Supporting Information
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Supporting Information for

One-pot Synthesis of Functionalized Benzimidazoles and 1H-Pyrimidines via Cascade Reactions of o-Aminoanilines or Naphthalene-1,8-diamine with Alkynes and p-Tolylsulfonyl Azide

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General Considerations

Infrared spectrums were obtained on a FTIR spectrometer. NMR specrums were recorded for $^1$H NMR at 400 MHz or 500 MHz, for $^{13}$C NMR at 100 MHz or 125 MHz. Chemical shifts are reported relative to residue peaks of d$_6$-DMSO (2.50 ppm for $^1$H and 40.0 for $^{13}$C). The following abbreviations are used to describe peak patterns where appropriate: s = single, d = double, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants are reported in Hertz (Hz). Low-resolution MS and HRMS were obtained using ESI ionization. Melting points were measured with micro melting point apparatus.

General Procedure for the Synthesis of Benzimidazoles 5.

\[
\begin{align*}
\text{1. CuI, Et}_3\text{N} \\
\text{2. H}^+ \\
\text{TsN}_3 & \quad \text{1} \quad \text{2} \quad \text{3} \\
\text{R}^1 & \quad \text{N} & \quad \text{NHR}^2 \\
\text{R}^2 & \quad \text{R}^3 \\
\rightarrow \\
\text{R}^1 & \quad \text{N} & \quad \text{N} \\
\text{R}^2 & \quad \text{R}^3 \\
\end{align*}
\]

To a solution of $p$-tolylsulfonyl azide (2.2 mmol), terminal alkynes (2.1 mmol), ortho-aminooanilines (2 mmol), CuI (0.2 mmol) in MeCN (10 mL) in Schlenk tube was added dropwise TEA (2 mmol). The reaction was stirred at room temperature under N$_2$ for 6 h. Then, conc. H$_2$SO$_4$ (98 %, 0.4 mL) was added to the reaction mixture, the resulting solution was heated under reflux for 4 h. After cooled to room temperature, the solution was poured into water (20 mL), neutralized with K$_2$CO$_3$. MeCN was removed in vacuum, and then the resulting solution was extracted with ethyl acetate (5 mL×3). The organic layer was combined, dried over anhydrous sodium sulfate. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (from 2:1 to 1:2).


\[
\begin{align*}
\text{1. CuI, Et}_3\text{N} \\
\text{2. H}^+ \\
\text{TsN}_3 & \quad \text{1} \quad \text{2} \quad \text{3} \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{R} & \quad \text{R} \\
\rightarrow \\
\text{R} & \quad \text{N} & \quad \text{N} \\
\end{align*}
\]

To a solution of $p$-tolylsulfonyl azide (2.2 mmol), terminal alkynes (2.1 mmol), naphthalene-1,8-diamine (2 mmol), CuI (0.2 mmol) in MeCN (10 mL) in Schlenk tube was added dropwise TEA (2 mmol). The reaction was stirred at room temperature under N$_2$ for 6 h. Then, conc. H$_2$SO$_4$ (98 %, 0.4 mL) was added to the reaction mixture, the resulting solution was heated under reflux for 4 h. After cooled to room temperature, the solution was poured into water (20 mL), neutralized with
K₂CO₃. The organic solvent was removed in vacuum, and then the resulting solution was extracted with ethyl acetate (5 mL×3). The organic layer was combined, dried over anhydrous sodium sulfate. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (3:1).

**Characterization Data**

*N-(2-aminophenyl)-2-phenyl-N'-tosylacetimid amide (4a)*

![Structure of 4a and 4a']

(4a/4a' ≈ 10/1)

Yellow syrup liquid. ¹H NMR (500 MHz, d⁶-DMSO): δ 2.31 (2.7H, s), 2.38 (0.27H, s), 3.66 (0.16H, s), 4.31 (1.8H, s), 4.93 (2.0H, br), 6.46 (0.09H, t, J = 7.0 Hz), 6.55(0.92H, t, J = 7.5 Hz), 6.67(0.10H, d, J = 7.5 Hz), 6.76 (0.98H, d, J = 7.5 Hz), 6.88-6.89 (0.19H, m), 6.97-7.00 (1.9H, m), 7.04-7.14 (0.47H, m), 7.21 (1.9H, d, J = 7.5 Hz), 7.25-7.28 (0.93H, m), 7.35 (2.0 H, t, J = 7.2 Hz), 7.43 (1.9H, d, J = 7.2 Hz), 7.51 (1.8H, d, J = 8.0 Hz), 7.72-7.70 (0.36H, m), 9.66 (0.09H, brs), 9.87 (0.91H, brs); ¹³C NMR (125 MHz, d⁶-DMSO) δ 21.37, 38.92, 116.47, 116.54, 122.50, 126.12, 126.66, 127.16, 127.36, 128.13, 128.52, 128.93, 129.18, 129.53, 129.71, 129.80, 136.21, 141.46, 142.06, 143.72, 165.72; IR (KBr, cm⁻¹) 3362, 3266, 3062, 3031, 2922, 1626, 1571, 1533, 1497, 1459, 1398, 1273, 1142, 1089, 1031, 1017, 984, 814, 751, 697, 669, 591, 555; MS (ESI) m/z: 378.0 ([M-H]⁻); HRMS (ESI) m/z calcd for C₂₁H₂₂N₃O₂S ([M+H]+), 380.1427; found 380.1430.

2-Benzyl-1H-benzo[d]imidazole (5a)

![Structure of 5a]

White solid. M.p.187-188 °C. ¹H NMR (400 MHz, d⁶-DMSO) δ 4.18 (2H, s), 7.11-7.13 (2H, m), 7.20-7.24 (1H, m), 7.29-7.35 (4H, m), 7.48 (2H, brs), 12.32 (1H, brs); ¹³C NMR (100 MHz, d⁶-DMSO) δ 35.36, 121.68, 126.90, 128.86, 129.15,
138.06, 153.92; IR (KBr, cm⁻¹) 3432, 3083, 3050, 2837, 2738, 2687, 2637, 1624, 1588, 1536, 1493, 1457, 1447, 1427, 1323, 1271, 1224, 1196, 1148, 1024, 1013, 1001, 926, 890, 848, 768, 749, 723, 695, 670, 619, 565; MS (ESI) m/z: 209.0 ([M+H]+); HRMS (ESI) m/z calcd for C₁₄H₁₃N₂ ([M+H]+), 209.1073; found 209.1073.

2-(4-Methoxybenzyl)-1H-benzo[d]imidazole (5b)

Slightly yellow solid. M.p. 165-166 °C. ¹H NMR (400 MHz, d₆-DMSO) δ 3.71 (3H, s), 4.10 (2H, s), 6.88 (2H, d, J = 8.8 Hz), 7.10-7.13 (2H, m), 7.25 (2H, d, J = 8.4 Hz), 7.47 (2H, brs), 12.24 (1H, brs); ¹³C NMR (125 MHz, d₆-DMSO) δ 34.48, 55.43, 114.30, 114.85, 121.55, 129.91, 130.13, 139.22, 154.28, 158.41; IR (KBr, cm⁻¹) 3436, 2999, 2937, 2901, 2841, 2759, 1611, 1584, 1537, 1512, 1456, 1442, 1412, 1326, 1305, 1271, 1244, 1184, 1105, 1029, 1000, 922, 838, 814, 769, 752, 729, 715, 573, 511; MS (ESI) m/z: 239.0 ([M+H]+); HRMS (ESI) m/z calcd for C₁₅H₁₅N₂O ([M+H]+), 239.1179; found 239.1179.

2-(4-tert-Butylbenzyl)-1H-benzo[d]imidazole (5c)

Slightly yellow solid. M.p. 169-171 °C. ¹H NMR (400 MHz, d₆-DMSO) δ 1.24 (9H, s), 4.13 (2H, s), 7.09-7.13 (2H, m), 7.25 (2H, d, J = 8.0 Hz), 7.32 (2H, d, J = 8.0 Hz), 7.46-7.48 (2H, m), 12.27 (1H, brs); ¹³C NMR (125 MHz, d₆-DMSO) δ 31.48, 34.42, 34.86, 34.86, 114.84, 121.54, 125.52, 128.71, 134.96, 139.27, 149.20, 154.04; IR (KBr, cm⁻¹) 3399, 3057, 2964, 2905, 2866, 2775, 1624, 1593, 1540, 1517, 1456, 1434, 1422, 1363, 1310, 1271, 1222, 1203, 1171, 1150, 1109, 1024, 1000, 830, 808, 767, 745, 735, 715,
567; MS (ESI) m/z: 265.0 ([M+H]+); HRMS (ESI) m/z calcd for C_{18}H_{21}N_{2} ([M+H]^+), 265.1699; found 265.1700.

2-(2-Chlorobenzyl)-1H-benzo[d]imidazole (5d)

White solid. M.p. 215-217 °C. \(^1\)H NMR (400 MHz, d\(_6\)-DMSO) δ 4.31 (2H, s), 7.11-7.13 (2H, m), 7.30-7.32 (2H, m), 7.37-7.40 (1H, m), 7.45-7.49 (3H, m), 12.32 (1H, brs); \(^{13}\)C NMR (125 MHz, d\(_6\)-DMSO) δ 33.34, 115.13, 121.93, 127.88, 129.18, 129.86, 132.02, 133.88, 135.78, 152.76; IR (KBr, cm\(^{-1}\)) 3415, 3089, 3049, 3002, 2950, 2911, 2853, 2806, 2756, 1623, 1540, 1483, 1472, 1457, 1444, 1419, 1326, 1271, 1218, 1196, 1052, 1031, 1003, 931, 850, 751, 739, 684, 610; MS (ESI) m/z: 243.3 ([M+H]^+); HRMS (ESI) m/z calcd for C\(_{14}\)H\(_{12}\)ClN\(_{2}\) ([M+H]^+), 243.0684; found 243.0685.

2-(3-Chlorobenzyl)-1H-benzo[d]imidazole (5e)

White solid. M.p. 182-183 °C. \(^1\)H NMR (400 MHz, d\(_6\)-DMSO) δ 4.20 (2H, s), 7.11-7.15 (2H, m), 7.28-7.36 (3H, m), 7.43 (1H, s), 7.48-7.51 (2H, m), 12.24 (1H, brs); \(^{13}\)C NMR (125 MHz, d\(_6\)-DMSO) δ 34.97, 115.24, 122.18, 127.20, 128.12, 130.93, 133.70, 140.54, 153.54; IR (KBr, cm\(^{-1}\)) 3431, 3055, 3026, 2995, 2935, 2840, 2742, 2687, 2637, 2523, 1617, 1598, 1577, 1487, 1477, 1454, 1445, 1385, 1317, 1299, 1273, 1220, 1203, 1166, 1150, 1093, 1080, 1027, 1002, 886, 864, 794, 769, 746, 685, 661, 616, 535; MS (ESI) m/z: 243.3 ([M+H]^+); HRMS (ESI) m/z calcd for C\(_{14}\)H\(_{12}\)ClN\(_{2}\) ([M+H]^+), 243.0684; found 243.0683.

2-(4-Chlorobenzyl)-1H-benzo[d]imidazole (5f)
White solid. M.p. 189-191 °C. \(^1\)H NMR (400 MHz, d\(^6\)-DMSO) \(\delta\) 4.18 (2H, s), 7.10-7.14 (2H, m), 7.34-7.39 (4H, m), 7.48 (1H, brs), 12.33 (1H, brs); \(^{13}\)C NMR (100 MHz, d\(^6\)-DMSO) \(\delta\) 34.56, 121.71, 128.76, 131.04, 131.64, 136.98, 153.47; IR (KBr, cm\(^{-1}\)) 3414, 3088, 3055, 2838, 2733, 2687, 2631, 1625, 1591, 1539, 1491, 1456, 1440, 1425, 1388, 1322, 1271, 1225, 1196, 1178, 1151, 1109, 1095, 1026, 1016, 1002, 962, 924, 890, 837, 819, 801, 766, 755, 745, 683, 617, 539; MS (ESI) m/z: 243.1 ([M+H]\(^+\)); HRMS (ESI) m/z calcd for C\(_{14}\)H\(_{12}\)ClN\(_2\) ([M+H]\(^+\)), 243.0684; found 243.0685.

2-Pentyl-1\(^H\)-benzo[d]imidazole (5g)

![Structure of 2-Pentyl-1H-benzo[d]imidazole (5g)](image)

White solid. M.p. 162-163 °C. \(^1\)H NMR (400 MHz, d\(^6\)-DMSO) \(\delta\) 0.85 (3H, t, \(J = 6.2\) Hz), 1.28-1.31 (4H, m), 1.72-1.80 (2H, m), 2.79 (2H, t, \(J = 7.4\) Hz), 7.07-7.12 (2H, m), 7.45-7.47 (2H, m), 12.21 (1H, brs); \(^{13}\)C NMR (125 MHz, d\(^6\)-DMSO) \(\delta\) 14.16, 22.19, 27.64, 28.90, 31.28, 114.77, 121.41, 139.18, 155.59; IR (KBr, cm\(^{-1}\)) 3432, 3050, 2952, 2867, 2733, 2673, 1623, 1590, 1538, 1482, 1456, 1436, 1420, 1379, 1351, 1315, 1272, 1234, 1224, 1200, 1154, 1109, 1021, 1000, 966, 929, 900, 842, 769, 751, 742, 737, 617; MS (ESI) m/z: 189.0 ([M+H]\(^+\)); HRMS (ESI) m/z calcd for C\(_{14}\)H\(_{17}\)N\(_2\) ([M+H]\(^+\)), 189.1386; found 189.1377.

2-Hexyl-1\(^H\)-benzo[d]imidazole (5h)

![Structure of 2-Hexyl-1H-benzo[d]imidazole (5h)](image)

White solid. M.p. 136-138 °C. \(^1\)H NMR (400 MHz, d\(^6\)-DMSO) \(\delta\) 0.84 (3H, t, \(J = 7.0\) Hz), 1.27-1.33 (6H, m), 1.71-1.78 (2H, m), 2.79 (2H, t, \(J = 7.8\) Hz), 7.07-7.11 (2H,
m), 7.45 (2H, m), 12.19 (1H, brs); $^{13}$C NMR (100 MHz, d$_6$-DMSO) δ 14.34, 22.43, 27.99, 28.80, 28.98, 31.42, 121.42, 155.57; IR (KBr, cm$^{-1}$) 3434, 3051, 2952, 2928, 2856, 2734, 2685, 1623, 1590, 1539, 1482, 1455, 1422, 1375, 1317, 1274, 1259, 1225, 1201, 1182, 1157, 1109, 1030, 1002, 933, 768, 751, 739, 617; MS (ESI) m/z: 203.2 ([M+H]$^+$); HRMS (ESI) m/z calcd for C$_{13}$H$_{19}$N$_2$ ([M+H]$^+$), 203.1543; found 203.1533.

2-Heptyl-1$H$-benzo[d]imidazole (5i)

White solid. M.p. 143-145 °C. $^1$H NMR (400 MHz, d$_6$-DMSO) δ 0.84 (3H, t, $J$ = 6.4 Hz), 1.24- 1.30 (8H, m), 1.72-1.77 (2H, m), 2.79 (2H, t, $J$ = 7.4 Hz), 7.07-7.11 (2H, m), 7.45 (2H, brs), 12.19 (1H, brs); $^{13}$C NMR (100 MHz, d$_6$-DMSO) δ14.36, 22.52, 28.03, 28.86, 28.97, 29.09, 31.60, 121.36, 155.56; IR (KBr, cm$^{-1}$) 3431, 3086, 3053, 2955, 2927, 2855, 2739, 2679, 1623, 1590, 1541, 1482, 1455, 1423, 1377, 1319, 1273, 1223, 1200, 1109, 1029, 1002, 928, 766, 751, 737, 617; MS (ESI) m/z: 217.7 ([M+H]$^+$); HRMS (ESI) m/z calcd for C$_{14}$H$_{21}$N$_2$ ([M+H]$^+$), 217.1699; found 217.1696.

2-Octyl-1$H$-benzo[d]imidazole (5j)

White solid. M.p. 140-142 °C. $^1$H NMR (400 MHz, d$_6$-DMSO) δ0.83 (3H, t, $J$ = 7.0 Hz), 1.22- 1.30 (10H, m), 1.71-1.79 (2H, m), 2.78 (2H, t, $J$ = 7.4 Hz), 7.07-7.11 (2H, m), 7.44-7.46 (2H, m), 12.21 (1H, brs); $^{13}$C NMR (100 MHz, d$_6$-DMSO) δ14.36, 22.53, 28.04, 28.98, 29.04, 29.13, 29.17, 31.71, 121.39, 155.55; IR (KBr, cm$^{-1}$) 3434, 3051, 2926, 2855, 2733, 2667, 1624, 1590, 1538, 1481, 1449, 1435, 1419, 1377, 1315, 1272, 1224, 1197, 1109, 1023, 1001, 929, 911, 841, 769, 752, 741, 617; MS (ESI) m/z: 231.5 ([M+H]$^+$); HRMS (ESI) m/z calcd for C$_{15}$H$_{23}$N$_2$ ([M+H]$^+$), 231.1845; found 231.1845.
2-Nonyl-1H-benzo[d]imidazole (5k)

White solid. M.p. 126-128 °C. $^1$H NMR (400 MHz, d$_6$-DMSO) $\delta$ 0.83 (3H, t, $J$ = 6.8 Hz), 1.22- 1.28 (12H, m), 1.73-1.76 (2H, m), 2.78 (2H, t, $J$ = 7.6 Hz), 7.01-7.11 (2H, m), 7.44-7.46 (2H, m), 12.19 (1H, brs); $^{13}$C NMR (100 MHz, d$_6$-DMSO) $\delta$ 14.37, 22.54, 28.02, 28.97, 29.14, 29.21, 29.34, 31.72, 121.40, 155.57; IR (KBr, cm$^{-1}$) 3433, 3088, 3052, 2925, 2770, 1622, 1591, 1542, 1482, 1454, 1421, 1321, 1218, 1198, 1111, 1028, 1004, 928, 902, 752, 739, 617; MS (ESI) m/z: 245.2 ([M+H]$^+$); HRMS (ESI) m/z calcd for C$_{16}$H$_{25}$N$_2$ ([M+H]$^+$), 245.2012; found 245.2002.

2-Methyl-1H-benzo[d]imidazole (5l)

White solid. M.p. 176-177 °C. $^1$H NMR (400 MHz, d$_6$-DMSO) $\delta$ 0.85 (3H, t, $J$ = 6.2 Hz), 1.28- 1.31 (4H, m), 1.72-1.80 (2H, m), 2.79 (2H, t, $J$ = 7.4 Hz), 7.07-7.12 (2H, m), 7.45-7.47 (2H, m), 12.21 (1H, brs); $^{13}$C NMR (100 MHz, d$_6$-DMSO) $\delta$ 14.26, 22.29, 27.72, 28.94, 31.32, 121.42, 155.58; IR (KBr, cm$^{-1}$) 3448, 3098, 3063, 2996, 2917, 2876, 2848, 2788, 2679, 1622, 1592, 1557, 1488, 1464, 1450, 1418, 1387, 1361, 1272, 1219, 1044, 1028, 1004, 924, 897, 836, 766, 737, 675, 625, 618; MS (ESI) m/z: 133.0 ([M+H]$^+$); HRMS (ESI) m/z calcd for C$_8$H$_9$N$_2$ ([M+H]$^+$), 133.0760; found 133.0759.

2-(4-Chlorobenzyl)-5,6-dimethyl-1H-benzo[d]imidazole (5m)

Slightly yellow solid. M.p. 199-201 °C. $^1$H NMR (400 MHz, d$_6$-DMSO) $\delta$ 2.26 (6H, s),
4.13 (2H, s), 7.24 (1H, s), 7.31-7.37 (4H, m), 12.08 (1H, brs); \(^{13}\)C NMR (125 MHz, d\(^6\)-DMSO) \(\delta\) 20.41, 34.69, 115.36, 128.94, 130.38, 131.13, 131.85, 137.29, 152.77; IR (KBr, cm\(^{-1}\)) 3430, 3134, 3098, 3050, 2967, 2938, 2880, 1630, 1585, 1542, 1491, 1466, 1441, 1418, 1406, 1385, 1306, 1243, 1188, 1172, 1165, 1091, 1026, 1017, 999, 917, 872, 853, 804, 694; MS (ESI) m/z: 271.6 ([M+H]\(^+\)); HRMS (ESI) m/z calcd for C\(_{16}\)H\(_{16}\)ClN\(_2\) ([M+H]\(^+\)), 271.0997; found 271.0995.

2-(4-Chlorobenzyl)-5,6-dichloro-1\(^{H}\)-benzo[d]imidazole (5n)

![Chemical structure](attachment:image)

Pink solid. M.p. 214-215 °C. \(^1\)H NMR (400 MHz, d\(^6\)-DMSO) \(\delta\) 4.19 (2H, s), 7.33-7.39 (4H, m), 7.69 (1H, s), 7.80 (1H, s), 12.63 (1H, brs); \(^{13}\)C NMR (100 MHz, d\(^6\)-DMSO) \(\delta\) 34.45, 122.98, 129.90, 124.04, 124.48, 128.89, 131.20, 131.85, 134.36, 136.42, 143.48, 156.57; IR (KBr, cm\(^{-1}\)) 3420, 3093, 3006, 2939, 2848, 2775, 2679, 1627, 1578, 1534, 1492, 1446, 1400, 1346, 1295, 1225, 1169, 1097, 1017, 971, 913, 870, 847, 803, 762, 690, 655, 542, 503; MS (ESI) m/z: 311.0 ([M+H]\(^+\)); HRMS (ESI) m/z calcd for C\(_{16}\)H\(_{10}\)Cl\(_3\)N\(_2\) ([M+H]\(^+\)), 310.9904; found 310.9908.

2-(2-Chlorobenzyl)-1-methyl-1\(^{H}\)-benzo[d]imidazole (5o)

![Chemical structure](attachment:image)

Slightly yellow solid. M.p. 119-121 °C. \(^1\)H NMR (400 MHz, d\(^6\)-DMSO) \(\delta\) 3.76 (3H, s), 4.37 (2H, s), 7.13-7.25 (3H, m), 7.27-7.31 (2H, m), 7.47-7.55 (3H, m); \(^{13}\)C NMR (100 MHz, d\(^6\)-DMSO) \(\delta\) 30.14, 31.35, 110.31, 118.93, 121.72, 122.12, 127.77, 129.01, 129.71, 131.64, 133.62, 135.25, 136.22, 142.67, 153.02; IR (KBr, cm\(^{-1}\)) 3448, 3056, 2914, 1616, 1589, 1572, 1517, 1473, 1437, 1421, 1396, 1331, 1321, 1302, 1286, 1266, 1238, 1209, 1160, 1149, 1123, 1094, 1054, 1038, 1005, 926, 871, 845, 808, 768, 753, 743, 729, 698, 691, 660, 574, 541, 523; MS (ESI) m/z: 257.1 ([M+H]\(^+\)); HRMS (ESI) m/z calcd for C\(_{17}\)H\(_{15}\)Cl\(_2\)N\(_2\) ([M+H]\(^+\)), 257.1006; found 257.1008.
m/z calcd for C$_{15}$H$_{14}$ClN$_2$ ([M+H]$^+$), 257.0840; found 257.0843.

2-(3-Chlorobenzyl)-1-methyl-1$H$-benzo[d]imidazole (5p)

Slightly yellow solid. M.p. 80-82 °C. $^1$H NMR (400 MHz, d$_6$-DMSO) δ 3.71 (3H, s), 4.32 (2H, s), 7.14-7.38 (6H, m), 7.47 (1H, d, J = 7.6 Hz), 7.59 (1H, d, J = 8.0 Hz); $^{13}$C NMR (100 MHz, d$_6$-DMSO) δ 30.19, 32.84, 110.35, 118.98, 121.79, 122.18, 127.02, 128.00, 129.09, 130.78, 133.51, 136.26, 139.84, 142.65, 153.54; IR (KBr, cm$^{-1}$) 3448, 3059, 2942, 1917, 1876, 1797, 1758, 1616, 1597, 1573, 1498, 1471, 1438, 1400, 1333, 1287, 1236, 1190, 1169, 1122, 1090, 1080, 1007, 921, 890, 860, 850, 794, 762, 744, 726, 681, 633, 589, 577, 569, 535, 526; MS (ESI) m/z: 257.2 ([M+H]$^+$); HRMS (ESI) m/z calcd for C$_{15}$H$_{14}$ClN$_2$ ([M+H]$^+$), 257.0840; found 257.0843.

2-(4-Chlorobenzyl)-1-methyl-1$H$-benzo[d]imidazole (5q)

Slightly yellow solid. M.p. 117-119 °C. $^1$H NMR (400 MHz, d$_6$-DMSO) δ 3.69 (3H, s), 4.30 (2H, s), 7.14-7.22 (2H, m), 7.30 (2H, d, J = 8.4 Hz), 7.37 (2H, d, J = 8.4 Hz), 7.47 (1H, d, J = 7.6 Hz), 7.57 (1H, d, J = 6.8 Hz); $^{13}$C NMR (100 MHz, d$_6$-DMSO) δ 30.18, 32.66, 110.31, 118.94, 121.76, 122.14, 128.90, 131.06, 131.68, 136.30, 136.33, 142.64, 153.74; IR (KBr, cm$^{-1}$) 3447, 3041, 2940, 1786, 1614, 1601, 1509, 1492, 1480, 1469, 1442, 1421, 1412, 1402, 1334, 1316, 1302, 1285, 1274, 1237, 1208, 1196, 1178, 1151, 1126, 1094, 1080, 1016, 1007, 972, 945, 922, 911, 890, 842, 804, 766, 749, 710, 679, 670, 559, 513; MS (ESI) m/z: 257.2 ([M+H]$^+$); HRMS (ESI) m/z calcd for C$_{15}$H$_{14}$ClN$_2$ ([M+H]$^+$), 257.0840; found 257.0842.
2-(3-Chlorobenzyl)-1H-Pyrimidine (7a)

Yellow solid. M.p. 171-173 °C. $^1$H NMR (400 MHz, d$_6$-DMSO) δ 3.59 (2H, s), 6.34-6.50 (2H, br), 6.97-7.09 (4H, m), 7.32-7.39 (3H, m), 7.46 (1H, s), 10.64 (1H, brs); $^{13}$C NMR (125 MHz, d$_6$-DMSO) δ 40.95, 118.82, 121.83, 127.21, 127.98, 128.85, 129.13, 130.76, 133.48, 135.56, 139.73, 156.03; IR (KBr, cm$^{-1}$) 3404, 3047, 2813, 1639, 1609, 1597, 1542, 1479, 1445, 1433, 1416, 1369, 1341, 1300, 1241, 1174, 1094, 1078, 1052, 1032, 991, 866, 824, 786, 770, 759, 709, 682, 632; MS (ESI) m/z: 291.1 ([M-H]$^-$); HRMS (ESI) m/z calcd for C$_{18}$H$_{14}$ClN$_2$ ([M+H]$^+$), 293.0840; found 293.0842.

2-(4-Chlorobenzyl)-1H-Pyrimidine (7b)

Yellow solid. M.p. 183-185 °C. $^1$H NMR (400 MHz, d$_6$-DMSO) δ 3.57 (2H, s), 6.30-6.53 (2H, br), 6.98 (2H, d, $J$ = 8.0 Hz), 7.09 (2H, br), 7.38-7.43 (4H, m), 10.64 (1H, brs); $^{13}$C NMR (125 MHz, d$_6$-DMSO) δ 40.80, 108.42, 119.08, 121.94, 128.75, 129.00, 131.22, 132.16, 135.68, 136.27, 156.58; IR (KBr, cm$^{-1}$) 3398, 3047, 2927, 2823, 1918, 1635, 1594, 1535, 1491, 1476, 1442, 1425, 1413, 1373, 1342, 1309, 1291, 1238, 1182, 1165, 1092, 1051, 1030, 1017, 988, 825, 805, 793, 765, 713, 692, 616, 512; MS (ESI) m/z: 291.1 ([M-H]$^-$); HRMS (ESI) m/z calcd for C$_{18}$H$_{14}$ClN$_2$ ([M+H]$^+$), 293.0840; found 293.0829.
2-pentyl-1H-Pyrimidine (7c)

Yellow solid. M.p. 136-138 °C. $^1$H NMR (400 MHz, d$_6$-DMSO) $\delta$ 0.87 (3H, t, $J = 7.0$ Hz), 1.29-1.33 (4H, m), 1.62-1.66 (2H, m), 2.23 (2H, m, $J = 7.6$ Hz), 6.40 (2H, br), 6.95 (2H, d), 7.06-7.10 (2H, m), 10.42 (1H, brs); $^{13}$C NMR (125 MHz, d$_6$-DMSO) $\delta$ 14.15, 22.20, 26.55, 31.20, 35.02, 118.19, 121.80, 128.62, 135.49, 157.76; IR (KBr, cm$^{-1}$) 3410, 3049, 2955, 2928, 2868, 1910, 1639, 1605, 1540, 1477, 1442, 1415, 1373, 1340, 1290, 1241, 1178, 1163, 1092, 1055, 1030, 825, 768, 623, 592; MS (ESI) m/z: 239.2 ([M+H]$^+$); HRMS (ESI) m/z calcd for C$_{16}$H$_{19}$N$_2$ ([M+H]$^+$), 239.1543; found 239.1532.
Copies of NMR Spectra
\[ 4a/4a' \sim 10/1 \]

in \( d^2\text{-DMSO+D}_2\text{O} \)
$4a/4a' \sim 10/1$

in $d^6$-DMSO
4a/4a' ~ 10/1
in d6-DMSO
2-benzyl 1H benzo[d]imidazole
2-(4-methoxybenzyl)-1H-benzo[d]imidazole
2-(4-tert-butylibenzyl)-1-\(\beta\)-benzo[\(\beta\)]imidazole
2-(2-chlorobenzyl)-1H benzimidazole
2-(3-chlorobenzyl)-1H-benzo[d]imidazole
2-(3-chlorobenzyl)-1H-benzo[d]imidazole
2-(4-chlorobenzyl)-1-Me-benzo[d]imidazole
2-(4-Chlorobenzyl) 1H-benzo[d]imidazole
2-pentyl-1H-benzo[d]imidazole
2-hexyl-1H-benzod[1]imidazole
2-heptyl-1H-benzo[d]imidazole
2-heptyl-1H-benzo[d]imidazole
2-octyl-1H-benzo[d]imidazole
2-ethyl-1H benz[d]imidazole
2-methyl-1H-benzo[d]imidazole
2-methyl-1H-benzo[d]imidazole
2-(4-chlorobenzyl)-5,6-dimethyl-1H-benzodimidazole
5,6-dichloro-2-(4-chlorobenzyl)-1H-benzo[d]imidazole
2-(2-chlorobenzyl)-1-methyl-1H-benz[de]imidazole
2-(3-chlorobenzyl)-1-methyl-1H-benzo[d]imidazole
2-(3-chlorobenzyl)-1-methyl-1H-henzo[cf]imidazole
2-(4-chlorobenzyl)-1-methyl-1H-benzo[d]imidazole
2-(4-chlorobenzyl)-1-methyl-1H-benzimidazole
2-pentyl-1H-perimidine