Supporting Information

Synthesis of Benzimidazoles via Iron-Catalyzed Aerobic Oxidation Reaction of Imine Derivatives with *o*-phenylenediamine

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Experimental Section

All starting materials were purchased from commercial sources and used without further treatment. Melting points were determined on a Thomas Hoover capillary apparatus and were uncorrected. All known compounds were identified by appropriate technique such as ¹H NMR and compared with previously reported data. ¹H NMR (500 MHz) was recorded on a Bruker 500 spectrometer with tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on an Agilent technologies 6110 quadrupole LC/MS equipped with an electrospray ionization (ESI) probe operating in positive ion mode. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. All the products are the known compounds.

Typical Procedure for oxidative synthesis of benzimidazoles

A mixture of 1.5 mmol *o*-phenylenediamine, and 1 mmol imine, 5 mol% Fe(NO₃)₃·9H₂O, and 5 ml MeCN were mixed in a 10 ml three-necked flask, one necked is equipped with a condenser, another is equipped with a thermometer with a condenser, and then stirred rapidly open to air at 80 °C for 12 hours. The reaction progress was monitored by TLC. After completion of the reaction, the residue was directly purified by column chromatograph on a silica gel using hexane/ethyl acetate (7:3) as eluent to afford the pure product.

2-Phenyl-1H-benzimidazole

m.p. 294-296 °C (lit.¹ m.p. 295-297 °C); ¹H NMR (DMSO-d₆, 500 MHz): δ 12.82 (s, 1H, NH), 8.20-8.15 (m, 2H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.58-7.46 (m, 4H), 7.24-7.17 (m, 2H). MS (m/z)

[M+H]⁺: 195.

2-(4-fluorophenyl)-1H-benzimidazole

m.p. 296-298 °C (lit.⁴ m.p. 246-251 °C); ¹H NMR (DMSO-d₆, 500 MHz): δ 12.90 (s, 1H, NH), 8.24-8.19 (m, 2H), 7.65 (d, 1H, *J* = 7.50 Hz), 7.52 (m, 1H, *J* = 7.00 Hz), 7.39 (t, 2H, *J*₁ = 9.00 Hz, *J*₂ = 8.50 Hz), 7.19 (t, 2H, *J*₁ = 8.00 Hz, *J*₂ = 8.50 Hz). MS (m/z) [M+H]⁺: 213.

2-(4-bromophenyl)-1H-benzimidazole

m.p. 296-298 °C (lit.⁴ m.p. 298-299 °C); ¹H NMR (DMSO-d₆, 500 MHz): δ 12.98 (s, 1H, NH), 8.12 (d, 2H), 7.77 (d, 2H), 7.66-7.54 (m, 2H), 7.21 (d, 2H). MS (m/z) [M+H]⁺: 274.

2-(4-chlorophenyl)-1H-benzimidazole

m.p. 292-293 °C (lit.¹ m.p. 292-294 °C); ¹H NMR (DMSO-d₆, 500 MHz): δ 12.99 (s, 1H, NH), 8.21-8.18 (m, 2H), 7.75-7.62 (m, 4H), 7.26-7.22 (m, 2H). MS (m/z) [M+H]⁺: 229.

2-(2-chlorophenyl)-1H-benzimidazole

m.p. 233-234 °C (lit.⁵ m.p. 233-234 °C); ¹H NMR (DMSO-d₆, 500 MHz): δ 12.71 (s, 1H, NH), 7.90 (dd, 1H, *J* = 2.0 Hz, *J* = 2.2 Hz), 7.70 (d, 1H, *J* = 7.8 Hz), 7.67-7.63 (m, 1H), 7.60-7.48 (m, 3H), 7.30-7.18 (m, 2H). MS (m/z) [M+H]⁺: 229.

2-(2,4-dichlorophenyl)-1H-benzimidazole

m.p. 217-219 °C (lit.⁵ m.p. 218-220 °C); ¹H NMR (DMSO-d₆, 500 MHz): δ 12.78 (s, 1H, NH), 7.93 (d, 1H, *J* = 8.4 Hz), 7.84 (d, 1H, *J* = 2.1 Hz), 7.63-7.55 (m, 3H), 7.25-7.23 (m, 2H). MS (m/z) [M+H]⁺: 263.

2-(4-nitrophenyl)-1H-benzimidazole

m.p. 320-322 °C (lit.⁴ m.p. 321-322 °C); ¹H NMR (DMSO-d₆, 500 MHz): δ 12.29 (s, 1H, NH), 8.46-8.39 (m, 4H), 7.73 (d, 1H, *J* = 7.6 Hz), 7.59 (d, 1H, *J* = 7.5 Hz), 7.33-7.20 (m, 2H). MS (m/z) [M+H]⁺: 240.

2-(4-Methoxyphenyl)-1H-benzimidazole

m.p. 224-226 °C (lit.¹ m.p. 295-297 °C); ¹H NMR (DMSO-d₆, 500 MHz): δ 12.73 (s, 1H, NH), 8.10 (d, 2H, *J* = 8.8 Hz), 7.60 (d, 1H, *J* = 7.5 Hz), 7.48 (d, 1H, *J* = 7.3 Hz), 7.19-7.08 (m, 4H), 3.82-3.84 (s, 3H). MS (m/z) [M+H]⁺: 225.

2-(4-Dimethylaminophenyl)-1H-benzimidazole

m.p. 273-275 °C (lit.⁶ m.p. 273-275 °C); ¹H NMR (DMSO-d₆, 500 MHz): δ 12.52 (s, 1H, NH), 7.98 (d, 2H, *J* = 8.9 Hz), 7.54 (s, 1H), 7.43 (s, 1H), 7.15-7.07 (m, 2H), 6.82 (d, 2H, *J* = 9.0 Hz),

2.99 (s, 6H). MS (m/z) [M+H]⁺: 238.

2-(4-Isopropylphenyl)-1H-benzimidazole

m.p. 258-260 °C (lit.⁹ m.p. 259-260 °C); ¹H NMR (DMSO-d₆, 500 MHz) δ 12.79 (s, 1H), 8.18 (d, 2H, *J* = 8.15 Hz), 7.63 (d, 1H, *J* = 7.55 Hz), 7.49 (d, 1H, *J* = 7.45 Hz), 7.40 (d, 2H, *J* = 8.15 Hz), 7.22-7.11 (m, 2H), 2.99-2.89 (m, 1H), 1.22 (d, 6H, *J* = 6.9 Hz). MS (m/z) [M+H]⁺: 237.

2-(3, 4, 5-trimethoxyphenyl)-1H-benzimidazole

m.p. 255-256 °C (lit.² m.p. 254-256 °C); ¹H NMR (DMSO-d₆, 500 MHz) δ 12.87 (s, 1H), 7.65 (d, 1H, *J* = 7.7 Hz), 7.53 (t, 3H, *J* = 6.8 Hz), 7.24-7.15 (m, 2H), 3.89 (s, 6H), 3.72 (s, 3H). MS (m/z) [M+H]⁺: 285.

2-(1-Naphthyl)-1H-benzimidazole

m.p. 216-218 °C (lit.¹⁰ m.p. 217 °C); ¹H NMR (DMSO-d₆) δ 12.90 (s, 1H), 9.09 (d, 1H, *J* = 8.3 Hz), 8.09 (d, 1H, *J* = 8.2 Hz), 8.05-7.97 (m, 2H), 7.76 (d, 1H, *J* = 7.7 Hz), 7.70-7.53 (m, 4H), 7.29-7.20 (m, 2H). MS (m/z) [M+H]⁺: 245.

2-styryl-1H-benzimidazole

m.p. 202-204 °C (lit.¹¹ m.p. 201-203 °C); ¹H NMR (DMSO-d₆) δ 12.61 (s, 1H), 7.65 (t, 3H, *J* = 8.5 Hz), 7.51 (s, 2H), 7.42 (t, 2H, *J* = 7.53 Hz), 7.35 (t, 1H, *J* = 7.28 Hz), 7.23-7.13 (m, 3H). MS (m/z) [M+H]⁺: 221.

2-Furyl-1H-benzimidazole

m.p. 285-286 °C (lit.⁶ m.p. 285-287 °C); ¹H NMR (DMSO-d₆) δ 12.96 (s, 1H), 7.95 (d, 1H, *J* = 1.1 Hz), 7.63 (d, 1H, *J* = 7.5 Hz), 7.50 (d, 1H, *J* = 7.5 Hz), 7.23-7.19 (m, 3H), 6.75-6.73 (m, 1H). MS (m/z) [M+H]⁺: 185.

2-(5-methylfuryl)-1H-benzimidazole

m.p. 176-178 °C (lit.⁷ m.p. 175-177 °C); ¹H NMR (DMSO-d₆) δ 12.78 (s, 1H), 7.57 (s, 1H), 7.47 (s, 1H), 7.17 (s, 2H), 7.07 (d, 1H, *J* = 3.2 Hz), 6.34 (d, 1H, *J* = 3.0 Hz), 2.41 (s, 3H). MS (m/z) [M+H]⁺: 199.

2-(Pyridin-2-yl)-1H-benzimidazole

m.p. 218-219 °C (lit.¹² m.p. 219-220 °C); ¹H NMR (DMSO-d₆) δ 13.07 (s, 1H), 8.71 (d, 1H, *J* = 4.6 Hz), 8.31 (d, 1H, *J* = 7.85 Hz), 8.02-7.94 (m, 1H), 7.69 (d, 1H, *J* = 7.8 Hz), 7.52 (t, 2H, *J* = 8.85 Hz), 7.27-7.15 (m, 2H). MS (m/z) [M+H]⁺: 196.

2-Phenyl-5-Chloro- 1H-benzimidazole

m.p. 212-214 °C (lit.¹ m.p. 212-214 °C); ¹H NMR (DMSO-d₆) δ 13.08 (s, 1H), 8.14 (d, 2H, *J* =7.3 Hz), 7.77-7.44 (m, 5H), 7.21 (d, 1H, *J*=8.2 Hz). MS (m/z) [M+H]⁺: 229.

2-Phenyl-5-Nitro- 1H-benzimidazole

m.p. 208-209 °C (lit.¹ m.p. 208-210 °C); ¹H NMR (DMSO-d₆) δ 13.61 (s, 1H), 8.48 (s, 1H), 8.22 (dd, 2H, *J*₁ =1.7 Hz, *J*₂ =1.3 Hz), 8.14 (dd, 1H, *J*₁ =2.2 Hz, *J*₂ =2.2 Hz), 7.77 (d, 1H, *J* =8.3 Hz), 7.63-7.55 (m, 3H). MS (m/z) [M+H]⁺: 240.

2-heptyl-1H-benzimidazole

m.p. 143-144°C (lit.¹³ m.p. 143-145°C); ¹H NMR (DMSO-d₆) δ 12.13 (s, 1H), 7.45 (s, 2H), 7.20-7.00 (m, 2H), 2.79 (t, 2H, *J*₁ =7.50 Hz, *J*₂ =7.55 Hz), 1.75 (t, 2H, *J*₁ =6.80 Hz, *J*₂ =7.10 Hz), 1.40-1.18 (m, 8H), 0.85 (t, 3H, *J*₁ =6.40 Hz, *J*₂ =6.95 Hz). MS (m/z) [M+H]⁺: 217.

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¹H NMR and MS Spectra of all the Products

¹H NMR spectrum (500 MHz, DMSO) of 2-Phenyl-1H-benzimidazole

MS spectrum of 2-Phenyl-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-fluorophenyl)-1H-benzimidazole

20140620-YJT-3 #69 RT: 0.85 AV: 1 NL: 2.48E7
T: + c Q1MS [150.00-350.10]

MS spectrum of 2-(4-fluorophenyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-bromophenyl)-1H-benzimidazole

MS spectrum of 2-(4-bromophenyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-chlorophenyl)-1H-benzimidazole

MS spectrum of 2-(4-chlorophenyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(2-chlorophenyl)-1H-benzimidazole

MS spectrum of 2-(2-chlorophenyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(2,4-dichlorophenyl)-1H-benzimidazole

MS spectrum of 2-(2,4-dichlorophenyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-nitrophenyl)-1H-benzimidazole

MS spectrum of 2-(4-nitrophenyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-Methoxyphenyl)-1H-benzimidazole

MS spectrum of 2-(4-Methoxyphenyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-Dimethylaminophenyl)-1H-benzimidazole

MS spectrum of 2-(4-Dimethylaminophenyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-Isopropylphenyl)-1H-benzimidazole

20131022-YUJIATAO-1-1 #37 RT: 0.40 AV: 1 NL: 4.04E7
T: + c Q1MS [90.00-300.10]

MS spectrum of 2-(4-Isopropylphenyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(3, 4, 5-trimethoxyphenyl)-1H-benzimidazole

MS spectrum of 2-(3, 4, 5-trimethoxyphenyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(1-Naphtyl)-1H-benzimidazole

20131022-YUJIATAO-2-1 #74 RT: 0.79 AV: 1 NL: 1.52E7
T: + c Q1MS [90.00-300.10]

MS spectrum of 2-(1-Naphtyl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-styryl-1H-benzimidazole

20131022-YUJIATAO-4 #79 RT: 0.85 AV: 1 NL: 3.15E6
T: + c QIMS [90.00-300.10]

MS spectrum of 2-styryl-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-Furyl-1H-benzimidazole

MS spectrum of 2-Furyl-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(5-methylfuryl)-1H-benzimidazole

MS spectrum of 2-(5-methylfuryl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-(Pyridin-2-yl)-1H-benzimidazole

20131022-YUJIATAO-3 #209 RT: 2.42 AV: 1 NL: 1.82E7
T: + c Q1MS [90.00-300.10]

MS spectrum of 2-(Pyridin-2-yl)-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-Phenyl-5-Nitro-1H-benzimidazole

MS spectrum of 2-Phenyl-5-Nitro-1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-Phenyl-5-Chloro-1H-benzimidazole

20131011-jiangtao #41 RT: 0.47 AV: 1 NL: 3.89E6
T: + c Q1MS [85.00-300.10]

MS spectrum of 2-Phenyl-5-Chloro- 1H-benzimidazole

¹H NMR spectrum (500 MHz, DMSO) of 2-heptylbenzimidazole.

20131022-YUJIATAO-4 #268 RT: 3.20 AV: 1 NL: 5.13E4
T: - c Full ms2 219.00@35.00 [30.00-240.00]

MS spectrum of 2-heptylbenzimidazole.