

Montmorillonite K10: An efficient organo- heterogeneous catalyst for synthesis of Benzimidazole Derivatives.

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Electronic Supplementary Material

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Experimental Section

Montmorillonite K10 clay and all chemicals reagent obtained from Sigma-Aldrich.. The chemical composition (wt%) of the clay (main elements) was SiO₂: 67.6; Al₂O₃: 14.6; Fe₂O₃: 2.9; MgO: 1.8.

All reactions were monitored by GC-MS Shimadzu workstation. It is constituted by a GC 2010 (equipped with a 30 m-QUADREX 007-5MS capillary column, operating in the “split” mode, 1 mL min⁻¹ flow of He as carrier gas).

¹H-NMR and ¹³C-NMR spectra were recorded at 300 MHz and at 75 MHz respectively, using a Bruker WM 300 system. The samples solubilized in CDCl₃ using tetramethylsilane (TMS) as reference (δ 0.00). Chemical shifts are given in parts per million (ppm) and coupling constants (J) are given in hertz. For ¹³C-NMR the chemical shifts are relative to CDCl₃ (δ 77.0).

Synthos 3000 instrument from Anton Paar, equipped with a 4 × 24MG5 Rotor, used for the MW-assisted reactions. An external IR sensor monitors the temperature at the base of each reaction vessel.

General Procedure for the Synthesis of 1,2-Substituted Benzimidazoles 1a-8a.

The aldehyde (2 mmol) was added to the *o*-PDA (1 mmol) and MK10 (20 mg). The obtained mixture reaction was reacted for 5 min under microwave assisted, at a temperature of 60 °C (IR Limit). After completion conversion of *o*-phenilendiammine, the MK10 was separated from the reaction mixture by filtration and washed with ethyl acetate (4x3 mL). The products were isolated after evaporation of the solvent to afford compounds in 90-99 % yields. The NMR spectral data were accordance with those reported in the literature [50].

General Procedure for the Synthesis of 2-Substituted Benzimidazoles 1b-8b.

The synthesis procedure of the mono-substituted imidazoles derived is carried out under the same conditions used for the synthesis of the 1,2-substituted benzimidazoles. In this case, however, the aldehydes are used in an amount equal to 1mmol. After completion conversion of *o*-PDA in the 2-monosubstituted benzimidazoles (5 minutes), the products were isolated as previously described.

Catalyst recycling

The MK10 was separated from the reaction mixture by a rapid filtration and washed with ethyl acetate (3 mL) for four times and dried in a oven (50 °C).

¹H NMR and ¹³C NMR of compounds 1a-3a, 6a-8a

1-Benzyl-2-phenyl-1H-benzimidazole (1a): ¹H NMR (300 MHz, CDCl₃, δ ppm (J, Hz): 7.87 (d, J=7.8 Hz, 1 H), 7.71 (d, J=7.8 Hz, 2 H), 7.50–7.44 (m, 3 H), 7.34–7.20 (m, 6 H), 7.10 (d, J=6.7 Hz, 2 H), 5.48 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ ppm: 154.2, 143.1, 136.2, 136.0, 130.0, 129.7, 129.1, 129.0, 128.5, 127.6, 125.8, 122.8, 122.5, 119.8, 110.1, 48.2.

1-(4-Methylbenzyl)-2-(4-methylphenyl)-1H-benzimidazole (2a): ¹H NMR (400 MHz, CDCl₃) δ ppm (J, Hz): 8.03 (d, J = 8 Hz, 1H), 7.74 (d, J = 7.7 Hz, 2H), 7.31–7.18 (m, 6H), 7.13 (d, J = 7.7 Hz, 2H), 7.99 (d, J = 7.7 Hz, 2H), 5.42 (s, 2H), 2.65 (s, 3H), 2.40 (s, 3H). ¹³C NMR (400 MHz, CDCl₃) δ ppm: 136.2, 135.8, 130.1, 129.3, 129.1, 128.8, 127.8, 125.9, 123.2, 122.9, 119.9, 110.5, 96.1, 77.6, 76.9, 76.3, 47.8, 47.6, 21.7.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzimidazole (3a): ¹H NMR (400 MHz, DMSO-d₆) δ ppm (J, Hz): 7.83 (d, J = 8.6 Hz, 1H) 7.63 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.5 Hz, 1H), 7.25–7.19 (m, 2H), 7.09 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 5.38 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H); ¹³C NMR (75

MHz, DMSO-d₆) δ ppm: 160.5, 159.0, 154.8, 143.2, 138.5, 135.7, 130.1, 128.3, 127.3, 127.2, 122.3, 122.4, 122.4, 119.5, 114.0, 110.1, 55.3, 55.2, 47.8, 39.5.

2-Ethyl-1-propyl-1H-benzimidazole (6a): ¹H NMR (300 MHz, CDCl₃) δ ppm (J, Hz): 7.39-7.24, (d, 4H, J = 9.18 Hz), 4.18-4.14 (m, 2H), 3.15-3.11 (m, 2H), 1.92-1.89 (m, 2H), 1.58-1.54 (m, 3H), 1.02-0.90 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 158.0, 141.7, 134.7, 122.1, 121.1, 120.1, 107.6, 47.2, 20.1, 18.5, 10.3, 9.9.

1-Ethyl-2-methyl-1H-benzimidazole (7a): ¹H NMR (300 MHz, CDCl₃) δ ppm (J, Hz): 7.71-7.25, (m, 4H), 4.22-4.16 (s, 2H), 2.64 (s, 3H), 1.44-1.41 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 151.0, 142.6, 134.6, 121.9, 121.7, 119.0, 108.9, 38.5, 14.9, 13.7.

2-Benzyl-1-phenethyl-1H-benzimidazole (8a): ¹H NMR (300 MHz, CDCl₃) δ ppm (J, Hz): 7.78 (s, 2H), 7.28-7.25 (m, 10 H), 7.00 (s, 2H), 4.15 (s, 2 H), 3.94 (s, 2H), 2.80-2.76 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 153.2, 142.7, 137.8, 136.4, 136.1, 135.1, 128.9, 128.6, 128.4, 127.0, 126.4, 122.4, 122.0, 120.0, 109.4, 65.8, 35.6, 34.4.

¹H NMR and ¹³C NMR of compounds 1b-8b

2-Phenyl-1H-benzimidazole (1b): ¹H NMR (300 MHz, DMSO-d₆) δ ppm (J, Hz): 12.90 (br s, 1H), 8.20 (d, J = 9.0 Hz, 2H), 7.70 (d, J = 7.2 Hz, 1H), 7.60-7.45 (m, 4H), 7.23-7.19 (m, 2H); ¹³C NMR (75 MHz, DMSO-d₆) δ ppm: 151.0, 143.6, 135.0, 130.1, 129.8, 129.0, 126.4, 122.5, 121.5, 118.1, 111.2.

2-(4-Methylphenyl)-1H-benzimidazole (2b): ¹H NMR (300 MHz, DMSO-d₆) δ ppm (J, Hz): 12.85 (br s, 1H), 8.05 (d, J = 7.2 Hz, 2H), 7.65 (s, 1H), 7.51 (s, 1H), 7.36 (d, J = 6.8 Hz, 2H), 7.19 (s, 2H), 2.37 (s, 3H); ¹³C NMR (75 MHz, DMSO-d₆) δ ppm: 151.4, 143.7, 139.6, 135.0, 129.0, 127.3, 126.4, 122.4, 120.9, 118.7, 111.2, 21.0.

2-(4-Methoxyphenyl)-1H-benzimidazole (3b): ¹H NMR (300 MHz, DMSO-d₆) δ ppm (J, Hz): 12.70 (br s, 1H), 8.15 (d, J = 7.2 Hz, 2H), 7.60 (s, 2H), 7.20-7.10 (m, 4H), 3.83 (s, 3H); ¹³C NMR (75 MHz, DMSO-d₆) δ ppm: 160.4, 151.3, 128.0, 122.5, 121.7, 114.4, 114.3, 111.2, 55.3, 14.0.

2-(4-Chlorophenyl)-1H-benzimidazole (4b): ¹H NMR (300 MHz, DMSO-d₆) δ ppm (J, Hz): 12.97 (br s, 1H), 8.19 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.23-7.20 (m, 2H); ¹³C NMR (75 MHz, DMSO-d₆) δ ppm: 150.1, 143.7, 135.0, 134.4, 129.0, 128.7, 128.1, 122.7, 121.8, 118.9, 111.4.

2-(4-Nitrophenyl)-1H-benzimidazole (5b): ¹H NMR (300 MHz, DMSO-d₆) δ ppm (J, Hz): 13.30 (br s, 1H), 8.40-8.37 (m, 4H), 7.67 (s, 2H), 7.27 (s, 2H); ¹³C NMR (75 MHz, DMSO-d₆) δ ppm: 150.0, 149.0, 147.7, 136.0, 134.5, 127.32, 127.3, 124.14, 124.1, 122.9, 114.9.

2-Ethyl-1H-benzimidazole (6b): ¹H NMR (300 MHz, CDCl₃) δ ppm (J, Hz): 11.50 (s, 1H), 7.57-7.54 (d, 2H, J = 9.20 Hz), 7.25-7.19 (d, 2H, J = 9.18 Hz), 3.10-2.95 (m, 2H), 1.46-1.40 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 156.8, 138.6, 130.1, 114.6, 22.6, 12.4.

2-Methyl-1H-benzimidazole (7b): ¹H NMR (300 MHz, CDCl₃) δ ppm (J, Hz): 11.59 (s, 1H), 7.56-7.55 (d, 2H, J = 9.20 Hz), 7.25-7.20 (d, 2H, J = 9.20 Hz), 2.68 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 148.2, 138.0, 122.0, 114.2, 14.0.

2-Benzyl-1H-benzimidazole (8b): ¹H NMR (300 MHz, CDCl₃) δ ppm (J, Hz): 7.50-7.15 (m, 9H), 4.29 (s, 2H). ¹³C NMR (75 MHz, CDCl₃) δ ppm: 162.5, 153.2, 137.1, 128.4, 128.4, 128.5, 128.0, 128.1, 122.1, 33.4.