Supporting Information

Copper(I)- Promoted C-N Cross-Coupling of N-Heterocyclic Compounds with 1,2-Di(pyrimidin-2-yl) Disulfides

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1. **General**

$^1$H NMR and $^{13}$C NMR data analyses were performed with a Varian Mercury plus-400 instrument and plus-600 instrument unless otherwise specified. Dual-beam infrared spectrophotometer CDCl$_3$ as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the $^1$H NMR spectrum as 0.00 ppm. The data of $^1$H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (J values) in Hz and integration. Chemical shift for $^{13}$C NMR spectra were recorded in ppm from TMS using the central peak of CDCl$_3$ (77.0 ppm) as the internal standard. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Melting points were measured with an XT-4 apparatus. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and Orbitrap Elite mass spectrometer. Column chromatography was generally performed on silica gel (200–300 mesh) and TLC analyses were conducted on silica gel GF254 plates.
2 Experimental details and characterization data for all compounds.

2.1 General procedure for the synthesis of 3a (Scheme 1). Under an atmosphere of nitrogen, disulfide 1a (1 mmol, 0.546 g), indole 2a (3 mmol, 0.351 g), CuTC (1.0 mmol, 0.191 g) and Cs₂CO₃ (3.0 mmol, 0.978 g) were added to an oven-dried Schlenk tube. The tube was stoppered and degassed with nitrogen three times. Water-free dioxane (3 mL) was added by syringe and the mixture was stirred for 12 h at 120°C and the reaction was monitored by TLC analysis. Then, 2 mL diluted hydrochloric acid were added to the mixture to quench the reaction and extracted with ethyl acetate (3×100 mL). The combined organic layers were washed with aqueous NaHCO₃ and brine, dried over MgSO₄, filtered, and the volatiles were removed in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:30) to give the corresponding products.

Scheme 1: Synthesis of intermediate product 3a.

2.2 General procedure for the synthesis of 4a (Scheme 2). Under an atmosphere of nitrogen, disulfide 1a (1 mmol, 0.546 g), 2-methylindole 2b (3 mmol, 0.393 g), CuTC (1.0 mmol, 0.191 g), Ni(dppp)Cl₂ (0.1 mol, 0.054 g) and Cs₂CO₃ (3.0 mmol, 0.978 g) were added to an oven-dried Schlenk tube. The tube was stoppered and degassed with nitrogen three times. Water-free dioxane (3 mL) was added by syringe and the mixture was stirred for 12 h at 120°C and the reaction was monitored by TLC analysis. Then, 2 mL diluted hydrochloric acid were added to the mixture to quench the reaction and extracted with ethyl acetate (3×100 mL). The combined organic layers were washed with aqueous NaHCO₃ and brine, dried over MgSO₄, filtered, and the volatiles were removed in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/ petroleum ether 1:30) to give the corresponding products.

Scheme 2: Synthesis of intermediate product 5a.
2.3 Characterization Data for the Isolated Products.

**Ethyl 2-(1H-indol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3a).** Colorless crystal, mp 135–137 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.88 (d, \(J=8.4\) Hz, 1H, ArH), 8.37 (d, \(J=3.6\) Hz, 1H, ArH), 7.77–7.75 (m, 2H, ArH), 7.62 (d, \(J=7.8\) Hz, 1H, CH), 7.53–7.50 (m, 3H, ArH), 7.34 (t, \(J=7.8\) Hz, 1H, ArH), 7.25 (t, \(J=7.2\) Hz, 1H, ArH), 6.71 (d, \(J=3.6\) Hz, 1H, CH), 4.20 (q, \(J=7.2\) Hz, 2H, OCH\(_2\)), 2.70 (s, 3H, CH\(_3\)), 1.07 (t, \(J=7.2\) Hz, 3H, CH\(_2\)CH\(_3\)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 168.12, 167.31, 165.39, 156.44, 138.06, 135.48, 131.49, 130.13, 128.52 (2 C), 128.36 (2 C), 126.04, 123.74, 122.31, 120.81, 120.57, 116.62, 107.24, 61.69, 22.97, 13.64. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{22}\)H\(_{20}\)N\(_3\)O\(_2\) 358.1550 [M+H]\(^+\), Found 358.1553.

**Ethyl 2-(1H-indol-1-yl)-4-methyl-6-(p-tolyl)pyrimidine-5-carboxylate (3b).** Colorless crystal, mp 91–93 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.89 (d, \(J=8.4\) Hz, 1H, ArH), 8.38 (d, \(J=3.6\) Hz, 1H, ArH), 7.68 (d, \(J=8.4\) Hz, 2H, ArH), 7.63 (d, \(J=7.8\) Hz, 1H, CH), 7.36–7.31 (m, 3H, ArH), 7.25 (t, \(J=7.2\) Hz, 1H, ArH), 6.71 (d, \(J=3.6\) Hz, 1H, CH), 4.24 (q, \(J=7.2\) Hz, 2H, OCH\(_2\)), 2.69 (s, 3H, CH\(_3\)), 2.45 (s, 3H, Ar-CH\(_3\)), 1.14 (t, \(J=7.2\) Hz, 3H, CH\(_2\)CH\(_3\)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 168.36, 167.07, 165.19, 156.43, 140.52, 135.50, 135.15, 131.48, 129.27 (2 C), 128.38 (2 C), 126.07, 123.71, 122.26, 120.81, 120.44, 116.65, 107.13, 61.70, 22.95, 21.45, 13.74. HRMS (ESI\(^+\)) m/z: Calcd for C\(_{23}\)H\(_{22}\)N\(_3\)O\(_2\) 372.1707 [M+H]\(^+\), Found 372.1710.

**Ethyl 4-(4-fluorophenyl)-2-(1H-indol-1-yl)-6-methylpyrimidine-5-carboxylate (3c).** Yellow oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.83 (d, \(J=8.4\) Hz, 1H, ArH), 8.34 (d, \(J=3.6\) Hz, 1H, ArH), 7.76–7.74 (m, 2H, ArH), 7.61 (d, \(J=7.8\) Hz, 1H, CH), 7.33 (t, \(J=7.2\) Hz, 1H, ArH), 7.25–7.18 (m, 3H, ArH), 6.70 (d, \(J=3.6\) Hz, 1H, CH), 4.22 (q, \(J=7.2\) Hz, 2H, OCH\(_2\)), 2.69 (s, 3H, CH\(_3\)), 1.12 (t, \(J=7.2\) Hz, 3H, CH\(_2\)CH\(_3\)); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 168.03, 167.42, 164.10, 156.38, 135.44, 131.49,
Ethyl 4-(2-chlorophenyl)-2-(1H-indol-1-yl)-6-methylpyrimidine-5-carboxylate (3d). Colorless crystal, mp 137–139 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.80 (d, $J$=8.4 Hz, 1H, ArH), 8.31 (d, $J$=3.6 Hz, 1H, ArH), 7.60 (d, $J$=7.8 Hz, 1H, CH), 7.49 (d, $J$=7.8 Hz, 1H, ArH), 7.42-7.38 (m, 3H, ArH), 7.30 (t, $J$=7.8 Hz, 1H, ArH), 7.23 (t, $J$=7.2 Hz, 1H, ArH), 6.69 (d, $J$=3.6 Hz, 1H, CH), 4.08 (q, $J$=7.2 Hz, 2H, OCH$_2$), 2.80 (s, 3H, CH$_3$), 0.93 (t, $J$=7.2 Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 168.77, 166.27, 165.44, 156.31, 137.94, 135.44, 132.15, 131.51, 130.12, 129.98, 129.54, 126.64, 126.05, 123.83, 122.46, 120.83, 120.80, 116.70, 107.58, 61.34, 23.89, 13.42. HRMS (ESI$^+$) m/z: Calcd for C$_{22}$H$_{19}$FN$_3$O$_2$ 392.1160 [M+H]$^+$, Found 392.1158.

Ethyl 4-(4-chlorophenyl)-2-(1H-indol-1-yl)-6-methylpyrimidine-5-carboxylate (3e). Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.81 (d, $J$=7.8 Hz, 1H, ArH), 8.33 (d, $J$=3.6 Hz, 1H, ArH), 7.69 (d, $J$=8.4 Hz, 2H, ArH), 7.61 (d, $J$=7.8 Hz, 1H, CH), 7.48 (d, $J$=7.8 Hz, 2H, ArH), 7.33 (t, $J$=7.8 Hz, 1H, ArH), 7.25–7.23 (m, 1H, ArH), 6.70 (d, $J$=3.0 Hz, 1H, CH), 4.22 (q, $J$=7.2 Hz, 2H, OCH$_2$), 2.69 (s, 3H, CH$_3$), 1.13 (t, $J$=7.2 Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 167.89, 167.56, 164.08, 156.42, 156.49, 136.43, 135.43, 131.49, 129.73 (2 C), 128.80 (2 C), 125.95, 123.80, 122.41, 120.87, 120.37, 116.52, 107.43, 61.83, 23.00, 13.73. HRMS (ESI$^+$) m/z: Calcd for C$_{22}$H$_{19}$ClN$_3$O$_2$ 392.1160 [M+H]$^+$, Found 392.1163.

Ethyl 4-(4-bromophenyl)-2-(1H-indol-1-yl)-6-methylpyrimidine-5-carboxylate (3f). Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.81 (d, $J$=8.4 Hz, 1H, ArH), 8.33 (d, $J$=3.6 Hz, 1H, ArH), 7.65-7.61 (m, 5H, ArH, CH), 7.33 (t, $J$=7.2 Hz, 1H, ArH), 7.26–7.23(m, 1H, ArH), 6.70 (d, $J$=3.6 Hz,
1H, CH), 4.22 (q, J=7.2 Hz, 2H, OCH$_2$), 2.69 (s, 3H, CH$_3$), 1.13 (t, J=7.2 Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 167.86, 167.59, 164.15, 156.42, 136.91, 135.42, 131.76 (2 C), 131.49, 129.95 (2 C), 125.94, 124.82, 123.80, 122.42, 120.88, 120.33, 116.53, 107.44, 61.85, 23.01, 13.73.

HRMS (ESI$^+$) m/z: Calcd for C$_{22}$H$_{19}$BrN$_3$O$_2$ 436.0655 [M+H]$^+$, Found 436.0654.

**Ethyl 2-(1H-indol-1-yl)-4-methyl-6-(3-nitrophenyl)pyrimidine-5-carboxylate (3g).** Colorless crystal, mp 120–122 °C. $^1$H NMR (600 MHz, CDCl$_3$): δ 8.79 (d, J=8.4 Hz, 1H, ArH), 8.61 (s, 1H, ArH), 8.38–8.37 (m, 1H, ArH), 8.08 (d, J=7.2 Hz, 1H, ArH), 7.69 (t, J=7.8 Hz, 1H, ArH), 7.62 (d, J=7.8 Hz, 1H, CH), 7.34 (t, J=7.8 Hz, 1H, ArH), 7.26–7.24 (m, 1H, ArH), 6.72 (d, J=3.6 Hz, 1H, CH), 4.26 (q, J=7.2 Hz, 2H, OCH$_2$), 2.73 (s, 3H, CH$_3$), 1.16 (t, J=7.2 Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 168.20, 167.32, 162.78, 156.49, 148.29, 139.53, 135.39, 134.29, 131.55, 129.64, 125.88, 124.73, 123.96, 123.46, 122.62, 120.97, 120.43, 116.49, 107.84, 62.08, 23.21, 13.76.

HRMS (ESI$^+$) m/z: Calcd for C$_{22}$H$_{19}$N$_4$O$_4$ 403.1401 [M+H]$^+$, Found 403.1403.

**Methyl 2-(1H-indol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3h).** Yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.86 (d, J=8.4 Hz, 1H, ArH), 8.36 (d, J=3.6 Hz, 1H, ArH), 7.76–7.74 (m, 2H, ArH), 7.61 (d, J=7.8 Hz, 1H, CH), 7.52–7.51 (m, 3H, ArH), 7.33 (t, J=7.8 Hz, 1H, ArH), 7.23 (d, J=7.8 Hz, 1H, ArH), 6.70 (d, J=3.6 Hz, 1H, CH), 3.70 (s, 3H, OCH$_3$), 2.69 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 168.70, 167.38, 165.23, 156.50, 137.90, 135.46, 131.48, 130.26, 128.59 (2 C), 128.26 (2 C), 126.02, 123.75, 122.33, 120.82, 120.19, 116.60, 107.29, 52.47, 23.00. HRMS (ESI$^+$) m/z: Calcd for C$_{21}$H$_{18}$N$_3$O$_2$ 344.1394 [M+H]$^+$, Found 344.1397.

**Ethyl 2-(1H-indol-1-yl)-4-isopropyl-6-phenylpyrimidine-5-carboxylate (3i).** Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$): δ 8.89 (d, J=8.4 Hz, 1H, ArH), 8.40 (d, J=3.0 Hz, 1H, ArH), 7.76 (d, J=7.2 Hz, 2H, ArH), 7.63 (d, J=7.8 Hz, 1H, CH), 7.51–7.50 (m, 3H, ArH), 7.34 (t, J=7.8 Hz, 1H, ArH), 7.24
(d, J=7.2 Hz, 1H, ArH), 6.71 (d, J=3.0 Hz, 1H, CH), 4.19 (q, J=7.2 Hz, 2H, OCH₂), 3.37–3.33 (m, 1H, CH), 1.45 [d, J=7.2 Hz, 6H, CH(CH₃)₂], 1.07 (t, J=7.2 Hz, 3H, CH₂CH₃); ¹³C NMR (150 MHz, CDCl₃): δ 175.07, 168.29, 165.25, 156.87, 138.14, 135.48, 131.45, 130.06, 128.51 (2 C), 128.33 (2 C), 126.10, 123.69, 122.20, 120.80, 120.03, 116.53, 107.06, 61.75, 33.88, 21.98 (2 C), 13.63. HRMS (ESI⁺) m/z: Calcd for C₂₄H₂₄N₃O₂ 386.1863 [M+H]⁺, Found 386.1860.

Ethyl 2-(1H-benzo[d]imidazol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3j). Colorless crystal, mp 111–113 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.16 (s, 1H, ArH), 8.63 (d, J = 7.8 Hz, 1H, CH), 7.87–7.84 (m, 2H, ArH), 7.75 (d, J = 7.2 Hz, 2H, ArH), 7.55–7.51 (m, 2H, ArH), 7.42–7.36 (m, 2H, ArH), 4.21 (q, J = 7.2 Hz, 2H, OCH₂), 2.72 (s, 3H, CH₃), 1.08 (t, J = 7.2 Hz, 3H, CH₂CH₃); ¹³C NMR (150 MHz, CDCl₃): δ 167.91, 167.55, 165.65, 154.94, 142.03, 137.30, 130.55, 130.30, 128.68 (2 C), 128.36 (2 C), 127.22, 124.72, 123.91, 122.56, 120.47, 115.83, 61.99, 22.89, 13.62. HRMS (ESI⁺) m/z: Calcd for C₂₁H₁₉N₄O₂ 359.1503 [M+H]⁺, Found 359.1505.

Ethyl 2-(1H-benzo[d]imidazol-1-yl)-4-(4-fluorophenyl)-6-methylpyrimidine-5-carboxylate (3k). Colorless crystal, mp 99–101 °C. ¹H NMR (600 MHz, CDCl₃): δ 9.12 (s, 1H, ArH), 8.58 (d, J=7.8 Hz, 1H, CH), 7.86–7.83 (m, 2H, ArH), 7.77–7.74 (m, 2H, ArH), 7.40–7.35 (m, 3H, ArH), 7.20 (t, J=8.4 Hz, 2H, ArH), 4.24 (q, J=7.2 Hz, 2H, OCH₂), 2.70 (s, 3H, CH₃), 1.14 (t, J=7.2 Hz, 3H, CH₂CH₃); ¹³C NMR (150 MHz, CDCl₃): δ 168.01, 167.47, 164.32, 154.97, 145.07, 141.96, 141.19, 130.56, 130.50, 130.28, 127.20, 124.74, 123.95, 120.50, 115.94, 115.80, 115.73, 112.45, 62.09, 22.89, 13.73. HRMS (ESI⁺) m/z: Calcd for C₂₁H₁₉FN₂O₂ 377.1408 [M+H]⁺, Found 377.1410.

Ethyl 2-(1H-benzo[d]imidazol-1-yl)-4-(2-chlorophenyl)-6-methylpyrimidine-5-carboxylate (3l). Colorless crystal, mp 111–113 °C. ¹H NMR (600 MHz, CDCl₃): δ 9.11 (s, 1H, ArH), 8.57–8.56 (m, 1H, CH), 7.83–7.81 (m, 1H, ArH), 7.51–7.49 (m, 1H, ArH), 7.44–7.33 (m, 5H, ArH), 4.10 (q, J=7.2 Hz, 2H, OCH₂), 2.72 (s, 3H, CH₃), 1.08 (t, J=7.2 Hz, 3H, CH₂CH₃); ¹³C NMR (150 MHz, CDCl₃): δ 175.07, 168.29, 165.25, 156.87, 138.14, 135.48, 131.45, 130.06, 128.51 (2 C), 128.33 (2 C), 126.10, 123.69, 122.20, 120.80, 120.03, 116.53, 107.06, 61.75, 33.88, 21.98 (2 C), 13.63. HRMS (ESI⁺) m/z: Calcd for C₂₄H₂₄N₃O₂ 386.1863 [M+H]⁺, Found 386.1860.
Hz, 2H, OCH2), 2.82 (s, 3H, CH3), 0.94 (t, J=7.2 Hz, 3H, CH2CH3); 13C NMR (150 MHz, CDCl3): δ 169.29, 165.75, 165.69, 154.91, 145.07, 142.03, 137.14, 132.14, 130.53, 129.95, 129.69, 127.20, 126.76, 124.78, 124.01, 123.02, 120.43, 115.92, 61.66, 23.75, 13.42.

HRMS (ESI+) m/z: Calcd for C21H18BrN4O2 393.1113 [M+H]+, Found 393.1110.

Ethyl 2-(1H-benzo[d]imidazol-1-yl)-4-(4-bromophenyl)-6-methylpyrimidine-5-carboxylate (3m).

Colorless crystal, mp 147–149 °C. 1H NMR (600 MHz, CDCl3): δ 9.12 (s, 1H, ArH), 8.57 (d, J=7.8 Hz, 1H, CH), 7.84 (d, J=7.8 Hz, 1H, ArH), 7.66 (d, J=8.4 Hz, 2H, ArH), 7.62 (d, J=9.0 Hz, 2H, ArH), 7.40–7.25 (m, 2H, ArH), 4.24 (q, J=7.2 Hz, 2H, OCH2), 2.71 (s, 3H, CH3), 1.15 (t, J=7.2 Hz, 3H, CH2CH3); 13C NMR (150 MHz, CDCl3): δ 168.19, 167.30, 164.40, 155.04, 145.07, 141.94, 136.13, 131.96 (2C), 129.93 (2C), 127.21, 125.36, 124.77, 124.00, 122.35, 120.53, 115.73, 62.16, 22.93, 13.73. HRMS (ESI+) m/z: Calcd for C21H18BrN4O2 437.0608 [M+H]+, Found 437.0604.

4.2.21 Ethyl 2-(1H-benzo[d]imidazol-1-yl)-4-methyl-6-(3-nitrophenyl)pyrimidine-5-carboxylate (3n).

Colorless crystal, mp 146–148 °C. 1H NMR (600 MHz, CDCl3): δ 9.12 (s, 1H, ArH), 8.61 (s, 1H, CH), 8.55 (d, J=7.8 Hz, 1H, ArH), 8.40 (d, J=7.8 Hz, 1H, ArH), 8.10 (d, J=7.8 Hz, 1H, ArH), 7.84 (d, J=7.8 Hz, 1H, ArH), 7.73 (t, J=7.8 Hz, 1H, ArH), 7.42–7.36 (m, 2H, ArH), 4.29 (q, J=7.2 Hz, 2H, OCH2), 2.75 (s, 3H, CH3), 1.19 (t, J=7.2 Hz, 3H, CH2CH3); 13C NMR (150 MHz, CDCl3): δ 168.81, 166.76, 162.97, 155.13, 148.34, 145.08, 141.87, 138.73, 134.28, 131.68, 129.89, 125.12, 124.92, 124.17, 123.43, 122.57, 120.62, 115.65, 62.43, 23.12, 13.76. HRMS (ESI+) m/z: Calcd for C21H18N3O4 404.1353 [M+H]+, Found 404.1356.

Ethyl 4-methyl-6-phenyl-2-(1H-1,2,4-triazol-1-yl)pyrimidine-5-carboxylate (3o). Colorless oil. 1H NMR (600 MHz, CDCl3) δ 9.28 (s, 1H, CH), 8.15 (s, 1H, CH), 7.69 (d, J = 6.6 Hz, 2H, ArH), 7.50 - 7.46 (m, 3H, ArH), 4.20 (q, J = 7.2 Hz, 2H, OCH2), 2.70 (m, 3H, ArH), 1.06 (t, J=7.2 Hz, 3H,
CH$_2$CH$_3$; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.73, 166.98, 165.94, 153.74, 153.14, 144.09, 136.48, 130.75, 128.62 (2 C), 128.35 (2 C), 124.68, 62.15, 22.78, 13.53. HRMS (ESI$^+$) m/z: Calcd for C$_{16}$H$_{15}$N$_3$O$_2$ 310.1299 [M+H]$^+$, Found 310.1302.

**Ethyl 4-methyl-6-(p-tolyl)-2-(1H-1,2,4-triazol-1-yl)pyrimidine-5-carboxylate (3p).** Colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 9.30 (s, 1H, CH), 8.18 (s, 1H, CH), 7.63 (d, $J = 7.8$ Hz, 2H, ArH), 7.29 (d, $J = 7.8$ Hz, 2H, ArH), 4.26 (q, $J = 7.2$ Hz, 2H, OCH$_2$), 2.71 (s, 3H), 2.42 (s, 3H), 1.14 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 168.58, 167.31, 165.77, 153.79, 153.19, 146.80, 141.43, 133.62, 129.43 (2 C), 128.43 (2 C), 124.51, 62.21, 22.83, 21.45, 13.69. HRMS (ESI$^+$) m/z: Calcd for C$_{17}$H$_{17}$N$_5$O$_2$ 324.1455 [M+H]$^+$, Found 324.1457.

**Ethyl 2-(1H-benzo[d][1,2,3]triazol-1-yl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3q).** Colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.61 (d, $J = 8.4$ Hz, 1H, ArH), 8.19 – 8.18 (m, 1H, ArH), 7.80 (d, $J = 7.2$ Hz, 2H, ArH), 7.69 (d, $J = 7.2$ Hz, 2H, ArH), 7.65 – 7.62 (m, 1H, ArH), 7.58 – 7.48 (m, 4H, ArH), 4.25 (q, $J = 7.2$ Hz, 2H, OCH$_2$), 2.82 (s, 3H, CH$_3$), 1.11 (t, $J = 6.6$ Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 168.58, 167.29, 165.89, 155.13, 146.80, 137.03, 131.87, 130.72, 129.38 (2 C), 128.47 (2 C), 125.28 (2 C), 124.08, 120.31, 114.99, 62.18, 23.02, 13.64. HRMS (ESI$^+$) m/z: Calcd for C$_{20}$H$_{17}$N$_5$O$_2$ 360.1455 [M+H]$^+$, Found 360.1457.

**Ethyl 2-(1H-benzo[d][1,2,3]triazol-1-yl)-4-(4-chlorophenyl)-6-methylpyrimidine-5-carboxylate (3r).** Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.50 (d, $J = 8.0$ Hz, 1H, ArH), 8.13 (d, $J = 8.0$ Hz, 1H, ArH), 7.69 (d, $J = 8.0$ Hz, 2H, ArH), 7.60 – 7.56 (m, 1H, ArH), 7.46 (d, $J = 8.0$ Hz, 3H, ArH), 4.22 (q, $J = 8.0$ Hz, 2H, OCH$_2$), 2.76 (s, 3H, CH$_3$), 1.12 (t, $J = 6$ Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.83, 167.12, 164.61, 155.16, 146.84, 137.25, 135.40, 131.87, 129.88 (2 C), 129.15 (2 C), 125.39 (2 C), 123.92, 120.42, 114.89, 62.38, 23.08, 13.77. HRMS (ESI$^+$) m/z: Calcd
for C_{29}H_{30}ClN_{5}O_{2} 394.1065 [M+H]^+, Found 394.1063.

Ethyl 4-methyl-2-(2-methyl-1H-indol-1-yl)-6-phenylpyrimidine-5-carboxylate (4a). Yellow oil. 1H NMR (600 MHz, CDCl₃): δ 8.30 (d, J=8.4 Hz, 1H, ArH), 7.68–7.66 (m, 2H, ArH), 7.55–7.54 (m, 3H, ArH), 7.48 (d, J=7.8 Hz, 1H, ArH), 7.16–7.13 (m, 2H, ArH), 6.51 (s, 1H, CH), 4.19 (q, J=7.2 Hz, 2H, OCH₂), 2.70 (s, 3H, CH₃), 2.62 (s, 3H, CH₃), 1.03 (t, J=7.2 Hz, 3H, CH₂); 13C NMR (150 MHz, CDCl₃): δ 168.12, 167.31, 165.39, 156.44, 138.06, 135.48, 131.49, 130.13, 128.52 (2 C), 128.36 (2 C), 126.04, 123.74, 122.31, 120.82, 120.57, 116.62, 107.24, 61.69, 22.97, 13.64, 13.63. HRMS (ESI+) m/z: Calcd for C_{29}H_{30}N_{5}O_{2} 372.1707 [M+H]^+, Found 372.1710.

Ethyl 4-methyl-2-(2-methyl-1H-indol-1-yl)-6-(p-tolyl)pyrimidine-5-carboxylate (4b). Yellow oil. 1H NMR (400 MHz, CDCl₃): δ 8.41 (d, J=8.0 Hz, 1H, ArH), 7.65 (d, J=8.0 Hz, 2H, ArH), 7.50 (d, J=7.2 Hz, 1H, ArH), 7.29 (d, J=7.6 Hz, 2H, ArH), 7.19 (t, J=7.2 Hz, 2H, ArH), 6.44 (s, 1H, CH), 4.26 (q, J=7.2 Hz, 2H, OCH₂), 2.78 (s, 3H, CH₃), 2.69 (s, 3H, Ar-CH₃), 2.43 (s, 3H, CH₂), 1.15 (t, J=7.2 Hz, 3H, CH₂); 13C NMR (100 MHz, CDCl₃): δ 167.88, 167.31, 163.82, 157.20, 137.91, 136.85, 136.65, 131.81, 129.95 (2 C), 129.63 (2 C), 124.92, 122.58, 122.14, 120.77, 119.51, 114.73, 107.63, 61.97, 29.67, 22.86, 17.40, 13.75. HRMS (ESI+) m/z: Calcd for C_{26}H_{26}N_{3}O_{2} 386.1863 [M+H]^+, Found 386.1865.

Ethyl 4-(4-fluorophenyl)-6-methyl-2-(2-methyl-1H-indol-1-yl) pyrimidine-5- carboxylate (4c). Colorless crystal, mp 105–107 °C. 1H NMR (400 MHz, CDCl₃): δ 8.40 (d, J=7.6 Hz, 1H, ArH), 7.77–7.73 (m, 2H, ArH), 7.51–7.49 (m, 1H, ArH), 7.22–7.16 (m, 4H, ArH), 6.44 (s, 1H, CH), 4.25 (q, J=7.2 Hz, 2H, OCH₂), 2.77 (s, 3H, CH₃), 2.70 (s, 3H, CH₃), 1.15 (t, J=7.2 Hz, 3H, CH₂); 13C NMR (100 MHz, CDCl₃): δ 168.05, 167.17, 163.80, 157.15, 137.90, 136.87, 130.51, 130.46 (2
Ethyl 4-(4-chlorophenyl)-6-methyl-2-(2-methyl-1H-indol-1-yl)pyrimidine-5-carboxylate  (4d).

Yellow oil. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.40 (d, $J$=7.8 Hz, 1H, ArH), 7.68 (d, $J$=9.0 Hz, 2H, ArH), 7.50 (d, $J$=7.8 Hz, 1H, ArH), 7.47 (d, $J$=8.4 Hz, 2H, ArH), 7.21-7.18 (m, 2H, ArH), 6.44 (s, 1H, CH), 4.25 (q, $J$=7.1 Hz, 2H, OCH$_2$), 2.76 (s, 3H, CH$_3$), 2.71 (s, 3H, CH$_3$), 1.16 (t, $J$=7.2 Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 167.90, 167.28, 163.75, 157.19, 137.90, 136.86, 136.56, 136.18, 129.74 (2 C), 129.63 (2 C), 128.84, 122.57, 122.13, 120.81, 119.50, 114.71, 107.61, 61.96, 22.85, 17.38, 13.74. HRMS (ESI$^+$) m/z: Calcld for C$_{23}$H$_{21}$F$_3$N$_3$O$_2$ 390.1612 [M+H]$^+$, Found 390.1608.

Ethyl 4-(4-bromophenyl)-6-methyl-2-(2-methyl-1H-indol-1-yl)pyrimidine-5-carboxylate  (4e).

Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.40 (d, $J$=8.4 Hz, 1H, ArH), 7.65–7.60 (m, 3H, ArH), 7.51–7.45 (m, 2H, ArH), 7.22–7.19 (m, 2H, ArH), 6.45 (s, 1H, CH), 4.25 (q, $J$=7.2 Hz, 2H, OCH$_2$), 2.77 (s, 3H, CH$_3$), 2.71 (s, 3H, CH$_3$), 1.16 (t, $J$=7.2 Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.88, 167.31, 163.82, 157.20, 137.91, 136.85, 136.65, 131.81, 129.95 (2 C), 129.63 (2 C), 124.92, 122.58, 122.14, 120.77, 119.51, 114.73, 107.63, 61.97, 22.86, 17.40, 13.75. HRMS (ESI$^+$) m/z: Calcd for C$_{23}$H$_{21}$BrN$_3$O$_2$ 450.0812 [M+H]$^+$, Found 450.0815.

$^1$H and $^{13}$C Spectra of compound 3a (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3a (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3b (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3b (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3c (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3c (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3d (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3d (CDCl$_3$, 150MHz)
\(^1\)H NMR Spectra of compound 3e (CDCl\(_3\), 600 MHz)

\[^{13}\text{C} \text{NMR} \text{ Spectra of compound 3e (CDCl}_3\text{, 150 MHz)\)}}
$^1$H NMR Spectra of compound 3f (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3f (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3g (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3g (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3h (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectra of compound 3h (CDCl$_3$, 100 MHz)
$^1$H NMR Spectra of compound 3i (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3i (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3j (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3j (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3k (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3k (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3l (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3l (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3m (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3m (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3n (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3n (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3o (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3o (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 3p (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 3p (CDCl$_3$, 150 MHz)
\(^1\)H NMR Spectra of compound 3q (CDCl\(_3\), 400 MHz)

\(^{13}\)C NMR Spectra of compound 3q (CDCl\(_3\), 100 MHz)
$^1$H NMR Spectra of compound 3r (CDCl₃, 400 MHz)

$^{13}$C NMR Spectra of compound 3r (CDCl₃, 100 MHz)
$^1$H NMR Spectra of compound 4a (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 4a (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 4b (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectra of compound 4b (CDCl$_3$, 100 MHz)
$^1$H NMR Spectra of compound 4c (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectra of compound 4c (CDCl$_3$, 100 MHz)
$^1$H NMR Spectra of compound 4d (CDCl$_3$, 600 MHz)

$^{13}$C NMR Spectra of compound 4d (CDCl$_3$, 150 MHz)
$^1$H NMR Spectra of compound 4e (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectra of compound 4e (CDCl$_3$, 100 MHz)