

**Green synthesis of benzonitrile using ionic liquid with multiple roles
as the recycling agent**

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Calculation of the H_0 value of the ILs

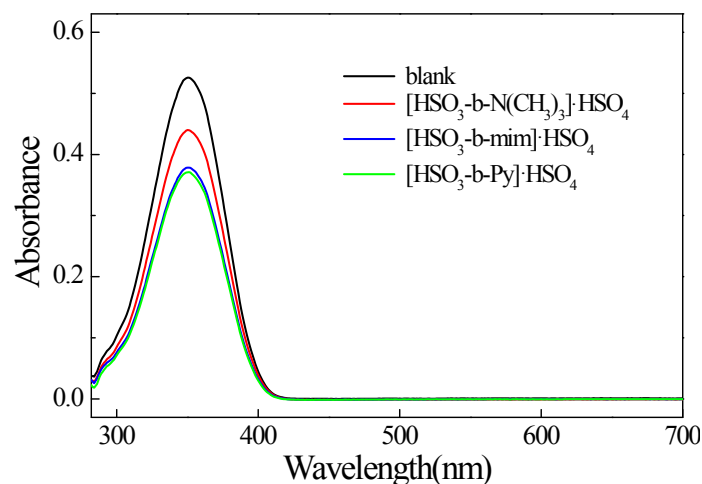


Fig. S1 Absorbance spectra of 4-nitroaniline in dichloromethane after addition of ionic liquids

With the increasing of acid strength, the absorbance of the unprotonated basic indicator decreased. H_0 of the ILs could be calculated based on the ratio of the absorbance of the unprotonated indicator to that of the protonated indicator. The calculation equation of H_0 could be expressed as Equation (1). Where, $[I]$ and $[IH^+]$ are separately the molar concentration of the unprotonated and the protonated form of an indicator in the ILs. In this work, the H_0 value of the ILs was determined with the same concentration of 4-nitroaniline (5mg/L) and ILs (5mmol/L) in CH_2Cl_2 .

$$H_0 = pK(I)_{aq} + \log\left(\frac{[I]}{[IH^+]}\right) \quad (1)$$

Figure S2-S5 1H and ^{13}C NMR spectra of the fresh and recovered $[HSO_3\text{-b-Py}]\cdot HSO_4$

Fresh:

1H NMR (400MHz; D_2O) 1.55(t, 2H), 1.92(t, 2H), 2.71(m, 2H), 4.41(t, 2H), 7.83(d, 2H), 8.30(s, 1H), 8.61(d, 2H)

^{13}C NMR (300MHz, D_2O) 20.8, 29.2, 49.9, 61.0, 128.2, 144.1, 145.6

Recovered:

^1H NMR (400MHz; D_2O) 1.66(m, 2H), 2.02(m, 2H), 2.82(m, 2H), 4.51(t, 2H), 7.93(t, 2H), 8.40(t, 1H), 8.72(d, 2H)

^{13}C NMR (300MHz, D_2O) 20.8, 29.3, 49.9, 61.1, 128.3, 144.2, 145.6

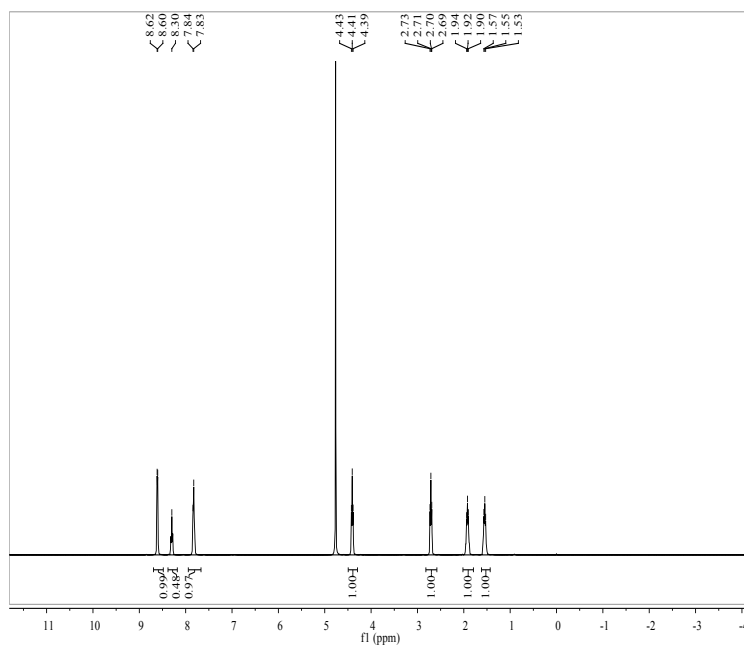


Fig. S2 ^1H NMR spectra of the fresh $[\text{HSO}_3\text{-b-Py}]\cdot\text{HSO}_4$ (D_2O)

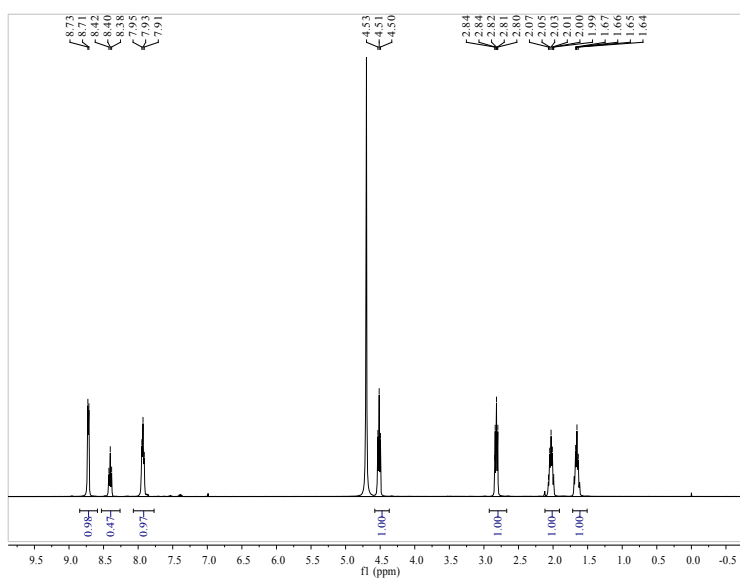


Fig. S3 ^1H NMR spectra of the recovered $[\text{HSO}_3\text{-b-Py}]\cdot\text{HSO}_4$ (D_2O)

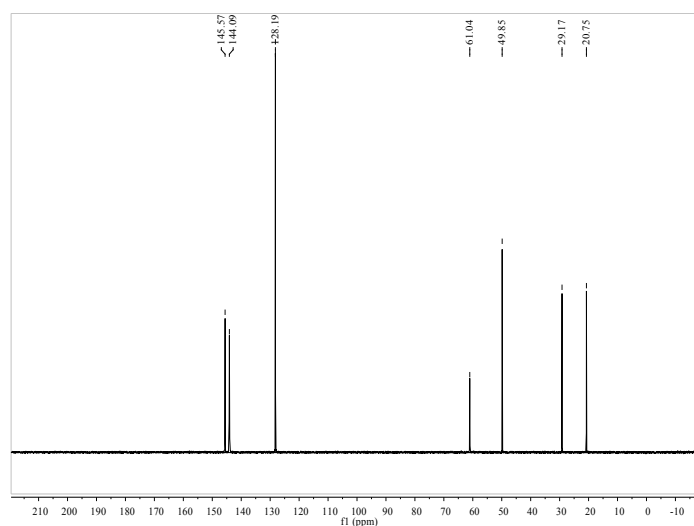


Fig. S4 ^{13}C NMR spectra of the fresh $[\text{HSO}_3\text{-b-Py}]\cdot\text{HSO}_4$ (D_2O)

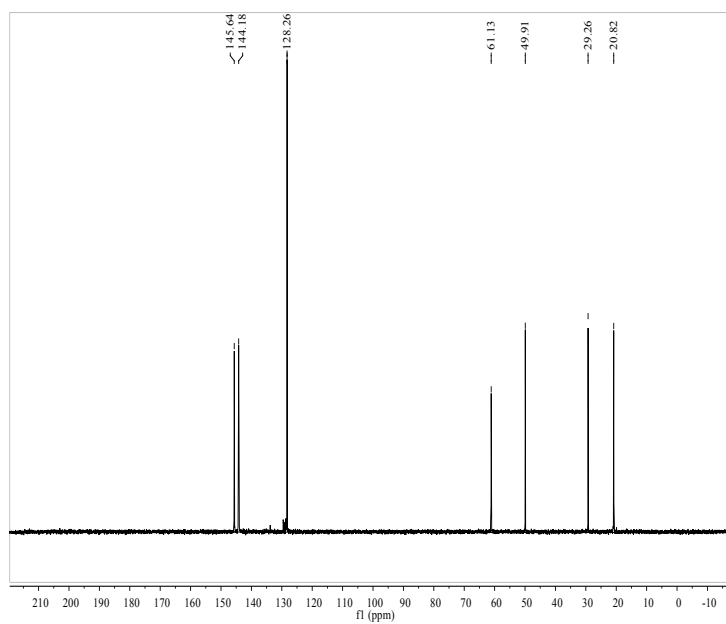


Fig. S5 ^{13}C NMR spectra of the recovered $[\text{HSO}_3\text{-b-Py}]\cdot\text{HSO}_4$ (D_2O)

Fig. S6-S9 ^1H and ^{13}C NMR spectra of the $(\text{NH}_2\text{OH})_2\cdot[\text{HSO}_3\text{-b-Py}]\cdot\text{HSO}_4$ obtained from the fresh and recovered $[\text{HSO}_3\text{-b-Py}]\cdot\text{HSO}_4$

Fresh:

^1H NMR (400MHz; D_2O) 1.75(m, 2H), 2.12(m, 2H), 2.91(t, 2H), 4.61(t, 2H), 8.02(t, 2H), 8.50(t, 1H), 8.81(d, 2H)

^{13}C NMR (300MHz, D_2O) 20.8, 29.2, 49.9, 61.0, 128.2, 144.1, 145.6

Recovered:

^1H NMR (400MHz; D_2O) 1.76(m, 2H), 2.13(t, 2H), 2.91(t, 2H), 4.61(t, 2H), 8.03(d, 2H), 8.50(t, 1H), 8.81(d, 2H)

^{13}C NMR (300 MHz, D_2O) 20.8, 29.3, 49.9, 61.2, 128.3, 144.2, 145.7

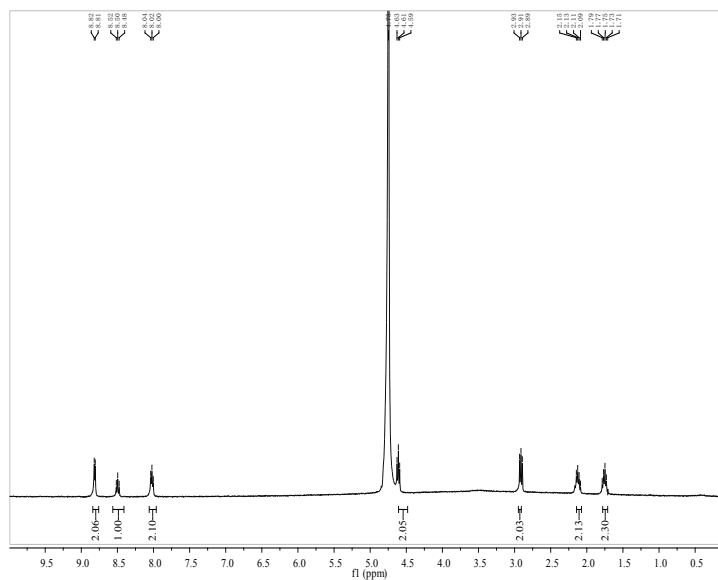


Fig. S6 ^1H NMR spectra of the $(\text{NH}_2\text{OH})_2 \cdot [\text{HSO}_3\text{-b-Py}] \cdot \text{HSO}_4$ obtained from the fresh $[\text{HSO}_3\text{-b-Py}] \cdot \text{HSO}_4$ (D_2O)

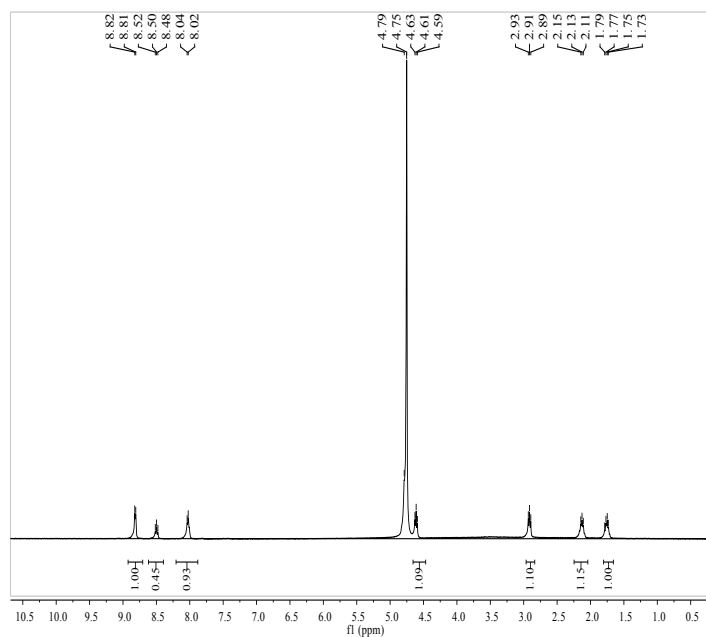


Fig. S7 ^1H NMR spectra of the $(\text{NH}_2\text{OH})_2 \cdot [\text{HSO}_3\text{-b-Py}] \cdot \text{HSO}_4$ obtained from the recovered $[\text{HSO}_3\text{-b-Py}] \cdot \text{HSO}_4$ (D_2O)

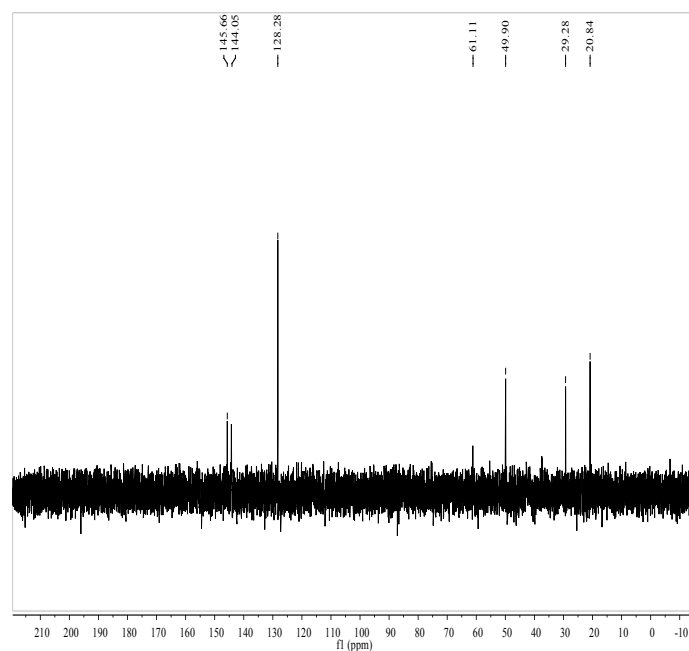


Fig. S8 ^{13}C NMR spectra of the $(\text{NH}_2\text{OH})_2 \cdot [\text{HSO}_3\text{-b-Py}] \cdot \text{HSO}_4$ obtained from the fresh $[\text{HSO}_3\text{-b-Py}] \cdot \text{HSO}_4$ (D_2O)

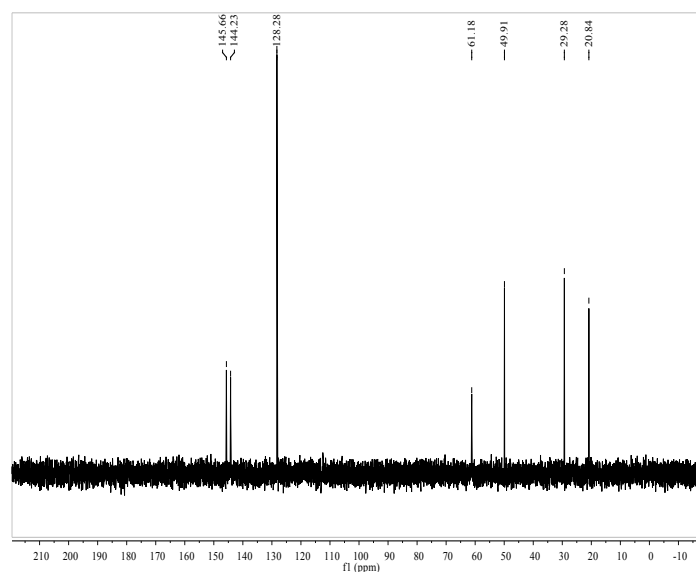


Fig. S9 ^{13}C NMR spectra of the $(\text{NH}_2\text{OH})_2 \cdot [\text{HSO}_3\text{-b-Py}] \cdot \text{HSO}_4$ obtained from the recovered $[\text{HSO}_3\text{-b-Py}] \cdot \text{HSO}_4$ (D_2O)

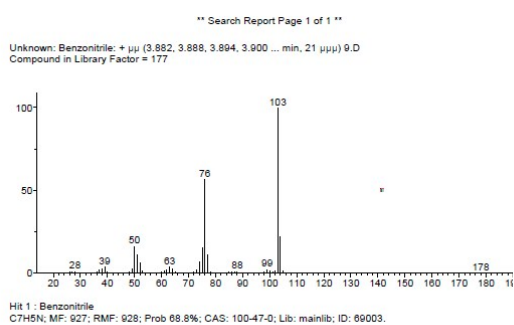
EI-MS and FT-IR of the selected nitriles

Benzonitrile, 4-nitrobenzonitrile, butyronitrile and pentanenitrile were prepared under optimal reaction conditions. After the reaction, the resulting mixture was cooled and separated into organic phase and aqueous phase automatically. The organic phase was

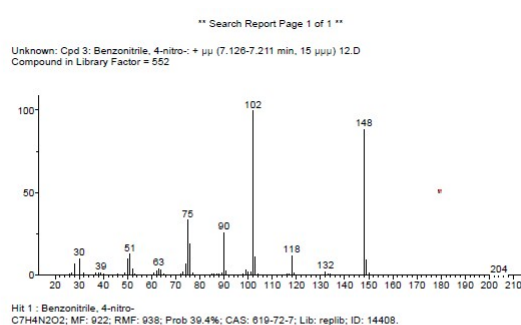
distilled with a rotary evaporator under vacuum to get the corresponding nitriles. The EI-MS and FT-IR of these nitriles were presented as follows.

(1) EI-MS

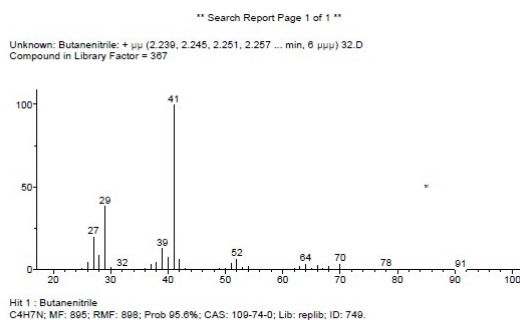
The products were identified qualitatively by Agilent 7890B-5977A GC-MS (Agilent Technologies Inc., USA) with a HP-5MS column. The analysis conditions were as follows: He as carrier, injection port temperature of 250°C and the program-controlled column temperature: initial temperature was set at 90°C for 2 min and then increased with a rate of 15°C min⁻¹ to 225°C and held for 2min. Mass spectra were collected with an ion source temperature of 230°C and a scan range of 20-550 m/z.



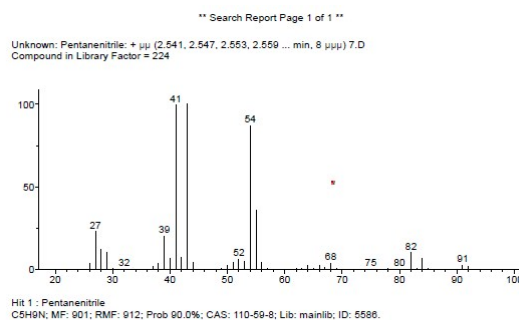
Benzonitrile



4-Nitrobenzonitrile



Butyronitrile



Pentanitrile

(2) FT-IR

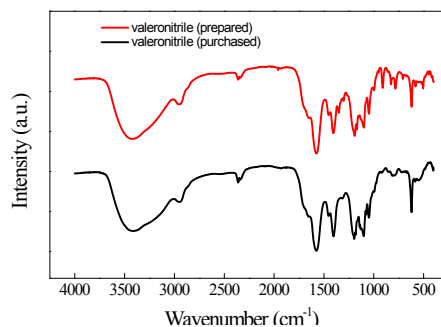
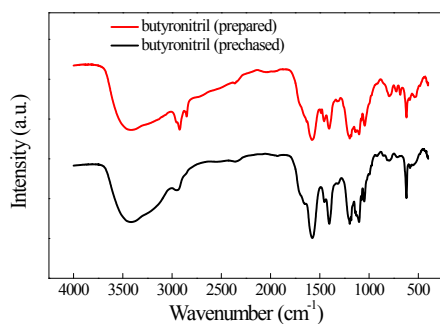
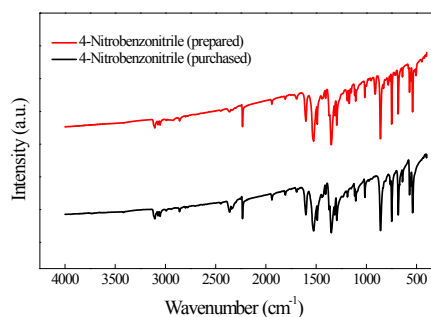
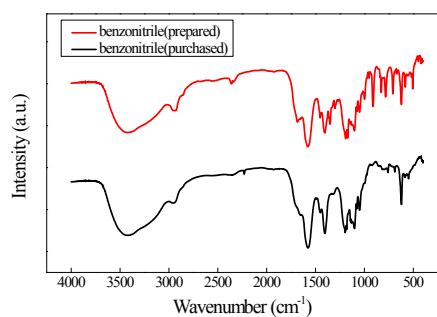
The FT-IR spectra of the benzonitrile, 4-nitrobenzonitrile, butyronitrile and pentanenitrile was presented and compared with those of the standard sample. The results indicated that they were much the same.

Benzonitrile: ν : 2330cm^{-1} (CN)

4-Nitrobenzonitrile: ν : 2228cm^{-1} (CN); $1530\&1346\text{ cm}^{-1}$ (NO_2)

Butyronitrile: ν : 2228cm^{-1} (CN)

Pentanenitrile: ν : 2328cm^{-1} (CN)



FT-IR spectra of the benzonitrile, 4-nitrobenzonitrile, butyronitrile and pentanenitrile