Electronic Supplementary Information (ESI)

Selective conversion of chitin to levulinic acid catalyzed by ionic liquid: distinctive effect of *N*-acetyl groups

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1. Characterisation of ionic liquids

1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ([C_3SO_3Hmim]HSO_4): δ_H(400 MHz; D_2O) 8.26 (1 H, s, N-CH-N), 7.05 (1 H, s, CH-N), 6.99 (1 H, s, CH-N), 3.89 (2 H, t, *J* 7, N-CH_2), 3.43 (3 H, s, N-CH_3), 2.46 (2 H, t, *J* 7, CH_2-S), 1.80-1.88 (2 H, m, CH_2); δ_C(101 MHz; D_2O) 135.6, 123.2, 121.7, 47.2, 46.7, 35.2, 24.5.

1-methyl-3-(3-sulfopropyl)imidazolium methanesulfonate ([C_3SO_3Hmim]CH_3SO_3): δ_H(500 MHz; D_2O) 8.75 (1 H, s, N-CH-N), 7.52 (1 H, s, CH-N), 7.44 (1 H, s, CH-N), 4.36 (2 H, t, *J* 7, N-CH_2), 3.89 (3 H, s, N-CH_3), 2.92 (2 H, t, *J* 7, CH_2-S), 2.80 (3 H, s, CH_3-S), 2.28-2.34 (2 H, m, CH_2); δ_C(125 MHz; D_2O) 135.6, 123.3, 121.7, 47.2, 46.8, 38.1, 35.3, 24.6.

1-methyl-3-(3-sulfopropyl)imidazolium phenylsulfonate ([C_3SO_3Hmim]$PhSO_3$): δ_H(400 MHz; D_2O) 8.31 (1 H, s, N-CH-N), 7.48 (2 H, d, *J* 7, 2CH), 7.18-7.26 (3 H, m, 3CH), 7.11 (1 H, s, CH-N), 7.04 (1 H, s, CH-N), 3.97 (2 H, t, *J* 7, N-CH_2), 3.51 (3 H, s, N-CH_3), 2.60 (2 H, t, *J* 7, CH_2-S), 1.93-2.00 (2 H, m, CH_2); δ_C(101 MHz; D_2O) 142.5, 135.8, 131.4, 128.9, 125.2, 123.6, 122.0, 47.6, 47.2, 35.7, 25.0.

1-methyl-3-(3-sulfopropyl)imidazolium 1-naphthalenesulfonate ([C_3SO_3Hmim]1-NS): δ_H(400 MHz; D_2O) 8.25 (1 H, d, *J* 8, CH), 7.83 (1 H, s, N-CH-N), 7.71 (1 H, d, *J* 7, CH), 7.41 (1 H, d, *J* 8, CH), 7.35 (1 H, d, *J* 8, CH), 7.24 (1 H, t, *J* 8, CH), 7.09 (1 H, t, *J* 7, CH), 7.04 (1 H, t, *J* 8 Hz, CH), 6.63 (1 H, s, CH-N), 6.53 (1 H, s, CH-N), 3.58 (2 H, t, *J* 7, N-CH_2), 3.13 (3 H, s, N-CH_3), 2.44 (2 H, t, *J* 7, CH_2-S), 1.72-1.75 (2 H, m, CH_2); δ_C(101 MHz; D_2O) 138.2, 135.1, 133.5, 132.0, 128.5, 127.7, 127.4, 126.5, 125.7, 125.0, 124.4, 123.2, 123.1, 121.5, 121.4, 47.3, 47.1, 35.3, 24.8.

1-methyl-3-(3-sulfopropyl)imidazolium dihydrogen phosphate ([C_3SO_3Hmim]H_2PO_4): δ_H(500 MHz; D_2O) 8.78 (1 H, s, N-CH-N), 7.55 (1 H, s, CH-N), 7.48 (1 H, s, CH-N), 4.40 (2 H, t, *J* 7, N-CH_2), 3.93 (3 H, s, N-CH_3), 2.96 (2 H, t, *J* 8, CH_2-S), 2.32-2.38 (2 H, m, CH_2); δ_C(125 MHz; D_2O) 135.7, 123.5, 121.9, 47.5, 47.1, 35.5, 24.8.

1-methyl-3-(3-sulfopropyl)imidazolium chloride ([C_3SO_3Hmim]Cl): δ_H(500 MHz; D_2O) 8.79 (1 H, s, N-CH-N), 7.56 (1 H, s, CH-N), 7.49 (1 H, s, CH-N), 4.40 (2 H, t, *J* 7, N-CH_2), 3.94 (3 H, s, N-CH_3), 2.96 (2 H, t, *J* 7, CH_2-S), 2.33-2.39 (2 H, m, CH_2); δ_C(101 MHz; D_2O) 136.0, 123.6, 122.4, 47.6, 47.2, 35.7, 25.0.

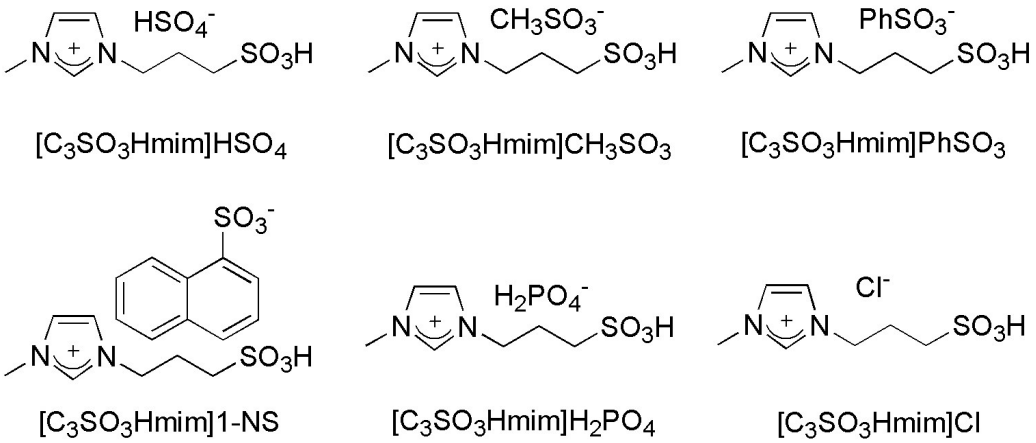

Fig. S1 Chemical structures of acidic ionic liquids.

2. Characterisation of reaction mixture and solid residues

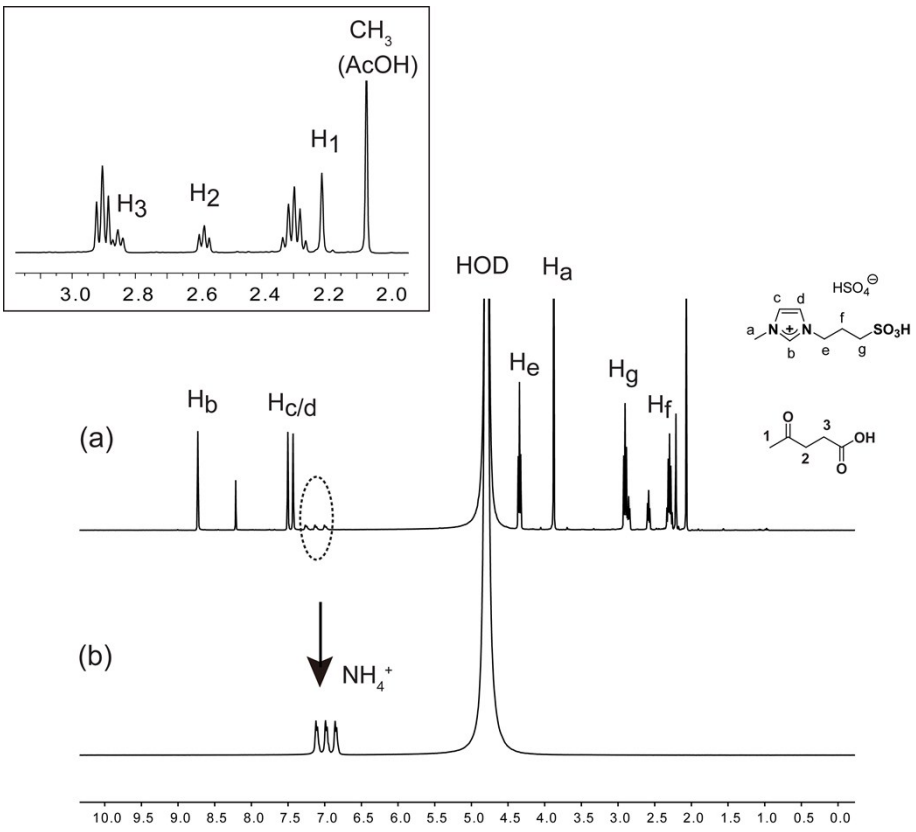

Fig. S2 ^{1}H NMR spectra (in D_2O) of (a) reaction mixture (Conditions: 500 mg chitin, 1.000 g $[C_3SO_3Hmim]HSO_4$, 6.000 g H_2O, 180 ℃, 5 h) and (b) standard NH_4HSO_4.

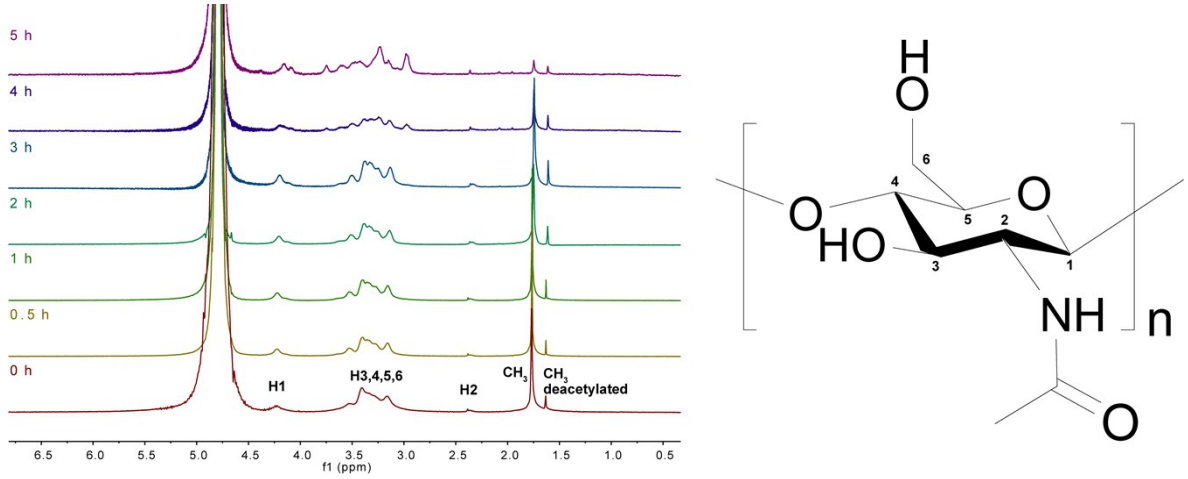

Fig. S3 ^{1}H NMR spectra of solid residues dissolved in 8 wt% of NaOH/4 wt% of urea (D_2O, -30℃).[1] Conditions: 250 mg chitin, 1.000 g $[C_3SO_3Hmim]HSO_4$, 6.000 g H_2O, 180 ℃.

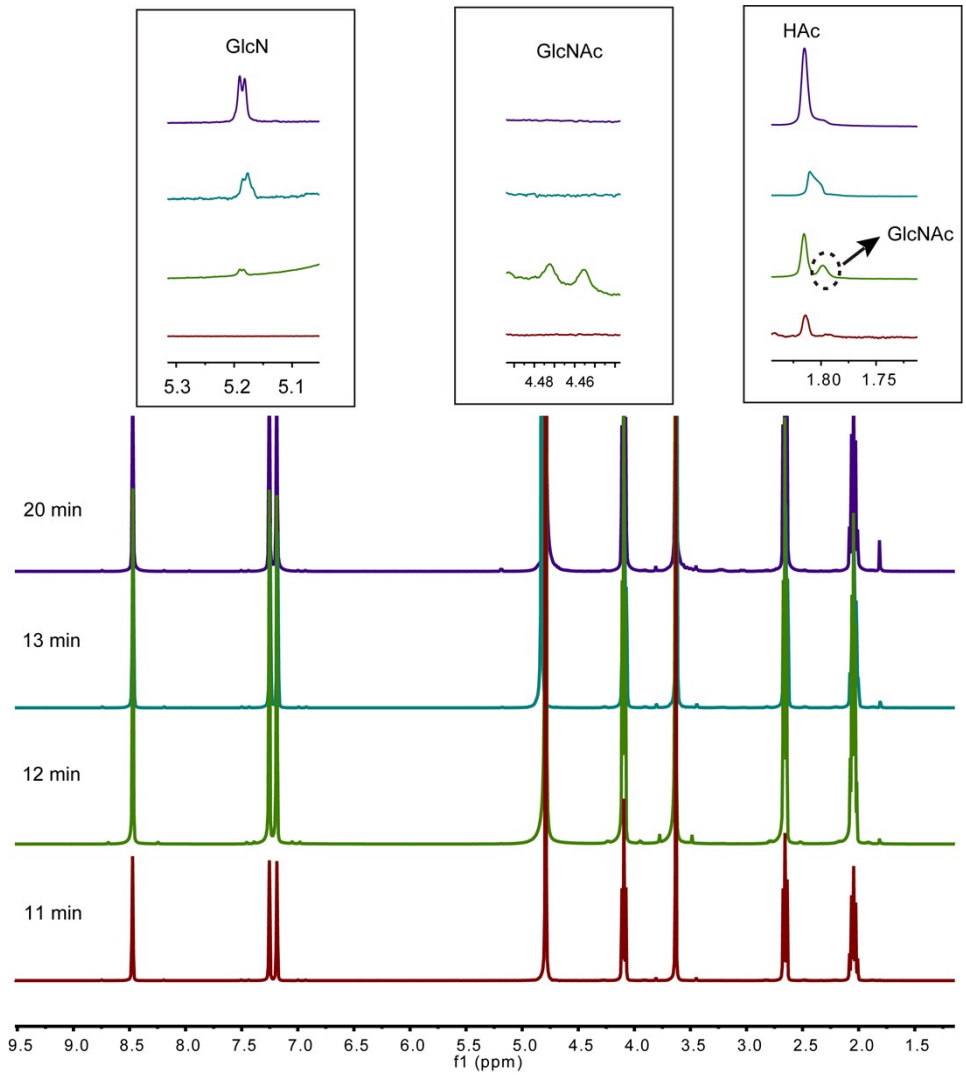

Fig. S4 ^{1}H NMR spectra of the reaction mixture in D_2O. Conditions: 250 mg chitin, 1.000 g $[C_3SO_3Hmim]HSO_4$, 6.000 g H_2O, 180 ℃.

3. Characterisation of levulinic acid product

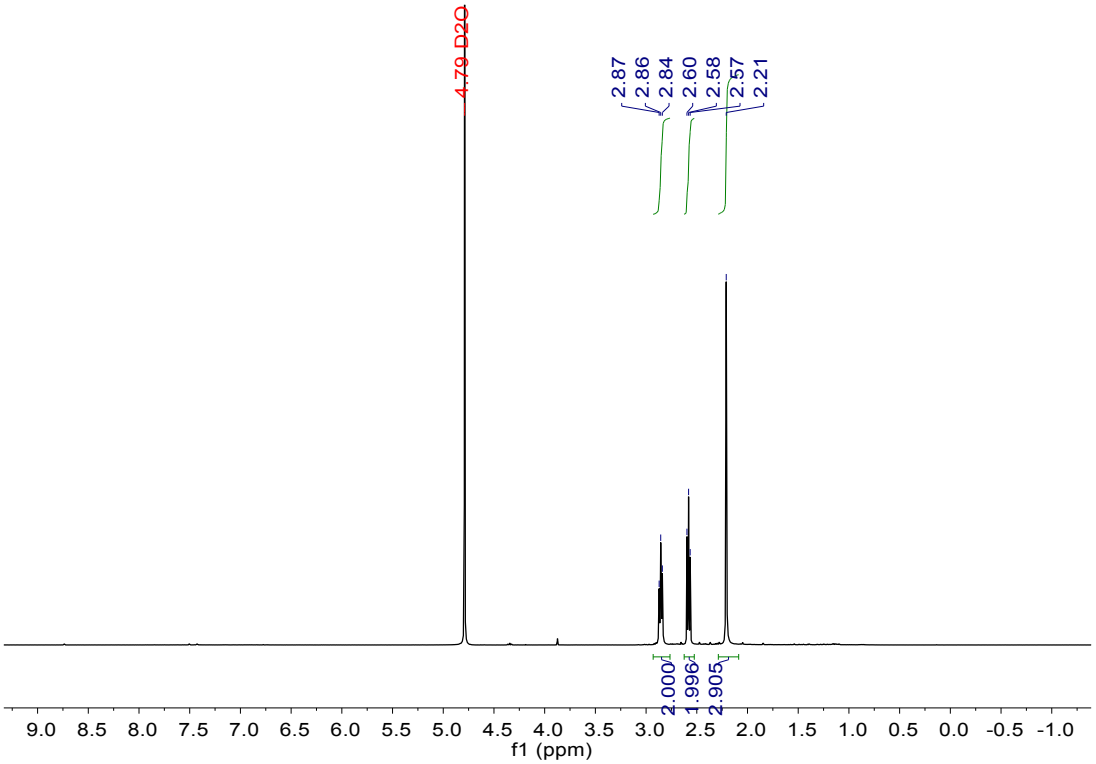

Fig. S5 ^{1}H NMR spectrum of isolated levulinic acid (D_2O).

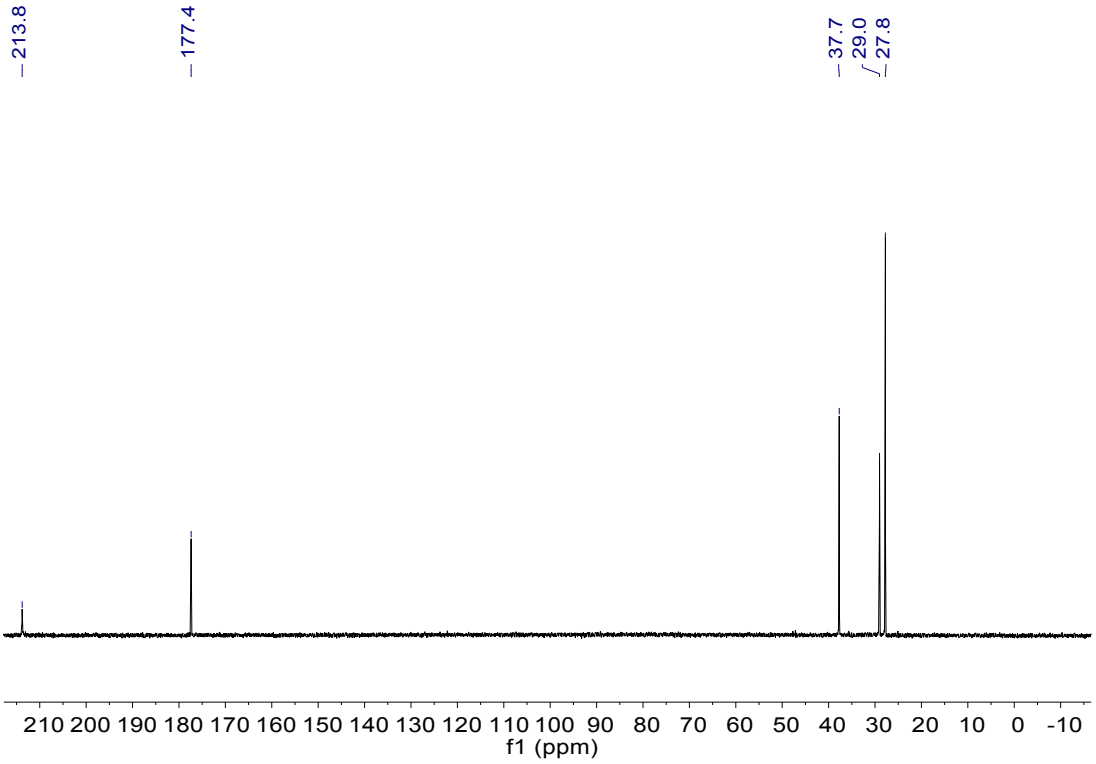

Fig. S6 ^{13}C NMR spectrum of isolated levulinic acid (D_2O).

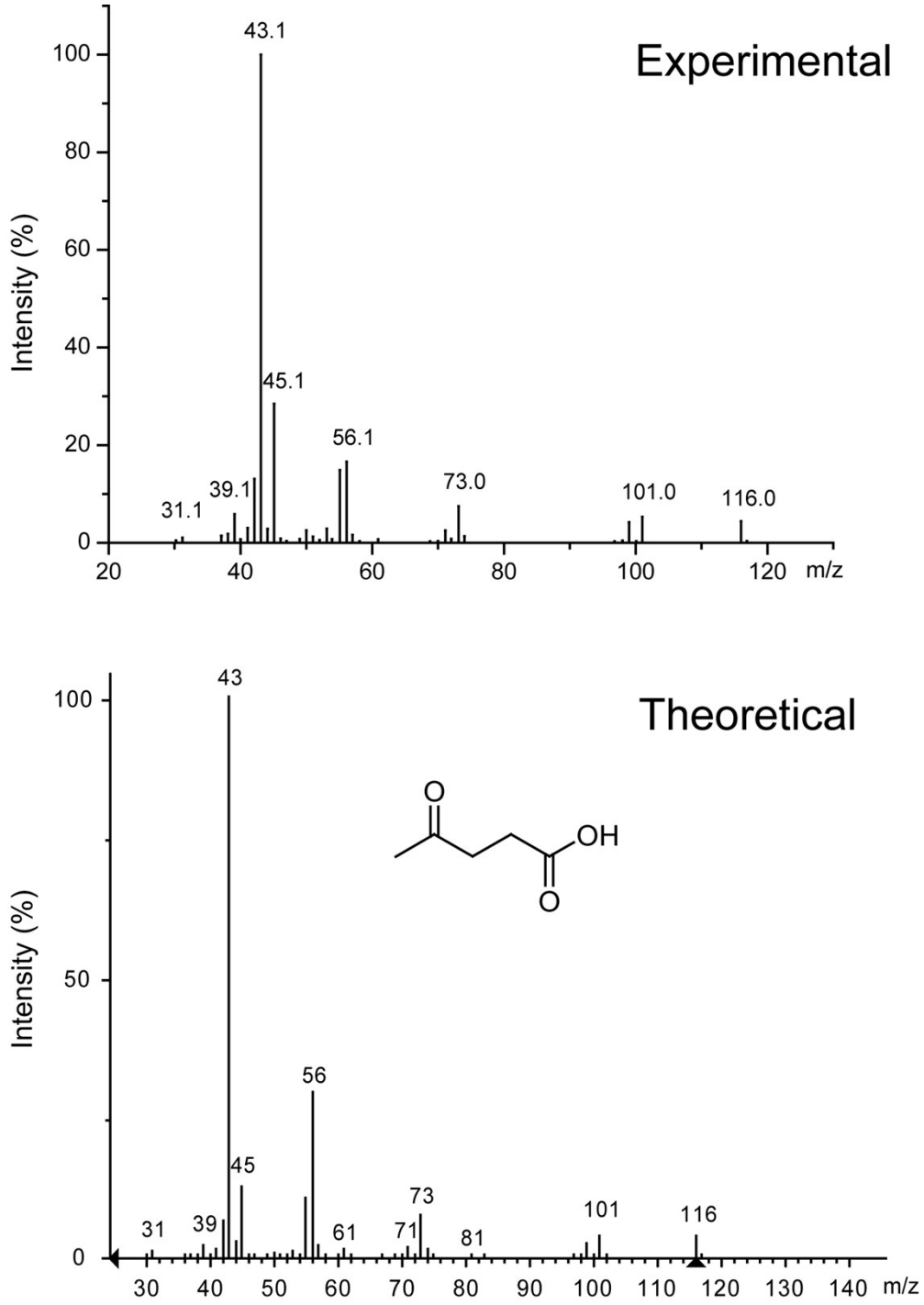

Fig. S7 Experimentally detected and theoretical mass spectra of levulinic acid.

References:

(1) (a) Fang, Y.; Zhang, R.; Duan, B.; Liu, M.; Lu, A.; Zhang, L. Recyclable universal solvents for chitin to chitosan with various degrees of acetylation and construction of robust hydrogels. *ACS Sustainable Chemistry & Engineering* **2017**, *5*, 2725-2733. (b) Gong, P.; Wang, J.; Liu, B.; Ru, G.; Feng, J. Dissolution of chitin in aqueous KOH. *Cellulose* **2016**, *23*, 1705-1711.