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## SYNTHESIS OF *N*3-SUBSTITUTED QUINAZOLINE-2,4-DIONES VIA C-4 AMINATION-CYCLIZATION OF ISATOIC ANHYDRIDES

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Dedicated to the 80th anniversary of Prof. Dr. Somsak Ruchirawat

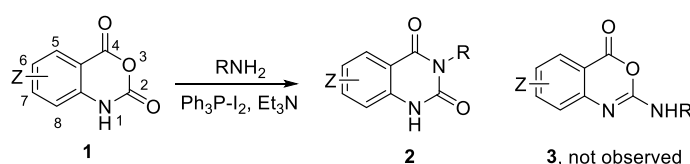
**Abstract** – A direct approach for the synthesis of *N*3-substituted quinazoline-2,4-diones via condensation of isatoic anhydrides with amines mediated by Ph<sub>3</sub>P-I<sub>2</sub> was reported. Instead of the expected benzoxazinones, the reaction proceeds with an amine attack at the C-4 position of isatoic anhydrides leading to quinazoline-2,4-diones upon heating in the presence of base. This one-pot process enables a rapid construction of a broad range of quinazoline-2,4-dione derivatives using simple, readily available, and low-cost reagents with no extra carbonylating agent needed.

Quinazolinediones represent one of the most important structural motifs in medicinal chemistry. They have been shown to exhibit a broad range of pharmacological and biological activities. Some examples include antihypertensive,<sup>1</sup> antimicrobial,<sup>2</sup> antimalarial,<sup>3</sup> antiviral,<sup>4</sup> and anticancer properties.<sup>5</sup> Regarding their promising potential in drug discovery and development, numerous synthetic methods have been developed to gain access to these heterocyclic systems using various synthetic precursors such as anthranilic acids,<sup>6</sup>

*o*-halobenzoates,<sup>7</sup> 2-aminobenzonitriles,<sup>8</sup> 2-haloanilines,<sup>9</sup> benzamides,<sup>10</sup> *o*-halophenylureas or carbodiimides,<sup>11</sup> and 2,3-unsubstituted indoles/indolines.<sup>12</sup>

Apart from these substrates, isatoic anhydride is also another versatile building block toward quinazolinediones due to their ready availability and ease of reactions with electrophiles or nucleophiles.<sup>13</sup> Upon treatment with an amine, the reaction of isatoic anhydride generally proceeds with a loss of carbon dioxide giving *N*-substituted anthranilamide as the main product.<sup>13e</sup> Thus, the commonly applied approaches toward *N*3-substituted quinazolinediones mostly involve carbonylation of the preformed anthranilamides with carbonylating agents such as CDI,<sup>14</sup> triphosgene,<sup>15</sup> trichloroacetyl chloride,<sup>16</sup> di-*tert*-butyl decarbonate,<sup>17</sup> or (thio)urea.<sup>18</sup> Alternatively, cycloaddition between *N*-methylisatoic anhydrides and isocyanates under metal-catalyzed conditions could provide *N,N'*-disubstituted quinazolinediones in one step.<sup>19</sup>

In our continuing study involving phosphonium-mediated synthesis, our attention has now focused on the synthesis of biologically active heterocycles.<sup>20</sup> In attempts to synthesize benzoxazinones via deoxygenative amination at the C-2 position of isatoic anhydrides in the presence of Ph<sub>3</sub>P-I<sub>2</sub>, we have discovered that quinazolinediones **2** were obtained without detectable amount of the expected benzoxazinone products **3**. Herein, we wish to report a new approach toward quinazolinediones **2** which enables rapid access to a broad range of *N*3-substituted derivatives using isatoic anhydrides and amines as the easily available and cost-effective starting materials without additional CO source<sup>14-18</sup> (Scheme 1).



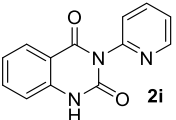
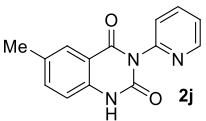
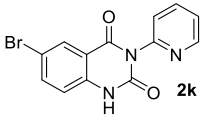
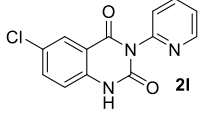
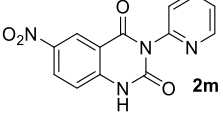
**Scheme 1**

According to Table 1, the reaction between isatoic anhydride (**1a**) and aniline in the presence of Ph<sub>3</sub>P-I<sub>2</sub> and triethylamine proceeded upon heating in toluene to afford quinazolinedione **2a** in high yield (entry 1). Similar outcomes were observed when the reaction was carried out using different aryl amines (entries 2-6). When comparing with anilines containing electron-withdrawing substituent (eg. -Cl, -CF<sub>3</sub>, -NO<sub>2</sub>), electron-rich amines such as those bearing -OMe, -Me are more effective leading to higher yields of **2b** and **2c**. While sterically hindered 1-naphthylamine gave relatively lower yield of **2g**, the reaction of benzylamine proceeded smoothly to afford 3-benzylquinazolinedione **2h** in high yield (entries 7 and 8). In addition, the reaction conditions were compatible with a range of differently substituted isatoic anhydrides. As shown in Table 1 (entries 9-12), the substrates with both electron-donating and electron-withdrawing

groups condensed with 2-aminopyridine giving 3-(pyridin-2-yl)quinazolinone derivatives in moderate to good yields. Only in the case when a strong electron-withdrawing  $-\text{NO}_2$  group is *para* to N-1 of **1e**, a complex mixture was obtained in which the desired product **2m** was not isolated (entry 13).

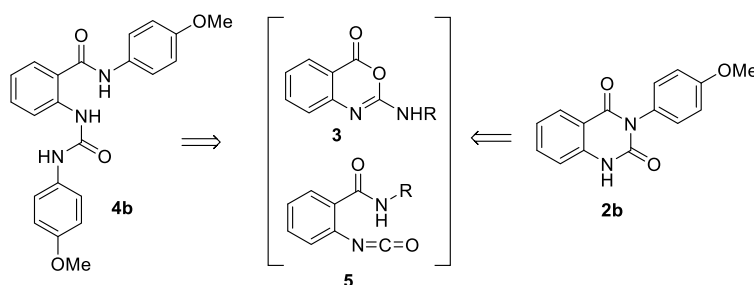
**Table 1.** Reaction of isatoic anhydride **1** with amines

Entry	<b>1</b> (6-Z = )	RNH <sub>2</sub>	<b>2</b>	Yield of <b>2</b> <sup>a,b</sup> (%)	mp (°C) <sup>[lit.]</sup>
1	<b>1a</b> (H)	PhNH <sub>2</sub>		75	280-282 <sup>11</sup>
2	<b>1a</b> (H)	4-MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>		78 <sup>c</sup>	299-300 <sup>21</sup>
3	<b>1a</b> (H)	4-MeC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>		89	260-261 <sup>22</sup>
4	<b>1a</b> (H)	4-ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>		69	296-297 <sup>21</sup>
5	<b>1a</b> (H)	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>		56	290-292 <sup>23</sup>
6	<b>1a</b> (H)	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>		21	299-300 <sup>24</sup>
7	<b>1a</b> (H)	1-naphthylamine		62	268-269 <sup>25</sup>
8	<b>1a</b> (H)	BnNH <sub>2</sub>		81	227-228 <sup>6</sup>

9	<b>1a</b> (H)	2-aminopyridine		80	254-256 <sup>12</sup>
10	<b>1b</b> (Me)	2-aminopyridine		85	277-279 <sup>12</sup>
11	<b>1c</b> (Br)	2-aminopyridine		73	332-335 <sup>12</sup>
12	<b>1d</b> (Cl)	2-aminopyridine		69	313-315 <sup>12</sup>
13	<b>1e</b> (NO <sub>2</sub> )	2-aminopyridine		complex mixture	<sup>12</sup>

<sup>a</sup>All known products were identified and characterized by comparison of their physical and spectral data with those of authentic samples. <sup>b</sup>Isolated yield. <sup>c</sup>The reaction was carried out at 110 °C for 3 h.

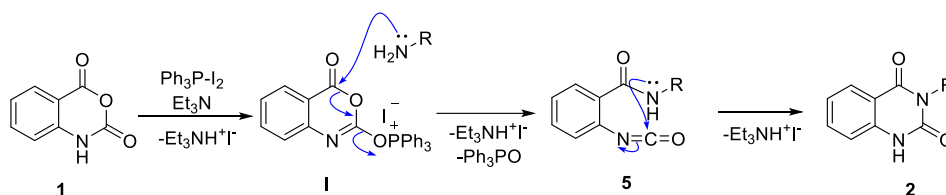
Notably, in accordance with other studies,<sup>13</sup> the reaction of **1a** with aniline in the absence of the Ph<sub>3</sub>P-I<sub>2</sub> combination proceeded with loss of carbon dioxide to give 2-amino-*N*-phenylbenzamide. It is also worth mentioning that, when the standard reaction conditions were applied in the synthesis of **2b**, significant amount of *o*-ureidobenzamide **4b** was isolated as a competing product implying either benzoxazinone **3** or 2-isocyanatobenzamide species **5** as a possible reaction intermediate (Figure 1). Nevertheless, among all the tested substrates, the corresponding benzoxazinone products **3** have never been observed during the course of the reaction. These results indicated that the Ph<sub>3</sub>P-I<sub>2</sub>-mediated reaction of isatoic anhydride (**1**) proceeded primarily through an initial C-2 phosphorylation before an amine attack at the C-4 position.



**Figure 1**

The reaction mechanism for the formation of quinazoline-2,4-diones **2** is thus proposed as depicted in Scheme 2. The reaction presumably begins by C-2 activation of **1** to produce phosphonium iodide **I**.<sup>26</sup>

Subsequent nucleophilic attack of an amine to the C-4 carbonyl of **1** then leads to benzoxazinone ring opening with a release of  $\text{Ph}_3\text{PO}$ . Cyclization of the formed isocyanate intermediate **5** via C-N bond formation finally furnishes the cyclized product **2**.<sup>27</sup>



**Scheme 2**

In summary, condensation reaction between isatoic anhydrides and amines in the presence of  $\text{Ph}_3\text{P-I}_2$  as an activator proceeds with an amine attack at C-4 of **1** to afford *N*<sup>3</sup>-substituted quinazolinediones **2**. Various quinazolinedione derivatives with *N*-aryl, *N*-alkyl, and *N*-heteroaryl can be efficiently prepared in satisfactory yields. The method offers several benefits using simple and readily available substrates as well as low-cost reagents under transition-metal-free conditions, while a broad scope of substrates can be tolerated.

## EXPERIMENTAL

All reagents were purchased from Sigma-Aldrich or TCI and used without further purification. All reactions were run in flame- or oven-dried glassware under  $\text{N}_2$  gas. Thin-layer chromatography was carried out on silica gel plates (60F<sub>254</sub>, MERCK, Germany) and visualized under UV light (254 nm). Column chromatography was performed over silica gel 60 (70–230 mesh, MERCK, Germany). Melting points were determined using Mettler Toledo DSC equipment at a heating rate of 6 °C/min and are uncorrected. NMR spectra were recorded using a Bruker AVANCE™ (400 and 500 MHz for <sup>1</sup>H). Chemical shifts were reported in parts per million (ppm,  $\delta$ ) downfield from tetramethylsilane (TMS). Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qui), sextet (sex), septet (sep), multiplet (m), broad (br), doublet of doublets (dd), triplet of doublets (td) and doublet of doublet of doublets (ddd). High-resolution mass spectra (HRMS) were recorded using the Agilent 6546 LC/Q-TOF via the electrospray ionization (ESI).

### General procedure for the synthesis of *N*<sup>3</sup>-substituted quinazolinediones **2**

Iodine (0.1514 g, 0.597 mmol) and triphenylphosphine (0.1566 g, 0.597 mmol) were mixed in 15 mL pressure tube before adding freshly distilled  $\text{CH}_2\text{Cl}_2$  (2 mL), followed by isatoic anhydride **1** (0.398 mmol) at 0 °C. After that, triethylamine (0.22 mL, 1.59 mmol) was added, and the mixture was sonicated briefly before adding amine (0.4776 mmol). After stirring for 10 min at 25 °C, toluene (1 mL) was added before

stirring in a preset oil bath at 120 °C. The progress of the reaction was monitored by thin-layer chromatography. After reaction completion (3-6 h), the solution was cooled, and the crude mixture was concentrated under reduced pressure before purification by column chromatography (CC) using EtOAc/hexanes as the eluent.

**3-Phenylquinazoline-2,4(1H,3H)-dione (2a):**<sup>11</sup> White solid (0.0712 g, 75% yield); mp 280-282 °C;  $R_f$  0.35 (10% EtOAc/hexanes);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3 + \text{CD}_3\text{OD}$  (2 drops))  $\delta$  8.12 (d,  $J = 8.0$  Hz, 1H), 7.59 (t,  $J = 8.0$  Hz, 1H), 7.53 (t,  $J = 7.5$  Hz, 2H), 7.48 (t,  $J = 7.5$  Hz, 1H), 7.29 (d,  $J = 7.5$  Hz, 2H), 7.22 (d,  $J = 8.0$  Hz, 1H), 7.05 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3 + \text{CD}_3\text{OD}$  (2 drops))  $\delta$  163.0, 151.4, 139.2, 135.4, 134.8, 129.4, 128.8, 128.47, 128.46, 123.3, 115.2, 114.6.

**3-(4-Methoxyphenyl)quinazoline-2,4(1H,3H)-dione (2b):**<sup>21</sup> White solid (0.0831 g, 78% yield); mp 299-300 °C;  $R_f$  0.35 (10% EtOAc/hexanes);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.23 (s, 1H), 8.00 (t,  $J = 2.0$  Hz, 1H), 7.91 (d,  $J = 8.0$  Hz, 1H), 7.68 – 7.64 (m, 3H), 7.56 (t,  $J = 8.0$  Hz, 1H), 6.94 (d,  $J = 9.5$  Hz, 1H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  164.1, 156.2, 137.5, 133.7, 132.4, 131.7, 130.8, 127.8, 126.8, 122.5, 114.3, 55.7.

**3-(*p*-Tolyl)quinazoline-2,4(1H,3H)-dione (2c):**<sup>22</sup> White solid (0.0894 g, 89% yield); mp 260-261 °C;  $R_f$  0.34 (10% EtOAc/hexanes);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  11.53 (s, 1H), 7.94 (d,  $J = 8.0$  Hz, 1H), 7.69 (t,  $J = 8.0$  Hz, 1H), 7.28 (d,  $J = 8.0$  Hz, 2H), 7.25 – 7.19 (m, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 2.38 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  162.7, 150.7, 140.3, 137.9, 133.6, 129.8, 129.2, 128.0, 122.9, 115.7, 114.8, 21.2.

**3-(4-Chlorophenyl)quinazoline-2,4(1H,3H)-dione (2d):**<sup>21</sup> White solid (0.0749 g, 69% yield); mp 296-297 °C;  $R_f$  0.36 (10% EtOAc/hexanes);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  11.59 (s, 1H), 7.94 (d,  $J = 8.0$  Hz, 0H), 7.71 (t,  $J = 8.0$  Hz, 1H), 7.56 (d,  $J = 8.5$  Hz, 2H), 7.39 (d,  $J = 8.5$  Hz, 1H), 7.25 (d,  $J = 8.0$  Hz, 1H), 7.23 (t,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  162.6, 150.5, 140.3, 135.7, 135.1, 133.2, 131.5, 129.3, 128.0, 123.0, 115.7, 114.8.

**3-(3-(Trifluoromethyl)phenyl)quinazoline-2,4(1H,3H)-dione (2e):**<sup>23</sup> White solid (0.0682 g, 56% yield); mp 290-292 °C;  $R_f$  0.33 (10% EtOAc/hexanes);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  11.64 (s, 1H), 7.96 (dd,  $J = 8.0, 1.5$  Hz, 1H), 7.84 (s, 1H), 7.82 (d,  $J = 8.0$  Hz, 1H), 7.76 – 7.69 (m, 3H), 7.27 – 7.23 (m, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  162.7, 150.6, 140.3, 137.1, 135.8, 134.1, 130.5, 130.2 (q,  $^2J_{CF} = 27.5$  Hz) 128.7 (q,  $^1J_{CF} = 261.3$  Hz), 128.0, 126.7 (q,  $^3J_{CF} = 3.9$  Hz), 125.4 (d,  $^3J_{CF} = 4.5$  Hz), 123.3, 123.1, 115.8, 114.8.

**3-(4-Nitrophenyl)quinazoline-2,4(1H,3H)-dione (2f):**<sup>24</sup> White solid (0.0239 g, 21% yield); mp 299-300 °C;  $R_f$  0.38 (30% EtOAc/hexanes);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3 + \text{CD}_3\text{OD}$  (2 drops))  $\delta$  8.25 (d,  $J = 9.5$  Hz, 1H), 7.93 – 7.81 (m, 3H), 7.82 (d,  $J = 8.0$  Hz, 1H), 7.56 (d,  $J = 8.0$  Hz, 1H), 7.46 (t,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}$

NMR (125 MHz, CDCl<sub>3</sub> + CD<sub>3</sub>OD (2 drops))  $\delta$  165.2, 144.2, 143.7, 136.1, 134.9, 132.4, 130.2, 127.7, 125.8, 125.1, 119.9, 119.8.

**3-(Naphthalen-1-yl)quinazoline-2,4(1H,3H)-dione (2g):**<sup>25</sup> White solid (0.0711 g, 62% yield); mp 268-269 °C; *R<sub>f</sub>* 0.32 (10% EtOAc/hexanes); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.75 (s, 1H), 8.06 (dd, *J* = 8.5, 1.5 Hz, 2H), 8.02 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.76 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 7.72 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.66 (t, *J* = 8.5 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.52 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 (td, *J* = 8.0, 1.5 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  163.0, 150.8, 140.7, 135.9, 134.4, 133.0, 130.6, 129.2, 128.7, 128.2, 127.6, 127.4, 126.7, 126.2, 123.1, 122.8, 115.9, 114.8.

**3-Benzylquinazoline-2,4(1H,3H)-dione (2h):**<sup>6</sup> White solid (0.0813 g, 81% yield); mp 227-228 °C; *R<sub>f</sub>* 0.34 (10% EtOAc/hexanes); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.53 (s, 1H), 7.94 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.66 (td, *J* = 8.0, 1.5 Hz, 1H), 7.33 – 7.29 (m, 4H), 7.25 – 7.19 (m, 3H), 5.10 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  162.4, 150.7, 139.9, 137.8, 135.6, 128.8, 127.95, 127.92, 127.5, 123.1, 115.7, 114.1, 43.6.

**3-(Pyridin-2-yl)quinazoline-2,4(1H,3H)-dione (2i):**<sup>12</sup> White solid (0.0762 g, 80% yield); mp 254-256 °C; *R<sub>f</sub>* 0.41 (40% EtOAc/hexanes); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  10.80 (s, 1H), 8.67 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.94 (td, *J* = 8.0, 1.5 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  162.8, 150.9, 149.7, 148.7, 139.4, 139.0, 135.5, 128.3, 124.34, 124.28, 123.4, 115.4, 114.5.

**6-Methyl-3-(pyridin-2-yl)quinazoline-2,4(1H,3H)-dione (2j):**<sup>12</sup> White solid (0.0855 g, 85% yield); mp 277-279 °C; *R<sub>f</sub>* 0.29 (60% EtOAc/hexanes); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.57 (s, 1H), 8.66 – 8.53 (m, 1H), 8.00 (td, *J* = 8.0, 2.0 Hz, 1H), 7.75 (dd, *J* = 2.2, 1.0 Hz, 1H), 7.55 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.52 – 7.50 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 3.37 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  162.6, 150.4, 149.83, 149.79, 139.2, 138.3, 137.0, 132.5, 127.3, 124.9, 124.6, 115.9, 114.5, 20.7.

**6-Bromo-3-(pyridin-2-yl)quinazoline-2,4(1H,3H)-dione (2k):**<sup>12</sup> White solid (0.0924 g, 73% yield); mp 332-335 °C; *R<sub>f</sub>* 0.39 (60% EtOAc/hexanes); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.80 (s, 1H), 8.62 – 8.61 (m, 1H), 8.03 – 8.00 (m, 2H), 7.90 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  161.5, 150.1, 149.8, 149.5, 139.7, 139.3, 138.5, 129.8, 124.83, 124.75, 118.4, 116.5, 114.7.

**6-Chloro-3-(pyridin-2-yl)quinazoline-2,4(1H,3H)-dione (2l):**<sup>12</sup> White solid (0.0753 g, 69% yield); mp 313-315 °C; *R<sub>f</sub>* 0.37 (60% EtOAc/hexanes); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.80 (s, 1H), 8.62 – 8.61 (m, 1H), 8.02 (td, *J* = 8.0, 2.0 Hz, 1H), 7.89 (d, *J* = 2.5 Hz, 1H), 7.79 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.29 (d, *J* = 8.5 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  161.6, 150.1, 149.8, 149.5, 139.32, 139.26, 135.9, 127.2, 126.8, 124.83, 124.75, 118.2, 116.1.

*N*-(4-Methoxyphenyl)-2-(3-(4-methoxyphenyl)ureido)benzamide (**4b**):<sup>28</sup> White solid (0.0389 g, 25% yield); mp 212-213 °C; *R*<sub>f</sub> 0.30 (30% EtOAc/hexanes); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 10.36 (s, 1H), 9.68 (s, 1H), 9.49 (s, 1H), 8.25 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.74 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 2H), 7.48 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 7.41 (d, *J* = 9.0 Hz, 2H), 7.10 (td, *J* = 8.5, 1.5 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 3.76 (s, 3H), 3.72 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 167.4, 156.4, 155.0, 153.0, 140.0, 133.3, 132.2, 131.9, 128.8, 122.9, 122.8, 121.5, 121.2, 120.7, 114.4, 114.2, 55.7, 55.6.

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