

Synthesis of 2-alkyl substituted benzimidazoles under microwave irradiation: Anti-proliferative effect of some representative compounds on human histiocytic lymphoma cell U937

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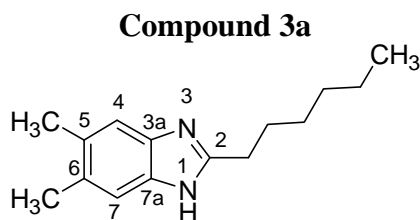
Supplementary Information Part 1

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1. General procedure for the synthesis of the benzimidazoles: A typical example is as follows. Heptanoic acid **1a** (0.14 ml, 1.0 mmol) was added to 4, 5-dimethyl-1, 2-phenylenediamine **2a** (136 mg, 1.0 mmol). 62% aqueous hexafluorophosphoric acid (0.01 ml, 0.1 mmol) was added. The reaction mixture was mixed thoroughly and then heated in a microwave for 5 minutes (600 Watt) at 115 °C. It was then allowed to cool down to room temperature. TLC was checked. Unfortunately, the starting amine and the product **3a** give the same RF value of 0.8 (100% ethyl acetate or at any other possible concentration of the running solvent). It is also true for compounds **3k**, **3l**, **3m**, **3n**, **3o**, **3p** and **3q**. For workup, 10% NaOH solution was added followed by rigorous titration. The solid which remained was filtered off, washed several times with distilled water and purified by recrystallisation from ethyl acetate and hexanes. The yield of compound **3a** was 96%.

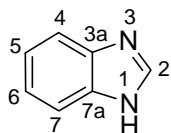
2. Characterization data of the synthesized compounds:



2-Hexyl-5,6-dimethyl-1H-benzimidazole (**3a**): sticky solid; ^1H NMR (300 MHz, CDCl_3): δ (ppm) 12.71 (s, 1H, N_1H), 7.25 (s, 2H, H_4 and H_7), 2.86 (t, $J = 7.5$ Hz, 2H, $\text{C}_2\text{-CH}_2$), 2.22 (s, 6H, $\text{C}_5\text{-CH}_3$ and $\text{C}_6\text{-CH}_3$), 1.79-1.69 (m, 2H, $\text{C}_2\text{-CH}_2\text{-CH}_2$), 1.20-1.05 (m, 6H, $\text{C}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$) and 0.75 (br s, 3H, $\text{C}_2\text{-(CH}_2)_5\text{-CH}_3$); ^{13}C NMR (75 MHz, CDCl_3): δ 155.2 (C_2), 137.0 (C_{3a} and C_{7a}), 130.6 (C_5 and C_6), 114.7 (C_4 and C_7), 31.4 ($\text{C}_2\text{-CH}_2$), 29.2 ($\text{C}_2\text{-CH}_2\text{-CH}_2$), 29.0 ($\text{C}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 28.5 ($\text{C}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 22.4 ($\text{C}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 20.1 ($\text{C}_5\text{-CH}_3$ and $\text{C}_6\text{-CH}_3$).

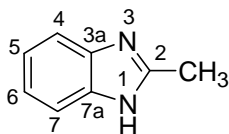
$\underline{\text{C}}\text{H}_3$ and $\text{C}_6\text{-}\underline{\text{C}}\text{H}_3$) and 13.8 ($\text{C}_2\text{-(CH}_2\text{)}_5\text{-}\underline{\text{C}}\text{H}_3$); IR(KBr) 2927, 1451 and 1020 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{N}_2$: C, 78.21; H, 9.63; N, 12.16. Found: C, 78.21; H, 9.61; N, 12.15; Yield: 96%

Compound 3b



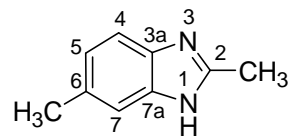
1H-Benzoimidazole (**3b**): brown solid; $170\text{ }^\circ\text{C}$ (m.p.); $^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ (ppm) 8.18 (s, 1H, $\text{C}_2\text{-H}$), 7.56-7.54 (m, 2H, H_5 and H_6) and 7.15-7.12 (m, 2H, H_4 and H_7); $^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$): δ 142.1 (C_2), 138.2 (C_{3a} and C_{7a}), 121.9 (C_5 and C_6) and 115.4 (C_4 and C_7); IR(KBr) 2793, 1407, 1245 and 744 cm^{-1} ; Anal. Calcd for $\text{C}_7\text{H}_6\text{N}_2$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.17; H, 5.11; N, 23.70; Yield: 90%

Compound 3c



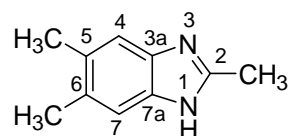
2-Methyl-1H-benzoimidazole (**3c**): brown solid; $175\text{-}176\text{ }^\circ\text{C}$ (m.p.); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) 7.57-7.51 (m, 2H, H_5 and H_6), 7.42 (br s, 1H, N_1H), 7.24-7.19 (m, 2H, H_4 and H_7) and 2.65 (s, 3H, $\text{C}_2\text{-CH}_3$); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 151.2 (C_2), 138.6 (C_{3a} and C_{7a}), 122.2 (C_5 and C_6), 114.5 (C_4 and C_7) and 14.9 ($\text{C}_2\text{-CH}_3$); IR(KBr) 2673, 1384, 1267 and 732 cm^{-1} ; Anal. Calcd for $\text{C}_8\text{H}_8\text{N}_2$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.70; H, 6.12; N, 21.20; Yield: 85%

Compound 3d



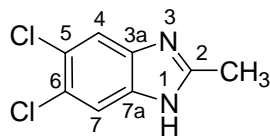
2,6-Dimethyl-1H-benzimidazole (**3d**): brown solid; 202 °C (m.p.); ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.92 (br s, 1H, N_1H), 7.45 (d, $J = 8.1$ Hz, 1H, H_4), 7.34 (s, 1H, H_7), 7.05 (d, $J = 8.1$ Hz, 1H, H_5), 2.63 (s, 3H, $\text{C}_2\text{-CH}_3$) and 2.44 (s, 3H, $\text{C}_6\text{-CH}_3$); ^{13}C NMR (75 MHz, CDCl_3): δ 151.0 (C_2), 138.1 (C_{3a}), 136.7 (C_{7a}), 132.0 (C_6), 123.7 (C_4), 114.2 (C_7), 113.9 (C_5), 21.5 ($\text{C}_6\text{-CH}_3$) and 14.7 ($\text{C}_2\text{-CH}_3$); IR(KBr) 2918, 1450, 1400, 1281, 1027 and 801 cm^{-1} ; Anal. Calcd for $\text{C}_9\text{H}_{10}\text{N}_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.94; H, 6.89; N, 19.17; Yield: 76%

Compound 3e



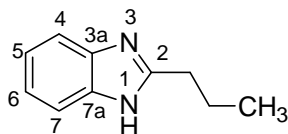
2,5,6-Trimethyl-1H-benzimidazole (**3e**): light brown solid; 229-231 °C (m.p.); ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ (ppm) 11.86 (br s, 1H, N_1H), 7.16 (s, 2H, H_4 and H_7), 2.38 (s, 3H, $\text{C}_2\text{-CH}_3$) and 2.22 (s, 6H, $\text{C}_5\text{-CH}_3$ and $\text{C}_6\text{-CH}_3$); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 150.3 (C_2 , C_{3a} and C_{7a}), 129.2 (C_4 , C_5 , C_6 and C_7), 20.0 ($\text{C}_5\text{-CH}_3$ and $\text{C}_6\text{-CH}_3$) and 14.7 ($\text{C}_2\text{-CH}_3$); IR(KBr) 2922, 1458, 1389, 1010 and 856 cm^{-1} ; Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.99; H, 7.56; N, 17.49; Yield: 90%

Compound 3f



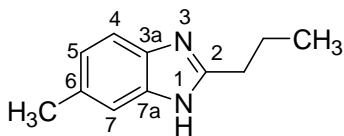
5,6-Dichloro-2-methyl-1H-benzimidazole (**3f**): grey solid; 249 °C (m.p.); ^1H NMR (300 MHz, DMSO- d_6): δ (ppm) 12.49 (br s, 1H, N_1H), 7.69 (s, 2H, H_4 and H_7) and 2.48 ($\text{C}_2\text{-CH}_3$); ^{13}C NMR (75 MHz, DMSO- d_6): δ 154.9 (C_2 , C_{3a} and C_{7a}), 123.9 (C_4 , C_5 , C_6 and C_7) and 15.1 (CH_3); IR(KBr) 3110, 1446, 1373, 1019 and 859 cm^{-1} ; Anal. Calcd for $\text{C}_8\text{H}_6\text{Cl}_2\text{N}_2$: C, 47.79; H, 3.01; Cl, 35.27; N, 13.93. Found: C, 47.80; H, 3.01; Cl, 35.25; N, 13.93; Yield: 65%

Compound 3g



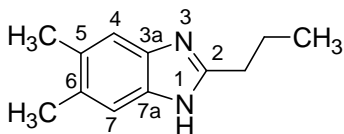
2-Propyl-1H-benzimidazole (**3g**): brown solid; 160-162 °C (m.p.); ^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.94 (br s, 1H, N_1H), 7.61-7.58 (m, 2H, H_5 and H_6), 7.28-7.24 (m, 2H, H_4 and H_7), 2.98 (t, $J = 7.5$ Hz, 2H, $\text{C}_2\text{-CH}_2$), 1.99-1.87 (m, 2H, $\text{C}_2\text{-CH}_2\text{-CH}_2$) and 1.00 (t, $J = 7.5$ Hz, 3H, $\text{C}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$); ^{13}C NMR (75 MHz, CDCl_3): δ 155.0 (C_2), 137.7 (C_{3a} and C_{7a}), 122.5 (C_5 and C_6), 114.5 (C_4 and C_7), 30.9 ($\text{C}_2\text{-CH}_2$), 21.6 ($\text{C}_2\text{-CH}_2\text{-CH}_2$) and 13.8 ($\text{C}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$); IR(KBr) 2958, 1427, 1268 and 745 cm^{-1} ; Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.98; H, 7.56; N, 17.47; Yield: 80%

Compound 3h



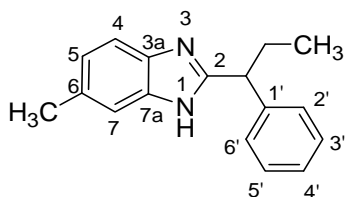
6-Methyl-2-propyl-1H-benzimidazole (**3h**): light brown solid; 153-154 °C (m.p.); ¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.08 (br s, 1H, N₁H), 7.44 (d, *J* = 8.1 Hz, 1H, H₄), 7.33 (s, 1H, H₇), 7.04 (d, *J* = 8.1 Hz, 1H, H₅), 2.90 (t, *J* = 7.5 Hz, 2H, C₂-CH₂), 2.44 (s, 3H, C₆-CH₃), 1.94-1.81 (m, 2H, C₂-CH₂-CH₂) and 0.97 (t, *J* = 7.5 Hz, 3H, C₂-CH₂-CH₂-CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 155.1 (C₂), 138.4 (C_{3a}), 137.0 (C_{7a}), 131.8 (C₆), 123.4 (C₄), 114.4 (C₇), 114.1 (C₅), 31.2 (C₂-CH₂), 21.7 (C₂-CH₂-CH₂), 21.6 (C₆-CH₃) and 13.8 (C₂-CH₂-CH₂-CH₃); IR(KBr) 2959, 1446, 1281 and 798 cm⁻¹; Anal. Calcd for C₁₁H₁₄N₂: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.81; H, 8.11; N, 16.08; Yield: 78%

Compound 3i



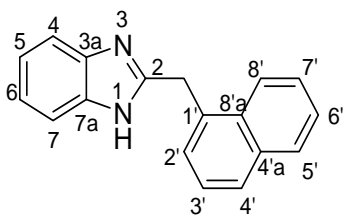
5,6-Dimethyl-2-propyl-1H-benzimidazole (**3i**): light brown solid; 167 °C (m.p.); ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 11.86 (br s, 1H, N₁H), 7.17 (s, 2H, H₄ and H₇), 2.68 (t, *J* = 7.5 Hz, 2H, C₂-CH₂), 2.23 (s, 6H, C₅-CH₃ and C₆-CH₃), 1.77-1.67 (m, 2H, C₂-CH₂-CH₂) and 0.88 (t, *J* = 7.5 Hz, 3H, C₂-CH₂-CH₂-CH₃); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 154.1 (C₂), 137.2 (C_{3a} and C_{7a}), 129.4 (C₅ and C₆), 114.6 (C₄ and C₇), 30.9 (C₂-CH₂), 21.5 (C₂-CH₂-CH₂), 20.3 (C₅-CH₃ and C₆-CH₃) and 14.1 (C₂-CH₂-CH₂-CH₃); IR(KBr) 2970, 1454, 1406, 1304, 1002 and 852 cm⁻¹; Anal. Calcd for C₁₂H₁₆N₂: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.55; H, 8.57; N, 14.89; Yield: 95%

Compound 3j



6-Methyl-2-(1-phenyl-propyl)-1H-benzimidazole (**3j**): brown solid; 120 °C (m.p.); ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.88 (br s, 1H, N₁H), 7.43 (d, *J* = 8.1 Hz, 1H, H₄), 7.33-7.14 (m, 6H, H₇, H_{2'}, H_{3'}, H_{4'}, H_{5'} and H_{6'}), 7.04 (d, *J* = 8.1 Hz, 1H, H₅), 4.14 (t, *J* = 7.5 Hz, 1H, C₂-CH-CH₂-CH₃), 2.52-2.42 (m, 4H, C₆-CH₃ and ½ C₂-CH-CH₂-CH₃), 2.32-2.11 (m, 1H, ½ C₂-CH-CH₂-CH₃) and 0.93 (t, *J* = 7.5 Hz, 1H, C₂-CH-CH₂-CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 156.3 (C₂), 140.7 (C₁), 137.3 (C_{3a}), 135.9 (C_{7a}), 132.5 (C₆), 128.8 (C_{2'} and C_{6'}), 128.0 (C_{3'} and C_{5'}), 127.2 (C_{4'}), 124.1 (C₄), 114.6 (C₇), 114.2 (C₅), 47.8 (C₂-CH-CH₂-CH₃), 27.5 (C₂-CH-CH₂-CH₃), 21.5 (C₆-CH₃) and 12.3 (C₂-CH-CH₂-CH₃); IR(KBr) 2928, 1449, 1278, 807 and 697 cm⁻¹; Anal. Calcd for C₁₇H₁₈N₂: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.57; H, 7.26; N, 11.19; Yield: 78%

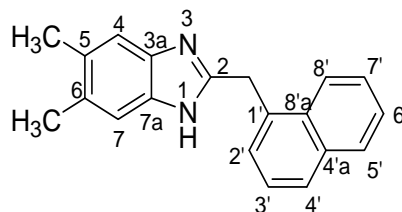
Compound 3k



2-Naphthalen-1-ylmethyl-1H-benzimidazole (**3k**): pale pink solid; 230-232 °C (m.p.); ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 12.18 (br s, 1H, NH), 8.18-8.16 (m, 1H, H_{8'}), 7.91-7.88 (m, 1H, H_{5'}), 7.84-7.80 (m, 1H, H_{4'}), 7.51-7.40 (m, 6H, H₅, H₆, H_{2'}, H_{3'}, H_{6'} and H_{7'}), 7.07-7.04 (m, 2H, H₄ and H₇), 4.60 (s, 2H, CH₂) and 3.32 (s, 6H, CH₃); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 153.5 (C₂), 133.6 (C_{3a}, C_{7a} and C₁), 133.5 (C_{4'a}), 131.7 (C_{8'a}), 128.5 (C_{5'}), 127.4 (C₄ and C_{4'}), 126.3

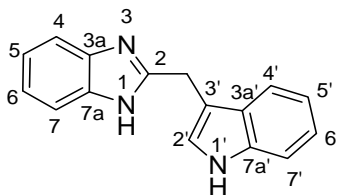
(C_{3'}), 125.8 (C₇ and C_{7'}), 125.7 (C_{6'}), 124.1 (C_{8'}), 121.3 (C₅ and C₆) and 32.8 (CH₂); IR(KBr) 2740, 1426, 778 and 742 cm⁻¹; Anal. Calcd for C₁₈H₁₄N₂: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.70; H, 5.44; N, 10.83; Yield: 75%

Compound 31



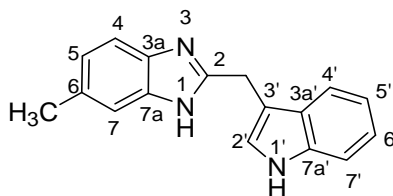
5,6-Dimethyl-2-naphthalen-1-ylmethyl-1H-benzimidazole (**31**): light brown solid; 218 °C (m.p.); ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 11.90 (br s, 1H, NH), 8.17-8.14 (m, 1H, H_{8'}), 7.90-7.87 (m, 1H, H_{5'}), 7.82-7.80 (m, 1H, H_{4'}), 7.48-7.42 (m, 4H, H_{2'}, H_{3'}, H_{6'} and H_{7'}), 7.17 (s, 2H, H₄ and H₇), 4.55 (s, 2H, CH₂) and 2.22 (s, 6H, CH₃); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 152.5 (C₂), 133.9 (C_{1'}), 133.5 (C_{4'a}), 131.7 (C_{8'a}), 129.5 (C_{3a} and C_{7a}), 128.5 (C_{5'}), 127.34 (C₄ and C_{4'}), 127.28 (C_{3'}), 126.2 (C_{2'}), 125.8 (C₇ and C_{7'}), 125.7 (C_{6'}), 124.1 (C_{8'}), 32.8 (CH₂) and 19.9 (CH₃); IR(KBr) 2923, 1448, 1012 and 781 cm⁻¹; Anal. Calcd for C₂₀H₁₈N₂: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.86; H, 6.35; N, 9.79; Yield: 80 %

Compound 3m



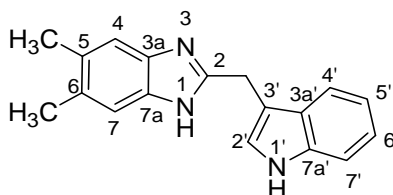
2-(1H-Indol-3-ylmethyl)-1H-benzoimidazole (**3m**): grey solid; 193-194 °C (m.p.); ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 10.97 (br s, 1H, N₁H), 7.47-7.41 (m, 3H, H₅, H₆ and H₄'), 7.33-7.27 (m, 2H, H₂' and H₇'), 7.09-6.97 (m, 3H, H₄, H₇ and H₆'), 6.89 (t, *J* = 7.1 Hz, 1H, H₅') and 4.26 (s, 2H, CH₂); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 154.4 (C₂), 136.3 (C_{7a}'), 127.0 (C_{3a}, C_{7a} and C_{3'a}'), 123.9 (C₂'), 121.4 (C₆'), 121.1 (C₅'), 118.5 (C₄'), 117.8 (C₇'), 114.5 (C₄ and C₇), 111.5 (C₅ and C₆), 109.8 (C₃') and 25.3 (CH₂); IR(KBr) 3409, 3150, 1449, 1092 and 741 cm⁻¹; Anal. Calcd for C₁₆H₁₃N₃: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.72; H, 5.30; N, 16.98; Yield: 70%

Compound 3n



2-(1H-Indol-3-ylmethyl)-6-methyl-1H-benzoimidazole (**3n**): grey solid; 90 °C (m.p.); ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 11.03 (s, 1H, N₁H), 7.41-7.32 (m, 4H, H₄, H₇, H₄' and H₇'), 7.07-7.01 (m, 2H, H₅ and H₆'), 6.91 (t, *J* = 7.2 Hz, 1H, H₅'), 4.37 (s, 2H, CH₂) and 2.37 (s, 3H, CH₃); ¹³C NMR (75 MHz, DMSO-*d*₆): δ 154.0 (C₂), 136.3 (C_{7a}'), 130.2 (C_{3a}, C_{7a} and C₆), 127.0 (C_{3'a}'), 123.7 (C₂'), 122.5 (C₆'), 121.1 (C₅'), 118.49 (C₄'), 118.46 (C₅ and C₇'), 111.4 (C₄ and C₇), 110.1 (C₃'), 25.4 (CH₂) and 21.3 (CH₃); IR(KBr) 3392 and 742 cm⁻¹; Anal. Calcd for C₁₇H₁₅N₃: C, 78.13; H, 5.79; N, 16.08. Found: C, 78.13; H, 5.78; N, 16.09; Yield: 75%

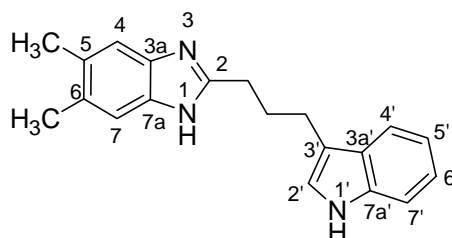
Compound 3o



2-(1H-Indol-3-ylmethyl)-5,6-dimethyl-1H-benzoimidazole (**3o**): light grey solid; 190 °C (m.p.);

^1H NMR (300 MHz, DMSO- d_6): δ (ppm) 11.60 (br s, 1H, N_1H), 10.90 (s, 1H, N_1H), 7.41 (d, $J = 7.8$ Hz, 1H, $\text{H}_{4'}$), 7.31 (d, $J = 8.2$ Hz, 1H, $\text{H}_{7'}$), 7.22 (d, $J = 2.1$ Hz, 1H, $\text{H}_{2'}$), 7.17 (s, 2H, H_4 and H_7), 7.01 (t, $J = 7.2$ Hz, 1H, $\text{H}_{6'}$), 6.88 (t, $J = 7.1$ Hz, 1H, $\text{H}_{5'}$), 4.19 (s, 2H, CH_2) and 2.22 (s, 6H, CH_3); ^{13}C NMR (75 MHz, DMSO- d_6): δ 153.6 (C_2), 136.4 (C_{7a}), 129.5 (C_{3a} and C_{7a}), 127.1 ($\text{C}_{3'}$ and $\text{C}_{3'a}$), 123.8 ($\text{C}_{2'}$), 121.2 ($\text{C}_{5'}$ and $\text{C}_{6'}$), 118.6 ($\text{C}_{4'}$), 111.6 (C_4 , C_7 and $\text{C}_{7'}$), 110.4 (C_5 and C_6), 25.5 (CH_2) and 20.1 (CH_3); IR(KBr) 3385, 2929, 1448 and 735 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{N}_3$: C, 78.52; H, 6.22; N, 15.26. Found: C, 78.51; H, 6.24; N, 15.25; Yield: 86%

Compound 3p

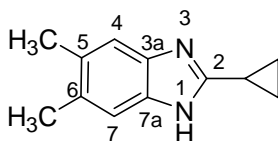


2-[3-(1H-Indol-3-yl)-propyl]-5,6-dimethyl-1H-benzoimidazole (**3p**): light grey solid; 96 °C

(m.p.); ^1H NMR (300 MHz, DMSO- d_6): δ (ppm) 10.77 (s, 1H, N_1H), 7.47 (d, $J = 7.7$ Hz, 1H, $\text{H}_{4'}$), 7.30 (d, $J = 8.0$ Hz, 1H, $\text{H}_{7'}$), 7.18 (s, 2H, H_4 and H_7), 7.11 (s, 1H, $\text{H}_{2'}$), 7.02 (t, $J = 7.2$ Hz, 1H, $\text{H}_{6'}$), 6.92 (t, $J = 7.2$ Hz, 1H, $\text{H}_{5'}$), 2.81-2.70 (m, 4H, $\text{C}_2\text{-CH}_2$ and $\text{C}_3\text{-CH}_2$), 2.23 (s, 6H, CH_3) and 2.13-2.06 (m, 2H, $\text{C}_2\text{-CH}_2\text{-CH}_2$); ^{13}C NMR (75 MHz, DMSO- d_6): δ 154.2 (C_2), 136.4 (C_{7a}),

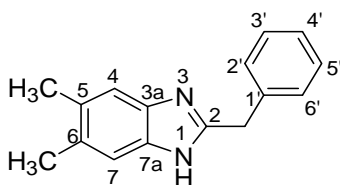
129.2 (C_{3a} and C_{7a}), 127.3 ($C_{3'}$ and $C_{3'a}$), 122.4 ($C_{2'}$), 120.9 (C_6'), 118.4 ($C_{4'}$), 118.2 ($C_{5'}$), 114.1 (C_4 , C_5 , C_6 and C_7), 111.4 (C_7), 28.5 (C_2 - $\underline{CH_2}$ - $\underline{CH_2}$), 24.4 ($C_{3'}$ - $\underline{CH_2}$) and 20.0 ($\underline{CH_3}$); IR(KBr) 3409 and 743 cm^{-1} ; Anal. Calcd for $C_{20}H_{21}N_3$: C, 79.17; H, 6.98; N, 13.85. Found: C, 79.16; H, 6.97; N, 13.87; Yield: 79%

Compound 3q



2-Cyclopropyl-5,6-dimethyl-1H-benzimidazole (**3q**): light brown solid; 220 °C (m.p.); ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ (ppm) 11.86 (br s, 1H, N_1H), 7.12 (s, 2H, H_4 and H_7), 2.22 (s, 6H, C_5 - $\underline{\text{CH}_3}$ and C_6 - $\underline{\text{CH}_3}$), 2.03-1.98 (m, 1H, cyclopropyl $\underline{\text{CH}}$) and 0.97-0.93 (m, 4H, cyclopropyl $\underline{\text{CH}_2}$); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 155.9 (C_2), 129.0 (C_{3a} and C_{7a}), 117.8 (C_4 , C_5 , C_6 and C_7), 19.9 (C_5 - $\underline{\text{CH}_3}$ and C_6 - $\underline{\text{CH}_3}$), 9.5 (cyclopropyl $\underline{\text{CH}}$) and 8.5 (cyclopropyl $\underline{\text{CH}_2}$); IR(KBr) 2896, 1437, 1307, 998 and 853 cm^{-1} ; Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.39; H, 7.60; N, 15.03; Yield: 90%

Compound 3r



2-Benzyl-5,6-dimethyl-1H-benzimidazole (**3r**): greenish-brown solid; 104-105 °C (m.p.); ^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.29-7.26 (m, 7H, H_4 , H_7 , $\text{H}_{2'}$, $\text{H}_{3'}$, $\text{H}_{4'}$, $\text{H}_{5'}$ and $\text{H}_{6'}$), 4.23 (s, 2H, $\underline{\text{CH}_2}$) and 2.35 (C_5 - $\underline{\text{CH}_3}$ and C_6 - $\underline{\text{CH}_3}$); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 152.4 (C_2), 136.3

(C_{3a}), 136.2 (C_{7a}), 131.6 (C_{1'}), 128.93 (C_{2'} and C_{6'}), 128.87 (C_{3'} and C_{5'}), 127.2 (C_{4'}), 114.8 (C₄ and C₇), 35.3 (CH₂) and 20.2 (C₅-CH₃ and C₆-CH₃); IR(KBr) 1636, 1463, 1444, 1422, 1313 and 721 cm⁻¹; Anal. Calcd for C₁₆H₁₆N₂: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.33; H, 6.83; N, 11.84; Yield: 95%