Supporting Information

Iron-catalyzed highly efficient aerobic oxidative synthesis of benzimidazoles, benzoxazoles and benzothiazoles direct from aromatic primary amines under solvent-free conditions in the open air

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Experimental section

General Methods.

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 are 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. Yields refer to the isolated yields of the products after

purification by silica-gel column chromatography (300 mesh). All starting chemicals are commercially available.

Experimental Procedures for Synthesis of Benzimidazoles

A mixture of 4mmol *o*-phenylenediamine, 2-aminophenol or 2-amino-thiophenole and 4.8mmol amine, 5mol% Fe(NO₃)₃, 5mol% TEMPO were mixed in a 5-ml three-necked flask, and then stirred rapidly open to air at 110 °C for several 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 (Table 2, entry 1)

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-bromophenyl)-1H-benzimidazole (Table 2, entry 2)

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 (Table 2, entry 3)

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 (Table 2, entry 4)

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 (Table 2, entry 5)

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 (Table 2, entry 6)

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 (Table 2, entry 7)

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 (Table 2, entry 8)

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 (Table 2, entry 9)

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 (Table 2, entry 10).

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-Naphtyl)-1H-benzimidazole (Table 2, entry 11).

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 (Table 2, entry 12).

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 (Table 2, entry 13).

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 (Table 2, entry 14)

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 (Table 2, entry 15).

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 (Table 2,entry 16)

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 (Table 2,entry 17)

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-phenylbenzoxazole (Table 2,entry 18)

m.p. 96-98 °C (lit.⁸ m.p. 208-210 °C); ¹H NMR (DMSO-d₆) δ 8.21 (dd, 2H, J_1 =1.5 Hz, J_2 =2.0 Hz), 7.84-7.77 (m, 2H), 7.67-7.60 (m, 3H), 7.46-7.39 (m, 2H). MS (m/z) [M+H]⁺: 196.

2-(4-chlorophenyl)- benzoxazole (Table 2,entry 19)

m.p. 145-146 °C (lit.⁸ m.p. 144-145 °C); ¹H NMR (DMSO-d₆) δ 8.19 (d, 2H, J =8.5 Hz), 7.87-7.75 (m, 2H), 7.68 (d, 2H, J =8.5 Hz), 7.50-7.37 (m, 2H). MS (m/z) [M+H]⁺: 230.

2-(4-methoxyphenyl)- benzoxazole (Table 2,entry 20)

m.p. 97-98 °C (lit.⁸ m.p. 97-98 °C); ¹H NMR (DMSO-d₆) δ 8.17-8.12 (m, 2H), 7.78-7.72 (m, 2H), 7.42-7.36 (m, 2H), 7.19-7.14 (m, 2H), 3.87 (s, 3H). MS (m/z) [M+H]⁺: 226.

2-phenylbenzothiazole (Table 2,entry 21)

m.p. 110-112 °C (lit.⁸ m.p. 111-112 °C); ¹H NMR (DMSO-d₆): δ 8.14 (d, 1H, J =8.0 Hz), 8.12-8.05 (m, 3H), 7.60-7.52 (m, 4H), 7.49-7.44 (m, 1H). MS (m/z) [M+H]⁺: 212.

2-(4-chlorophenyl)-benzothiazole (Table 2,entry 22)

m.p. 111-113 °C (lit.⁸ m.p. 110-112 °C); ¹H NMR (DMSO-d₆): δ 8.74 (s, 1H), 8.02 (d, 2H, J =8.5 Hz), 7.64 (d, 2H, J =8.4 Hz), 7.57-7.52 (m, 1H), 7.35-7.22 (m, 3H). MS (m/z) [M+H]⁺: 246.

2-(4-nitrophenyl)-benzothiazole (Table 2,entry 23)

m.p. 228-230 °C (lit.⁸ m.p. 228-229 °C); ¹H NMR (DMSO-d₆): δ 8.43-8.34 (m, 4H), 8.23 (d, 1H,

$J = 7.9$ Hz), 8.15 (d, 1H, $J = 8.1$ Hz), 7.61 (t, 1H, $J = 7.6$ Hz), 7.54 (t, 1H, $J = 7.6$ Hz). MS (m/z) [M+H]⁺: 257.

References

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¹H NMR and MS Spectra of all the Products

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

MS spectrum of 2-Phenyl-1H-benzimidazole (Table 2, entry 1)

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

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

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-chlorophenyl)-1H-benzimidazole (Table 2, entry 3)

MS spectrum of 2-(4-chlorophenyl)-1H-benzimidazole (Table 2, entry 3)

¹H NMR spectrum (500 MHz, DMSO) of 2-(2,4-dichlorophenyl)-1H-benzimidazole (Table 2, entry 5)

MS spectrum of 2-(2,4-dichlorophenyl)-1H-benzimidazole (Table 2, entry 5)

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-nitrophenyl)-1H-benzimidazole (Table 2, entry 6)

MS spectrum of 2-(4-nitrophenyl)-1H-benzimidazole (Table 2, entry 6)

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-Methoxyphenyl)-1H-benzimidazole (Table 2, entry 7)

MS spectrum of 2-(4-Methoxyphenyl)-1H-benzimidazole (Table 2, entry 7)

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-Dimethylaminophenyl)-1H-benzimidazole (Table 2, entry 8)

MS spectrum of 2-(4-Dimethylaminophenyl)-1H-benzimidazole (Table 2, entry 8)

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-Isopropylphenyl)-1H-benzimidazole (Table 2, entry 9)

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

MS spectrum of 2-(4-Isopropylphenyl)-1H-benzimidazole (Table 2, entry 9)

¹H NMR spectrum (500 MHz, DMSO) of 2-(3, 4, 5-trimethoxyphenyl)-1H-benzimidazole (Table 2, entry 10)

MS spectrum of 2-(3, 4, 5-trimethoxyphenyl)-1H-benzimidazole (Table 2, entry 10)

¹H NMR spectrum (500 MHz, DMSO) of 2-(1-Naphtyl)-1H-benzimidazole (Table 2, entry 11)

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 (Table 2, entry 11)

¹H NMR spectrum (500 MHz, DMSO) of 2-styryl-1H-benzimidazole (Table 2, entry 12)

20131022-YUJIATAO-4 #79 RT: 0.85 AV: 1 NL: 3.15E6
T: + c Q1MS [90.00-300.10]

MS spectrum of 2-styryl-1H-benzimidazole (Table 2, entry 12)

¹H NMR spectrum (500 MHz, DMSO) of 2-Furyl-1H-benzimidazole (Table 2, entry 13)

MS spectrum of 2-Furyl-1H-benzimidazole (Table 2, entry 13)

¹H NMR spectrum (500 MHz, DMSO) of 2-(5-methylfuryl)-1H-benzimidazole (Table 2, entry 14)

MS spectrum of 2-(5-methylfuryl)-1H-benzimidazole (Table 2, entry 14)

¹H NMR spectrum (500 MHz, DMSO) of 2-(Pyridin-2-yl)-1H-benzimidazole (Table 2, entry 15)

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 (Table 2, entry 15)

¹H NMR spectrum (500 MHz, DMSO) of 2-Phenyl-5-Chloro-1H-benzimidazole (Table 2,entry 16)

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

MS spectrum of 2-Phenyl-5-Chloro- 1H-benzimidazole (Table 2,entry 16)

¹H NMR spectrum (500 MHz, DMSO) of 2-Phenyl-5-Nitro- 1H-benzimidazole (Table 2,entry 17)

MS spectrum of 2-Phenyl-5-Nitro- 1H-benzimidazole (Table 2,entry 17)

¹H NMR spectrum (500 MHz, DMSO) of 2-phenylbenzoxazole (Table 2,entry 18)

MS spectrum of 2-phenylbenzoxazole (Table 2,entry 18)

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-methoxyphenyl)-benzoxazole (Table 2, entry 20)

MS spectrum of 2-(4-methoxyphenyl)-benzoxazole (Table 2, entry 20)

¹H NMR spectrum (500 MHz, DMSO) of 2-phenylbenzothiazole (Table 2, entry 21)

MS spectrum of 2-phenylbenzothiazole (Table 2, entry 21)

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-chlorophenyl)-benzothiazole (Table 2,entry 22)

MS spectrum of 2-(4-chlorophenyl)-benzothiazole (Table 2,entry 22)

¹H NMR spectrum (500 MHz, DMSO) of 2-(4-nitrophenyl)-benzothiazole (Table 2,entry 23)

MS spectrum of 2-(4-nitrophenyl)-benzothiazole (Table 2,entry 23)