Supporting Information

HIGHLY CHEMOSELECTIVE SYNTHESIS OF BENZIMIDAZOLES IN SC(OTF)$_3$-CATALYZED SYSTEM

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1. Measurement

^{1}H and ^{13}C NMR spectrums were recored on Bruker ARX 400 for proton. For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent of $CDCl_3$ (δ: 77.36 ppm), DMSO-d_6 (δ: 40.45) and $(CD_3)_2CO$ (δ: 30.60, 205.87) used as an internal reference. And ^{1}H NMR were reported downfield from $CDCl_3$ (δ: 7.27 ppm), DMSO-d_6 (δ: 2.49), and $(CD_3)_2CO$ (δ: 2.09) Column chromatographies were performed with silica gel (200-300 mesh ASTM).

2. General experimental procedure

2.1 A typical experimental procedure of 1,2-disustituted benzimidazoles

A mixture of $Sc(OTf)_3$ (98.4 mg, 0.2 mmol) and EtOH (5mL) were well stirred until the solid dissolved completely at reflux condition; then o-phenylenediamine **1a** (129.8mg, 1.2 mmol) and benzaldehyde **2a** (202 uL, 2.0 mmol) was added into the above mixture. The reaction was monitored by TLC. The reaction mixture was cooled to r.t., and then evaporated in vacuum. The product purified by column chromatography (PE-EtOAc= 5:1) to give light yellow solid 3a (269.6 mg, 95%). **3b-3j** were synthesized through the same procedure and characterized by ^{1}H NMR and ^{13}C NMR.

2.2 A typical experimental procedure of 2-sustituted benzimidazoles

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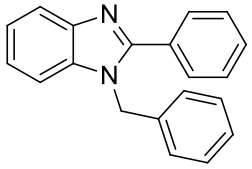
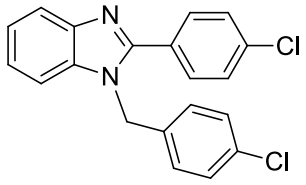
A mixture of o-phenylenediamine **1a** (129.8mg, 1.2 mmol), $Sc(OTf)_3$ (73.8 mg, 0.15 mmol) and EtOH (15 mL) wre well stirred until the solid dissolved completely at reflux condition. Benzaldehyde **2b** (101 uL, 1.0 mmol) and H_2O_2 (61 uL, 30 wt%, 2mmol) was diluted to 20 mL EtOH, and dropwised into the preprocessed mixture. After TLC showed the reaction to be complete, the reaction mixture was cooled to r.t., and then evaporated in vacuum. The product purified by column chromatography (PE-EtOAc= 4:1) to give light yellow solid 4a (160.6 mg, 90%). **4b-4k** were synthesized through the same procedure characterized by ^{1}H NMR and ^{13}C NMR.

3. Spectral data

1-benzyl-2-phenyl-1H-benzo[d]imidazole 3a Light yellow solid (269.6 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.88 (d, *J* = 8 Hz, 1 H), 7.48-7.45 (m, 3 H), 7.34-7.30 (m, 4 H), 7.25-7.21 (m, 2 H), 7.11 (d, *J* = 7.2 Hz, 2 H), 5.47 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ= 154.22, 143.23, 136.44, 136.11, 130.12, 129.97, 129.30, 129.11, 128.81, 127.83, 126.01, 123.10, 122.74, 120.03, 110.61, 48.41.

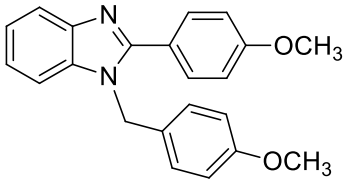


1-(4-chlorobenzyl)-2-(4-chlorophenyl)-1H-benzo[d]imidazole 3b Light yellow solid (324.2 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.88 (d, *J* = 8 Hz, 1 H), 7.60-7.58(m, 2 H), 7.45-7.43 (m, 2 H), 7.36-7.27 (m, 4 H), 7.20 (d, *J* = 8 Hz, 1 H), 7.02 (d, *J* = 8.4 Hz, 2 H), 5.40 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$,25°C, TMS): δ =152.90, 143.14, 136.36, 135.96, 134.68, 133.87, 130.47, 129.41, 129.12, 128.41, 127.29, 123.50, 123.07, 120.22, 110.34, 47.82.

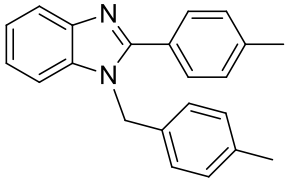


1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]imidazole 3c Yellow solid (326.9 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.84 (d, *J* = 8 Hz, 1 H), 7.65-7.63(m, 2 H), 7.31-7.27 (m, 1 H), 7.24-7.21 (m, 2 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 7.00-6.96 (m, 2 H), 6.86-6.84 (m, 2 H), 5.38 (s, 2 H), 3.85(s, 3 H), 3.70(s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$,25°C, TMS): δ = 160.90, 159.12, 154.14, 143.22, 136.13, 130.72, 128.51, 127.23, 122.74, 122.53, 122.49, 119.74, 114.44, 114.20, 110.45, 55.40,

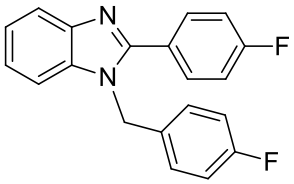
55.32, 47.90.



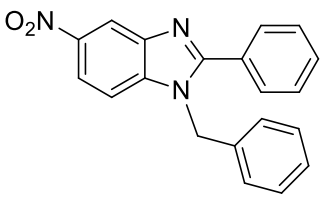
1-(4-methylbenzyl)-2-p-tolyl-1H-benzo[d]imidazole 3d Yellow solid (290.3 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=7.86 (d, J=8 Hz, 1 H), 7.59 (d, *J* = 8 Hz, 2 H), 7.31-7.27 (m, 1 H), 7.25-7.24 (m ,2 H), 7.21-7.16 (m, 2 H), 7.13(d, *J* = 8 Hz, 2 H), 6.99 (d, *J* = 8 Hz, 2 H), 5.40 (s, 1 H), 2.40 (s, 3 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 154.38, 143.22, 140.05, 137.46, 136.14, 133.50, 129.73, 129.48, 129.19, 127.22, 125.93, 122.86, 122.58, 119.85 (s), 110.55 (s), 48.22, 21.48, 21.14.



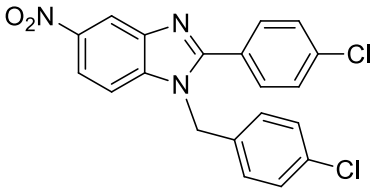
1-(4-fluorobenzyl)-2-(4-fluorophenyl)-1H-benzo[d]imidazole 3e Yellow solid (307.1 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ= 7.86 (d, *J* = 7.6 Hz, 1 H), 7.66-7.63 (m, 2 H), 7.34-7.28 (m, 2 H), 7.24-7.20 (m, 1 H), 7.17-7.13 (m, 2 H), 7.07-6.99 (m, 4 H), 5.40 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ= 162.54, 161.08, 153.11, 143.07, 135.90, 131.95, 131.24, 127.64, 126.17, 123.33, 122.96, 120.11, 116.22 116.01 , 110.36, 47.74.



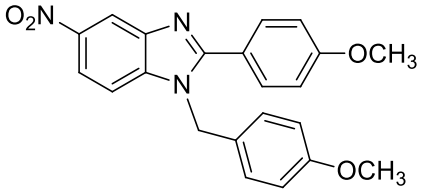
1-benzyl-5-nitro-2-phenyl-1H-benzo[d]imidazole 3f Yellow solid (277.4 mg,84%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=8.25 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1 H), 8.18 (d, *J* = 2 Hz, 2 H), 7.90 (d, *J* = 8.8 Hz, 1 H), 7.73-7.70 (m, 2 H), 7.55-7.48 (m, 3 H), 7.39-7.32 (m, 3 H), 7.10-7.07 (m, 2 H), 5.55 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$,25°C, TMS): δ = 158.87, 147.65, 143.70, 135.45, 135.19, 130.94, 129.42, 129.36, 129.30, 129.09, 125.88, 120.03, 118.73, 107.47, 48.84.



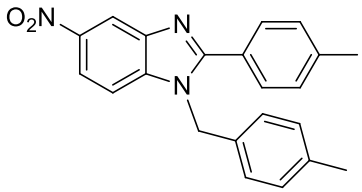
1-(4-chlorobenzyl)-2-(4-chlorophenyl)-5-nitro-1H-benzo[d]imidazole 3g Yellow solid **(**362.4 mg,91%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=8.27 (dd, *J* = 9.0 Hz, *J* = 2 Hz, 1 H), 8.17 (d, *J* = 1.6 Hz, 2 H), 7.65-7.60 (m, 2 H), 7.51-7.49 (m ,2 H), 7.37-7.34 (m, 2 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 5.49 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ= 145.26, 140.50, 137.54, 134.42, 130.50, 129.74, 129.52, 129.15, 128.96, 127.15, 118.81, 103.82, 98.95, 82.60, 48.18.



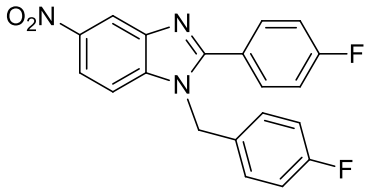
1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-5-nitro-1H-benzo[d]imidazole 3h Yellow solid (342.6 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=8.23 (dd, *J* = 8.8 Hz, *J* = 2 Hz, 1 H), 8.17 (d, *J* = 2 Hz, 1 H), 7.86 (d, *J* = 8.8 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.02 (dd, *J* = 8.8 Hz, *J* = 4 Hz, 2 H),6.88 (d, *J* = 8.4 Hz, 2 H), 5.48 (s, 2 H), 3.87 (s, 3 H), 3.80 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 160.87, 159.10, 158.97, 146.54, 140.74, 139.71, 129.77, 129.11, 128.91, 128.13, 127.59, 119.00, 114.25, 114.14, 114.06, 55.32, 47.93, 47.26.



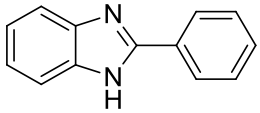
1-(4-methylbenzyl)-5-nitro-2-(p-tolyl)-1H-benzo[d]imidazole 3i Yellow solid (303.7 mg , 85%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=8.23 (dd, *J* = 8.8 Hz, *J* = 2 Hz, 1 H), 8.15 (d, *J* = 2 Hz, 1 H), 7.88 (d, *J* = 8.8 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 7.6 Hz, 2 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 5.50 (s, 2 H), 2.43 (s, 3 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 159.07, 147.73, 143.53, 141.31, 138.14, 135.49, 132.22, 130.04, 129.77, 129.22, 125.81, 119.79, 118.65, 107.45, 48.67, 27.38, 21.55, 21.14.



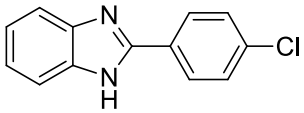
1-(4-fluorobenzyl)-2-(4-fluorophenyl)-5-nitro-1H-benzo[d]imidazole 3j Yellow solid (321.9 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ=8.24 (dd, *J* = 8.8 Hz, *J* = 2 Hz, 1 H), 8.18 (d, *J* = 2.0 Hz, 1 H), 7.90 (d, *J* = 9.2 Hz, 2 H), 7.70 (dd, *J* = 8.6 Hz, *J* = 5.6 Hz, 2 H), 7.24-7.19 (m, 2 H), 7.09-7.05 (m, 4 H), 5.50 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 165.57, 163.05, 157.75, 147.42 – 147.29, 143.83 – 143.71, 135.32, 131.4, 130.76, 127.59, 125.03, 120.17, 118.92, 116.73 – 116.53, 116.50 – 116.30, 107.25, 48.19.



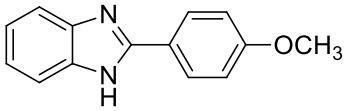
2-phenyl-1H-benzo[d]imidazole 4a Yellow solid (160.6 mg, 90%);^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25°C, TMS): δ=12.91(s, 1 H), 8.19-8.17(m, 2 H), 7.67-7.49 (m, 5 H), 7.21(s, br, 2H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$, 25°C, TMS): *δ* = 151.58, 143.38,135.50, 130.73, 130.29, 129.11, 126.87, 122.89, 121.20, 118.89, 111.84.



2-(4-chlorophenyl)-1H-benzo[d]imidazole 4b Yellow solid (208.8 mg, 92%); ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25°C, TMS): *δ* = 12.90 (s, 1H), 8.21 (d, *J* =8.4Hz, 2H), 7.64 (d, *J* = 8.4Hz, 4H), 7.23–7.20 (m, 2H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$, 25°C, TMS): *δ* = 150.56, 144.31, 135.02, 134.81, 129.50, 128.66, 128.22, 122.91, 122.50, 119.34, 111.69.

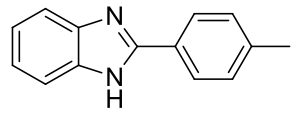


2-(4-methoxyphenyl)-1H-benzo[d]imidazole 4c Yellow solid (213.0 mg, 95%); ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25°C, TMS): *δ* = 7.45 (d, *J* = 7.2Hz, 1H), 7.24–7.20 (m, 2H), 7.08 (d, *J* = 8.8Hz, 2H), 6.96 (d, *J* = 8.4Hz, 2H), 6.83 (d, *J* = 8.8Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$, 25°C, TMS): *δ* = 160.80, 153.56, 143.27, 136.30, 129.27, 127.85, 122.47, 119.37, 114.68, 114.59, 111.48, 55.80.

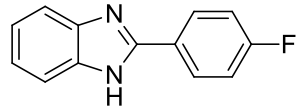


2-(p-tolyl)-1H-benzo[d]imidazole 4d Yellow solid (193.7 mg, 93%); ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25°C, TMS): *δ* = 12.81 (s, 1H), 8.06 (d, *J* = 7.8Hz, 2H), 7.55 (s,

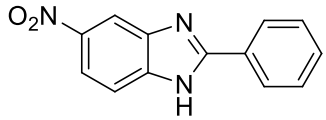
2H), 7.34 (d, *J* = 7.8Hz, 2H), 7.21–7.18 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$, 25°C, TMS): *δ* = 151.78, 144.28, 140.00, 135.36, 129.88, 127.86, 126.85, 122.69, 121.99, 119.12, 111.66, 21.33.



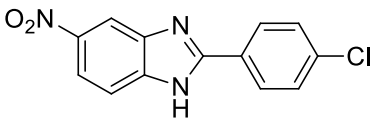
2-(4-fluorophenyl)-1H-benzo[d]imidazole 4e Brown solid (203.2 mg, 96%); ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25°C, TMS): δ= 12.92 (s, 1H), 8.25-8.21 (m, 2 H), 7.66-7.54 (m, 2 H), 7.43-7.38 (m, 2 H), 7.21-7.16 (m, 2 H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$, 25°C, TMS): δ = 164.78, 162.23, 150.91, 129.72, 129.60, 129.22, 129.10, 127.33, 122.58. 118.13, 116.88.



5-nitro-2-phenyl-1H-benzo[d]imidazole 4f Yellow solid (193.7 mg , 84%); ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25°C, TMS): δ= 13.55 (s, 1H), 8.40 (s, 1H), 8.14–8.1 (m, 2H), 8.09–8.04 (m, 1H), 7.70 (d, 1H), 7.54 (s, 1H), 7.52 (s, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*, 25°C, TMS): δ= 155.12, 143.10, 137.62, 131.37, 129.55, 129.42, 128.75, 127.37, 118.37, 110.71, 104.93.

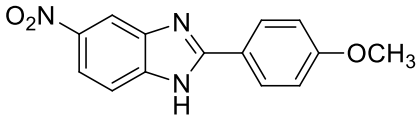


2-(4-chlorophenyl)-5-nitro-1H-benzo[d]imidazole 4g Yellow soloid (249.6 mg , 91%); ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25°C, TMS): δ=13.72 (s, 1 H), 8.51(s, br, 1 H), 8.24 (d, *J* = 8.8 Hz, 2 H), 8.16 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1 H), 7.80 (s, br, 1 H), 7.71 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO-*d6*, 25°C, TMS): δ= 155.13, 150.53, 143.50, 136.36, 131.46, 129.88, 129.32, 128.55, 118.92, 115.64, 112.65.

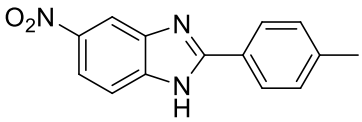


2-(4-methoxyphenyl)-5-nitro-1H-benzo[d]imidazole 4h Yellow solid (235.6 mg, 88%); ^{1}H NMR (400 MHz, Acetone, 25°C, TMS): δ= 12.50 (s, 1H), 8.48 (s, 1H), 8.21

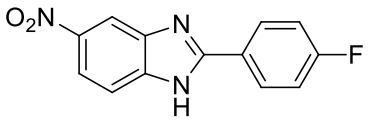
(t, *J* = 13.9 Hz, 2H), 8.16 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.76 (t, *J* = 17.8 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR(100 MHz, Acetone, 25°C, TMS): δ= 162.06, 143.71, 142.35, 128.70, 121.81, 117.76, 116.38, 114.35, 113.37, 100.35, 99.67 54.99.



5-nitro-2-(p-tolyl)-1H-benzo[d]imidazole 4i Yellow solid (216.3 mg, 85%); ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 25°C, TMS): δ= 13.45 (s, 1H), 8.10 (s, br, 1 H), 8.09 (dd, *J*$_1$ = 8.8 Hz, *J*$_2$ = 1 Hz, 1 H), 7.98 (d, *J* = 8.4 Hz, 2 H), 7.67 (s, br, 1 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 2.45 (s, 3 H); ^{13}C NMR(100 MHz, DMSO-*d*$_6$, 25°C, TMS): δ= 156.32, 136.37,130.12, 129.15, 127.77, 126.02, 118.67, 115.02, 112.81, 112.39, 109.91, 21.11.



2-(4-fluorophenyl)-5-nitro-1H-benzo[d]imidazole 4j Yellow solid (226.3 mg, 88%); ^{1}H NMR (400 MHz, Acetone, 25°C, TMS) δ 12.64 (s, 1H), 8.51 (s, 1H), 8.37 – 8.28 (m, 2H), 8.18 (dt, *J* = 8.9, 2.0 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.39 (td, *J* = 8.7, 1.7 Hz, 2H); ^{13}C NMR(100 MHz, Acetone, 25°C, TMS): ^{13}C NMR(100 MHz, Acetone, 25°C, TMS): δ= 165.55, 163.07, 154.84, 143.52, 139.38, 129.43,129.40, 125.98, 118.05, 116.09, 116.03.



2-(furan-2-yl)-1H-benzo[d]imidazole 4k Yellow solid (129.4 mg, 70%); ^{1}H NMR (400 MHz, DMSO-*d*6, 25°C, TMS): δ= 12.91 (brs, 1H)，7.94 (s, 1 H), 7.62 (d, *J* = 8.4 Hz, 1 H), 7.50 (d, 1H, J = 8.0 Hz), 7.25-7.18 (m, 3H), 6.77-6.74(m, 1 H); ^{13}C NMR (100 MHz, DMSO-*d*6, 25°C, TMS): δ= 146.00, 143.45, 143.45, 137.12, 134.16, 122.43, 121.56, 118.66, 112.33, 111.23, 110.34.