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## Supporting Materials

# Heterogeneously Biomimetic Aerobic Synthesis of 3-Iodoimidazo[1,2-*a*]pyridines via CuO<sub>x</sub>/OMS-2-catalyzed Tandem Cyclization/iodination and Their Late-stage Functionalization

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## Experimental

All reagents were purchased from commercial suppliers and used without further purification. Metal salts and catalyst supports were commercially available and were used directly. All experiments were carried out under air. Flash chromatography was carried out with Merck silica gel 60 (200-300 mesh). Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (400 and 100 MHz respectively) spectra were recorded in  $\text{CDCl}_3$ . Chemical shifts ( $\delta$ ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants ( $J$ ) are given in Hz. All heterogeneous catalysts are synthesized by wet impregnation in deionized water and  $\text{Cu}(\text{OH})_x/\text{OMS-2}$  is made by deposition-precipitation in water.

### Preparation of OMS-2<sup>[1]</sup>

5.89g of  $\text{KMnO}_4$  in 100 mL of deionized water was added to a solution of 8.8g of  $\text{MnSO}_4\cdot\text{H}_2\text{O}$  in 30 mL of deionized water and 3 mL concentrated  $\text{HNO}_3$ . The solution was refluxed at 100 °C for 24 h, and the product was filtered, washed, and dried at 120 °C for 8 hours. Finally, the dry OMS-2 was calcined in a muffle furnace at 350 °C for 2 hours. Then, the black powder OMS-2 was obtained.

BET surface area: 158.4870  $\text{m}^2/\text{g}$

Pore volume (BJH Adsorption): 0.5249  $\text{cm}^3/\text{g}$

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Pore size (BJH Adsorption): 127.058 Å

### **Preparation of CuO<sub>x</sub>/OMS-2**

Support OMS-2 (2g) was added to a 50 mL round-bottom flask. A solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.15g) in deionized water (10 mL) was added to OMS-2, and additional deionized water (10 mL) was added to wash down the sides of the flask. Then the flask was submerged into an ultrasound bath for 3h at room temperature and stirred for further 20h at room temperature. After that, the water was distilled under reduced pressure on a rotary evaporator at 80 °C for more than 2h. Finally, the black powder was dried into an oven at 110 °C for 4hour followed by calcination at 350 °C for 2hours. The Inductive Coupled Plasma Optical Emission Spectrum (ICP-OES) showed Cu content is 1.31 wt%.

BET surface area: 127.0775 m<sup>2</sup>/g

Pore volume (BJH Adsorption): 0.4751 cm<sup>3</sup>/g

Pore size (BJH Adsorption): 13.7224 nm

### **General procedure for CuO<sub>x</sub>/OMS-2-catalyzed cyclization/iodination tandem reaction**

CuO<sub>x</sub>/OMS-2 (6 mg, 0.2 mol%), 2-aminopyridine (0.6 mmol), acetophenone (0.5 mmol), I<sub>2</sub> (0.25 mmol) and DCB (1 mL) were added to a flask with a bar. The flask was stirred at 100 °C for 20h under air. After

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cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 4/1 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic analysis. HRMS were provided for all new compounds.

### **Synthesis of 4 via Suzuki Reaction<sup>[7]</sup>**

$\text{Pd}(\text{OAc})_2$  (10 mol%), xanphos (20 mol%),  $\text{K}_3\text{PO}_4$  (2.0 equiv.), 3a (0.5 mmol), phenylboronic acid (0.75 mmol) and toluene (2 mL) were added to a sealed tube. The tube was stirred at 120 °C for 20h under  $\text{N}_2$ . After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 4/1 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic analysis.

### **Synthesis of 4 via direct coupling<sup>[8]</sup>**

$\text{Pd}(\text{OAc})_2$  (5 mol%),  $\text{CuI}$  (10 mol%),  $\text{PPh}_3$  (10 mol%),  $\text{NaOtBu}$  (2.0 equiv.), 3a (0.5 mmol), benzene (5.0 equiv.) and 1,4-dioxane (2 mL) were

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added to a sealed tube. The tube was stirred at 110 °C for 20h under N<sub>2</sub>. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 4/1 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic analysis.

### **Synthesis of 5<sup>[9]</sup>**

AgNO<sub>3</sub>(10 mol%), N,N-DMEDA (10 mol%), KOtBu (2.0 equiv.), 3a (0.6 mmol), 2-aminopyridine (0.5 mmol) and DMSO (2 mL) were added to a sealed tube. The tube was stirred at 160 °C for 24h under N<sub>2</sub>. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 3/2 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic analysis.

### **Synthesis of 6<sup>[10]</sup>**

PdCl<sub>2</sub> (10 mol%), CuI (20 mol%), PPh<sub>3</sub> (20 mol%), 3a (0.5 mmol), phenylacetylene (1.25 mmol) and EtN<sub>3</sub> (2 mL) were added to a sealed

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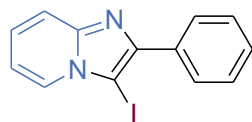
tube. The tube was stirred at 60 °C for 12h under N<sub>2</sub>. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 4/1 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic and HRMS analysis.

### **Synthesis of 7<sup>[11]</sup>**

Pd(OAc)<sub>2</sub> (5 mol%), Nixantphos (10 mol%), KN(SiMe<sub>3</sub>)<sub>2</sub> (3.0 equiv.), 3a (0.5 mmol), toluene (1.5 mmol) and 1,4-dioxane (2 mL) were added to a sealed tube. The tube was stirred at 110 °C for 24h under N<sub>2</sub>. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 4/1 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic analysis.

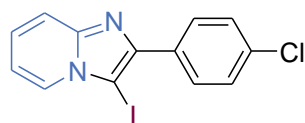
## Spectrum data of the products

### 3-iodo-2-phenylH-imidazo[1,2-a]pyridine (3a)<sup>[2]</sup>



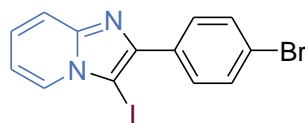
White solid, isolated yield 93%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 8.18(d, 1H, *J* = 6.9 Hz), 7.07(d, 2H, *J* = 7.3 Hz), 7.60(d, 1H, *J* = 9.0 Hz), 7.48(t, 2H, *J* = 7.6 Hz), 7.40(t, 1H, *J* = 7.4 Hz), 7.28-7.24(m, 1H), 6.88(t, 1H, *J* = 6.8 Hz); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 148.1, 148.0, 133.6, 128.6, 128.4, 128.3, 126.6, 125.6, 117.6, 113.2, 59.6.

### 2-(4-chlorophenyl)-3-iodoH-imidazo[1,2-a]pyridine (3b)



White solid, isolated yield 82%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 8.19(d, 1H, *J* = 6.8 Hz), 8.00(d, 2H, *J* = 8.4 Hz), 7.58(d, 1H, *J* = 9.2 Hz), 7.44-7.42(m, 2H), 7.24(t, 1H, *J* = 7.4 Hz), 6.91(t, 1H, *J* = 6.4 Hz); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 148.1, 146.9, 134.3, 132.1, 129.7, 128.6, 126.5, 125.8, 117.6, 113.3, 59.5. HRMS (ESI) *m/z*: Found: 354.9482. Calcd for C<sub>13</sub>H<sub>8</sub>ClIN<sub>2</sub>: (M+H)<sup>+</sup> 354.9493.

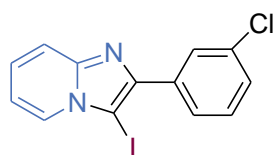
### 2-(4-bromophenyl)-3-iodoH-imidazo[1,2-a]pyridine (3c)



White solid, isolated yield 90%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 8.19(d,

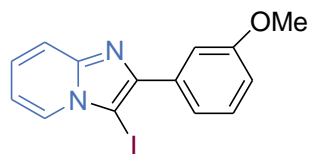
1H,  $J = 6.8$  Hz), 7.96(d, 2H,  $J = 8.8$  Hz), 7.60(d, 3H,  $J = 8.8$  Hz), 7.26(t, 1H,  $J = 1.2$  Hz), 6.92(t, 1H,  $J = 5.2$  Hz);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta = 148.1, 146.9, 132.5, 131.5, 129.6, 126.5, 125.8, 122.5, 117.6, 113.3, 59.5$ . HRMS (ESI)  $m/z$ : Found: 398.8997. Calcd for  $\text{C}_{13}\text{H}_8\text{BrIN}_2$ :  $(\text{M}+\text{H})^+$  398.8988.

### 2-(3-chlorophenyl)-3-iodoH-imidazo[1,2-a]pyridine (3d)



Pale yellow solid, isolated yield 89%.  $^1\text{H}$  NMR (400MHz,  $d$ -DMSO):  $\delta = 8.41(\text{d}, 1\text{H}, J = 6.8$  Hz), 8.15(s, 1H), 8.04(d, 1H,  $J = 6.8$  Hz), 7.59(d, 2H,  $J = 3.6$  Hz), 7.10(m, 2H), 6.96(m, 1H);  $^{13}\text{C}$  NMR (100MHz,  $d$ -DMSO):  $\delta = 148.5, 144.0, 138.8, 137.6, 136.2, 134.9, 134.4, 133.4, 132.4, 122.3, 118.9, 74.9$ . HRMS (ESI)  $m/z$ : Found: 354.9484. Calcd for  $\text{C}_{13}\text{H}_8\text{ClIN}_2$ :  $(\text{M}+\text{H})^+$  354.9493.

### 3-iodo-2-(3-methoxyphenyl)H-imidazo[1,2-a]pyridine (3e)

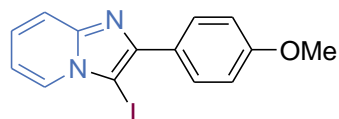


Pale yellow oil, isolated yield 73%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta = 8.16(\text{d}, 1\text{H}, J = 7.2$  Hz), 7.66-7.57(m, 3H), 7.37(t, 1H,  $J = 8.0$  Hz), 7.20(t, 1H,  $J = 6.8$  Hz), 6.94(q, 1H,  $J = 1.2$  Hz), 6.92-6.84(m, 1H), 3.87(s, 3H);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta = 159.4, 147.9, 147.7, 134.7, 129.3, 126.4, 125.5, 120.9, 117.4, 114.5, 113.4, 113.1, 55.3$ . HRMS (ESI)  $m/z$ : Found:



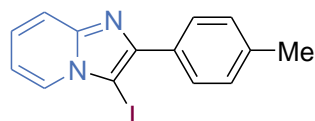
350.9987. Calcd for C<sub>14</sub>H<sub>11</sub>IN<sub>2</sub>O: (M+H)<sup>+</sup> 350.9989.

**3-iodo-2-(4-methoxyphenyl)H-imidazo[1,2-a]pyridine (3f)**



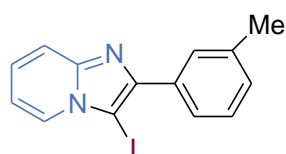
White solid, isolated yield 82%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 8.19(d, 1H, J = 7.6 Hz), 8.03-7.99(m, 2H), 7.58(d, 1H, J = 8.8 Hz), 7.26-7.21(m, 1H), 7.03(t, 2H, J = 2.8 Hz), 6.97(t, 1H, J = 6.8 Hz); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 159.7, 148.0, 147.9, 129.7, 126.6, 126.1, 125.3, 117.4, 113.8, 112.9, 58.6, 55.3. HRMS (ESI) m/z: Found: 350.9987. Calcd for C<sub>14</sub>H<sub>11</sub>IN<sub>2</sub>O: (M+H)<sup>+</sup> 350.9989.

**3-iodo-2-p-tolylH-imidazo[1,2-a]pyridine (3g)**



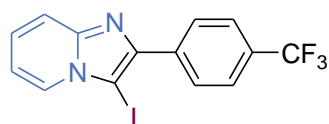
White solid, isolated yield 58%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 8.21(d, 1H, J = 6.8 Hz), 7.96(d, 2H, J = 8.0 Hz), 7.60(d, 1H, J = 8.8 Hz), 7.29(d, 2H, J = 8.0 Hz), 7.25(d, 1H, J = 7.2 Hz), 6.90(t, 1H, J = 6.4 Hz) 2.42(s, 3H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 148.1, 138.2, 130.7, 129.4, 129.1, 128.4, 127.1, 126.4, 125.4, 117.5, 113.0, 58.1, 21.3. HRMS (ESI) m/z: Found: 335.0049. Calcd for C<sub>14</sub>H<sub>11</sub>IN<sub>2</sub>: (M+H)<sup>+</sup> 335.0040.

**3-iodo-2-m-tolylH-imidazo[1,2-a]pyridine (3h)**



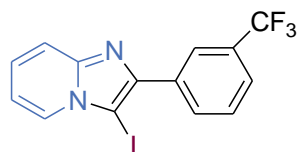
White solid, isolated yield 55%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta = 8.19(\text{d}, 1\text{H}, J = 6.8 \text{ Hz}), 7.87(\text{d}, 2\text{H}, J = 6.4 \text{ Hz}), 7.60(\text{d}, 1\text{H}, J = 9.2 \text{ Hz}), 7.45(\text{d}, 1\text{H}, J = 7.2 \text{ Hz}), 7.22-7.20(\text{m}, 2\text{H}), 6.89(\text{t}, 1\text{H}, J = 6.0 \text{ Hz}), 2.44(\text{s}, 3\text{H})$ ;  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta = 148.1, 147.9, 138.0, 133.6, 129.2, 129.0, 128.1, 126.4, 125.5, 117.5, 113.0, 59.6, 21.4$ . HRMS (ESI)  $m/z$ : Found: 335.0041. Calcd for  $\text{C}_{14}\text{H}_{11}\text{IN}_2$ :  $(\text{M}+\text{H})^+$  335.0040.

### 3-iodo-2-(4-(trifluoromethyl)phenyl)H-imidazo[1,2-a]pyridine (3i)



Yellow solid, isolated yield 88%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta = 8.52(\text{d}, 2\text{H}, J = 8.0 \text{ Hz}), 7.99(\text{d}, 2\text{H}, J = 8.0 \text{ Hz}), 7.59(\text{d}, 1\text{H}, J = 8.8 \text{ Hz}), 7.49(\text{d}, 1\text{H}, J = 8.0 \text{ Hz}), 7.26(\text{t}, 1\text{H}, J = 6.4 \text{ Hz})$ ;  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta = 148.2, 146.5, 137.1, 130.2, 129.9, 128.6, 126.0, 125.4, 125.3, 125.2, 125.1, 117.8, 113.5, 60.1$ . HRMS (ESI)  $m/z$ : Found: 388.9765. Calcd for  $\text{C}_{14}\text{H}_8\text{F}_3\text{IN}_2$ :  $(\text{M}+\text{H})^+$  388.9757.

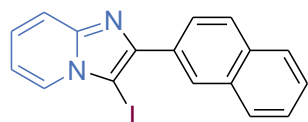
### 3-iodo-2-(3-(trifluoromethyl)phenyl)H-imidazo[1,2-a]pyridine (3j)



Pale yellow solid, isolated yield 85%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta = 8.31(\text{s}, 1\text{H}), 8.28-8.22(\text{m}, 2\text{H}), 7.64-7.62(\text{m}, 3\text{H}), 7.29-7.26(\text{m}, 1\text{H}), 6.96(\text{t}, 1\text{H}, J = 6.8 \text{ Hz})$ ;  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta = 148.3, 146.5, 134.4, 131.5, 130.9, 130.6, 128.8, 126.6, 125.9, 125.3, 124.9, 124.8,$

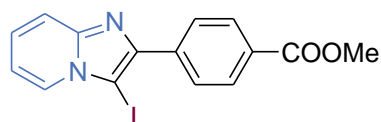
117.7, 113.5, 59.8. HRMS (ESI)  $m/z$ : Found: 388.9766. Calcd for  $C_{14}H_8F_3IN_2$ :  $(M+H)^+$  388.9757

**3-iodo-2-(naphthalen-2-yl)H-imidazo[1,2-a]pyridine (3k)<sup>[3]</sup>**



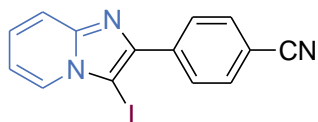
White solid, isolated yield 86%.  $^1H$  NMR (400MHz,  $CDCl_3$ ):  $\delta$  = 8.56 (s, 1H), 8.20(t, 2H,  $J$  = 6.0 Hz), 7.94(d, 2H,  $J$  = 8.0 Hz), 7.81(d, 1H,  $J$  = 6.8 Hz), 7.64(d, 1H,  $J$  = 9.2 Hz), 7.49(d, 2H,  $J$  = 6.0 Hz), 7.24(t, 1H,  $J$  = 6.8 Hz), 6.89(t, 1H,  $J$  = 6.8 Hz);  $^{13}C$  NMR (100MHz,  $CDCl_3$ ):  $\delta$  = 148.2, 147.9, 133.2, 133.1, 130.9, 128.4, 127.9, 127.7, 127.6, 126.5, 126.3, 126.2, 126.1, 125.6, 117.5, 113.2, 59.8.

**methyl 4-(3-iodoH-imidazo[1,2-a]pyridin-2-yl)benzoate (3l)**



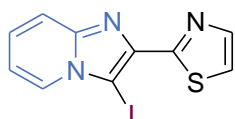
White solid, isolated yield 38%.  $^1H$  NMR (400MHz,  $CDCl_3$ ):  $\delta$  = 8.25(d, 1H,  $J$  = 6.8 Hz), 8.66(m, 3H), 7.64(d, 1H,  $J$  = 8.8 Hz), 7.31-7.30(m, 1H), 6.96(t, 1H,  $J$  = 6.8 Hz), 3.95(s, 3H);  $^{13}C$  NMR (100MHz,  $CDCl_3$ ):  $\delta$  = 166.9, 148.3, 146.9, 138.0, 129.7, 128.3, 127.3, 126.6, 125.9, 117.8, 113.5, 60.3, 52.1. HRMS (ESI)  $m/z$ : Found: 378.9952. Calcd for  $C_{15}H_{11}IN_2O_2$ :  $(M+H)^+$  378.9983.

**4-(3-iodoH-imidazo[1,2-a]pyridin-2-yl)benzotrile (3m)**



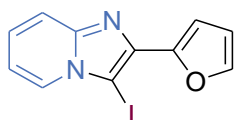
White solid, isolated yield 44%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.26-8.23(m, 3H), 7.76(d, 2H,  $J$  = 8.8 Hz), 7.63(d, 1H,  $J$  = 9.2 Hz), 7.32(t, 1H,  $J$  = 6.8 Hz), 6.98(t, 1H,  $J$  = 6.8 Hz);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.3, 145.8, 138.1, 132.2, 128.8, 126.4, 126.3, 118.8, 117.9, 113.7, 111.6, 60.5. HRMS (ESI)  $m/z$ : Found: 345.9868. Calcd for  $\text{C}_{14}\text{H}_8\text{IN}_3$ :  $(\text{M}+\text{H})^+$  345.9876.

### 3-iodo-2-(thiazol-2-yl)imidazo[1,2-a]pyridine (3n)



White solid, isolated yield 59%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.28(d, 1H,  $J$  = 7.2 Hz), 8.00(d, 1H,  $J$  = 3.6 Hz), 7.64(d, 1H,  $J$  = 9.2 Hz), 7.43(d, 1H,  $J$  = 3.2 Hz), 7.31(t, 1H,  $J$  = 6.8 Hz), 6.98(t, 1H,  $J$  = 6.8 Hz);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 162.4, 151.4, 147.8, 143.8, 141.9, 126.5, 119.9, 117.9, 113.9, 59.9. HRMS (ESI)  $m/z$ : Found: 327.9356. Calcd for  $\text{C}_{14}\text{H}_6\text{IN}_3\text{S}$ :  $(\text{M}+\text{H})^+$  327.9348.

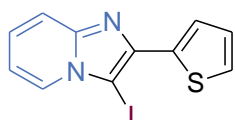
### 2-(furan-2-yl)-3-iodoimidazo[1,2-a]pyridine (3o)



White solid, isolated yield 61%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.19(d, 1H,  $J$  = 6.8 Hz), 7.62-7.58(m, 2H), 7.26(t, 1H,  $J$  = 6.8 Hz), 7.18-7.17(m,

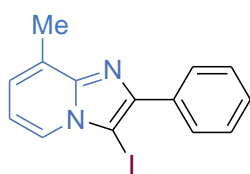
1H), 6.90(t, 1H,  $J = 7.2$  Hz), 6.56(q, 1H,  $J = 3.2$  Hz);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta = 148.1, 147.9, 142.8, 140.7, 126.3, 125.9, 117.5, 113.4, 111.7, 111.4, 108.9, 57.8$ . HRMS (ESI)  $m/z$ : Found: 310.9688. Calcd for  $\text{C}_{11}\text{H}_7\text{IN}_2\text{O}$ :  $(\text{M}+\text{H})^+$  310.9694.

### 3-iodo-2-(thiophen-2-yl)H-imidazo[1,2-a]pyridine (3p)

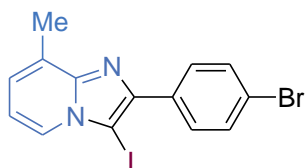


White solid, isolated yield 78%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta = 8.21\text{-}8.19(\text{m}, 1\text{H}), 7.96\text{-}7.94(\text{m}, 1\text{H}), 7.59\text{-}7.57(\text{m}, 1\text{H}), 7.37(\text{d}, 1\text{H}, J = 7.2$  Hz), 7.28-7.26(m, 1H), 7.23(t, 1H,  $J = 6.8$  Hz), 6.90(t, 1H,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta = 147.8, 137.5, 127.6, 127.1, 126.4, 126.3, 126.1, 126.7, 117.4, 113.4, 58.5$ . HRMS (ESI)  $m/z$ : Found: 326.9449. Calcd for  $\text{C}_{11}\text{H}_7\text{IN}_2\text{S}$ :  $(\text{M}+\text{H})^+$  326.9437.

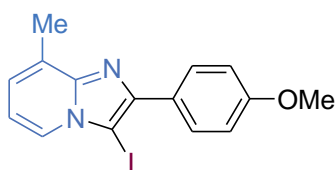
### 3-iodo-8-methyl-2-phenylH-imidazo[1,2-a]pyridine (3q)



White solid, isolated yield 97%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta = 8.09(\text{d}, 1\text{H}, J = 6.8$  Hz), 8.05(d, 2H,  $J = 6.8$  Hz), 7.48(m, 2H), 7.39(t, 1H,  $J = 7.2$  Hz), 7.05(d, 1H,  $J = 6.8$  Hz), 6.84(t, 1H,  $J = 6.8$  Hz), 2.68(s, 3H);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta = 148.5, 147.6, 133.9, 128.7, 128.3, 128.1, 127.6, 124.4, 124.2, 112.9, 59.9, 16.6$ . HRMS (ESI)  $m/z$ : Found: 335.0048. Calcd for  $\text{C}_{14}\text{H}_{11}\text{IN}_2$ :  $(\text{M}+\text{H})^+$  335.0040.

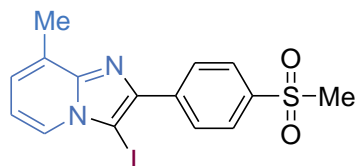
**2-(4-bromophenyl)-3-iodo-8-methylimidazo[1,2-a]pyridine (3r)**

White solid, isolated yield 98%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.06(d, 1H,  $J$  = 6.8 Hz), 7.95(d, 2H,  $J$  = 8.8 Hz), 7.59(d, 2H,  $J$  = 8.4 Hz), 7.04(d, 1H,  $J$  = 4.0 Hz), 6.83(t, 1H,  $J$  = 7.2 Hz), 2.65(s, 3H);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.5, 146.4, 132.8, 131.4, 130.1, 127.7, 124.4, 124.3, 122.4, 113.2, 59.8, 16.5. HRMS (ESI)  $m/z$ : Found: 412.9157. Calcd for  $\text{C}_{14}\text{H}_{10}\text{BrIN}_2$ : ( $\text{M}+\text{H}$ ) $^+$  412.9156.

**3-iodo-2-(4-methoxyphenyl)-8-methylimidazo[1,2-a]pyridine (3s)**

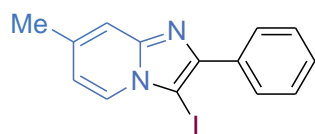
White solid, isolated yield 98%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.07(d, 1H,  $J$  = 6.8 Hz), 7.99(d, 2H,  $J$  = 6.4 Hz), 7.02(t, 3H,  $J$  = 7.6 Hz), 6.81(t, 1H,  $J$  = 6.8 Hz), 3.87(s, 3H), 2.66(s, 3H);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.6, 148.4, 147.5, 129.9, 127.4, 126.4, 124.3, 124.1, 113.8, 112.8, 59.1, 55.3, 16.5. HRMS (ESI)  $m/z$ : Found: 365.0137. Calcd for  $\text{C}_{15}\text{H}_{13}\text{IN}_2\text{O}$ : ( $\text{M}+\text{H}$ ) $^+$  365.0145.

**3-iodo-8-methyl-2-(4-(methylsulfonyl)phenyl)imidazo[1,2-a]pyridine (3t)**



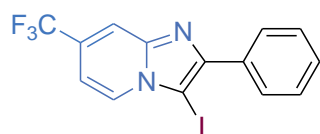
White solid, isolated yield 58%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.29(d, 2H,  $J$  = 6.8 Hz), 8.08(d, 1H,  $J$  = 6.8 Hz), 8.02(d, 2H,  $J$  = 6.8 Hz), 7.07(t, 1H,  $J$  = 4.4), 6.87(t, 1H,  $J$  = 6.8 Hz), 3.01(s, 3H), 2.65(s, 3H);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.6, 145.3, 139.5, 139.4, 129.2, 127.9, 127.4, 124.8, 124.5, 113.6, 60.9, 44.6, 16.4. HRMS (ESI)  $m/z$ : Found: 412.9757. Calcd for  $\text{C}_{15}\text{H}_{13}\text{IN}_2\text{O}_2\text{S}$ : ( $\text{M}+\text{H}$ ) $^+$  412.9762.

### 3-iodo-7-methyl-2-phenylimidazo[1,2-a]pyridine (3u)



White solid, isolated yield 83%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  8.10(d, 1H,  $J$  = 7.2 Hz), 8.05(d, 2H,  $J$  = 7.2 Hz), 7.49-7.46(m, 2H), 7.40-7.38(m, 2H), 7.63(d, 1H,  $J$  = 7.2 Hz), 2.46(s, 3H);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 148.5, 136.7, 133.7, 128.5, 128.3, 118.2, 127.2, 125.7, 116.1, 115.8, 58.5, 21.3. HRMS (ESI)  $m/z$ : Found: 335.0049. Calcd for  $\text{C}_{14}\text{H}_{11}\text{IN}_2$ : ( $\text{M}+\text{H}$ ) $^+$  335.0040.

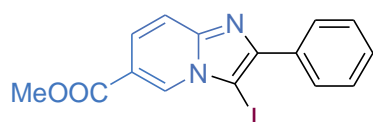
### 3-iodo-2-phenyl-7-(trifluoromethyl)imidazo[1,2-a]pyridine (3v)



Yellow solid, isolated yield 56%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.59(s, 1H), 8.06(d, 2H,  $J$  = 7.2 Hz), 7.72(d, 1H,  $J$  = 9.6 Hz), 7.52(t, 2H,  $J$  = 5.6

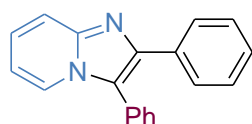
H<sub>z</sub>), 7.44(t, 2H, *J* = 6.4 Hz); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 149.9, 147.9, 132.8, 128.9, 128.5, 128.5, 125.6, 125.5, 124.7, 122.0, 121.5, 121.4, 118.3, 117.8, 117.5, 61.4. HRMS (ESI) *m/z*: Found: 388.9765. Calcd for C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>IN<sub>2</sub>: (M+H)<sup>+</sup> 388.9757.

### Methyl 3-iodo-2-phenylH-imidazo[1,2-a]pyridine-6-carboxylate (3w)



White solid, isolated yield 40%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 8.98(s, 1H), 8.07(d, 2H, *J* = 7.2 Hz), 7.81(d, 1H, *J* = 7.6 Hz), 7.63(d, 1H, *J* = 7.2 Hz), 7.49(d, 2H, *J* = 6.8 Hz), 7.43(d, 1H, *J* = 7.6 Hz), 3.99(s, 3H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 165.1, 149.8, 148.7, 132.9, 130.6, 128.8, 128.5, 128.4, 125.3, 117.2, 116.9, 60.9, 52.6. HRMS (ESI) *m/z*: Found: 378.9952. Calcd for C<sub>15</sub>H<sub>11</sub>IN<sub>2</sub>O<sub>2</sub>: (M+H)<sup>+</sup> 378.9983.

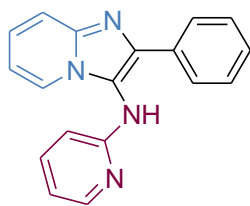
### 2,3-diphenylH-imidazo[1,2-a]pyridine (4)<sup>[4]</sup>



White solid, isolated yield 85%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ = 7.98(d, 1H, *J* = 6.8 Hz), 7.73-7.67(m, 3H), 7.57-7.54(m, 3H), 7.53-7.46(m, 3H), 7.32-7.20(m, 3H), 6.78(t, 1H, *J* = 6.8 Hz); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ = 144.6, 141.7, 133.1, 130.7, 130.0, 129.5, 129.0, 128.4, 128.3, 128.2, 125.4, 123.2, 121.1, 117.3, 112.7.

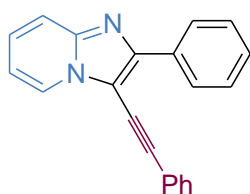
### 2-phenyl-N-(pyridin-2-yl)H-imidazo[1,2-a]pyridin-3-amine (5)<sup>[5]</sup>





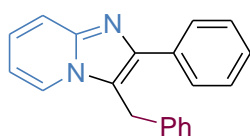
White solid, isolated yield 85%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.14(d, 1H,  $J$  = 4.4 Hz), 8.05(d, 2H,  $J$  = 7.2 Hz), 7.87(d, 1H,  $J$  = 6.8 Hz), 7.66(d, 1H,  $J$  = 8.8 Hz), 7.36-7.33(m, 3H), 7.29-7.26(m, 2H), 6.79-6.63(m, 2H), 6.12(d, 1H,  $J$  = 8.4 Hz) ;  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 156.9, 148.8, 142.8, 138.6, 137.7, 133.1, 128.5, 127.8, 126.8, 125.1, 122.5, 117.6, 115.4, 113.8, 112.3, 106.5.

### 2-phenyl-3-(2-phenylethynyl)H-imidazo[1,2-a]pyridine (6)



White solid, isolated yield 95%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.39-8.36-7.87(m, 3H), 7.60(d, 1H,  $J$  = 2.0 Hz), 7.50(d, 2H,  $J$  = 3.2 Hz), 7.42-7.40(m, 2H), 7.42-7.31(m, 4H), 7.28-7.24(m, 1H), 6.93(t, 1H,  $J$  = 6.8 Hz);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  = 147.9, 145.2, 133.5, 131.2, 128.8, 128.7, 128.6, 128.5, 127.2, 127.1, 126.3, 125.1, 122.7, 117.5, 112.9, 104.7, 101.2. HRMS (ESI)  $m/z$ : Found: 295.1268. Calcd for  $\text{C}_{21}\text{H}_{14}\text{N}_2$ :  $(\text{M}+\text{H})^+$  295.1273.

### 3-benzyl-2-phenylH-imidazo[1,2-a]pyridine (7)<sup>[6]</sup>



White solid, isolated yield 48%.  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ):  $\delta = 7.79(\text{d}, 2\text{H}, J = 7.2 \text{ Hz}), 7.64(\text{t}, 2\text{H}, J = 8.8 \text{ Hz}), 7.40(\text{t}, 2\text{H}, J = 7.2 \text{ Hz}), 7.26\text{-}7.24(\text{m}, 3\text{H}), 7.11\text{-}7.09(\text{m}, 3\text{H}), 6.61(\text{t}, 1\text{H}, J = 6.8 \text{ Hz}), 4.44(\text{s}, 2\text{H});$   
 $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta = 144.7, 143.9, 136.6, 134.4, 128.8, 128.4, 127.9, 127.5, 127.4, 126.7, 123.2, 117.5, 117.4, 111.9, 29.6.$

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