

## Supporting Information

### KI-Catalyzed oxidative cyclization of $\alpha$ -keto acids and 2-hydrazinopyridines: Efficient one-pot synthesis of 1,2,4-triazolo[4,3-*a*]pyridines

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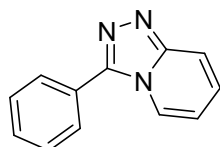
## 1. General Experimental Information.

All solvents and reagents were obtained from commercial sources and used without further purification.  $^1\text{H}$  NMR spectra obtained with tetramethylsilane (TMS,  $\delta = 0$  ppm) as internal standard in  $\text{CDCl}_3$  using a Agilent DD2 400-MR spectrometer (400 MHz). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant (J) and integration.  $^{13}\text{C}$  NMR spectra were recorded on Agilent DD2 400-MR spectrometer (100 MHz). The chemical shifts were determined in the  $\delta$ -scale relative to  $\text{CDCl}_3$  ( $\delta = 77.0$  ppm). HR MS were recorded on an AB SCIEX TOFTM 4600 MS equipped with an electrospray ionization (ESI) probe operating in positive ion mode. Silica gel (200–300 mesh) was used for column chromatographic separations and purifications. Petroleum ether (PE) refers to the fraction boiling at 60–90 °C.

## 2. Experimental Procedures

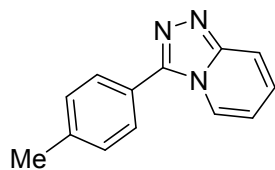
A sealed tube was charged with  $\alpha$ -keto acids **1** (0.5 mmol) and 2-hydrazine pyridines **2** (0.5 mmol), KI (0.1 mmol),  $\text{Na}_2\text{CO}_3$  (1 mmol), 1,4-dioxane (2 mL), and then TBHP (1 mmol) was added. The reaction mixture was stirred at 130 °C for 12 h. Then the mixture was cooled to room temperature, 20 mL water was added to the mixture, which was extracted with ethyl acetate ( $3 \times 10$  mL). The organic layer was combined and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent under reduced pressure, the residue was separated by flash column chromatography to afford the pure product **4** (PE : EA = 1 : 1).

## 3. Characterization Data for the Products

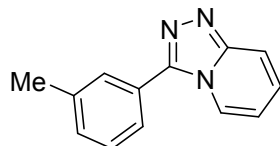


**3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (4a).** Light yellow solid (80 mg, 82% yield). mp 170–171 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.56 (d,  $J = 7.0$  Hz, 1H), 7.91 (d,  $J = 6.5$  Hz, 2H), 7.81 (d,  $J = 9.3$  Hz, 1H), 7.59–7.65 (m, 3H), 7.41–7.45 (m, 1H), 7.02 (t,  $J = 6.7$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.0, 146.0, 129.9, 129.2, 128.0, 127.9, 126.6, 123.8, 115.6, 114.4. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_3$  [ $\text{M} + \text{H}$ ] $^+$

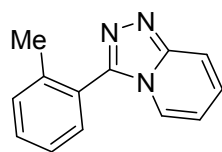
196.0869, found: 196.0868.



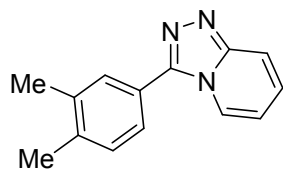
**3-(p-tolyl)-[1,2,4]triazolo[4,3-a]pyridine (4b).** Light yellow solid (75 mg, 72% yield). mp 160-161 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.26 (d, *J* = 7.1 Hz, 1H), 7.82 (d, *J* = 9.3 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.24-7.29 (m, 2H), 6.85 (t, *J* = 6.4 Hz, 1H), 2.47 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 140.6, 130.1, 128.3, 127.0, 124.0, 123.9, 122.8, 117.0, 114.2, 110.2, 21.7. HRMS (ESI): *m/z* calcd for C<sub>13</sub>H<sub>12</sub>N<sub>3</sub> [M + H]<sup>+</sup> 210.1026, found: 210.1025.



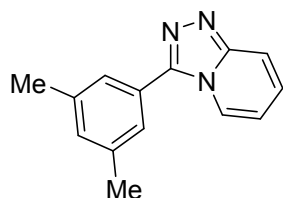
**3-(m-tolyl)-[1,2,4]triazolo[4,3-a]pyridine (4c).** Light yellow solid (73 mg, 70% yield). mp 52-53 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.21 (d, *J* = 7.1 Hz, 1H), 7.70 (d, *J* = 9.3 Hz, 1H), 7.57 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.17-7.22 (m, 1H), 6.79 (t, *J* = 7.3 Hz, 1H), 2.37 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.4, 146.8, 139.2, 130.9, 129.1, 128.9, 127.1, 126.4, 125.0, 122.7, 116.5, 114.2, 21.4. HRMS (ESI): *m/z* calcd for C<sub>13</sub>H<sub>12</sub>N<sub>3</sub> [M + H]<sup>+</sup> 210.1026, found: 210.1030.



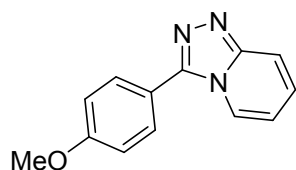
**3-(o-tolyl)-[1,2,4]triazolo[4,3-a]pyridine (4d).** Light brown solid (42 mg, 40% yield). mp 132-135 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.74 (t, *J* = 7.9 Hz, 1H), 7.34-7.40 (m, 3H), 7.28-7.32 (m, 1H), 7.21-7.26 (m, 1H), 6.78 (t, *J* = 6.8 Hz, 1H), 2.20 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 149.9, 146.3, 138.6, 131.1, 130.5, 130.2, 127.1, 126.3, 125.6, 122.7, 116.5, 114.0, 19.7. HRMS (ESI): *m/z* calcd for C<sub>13</sub>H<sub>12</sub>N<sub>3</sub> [M + H]<sup>+</sup> 210.1026, found: 210.1024.



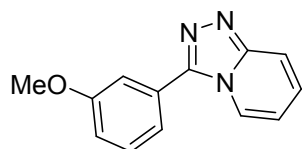
**3-(3,4-dimethylphenyl)-[1,2,4]triazolo[4,3-a]pyridine (4e).** Brown solid (93 mg, 83% yield). mp 131-133 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.28 (d, *J* = 7.1 Hz, 1H), 7.82 (d, *J* = 9.3 Hz, 1H), 7.41 (s, 1H), 7.32-7.35 (m, 1H), 7.25-7.29 (m, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.85 (t, *J* = 7.3 Hz, 1H), 3.97 (s, 3H), 3.97 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.8, 150.0, 146.9, 144.2, 127.0, 122.8, 120.5, 119.4, 117.1, 114.2, 112.1, 111.5, 56.3, 56.2. HRMS (ESI): *m/z* calcd for C<sub>14</sub>H<sub>14</sub>N<sub>3</sub> [M + H]<sup>+</sup> 224.1182, found: 224.1180.



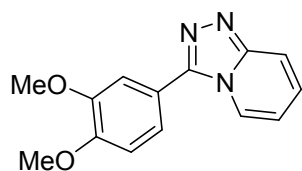
**3-(3,5-dimethylphenyl)-[1,2,4]triazolo[4,3-a]pyridine (4f).** Brown solid (84 mg, 75% yield). mp 160-161 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.27 (d, *J* = 7.1 Hz, 1H), 7.79 (d, *J* = 9.3 Hz, 1H), 7.42 (s, 2H), 7.23-7.27 (m, 1H), 7.16 (s, 1H), 6.84 (t, *J* = 7.3 Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.6, 147.2, 139.2, 132.0, 127.0, 126.6, 126.0, 122.9, 116.9, 114.1, 21.4. HRMS (ESI): *m/z* calcd for C<sub>14</sub>H<sub>14</sub>N<sub>3</sub> [M + H]<sup>+</sup> 224.1182, found: 224.1182.



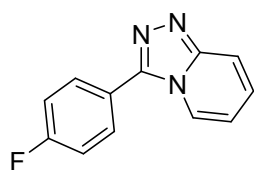
**3-(4-methoxyphenyl)-[1,2,4]triazolo[4,3-a]pyridine (4g).** Brown solid (77 mg, 68% yield). mp 114-116 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.22 (d, *J* = 7.1 Hz, 1H), 7.74-7.81 (m, 3H), 7.23-7.27 (m, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 3.89 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.2, 150.5, 146.8, 129.9, 127.0, 122.7, 119.0, 117.0, 114.9, 114.1, 55.6. HRMS (ESI): *m/z* calcd for C<sub>13</sub>H<sub>12</sub>N<sub>3</sub>O [M + H]<sup>+</sup> 226.0975, found: 226.0972.



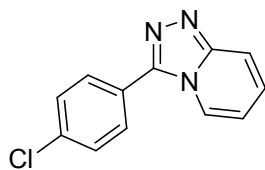
**3-(3-methoxyphenyl)-[1,2,4]triazolo[4,3-a]pyridine (4h).** Brown solid (73 mg, 65% yield). mp 58-59 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.29 (d, *J* = 7.0 Hz, 1H), 7.79 (d, *J* = 9.3 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.04-7.07 (m, 1H), 6.85 (t, *J* = 6.7 Hz, 1H), 3.86 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.4, 150.6, 146.7, 130.4, 127.9, 127.2, 122.9, 120.2, 116.9, 116.4, 114.3, 113.9, 55.6. HRMS (ESI): *m/z* calcd for C<sub>13</sub>H<sub>12</sub>N<sub>3</sub>O [M + H]<sup>+</sup> 226.0975, found: 226.0974.



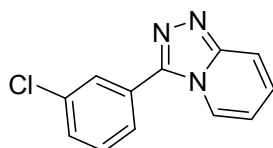
**3-(3,4-dimethoxyphenyl)-[1,2,4]triazolo[4,3-a]pyridine (4i).** Brown solid (79 mg, 62% yield). mp 149-150 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.28 (d, *J* = 7.1 Hz, 1H), 7.82 (d, *J* = 9.3 Hz, 1H), 7.40 (s, 1H), 7.31-7.334 (m, 1H), 7.25-7.29 (m, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.86 (t, *J* = 7.3 Hz, 1H), 3.97 (s, 3H), 3.96 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.9, 150.0, 127.2, 122.8, 120.5, 119.2, 117.0, 114.3, 112.1, 111.5, 56.3, 56.2. HRMS (ESI): *m/z* calcd for C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub> [M + H]<sup>+</sup> 256.1081, found: 256.1081.



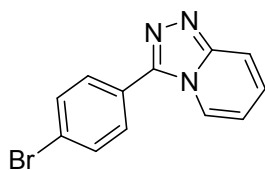
**3-(4-fluorophenyl)-[1,2,4]triazolo[4,3-a]pyridine (4j).** Light brown solid (54 mg, 51% yield). mp 159-162 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.21 (d, *J* = 7.0 Hz, 1H), 7.78-7.82 (m, 3H), 7.23-7.29 (m, 3H), 6.87 (t, *J* = 7.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.1, 162.6, 150.6, 146.0, 130.4, 128.8 (d, *J*<sub>C-F</sub> = 326.9 Hz), 122.9 (d, *J*<sub>C-F</sub> = 3.4 Hz), 122.5, 116.8, 116.6, 115.7 (d, *J*<sub>C-F</sub> = 248.3 Hz). HRMS (ESI): *m/z* calcd for C<sub>12</sub>H<sub>9</sub>FN<sub>3</sub> [M + H]<sup>+</sup> 214.0775, found: 214.0779.



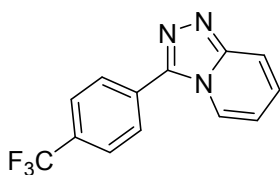
**3-(4-chlorophenyl)-[1,2,4]triazolo[4,3-a]pyridine (4k).** Light brown solid (64 mg, 56% yield). mp 201-202 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.24 (d, *J* = 7.1 Hz, 1H), 7.85 (d, *J* = 9.3 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.28-7.32 (m, 1H), 6.90 (t, *J* = 6.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.8, 145.9, 136.6, 129.8, 129.6, 127.3, 125.3, 122.5, 117.2, 114.6. HRMS (ESI): *m/z* calcd for C<sub>12</sub>H<sub>9</sub>ClN<sub>3</sub> [M + H]<sup>+</sup> 230.0480, found: 230.0477.



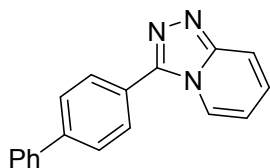
**3-(3-chlorophenyl)-[1,2,4]triazolo[4,3-a]pyridine (4l).** Light yellow solid (60 mg, 52% yield). mp 159-161 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.26 (d, *J* = 7.1 Hz, 1H), 7.80 (d, *J* = 9.3 Hz, 2H), 7.69-7.72 (m, 1H), 7.49-7.50 (m, 2H), 7.27-7.31 (m, 1H), 6.90 (t, *J* = 7.3 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.8, 145.5, 135.4, 130.7, 130.4, 128.5, 128.3, 127.4, 126.3, 122.5, 117.0, 114.7. HRMS (ESI): *m/z* calcd for C<sub>12</sub>H<sub>9</sub>ClN<sub>3</sub> [M + H]<sup>+</sup> 230.0480, found: 230.0476.



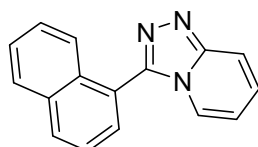
**3-(4-bromophenyl)-[1,2,4]triazolo[4,3-a]pyridine (4m).** Brown solid (93 mg, 68% yield). mp 198-200 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.24 (d, *J* = 7.1 Hz, 1H), 7.85 (d, *J* = 9.3 Hz, 1H), 7.73 (s, 4H), 7.28-7.33 (m, 1H), 6.90 (t, *J* = 7.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 132.8, 129.8, 127.3, 125.8, 124.8, 122.5, 117.2, 114.7. HRMS (ESI): *m/z* calcd for C<sub>12</sub>H<sub>8</sub>BrN<sub>3</sub>Na [M + Na]<sup>+</sup> 295.9794, found: 295.9794.



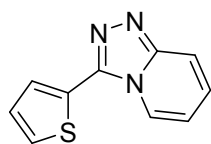
**3-(4-(trifluoromethyl)phenyl)-[1,2,4]triazolo[4,3-a]pyridine (4n).** Brown solid (55 mg, 42% yield). mp 215-218 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.30 (d, *J* = 7.1 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 2H), 7.87 (t, *J* = 7.7 Hz, 3H), 7.31-7.36 (m, 1H), 6.94 (t, *J* = 7.3 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 151.0, 146.6, 132.2 (d, *J*<sub>C-F</sub> = 32.9 Hz), 130.4, 128.6, 127.6, 126.5 (q, *J*<sub>C-F</sub> = 38 Hz), 125.2, 122.5, 117.2, 115.0. HRMS (ESI): *m/z* calcd for C<sub>13</sub>H<sub>9</sub>F<sub>3</sub>N<sub>3</sub> [M + H]<sup>+</sup> 246.0743, found: 246.0743.



**3-([1,1'-biphenyl]-4-yl)-[1,2,4]triazolo[4,3-a]pyridine (4o).** Brown solid (96 mg, 71% yield). mp 158-160 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.33 (d, *J* = 7.1 Hz, 1H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.81 (t, *J* = 10.5 Hz, 3H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.26-7.30 (m, 1H), 6.88 (t, *J* = 7.3 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.7, 146.7, 143.1, 140.1, 129.1, 128.7, 128.1, 128.0, 127.2, 127.1, 125.6, 122.8, 117.0, 114.4. HRMS (ESI): *m/z* calcd for C<sub>18</sub>H<sub>14</sub>N<sub>3</sub> [M + H]<sup>+</sup> 272.1182, found: 272.1184.

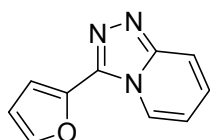


**3-(naphthalen-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (4p).** Brown oil (53 mg, 43% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 9.3 Hz, 1H), 7.74 (d, *J* = 7.0 Hz, 2H), 7.59-7.67 (m, 2H), 7.54 (t, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 8.3 Hz, 1H), 7.26-7.30 (m, 1H), 6.75 (t, *J* = 7.3 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.4, 145.8, 134.0, 131.6, 131.2, 129.1, 128.8, 127.6, 127.4, 126.8, 125.4, 125.1, 123.6, 123.1, 116.7, 114.0. HRMS (ESI): *m/z* calcd for C<sub>16</sub>H<sub>12</sub>N<sub>3</sub> [M + H]<sup>+</sup> 246.1026, found: 246.1027.

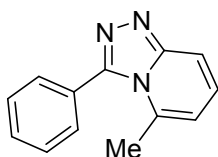


**3-(thiophen-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (4q).** Brown solid (49 mg, 49%

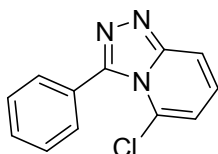
yield). mp 152-154 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.39 (d, *J* = 7.1 Hz, 1H), 7.84 (d, *J* = 9.3 Hz, 1H), 7.66-7.67 (m, 1H), 7.56-7.58 (m, 1H), 7.25-7.32 (m, 2H), 6.94 (t, *J* = 7.3 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 128.2, 128.1, 127.7, 127.3, 127.2, 126.3, 122.9, 117.1, 115.6, 114.7. HRMS (ESI): *m/z* calcd for C<sub>10</sub>H<sub>8</sub>N<sub>3</sub>S [M + H]<sup>+</sup> 202.0433, found: 202.0432.



**3-(furan-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (4r).** Brown solid (60 mg, 65% yield). mp 99-100 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.73 (d, *J* = 7.1 Hz, 1H), 7.81 (d, *J* = 9.3 Hz, 1H), 7.66-7.67 (m, 1H), 7.25-7.31 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.64-6.65 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.1, 143.6, 143.1, 127.4, 124.4, 116.8, 114.6, 112.2, 111.2. HRMS (ESI): *m/z* calcd for C<sub>10</sub>H<sub>8</sub>N<sub>3</sub>O [M + H]<sup>+</sup> 186.0662, found: 186.0659.



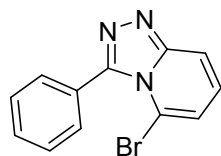
**5-methyl-3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (4t).** Yellow solid (37 mg, 35% yield). mp 145-147 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.69 (d, *J* = 9.3 Hz, 1H), 7.52-7.56 (m, 3H), 7.45-7.49 (m, 2H), 7.15-7.19 (m, 1H), 6.52 (d, *J* = 6.6 Hz, 1H), 2.17 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 151.5, 147.4, 135.0, 131.2, 130.2, 129.7, 128.0, 127.5, 114.8, 114.6, 21.0. HRMS (ESI): *m/z* calcd for C<sub>13</sub>H<sub>12</sub>N<sub>3</sub> [M + H]<sup>+</sup> 210.1026, found: 210.1023.



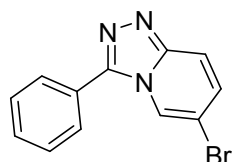
**5-chloro-3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (4u).** Light brown solid (85 mg, 74% yield). mp 144-146 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.80 (d, *J* = 9.2 Hz, 1H), 7.60 (d, *J* = 6.8 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45-7.51 (m, 2H), 7.21-7.26 (m, 1H), 6.85-6.87 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 151.9, 147.6, 131.5, 130.2, 128.5,



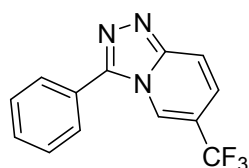
127.8, 127.6, 126.0, 115.7, 115.2. HRMS (ESI):  $m/z$  calcd for  $C_{12}H_9ClN_3$   $[M + H]^+$  230.0480, found: 230.0479.



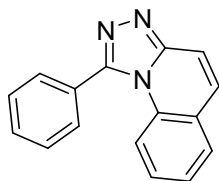
**5-bromo-3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (4v).** Brown solid (78 mg, 58% yield). mp 151-153 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.84 (d,  $J = 9.1$  Hz, 1H), 7.53-7.59 (m, 3H), 7.47 (t,  $J = 7.3$  Hz, 2H), 7.12-7.16 (m, 1H), 7.05 (t,  $J = 8.0$  Hz, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  151.6, 148.3, 131.9, 130.4, 128.4, 127.7, 120.0, 116.2, 112.6, 110.2. HRMS (ESI):  $m/z$  calcd for  $C_{12}H_9BrN_3$   $[M + H]^+$  273.9974, found: 273.9964.



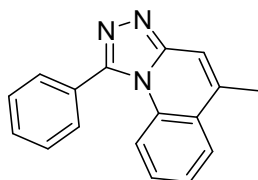
**6-bromo-3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (4w).** Brown solid (93 mg, 68% yield). mp 174-176 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.40 (s, 1H), 7.80 (d,  $J = 6.3$  Hz, 2H), 7.72 (d,  $J = 9.7$  Hz, 1H), 7.56-7.62 (m, 3H), 7.33-7.33 (m, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  149.2, 146.8, 130.9, 130.7, 129.6, 128.4, 126.2, 122.7, 117.6, 109.6. HRMS (ESI):  $m/z$  calcd for  $C_{12}H_9BrN_3$   $[M + H]^+$  273.9974, found: 273.9970.



**3-phenyl-6-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine (4x).** Light yellow solid (66 mg, 50% yield). mp 93-94 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.59 (dd,  $J = 2.6, 1.3$  Hz, 1H), 7.94 (d,  $J = 9.6$  Hz, 1H), 7.81-7.83 (m, 2H), 7.62-7.64 (m, 3H), 7.39-7.42 (m, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  149.1 (d,  $J_{C-F} = 190$  Hz), 131.1, 129.8, 128.5, 125.8, 123.0 (d,  $J_{C-F} = 272$  Hz), 123.1 (q,  $J_{C-F} = 2.4$  Hz), 122.3 (q,  $J_{C-F} = 6.0$  Hz), 119.1 (d,  $J_{C-F} = 34$  Hz), 118.2. HRMS (ESI):  $m/z$  calcd for  $C_{13}H_9F_3N_3$   $[M + H]^+$  264.0743, found: 264.0738.



**1-phenyl-[1,2,4]triazolo[4,3-a]quinoline (4y).** Yellow solid (76 mg, 62% yield). mp 137-138 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 9.2$  Hz, 1H), 7.68-7.71 (m, 3H), 7.53-7.63 (m, 5H), 7.45 (t,  $J = 7.1$ Hz, 1H), 7.33 (t,  $J = 7.9$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.0, 149.2, 132.0, 130.7, 130.1, 129.8, 129.7, 129.4, 129.2, 129.1, 126.3, 124.8, 116.9, 115.3. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_3$   $[\text{M} + \text{H}]^+$  246.1026, found: 246.1024.



**5-methyl-1-phenyl-[1,2,4]triazolo[4,3-a]quinoline (4z).** Yellow solid (91 mg, 70% yield). mp 144-146 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 (d,  $J = 8.1$  Hz, 1H), 7.66-7.68 (m, 2H), 7.58-7.62 (m, 4H), 7.53 (s, 1H), 7.48 (t,  $J = 7.6$  Hz, 1H), 7.33 (t,  $J = 7.2$  Hz, 1H), 2.64 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.8, 148.9, 136.7, 131.9, 130.5, 130.1, 129.9, 129.2, 128.8, 126.1, 126.0, 125.3, 117.1, 114.2, 19.8. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{13}\text{N}_3\text{Na}$   $[\text{M} + \text{Na}]^+$  282.1002, found: 282.0991.

## 4. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

