Supporting Information

Direct conversion of chitosan to 5-hydroxymethylfurfural in water

using Brønsted-Lewis acidic ionic liquids as catalysts

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Fig S1. ¹H NMR (400 MHz, D₂O) spectrum of [Hmim][HSO₄]: δ 8.55 (s, 1H, imidazolyl-H), 7.33 (s, 2H, imidazolyl-H), 3.82 (s, 3H, CH₃).

Anal. Calcd. for C₄H₈O₄N₂S: C 26.66; H 4.48; N 15.55; S 17.80; Found: C 26.63; H 4.50; N 15.51; S 17.84.



Fig S2. ¹H NMR (400 MHz, D₂O) spectrum of [Hmim][HSO₄]-NiCl₂: δ 8.48 (s, 1H,

imidazolyl-H), 7.26 (s, 2H, imidazolyl-H), 3.74 (s, 3H, CH₃)



Fig S3. ¹H NMR (400 MHz, D₂O) spectrum of [Hmim][Cl]: δ 8.59 (s, 1H, imidazolyl-H),
7.37 (s, 2H, imidazolyl-H), 3.85 (s, 3H, CH3).

Anal. Calcd. for C₄H₇N₂Cl: C 40.52; H 5.95; N 23.63. Found: C 40.53; H 5.97; N 23.61.



Fig S4. ¹H NMR (400 MHz, D₂O) spectrum of [HSO₃-b-N-(C₂H₅)₃][Cl]: δ 3.17 (q, *J* = 7.2 Hz, 6H,CH₂), 3.10 (t, *J* = 9.2 Hz, 2H,CH₂), 2.85 (t, *J* = 6.8 Hz, 2H,CH₂), 1.74-1.61 (m, 4H,CH₂), 1.15 (t, *J* = 7.2 Hz, 9H,CH₃).

Anal. Calcd. for C₁₀H₂₄NO₃SCI: C 43.86; H 8.83; N 5.12; S 11.71. Found: C 43.84; H 8.82; N 5.15; S 11.69.



Fig S5. ¹H NMR (400 MHz, D₂O) spectrum of [HSO₃-b-N-(C₂H₅)₃][Cl]-ZnCl₂: δ 3.13 (q, *J* = 7.2 Hz, 6H,CH₂), 3.06 (t, *J* = 9.2 Hz, 2H,CH₂), 2.82 (t, *J* = 6.8 Hz, 2H,CH₂), 1.74-1.61 (m, 4H,CH₂), 1.11 (t, *J* = 7.2 Hz, 9H,CH₃).



Fig S6. FT-IR spectra of samples using pyridine as probe. (1) Pure pyridine; (2) Pyridine/[Hmim][HSO₄]- 0.5 FeCl₂; (3) Pyridine/[Hmim][HSO₄]- 0.7 FeCl₂. Pyridine is 1/2 in volume.



Fig S7. FT-IR spectra of samples using acetonitrile as probe. (1) Pure acetonitrile; (2) Acetonitrile/[Hmim][HSO₄]- 0.5 FeCl₂; (3) Acetonitrile/[Hmim][HSO₄]- 0.7 FeCl₂. Acetonitrile is 1/2 in volume.



Fig S8. TGA curves of Brønsted-Lewis acidic ionic liquid. (1) [Hmim][HSO₄]; (2) [Hmim][HSO₄]- 0.5 FeCl₂; (3) [Hmim][HSO₄]- 0.7 FeCl₂. (NOTE: The position of the [Hmim][HSO₄]- 0.7 FeCl₂ isotherm is shifted.)