Supporting Information

Lewis acidic ionic liquids of crown ether complex cations: preparation and applications in organic reactions

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1. Characterization data of Lewis acidic ionic liquids and part compounds

1.1 The data of Lewis acidic ionic liquids

[18-C-6K][AlCl₄] (A) FT-IR (cm⁻¹) 3427.8 (m), 2916.5 (m), 1476.0 (w), 1353.5 (w), 1115.4 (s), 945.6 (m); Raman (cm⁻¹): 359; Elemental analysis calcd for C₁₂H₂₄Cl₄AlKO₆·CH₃CH₂OH·H₂O (%): C 31.36, H 6.01; found: C 31.70, H 6.34; MS (ESI) m/z: calcd for [M]⁻ 168.79, found 168.86.

[18-C-6K][FeCl₄] (B) FT-IR (cm⁻¹) 3431.0 (m), 2896.4 (m), 1634.5 (w), 1351.2 (w), 1105.1 (s), 961.8 (m); Raman (cm⁻¹): 332; Elemental analysis calcd for C₁₂H₂₄Cl₄FeKO₆·H₂O·CH₂Cl₂ (%) C 25.85, H 4.67; found: C 25.81, H 4.61; MS (ESI) m/z: calcd for [M]⁻ 197.66, found 197.85.

[18-C-6K][ZnCl₃] (C) FT-IR (cm⁻¹) 3412.9 (m), 2899.7 (m), 1648.8 (w), 1353.6 (w), 1110.3 (s), 962.8 (m); Raman (cm⁻¹): 289; Elemental analysis calcd for C₁₂H₂₄Cl₃ZnKO₆·CH₃CH₂OH·H₂O: C 31.18, H 5.98; found: C 30.82, H 5.75; MS (ESI) m/z: calcd for [M]⁻ 171.75, found 170.87.
[15-C-5Na][FeCl₄] (D) FT-IR (cm⁻¹) 3429.0 (m), 2922.7 (m), 1475.0 (w), 1353.2 (w), 1117.2 (s),
947.9 (w); Raman (cm⁻¹): 329; Elemental analysis calcd for C₁₀H₂₆Cl₄FeNaO₅ (%)·2H₂O: C 25.18,
H 5.07 found C 25.31, H 5.22; MS (ESI) m/z: calcd [M]⁻ 197.66, found 197.83.

[15-C-5Na][ZnCl₃] (E) FT-IR (cm⁻¹) 3441.1 (m), 2922.1 (m), 1477.8 (w), 1352.4 (w), 1113.6 (s),
946.3 (m); Raman (cm⁻¹): 287; Elemental analysis calcd for C₁₀H₂₆Cl₃ZnNaO₅·1/3CH₃CH₂OH
(%): C 29.77, H 5.15 found: C 30.03, H 4.75; MS (ESI) m/z: calcd for [M]⁻ 170.75, found 170.87.

[18-C-6K]⁺ MS (ESI) m/z: calcd for [M]⁺ 303.12, found 303.11.


1.2 ¹H NMR data of target compounds

2-phenyl-1H-benzo[d]imidazole (3a) ¹H NMR (300 MHz, DMSO-ᴅ) δ = 12.94(s, 1H),
8.19 (d, J=7.1Hz 1H), 7.80-7.33(m, 3H), 7.22 (dd, J=6.0, 2.8Hz, 1H) ppm;

1-benzyl-2-phenyl-1H-benzo[d]imidazole (4a) ¹H NMR (300 MHz, DMSO-ᴅ) δ = 10.83
(s, 1H), 7.37 (dd, J=10.0, 4.8 Hz, 1H), 7.27 (t, J = 7.5Hz, 1H), 7.18 (d, J=7.3, 1H), 7.07-
6.99 (m, 1H), 5.84(s, 1H) ppm;

3,3'-(phenylmethylene)bis(1H-indole) (6a) ¹H NMR (300 MHz, CDCl₃) δ = 7.89 (d, J =
8.4Hz, 1H), 7.70 (dd, J = 6.9, 1.8Hz, 2H), 7.48 (m, 3H), 7.33 (m, 4H), 7.24 (dd, J =6.6,
1.2Hz, 2H), 7.12 (dd, J=8.4, 2.4Hz, 2H), 5.47 (s, 2H);
2. FT-IR, MS, TGA-DSC of Lewis acidic ionic liquids

2.1 FT-IR of Lewis acidic ionic liquids

Figure S1 IR spectrum of A
Figure S2 IR spectrum of B
Figure S3 IR spectrum of C
Figure S4 IR spectrum of D
Figure S5 IR spectrum of E
2.2 MS of Lewis acidic ionic liquids
Figure S6 MS of IL catalyst cation [18-C-6K]$^+$
Figure S7 MS of IL catalyst cation [15-C-5Na]^+
Figure S8 MS of A anion [AlCl₄]⁻
Figure S9 MS of B anion [FeCl$_4$]$^-$
Figure S10 MS of C anion [ZnCl$_3$]$^-$

Figure S11 MS of D anion [FeCl$_4$]$^-$
Figure S12 MS of E anion [ZnCl$_3$]$^-$
2.3 TGA-DSC of Lewis acidic ionic liquids

Figure S13 TGA-DSC of A
Figure S14 TGA-DSC of B
Figure S15 TGA-DSC of C

Figure S16 TGA-DSC of D
Figure S17 TGA-DSC of E
3. $^1$H NMR of part compounds

$^1$H NMR 2-phenyl-1H-benzo[d]imidazole (3a)
$^{1}$H NMR 1-benzyl-2-phenyl-1H-benzo[d]imidazole (4a)

$^{1}$H NMR 3,3'-(phenylmethylene)bis(1H-indole) (6a)

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