

## Supporting Information

### Copper-catalyzed cascade synthesis of benzimidazoquinazoline derivatives under mild condition

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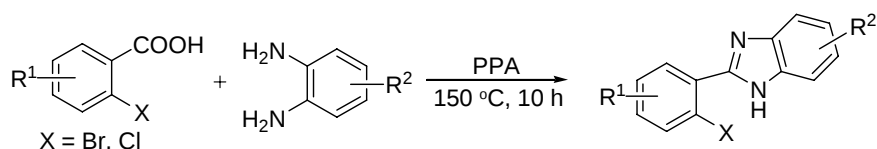
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## General experimental procedures

All reactions were carried out under nitrogen atmosphere. Proton and carbon magnetic resonance spectra ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) were recorded using tetramethylsilane (TMS) in the solvent of  $\text{CDCl}_3$  as the internal standard ( $^1\text{H}$  NMR: TMS at 0.00 ppm,  $\text{CHCl}_3$  at 7.26 ppm;  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$  at 77.2 ppm) or were recorded using tetramethylsilane (TMS) in the solvent of  $\text{DMSO}-d_6$  as the internal standard ( $^1\text{H}$  NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm;  $^{13}\text{C}$  NMR: DMSO at 39.5 ppm).

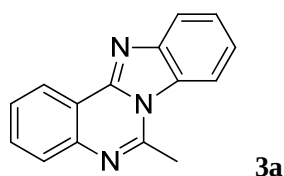
## General procedure for synthesis of compounds 1a-e<sup>1-3</sup>



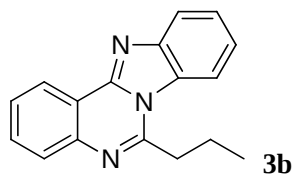
Substituted 2-halobenzoic acid (10 mmol) and substituted 1,2-phenylenediamine (10 mmol) were added to a flask charged with polyphosphoric acid (PPA) (14 g) and a magnetic stirrer, and the mixture was stirred at 150 °C for 10 h. The reaction solution was poured into crushed ice and kept in a refrigerator overnight. The resulting solid precipitate was filtered and added to 1M  $\text{Na}_2\text{CO}_3$  aqueous solution (about 50 mL) till no gas was released, and the mixture was stirred for 30 min. The precipitate was filtered and dried under an infrared lamp, and then purified by column chromatography on silica gel to provide the desired white solid product (Eluent: petroleum ether/ethyl acetate = 2:1). Yield: 60 ~ 80%.

**General procedure for synthesis of compounds 3a-s.** Substituted 2-(2-halophenyl)benzimidazole (**1**, 0.5 mmol), amidine or guanidine hydrochloride (**2**, 0.75 mmol), CuI (0.05 mmol, 10 mg),  $\text{K}_3\text{PO}_4$  (1.5 mmol, 318 mg) were added to a 10 mL two-neck round bottom flask charged with a magnetic stirrer. The flask was evacuated and backfilled with nitrogen, and then solvent (1.5 mL of DMSO and 0.5 mL of  $\text{CH}_2\text{Cl}_2$  for entries 1-17; 2 mL of DMSO for others in Table 2) was added to the flask under a stream of nitrogen. The mixture was stirred at room temperature (entries 1-17 in Table 2), 100 °C (entries 18-23 in Table 2) or 80 °C (entries 24 and 25

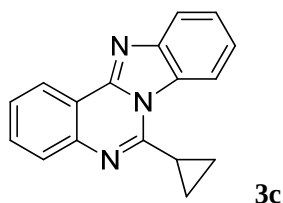
in Table 2) under nitrogen atmosphere for 16 ~ 26 h. After completion of the reaction, the mixture was filtered, and the residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 3 mL). The combined filtrate was concentrated with the aid of a rotary evaporator, and the residue was purified by column chromatography on silica gel to provide the desired product (**3a-s**).



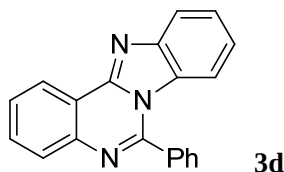
**6-Methylbenzo[4,5]imidazo[1,2-c]quinazoline (3a).**<sup>4</sup> Eluent: petroleum ether/ethyl acetate (3:1). Yield: 111 mg (95%) using 2-(2-bromophenyl)-1*H*-benzo[*d*]imidazole as the substrate; 93 mg (80%) using 2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole as the substrate. White solid, mp 175-177 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.64-8.59 (dd, 1H, *J* = 7.9, 1.4 Hz), 7.95 (t, 2H, *J* = 8.6 Hz), 7.83 (d, 1H, *J* = 7.9 Hz), 7.76-7.68 (m, 1H), 7.64-7.56 (m, 1H), 7.54-7.46 (m, 1H), 7.41-7.33 (m, 1H), 3.12 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 147.7, 144.4, 142.3, 131.7, 129.4, 127.7, 127.4, 125.6, 124.1, 123.0, 120.2, 118.1, 114.0, 24.1. [M+H]<sup>+</sup> *m/z* 234.0.



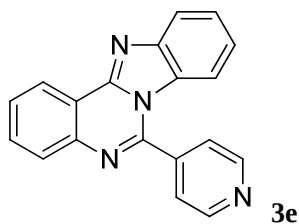
**6-Propylbenzo[4,5]imidazo[1,2-c]quinazoline (3b).**<sup>4</sup> Eluent: petroleum ether/ethyl acetate (5:1). Yield: 114 mg (87%) using 2-(2-bromophenyl)-1*H*-benzo[*d*]imidazole as the substrate; 100 mg (76%) using 2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole as the substrate. White solid, mp 110-111 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.56 (d, 1H, *J* = 7.9 Hz), 7.91 (d, 1H, *J* = 8.3 Hz), 7.78 (t, 2H, *J* = 7.2 Hz), 7.65 (t, 1H, *J* = 7.2 Hz), 7.53 (t, 1H, *J* = 7.6 Hz), 7.43 (t, 1H, *J* = 7.2 Hz), 7.30 (t, 1H, *J* = 7.6 Hz), 3.22 (t, 2H, *J* = 7.6 Hz), 2.08-1.93 (m, 2H), 1.17 (t, 3H, *J* = 7.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 150.5, 147.8, 144.3, 142.1, 131.5, 128.8, 127.5, 125.3, 124.0, 122.9, 120.1, 118.0, 114.2, 37.7, 19.2, 13.9. [M+H]<sup>+</sup> *m/z* 262.1.



**6-Cyclopropylbenzo[4,5]imidazo[1,2-c]quinazoline (3c).** Eluent: petroleum ether/ethyl acetate (5:1). Yield: 112.5 mg (87%) using 2-(2-bromophenyl)-1*H*-benzo[*d*]imidazole as the substrate; 80 mg (62%) using 2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole as the substrate. White solid, mp 166-167 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.65 (d, 1H, *J* = 7.9 Hz), 8.31 (d, 1H, *J* = 8.3 Hz), 8.03 (d, 1H, *J* = 7.9 Hz), 7.83 (d, 1H, *J* = 8.3 Hz), 7.71 (t, 1H, *J* = 7.2 Hz), 7.62-7.52 (m, 2H), 7.43 (t, 1H, *J* = 7.9 Hz), 2.78-2.66 (m, 1H), 1.58-1.46 (m, 2H), 1.40-1.28 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 150.9, 148.0, 144.5, 142.3, 131.6, 129.4, 127.6, 127.5, 125.5, 124.1, 122.9, 120.1, 118.2, 114.7, 16.1, 7.9. [M+H]<sup>+</sup> *m/z* 260.1.

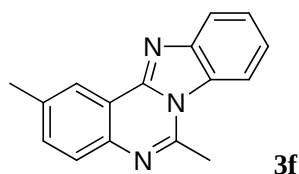


**6-Phenylbenzo[4,5]imidazo[1,2-c]quinazoline (3d).**<sup>4</sup> Eluent: petroleum ether/ethyl acetate (5:1). Yield: 127 mg (86%) using 2-(2-bromophenyl)-1*H*-benzo[*d*]imidazole as the substrate; 68 mg (46%) using 2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole as the substrate. White solid, mp 247-249 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.75-8.69 (dd, 1H, *J* = 7.9, 1.4 Hz), 8.00-7.92 (m, 2H), 7.80-7.60 (m, 7H), 7.48-7.38 (m, 1H), 7.12-7.02 (m, 1H), 6.59 (d, 1H, *J* = 8.3 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 148.6, 148.1, 144.4, 142.4, 134.3, 131.9, 131.1, 129.4, 128.5, 128.4, 128.3, 125.7, 124.3, 122.6, 120.0, 118.5, 114.4. ESIMS [M+H]<sup>+</sup> *m/z* 296.1.

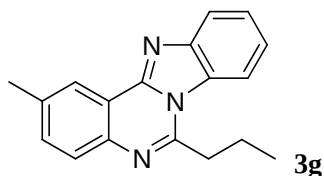


**6-(Pyridin-4-yl)benzo[4,5]imidazo[1,2-c]quinazoline (3e).** Eluent: petroleum ether/ethyl acetate (1:1). Yield: 110 mg (74%) using

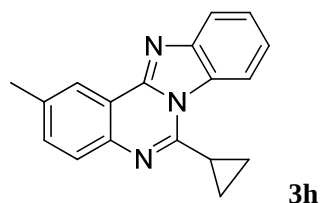
2-(2-bromophenyl)-1*H*-benzo[*d*]imidazole as the substrate; 79 mg (53%) using 2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole as the substrate. White solid, mp 253-255 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 9.00-8.95 (m, 2H), 8.77-8.71 (dd, 1H, *J* = 7.9, 1.4 Hz), 7.95-7.02 (m, 2H), 7.85-7.68 (m, 4H), 7.53-7.45 (m, 1H), 7.20-7.12 (m, 1H), 6.72 (d, 1H, *J* = 8.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 151.1, 147.8, 145.9, 144.5, 142.1, 141.8, 132.2, 129.0, 128.7, 128.4, 126.1, 124.4, 123.0, 122.9, 120.4, 118.6, 113.9. [M+H]<sup>+</sup> *m/z* 297.2.



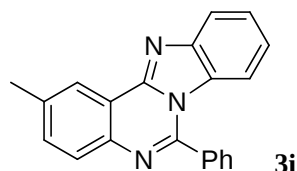
**2,6-Dimethylbenzo[4,5]imidazo[1,2-*c*]quinazoline (3f).** Eluent: petroleum ether/ethyl acetate (3:1). Yield: 104 mg (84%). White solid, mp 173-175 °C. <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300 MHz): δ 8.39 (s, 1H), 8.00-7.88 (m, 2H), 7.70 (d, 1H, *J* = 8.3 Hz), 7.56-7.30 (m, 3H), 3.08 (s, 3H), 2.53 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 147.7, 146.8, 144.3, 140.3, 137.9, 133.2, 129.4, 127.1, 125.4, 123.6, 122.8, 120.1, 117.7, 114.0, 24.1, 21.6. [M+H]<sup>+</sup> *m/z* 248.1.



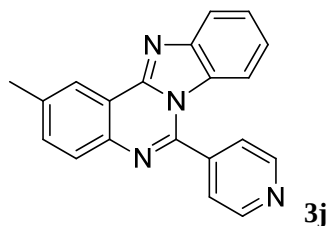
**2-Methyl-6-propylbenzo[4,5]imidazo[1,2-*c*]quinazoline (3g).** Eluent: petroleum ether/ethyl acetate (5:1). Yield: 106 mg (77%). White solid, mp 175-177 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.36 (s, 1H), 7.92 (d, 1H, *J* = 7.9 Hz), 7.80 (d, 1H, *J* = 8.6 Hz), 7.69 (d, 1H, *J* = 8.3 Hz), 7.50-7.42 (m, 2H), 7.37-7.29 (m, 1H), 3.23 (t, 2H, *J* = 7.6 Hz), 2.50 (s, 3H), 2.08-1.94 (m, 2H), 1.18 (t, 3H, *J* = 7.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 149.7, 147.9, 144.3, 140.2, 137.8, 133.0, 129.0, 127.3, 125.3, 123.6, 122.8, 120.1, 117.7, 114.2, 37.7, 21.5, 19.3, 13.9. [M+H]<sup>+</sup> *m/z* 276.1.



**6-Cyclopropyl-2-methylbenzo[4,5]imidazo[1,2-c]quinazoline (3h).** Eluent: petroleum ether/ethyl acetate (5:1). Yield: 83 mg (61%). White solid, mp 173-174 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.36 (s, 1H), 8.19 (d, 1H, *J* = 8.3 Hz), 7.95 (d, 1H, *J* = 8.3 Hz), 7.63 (d, 1H, *J* = 8.6 Hz), 7.51-7.29 (m, 3H), 2.63-2.53 (m, 1H), 2.48 (s, 3H), 1.48-1.40 (m, 2H), 1.29-1.21 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 150.0, 147.9, 144.4, 140.3, 137.7, 133.0, 129.4, 127.3, 125.3, 123.6, 122.6, 119.9, 117.8, 114.6, 21.5, 16.1, 7.8. [M+H]<sup>+</sup> *m/z* 274.1.

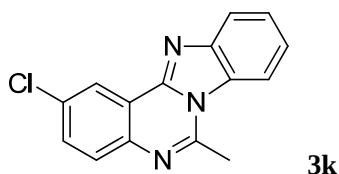


**2-Methyl-6-phenylbenzo[4,5]imidazo[1,2-c]quinazoline (3i).** Eluent: petroleum ether/ethyl acetate (5:1). Yield: 106 mg (69%). White solid, mp 251-253 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.55 (s, 1H), 7.97 (d, 1H, *J* = 7.9 Hz), 7.88 (d, 1H, *J* = 8.3 Hz), 7.78-7.56 (m, 6H), 7.44 (t, 1H, *J* = 8.1 Hz), 7.09 (t, 1H, *J* = 8.3 Hz), 6.60 (d, 1H, *J* = 8.3 Hz), 2.60 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): δ 148.1, 147.8, 144.5, 140.5, 138.8, 134.5, 133.4, 131.0, 129.4, 128.5, 128.1, 125.6, 123.9, 122.5, 120.0, 118.2, 114.4, 21.7. [M+H]<sup>+</sup> *m/z* 310.1.

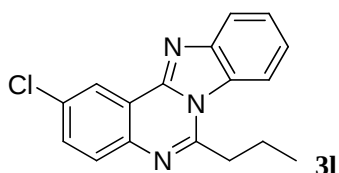


**2-Methyl-6-(pyridin-4-yl)benzo[4,5]imidazo[1,2-c]quinazoline (3j).** Eluent: petroleum ether/ethyl acetate (1:1). Yield: 102 mg (66%). White solid, mp 243-245 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.97 (s, 2H), 8.51 (s, 1H), 7.96 (d, 1H, *J* = 8.3 Hz), 7.84 (d, 1H, *J* = 8.3 Hz), 7.71 (d, 2H, *J* = 5.2 Hz), 7.59 (d, 1H, *J* = 8.3 Hz), 7.46 (t, 1H, *J* = 7.6 Hz), 7.13 (t, 1H, *J* = 7.9 Hz), 6.71 (d, 1H, *J* = 8.6 Hz), 2.60 (s, 3H). <sup>13</sup>C NMR

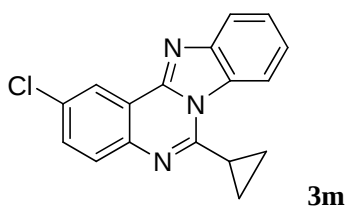
(CDCl<sub>3</sub>, 300 MHz):  $\delta$  151.0, 147.8, 145.0, 144.4, 141.9, 140.1, 139.5, 133.6, 128.7, 128.1, 125.9, 123.9, 123.0, 122.8, 120.3, 118.2, 113.9, 21.8. [M+H]<sup>+</sup> m/z 311.2.



**2-Chloro-6-methylbenzo[4,5]imidazo[1,2-c]quinazoline (3k).** Eluent: petroleum ether/ethyl acetate (3:1). Yield: 107 mg (80%). White solid, mp 209-210 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.48 (d, 1H, *J* = 2.1 Hz), 7.93-7.83 (m, 2H), 7.68 (d, 1H, *J* = 8.6 Hz), 7.60-7.53 (dd, 1H, *J* = 8.6, 2.1 Hz), 7.48 (t, 1H, *J* = 7.6 Hz), 7.35 (t, 1H, *J* = 7.9 Hz), 3.05 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  147.8, 146.3, 144.2, 140.5, 133.3, 132.0, 129.2, 128.9, 125.7, 123.4, 120.3, 119.0, 114.0, 24.0. [M+H]<sup>+</sup> m/z 294.2.

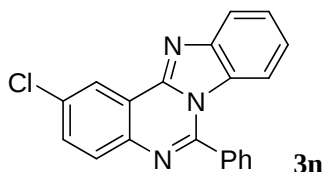


**2-Chloro-6-propylbenzo[4,5]imidazo[1,2-c]quinazoline (3l).** Eluent: petroleum ether/ethyl acetate (5:1). Yield: 99 mg (67%). White solid, mp 156-158 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.48 (s, 1H), 7.95-7.31 (m, 6H), 3.31-3.15 (m, 2H), 2.11-1.94 (m, 2H), 1.19 (t, 3H, *J* = 7.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  150.7, 146.6, 144.2, 140.4, 133.2, 131.9, 129.1, 128.8, 125.6, 123.4, 120.3, 119.0, 114.3, 37.7, 19.1, 13.9. [M+H]<sup>+</sup> m/z 296.2.

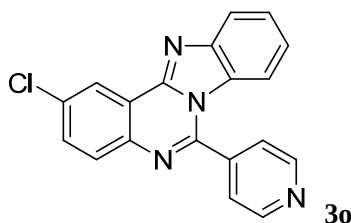


**2-Chloro-6-cyclopropylbenzo[4,5]imidazo[1,2-c]quinazoline (3m).** Eluent: petroleum ether/ethyl acetate (5:1). Yield: 89 mg (61%). White solid, mp 233-235 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.63 (d, 1H, *J* = 2.1 Hz), 8.32 (d, 1H, *J* = 8.3 Hz), 8.02 (d, 1H, *J* = 8.3 Hz), 7.76 (d, 1H, *J* = 8.6 Hz), 7.68-7.54 (m, 2H), 7.47 (t, 1H, *J* = 7.6 Hz), 2.80-2.66 (m, 1H), 1.57-1.47 (m, 2H), 1.41-1.31 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  151.3, 146.9, 144.5, 140.7, 133.2, 132.0, 129.4, 129.2, 125.8, 123.6, 123.4,

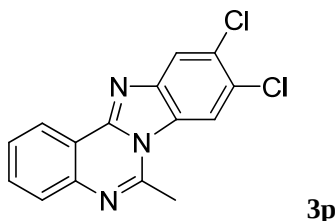
120.4, 119.3, 114.7, 16.1, 8.1.  $[M+H]^+$   $m/z$  268.1.



**2-Chloro-6-phenylbenzo[4,5]imidazo[1,2-c]quinazoline (3n).** Eluent: petroleum ether/ethyl acetate (5:1). Yield: 82 mg (50%). White solid, mp 236-238 °C.  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  8.71 (d, 1H,  $J = 2.4$  Hz), 7.99-7.89 (m, 2H), 7.78-7.64 (m, 6H), 7.51-7.43 (m, 1H), 7.16-7.08 (m, 1H), 6.63 (d, 1H,  $J = 8.6$  Hz).  $^{13}C$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  148.8, 147.0, 144.4, 140.8, 134.1, 132.3, 131.2, 129.8, 128.4, 126.0, 123.7, 123.1, 120.2, 119.6, 114.5.  $[M+H]^+$   $m/z$  330.3.

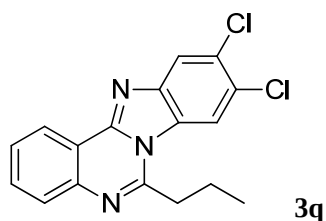


**2-Chloro-6-(pyridin-4-yl)benzo[4,5]imidazo[1,2-c]quinazoline (3o).** Eluent: petroleum ether/ethyl acetate (1:1). Yield: 99 mg (60%). White solid, mp 272-274 °C.  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  8.99 (d, 2H,  $J = 5.9$  Hz), 8.69 (d, 1H,  $J = 2.4$  Hz), 8.02-7.87 (m, 2H), 7.78-7.68 (m, 3H), 7.49 (t, 1H,  $J = 7.6$  Hz), 7.17 (t, 1H,  $J = 7.9$  Hz), 6.73 (d, 1H,  $J = 8.3$  Hz).  $^{13}C$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  151.1, 146.6, 146.0, 144.3, 141.5, 140.4, 134.8, 132.5, 129.9, 128.6, 126.3, 123.7, 123.4, 122.8, 120.5, 119.6, 113.9.  $[M+H]^+$   $m/z$  331.2.

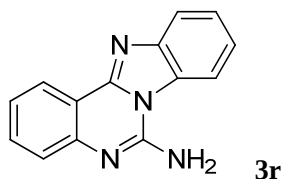


**9,10-Dichloro-6-methylbenzo[4,5]imidazo[1,2-c]quinazoline (3p).** Eluent: petroleum ether/ethyl acetate (3:1). Yield: 95 mg (63%). White solid, mp 269-271 °C.  $^1H$  NMR ( $CDCl_3$ , 600 MHz):  $\delta$  8.63 (d, 1H,  $J = 7.6$  Hz), 8.14 (s, 1H), 8.09 (s, 1H), 7.90 (d, 1H,  $J = 8.2$  Hz), 7.80 (t, 1H,  $J = 8.2$  Hz), 7.67 (t, 1H,  $J = 7.6$  Hz), 3.18 (s, 3H).

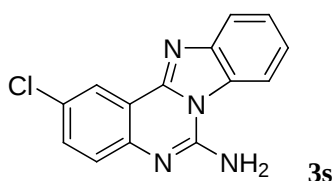
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  149.5, 146.9, 143.9, 142.5, 132.5, 130.0, 128.5, 128.2, 127.7, 127.0, 124.3, 121.2, 117.8, 115.4, 24.0.  $[\text{M}+\text{H}]^+$   $m/z$  303.4.



**9,10-Dichloro-6-propylbenzo[4,5]imidazo[1,2-c]quinazoline (3q).** Eluent: petroleum ether/ethyl acetate (5:1). Yield: 94 mg (57%). White solid, mp 199-201 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.50 (d, 1H,  $J = 7.9$  Hz), 7.96, 7.92 (ss, 2H), 7.84 (d, 1H,  $J = 8.3$  Hz), 7.74 (t, 1H,  $J = 7.2$  Hz), 7.59 (t, 1H,  $J = 7.6$  Hz), 3.23 (t, 2H,  $J = 7.6$  Hz), 2.15-1.99 (m, 2H), 1.24 (t, 3H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  149.7, 149.5, 143.6, 142.2, 132.3, 129.8, 128.0, 127.8, 126.8, 124.2, 121.0, 117.6, 115.6, 37.5, 19.0, 13.9.  $[\text{M}+\text{H}]^+$   $m/z$  331.3.

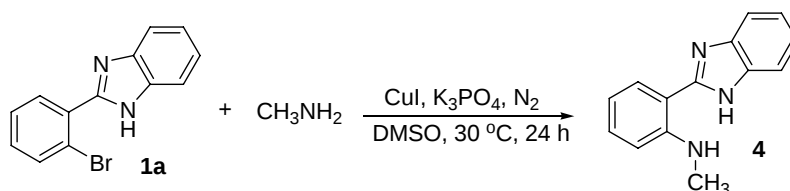


**Benzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3r).**<sup>5</sup> Eluent: petroleum ether/ethyl acetate (1:1). Yield: 87 mg (74%) using 2-(2-bromophenyl)-1H-benzo[d]imidazole as the substrate; 78 mg (67%) using 2-(2-chlorophenyl)-1H-benzo[d]imidazole as the substrate. White solid, mp > 300 °C.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 300 MHz):  $\delta$  8.51-8.38 (m, 2H), 7.94 (d, 1H,  $J = 7.9$  Hz), 7.73-7.35 (m, 7H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ , 300 MHz):  $\delta$  149.0, 147.0, 145.2, 144.4, 132.3, 128.7, 125.6, 124.9, 124.3, 123.7, 122.9, 119.6, 115.2, 114.8.  $[\text{M}+\text{H}]^+$   $m/z$  235.1.



**2-Chlorobenzo[4,5]imidazo[1,2-c]quinazolin-6-amine (3s).** Eluent: petroleum ether/ethyl acetate (1:1). Yield: 87 mg (65%). White solid, mp > 300 °C.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 300 MHz):  $\delta$  8.46 (d, 1H,  $J = 8.3$  Hz), 8.32 (d, 1H,  $J = 2.4$  Hz), 7.93 (d,

1H,  $J = 7.9$  Hz), 7.70-7.44 (m, 6H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 300 MHz):  $\delta$  147.9, 147.3, 144.3, 144.0, 132.3, 128.7, 127.4, 126.9, 125.8, 123.3, 123.1, 119.8, 114.9.  $[\text{M}+\text{H}]^+$   $m/z$  269.3.



**Reaction of 2-(2-bromophenyl)-1H-benzo[d]imidazole (1a) with methylamine.** In order to explore the copper-catalyzed mechanism for synthesis of benzimidazoquinazoline derivatives, we performed reaction of 2-(2-bromophenyl)-1H-benzo[d]imidazole (1a) with methylamine under the standard condition, and the corresponding N-arylation product 4 was obtained. The result implied that the cascade reactions can first undergo N-arylation procedure during synthesis of benzimidazoquinazoline derivatives.

**2-(1H-Benzo[d]imidazol-2-yl)-N-methylaniline (4).** Eluent: petroleum ether/ethyl acetate (2:1). Yield: 53 mg (47%). White solid, mp 212-214 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ , 600 MHz):  $\delta$  12.75 (s, 1H), 9.01 (s, 1H), 7.92 (d, 1H,  $J = 8.3$  Hz), 7.74-7.48 (m, 2H), 7.34-7.16 (m, 3H), 6.79-6.70 (m, 2H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 600 MHz):  $\delta$  152.9, 149.1, 143.2, 134.0, 132.6, 131.6, 130.9, 127.9, 123.0, 122.1, 118.7, 115.0, 111.0, 29.9.  $[\text{M}+\text{H}]^+$   $m/z$  224.6.

## References

- 1 K. Rajender Reddy, G. Gopi Krishna. *Tetrahedron Lett.*, 2005, **46**, 661-663.
- 2 B. Das, B. S. Kanth, K. R. Reddy, A. S. Kumar. *J. Heterocyclic Chem.*, 2008, **45**, 1499-1502.
- 3 D. Saha, A. Saha, B. C. Ranu. *Green Chem.* 2009, **11**, 733-737.
- 4 M. S. Khajavi, K. Rad-Moghadam, H. Hazarkhani. *Synth. Commun.*, 1999, **29**, 2617-2624.
- 5 J. A. Bleda, P. M. Fresneda, R. Orenes, P. Molina, *Eur. J. Org. Chem.*, 2009, **15**, 2490-2504.

