Supporting Information

A general and practical Oxidative Coupling of *o*-phenylenediamine with Arylmethylamines to the Synthesis of Benzimidazoles under Catalyst-free and Solvent-free Conditions

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Characterization Data for the Products

2-Phenyl-1H-benzimidazole (2a)

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 (2b)

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 (2c)

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 (2d)

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 (2e)

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 (2f)

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 (2g)

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), 3.83 (s, 3H). MS (m/z) [M+H]⁺: 225.

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

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 (2i)

m.p. 258-260 °C (lit.⁹ m.p. 259-260 °C); ¹H NMR (DMSO-d₆, 500 MHz) δ 12.79 (s, 1H), 8.08 (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 (2j).

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 (2k).

m.p. 216-218 °C (lit.¹⁰ m.p. 217 °C); ¹H NMR (DMSO-d₆) δ 12.90 (s, 1H), 9.08 (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 (2l).

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 (2m).

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 (2n)

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 (2o).

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-Nitro- 1H-benzimidazole (2p)

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-Phenyl-5-Chloro- 1H-benzimidazole (2q)

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-phenylbenzoxazole (2r)

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-phenylbenzothiazole (2s)

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.

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¹H NMR and MS Spectra of all the Products

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

MS spectrum of 2-Phenyl-1H-benzimidazole (2a)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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 (2i)

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

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

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

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 (2k)

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

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 (2I)

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

MS spectrum of 2-Furyl-1H-benzimidazole (2m)

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

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

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

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 (2o)

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

MS spectrum of 2-Phenyl-5-Nitro- 1H-benzimidazole (2p)

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

¹H NMR spectrum (500 MHz, DMSO) of 2-phenylbenzoxazole (2r)

MS spectrum of 2-phenylbenzoxazole (2r)

¹H NMR spectrum (500 MHz, DMSO) of 2-phenylbenzothiazole (2s)

MS spectrum of 2-phenylbenzothiazole (2s)