7.26 (m, 1H), 7.09 (t, J = 15.0 Hz, 2H), 6.51 (s, 1H), 4.75 (s, 1H), 3.85 (q, J = 6.6 Hz, 2H), 3.07 (t, J = 14.4 Hz, 2H), 2.78 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 155.17, 149.71, 147.41, 139.81, 139.00, 134.48, 129.59, 129.36, 128.93, 128.57, 128.31, 127.97, 126.29, 123.64, 122.10, 121.49, 111.42, 43.08, 35.70, 18.42. HRMS (ESI+) m/z: Calcd for C₂₄H₂₃N₂ 338.1856 [M+H]⁺, Found: 339.1852.
6-Chloro-N-phenethyl-4-phenylquinolin-2-amine (4r). Oil (68 %, 0.121 g). \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ: 7.69 (d, J = 9.0 Hz, 1H), 7.57 (d, J = 2.4 Hz, 1H), 7.52 - 7.45 (m, 4H), 7.43 - 7.40 (m, 2H), 7.33 - 7.31 (m, 2H), 7.28 - 7.22 (m, 3H), 6.51 (s, 1H), 4.91 (s, 1H), 3.80 (q, J = 6.6 Hz, 2H), 3.00 (t, J = 14.4 Hz, 2H). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) δ: 156.35, 148.87, 147.05, 139.20, 137.77, 130.01, 129.14, 128.84, 128.63, 128.59, 128.44, 128.00, 127.35, 126.46, 124.61, 123.13, 112.15, 42.80, 35.75. HRMS (ESI+) m/z: Calcd for C\textsubscript{23}H\textsubscript{20}ClN\textsubscript{2} 359.1310 [M+H]\textsuperscript{+}, Found: 359.1314.

N-(6-methoxy-4-phenylquinolin-2-yl)benzamide (4s). Solid (75 %, 0.126 g); mp 140-142 °C. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ: 9.13 (s, 1H), 8.54 (s, 1H), 7.98 (d, J = 7.2 Hz, 2H), 7.77 (d, J = 9.0 Hz, 1H), 7.62 (s, 1H), 7.57 - 7.43 (m, 9H), 2.42 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 166.69, 151.19, 150.80, 146.18, 138.91, 135.75, 134.87, 132.94, 132.73, 130.26, 129.44, 129.17, 129.07, 128.08, 128.0, 125.70, 125.47, 115.34, 22.36. HRMS (ESI+) m/z: Calcd for C\textsubscript{23}H\textsubscript{19}N\textsubscript{2}O 334.1492 [M+H]\textsuperscript{+}, Found: 334.1499.

N-(6-methoxy-4-phenylquinolin-2-yl)benzamide (4t). Solid (78 %, 0.138 g); mp 174-176 °C. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ: 8.80 (s, 1H), 8.53 (s, 1H), 7.99 - 7.96 (m, 2H), 7.81 (d, J = 9.0 Hz, 1H), 7.60 - 7.56 (m, 3H), 7.55 - 7.48 (m, 5H), 7.35 (dd, J = 3.0, 3.0 Hz, 1H), 7.19 (d, J = 4.2 Hz, 1H), 3.78 (s, 3H). \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) δ: 165.78, 157.04, 149.83, 148.91, 142.91, 138.33, 134.27, 132.26, 129.38, 129.15, 128.82, 128.58, 128.42, 127.24, 125.87, 122.09, 114.79, 104.34, 55.45. HRMS (ESI+) m/z: Calcd for C\textsubscript{23}H\textsubscript{19}N\textsubscript{2}O 355.1441 [M+H]\textsuperscript{+}, Found: 355.1445.
Methyl-N-phenylquinolin-2-amine (4u). Oil (65 %, 0.076 g). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 7.82 - 7.78 (m, 2H), 7.60 - 7.54 (m, 3H), 7.38 - 7.27 (m, 4H), 7.20 (s, 1H), 7.10 - 7.07 (m, 1H), 6.84 (d, J = 1.2 Hz, 1H), 2.58 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 154.13, 145.82, 140.24, 129.55, 129.35, 129.21, 127.01, 124.44, 123.58, 122.99, 122.92, 120.55, 111.73, 18.92. HRMS (ESI+) m/z: Calcd for C$_{16}$H$_{15}$N$_2$ 235.1230 [M+H]$^+$, Found: 235.1234.

4-Methyl-N-(p-tolyl)quinolin-2-amine (4v). Oil (73 %, 0.095 g). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 7.81 - 7.77 (m, 2H), 7.57 (m, 1H), 7.42 - 7.39 (m, 2H), 7.32-7.29 (m, 1H), 7.18 (d, J = 6.0 Hz, 2H), 6.98 (s, 1H), 6.80 (s, 1H), 2.56 (s, 3H), 2.36 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 154.77, 147.78, 145.57, 137.65, 132.85, 129.77, 129.44, 127.04, 124.42, 123.59, 122.64, 121.35, 111.45, 20.88, 18.90. HRMS (ESI+) m/z: Calcd for C$_{17}$H$_{17}$N$_2$ 249.1386 [M+H]$^+$, Found: 249.1390.

N-(4-fluorophenyl)-4-methylquinolin-2-amine (4w). Oil (80 %, 0.1 g). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 7.80 (dd, J = 1.8, 1.2Hz, 1H), 7.76 (d, J =0.8 Hz, 1H), 7.58-7.55 (m, 1H), 7.53 - 7.51 (m, 2H), 7.32-7.30 (m, 1H), 7.06 - 7.02 (m, 2H), 6.71 (s, 1H), 2.56 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 159.72, 158.12, 154.27, 147.22, 145.97, 136.22, 129.61, 126.89, 123.60, 122.94, 122.69, 115.85, 111.54, 18.90. HRMS (ESI+) m/z: Calcd for C$_{16}$H$_{14}$FN$_2$ 253.1136 [M+H]$^+$, Found: 253.1140.

N-benzyl-4-methylquinolin-2-amine (4x). Oil (46 %, 0.057 g). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$: 7.77 (dd, J= 1.8, 1.2 Hz, 1H), 7.73 (dd, J= 1.2, 1.2 Hz, 1H), 7.54 (m, 1H), 7.41 (d, J= 7.8 Hz, 2H), 7.34 - 7.30 (m, 2H), 7.30 - 7.23 (m, 2H), 6.48 (s, 1H), 5.01 (s, 1H), 4.72 (d, J= 5.4 Hz, 2H), 2.54 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$: 156.58, 147.97, 145.10, 139.52, 129.30, 128.61, 127.75, 127.24, 126.69, 123.95, 123.57, 121.92, 111.42, 45.74, 18.82. HRMS (ESI+) m/z: Calcd for C$_{17}$H$_{17}$N$_2$ 249.1386 [M+H]$^+$, Found: 249.1390.
4-Methyl-N-phenethylquinolin-2-amine (4y). Oil (49 %, 0.064 g). $^1$H NMR (600 MHz, CDCl$_3$) δ: 7.76 (dd, J = 1.2, 1.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.55 - 7.52 (m, 1H), 7.34 - 7.32 (m, 2H), 7.29 - 7.23 (m, 4H), 6.43 (s, 1H), 4.75 (s, 1H), 3.78 (q, J = 6.6 Hz, 2H), 2.99 (t, J = 13.8 Hz, 2H), 2.54 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 156.59, 148.03, 144.91, 139.44, 129.26, 128.88, 128.59, 126.63, 126.38, 123.81, 123.57, 121.81, 111.57, 42.76, 35.84, 18.79. HRMS (ESI+) m/z: Calcd for C$_{18}$H$_{19}$N$_2$ 263.1543 [M+H]$^+$, Found: 263.1540.

4-Methyl-N-pentylquinolin-2-amine (4z). Oil (53 %, 0.057 g). $^1$H NMR (600 MHz, CDCl$_3$) δ: 7.74 (d, J = 6.0 Hz, 1H), 7.66 (d, J = 6.0 Hz, 1H), 7.51 (t, J = 12.0 Hz, 1H), 7.23 - 7.19 (m, 1H), 6.49 (s, 1H), 4.71 (s, 1H), 3.45 (q, J = 1.8 Hz, 2H), 2.55 (s, 3H), 1.66 - 1.61 (m, 2H), 1.48 - 1.42 (m, 2H), 0.97 (t, J = 1.8 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 156.96, 148.03, 144.97, 129.25, 126.39, 123.67, 123.54, 121.61, 111.01, 41.49, 31.94, 20.20, 18.85, 13.88. HRMS (ESI+) m/z: Calcd for C$_{14}$H$_{19}$N$_2$ 215.1543 [M+H]$^+$, Found: 215.1548.

Heptyl-4-methylquinolin-2-amine (4A). Oil (48 %, 0.061 g). $^1$H NMR (600 MHz, CDCl$_3$) δ: 7.74 (dd, J = 1.8, 1.2 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.52 - 7.50 (m, 1H), 7.22 - 7.20 (m, 1H), 6.48 (s, 1H), 4.70 (s, 1H), 3.44 (td, J = 7.8, 6.6 Hz, 2H), 2.55 (s, 3H), 1.67 - 1.62 (m, 2H), 1.44 - 1.38 (m, 2H), 1.37 - 1.27 (m, 6H), 0.89 (t, J = 13.2 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 156.98, 148.10, 144.90, 129.22, 126.45, 123.69, 123.53, 121.59, 111.05, 41.79, 31.80, 29.83, 29.08, 27.03, 22.61, 18.83, 14.07. HRMS (ESI+) m/z: Calcd for C$_{17}$H$_{25}$N$_2$ 257.2012 [M+H]$^+$, Found: 257.2016.

1.8 References
1.9 Copies of $^1$H and $^{13}$C Spectra for products

$^1$H and $^{13}$C Spectra of compound 3a (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3b (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3c (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3d (CDCl$_3$, 600 MHz)
$^1\text{H}$ and $^{13}\text{C}$ Spectra of compound 3e (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3f (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3g (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3i (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3j (CDCl$_3$, 600 MHz)
$^{1}$H and $^{13}$C Spectra of compound 3k (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3l (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3m (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3n (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3o (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3p (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3q (CDCl$_3$, 600 MHz)
\( ^1H \) (F) and \( ^{13}C \) Spectra of compound 3r (CDCl\(_3\), 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3s (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 3t (CDCl$_3$, 600 MHz)
$^{1}\text{H}$ and $^{13}\text{C}$ Spectra of compound 3u (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4a (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4b (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4c (CDCl$_3$, 400 MHz)
$^1$H and $^{13}$C Spectra of compound 4d (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4e (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4f (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4g (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4h (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4i (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4j (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4k (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4l (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4m (CDCl$_3$, 600 MHz)
$^{1}\text{H}$ and $^{13}\text{C}$ Spectra of compound 4n (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4o (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4p (CDCl$_3$, 400 MHz)
$^1$H and $^{13}$C Spectra of compound 4q (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4r (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4s (CDCl$_3$, 600 MHz)
$^1\text{H}$ and $^{13}\text{C}$ Spectra of compound 4t (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4u (CDCl$_3$, 600 MHz)
$^1\text{H}$ and $^{13}\text{C}$ Spectra of compound 4v (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4w (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4x (CDCl₃, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4y (CDCl$_3$, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4z (CDCl₃, 600 MHz)
$^1$H and $^{13}$C Spectra of compound 4A (CDCl$_3$, 600 MHz)