

Copper (II) oxide nanoparticles: as a highly active and reusable heterogeneous catalyst for the construction of phenyl-1*H*-pyrazolo[3,4-*b*]pyridine derivatives under solvent-free conditions

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Supporting information (¹H and ¹³C NMR spectra of isolated compounds)

General procedure for the synthesis of 6-(4-bromophenyl)-4-(4-chlorophenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine (4a).

A mixture of 3-methyl-1-phenyl-1*H*-pyrazol-5-amine (**1**, 1.0 equiv.), 4-bromobenzaldehyde (**2a**, 1.0 equiv.) and 4-chloro-1-ethynylbenzene (**3a**, 1.0 equiv.) in the presence of CuO NPs (10 mol %) in neat conditions at 80 °C for 90 minutes. The completion of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature followed by addition of ethyl acetate (10 mL) and catalyst was recovered by filtration. The filtrate was denser under reduced pressure and obtained solid product was washed with hexane and recrystallized from ethanol to afford the pure product. The precipitated CuO NPs was washed with methanol twice and then dried under vacuum before reuse.

6-(4-bromophenyl)-4-(4-chlorophenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine

(4a). Yield 95%; light yellow powder; mp 160-162 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.35 (dd, *J* = 1.8, 8.3 Hz, 2H), 8.07 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.66-7.63 (m, 1H), 7.60-7.58 (m, 1H), 7.54-7.48 (m, 3H), 7.46-7.42 (m, 3H), 7.39-7.36 (m, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 2.28 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 155.5, 151.6, 144.5, 142.3, 141.9, 139.5, 137.2, 136.1, 132.4, 129.9, 129.2, 129.2, 128.9, 125.9, 121.3, 118.5, 114.7, 113.0, 15.5 ppm. HRMS (ESI, *m/z*): calcd for C₂₅H₁₇BrClN₃ (M+H⁺) 474.7796; found: 474.7790.

4-(4-(4-chlorophenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridin-6-yl)benzonitrile

(4b). Yield 93%; light yellow powder; mp 155-157 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.35 (d, *J* = 8.3 Hz, 2H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 3H), 7.34-7.30 (m, 1H), 2.27 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 155.5, 151.6, 144.5, 142.4, 141.9, 139.5, 137.2, 136.1, 132.4, 129.9, 129.2, 129.2, 128.9, 125.9, 121.3, 118.5, 114.7, 113.0, 15.5 ppm. HRMS (ESI, *m/z*): calcd for C₂₆H₁₇ClN₄ (M+H⁺) 420.1142; found: 420.1135.

4-(4-chlorophenyl)-3-methyl-1-phenyl-6-p-tolyl-1H-pyrazolo[3,4-b]pyridine (4c). Yield 95%; light yellow powder; mp 140-142 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.37 (dd, *J* = 1.8, 8.3 Hz, 2H), 8.10 (dd, *J* = 1.9, 8.3 Hz, 2H), 7.55-7.51 (m, 2H), 7.47-7.42 (m, 4H), 7.33-7.26 (m, 4H), 2.46 (s, 3H), 2.31 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 155.2, 151.7, 147.1, 142.7, 139.8, 139.0, 137.7, 135.7, 134.9, 130.5, 129.7, 129.2, 129.1, 128.9, 128.7, 127.6, 125.5, 121.1, 115.1, 114.1, 21.5, 15.6 ppm. HRMS (ESI, *m/z*): calcd for C₂₆H₂₀ClN₃ (M+H⁺) 409.1346; found: 409.1340.

4-(4-(4-chlorophenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridin-6-yl)-N,N-

dimethylbenzenamine (4d). Yield 92%; light yellow powder; mp 161-163 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 8.3 Hz, 2H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.46-7.41 (m, 5H), 7.29-7.24 (m, 1H), 6.81 (d, *J* = 8.3 Hz, 2H), 3.04 (s, 6H), 2.41 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 155.1, 151.9, 150.9, 147.5, 142.9, 139.9, 138.0, 135.5, 130.3, 129.1, 129.0, 128.9, 125.4, 125.2, 121.1, 114.9, 114.1, 111.9, 40.5, 16.0 ppm. HRMS (ESI, *m/z*): calcd for C₂₇H₂₃ClN₄ (M+H⁺) 438.1611; found: 438.1604.

4-(4-chlorophenyl)-6-(4-ethoxyphenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine

(4e). Yield 96%; light yellow powder; mp 154-156 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 8.3 Hz, 2H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.47-7.44 (m, 5H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 4.15-4.10 (q, 2H), 2.34 (s, 3H), 1.48 (t, *J* = 6.9 Hz, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 159.8, 155.2, 151.7, 146.9, 142.7, 139.8, 137.8, 135.6, 130.5, 129.9, 125.5, 121.1, 115.1, 114.5 ppm. HRMS (ESI, *m/z*): calcd for C₂₇H₂₂ClN₃O (M+H⁺) 439.1451; found: 439.1446.

4-(4-chlorophenyl)-6-(4-methoxyphenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine

(4f). Yield 93%; light yellow powder; mp 168-170 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.37 (dd, *J* = 1.9, 8.3 Hz, 2H), 8.09 (dd, *J* = 1.9, 8.3 Hz, 2H), 7.55-7.50 (m, 3H), 7.47-7.41 (m, 4H), 7.33-7.28 (m, 3H), 3.81 (s, 3H), 2.31 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 165.2, 160.5, 152.8, 146.1, 146.0, 142.4, 139.1, 137.4, 134.7, 131.5, 130.6, 129.1, 126.4, 123.4, 121.6, 121.4, 120.0, 115.8, 113.4, 55.4, 15.3 ppm. HRMS (ESI, *m/z*): calcd for C₂₆H₂₀ClN₃O (M+H⁺) 425.1295; found: 425.1288.

4-(4-chlorophenyl)-6-(4-isopropylphenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine

(4g). Yield 94%; light yellow powder; mp 126-128 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.56-7.49 (m, 3H), 7.46 (d, *J* = 8.3 Hz, 4H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 3.08-2.97 (m, 1H), 2.34 (s, 3H), 1.34 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 155.2, 151.7, 149.9, 147.1, 142.8, 139.8, 137.8, 135.7, 135.2, 129.2, 128.9, 126.6, 125.6, 121.8, 115.2, 114.1, 34.1, 24.1, 15.7 ppm. HRMS (ESI, *m/z*): calcd for C₂₈H₂₄ClN₃ (M+H⁺) 437.1659; found: 437.1651.

4-(4-chlorophenyl)-6-(3,4,5-trimethoxyphenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-

b]pyridine (4h). Yield 93%; light yellow powder; mp 206-208 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.37 (d, *J* = 8.3 Hz, 2H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 3H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.73 (s, 2H), 3.96 (s, 3H), 3.93 (s, 6H), 2.39 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 164.6, 153.6, 146.4, 145.7, 139.3, 139.1, 137.2, 137.2, 137.0, 136.6, 128.9, 128.6, 122.4, 106.1, 104.2, 60.9, 56.2, 12.9 ppm. HRMS (ESI, *m/z*): calcd for C₂₈H₂₄ClN₃O₃ (M+H⁺) 485.1506; found: 485.1500.

6-(2-bromophenyl)-4-(3-methoxyphenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine (4i). Yield 90%; light yellow powder; mp 144-146 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.45 (d, *J* = 8.3 Hz, 2H), 8.38 (d, *J* = 8.3 Hz, 1H), 7.79 (s, 1H), 7.74-7.71 (m, 2H), 7.54-7.47 (m, 3H), 7.42-7.37 (m, 3H), 7.27-7.22 (m, 2H), 3.88 (s, 3H), 2.15 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 160.1, 156.4, 151.3, 144.8, 142.7, 140.5, 139.8, 132.9, 130.7, 130.3, 129.9, 129.1, 129.0, 127.4, 125.4, 122.8, 121.2, 120.8, 120.1, 115.3, 114.9, 113.1, 55.4, 14.0 ppm. HRMS (ESI, *m/z*): calcd for C₂₆H₂₀BrN₃O (M+H⁺) 470.3605; found: 470.3600.

6-(5-bromo-2-fluorophenyl)-4-(3-methoxyphenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine (4j). Yield 91%; light yellow powder; mp 138-140 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.40-8.39 (m, 2H), 7.75-7.70 (m, 2H), 7.60-7.58 (m, 2H), 7.55-7.50 (m, 2H), 7.40 (m, 1H), 7.30-7.27 (m, 1H), 7.12-7.00 (m, 3H), 3.89 (s, 3H), 2.31 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 160.2, 156.5, 151.2, 146.4, 142.3, 140.3, 138.2, 134.0, 129.9, 129.6, 129.1, 125.6, 121.7, 121.2, 120.1, 115.8, 113.2, 55.4, 14.1 ppm. HRMS (ESI, *m/z*): calcd for C₂₆H₁₉BrFN₃O (M+H⁺) 488.3509; found: 488.3503.

4-(4-(4-bromophenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridin-6-yl)benzonitrile (4k). Yield 92%; light yellow powder; mp 203-205 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.33 (d, *J* = 8.3 Hz, 2H), 8.25 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.56-7.51 (m, 3H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 2.31 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 154.1, 151.5, 145.8, 143.1, 142.4, 139.5, 136.3, 132.7, 131.8, 130.7, 129.2, 128.1, 125.9, 123.6, 121.2, 118.8, 115.3, 114.3, 113.0, 15.6 ppm. HRMS (ESI, *m/z*): calcd for C₂₆H₁₇BrN₄ (M+H⁺) 465.3439; found: 465.3432.

4-(4-bromophenyl)-6-(4-fluorophenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine (4l). Yield 91%; light yellow powder; mp 167-169 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.35 (d, *J* = 8.3 Hz, 2H), 8.14-8.10 (m, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.66-7.57 (m, 5H), 7.43-7.36 (m, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.24-7.13 (m, 2H), 2.28 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 163.2 (d, *J* = 241.3 Hz), 155.2, 151.6, 145.7, 139.7, 137.9, 136.8, 135.3, 133.7, 132.0, 131.7, 130.9, 129.5, 129.4, 129.2, 125.7, 121.1, 116.0, 115.7, 115.0, 114.8 ppm. HRMS (ESI, *m/z*): calcd for C₂₅H₁₇BrFN₃ (M+H⁺) 458.3249; found: 458.3242.

4-(4-bromophenyl)-6-(4-isopropylphenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine (m). Yield 92%; light yellow powder; mp 131-133 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 8.3 Hz, 2H), 8.05 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.56-7.51 (m, 3H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 3.06-2.99 (m, 1H), 2.34 (s, 3H), 1.34 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 155.3, 151.8, 150.0, 147.1, 142.8, 139.8, 138.2, 135.3, 132.0, 129.2, 129.1, 126.6, 125.6, 124.1, 121.1, 115.2, 114.1, 34.1, 24.1, 15.6 ppm. HRMS (ESI, *m/z*): calcd for C₂₈H₂₄BrN₃ (M+H⁺) 482.4143; found: 482.4138.

4-(4-(4-bromophenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridin-6-yl)phenol (4n). Yield 92%; light yellow powder; mp 130-132 °C. ¹H-NMR (400 MHz, CDCl₃): δ 9.32 (s, 1H), 8.37 (d, *J* = 8.3 Hz, 2H), 8.04 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.55-7.51 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 2H), 2.36 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 158.1, 154.5, 146.9, 142.4, 139.4, 139.4, 137.8, 131.5, 130.0, 128.7, 128.6, 125.0, 123.3, 120.5, 115.2, 114.5, 15.3 ppm. HRMS (ESI, *m/z*): calcd for C₂₅H₁₈BrN₃O (M+H⁺) 456.3339; found: 456.3333.

4-(4-bromophenyl)-6-(4-ethoxyphenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]pyridine (4o). Yield 95%; light yellow powder; mp 128-130 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.37 (d, *J* = 8.3 Hz, 2H), 8.04 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 3H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.15-4.1 (m, 2H), 2.34 (s, 3H), 1.34 (d, *J* = 6.6 Hz, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 159.7, 155.3, 151.7, 146.9, 142.7, 139.8, 138.2, 132.0, 131.7, 130.5, 129.2, 129.1, 125.5, 121.1, 115.0, 114.5, 63.8, 15.7, 15.0 ppm. HRMS (ESI, *m/z*): calcd for C₂₇H₂₂BrN₃O (M+H⁺) 484.3871; found: 484.3865.

3-methyl-6-(2,5-dimethylphenyl)-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine (4p). Yield 90%; light yellow powder; mp 116-118 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.43 (d, *J* = 8.3 Hz, 2H), 8.19 (d, *J* = 8.3 Hz, 2H), 7.56-7.46 (m, 7H), 7.30-7.22 (m, 3H), 2.39 (s, 3H), 2.10 (s, 6H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 156.7, 151.6, 146.6, 143.1, 140.0, 137.2, 135.4, 132.5, 130.1, 129.7, 129.6, 129.4, 129.1, 128.9, 127.7, 125.4, 120.9, 115.2, 114.6, 21.1, 13.9 ppm. HRMS (ESI, *m/z*): calcd for C₂₇H₂₃N₃ (M+H⁺) 389.1892; found: 389.1886.

6-(3-bromophenyl)-3-methyl-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine (4q). Yield 91%; light yellow powder; mp 134-136 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.40 (d, *J* = 8.3 Hz, 2H), 8.15 (d, *J* = 8.2 Hz, 2H), 7.69 (s, 1H), 7.64-7.62 (m, 1H), 7.55-7.44 (m, 7H), 7.37 (t, *J* = 7.3

Hz, 1H), 7.30 (t, $J = 7.3$ Hz, 1H), 2.30 (s, 3H) ppm. ^{13}C -NMR (100 MHz, CDCl_3): 156.6, 151.6, 144.8, 142.2, 139.8, 139.7, 139.0, 132.1, 131.9, 130.0, 129.7, 129.1, 128.9, 127.8, 127.7, 125.6, 122.6, 121.1, 115.2, 15.6 ppm. HRMS (ESI, m/z): calcd for $\text{C}_{25}\text{H}_{18}\text{BrN}_3$ ($\text{M}+\text{H}^+$) 440.3345; found: 440.3338.

6-(3-chlorophenyl)-3-methyl-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine (4r). Yield 90%; light yellow powder; mp 107-109 °C. ^1H -NMR (400 MHz, CDCl_3): δ 8.40 (d, $J = 8.3$ Hz, 2H), 8.16 (d, $J = 8.2$ Hz, 2H), 7.53-7.43 (m, 10H), 7.29 (t, $J = 7.3$ Hz, 1H), 2.30 (s, 3H) ppm. ^{13}C -NMR (100 MHz, CDCl_3): 156.7, 151.8, 145.0, 142.3, 138.9, 134.6, 129.8, 129.7, 129.3, 129.1, 129.0, 127.7, 127.4, 125.6, 121.1, 115.2, 115.1, 15.5 ppm. HRMS (ESI, m/z): calcd for $\text{C}_{25}\text{H}_{18}\text{ClN}_3$ ($\text{M}+\text{H}^+$) 395.1189; found: 395.1183.

3-methyl-6-(2,6-dimethylphenyl)-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine (4s). Yield 89%; light yellow powder; mp 192-194 °C. ^1H -NMR (400 MHz, CDCl_3): δ 8.34 (d, $J = 8.3$ Hz, 2H), 7.52-7.43 (m, 8H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.14 (t, $J = 8.1$ Hz, 2H), 7.05 (s, 1H), 2.36 (s, 3H), 2.17 (s, 6H) ppm. ^{13}C -NMR (100 MHz, CDCl_3): 159.2, 151.8, 146.2, 142.5, 140.7, 139.9, 137.7, 136.2, 129.3, 129.1, 128.9, 128.5, 128.1, 127.8, 125.5, 121.1, 119.5, 113.3, 20.7, 15.7 ppm. HRMS (ESI, m/z): calcd for $\text{C}_{27}\text{H}_{23}\text{N}_3$ ($\text{M}+\text{H}^+$) 389.1892; found: 389.1885.

6-(3-fluorophenyl)-3-methyl-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine (4t). Yield 92%; light yellow powder; mp 102-104 °C. ^1H -NMR (400 MHz, CDCl_3): δ 8.41 (m, 2H), 8.16 (m, 2H), 7.53-7.49 (m, 7H), 7.29 (d, $J = 7.3$ Hz, 2H), 7.27-7.20 (m, 2H), 2.30 (s, 3H) ppm. ^{13}C -NMR (100 MHz, CDCl_3): 162.7 (d, $J = 240.3$), 156.6, 151.7, 145.0, 142.3, 139.8, 139.0, 130.2, 130.1, 129.7, 129.1, 128.9, 128.7, 128.1, 127.7, 125.5, 125.0, 121.1, 116.4, 116.2, 115.9, 115.7, 115.2, 113.6, 15.5 ppm. HRMS (ESI, m/z): calcd for $\text{C}_{25}\text{H}_{18}\text{FN}_3$ ($\text{M}+\text{H}^+$) 379.1485; found: 379.1478.

6-(3-methoxyphenyl)-3-methyl-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine (4u). Yield 94%; light yellow powder; mp 99-101 °C. ^1H -NMR (400 MHz, CDCl_3): δ 8.42 (d, $J = 8.3$ Hz, 2H), 8.17 (d, $J = 8.2$ Hz, 2H), 7.56-7.42 (m, 8H), 7.28 (t, $J = 7.3$ Hz, 1H), 7.11-7.02 (m, 2H), 3.86 (s, 3H), 2.33 (s, 3H) ppm. ^{13}C -NMR (100 MHz, CDCl_3): 159.5, 156.5, 146.5, 142.6, 139.9, 139.2, 129.5, 129.1, 128.9, 127.7, 125.4, 121.6, 121.0, 115.3, 114.8, 114.3, 55.5, 15.5 ppm. HRMS (ESI, m/z): calcd for $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}$ ($\text{M}+\text{H}^+$) 391.1685; found: 391.1678.

4-(3-methyl-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridin-6-yl)benzonitrile (4v). Yield 92%; light yellow powder; mp 197-199 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 8.3 Hz, 2H), 8.14 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.55-7.46 (m, 6H), 7.30 (t, *J* = 7.3 Hz, 1H), 2.33 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 156.6, 151.5, 144.2, 142.4, 141.8, 139.6, 138.7, 132.2, 129.9, 129.8, 129.1, 129.0, 127.6, 125.7, 121.1, 118.5, 115.0, 113.1, 112.8, 15.5 ppm. HRMS (ESI, *m/z*): calcd for C₂₆H₁₈N₄ (M+H⁺) 386.1531; found: 386.1525.

6-(4-isopropylphenyl)-3-methyl-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine (4w). Yield 93%; light yellow powder; mp 113-115 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.42 (d, *J* = 8.3 Hz, 2H), 8.17 (d, *J* = 8.2 Hz, 2H), 7.55-7.44 (m, 8H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 3.04-2.97 (m, 1H), 2.33 (s, 3H), 1.33 (d, *J* = 6.6 Hz, 6H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 156.5, 149.8, 146.9, 142.7, 140.0, 139.4, 135.4, 129.5, 129.2, 129.1, 128.9, 127.7, 126.5, 125.4, 121.1, 115.5, 34.1, 24.1, 15.7 ppm. HRMS (ESI, *m/z*): calcd for C₂₈H₂₅N₃ (M+H⁺) 403.2048; found: 403.2040.

6-(4-ethoxyphenyl)-3-methyl-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine (4x). Yield 94%; white powder; mp 141-143 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.42 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.2 Hz, 2H), 7.54-7.42 (m, 8H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.11-4.06 (q, 2H), 2.33 (s, 3H), 1.46 (t, *J* = 6.9 Hz, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 159.6, 156.4, 151.8, 146.5, 142.6, 139.9, 139.3, 130.4, 130.0, 129.4, 129.0, 128.8, 127.6, 125.3, 121.0, 115.4, 114.3, 63.7, 15.7, 14.9 ppm. HRMS (ESI, *m/z*): calcd for C₂₇H₂₃N₃O (M+H⁺) 405.1841; found: 405.1835.

6-(3,4,5-trimethoxyphenyl)-3-methyl-1,4-diphenyl-1H-pyrazolo[3,4-b]pyridine (4y). Yield 95%; white powder; mp 145-147 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.41 (d, *J* = 8.3 Hz, 2H), 8.19 (d, *J* = 8.2 Hz, 2H), 7.55-7.47 (m, 6H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.74 (s, 2H), 3.97 (s, 3H), 3.92 (s, 6H), 2.39 (s, 3H) ppm. ¹³C-NMR (100 MHz, CDCl₃): 157.2, 153.9, 152.3, 147.3, 143.1, 140.5, 139.8, 134.0, 130.3, 129.7, 129.6, 128.4, 126.2, 121.7, 115.9, 113.9, 107.1, 61.8, 57.0, 16.4 ppm. HRMS (ESI, *m/z*): calcd for C₂₈H₂₅N₃O₃ (M+H⁺) 451.1896; found: 451.1891.



































































































