**A Simple and Efficient One-Pot Synthesis of 2- Substituted Benzimidazoles from θ -
Diaminoarene and Aryl Aldehydes**

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Supporting Information

1. General.

All chemical reagents were obtained from Sigma Aldrich and were used without further purification. Melting points were determined in open capillaries and are uncorrected. Infrared (IR) spectra were recorded using FT-IR Bruker Alpha spectrometer, ESI-Mass spectra were recorded on Finnigan Matt Mass spectrometer and NMR (¹H and ¹³C) spectra were recorded with a Bruker Ascend 300 and 400 MHz spectrometer.

2. General experimental procedure for 2- Substituted Benzimidazoles:

To a stirred solution of θ -diaminoarene (1.0 mmol), aryl aldehyde (1.1 mmol), iodine (0.1 mmol), 20 mol% UHP and DMSO (5 mL) was heated to 70 °C for specified time. After completion of the reaction as indicated by TLC, it was cooled to room temperature, aqueous sodium carbonate solution was added and extracted with EtOAc (2×25 mL). The combined organic layer were washed with brine solution (2×25 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to get crude. The crude was purified by silica gel column chromatography using ethyl acetate: hexane (3:7) to afford the pure product.

Characterization data of synthesized compounds:

2-phenyl-1H-benzo[d]imidazole (3a)¹. White solid, Mp: 292-294 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.22 (d, *J* = 7.2 Hz, 2H), δ 7.40-7.72 (m, 5H), δ 8.19 (d, *J* = 7.1 Hz, 2H), 12.84 (br, s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 111.5, 118.8, 121.7, 122.1, 126.4, 128.4, 129.6, 130.5, 134.2, 142.7, 151.1. MS(ESI): *m/z* 195 [M + H]⁺. Anal. Calcd for C₁₃H₁₀N₂: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.36; H, 5.21; N, 14.43.

2-p-tolyl-1H-benzo[d]imidazole (3b)¹. White solid. Mp: 276 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 2.63 (s, 3H), 7.16-7.23 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.62 (s, 2H), 8.13 (d, *J* = 8.0 Hz, 2H), 12.78 (br, s, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 20.6, 111.0, 118.6, 121.6, 122.3, 126.8, 127.6, 129.4, 139.5, 151.4. MS(ESI): *m/z* 209 [M + H]⁺. Anal. Calcd for C₁₄H₁₂N₂: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.76; H, 5.80; N, 13.44.

2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3c)¹. White solid. Mp: 223-225 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 3.86 (s, 3H), 7.09-7.21 (m, 4H), 7.53-7.57 (m, 2H), 8.08-8.20 (m, 2H), 12.81 (br, s, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 55.5, 114.7, 121.6, 122.7, 127.9, 151.2, 160.5. MS(ESI): *m/z* 225 [M + H]⁺. Anal. Calcd. for C₁₄H₁₂N₂O: C, 74.98; H, 5.39; N, 12.49; O, 7.13. Found: C, 74.95; H, 5.38; N, 12.52; O, 7.15.

2-(2-methoxyphenyl)-1H-benzo[d]imidazole (3d)¹. off-white solid. Mp: 176-178 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 4.10 (s, 3H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.18-7.35 (m, 3H), 7.51 (t, *J* = 7.1 Hz, 1H), 7.54-7.69 (m, 2H), 8.38 (d, *J* = 7.55, 1H). ¹³C NMR (75 MHz, DMSO-

d_6): δ 55.6, 111.9, 118.2, 120.3, 121.7, 129.6, 130.9, 148.8, 156.8. MS(ESI): m/z 225 $[M + H]^+$. Anal. Calcd. for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49; O, 7.13. Found: C, 74.96; H, 5.40; N, 12.50; O, 7.14.

4-(1H-benzo[d]imidazol-2-yl)benzonitrile (3e)⁵. White solid. Mp: 261-263°C. 1H NMR (400MHz, DMSO- d_6): δ 7.31-7.22 (m, 2H), 7.58-7.57 (m, 1H), 7.72-7.71 (m, 1H), 8.02 (d, 2H, $J = 8.4$ Hz), 8.37 (d, 2H, $J = 8.4$ Hz), 13.17 (br, s, 1H). ^{13}C NMR (100 MHz, DMSO- d_6): δ 39.5, 112.1, 112.4, 119.1, 119.8, 122.7, 123.9, 127.4, 133.5, 134.7, 135.4, 144.2, 149.7. MS(ESI): m/z 220 $[M + H]^+$. Anal. Calcd. for $C_{14}H_9N_3$: C, 76.70; H, 4.14; N, 19.17. Found: C, 76.73; H, 4.12; N, 19.15.

2-(4-fluorophenyl)-1H-benzo[d]imidazole (3f)⁶. White solid. Mp: 247-249 °C. 1H NMR (300 MHz, DMSO- d_6) δ 7.19-7.17 (m, 2H), 7.39 (t, $J=8.7$ Hz, 2H), 7.65-7.56 (m, 2H), 8.20 (d, $J=8.7$ Hz, 1H), 8.22 (d, $J=8.7$ Hz, 1H), 12.94 (br s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 111.9, 116.4, 116.7, 119.1, 122.6, 123.1, 127.5, 129.5, 129.7, 151.0, 163.8. MS(ESI): m/z 213 $[M + H]^+$. Anal. Calcd. for $C_{13}H_9FN_2$: C, 73.57; H, 4.27; F, 8.95; N, 13.20. Found: C, 73.60; H, 4.28; F, 8.93; N, 13.19.

2-(2-fluorophenyl)-1H-benzo[d]imidazole (3g)⁴. Colourless solid. Mp: 272-275 °C. 1H NMR (400 MHz, DMSO- d_6) : 7.64-7.71 (m, 3H), 7.93 (t, 1H, $J = 8.0$ Hz), 8.14-8.16 (m, 2H), 8.25 (d, 1H, $J = 7.6$ Hz), 8.52 (d, 1H, $J = 8.0$ Hz), 8.65 (s, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) : δ 112.8, 117.6, 124.6, 125.8, 127.1, 129.3, 130.8, 131.4, 131.8, 132.3, 136.5, 168.4, 173.8. MS(ESI): m/z 248 $[M + H]^+$. Anal. Calcd. for $C_{13}H_9FN_2$: C, 73.57; H, 4.27; F, 8.95; N, 13.20. Found: C, 73.60; H, 4.28; F, 8.93; N, 13.19.

2-(4-chlorophenyl)-1H-benzo[d]imidazole (3h)¹. White solide. Mp: 290-291°C. ¹H NMR (300MHz, DMSO-*d*₆): δ 7.13-7.31 (m, 2H), 7.51-7.80 (m, 4H), 8.20 (d, *J* = 7.1 Hz, 2H), 12.96 (br, s, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 112.2, 118.6, 121.8, 122.3, 126.3, 128.8, 129.7, 130.3, 135.0, 143.0, 151.6. MS(ESI): *m/z* 228 [M + H]⁺. Anal. Calcd. for C₁₃H₉ClN₂: C, 68.28; H, 3.97; Cl, 15.50; N, 12.25. Found: C, 68.26; H, 3.96; Cl, 15.52; N, 12.26.

2-(2-chlorophenyl)-1H-benzo[d]imidazole (3i)¹. White solid. Mp: 232-234 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.19-7.30 (m, 2H), 7.50-7.74 (m, 5H), 7.80-7.91 (m, 1H), 12.70 (br s, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 122.0, 127.3, 129.8, 130.3, 130.5, 131.7, 131.8, 149.0. MS(ESI): *m/z* 229 [M + H]⁺. Anal. Calcd. for C₁₃H₉ClN₂: C, 68.28; H, 3.97; Cl, 15.50; N, 12.25. Found: C, 68.26; H, 3.96; Cl, 15.52; N, 12.26.

2-(3,4-difluorophenyl)-1H-benzo[d]imidazole (3j)⁴. Mp: 127-129 °C. ¹H NMR (300 MHz, DMSO-*d*₆) : δ 7.18-7.30 (m, 2H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.60-7.72 (m, 2H), 7.97-8.07 (m, 1H), 8.12-8.28 (m, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 111.5, 115.3, 118.2 (d, *J*_{CF} = 17.6 Hz), 118.6, 121.9, 122.8, 123.5, 127.8, 134.8, 143.5, 148.0, 149.7, 150.3. MS(ESI): *m/z* 231 [M + H]⁺. Anal. Calcd for C₁₃H₈F₂N₂: C, 67.82; H, 3.50; F, 16.51; N, 12.17. Found: C, 67.83; H, 3.50; F, 16.49; N, 12.18.

2-(4-bromophenyl)-1H-benzo[d]imidazole (3k)². pale yellow solid. Mp: 255-257 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.14-7.27 (m, 2H), 7.46-7.71 (m, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 8.15 (d, *J* = 8.5 Hz, 2H), 12.96 (bs, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 121.8, 123.3, 128.5, 129.3, 128.7, 130.7, 131.8, 150.1. MS(ESI): *m/z* 273 [M + H]⁺. Anal. Calcd. for C₁₃H₉BrN₂: C, 57.17; H, 3.32; Br, 29.26; N, 10.26. Found: C, 57.15; H, 3.31; Br, 29.29; N, 10.25.

2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole (3l)². Mp: 176-178 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.17-7.31 (m, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 8.42 (d, *J* = 8.1 Hz, 2H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 111.8, 120.0, 121.7, 123.1, 125.7, 127.0, 129.8, 133.6, 134.9, 143.6, 149.8. MS(ESI): *m/z* 263 [M + H]⁺. Anal. Calcd. for C₁₄H₉F₃N₂: C, 64.12; H, 3.46; F, 21.73; N, 10.68. Found: C, 64.13; H, 3.48; F, 21.72; N, 10.67.

2-(pyridin-2-yl)-1H-benzo[d]imidazole (3m)³. White solid. Mp: 221-223 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.14-7.30 (m, 2H), 7.46-7.60 (m, 2H), 7.74 (d, 1H), 8.00 (t, 1H), 8.32 (d, *J* = 7.2 Hz, 1H), 8.74 (d, *J* = 4.5 Hz, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 111.9, 119.2, 121.3, 121.7, 123.0, 124.6, 134.8, 136.7, 143.8, 148.9, 149.2, 150.8. MS(ESI): *m/z* 196 [M + H]⁺. Anal. Calcd. for C₁₂H₉N₃: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.80; H, 4.67; N, 21.53.

2-(1H-pyrrol-2-yl)-1H-benzo[d]imidazole (3n)⁴. Yellow color solid, Mp. 268-270 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 6.19 (d, *J* = 1.5 Hz, 1H), 6.82 (d, *J* = 3.5 Hz, 1H), 6.90 (d, *J* = 1.5 Hz, 1H), 7.11 (m, 2H), 7.43 (d, *J* = 4.5 Hz, 1H), 7.55 (d, *J* = 4.7 Hz, 1H), 11.81 (s, 1H, NH), 12.49 (s, 1H, NH); ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) 109.7, 110.8, 118.2, 121.4, 121.8, 123.2, 135.0, 144.3, 147.3; MS(ESI): *m/z* 184 [M + H]⁺. Anal. Calcd. for C₁₄H₈N₄O: C, 67.74; H, 3.25; N, 22.57. Found: C, 67.69; H, 3.29; N, 22.54.

2-(furan-2-yl)-1H-benzo[d]imidazole (3o)². Pale brown solid. Mp: 285-287 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 6.71 (dd, *J* = 3.3, 1.6 Hz, 1H), 7.20–7.19 (m, 3H), 7.54 (br s, 2H), 7.96 (dd, *J* = 1.6, 0.9 Hz, 1H), 12.91 (br s, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 111.6, 112.3, 118.7, 120.5, 122.8, 134.3, 143.7, 143.2, 146.1. MS(ESI): *m/z* 185 [M + H]⁺. Anal. Calcd. for C₁₁H₈N₂O: C, 71.73; H, 4.38; N, 15.21; O, 8.69. Found: C, 71.72; H, 4.40; N, 15.20; O, 8.68.

2-(thiophen-2-yl)-1H-benzo[d]imidazole (3p)². Pale yellow solid. Mp: 344-346 °C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.24–7.14 (m, 3H), 7.50 (dd, *J* = 7.0, 2.3 Hz, 1H), 7.62–7.59 (m, 1H), 7.72 (dd, *J* = 5.2, 1.3 Hz, 1H), 7.84 (dd, *J* = 3.5, 1.3 Hz, 1H), 12.98 (br s, 1H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 111.1, 118.5, 120.9, 122.6, 124.8, 128.3, 128.8, 131.9, 135.0, 143.6, 147.4. MS(ESI): *m/z* 201 [M + H]⁺. Anal. Calcd. for C₁₁H₈N₂S: C, 65.97; H, 4.03; N, 13.99; S, 16.01. Found: C, 65.94; H, 4.05; N, 13.97; S, 16.04.

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