Electronic Supplementary Information

Reactivity of hydroxylamine ionic liquid salts in direct synthesis of caprolactam from cyclohexanone under mild conditions

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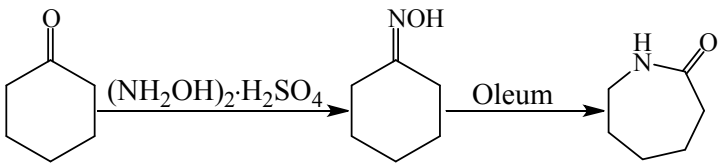
Schemes

Scheme S1 Traditional process for synthesis of CPL



Figures

Figure S1 (a-d) ^{1}H and ^{13}C NMR spectra of the two novel $(NH_2OH)_2{\cdot}$ILs

$(NH_2OH)_2{\cdot}[HSO_3\text{-b-}N(CH_3)_3]{\cdot}HSO_4$: δH (400 MHz; DMSO-$d_6$) 1.593(m, 2H), 1.766(t, 2H), 2.489(m, 2H), 3.025(s, 9H), 3.285(m, 2H), 8~9(bs, 20H).

$(NH_2OH)_2{\cdot}[HSO_3\text{-b-}N(CH_3)_3]{\cdot}HSO_4$: δC (400 MHz, D_2O) 20.945, 21.135, 49.889, 52.764, 65.769.

$(NH_2OH)_2{\cdot}[HSO_3\text{-b-Py}]{\cdot}HSO_4$: δH (400 MHz; DMSO-$d_6$) 1.562(t, 2H), 2.011(t, 2H), 2.505(t, 2H), 4.631(t, 2H), 8.173(t, 2H), 8~9(bs, 7H), 8.610(t, 1H), 9.109(d, 2H).

$(NH_2OH)_2{\cdot}[HSO_3\text{-b-Py}]{\cdot}HSO_4$: δC (400 MHz, D_2O) 20.783, 29.236, 49.871, 61.101, 128.233, 144.173, 145.613.

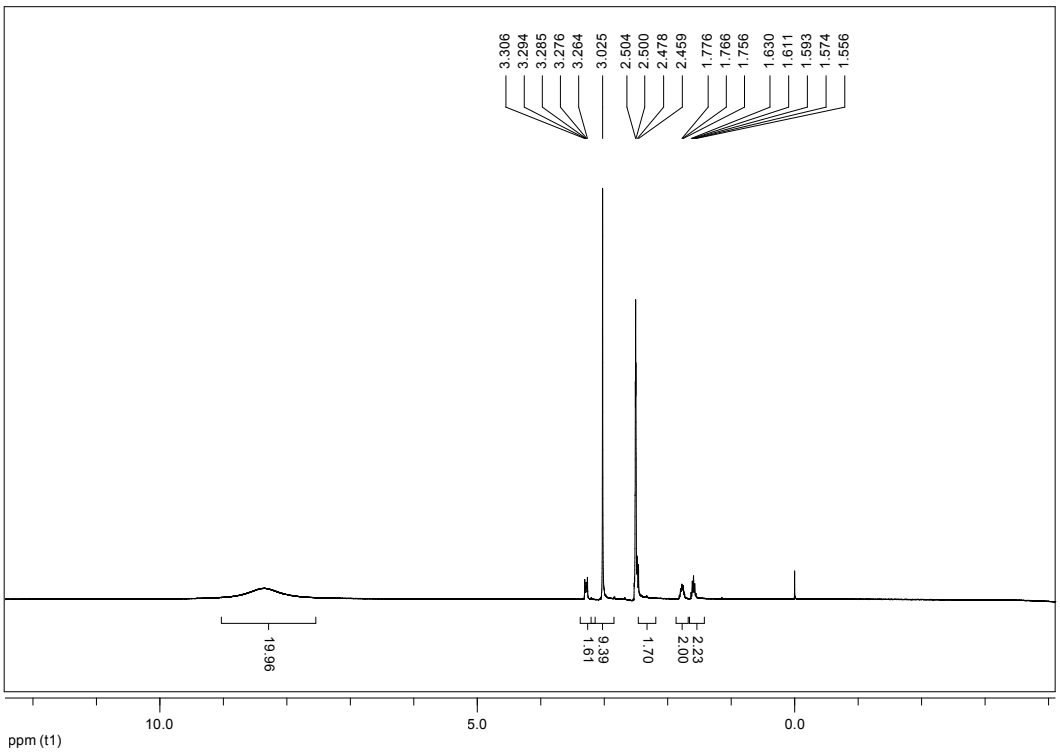


Figure S1 (a) ^{1}H NMR spectra of $(NH_2OH)_2 \cdot [HSO_3\text{-b-}N(CH_3)_3] \cdot HSO_4$ (DMSO-d_6)

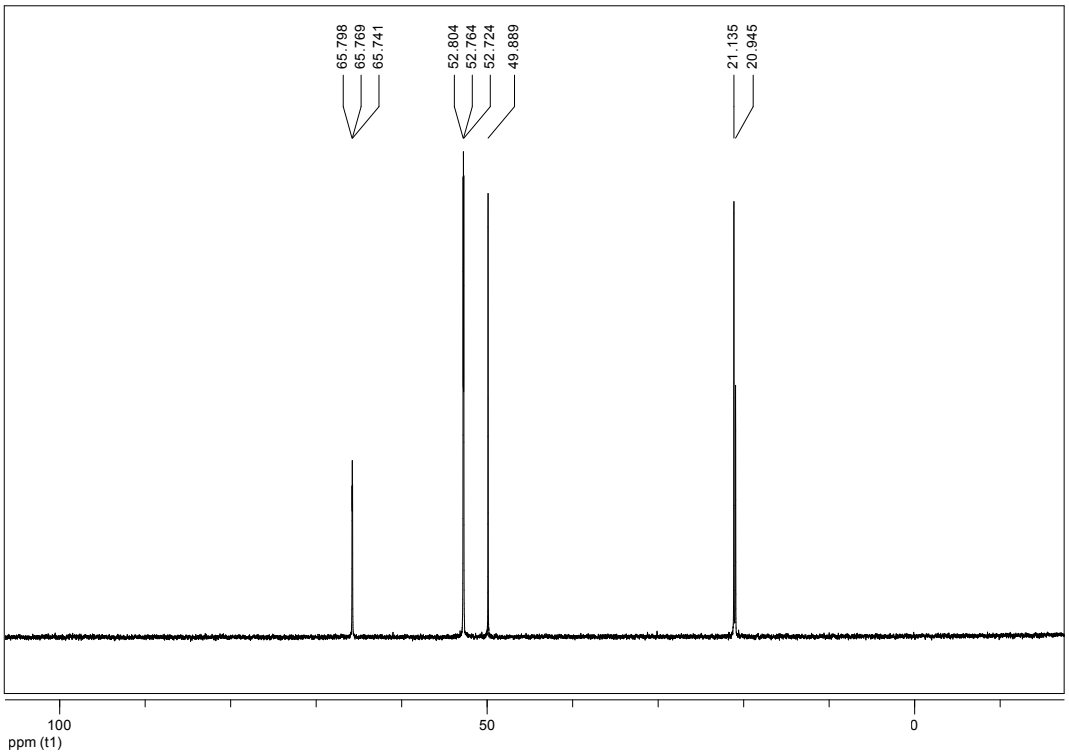


Figure S1 (b) ^{13}C NMR spectra of $(NH_2OH)_2 \cdot [HSO_3\text{-b-}N(CH_3)_3] \cdot HSO_4$ (D_2O)

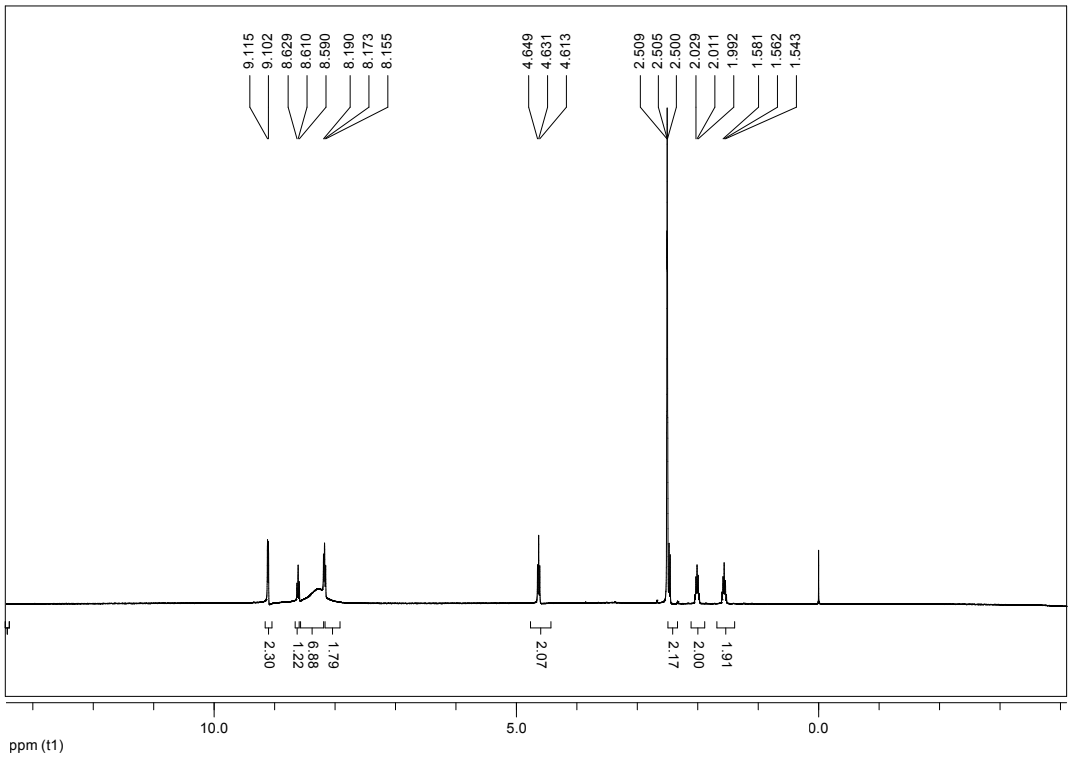


Figure S1 (c) ^{1}H NMR spectra of $(NH_2OH)_2 \cdot [HSO_3\text{-b-Py}] \cdot HSO_4$ (DMSO-d_6)

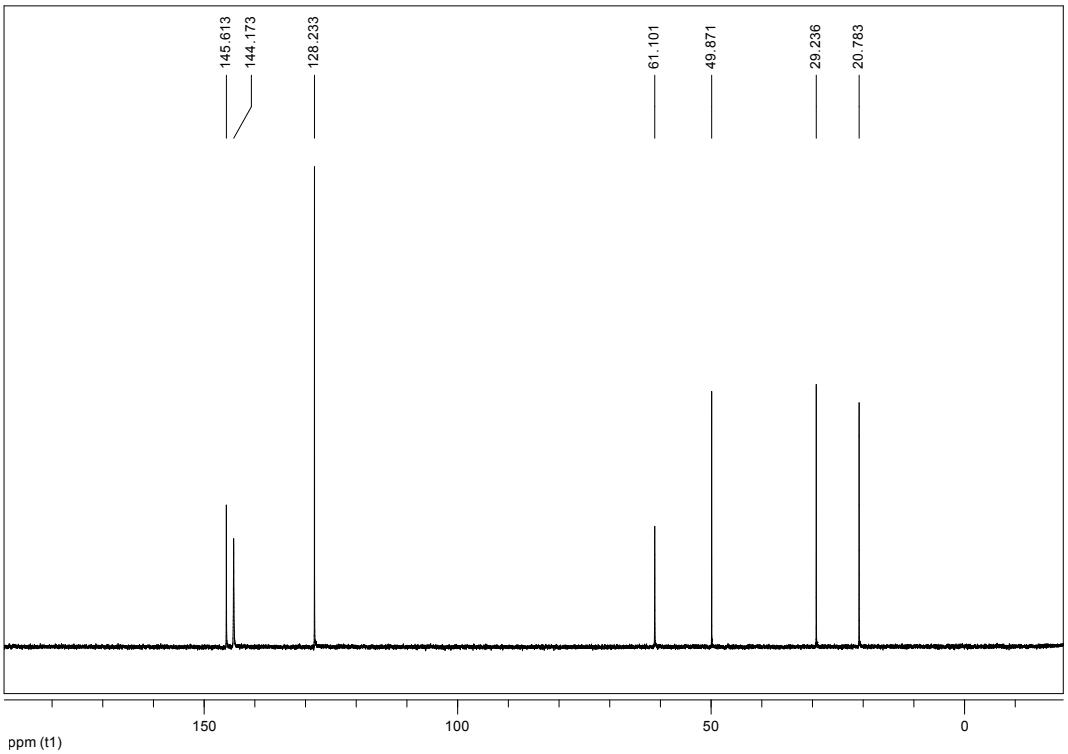


Figure S1 (d) ^{13}C NMR spectra of $(NH_2OH)_2 \cdot [HSO_3\text{-b-Py}] \cdot HSO_4$ (D_2O)

Tables

Table S1 Species and corresponding frequency values of the two $(NH_2OH)_2$·ILs (Raman spectra)

Species	Freequency (cm^{-1})
N-OH stretch	1011
OH bend, NH_3 rock	1190
NH_3 deformation	1617
NH_3 stretch	2973

Table S2 Beckmann rearrangement of COX to CPL under different conditions

No	$[HSO_3\text{-b-}(CH_3)_3]\cdot H_2SO_4$ (mmol)	$ZnCl_2$(mmol)	X_{COX} (%)	S_{CPL}(%)	S_{CYC}(%)
1	0	0	3.4	0	100
2	0.25	0	20.6	19.2	80.8
3	0	0.75	64.6	91.2	8.8
4	0.25	0.75	98.4	96.9	3.7

Reaction conditions: COX 5 mmol, $[HSO_3\text{-b-}(CH_3)_3]\cdot H_2SO_4$ 2.5 mmol, acetonitrile 10 mL, 80 °C, 4 h.