

Substrate-induced DMSO activation and involved reaction for rapid construction of substituted pyrimidines

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1. Experimental Reagents and Instruments

Unless otherwise noted, all reactions were carried out under air atmosphere, commercial materials and solvents were used without further purification. ^1H NMR and ^{13}C NMR spectra were measured on a 600 MHz spectrometer (^1H : 600 MHz, ^{13}C : 150 MHz) using CDCl_3 as the solvent at room temperature. Melting points were measured by using a Gongyi X-5 microscopy digital melting point apparatus and are uncorrected. High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with ESI mode. Flash column chromatography was performed on silica gel, 200–300 mesh.

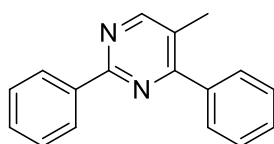
2. Experimental Procedures and Spectral Data of Compounds

2.1 General Procedure

A mixture of amidine hydrochlorides **1** (0.5 mmol), ketones **2** (0.2 mmol) and morphine (0.5 mmol) in DMSO (1.5 mL) was stirred at 140 °C for 15 h. After the reaction was finished, the mixture was added saturated sodium carbonate solution (10 mL) and extracted with ethyl acetate (30 mL*3 times), the organic phase was concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel using petroleum ether/EtOAc as the eluent to give the desired products **3**.

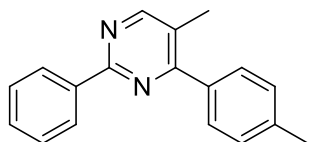
Note: The spectral data of the known compounds reported in this paper are consistent with those previously reported in the literatures.

2.2 Spectral Data of Compounds



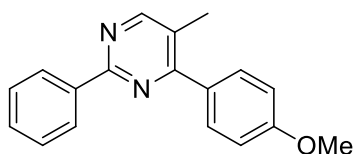
5-Methyl-2,4-diphenylpyrimidine (3aa)¹: White solid (41.4 mg, 84% yield); mp 83–84 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.68 (s, 1H), 8.51 (d, $J = 7.8$ Hz, 2H), 7.74 (d, $J = 7.8$ Hz, 2H), 7.54–7.47 (m, 6H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 165.0, 162.6, 159.3, 138.6, 137.9, 130.4, 129.4, 129.2, 128.6, 128.5, 128.2, 125.7, 17.1;

HRMS (ESI) m/z [M+H⁺] calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2$ 247.1235, found 247.1232.



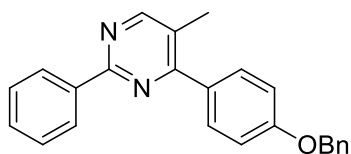
5-Methyl-2-phenyl-4-(p-tolyl)pyrimidine (3ab)¹: Light yellow solid (44.8 mg, 86% yield); mp 74–75°C; ¹H NMR (600 MHz, CDCl₃) δ 8.66 (s, 1H), 8.50 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.50-7.46 (m, 3H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 2.43 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 165.0, 162.6, 159.3, 139.5, 138.0, 135.8, 130.4, 129.22, 129.17, 128.6, 128.2, 125.6, 21.5, 17.3;

HRMS (ESI) m/z [M+H⁺] calcd for C₁₈H₁₇N₂ 261.1392, found 261.1388.



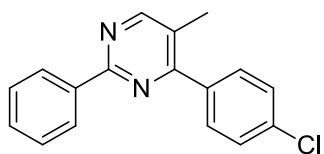
4-(4-Methoxyphenyl)-5-methyl-2-phenylpyrimidine (3ac)¹: Light yellow solid (43.1 mg, 78% yield); mp 117–118°C; ¹H NMR (600 MHz, CDCl₃) δ 8.63 (s, 1H), 8.50 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.49-7.45 (m, 3H), 7.04 (d, *J* = 7.8 Hz, 2H), 3.89 (s, 3H), 2.44 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 164.4, 162.5, 160.8, 159.3, 138.1, 131.1, 130.9, 130.2, 128.6, 128.1, 125.3, 113.9, 55.5, 17.5;

HRMS (ESI) m/z [M+H⁺] calcd for C₁₈H₁₇N₂O 277.1341, found 277.1340.



4-(4-(Benzyloxy)phenyl)-5-methyl-2-phenylpyrimidine (3ad): Yellow solid (45.8 mg, 65% yield); mp 121–122°C; ¹H NMR (600 MHz, CDCl₃) δ 8.64 (s, 1H), 8.50 (dd, *J* = 1.8, 7.8 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 2H), 7.50-7.47 (m, 5H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 9.0 Hz, 2H), 5.16 (s, 2H), 2.45 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 164.3, 162.6, 160.0, 159.3, 138.1, 136.9, 131.3, 130.9, 130.3, 128.8, 128.6, 128.2, 128.1, 127.6, 125.3, 114.8, 70.3, 17.5;

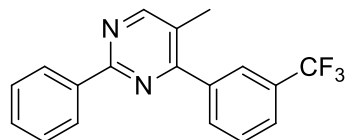
HRMS (ESI) m/z [M+H⁺] calcd for C₂₄H₂₁N₂O 353.1654, found 353.1652.



4-(4-Chlorophenyl)-5-methyl-2-phenylpyrimidine (3ae)¹: Light yellow solid (44.9 mg, 80% yield); mp 103–104°C; ¹H NMR (600 MHz, CDCl₃) δ 8.68 (s, 1H),

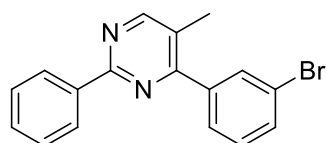
8.48-8.47 (m, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.50-7.47 (m, 5H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 163.8, 162.8, 159.6, 137.8, 137.0, 135.2, 130.7, 130.6, 128.8, 128.7, 128.2, 125.6, 17.2;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{Cl}$ 281.0846, found 281.0845.



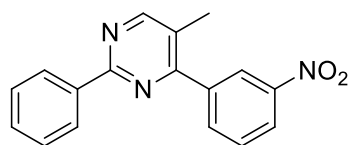
5-Methyl-2-phenyl-4-(3-(trifluoromethyl)phenyl)pyrimidine (3af): White solid (50.9 mg, 81% yield); mp 125–126 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.72 (s, 1H), 8.48 (d, $J = 7.2$ Hz, 2H), 8.01 (s, 1H), 7.92 (d, $J = 7.2$ Hz, 1H), 7.75 (d, $J = 7.8$ Hz, 1H), 7.65 (t, $J = 7.8$ Hz, 1H), 7.50-7.49 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 163.5, 162.9, 159.8, 139.4, 137.6, 132.5, 131.1 (q, $J = 33.0$ Hz), 130.7, 129.1, 128.7, 128.2, 126.3, 126.2 (q, $J = 4.5$ Hz), 125.7, 123.9 (q, $J = 271.5$ Hz), 17.0;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{18}\text{H}_{14}\text{F}_3\text{N}_2$ 315.1109, found 315.1104.



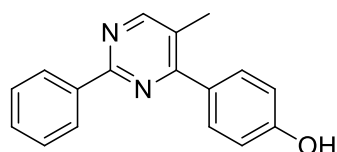
4-(3-Bromophenyl)-5-methyl-2-phenylpyrimidine (3ag): Yellow solid (44.3 mg, 68% yield); mp 130–131 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.69 (s, 1H), 8.49 (dd, $J = 7.8, 2.4$ Hz, 2H), 7.89 (s, 1H), 7.63 (t, $J = 7.8$ Hz, 2H), 7.50-7.47 (m, 3H), 7.38 (t, $J = 7.8$ Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 163.5, 162.8, 159.6, 140.6, 137.7, 132.4, 132.3, 130.6, 130.0, 128.6, 128.2, 127.8, 125.7, 122.7, 17.0;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{17}\text{H}_{14}\text{BrN}_2$ 326.0340, found 326.0341.



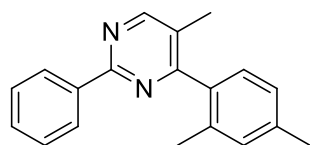
5-Methyl-4-(3-nitrophenyl)-2-phenylpyrimidine (3ah)¹: Yellow solid (33.8 mg, 58% yield); mp 138–139 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.74 (s, 1H), 8.62 (s, 1H), 8.49-8.47 (m, 2H), 8.35 (d, $J = 8.4$ Hz, 1H), 8.09 (d, $J = 7.2$ Hz, 1H), 7.71 (t, $J = 8.4$ Hz, 1H), 7.50-7.47 (m, 3H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 163.0, 162.3, 160.0, 148.4, 140.2, 137.4, 135.2, 130.8, 129.6, 128.7, 128.2, 125.7, 124.3, 124.2, 17.0;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_2$ 292.1086, found 292.1082.



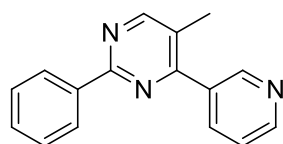
4-(5-Methyl-2-phenylpyrimidin-4-yl)phenol (3ai): White solid (21.0 mg, 40% yield); mp 120–121 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.63 (s, 1H), 8.47 (dd, $J = 8.4$, 2.4 Hz, 2H), 7.68 (d, $J = 9.0$ Hz, 2H), 7.49-7.46 (m, 3H), 6.95 (d, $J = 9.0$ Hz, 2H), 2.43 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 164.8, 162.5, 159.0, 157.7, 137.8, 131.1, 130.6, 130.5, 128.7, 128.2, 125.5, 115.6, 17.5;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}$ 263.1184, found 263.1183.



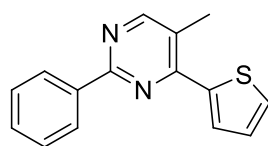
4-(2,4-Dimethylphenyl)-5-methyl-2-phenylpyrimidine (3aj): Colorless liquid (26.9 mg, 49% yield); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.68 (s, 1H), 8.46-8.44 (m, 2H), 7.48-7.45 (m, 3H), 7.16 (s, 1H), 7.14-7.11 (m, 2H), 2.40 (s, 3H), 2.18 (s, 3H), 2.16 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 167.3, 162.4, 158.5, 138.6, 138.0, 135.5, 135.4, 131.5, 130.3, 128.6, 128.4, 128.2, 126.9, 126.6, 21.4, 19.6, 16.1;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{19}\text{H}_{19}\text{N}_2$ 275.1548, found 275.1544.



5-Methyl-2-phenyl-4-(pyridin-3-yl)pyrimidine (3ak): Yellow liquid (36.1 mg, 73% yield); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.99 (d, $J = 1.2$ Hz, 1H), 8.73 (dd, $J = 4.8$, 1.2 Hz, 1H), 8.71 (s, 1H), 8.48 (dd, $J = 8.4$, 3.0 Hz, 2H), 8.09 (dt, $J = 7.8$, 1.2 Hz, 1H), 7.50-7.46 (m, 4H), 2.45 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 163.0, 162.1, 159.7, 150.3, 150.0, 137.5, 136.7, 134.4, 130.7, 128.7, 128.2, 125.9, 123.4, 17.0;

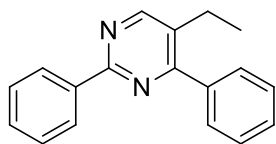
HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{16}\text{H}_{14}\text{N}_3$ 248.1188, found 248.1184.



5-Methyl-2-phenyl-4-(thiophen-2-yl)pyrimidine (3al): Light yellow liquid (38.9 mg, 77% yield); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.61 (s, 1H), 8.51 (dd, $J = 8.4$, 1.8 Hz, 2H), 7.77 (d, $J = 3.6$ Hz, 1H), 7.57 (d, $J = 4.8$ Hz, 1H), 7.52-7.47 (m, 3H), 7.21 (dd, J

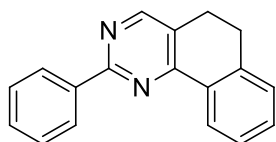
= 4.8, 3.6 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 162.3, 159.9, 157.3, 144.1, 137.7, 130.6, 130.1, 129.7, 128.6, 128.4, 128.2, 123.2, 18.4;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{S}$ 253.0799, found 253.0780.



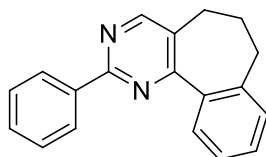
5-Ethyl-2,4-diphenylpyrimidine (3am)²: Colorless liquid (42.2 mg, 81% yield); ^1H NMR (600 MHz, CDCl_3) δ 8.73 (s, 1H), 8.48 (d, $J = 7.8$ Hz, 2H), 7.66 (d, $J = 7.8$ Hz, 2H), 7.52-7.46 (m, 6H), 2.79 (q, $J = 7.8$ Hz, 2H), 1.21 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 165.3, 162.4, 158.3, 138.8, 137.9, 131.7, 130.4, 129.2, 129.0, 128.6, 128.5, 128.2, 23.2, 15.1;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2$ 261.1392, found 261.1390.

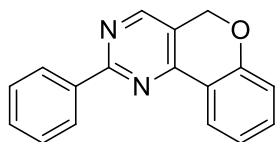


2-Phenyl-5,6-dihydrobenzo[h]quinazoline (3an)³: Light yellow solid (45.5 mg, 88% yield); mp 69–70 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.61 (s, 1H), 8.57-8.55 (m, 3H), 7.53-7.48 (m, 3H), 7.44-7.41 (m, 2H), 7.28-7.26 (m, 1H), 3.03-2.95 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 163.4, 159.4, 156.0, 139.5, 138.3, 132.9, 131.2, 130.4, 128.6, 128.3, 128.2, 127.5, 126.1, 125.9, 27.8, 24.5;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{18}\text{H}_{15}\text{N}_2$ 259.1235, found 259.1239.

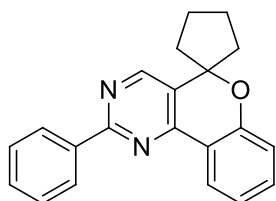


2-Phenyl-6,7-dihydro-5H-benzo[6,7]cyclohepta[1,2-d]pyrimidine (3ao): Light yellow solid (45.2 mg, 83% yield); mp 72–73 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.63 (s, 1H), 8.56 (dd, $J = 7.8, 1.8$ Hz, 2H), 7.91 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.52-7.43 (m, 5H), 7.30 (d, $J = 7.2$ Hz, 1H), 2.62 (t, $J = 7.2$ Hz, 2H), 2.54 (t, $J = 7.2$ Hz, 2H), 2.34-2.29 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.0, 163.5, 156.6, 140.3, 138.5, 138.1, 130.4, 130.2, 130.0, 129.2, 129.0, 128.6, 128.2, 127.1, 33.1, 31.3, 27.1; HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2$ 273.1392, found 273.1391.



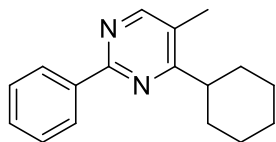
2-Phenyl-5H-chromeno[4,3-d]pyrimidine (3ap)³: Yellow solid (32.8 mg, 63% yield); mp 91–92 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.56-8.54 (m, 2H), 8.53 (s, 1H), 8.42 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.53-7.51 (m, 3H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.28 (s, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 164.8, 157.8, 155.9, 152.7, 137.9, 133.6, 130.8, 128.7, 128.4, 125.6, 122.6, 121.5, 120.4, 117.5, 65.7;

HRMS (ESI) m/z [M+H⁺] calcd for C₁₇H₁₃N₂O 261.1028, found 261.1025.



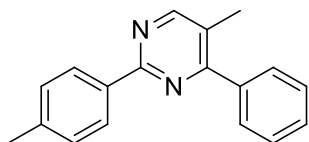
2-Phenylspiro[chromeno[4,3-d]pyrimidine-5,1'-cyclopentane] (3aq): Yellow solid (37.7 mg, 60% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.60 (s, 1H), 8.56 (dd, *J* = 7.8, 1.8 Hz, 2H), 8.44 (d, *J* = 7.2 Hz, 1H), 7.54-7.50 (m, 3H), 7.40 (td, *J* = 7.8, 1.2 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 2.40-2.37 (m, 2H), 2.07-2.05 (m, 2H), 2.02-1.97 (m, 2H), 1.90-1.87 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 163.8, 156.3, 155.2, 151.7, 137.9, 133.3, 130.7, 128.6, 128.3, 126.9, 125.5, 122.0, 121.3, 118.0, 87.8, 39.0, 24.0;

HRMS (ESI) m/z [M+H⁺] calcd for C₂₁H₁₉N₂O 315.1497, found 315.1501.

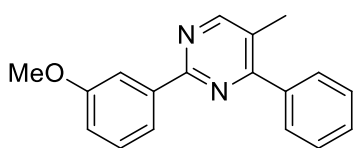


4-Cyclohexyl-5-methyl-2-phenylpyrimidine (3ar)¹: White solid (18.7 mg, 37% yield); mp 79–80 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.46-8.45 (m, 3H), 7.48-7.42 (m, 3H), 2.88-2.83 (m, 1H), 2.31 (s, 3H), 1.92-1.90 (m, 2H), 1.82-1.78 (m, 5H), 1.44-1.38 (m, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 172.3, 162.4, 157.5, 138.5, 130.1, 128.5, 128.1, 125.4, 42.3, 31.2, 26.6, 26.2, 15.2;

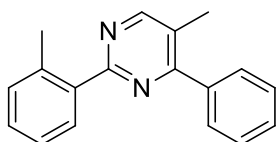
HRMS (ESI) m/z [M+H⁺] calcd for C₁₇H₂₁N₂ 253.1705, found 253.1706.



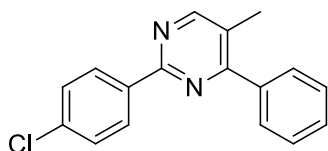
5-Methyl-4-phenyl-2-(p-tolyl)pyrimidine (3ba)¹: Light yellow solid (39.6 mg, 76% yield); mp 81–82 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.65 (s, 1H), 8.39 (d, *J* = 7.8 Hz, 2H), 7.74–7.73 (m, 2H), 7.53–7.47 (m, 3H), 7.28 (d, *J* = 7.8 Hz, 2H), 2.42 (s, 3H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (the ¹³C signal of one carbon overlaps) 165.0, 162.7, 159.3, 140.6, 138.7, 135.2, 129.4, 129.2, 128.5, 128.1, 125.4, 21.6, 17.2; HRMS (ESI) *m/z* [*M*+*H*⁺] calcd for C₁₈H₁₇N₂ 261.1392, found 261.1387.



2-(3-Methoxyphenyl)-5-methyl-4-phenylpyrimidine (3ca)¹: Light yellow solid (40.3 mg, 73% yield); mp 82–83 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.67 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 8.08 (t, *J* = 1.8 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.53–7.48 (m, 3H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.02 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.91 (s, 3H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 165.0, 162.4, 160.1, 159.3, 139.4, 138.6, 129.6, 129.4, 129.2, 128.4, 125.8, 120.8, 116.8, 113.0, 55.5, 17.2; HRMS (ESI) *m/z* [*M*+*H*⁺] calcd for C₁₈H₁₇N₂O 277.1341, found 277.1338.

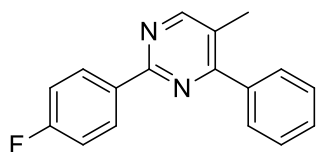


5-Methyl-4-phenyl-2-(o-tolyl)pyrimidine (3da): Light yellow liquid (31.3 mg, 60% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.72 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.72–7.70 (m, 2H), 7.52–7.46 (m, 3H), 7.34–7.29 (m, 3H), 2.62 (s, 3H), 2.45 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 165.5, 164.7, 159.1, 138.5, 138.4, 137.3, 131.3, 130.5, 129.4, 129.22, 129.18, 128.5, 126.0, 125.1, 21.4, 17.1; HRMS (ESI) *m/z* [*M*+*H*⁺] calcd for C₁₈H₁₇N₂ 261.1392, found 261.1389.



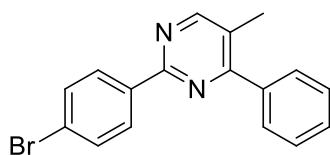
2-(4-Chlorophenyl)-5-methyl-4-phenylpyrimidine (3ea)¹: Light yellow solid (35.9 mg, 64% yield); mp 107–108 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.66 (s, 1H), 8.44 (d, *J* = 8.4 Hz, 2H), 7.72 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.54–7.50 (m, 3H), 7.44 (d, *J* = 8.4 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (the ¹³C signal of one carbon overlaps) 165.1, 161.7, 159.3, 138.4, 136.6, 136.4, 129.5, 129.2, 128.8, 128.5, 126.0, 17.2;

HRMS (ESI) m/z [M+H⁺] calcd for C₁₇H₁₄N₂Cl 281.0846, found 281.0839.



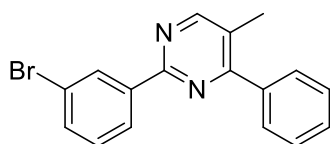
2-(4-Fluorophenyl)-5-methyl-4-phenylpyrimidine (3fa)¹: White solid (20.6 mg, 39% yield); mp 99–100 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.65 (s, 1H), 8.52–8.49 (m, 2H), 7.73–7.71 (m, 2H), 7.54–7.49 (m, 3H), 7.15 (t, *J* = 8.4 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 164.9, 164.5 (d, *J* = 248.5 Hz), 161.6, 159.2, 138.4, 133.9, 130.1 (d, *J* = 9.0 Hz), 129.3, 129.0, 128.3, 125.4, 115.3 (d, *J* = 21.5 Hz), 16.9 ;

HRMS (ESI) m/z [M+H⁺] calcd for C₁₇H₁₄N₂F 265.1141, found 265.1137.



2-(4-Bromophenyl)-5-methyl-4-phenylpyrimidine (3ga)¹: White solid (44.2 mg, 68% yield); mp 98–99 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.66 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 2H), 7.71 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.54–7.49 (m, 3H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 165.2, 161.8, 159.4, 138.5, 136.9, 131.8, 129.8, 129.5, 129.2, 128.5, 126.1, 125.2, 17.2;

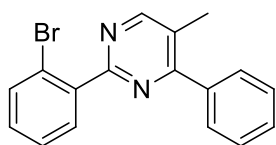
HRMS (ESI) m/z [M+H⁺] calcd for C₁₇H₁₄N₂Br 325.0340, found 325.0336.



2-(3-Bromophenyl)-5-methyl-4-phenylpyrimidine (3ha): White solid (41.0 mg, 63% yield); mp 96–97 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.67–8.66 (m, 2H), 8.43 (m,

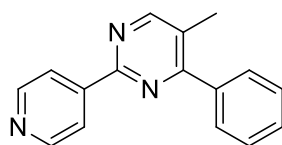
1H), 7.72-7.70 (m, 2H), 7.58-7.57 (m, 1H), 7.54-7.48 (m, 3H), 7.33 (t, $J = 7.8$ Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 165.2, 161.2, 159.4, 140.0, 138.4, 133.3, 131.2, 130.1, 129.6, 129.2, 128.5, 126.7, 126.4, 122.9, 17.2;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{17}\text{H}_{14}\text{BrN}_2$ 325.0340, found 325.0345.



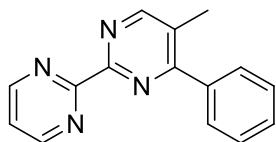
2-(2-Bromophenyl)-5-methyl-4-phenylpyrimidine (3ia): Light yellow liquid (38.4 mg, 59% yield); ^1H NMR (600 MHz, CDCl_3) δ 8.74 (s, 1H), 7.76-7.73 (m, 3H), 7.70 (d, $J = 7.8$ Hz, 1H), 7.51-7.47 (m, 3H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.28-7.25 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 165.0, 164.2, 159.1, 139.9, 138.1, 133.8, 131.7, 130.3, 129.5, 129.3, 128.5, 127.5, 126.1, 122.0, 17.2;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{17}\text{H}_{14}\text{BrN}_2$ 325.0340, found 325.0343.



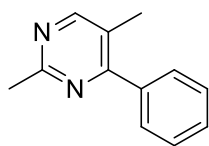
5-Methyl-4-phenyl-2-(pyridin-4-yl)pyrimidine (3ka)¹: Light yellow solid (31.1 mg, 67% yield); mp 115–116 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.75 (d, $J = 6.0$ Hz, 2H), 8.72 (s, 1H), 8.34 (d, $J = 6.0$ Hz, 2H), 7.72 (d, $J = 7.8$ Hz, 2H), 7.55-7.51 (m, 3H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 165.4, 160.6, 159.6, 150.5, 145.2, 138.1, 129.7, 129.2, 128.6, 127.6, 122.1, 17.3;

HRMS (ESI) m/z [$\text{M}+\text{H}^+$] calcd for $\text{C}_{16}\text{H}_{14}\text{N}_3$ 248.1188, found 248.1190.



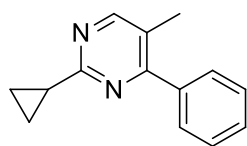
5-Methyl-4-phenyl-2,2'-bipyrimidine (3la): Yellow solid (37.7 mg, 76% yield); mp 126–127 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.98 (d, $J = 4.8$ Hz, 2H), 8.85 (s, 1H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.54-7.47 (m, 3H), 7.38 (t, $J = 4.8$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.6, 163.0, 160.6, 159.6, 158.1, 138.0, 129.5, 129.2, 128.8, 128.5, 121.2, 17.2;

HRMS (ESI) m/z [M+H⁺] calcd for C₁₅H₁₃N₄ 249.1140, found 249.1143.



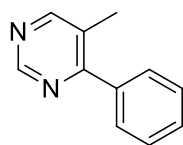
2,5-Dimethyl-4-phenylpyrimidine (3ma): Yellow liquid (16.0 mg, 43% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.51 (s, 1H), 7.57 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.49-7.44 (m, 3H), 2.75 (s, 3H), 2.32 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 165.8, 165.3, 158.9, 138.4, 129.3, 128.9, 128.6, 124.7, 25.8, 16.8;

HRMS (ESI) m/z [M+H⁺] calcd for C₁₂H₁₃N₂ 185.1079, found 185.1075.



2-Cyclopropyl-5-methyl-4-phenylpyrimidine (3na): Light yellow liquid (15.6 mg, 37% yield); ¹H NMR (600 MHz, CDCl₃) δ 8.43 (s, 1H), 7.60-7.58 (m, 2H), 7.48-7.42 (m, 3H), 2.30 (s, 3H), 2.29-2.25 (m, 1H), 1.16-1.13 (m, 2H), 1.05-1.02 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 169.7, 164.7, 158.8, 138.7, 129.2, 129.0, 128.4, 124.2, 18.0, 16.8, 10.4;

HRMS (ESI) m/z [M+H⁺] calcd for C₁₄H₁₅N₂ 211.1235, found 211.1231.



5-Methyl-2,4-diphenylpyrimidine (3oa)¹: Colorless liquid (17.4 mg, 51% yield); ¹H NMR (600 MHz, CDCl₃) δ 9.12 (s, 1H), 9.61 (s, 1H), 7.62-7.60 (m, 2H), 7.51-7.46 (m, 3H), 2.39 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 165.2, 158.8, 156.8, 138.0, 129.5, 128.9, 128.6, 128.3, 17.2;

HRMS (ESI) m/z [M+H⁺] calcd for C₁₁H₁₁N₂ 171.0922, found 171.0916.

3. References

1. C. Xu, S.-F. Jiang, X.-H. Wen, Q. Zhang, Z.-W. Zhou, Y. Wu, F.-C. Jia and A. Wu. *Adv. Synth. Catal.* 2018, **360**, 2267;
2. M. G. Barthakur, S. Gogoi, M. Dutta and R. C. Boruah. *Steroids*. 2009, **74**, 730.
3. J. Gogoi, P. Gogoi, P. Bezbaruan and R. C. Boruan. *Tetrahedron Lett.* 2013, **54**, 7136.

4. Copies for ^1H NMR and ^{13}C NMR of the Pyrimidines

