

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 6.342; 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 4.613; 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 5.751; 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 C₁₀H₂₀Cl₄FeNaO₅ (·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 C₁₀H₂₀Cl₃ZnNaO₅·1/3CH₃CH₂OH (%): 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.

[15-C-5Na]⁺ MS (ESI) m/z: calcd for [M]⁺ 243.12, found 243.09.

1.2 ¹H NMR data of target compounds

2-phenyl-1H-benzo[d]imidazole (**3a**) ¹H NMR (300 MHz, DMSO-*d*₆) 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-*d*₆) 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

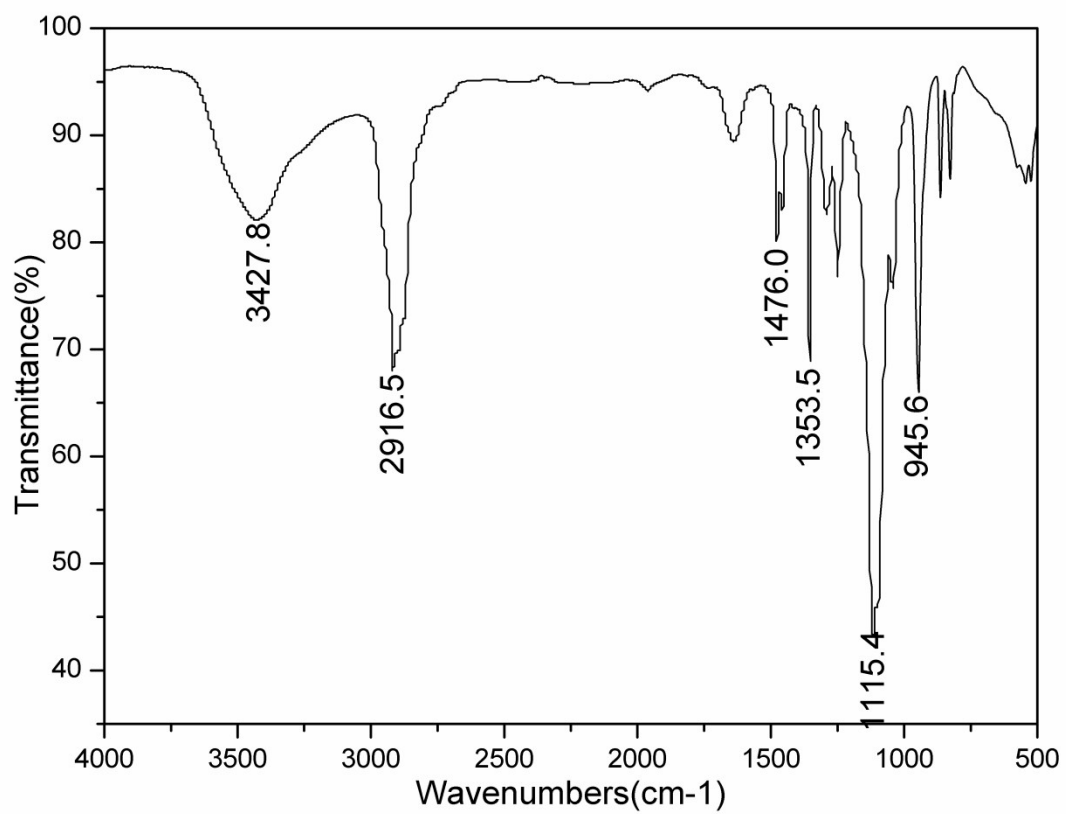


Figure S1 IR spectrum of A

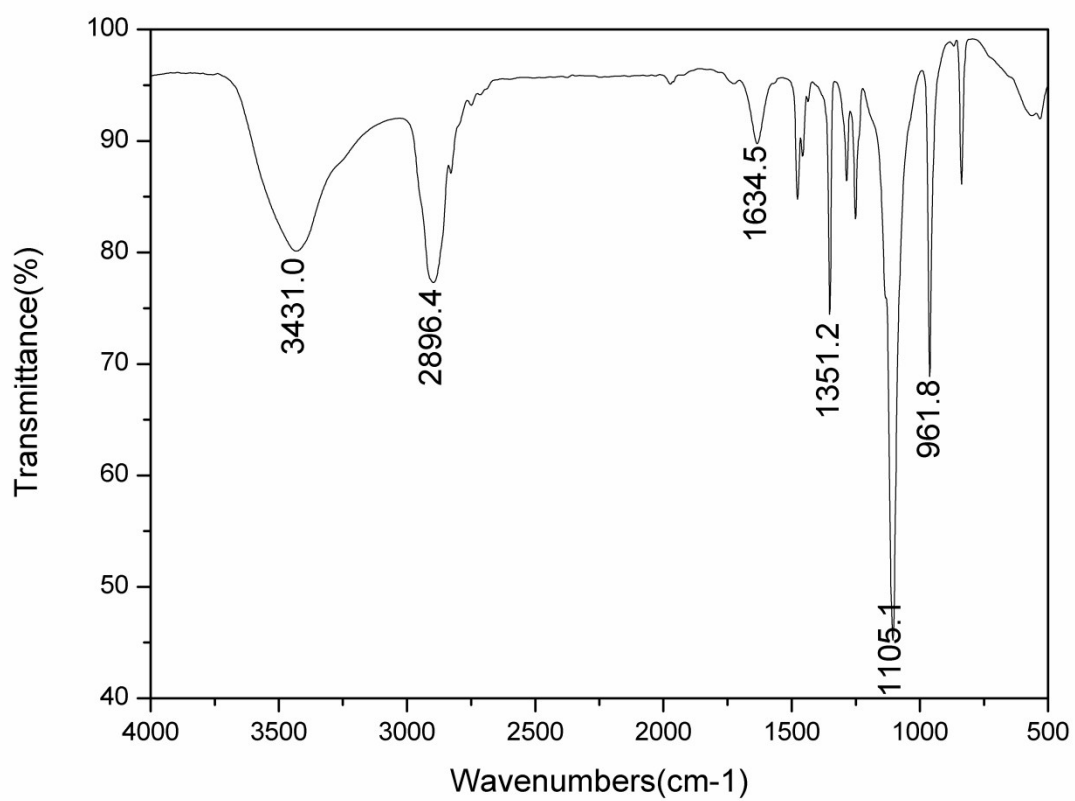


Figure S2 IR spectrum of B

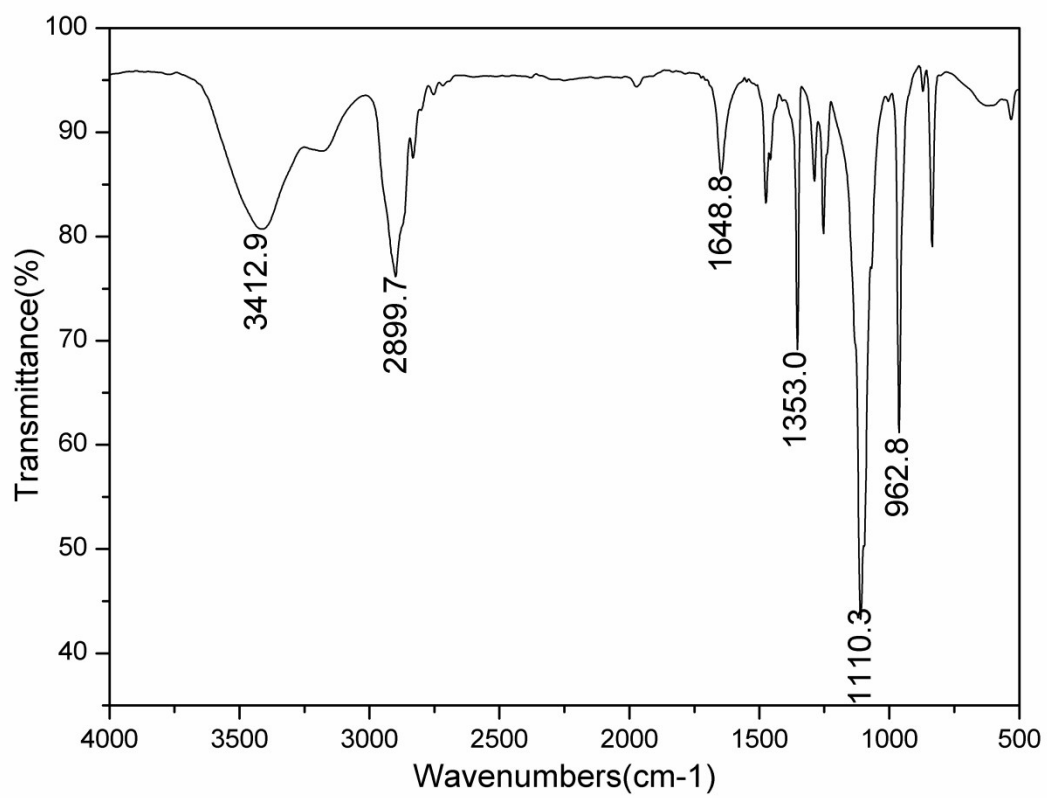


Figure S3 IR spectrum of C

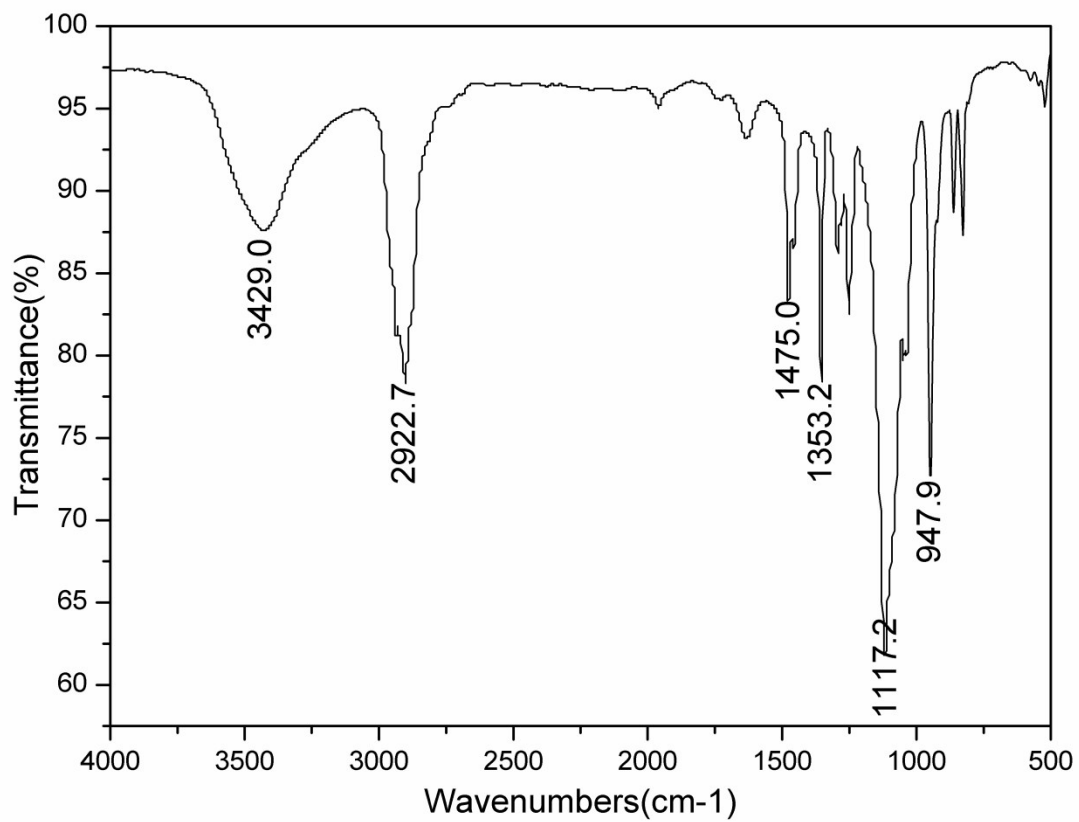


Figure S4 IR spectrum of D

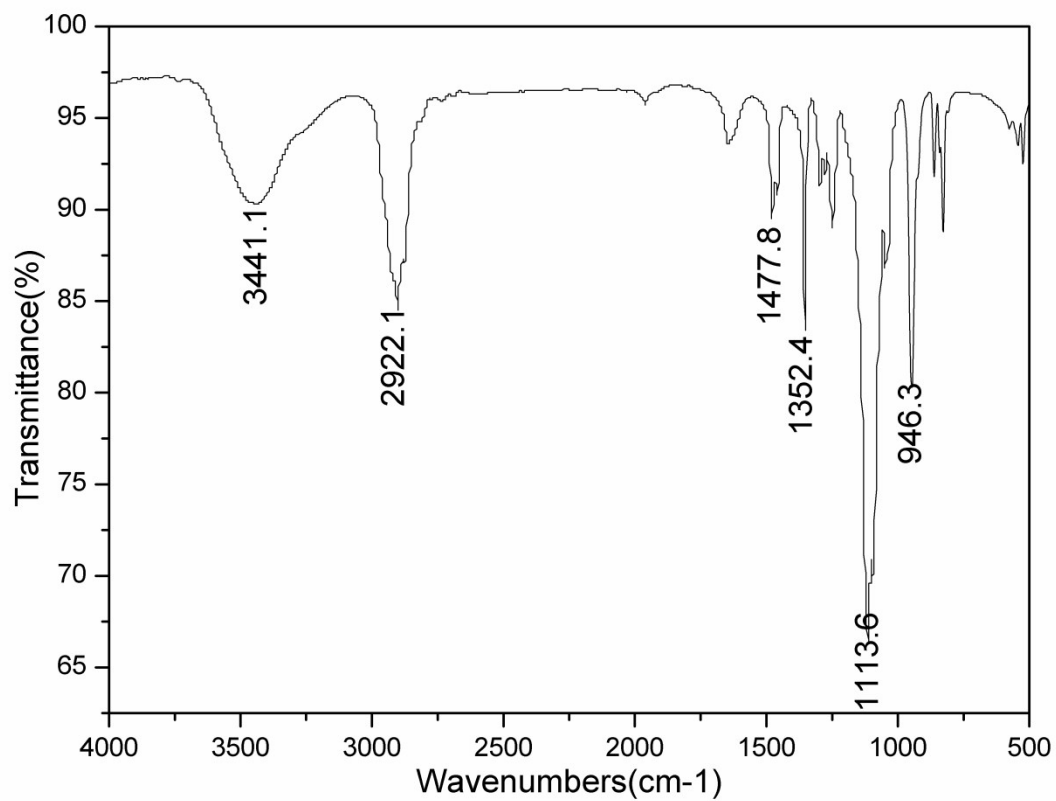


Figure S5 IR spectrum of E

2.2 MS of Lewis acidic ionic liquids

Generic Display Report

Analysis Info
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Acquisition Date 3/12/2014 4:43:08 PM
Operator BDAL@DE
Instrument micrOTOF

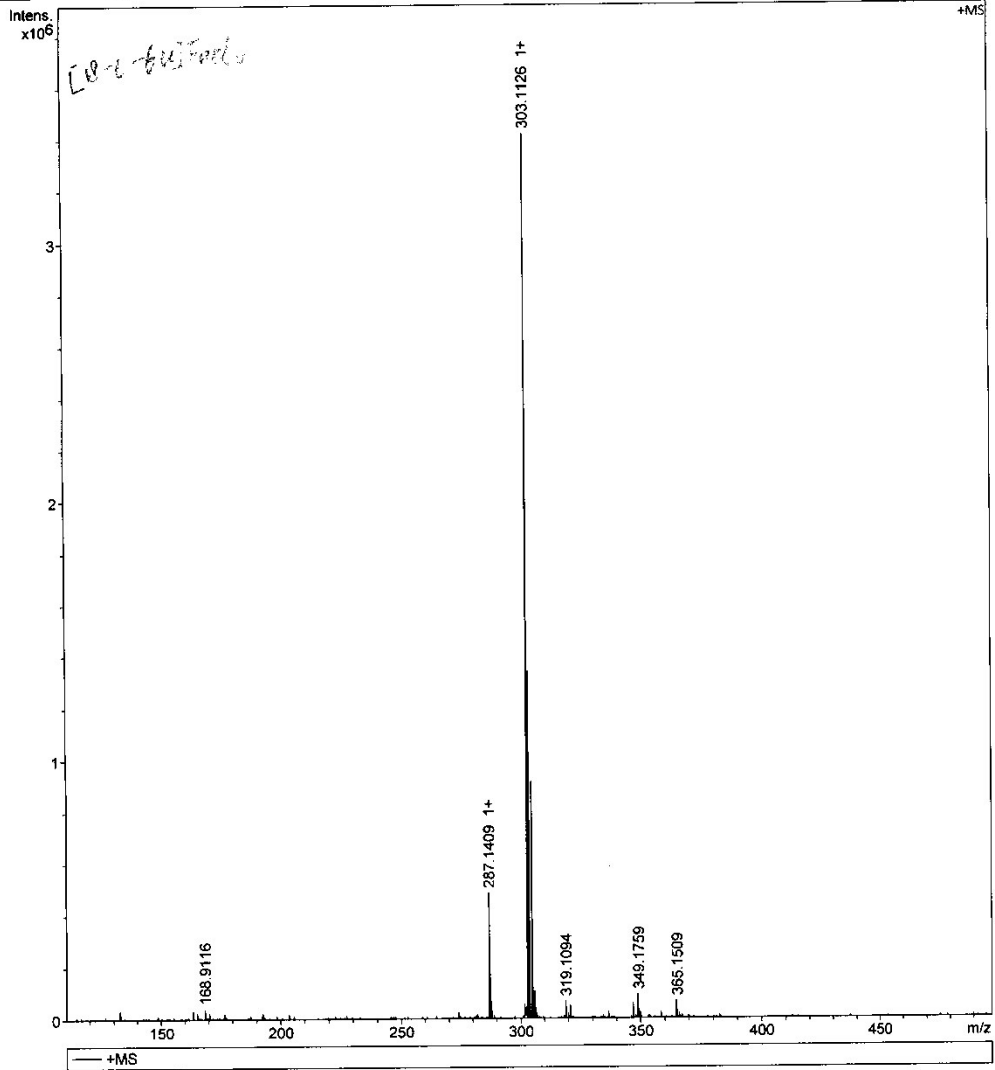


Figure S6 MS of IL catalyst cation [18-C-6K]⁺

Generic Display Report

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Instrument micrOTOF

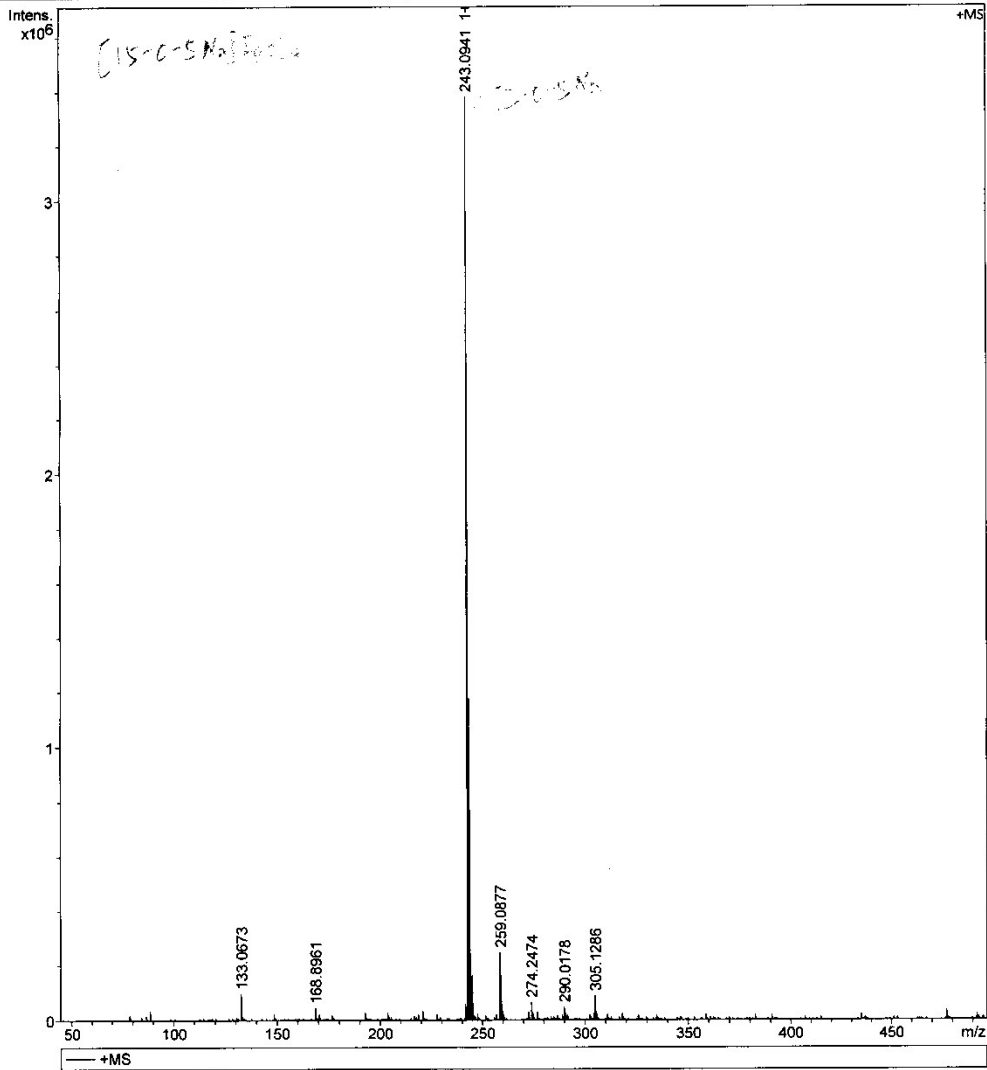


Figure S7 MS of IL catalyst cation [15-C-5Na]⁺

Generic Display Report

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Operator BDAL@DE
Instrument microTOF

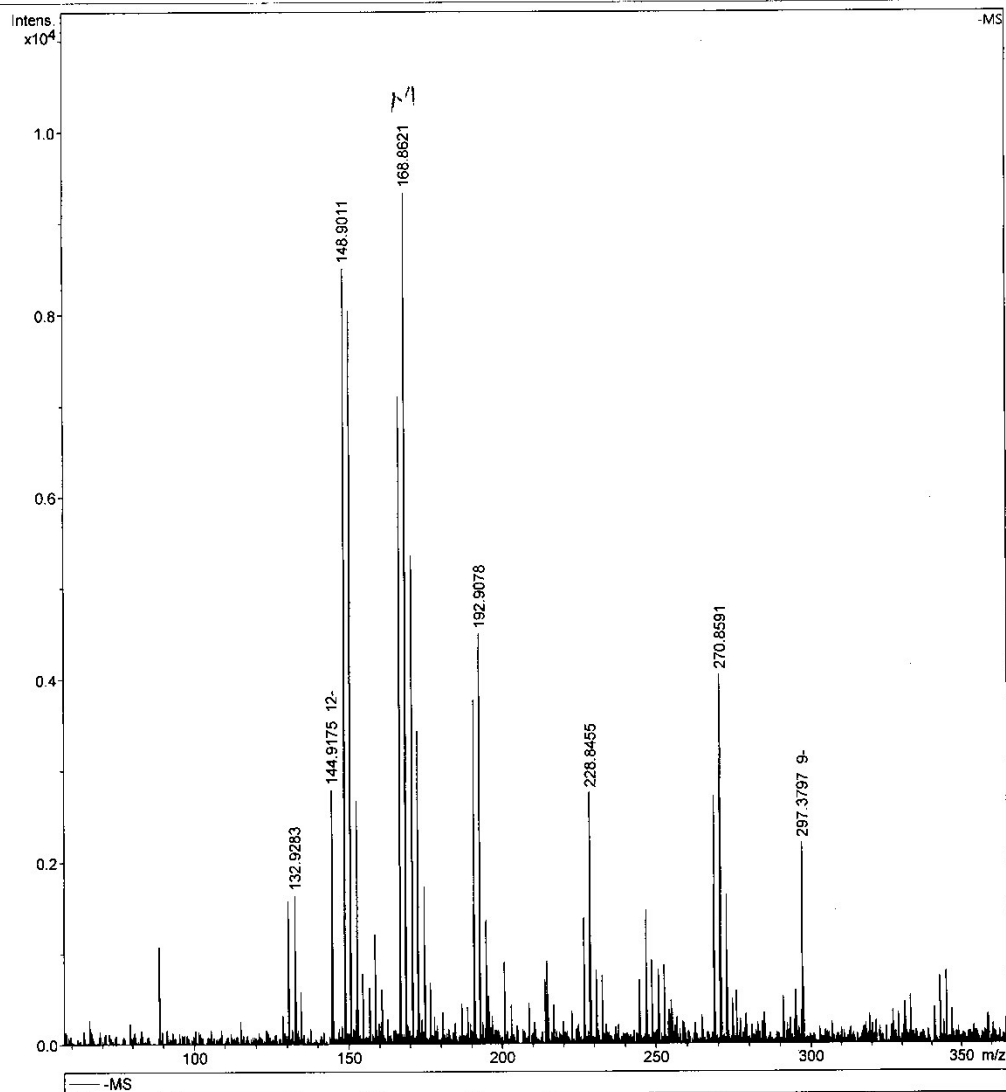


Figure S8 MS of A anion [AlCl₄]⁻

Generic Display Report

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Operator BDAL@DE
Instrument micrOTOF

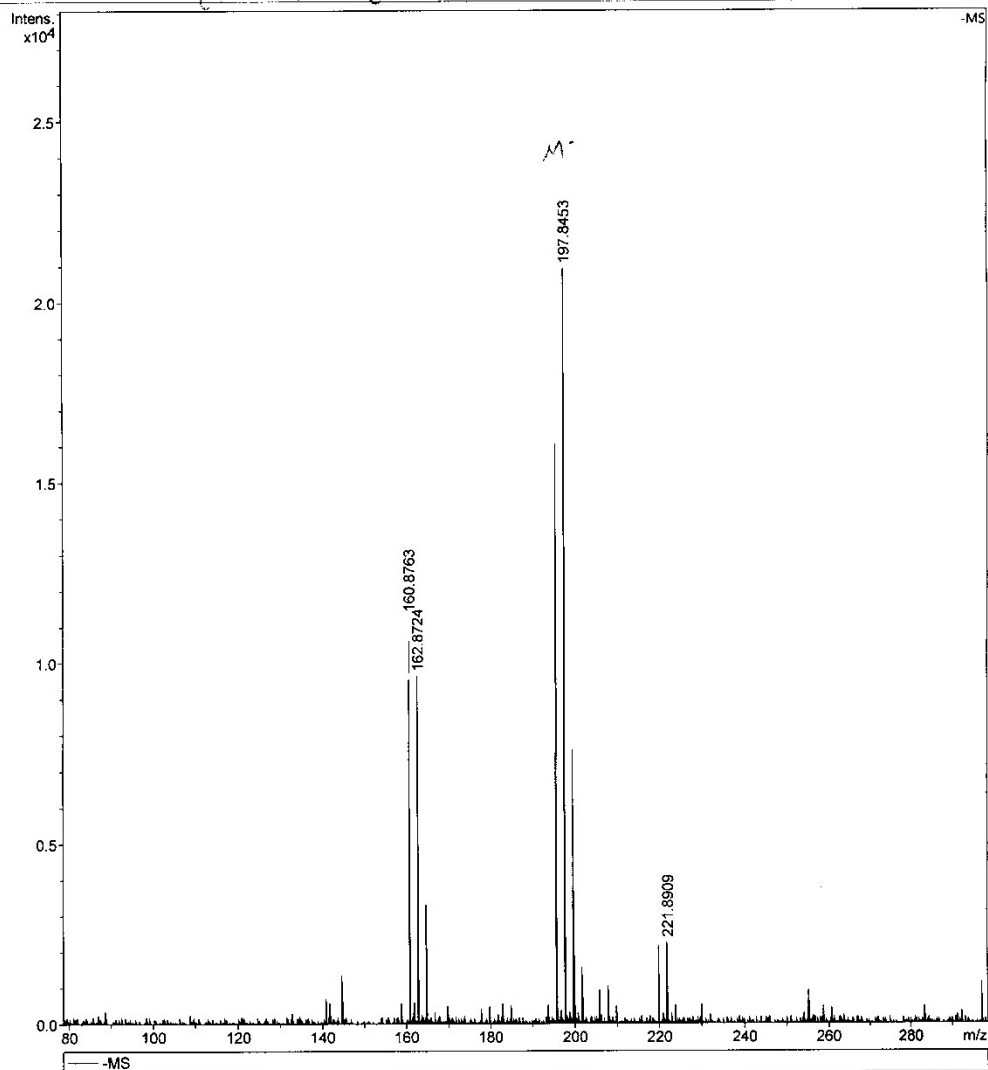


Figure S9 MS of B anion [FeCl₄]⁻

Generic Display Report

Analysis Info

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Acquisition Date 6/26/2014 4:54:12 PM

Operator BDAL@DE
Instrument micrOTOF

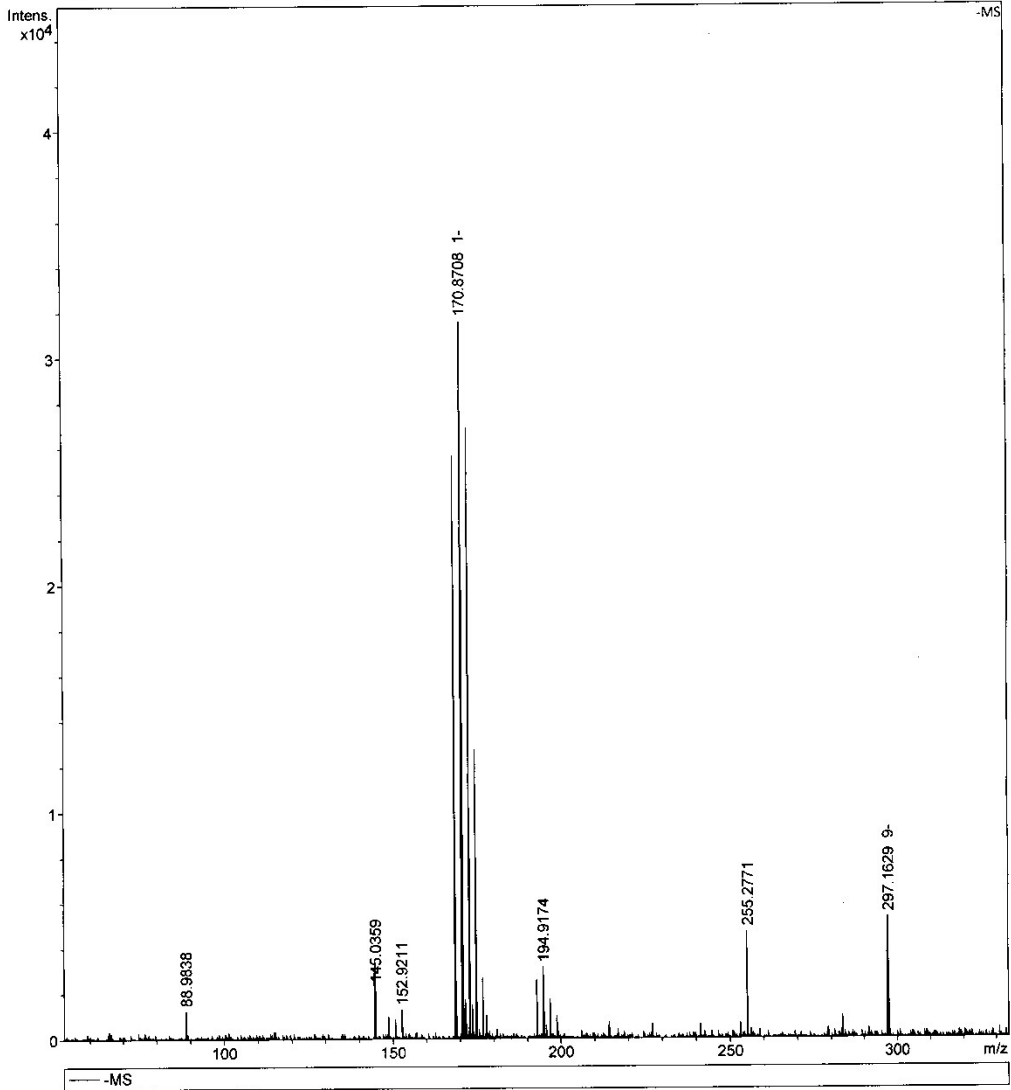


Figure S10 MS of C anion $[\text{ZnCl}_3]^-$

Generic Display Report

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Sample Name DEFAULT	
Comment	

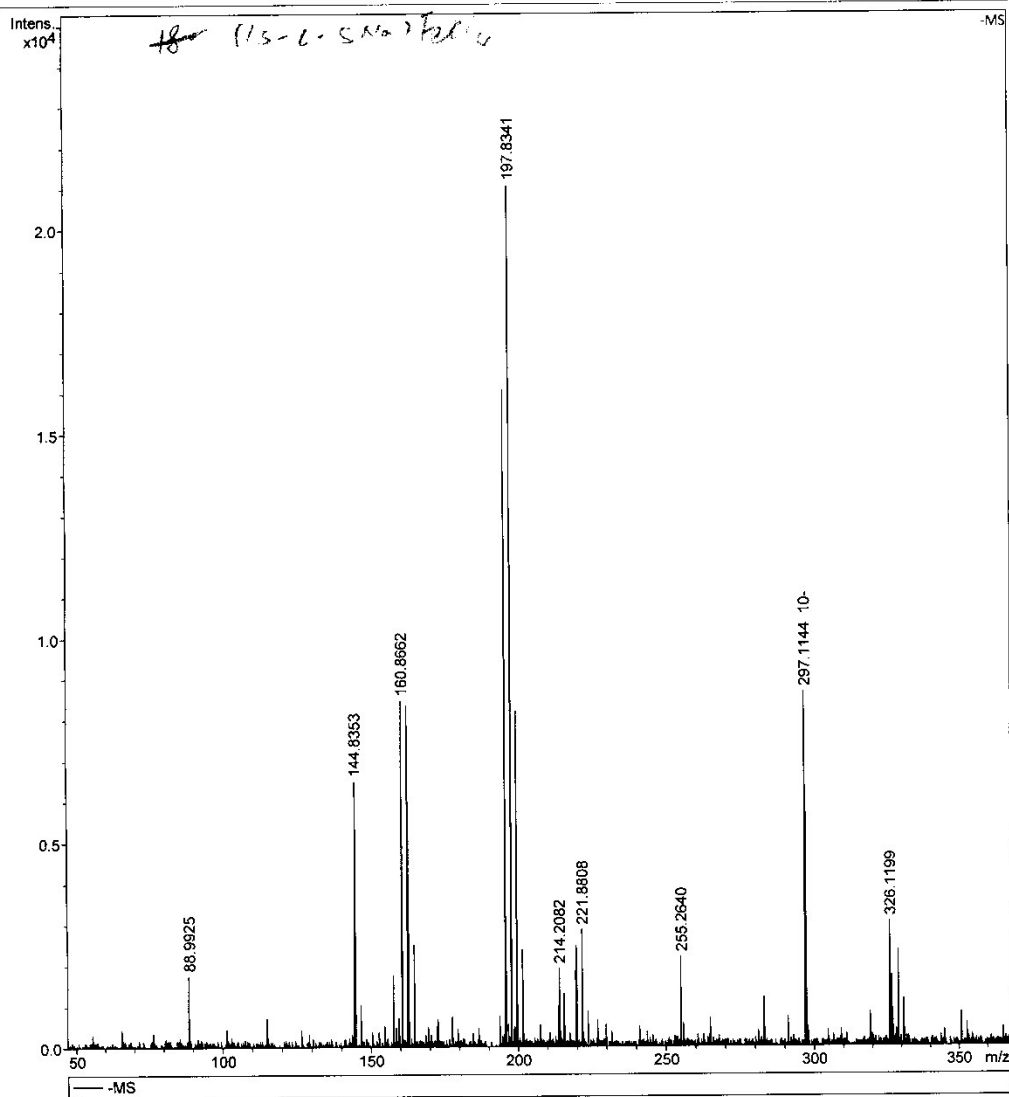


Figure S11 MS of D anion $[\text{FeCl}_4]^-$

Generic Display Report

Analysis Info

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Comment 15-C-SMA-1115

Acquisition Date 6/26/2014 4:57:37 PM

Operator BDAL@DE
Instrument micrOTOF

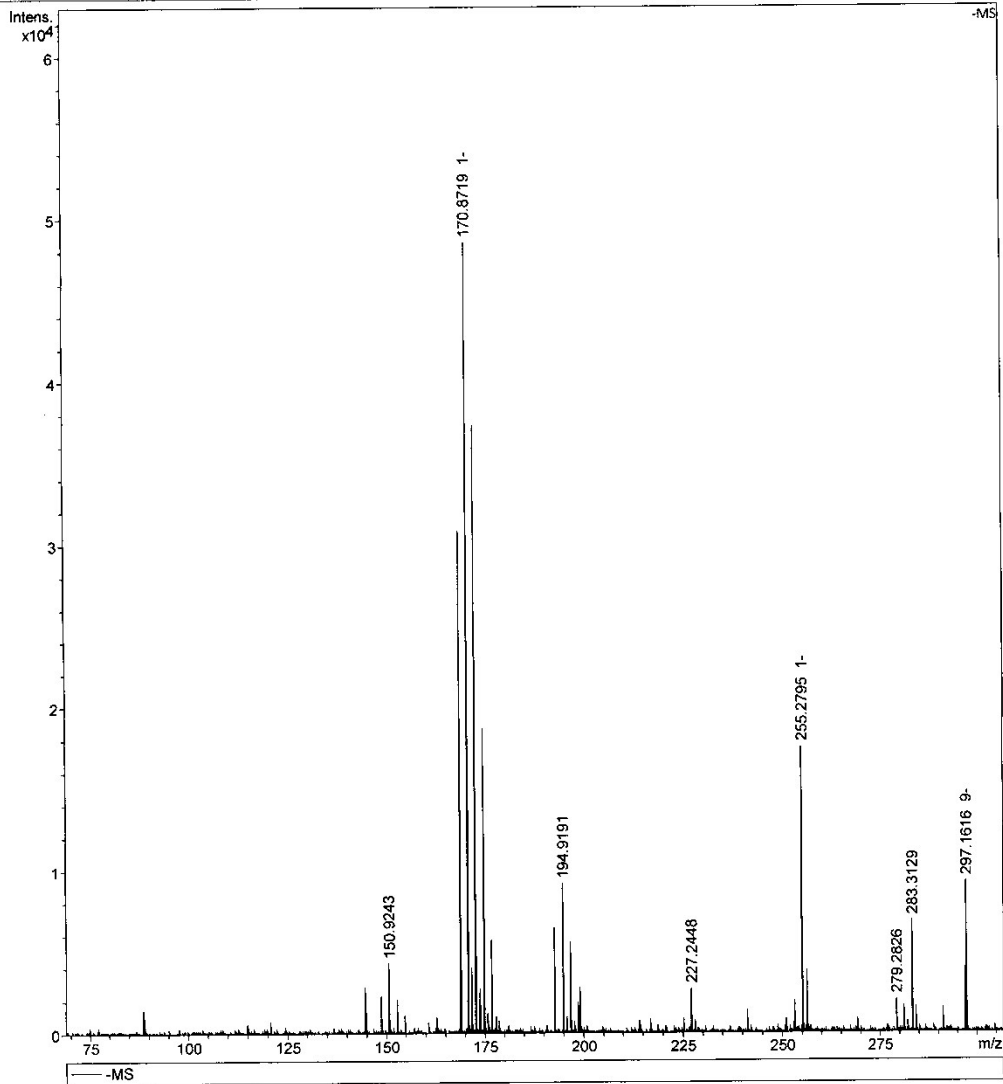


Figure S12 MS of E anion $[\text{ZnCl}_3]^-$

2.3 TGA-DSC of Lewis acidic ionic liquids

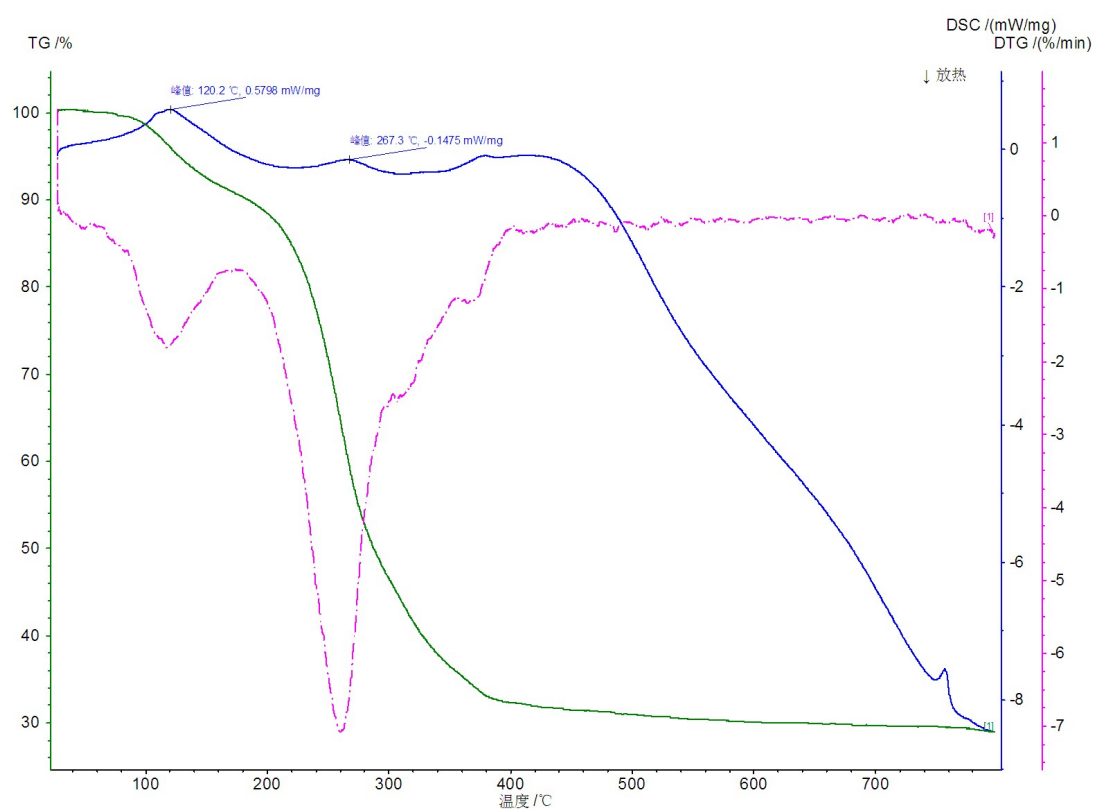


Figure S13 TGA-DSC of A

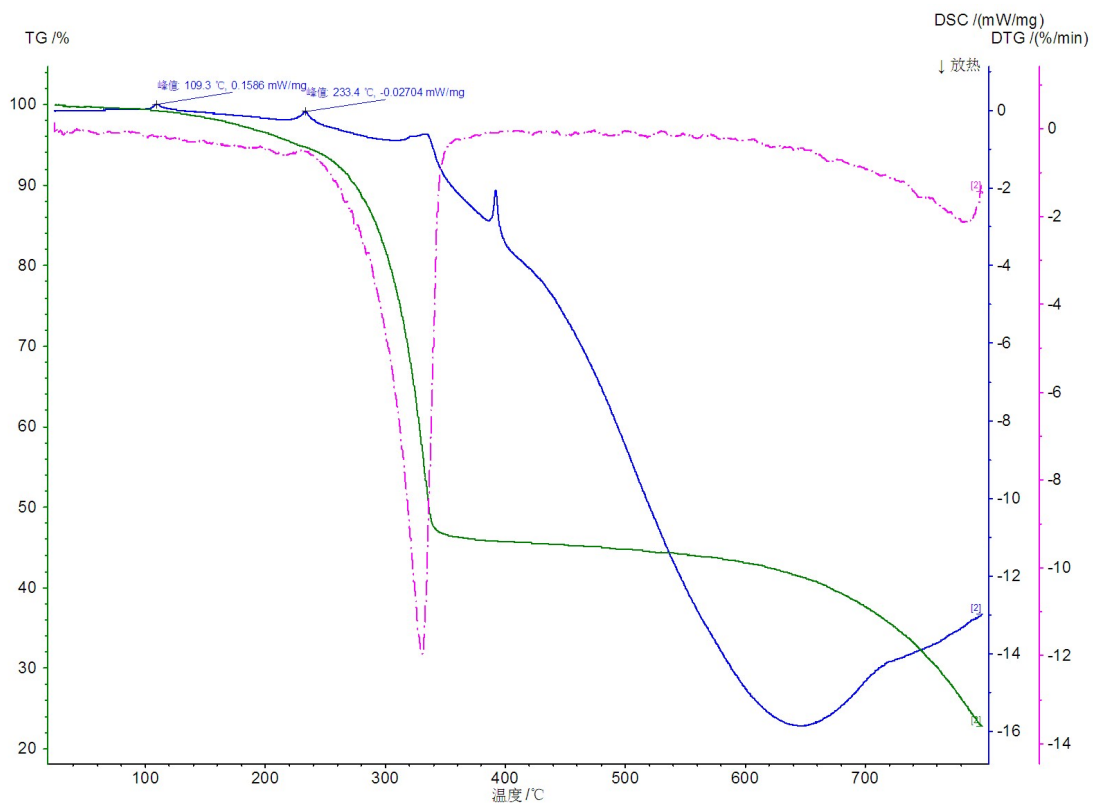


Figure S14 TGA-DSC of B

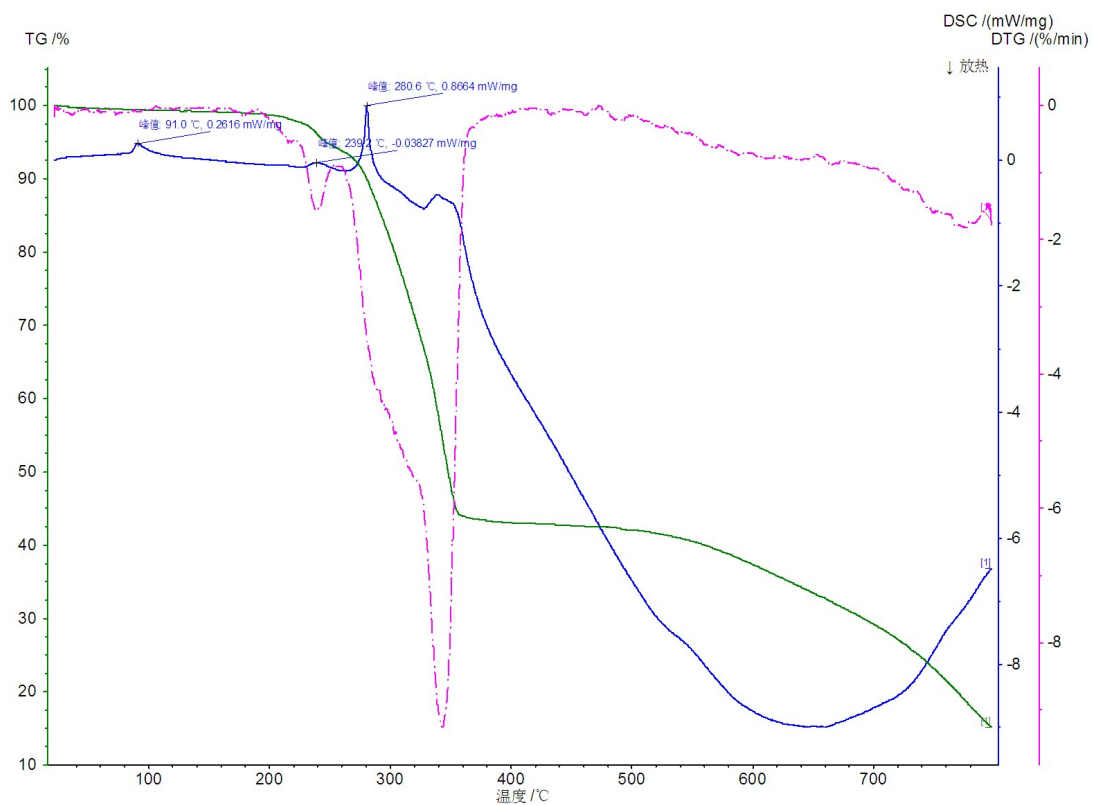


Figure S15 TGA-DSC of C

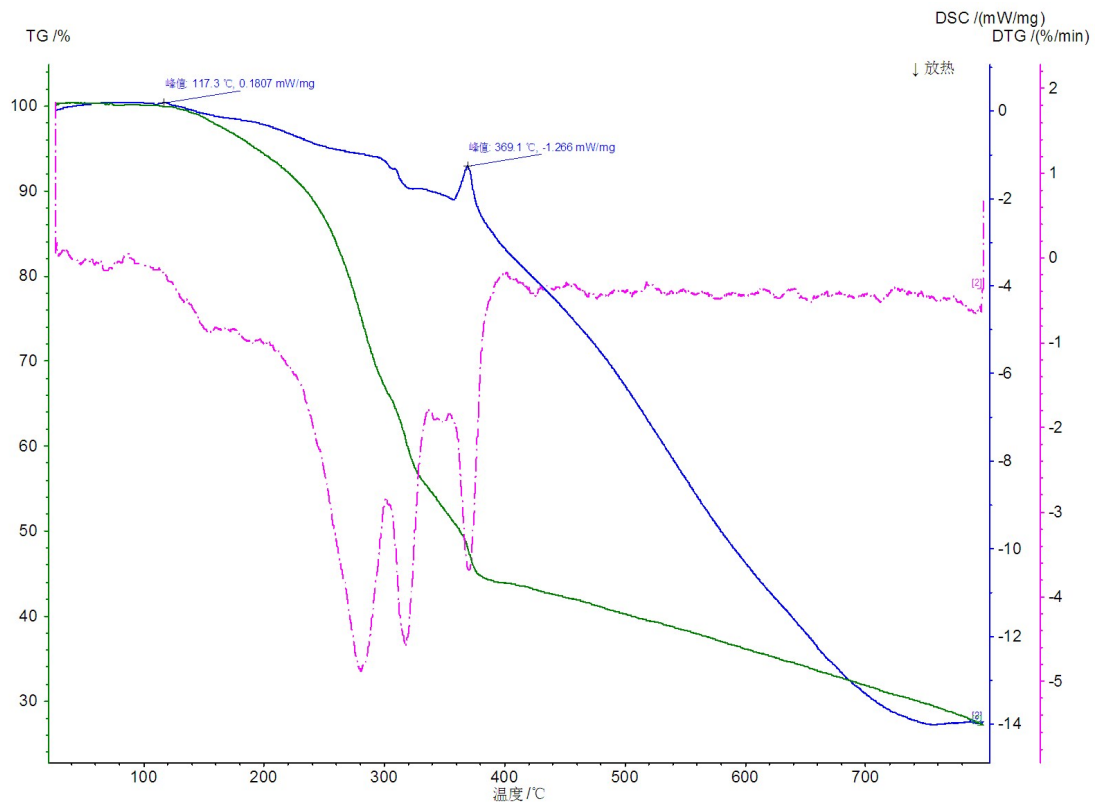


Figure S16 TGA-DSC of D

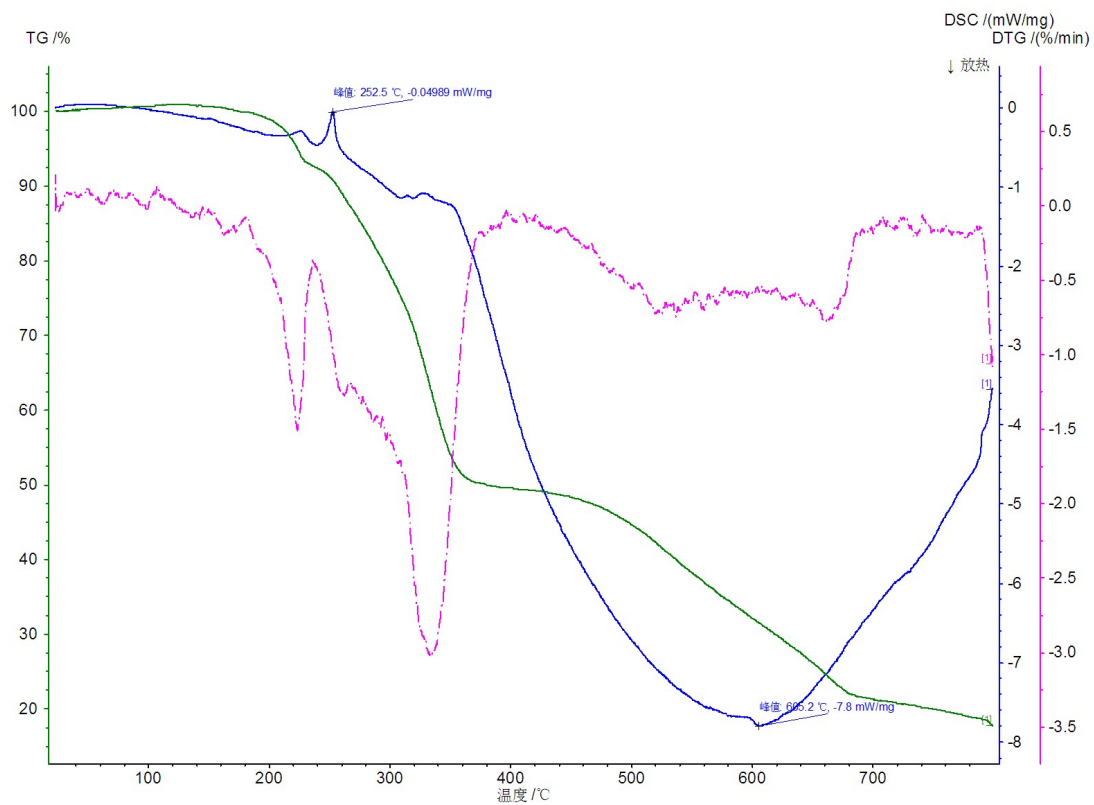
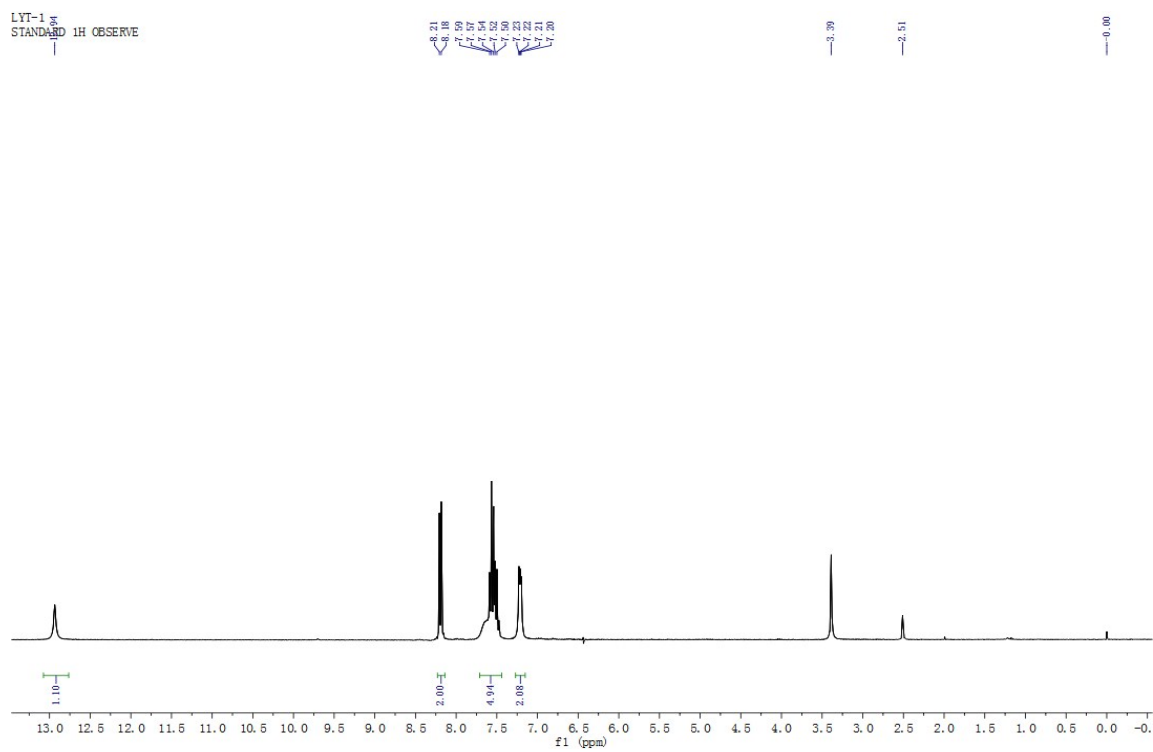
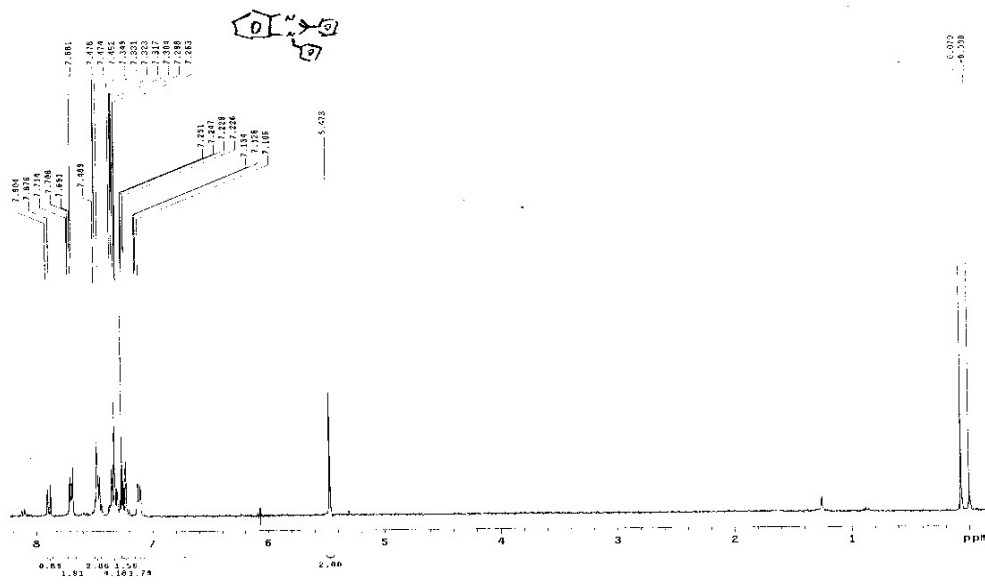


Figure S17 TGA-DSC of E

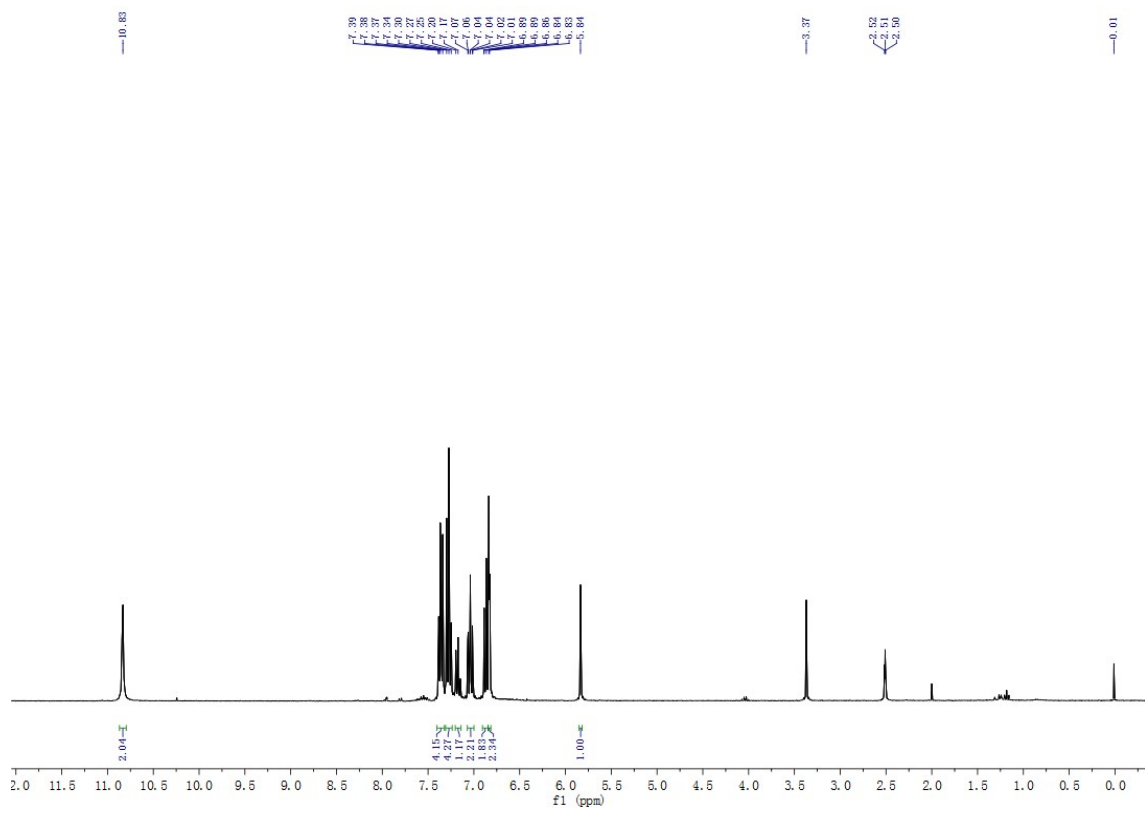
3. ¹H NMR of part compounds



¹H NMR 2-phenyl-1H-benzo[d]imidazole (**3a**)



¹H NMR 1-benzyl-2-phenyl-1H-benzo[d]imidazole (4a)



¹H NMR 3,3'-(phenylmethylene)bis(1H-indole) (6a)