Electronic Supplementary Material (ESI) for RSC Advances.

A Mechanistic Insight into Organocatalytic Properties of Imidazolium-Based Ionic Liquids and A Positive Co-Solvent Effect on Cellulose Modification Reactions in An Ionic Liquid

Ryohei Kakuchi[a], Ryo Ito[c], Shuhei Nomura[a], Hadi Abroshan[e], Kazuaki Ninomiya[b], Tomoyuki Ikai[c,d], Katsuhiro Maeda[c,d], Hyung Kim[e,f*] and Kenji Takahashi[a*]*

[a] Faculty of Natural System, Institute of Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan.

[b] Institute for Frontier Science Initiative, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

[c] Graduate School of Natural Science and Technology, College of Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

[d] Research Center for Sustainable Energy and Technology, College of Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

[e] Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA

[f] School of Computational Sciences, Korea Institute for Advanced Study, Seoul, 02455, Korea

Tel: +81 (0) 76-234-4828. E-mail: maeda@se.kanazawa-u.ac.jp, hjkim@cmu.edu and ktkenji@staff.kanazawa-u.ac.jp.

SUPPORTING INFORMATION

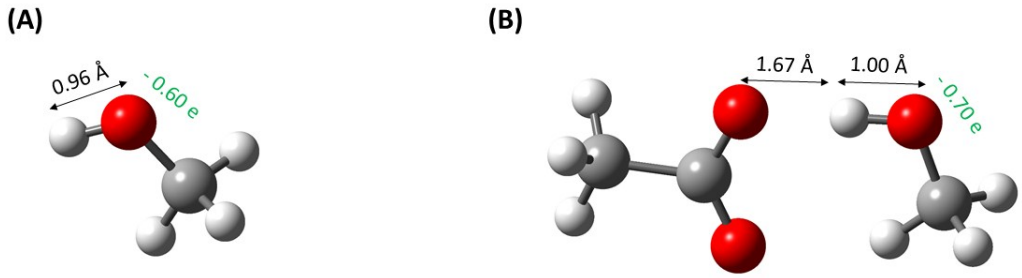

Figure S1. Optimized structure of (A) an isolated methanol molecule and (B) an acetate-methanol complex. Color code: O, C and H atoms are shown in red, dark grey, and light grey, respectively. The partial charge for the oxygen atom of methanol is given in green.

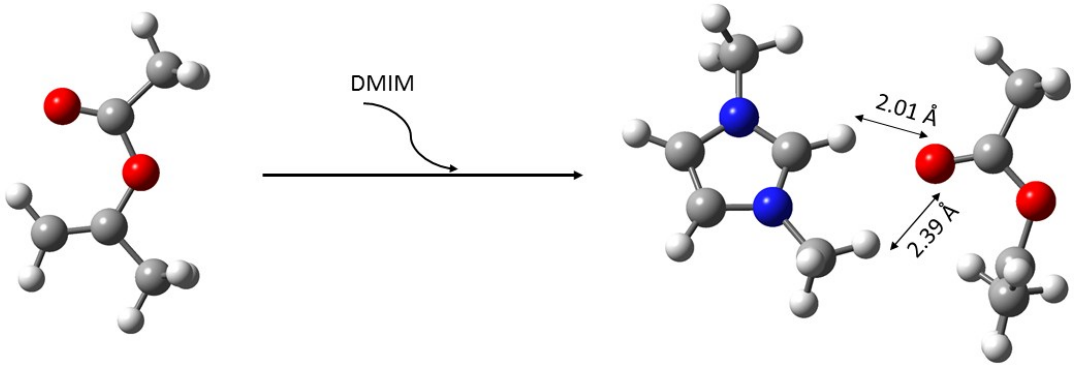

Figure S2. Deformation of isopropenyl acetate structure upon interaction with 1,3-dimethylimidazolium (DMIM). In the absence of DMIM, all carbon and oxygen atoms of the ester lie on a single plane; i.e., the plane defined by three C atoms of the isopropenyl group and the plane defined by two O and two C atoms of the acetate group are co-planar. Upon interaction with DMIM, the isopropenyl group twists along the O-C bond such that the two planes become perpendicular. Color code: O, N, C and H atoms are shown in red, blue, dark grey, and light grey, respectively.

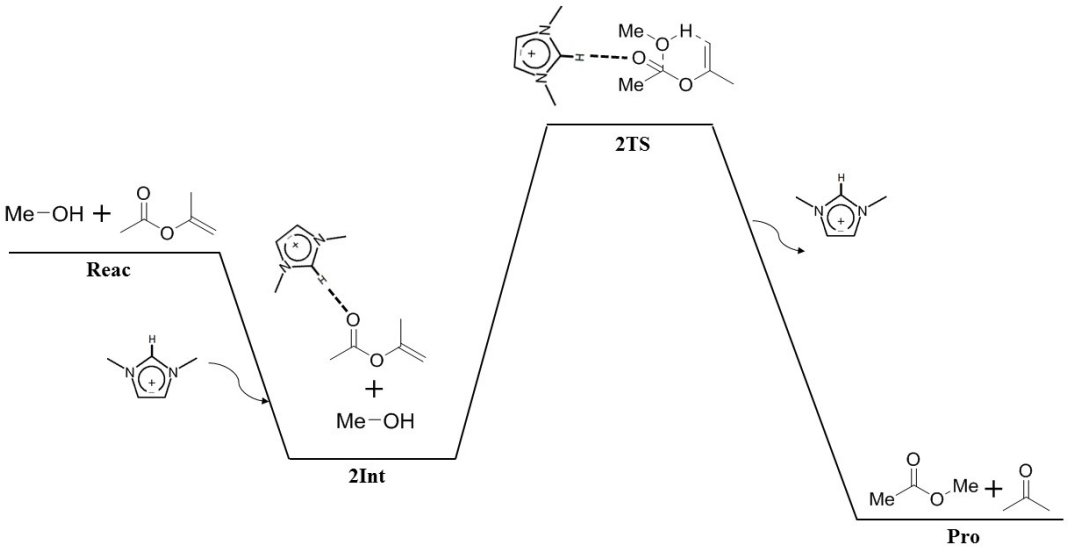

Figure S3. Proposed reaction Mechanism 2 for transesterification reactions in the presence of a 1,3-dimethylimidazolium cation. The calculated energies for different steps are given in Table S1.

Table S1. DFT results for ΔE for elementary steps of Mechanism 2 (Figure S-3).

Step	ΔE(kcal/mol)
Reac → 2Int	-15.8
2Int → 2TS	28.1
2TS → Pro	-37.3

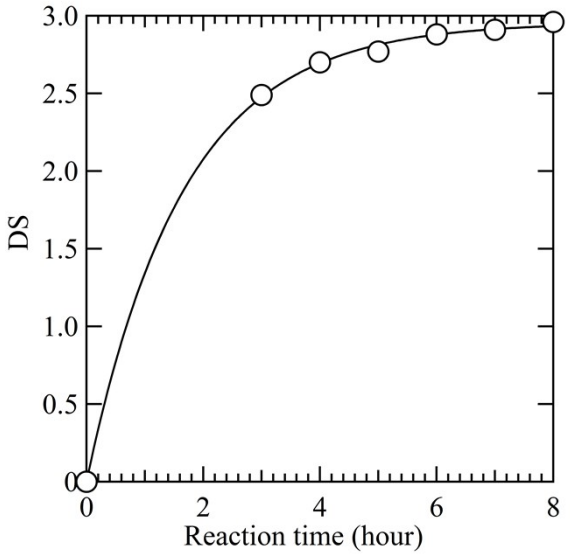

Figure S4. Effect of reaction time on the DS values (line; guidance) for cellulose modification reactions in EmimOAc/DMSO mixed solvent systems. The reaction conditions are as follows; Ar atmosphere; EmimOAc as a solvent and an organocatalyst; EmimOAc/cellulose (wt. ratio) = 2.5; initial [IPA]/[OH] = 2.45; 4 mL of DMSO was used as a co-solvent.