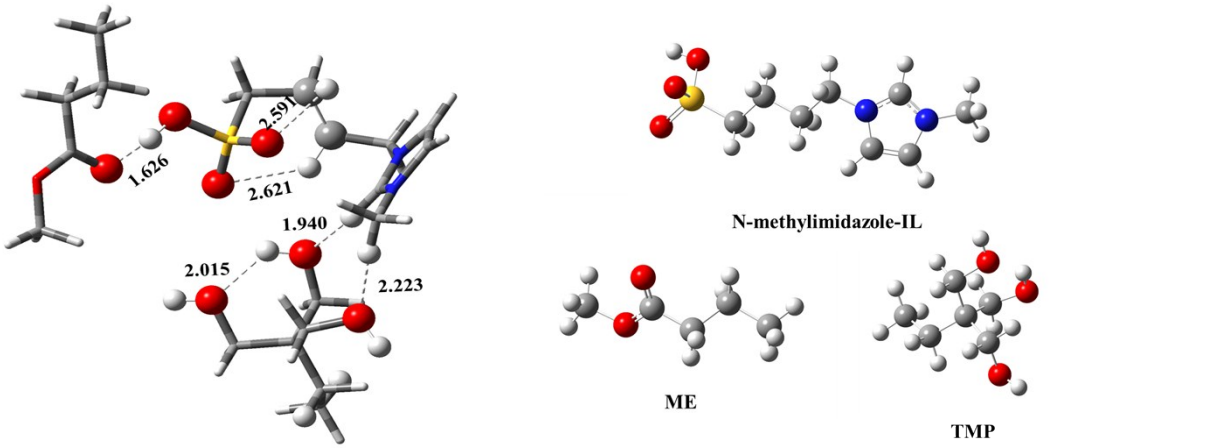
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Understanding the role of hydrogen bonding in Brønsted acidic ionic liquid-catalyzed transesterification: A combined theoretical and experimental investigation

Supplementary Figures



Relative E_{ZPE}*= 0 kJ /mol Relative $E_{ZPE(N\text{-}methylimidazole\text{-}IL+ME+TMP)}$*= 32.5 kJ /mol

Fig. S1 The most stable geometries of the N-methylimidazole-IL/TMP/ME mixture with intra- and inter-molecular hydrogen bonds (a1) and without hydrogen bonds (a2)

It can be seen that the relative energy E_{ZPE}* of geometry a2 was much higher, implying the significant contribution of HBs for stabilizing this system.

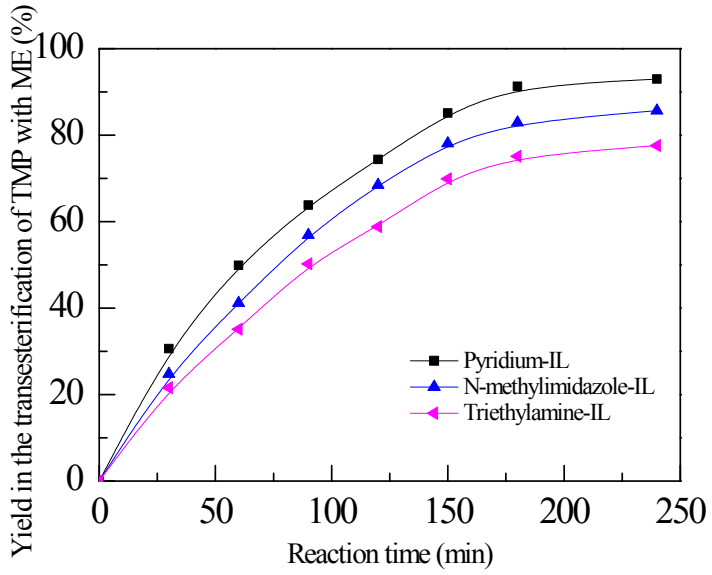


Fig. S2 Transesterification of TMP with ME catalyzed by these three ILs

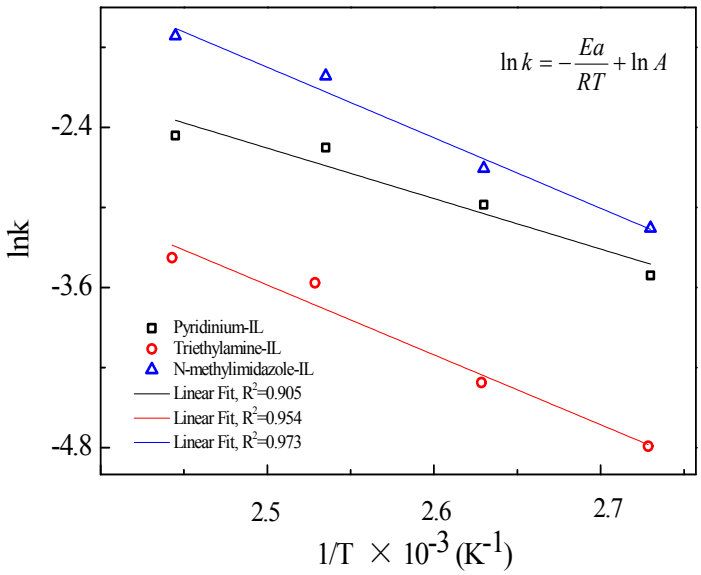


Fig. S3 Kinetics plot of lnk vs. 1/T for the triethylamine-IL catalyzed transesterification, the slope represents [-Ea/R] and the intercept represents lnA respectively.

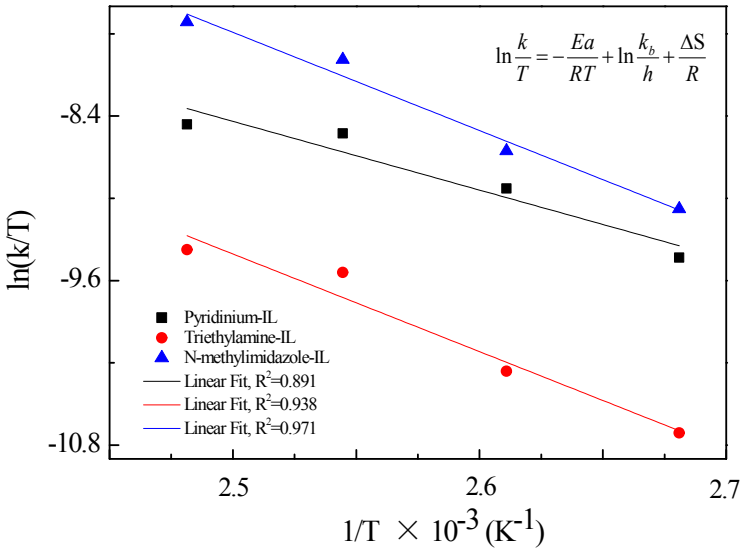


Fig. S4 Kinetics plot of ln(k/T) vs. 1/T for the triethylamine-IL catalyzed transesterification, the slope represents [-△H/R] and the intercept represents [ln(kB/h)+△S/R] in the Erying equation respectively.

Supplementary Table

Table S1 Binding energies (Δ E_{bin}) and normalized delocalization energies (DE_{na}) calculated for the three BAIL-containing systems at the B3LYP/6-311++G level of theory [a]

IL	Δ E_{bin} (kJ/mol)	DE_{na} (kJ/mol)
pyridinium-IL	132.56	80.2
triethylamine-IL	130.45	0
N-methylimidazole-IL	152.16	55.2

[a]The binding energies included BSSE and ZPVE corrections based on the results. The normalized delocalization energies were calculated according to the methods proposed by Sabine et al[54]

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Table S2 Comparison for the activation energy in the transesterification between DFT computed value and experiment result.

IL	Activation Energy ΔE (kJ/mol)			
	DFT computed result	DFT with HSO^4-	DFT with HSO^4- under implicit solvation	Experiment result
pyridinium-IL	199.6	157.3	116.8	108.3
triethylamine-IL	212.7	172.1	126.5	113.3
N-methylimidazole-IL	201.2	162.5	120.1	109.0