Supporting Information

Chemoselective epoxidation of substrate containing both electron rich and electron deficient olefins catalyzed by meso-tetraarylporphyrin iron(III) chlorides in imidazolium ionic liquids

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Experimental

The ionic liquids has been synthesised by the slight modification of the literature method.^[1]

Synthesis of 1-butyl-3-methylimidazolium chloride [bmim][Cl]

In a 100 ml round-bottom flask, 1-methylimidazole (0.3 mol, dried over MgSO₄) was mixed with *n*-butyl chloride (0.45 mol) and allowed to reflux for 24 h at 70 °C. The excess butyl chloride was distilled off and the residue was extracted thoroughly 2-3 times (100 ml each) with diethyl ether to remove the unreacted starting materials. A clear yellow viscous oily liquid of 1-butyl-3-methylimidazolium chloride was obtained in 94% yield (61.76 g). Further, the formation of ionic liquid [bmim][Cl] confirmed from the various spectroscopic data.

IR (Thin film, cm⁻¹): 3422, 3093, 3149, 2962, 2937, 2875, 2065, 1633, 1573, 1383, 1467, 1429, 1337, 1169, 1282, 1114, 1022, 842, 754, 622; ¹H NMR (D₂O, 60 MHz, δ ppm) : 0.72 (t, 3H, CH₃), 1.15 (m, 2H, CH₂), 1.81 (m, 2H, CH₂), 3.71 (s, 3H, N-CH₃), 4.09 (t, 2H, N-CH₂), 7.38 (s, 1H, NCH), 7.43 (s, 1H, NCH), 8.7 (s, 1H, N(H)CN).

Synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄]

Ionic liquid {[bmim][Cl], 0.25 mmol} was dissolved in dry acetone (50 ml) and stirred with NaBF₄ (5.0 g) at room temperature for 24 h to exchange the anion. The reaction mixture was filtered off to remove precipitated NaCl and excess NaBF₄. The acetone was evaporated on rotary evaporator under reduced pressure and vacuum dried to give [bmim][BF₄] in 97% yield.

IR (Thin film, cm⁻¹): 3150, 3094, 2874, 1631, 1571, 1464, 1382, 1168, 753; ¹H NMR (CDCl₃, 300 MHz, δ in ppm): 0.91 (t, *J*=7.12 Hz, 3H, CH₃), 1.35 (sexet, *J*=7.20 Hz, 2H, CH₂CH₃), 1.85 (q, *J*=7.20 Hz, 2H, NCH₂CH₂), 4.01 (s, 3H, NCH₃), 4.21 (t, *J*=7.11 Hz,

2H, NCH₂), 7.49 (s, 2H, C-4H & C-5H), 8.98 (s, 1H, C-2H); ¹³C NMR (300 MHz, δ in ppm, CDCl₃): 13.27, 19.23, 31.87, 36.13, 49.57, 122.49, 123.79, 136.12.

Synthesis of n-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆].

Ionic liquid ([bmim][Cl], 0.25 mmol) was dissolved in dry acetone (50 ml) and stirred with KPF₆ (5.0 g) at room temperature for 24 h to exchange the anion. The reaction mixture was filtered off to remove precipitated KCl and excess KPF₆. The acetone was evaporated on rotary evaporator under reduced pressure and vacuum dried to give [bmim][PF₆] in 98% yield.

IR (Thin film, cm⁻¹): 3156, 3098, 2878, 1635, 1574, 1467, 1383, 1172, 756; ¹H NMR (CDCl₃, 300 MHz, δ in ppm): 0.86 (br s, -CH₃), 1.21(br s, 2H, -CH₂CH₃), 1.81(q, *J*=7.20 Hz, 2H, NCH₂CH₂), 3.86 (br s, 3H, NCH₃), 4.18 (br s, -NCH₂), 7.50 (br s, 2H, H-4 & H-5), 8.75 (br s, 1H, H-2).

Synthesis of 1-butyl-3-methylimidazolium acetate [bmim][OAc].

Ionic liquid ([bmim][Cl], 0.25 mmol) was dissolved in dry acetone (50 ml) and stirred with NH_4OAc (5.0 g) at room temperature for 24 h to exchange the anion. The reaction mixture was filtered off to remove precipitated NH_4Cl and excess NH_4OAc . The acetone was evaporated on rotary evaporator under reduced pressure and vacuum dried to give [bmim][OAc] in 96% yield.

IR (Thin film, cm⁻¹): 3155, 3100, 2884, 1682, 1636, 1577, 1469, 1387, 1182; ¹H NMR (300 MHz: DMSO-d₆; δ in ppm): 1.02 (3H, t, -CH₃), 1.23 (2H, m, CH₂), 1.56 (3H, s, CH₃CO₂), 1.73 (2H, m, CH₂), 3.96 (3H, s, NCH₃), 4.17 (2H, t, NCH₂), 7.87 (1H, s, NCH), 7.95 (1H, s, NCH), 10.30 (1H, s, NCHN).



Figure 1. UV-Visible spectra of TAPFe(III)Cl with increasing concentration of $[Bmim][PF_6]$ in dichloromethane.



Figure 3.¹H NMR spectrum of **2a** in acetone- d_6 .



Figure 5. ¹H NMR spectrum of 2b in CDCl₃.







Figure 7. ¹H NMR spectrum of **3b** in CDCl₃.

ESR analysis

The intermediates responsible for the oxidation were prepared in an ESR sample tube by minor modification of reported method.^[2] The TAPFe(III)Cl complex (2 mM) in a [bmim][PF₆] was placed into an ESR tube, and the solution was cooled to -80 °C in a methanol-liquid nitrogen bath. Hydrogen peroxide (2 equivalent) or PhIO (2 equivalent) was slowly added to the solution. After 2 min., the solution in the ESR tube was immediately frozen to -80 °C and was subjected to ESR measurements. An identical reaction was performed at -80°C in the presence of substrates containing the electron rich and electron deficient olefins.



Figure 8. ESR Spectrum of $Cl_8TAPFe(III)Cl$ (2 mM) and oxidant (a) H_2O_2 (2 equivalents) or (b) PhIO (2 equivalents) in [bmim][PF₆] at temperature, -80°C, using microwave frequency, 9.47 GHz; microwave power, 0.5-1 mW; time constant, 82 ms; gain, 5x10² to 1x10⁴.

References

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