Biotransformation of Substituted Pyridines with Dioxygenase-containing Microorganisms.

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Electronic Supplementary Information.

Spectroscopic data for compounds 4a, 4c, 4d, 4e, 4f, 5a, 5b, 5c, 6a, 6c, 7a, 7c, 7d, 7e and **8**

2-Ethyl-3-hydroxypyridine (4a). δ_H (300 MHz, $CDCl_3$) 1.22 (3H, t, *J* = 7.4 Hz, CH_3), 2.85 (2H, q, *J* = 7.4 Hz, C<u>H</u>$_2$$CH_3$), 6.30 (1H, br. s, OH), 6.90 (1H, dd, *J* = 8.0 Hz, *J* = 4.8 Hz, 5-H), 7.05 (1H, d, *J* = 8.0 Hz, 4-H), 7.94 (1H, d, *J* = 4.8 Hz, 6-H); δ_C (75 MHz, $CDCl_3$) 11.6 (CH_3), 24.4 (CH_2), 121.3 (CH), 121. 7 (CH), 138.3 (CH), 150.4 (C), 150.7 (C); *m/z* (EI) 123 (M^+, 73%), 122 (M^+-H, 100%), 106 (M^+-OH, 35%).

3-Hydroxy-2-methylpyridine (4c). δ_H (500 MHz, d^6-DMSO) 2.37 (3H, s, CH_3), 7.08 (1H, dd, *J* = 8.1 Hz, *J* = 4.6 Hz, 5-H), 7.13 (1H, dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 4-H), 7.93 (1H, dd, *J* = 4.6 Hz, *J* = 1.4 Hz, 6-H), 9.72 (1H, s, OH); δ_C (125 MHz, d^6-DMSO) 19.9 CH_3), 121.6 (CH), 122.7 (CH), 140.6 (CH), 147.1 (C), 153.0 (C); *m/z* (EI) 109 (M^+, 100%), 94 (M^+ - CH_3, 10%).

2-Chloro-3-hydroxypyridine (4d). δ_H (500 MHz, CD_3OD) 7.22 (1H, dd, *J* = 8.0 Hz, *J* = 4.6 Hz, 5-H), 7.31 (1H, dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 4-H), 7.83 (1H, dd, *J* = 4.6 Hz, *J* = 1.5 Hz, 6-H); δ_C (125 MHz, CD_3OD) 125.7 (CH), 125.5 (CH), 139.1 (CH), 140.9 (C), 152.4 (C); *m/z* (EI) 131 (M^+ (^{37}Cl), 51%), 129 (M^+ (^{35}Cl), 100%), 93 (M^+ - Cl, 97%).

2-Bromo-3-hydroxypyridine (4e). δ_H (500 MHz, $CDCl_3$) 5.61 (1H, s, OH), 7.20 (1H, dd, *J* = 7.9 Hz, *J* = 4.6 Hz, 5-H), 7.29 (1H, d, *J* = 7.9 Hz, *J* = 1.6 Hz, 4-H), 7.98 (1H, d, *J* = 4.6 Hz, *J* = 1.6 Hz, 6-H); δ_C (125 MHz, $CDCl_3$) 121.8 (CH), 123.1 (CH), 129.8 (CH), 140.6 (C), 148.5 (C); *m/z* (EI) 176 (M^+ (^{81}Br), 67%), 174 (M^+ (^{79}Br), 70%), 173 (M^+ (^{79}Br) - H, 80%), 94 (M^+ -Br, 100%).

3-Hydroxypyridine (4f). δ_H (500 MHz, CD_3OD) 7.23 (2H, m, 4-H), 8.05 (1H, d, *J* = 3.7 Hz, 6-H), 8.25 (1H, s, 2-H); *m/z* (EI) 95 (M^+, 100%), 76 (60%), 41 (72%).

(*R*)-1-(2-Pyridyl)ethanol (5a). δ_H (500 MHz, $CDCl_3$) 1.35 (3H, d, *J* = 6.6 Hz, CH_3), 4.78 (1H, q, *J* = 6.6 Hz , C<u>H</u>OH), 5.27 (1H, br. s, OH), 6.99 (1H, m, 4-H), 7.27 (1H, d, *J* = 7.8 Hz , 3-H), 7.51 (1H, dt, *J* = 7.7 Hz, *J* = 1.8 Hz, 5-H), 8.28 (1H, dm, *J* = 4.1 Hz, 6-H); δ_C (125 MHz, $CDCl_3$) 22.0 (CH_3), 67.5 (CH), 117.7 (CH), 120.0 (CH), 135.0 (CH), 146.1 (C), 162.2 (CH); *m/z* (EI) 123 (M^+, 17%), 122 (M^+-H, 45%), 108 (M^+-CH_3, 93%), 106 (M^+-OH, 99%), 80 (M^+ - C_2H_3O, 100%); *CD* λ 269 nm Δε -0.138, λ 266 nm Δε +0.915, λ 262 nm Δε -0.129, λ 256 nm Δε +0.515, λ 239 nm Δε +4.519.

(*R*)-1-(2-Pyridyl)-1-propanol (5b). δ_H (500 MHz, $CDCl_3$) 0.95 (3H, t, *J* = 7.4 Hz, CH_3), 1.73 (1H, m, C<u>H</u>$_2$$CH_3$), 1.89 (1H, m, C<u>H</u>$_2$$CH_3$), 4.69 (1H, t, *J* = 5.8 Hz, C<u>H</u>OH), 7.18 (1H, m, 4-H), 7.27 (1H, d, *J* = 10.7 Hz, 3-H), 7.67 (1H, m, 5-H), 8.53 (1H, d, *J* = 4.7 Hz, 6-H); δ_C (125 MHz, $CDCl_3$) 9.8 (CH_3), 31.7 (CH_2), 74.2 (CH), 120.8 (CH), 122.6 (CH), 137.0 (CH), 148.5 (C), 162.4 (CH); *m/z* (EI) [silylated with BSTFA] 209 (M^+, 10%), 194 (M^+-CH_3, 56%), 180 (M^+-CH_2CH_3, 75%), 166 (100%); *CD* λ 268 nm Δε -0.123, λ 266 nm Δε +0.002, λ 263 nm Δε -0.009.

(2-Pyridyl)methanol (5c). δ_H (500 MHz, $CDCl_3$); 4.45 (1H, br. s, OH), 4.77 (2H, s, C<u>H</u>$_2$OH), 7.21 (1H, m, 5-H), 7.26 (1H, d, *J* = 7.6 Hz, 3-H), 7.68 (1H, m, 4-H), 8.56 (1H, d, *J* = 4.8 Hz, 6-H); δ_C (125 MHz, $CDCl_3$) 64.1 (CH_2), 120.6 (CH), 122.4 (CH), 136.7 (CH), 148.4 (C), 158.0 (CH); *m/z* (EI) 109 (M^+, 91%) 108 (M^+ - H, 100%), 80 (90%).

(*R*)-1-(3-Pyridyl)ethanol (6a). δ_H (500 MHz, $CDCl_3$) 1.53 (3H, d, *J* = 6.4 Hz, CH_3), 4.96 (1H, q, *J* = 6.4 Hz, C<u>H</u>OH), 7.29 (1H, m, 5-H), 7.74 (1H, dd, *J* = 7.9 Hz, *J* = 1.7 Hz, 4-H), 8.50 (1H, d, *J* = 4.7 Hz, 6-H), 8.59 (1H, s, 2-H); δ_C (125 MHz, $CDCl_3$) 25.2 (CH_3), 68.2 (CH), 123.1 (C), 133.1 (CH), 141.1 (CH), 147.5 (CH), 148.0 (CH); *m/z* (EI) 123 (M^+, 79%), 108 (M^+-CH_3, 99%), 80 (M^+-$COCH_3$, 100%).

(3-Pyridyl)methanol (6c). δ_H (500 MHz, $CDCl_3$) 4.63 (2H, s, C<u>H</u>$_2$OH), 7.20 (1H, m, 5-H), 7.65 (1H, d, *J* = 8.1 Hz, 4-H), 8.35 (1H, d, *J* = 4.8 Hz, 6-H), 8.41 (1H, s, 2-H); δ_C (125 MHz, $CDCl_3$) 62.2 (CH_2), 123.6 (C), 135.2 (CH), 137.0 (CH), 148.1 (CH), 148.7 (CH); *m/z* (EI) 109 (M^+, 87%), 108 (M^+ - H, 100%), 91 (M^+ - H_2O, 22%).

4-Ethyl-3-hydroxypyridine (7a). δ_H (500 MHz, $CDCl_3$) 1.19 (3H, t, *J* = 7.5 Hz, CH_3), 2.66 (2H, q, *J* = 7.5 Hz, C<u>H</u>$_2$CH$_3$), 7.08 (1H, d, *J* = 4.9 Hz, 5-H), 7.93 (1H, d, *J* = 4.9 Hz, 6-H), 8.18 (1H, s, 2-H); δ_C (125 MHz, $CDCl_3$) 11.3 (CH_3), 21.9 (CH_2), 123.8 (CH), 130.1 (C), 133.3 (CH), 145.1(CH), 154.0 (C); *m/z* (EI) 123 (M^+, 78%), 122 (M^+-H, 97%), 108 (M^+-CH_3, 100%), 94 (M^+-CH_2CH_3, 45%).

3-Hydroxy-4-methylpyridine (7c). δ_H (500 MHz, $CDCl_3$) 2.24 (3H, s, CH_3), 7.06 (1H, d, *J* = 4.9 Hz, 5-H), 7.88 (1H, d, *J* = 4.9 Hz, 6-H), 8.14 (1H, s, 2-H); δ_C (125 MHz, $CDCl_3$) 14.8 (CH_3), 125.4 (CH), 133.7 (C), 135.4 (CH), 137.7 (CH), 153.3 (C); *m/z* (EI) [Silylated using BSTFA] 181 (M^+, 64%), 166 (M^+-CH_3, 100%).

4-Chloro-3-hydroxypyridine (7d). δ_H (500 MHz, CD_3OD) 7.26 (1H, d, *J* = 5.0 Hz, 5-H), 7.84 (1H, d, *J* = 5.0 Hz, 6-H), 8.05 (1H, s, 2-H); δ_C (125 MHz, CD_3OD) 124.7 (CH), 130.3 (C), 137.2 (CH), 139.3 (CH), 150.7 (C); *m/z* (EI) 131 (M^+ (^{37}Cl), 46%), 129 (M^+ (^{35}Cl), 100%), 94 (M^+ - Cl, 10%).

4-Bromo-3-hydroxypyridine (7e). δ_H (500 MHz, $CDCl_3$) 7.54 (1H, d, *J* = 5.1 Hz, 5-H), 7.97 (1H, d, *J* = 5.1 Hz, 6-H), 8.28 (1H, s, 2-H); δ_C (125 MHz, $CDCl_3$) 121.9 (CH), 128.8 (C), 137.2 (CH), 140.8 (CH), 152.3 (C); *m/z* (EI) 175 (M^+ (^{81}Br), 92%), 173 (M^+ (^{79}Br), 100%), 93 (M^+ - Br, 45%).

5-Chloro-3-hydroxypyridine (8). δ_H (500 MHz, d^6-acetone) 7.14 (1H, s, 4-H), 8.0 (1H, s, 6-H), 8.07 (1H, s, 2-H); δ_C (125 MHz, d^6-acetone) 122.3 (C), 129.4 (CH), 136.5 (CH), 139.3 (CH), 151.8 (C); *m/z* (EI) 131 (M^+ (^{37}Cl), 34%), 129 (M^+ (^{35}Cl), 100%), 94 (M^+-Cl, 41%).