

## Supporting Information

### **Copper-Catalyzed Intramolecular Dehydrogenative Cyclization: Direct Access to Sensitive Formyl-Substituted imidazo[1,2-*a*]pyridines**

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#### Table of Contents

General Remarks	S2
Experimental Section	S 2-7
NMR Spectra	S 8-37

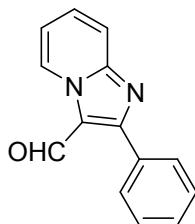
## General remark

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on 400MHz and 100MHz in CDCl<sub>3</sub>. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of their <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are provided. Products were purified by flash chromatography on 200–300 mesh silica gels. All melting points were determined without correction. The 1, 4-dioxane was purified before used. Other commercially available reagents and solvents were used without further purification except.

## Experimental Section

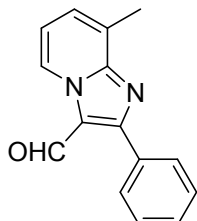
An oven-dried tube was charged with 0.3 mmol of cinnamaldehydes **1**, 0.6 mmol of aminopyridines **2**, CuI (0.03 mmol), ZnCl<sub>2</sub> (0.03 mmol), pyridine (0.03 mmol) and 2 mL DMSO. Then the reaction was stirred at 120 °C under air and the reaction time was monitored by TLC. After cooling to room temperature, the solvent was diluted with 10 ml H<sub>2</sub>O, and extracted with CH<sub>2</sub>Cl<sub>2</sub> 10ml×3, then washed with 10 ml of H<sub>2</sub>O, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then the solvent was evaporated in vacuo, the residues were purified by column chromatography, eluting with petroleum ether/EtOAc to afford the desired pyridines.

### 3-phenylimidazo[1,2-a]pyridine-2-carbaldehyde(3aa)



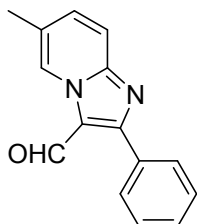
Yellow solid, melting point: 138-140 °C. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>) δ 10.07 (s, 1 H), 9.68-9.66 (d, *J* = 6.8 Hz, 1 H), 7.85-7.80 (m, 3 H), 7.61-7.51 (m, 4 H), 7.15-7.12 (m, 1 H). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>) δ 179.15, 158.25, 147.69, 132.33, 130.32, 129.78, 128.82, 128.75, 120.72, 117.39, 115.21. HRMS(ESI)*m/z* calcd for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 223.0865, found 223.0863.

### 8-methyl-3-phenylimidazo[1,2-a]pyridine-2-carbaldehyde(3ab)



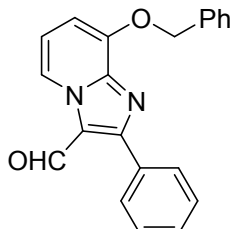
Yellow solid, melting point: 118-120 °C. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>) δ 10.04 (s, 1 H), 9.53-9.51 (d, *J* = 6.8 Hz, 1 H), 7.85-7.83 (m, 2 H), 7.55-7.50 (m, 3 H), 7.39-7.37 (d, *J* = 6.8 Hz, 1 H), 7.06-7.02 (t, *J* = 6.8 Hz, 1 H), 2.73 (s, 3 H). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>) δ 179.63, 157.95, 147.96, 132.67, 129.94, 129.65, 129.35, 128.84, 127.62, 126.49, 115.27, 17.01. HRMS(ESI)*m/z* calcd for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 237.1022, found 237.1020.

### 6-methyl-3-phenylimidazo[1,2-a]pyridine-2-carbaldehyde(3ac)



Yellow oil. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>) δ 10.04 (s, 1 H), 9.49 (s, 1 H), 7.83-7.81 (m, 2 H), 7.72-7.70 (d, 1 H), 7.56-7.50 (m, 3 H), 7.45-7.43 (m, 1 H), 2.45 (s, 3 H). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>) δ 179.47, 158.22, 146.72, 133.26, 132.54, 129.78, 129.70, 128.83, 126.83, 125.47, 120.59, 116.66, 18.34. HRMS(ESI)*m/z* calcd for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 237.1022, found 237.1021.

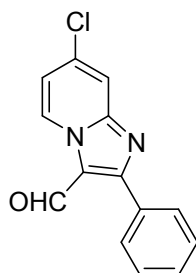
### 8-(benzyloxy)-2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde(3ae)



Yellow solid, melting point: 124-128 °C. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>) δ 10.05 (s, 1 H), 9.26-9.24 (m, 1 H), 7.88-7.85 (m, 2 H), 7.53-7.49 (m, 5 H), 6.94-6.91 (m, 1 H), 6.87-6.85 (m, 1 H), 5.45 (s, 2 H). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>) δ 179.79, 157.35, 147.47, 141.97, 135.75, 132.34, 130.04, 129.64, 128.71, 128.67, 128.23, 127.21, 121.50, 115.15, 109.57, 71.16. HRMS(ESI)*m/z* calcd for C<sub>21</sub>H<sub>16</sub>N

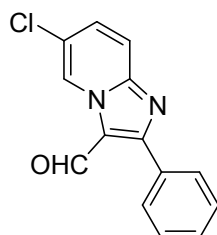
${}^2\text{O}_2[\text{M}+\text{H}]^+$  329.1284, **found** 329.1285.

### 7-chloro-3-phenylimidazo[1,2-a]pyridine-2-carbaldehyde(3af)



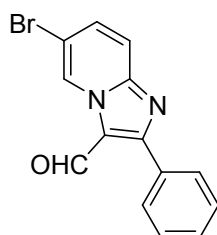
Yellow solid, melting point: 161-163 °C.  ${}^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.05 (s, 1 H), 9.59-9.57 (d,  $J$  = 7.2 Hz, 1 H), 7.83-7.78 (m, 3 H), 7.55-7.53 (m, 3 H), 7.11-7.09 (m, 1 H).  ${}^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.54, 158.84, 147.76, 136.97, 131.92, 130.07, 129.75, 128.94, 120.69, 116.62, 116.55. HRMS(ESI) $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{ClN}_2\text{O}$   $[\text{M}+\text{H}]^+$  257.0475 **found** 257.0477.

### 6-chloro-3-phenylimidazo[1,2-a]pyridine-2-carbaldehyde(3ag)



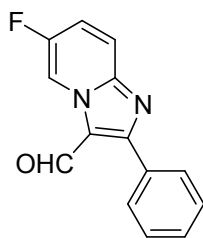
Yellow solid, melting point: 148-150 °C.  ${}^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.08 (s, 1 H), 9.76-9.75 (m, 1 H), 7.83-7.81 (m, 2 H), 7.76-7.74 (m, 1 H), 7.57-7.53 (m, 4 H).  ${}^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.72, 158.40, 146.01, 131.98, 131.55, 130.06, 129.75, 128.98, 126.77, 123.52, 120.84, 117.65. HRMS(ESI) $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{ClN}_2\text{O}$   $[\text{M}+\text{H}]^+$  257.0475 **found** 257.0474.

### 6-bromo-3-phenylimidazo[1,2-a]pyridine-2-carbaldehyde(3ah)



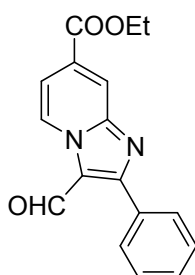
Yellow oil.  ${}^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.07 (s, 1 H), 9.85 (s, 1 H), 7.83-7.81 (m, 2 H), 7.71-7.63 (m, 2 H), 7.56-7.53 (m, 3 H).  ${}^{13}\text{C}$ NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.69, 158.21, 146.12, 133.71, 131.95, 130.05, 129.76, 128.97, 128.88, 120.70, 117.94, 109.97. HRMS(ESI) $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{BrN}_2\text{O}$   $[\text{M}+\text{H}]^+$  300.9971 **found** 300.9973.

### 6-fluoro-3-phenylimidazo[1,2-a]pyridine-2-carbaldehyde(3ai)



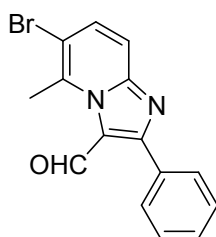
Yellow solid, melting point: 125-128 °C. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>) δ 10.07 (s, 1 H), 9.66 (d, 1 H), 7.82-7.77 (m, 3 H), 7.55-7.49 (m, 4 H). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>) δ 179.65, 158.86, 158.53, 158.50, 155.64, 153.25, 145.14, 129.90, 129.63, 128.90, 121.78, 121.54, 117.69, 117.60, 116.28, 115.86. HRMS(ESI)*m/z* calcd for C<sub>14</sub>H<sub>10</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> 241.0771 found 241.0774.

### ethyl 2-formyl-3-phenylimidazo[1,2-a]pyridine-7-carboxylate(3aj)



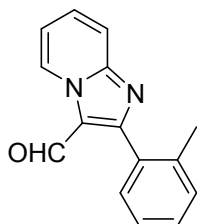
Yellow oil. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>) δ 10.13 (s, 1 H), 9.68-9.66 (m, *J* = 7.2 Hz, 1 H), 8.48 (s, 1 H), 7.86-7.83 (m, 2 H), 7.71-7.69 (m, 1 H), 7.58-7.54 (m, 3 H), 4.49-4.44 (q, *J* = 7.2 Hz, 2 H), 1.47-1.44 (t, *J* = 7.2 Hz, 3 H). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>) δ 179.97, 164.19, 158.93, 146.88, 131.97, 131.65, 130.03, 129.79, 128.94, 128.26, 121.25, 119.27, 114.39, 62.03, 14.17. HRMS(ESI)*m/z* calcd for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 295.1076 found 295.1074.

### 6-bromo-5-methyl-3-phenylimidazo[1,2-a]pyridine-2-carbaldehyde(3ak)



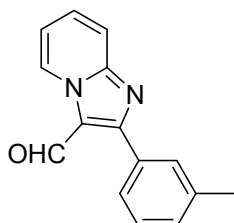
Yellow solid, melting point: 152-156 °C. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>) δ 9.82 (s, 1 H), 7.86-7.84 (m, 2 H), 7.77-7.75 (m, 1 H), 7.54-7.52 (t, 4 H), 3.00 (s, 3 H). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>) δ 178.79, 162.05, 149.21, 139.71, 135.19, 132.32, 130.21, 130.09, 128.80, 123.83, 115.59, 112.48, 23.30. HRMS(ESI)*m/z* calcd for C<sub>15</sub>H<sub>12</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> 315.0127 found 315.0123.

### 3-(*o*-tolyl)imidazo[1,2-a]pyridine-2-carbaldehyde(3ba)



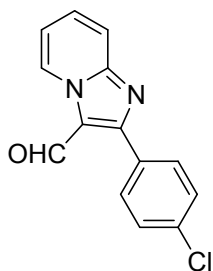
Yellow solid, melting point: 102-106 °C.  $^1\text{H NMR}$ (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.71 (s, 1 H), 9.64-9.62 (d,  $J$  = 6.8 Hz, 1 H), 7.82-7.79 (d, 1 H), 7.61-7.57 (m, 1 H), 7.43-7.27 (m, 4 H), 7.17-7.13 (t,  $J$  = 6.8 Hz, 1 H), 2.41 (s, 3H).  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.42, 159.09, 147.51, 137.53, 131.36, 131.28, 130.72, 130.16, 129.42, 128.51, 125.55, 121.50, 117.42, 115.21, 20.22. **HRMS(ESI) $m/z$  calcd for  $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  237.1022, found 237.1026.**

### 3-(*m*-tolyl)imidazo[1,2-*a*]pyridine-2-carbaldehyde (3ca)



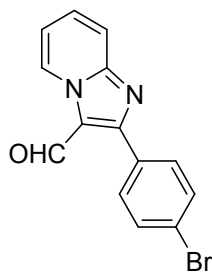
Yellow solid, melting point: 102-104 °C.  $^1\text{H NMR}$ (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.07 (s, 1 H), 9.67-9.65 (d,  $J$  = 6.8 Hz, 1 H), 7.82-7.79 (d,  $J$  = 8.8 Hz, 1 H), 7.68 (s, 1 H), 7.62-7.55 (m, 2 H), 7.44-7.40 (t, 1 H), 7.34-7.32 (d,  $J$  = 7.6 Hz, 1 H), 7.14-7.10 (m, 1 H), 2.46 (s, 3H).  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.65, 158.49, 147.70, 138.71, 132.24, 130.60, 130.34, 130.31, 128.78, 128.70, 127.03, 120.73, 117.38, 115.18, 21.38. **HRMS(ESI) $m/z$  calcd for  $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  237.1022, found 237.1024.**

### 3-(4-chlorophenyl)imidazo[1,2-*a*]pyridine-2-carbaldehyde (3da)



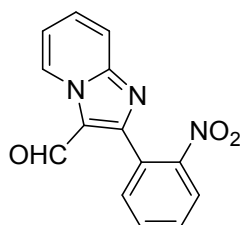
Yellow solid (18.5 mg, 15%), melting point: 130-132 °C.  $^1\text{H NMR}$ (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.05 (s, 1 H), 9.67-9.65 (d,  $J$  = 6.8 Hz, 1 H), 7.82-7.77 (t, 3 H), 7.62-7.58 (m, 1 H), 7.53-7.51 (d,  $J$  = 8.4 Hz, 2 H), 7.16-7.13 (t, 1 H).  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.07, 156.91, 147.74, 136.22, 130.97, 130.87, 130.57, 129.17, 128.82, 120.76, 117.47, 115.45. **HRMS(ESI) $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{ClN}_2\text{O}$   $[\text{M}+\text{H}]^+$  257.0475 found 257.0471.**

### 3-(4-bromophenyl)imidazo[1,2-*a*]pyridine-2-carbaldehyde (3ea)



White solid, melting point: 124-126 °C.  $^1\text{H NMR}$ (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.05 (s, 1 H), 9.67-9.65 (d,  $J$  = 6.8 Hz, 1 H), 7.82-7.80 (d,  $J$  = 8.8 Hz, 1 H), 7.73-7.66 (m, 4 H), 7.62-7.58 (m, 1 H), 7.17-7.13 (m, 1 H).  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.07, 156.95, 147.76, 132.14, 131.33, 131.22, 130.60, 128.83, 124.55, 120.75, 117.49, 115.48. **HRMS(ESI)** $m/z$  calcd for  $\text{C}_{15}\text{H}_{10}\text{BrN}_2\text{O}$   $[\text{M}+\text{H}]^+$  300.9971 **found** 300.9975.

### 3-(2-nitrophenyl)imidazo[1,2-a]pyridine-2-carbaldehyde (3fa)



Yellow solid, melting point: 120-122 °C.  $^1\text{H NMR}$ (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.80 (s, 1 H), 9.60-9.59 (d,  $J$  = 4 Hz, 1 H), 8.10-8.08 (d,  $J$  = 8 Hz, 1 H), 7.79-7.58 (m, 5 H), 7.20-7.16 (m, 1 H).  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.80, 154.16, 149.68, 147.59, 133.04, 132.56, 130.57, 130.48, 128.56, 127.21, 124.82, 121.28, 117.70, 115.77. **HRMS(ESI)** $m/z$  calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_3\text{O}_3$   $[\text{M}+\text{H}]^+$  268.0716, **found** 268.0719.

