Highly efficient synthesis of benzimidazoles using microwave irradiation.

Monica Nardi 1, \* Sonia Bonacci 1, Natividad Herrera Cano 2, Manuela Oliverio1 and Antonio Procopio1

1 Dipartimento di Scienze della Salute, Università Magna Græcia, Viale Europa, Germaneto,
88100 Catanzaro CZ, Italia; monica.nardi@unicz.it (M.N.); s.bonacci@unicz.it (S.B.); m.oliverio@unicz,it (M. O.); procopio@unicz.it (A. P.);

2 ICYTAC, CONICET and Universidad Nacional de Córdoba, Facultad de Ciencias Químicas, Departamento. Química Orgánica. Ciudad Universitaria, Bv. Juan Filloy s/n, 5000, Córdoba, Argentina; nhc@fcq.unc.edu.ar (N.H.C.)

**\*** Correspondence: monica.nardi@unicz.it (M.N.);

Tel. of M.N.: +39-0961-3694116

**Electronic Supplementary Material**

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**Experimental Section**

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-phenyl-2-Aryl(alkyl) Benzimidazoles 1a-11a.***

The aryl o alkyl aldehyde (1 mmol) was added to the *N*-phenil-*o*-phenilendiammine (1 mmol) and Er(OTf)3 (1% mol). The obtained mixture reaction was reacted for 5 min under microwave assisted, at a temperature of 60 °C (IR Limit). After completion conversion of *N*-phenil-*o*-phenilendiammine, the Er(OTf)3 was separated from the reaction mixture adding water and extracting the organic product with ethyl acetate (4x3 mL). The products were isolated after organic phases dried over Na2SO4, followed by evaporation under reduced pressure. Spectral data were in accordance with the literature [86]

***General Procedure for the Synthesis of 1-* *benzyl-2-Aryl-Benzimidazoles 1b-3b.***

The benzaldehyde or *p*-sostituited-benzaldehyde (1 mmol) was added to the *N*- benzyl-*o*-phenilendiammine (1 mmol) and Er(OTf)3 (1% mol). The obtained mixture reaction was reacted in the same reaction conditions previously reported (MW irradiation for 5 min). After completion conversion of *N*-phenil-*o*-phenilendiammine, the Er(OTf)3 was separated from the reaction mixture adding water and extracting the organic product with ethyl acetate (4x3 mL). The products were isolated after organic phases dried over Na2SO4, followed by evaporation under reduced pressure. Spectral data were in accordance with the literature [87].

***General Procedure for the Synthesis of 1-phenyl-2-Aryl(alkyl) Benzimidazoles 1a-11a.***

The aryl o alkyl aldehyde (1 mmol) was added to the *N*-phenil-*o*-phenilendiammine (1 mmol) and Er(OTf)3 (1% mmol). The obtained mixture reaction was reacted for 5 min under microwave assisted, at a temperature of 60 °C (IR Limit). After completion conversion of *N*-phenil-*o*-phenilendiammine, the Er(OTf)3 was separated from the reaction mixture adding water and extracting the organic product with ethyl acetate (4x3 mL). The products were isolated after organic phases dried over Na2SO4, followed by evaporation under reduced pressure. Spectral data were in accordance with the literature [86]

**1-Benzyl-2-phenyl-1*H*-benzimidazole (1b):** White solid; m.p. 132–134 °C, 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.Anal. Calcd for C20H16N2: C, 84.50; H, 5.63; N, 9.85 Found: C, 84.51; H, 5.69; N, 9.80

1**-Benzyl-2-(p-tolyl)-1H-benzimidazole (2b):** White solid (20 h, 54%). Mp: 129-131 o C. 1 H-NMR (300 MHz, CDCl3 ): δ = 7.87 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.31-7.27 (m, 4H), 7.24 (d, J = 8.0 Hz, 2H), 7.21-7.19 (m, 2H), 7.01 (d, J = 6.8 Hz, 2H), 5.43 (s, 2H), 2.39 (s, 3H); 13C NMR (75 MHz, CDCl3 ): δ = 154.34, 143.15, 140.10, 136.51, 136.09, 129.48, 129.17, 129.06, 127.75, 127.13, 125.98, 122.91, 122.63, 119.88, 110.49, 48.39, 21.45. HRMS calcd for C21H18N2 [(M+H)+ ]: 299.1543; found, 299.1550.

**1-Benzyl-2-(4-methoxyphenyl)-1H-benzo[d]imidazole (3b).** White solid (20 h, 62%). Mp: 133-135 o C. 1 H-NMR (300 MHz, CDCl3 ): δ = 7.86 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.4 Hz, 2H), 7.33-7.24 (m, 2H), 7.21 (dd, J = 14.8 Hz, 8.0 Hz, 2H), 7.09 (d, J = 6.8 Hz, 2H), 6.96-6.93 (m, 2H), 5.41 (s, 2H), 3.81 (s, 3H); 13C NMR (75 MHz, CDCl3 ): δ = 160.95, 154.18, 143.22, 136.55, 136.16, 130.70, 129.08, 127.75, 125.96, 122.79, 122.59, 122.41, 119.76, 114.23,110.40, 55.37, 48.38. HRMS calcd for C21H18N2O [(M+H)+ ]: 315.1492; found, 315.1496.