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SUPPLEMENTARY MATERIAL TO

Polystyrene-supported pyridinium chloroaluminate ionic liquid as a new heterogeneous Lewis acid catalyst for selective synthesis of benzimidazoles

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PHYSICAL AND SPECTRAL DATA OF THE OBTAINED COMPOUNDS

*2-Phenyl-1*H-*benzimidazole* (***1a***). m.p. 287–289 °C (Lit.[35]** 286–288 °C); IR (KBr, cm^{-1}): 1630 (C=N), 3438 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.16–7.27 (2H, *m*, aromatic), 7.51–7.65 (5H, *m*, aromatic), 8.30–8.33 (2H, *d*, *J* = = 7.1 Hz, aromatic), 12.92 (1H, *bs*, NH).

*6-Methyl-2-phenyl-1*H-*benzimidazole* (***1b***). m.p. 249–253 °C (Lit.[47] 246 °C); IR (KBr, cm^{-1}): 1625 (C=N), 3424 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / / ppm): 2.35 (3H, *s*, CH_3), 7.09–7.20 (4H, *m*, aromatic), 7.41–7.55 (4H, *m*, aromatic), 12.88 (1H, *bs*, NH).

*2-(4-Methylphenyl)-1*H-*benzimidazole* (***1c***). m.p. 265–267 °C (Lit.[40] 261––263 °C); IR (KBr, cm^{-1}): 1630 (C=N), 3430 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 2.30 (3H, *s*, CH_3), 7.20–7.36 (4H, *m*, aromatic), 7.49–7.56 (2H, *m*, aromatic), 7.95–8.09 (2H, *m*, aromatic), 12.85 (1H, *bs*, NH).

*6-Methyl-2-(4-methylphenyl)-1*H-*benzimidazole* (***1d***): m.p. 102–104 °C (Lit.[36] 101–102 °C); IR (KBr, cm^{-1}): 1620 (C=N), 3420 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 2.31 (3H, *s*, –CH_3), 2.40 (3H, *s*, –CH_3), 7.09–7.12 (3H, *m*, aromatic), 7.42 (1H, *s*, aromatic), 7.55 (1H, *d*, *J* = 8.0 Hz, aromatic), 8.20 (2H, *d*, *J* = 8.0 Hz, aromatic), 12.70 (1H, *bs*, NH).

*2-(4-Methoxyphenyl)-1*H-*benzimidazole* (***1e***). m.p. 228–231 °C (Lit.[30] 223––226 °C); IR (KBr, cm^{-1}): 1615 (C=N), 3430 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 3.72 (3H, *s*, –OCH_3), 7.13–7.21 (4H, *m*, aromatic), 7.45

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(1H, *s*, aromatic), 7.65 (1H, *s*, aromatic), 8.19 (2H, *d*, *J* = 1.7 Hz, aromatic), 12.10 (1H, *bs*, NH).

*2-(4-Chlorophenyl)-1*H*-benzimidazole (**1f**)*. m.p. 288–290 °C (Lit.[35] 284––286 °C); IR (KBr, cm^{-1}): 1628 (C=N), 3425 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.21–7.29 (2H, *m*, aromatic), 7.55–7.64 (4H, *m*, aromatic), 8.22 (2H, *d*, *J* = 8.5 Hz, aromatic), 12.96 (1H, *bs*, NH).

*6-Methyl-2-(4-chlorophenyl)-1*H*-benzimidazole (**1g**)*. m.p. 227–228 °C (Lit.[48] 224–225 °C); IR (KBr, cm^{-1}): 1630 (C=N), 3430 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 2.41 (3H, *s*, $–CH_3$), 7.31 (1H, *s*, aromatic), 7.64–7.79 (4H, *m*, aromatic), 8.31–8.36 (2H, *d*, *J* = 8.4 Hz, aromatic), 12.89 (1H, *bs*, NH).

*2-(2-Chlorophenyl)-1*H*-benzimidazole (**1h**)*. m.p. 230–232 °C (Lit.[40] 231–233 °C); IR (KBr, cm^{-1}): 1633 (C=N), 3429 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.25–7.30 (2H, *m*, aromatic), 7.51–7.61 (5H, *m*, aromatic), 7.89–7.93 (1H, *m*, aromatic), 12.64 (1H, *bs*, NH).

*2-(4-Bromophenyl)-1*H*-benzimidazole (**1i**)*. mp: 288–290 °C (Lit.[35] 283–284 °C); IR (KBr, cm^{-1}): 1624 (C=N), 3415 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / / ppm): 7.22–7.29 (2H, *m*, aromatic), 7.33–7.44 (6H, *m*, aromatic), 12.89 (1H, *bs*, NH).

*2-(3-Nitrophenyl)-1*H*-benzimidazole (**1j**)*. mp: 209–211 °C (Lit.[35] 207–208 °C); IR (KBr, cm^{-1}): 1340, 1550 (NO_2), 1624 (C=N), 3438 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.25–7.40 (4H, *m*, aromatic), 7.67–7.80 (4H, *m*, aromatic), 12.89 (1H, *bs*, NH).

*2-(4-Nitrophenyl)-1*H*-benzimidazole (**1k**)*. m.p. 310–312 °C (Lit.[40] 308–310 °C); IR (KBr, cm^{-1}): 1338, 1516 (NO_2), 1625 (C=N), 3418 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.32–7.44 (4H, *m*, aromatic), 8.02–8.15 (4H, *m*, aromatic), 12.87 (1H, *bs*, NH).

*2-(2-Hydroxyphenyl)-1*H*-benzimidazole (**1l**)*. mp: 242–243 °C (Lit.[35] 240––242 °C); IR (KBr, cm^{-1}):1622 (C=N), 3245, 3350, 3410 (NH, OH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.67–7.77 (4H, *m*, aromatic), 7.79–7.86 (3H, *m*, aromatic), 7.88 (1H, *s*, aromatic), 12.98 (2H, *bs*, NH, OH).

*2-(4-Hydroxyphenyl)-1*H*-benzimidazole (**1m**)*. m.p. 257–259 °C (Lit.[36] 254––255 °C); IR (KBr, cm^{-1}): 1625 (C=N), 3250, 3340, 3415 (NH, OH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.61–7.71 (4H, *m*, aromatic), 7.73–7.79 (2H, *m*, aromatic), 7.81–7.86 (2H, *m*, aromatic), 9.89 (1H, *bs*, OH), 12.71 (1H, *bs*, NH).

*2-(3-Hydroxyphenyl)-1*H*-benzimidazole (**1n**)*. m.p. 184–187 °C (Lit.[36] 182––183 °C); IR (KBr, cm^{-1}):1622 (C=N), 3268, 3360, 3418 (NH, OH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.57–7.67 (4H, *m*, aromatic), 7.69–7.76 (3H, *m*, aromatic), 7.79 (1H, *s*, aromatic), 9.85 (1H, *bs*, OH), 12.66 (1H, *bs*, NH).

*4-(1*H*-Benzimidazol-2-yl)benzonitrile (**1o**)*. m.p. 263–265 °C (Lit.[36] 262 °C); IR (KBr, cm^{-1}): 1618 (C=N), 2220 (CN), 3420 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.23–7.27 (2H, *m*, aromatic), 7.51–7.65 (2H, *m*, aromatic),

8.02–8.08 (2H, *d*, *J* = 8.4 Hz, aromatic), 8.40–8.46 (2H, *d*, *J* = 8.4 Hz, aromatic), 13.09 (1H, *bs*, NH).

*2-(2-Naphthyl)-1*H-*benzimidazole* (***2***). m.p. 218–219 °C (Lit.[36] 217 °C); IR (KBr, cm^{-1}): 1625 (C=N), 3430 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.25–7.29 (2H, *m*, aromatic), 7.49–7.57 (4H, *m*, aromatic), 8.02–8.11 (3H, *m*, aromatic), 8.37–8.41 (1H, *dd*, J_1 = 8.1, J_2 = 2.2 Hz, aromatic), 8.85 (1H, *s*, aromatic), 13.10 (1H, *bs*, NH).

*2-Benzyl-1*H-*benzimidazole* (***3***). m.p. 185–188 °C (Lit.[39] 184–186 °C); IR (KBr, cm^{-1}): 1623 (C=N), 3427 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.20 (2H, *s*, $–CH_2–$), 7.17–7.20 (2H, *d*, *J* = 7.3 Hz, aromatic), 7.25–7.27 (1H, *m*, aromatic), 7.36–7.41 (4H, *m*, aromatic), 7.45–7.47 (1H, *d*, *J* = 6.4 Hz, aromatic), 7.55–7.57 (1H, *d*, *J* = 8.9 Hz, aromatic), 12.27 (1H, *bs*, NH).

*6-Methyl-2-benzyl-1*H-*benzimidazole* (***4***). m.p. 144–147 °C (Lit.[49] 139–140 °C); IR (KBr, cm^{-1}): 1625 (C=N), 3430 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 4.15 (2H, *s*, $–CH_2–$), 7.15–7.18 (2H, *d*, *J* = 7.3 Hz, aromatic), 7.36––7.41 (5H, *m*, aromatic), 7.55–7.57 (1H, *d*, *J* = 8.9 Hz, aromatic), 12.31 (1H, *bs*, NH).

*2-Cyclohexyl-1*H-*benzimidazole* (***5***). m.p. 284–286 °C (Lit.[32] 282–283 °C); IR (KBr, cm^{-1}): 1630 (C=N), 3420 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / / ppm): 1.30–1.51 (2H, *m*, cyclohexyl ring), 1.66–1.77 (2H, *m*, cyclohexyl ring), 1.83–1.87 (2H, *m*, cyclohexyl ring), 2.05–2.15 (3H, *m*, cyclohexyl ring), 2.89––2.99 (2H, *m*, cyclohexyl ring), 7.15–7.20 (2H, *m*, aromatic), 7.53–7.59 (2H, *m*, aromatic), 11.55 (1H, *bs*, NH).

*2-Butyl-1*H-*benzimidazole* (***6***). m.p. 149–152 °C (Lit.[50] 148–149 °C); IR (KBr, cm^{-1}): 1630 (C=N), 3438 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 1.01–1.03 (3H, *t*, *J* = 7.3 Hz, CH_3), 1.44–1.46 (2H, *sext*, *J* = 7.0 Hz, $–CH_2–$), 1.89–1.91 (2H, *quin*, *J* = 7.0 Hz, $–CH_2–$), 2.95–2.98 (2H, *t*, *J* = 7.0 Hz, $–CH_2–$), 7.29–7.36 (4H, *m*, aromatic), 9.44 (1H, *bs*, NH).

*2-Styryl-1*H-*benzimidazole* (***7***). m.p. 200–202 °C (Lit.[31] 201–203 °C); IR (KBr, cm^{-1}): 1620 (C=N), 3425 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.20–7.30 (4H, *m*, aromatic), 7.31–7.33 (1H, *d*, *J* = 16.8 Hz, CH), 7.59–7.69 (5H, *m*, aromatic), 7.71–7.73 (1H, *d*, *J* = 16.8 Hz, CH), 12.99 (1H, *bs*, NH).

*2-(2-Pyridyl)-1*H-*benzimidazole* (***8***). m.p. 220–221 °C (Lit.[30] 216–219 °C); IR (KBr, cm^{-1}): 1625 (C=N), 3435 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / / ppm): 7.20–7.25 (2H, *m*, aromatic), 7.51–7.60 (3H, *m*, aromatic), 8.05–8.10 (1H, *dd*, J_1 = 7.5, J_2 = 1.6 Hz, aromatic), 8.25–8.27 (1H, *m*, aromatic), 8.76–8.79 (1H, *d*, *J* = 6.4 Hz, aromatic), 13.07 (1H, *bs*, NH).

*2-(2-Furyl)-1*H-*benzimidazole* (***9***). m.p. 289–291 °C (Lit.[36] 287–288 °C); IR (KBr, cm^{-1}): 1625 (C=N), 3425 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 6.78 (2H, *s*, aromatic), 7.50 (1H, *s*, aromatic), 7.60–7.70 (4H, *m*, aromatic), 12.89 (1H, *bs*, NH).

*2-(2-Thienyl)-1*H-*benzimidazole (**10**)*. m.p. 327–329 °C (Lit.[30] 330 °C); IR (KBr, cm^{-1}): 1624 (C=N), 3445 (NH); ^{1}H-NMR (300 MHz, DMSO-d_6, δ / ppm): 7.15–7.22 (3H, *m*, aromatic), 7.52–7.61 (2H, *m*, aromatic), 7.79–7.86 (2H, *m*, aromatic), 12.97 (1H, *bs*, NH).