Electronic Supplementary Information (ESI)

New Eutectic Ionic Liquids for Lipase Activation and Enzymatic Preparation of Biodiesel

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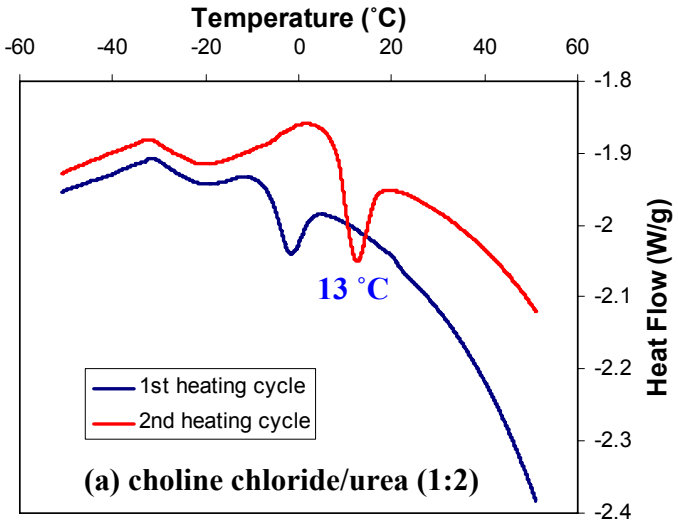

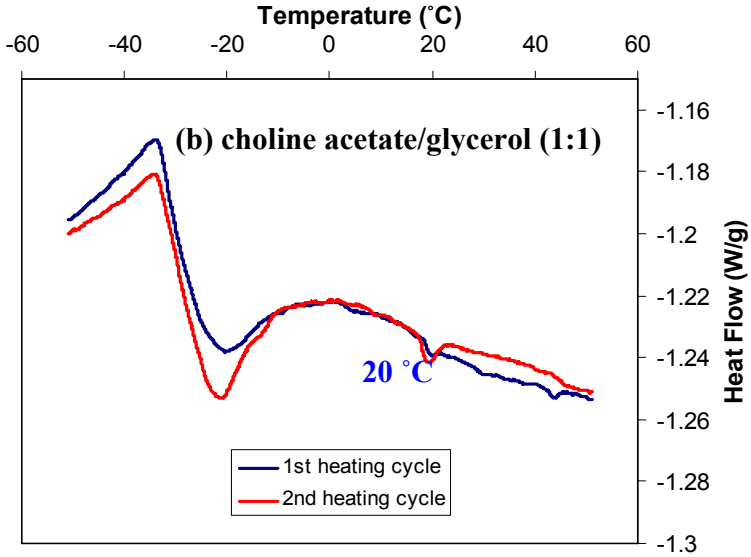

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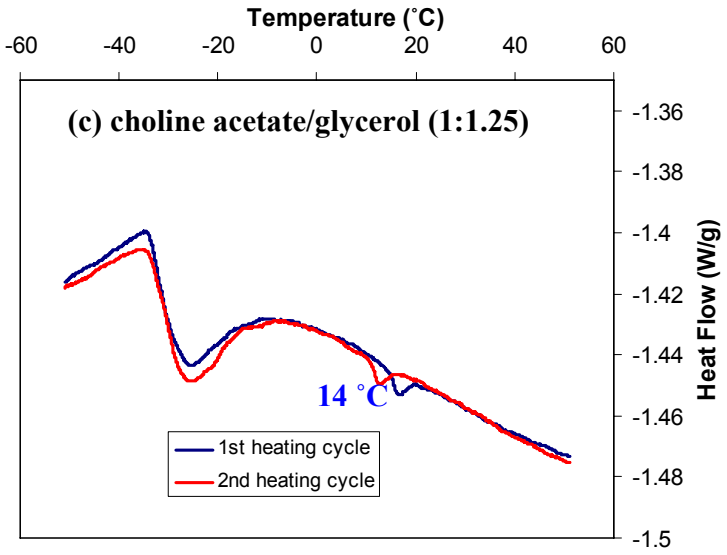
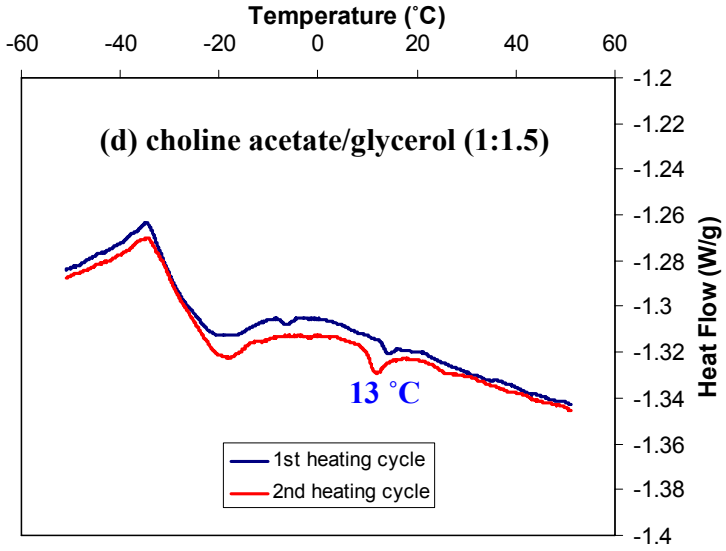
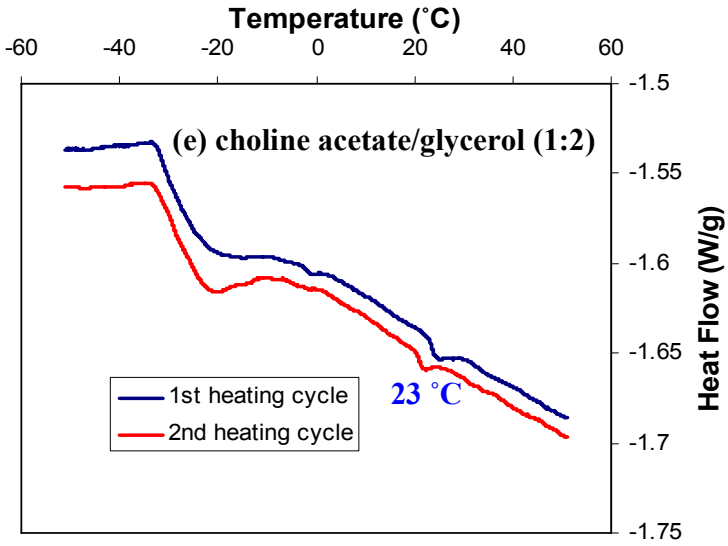
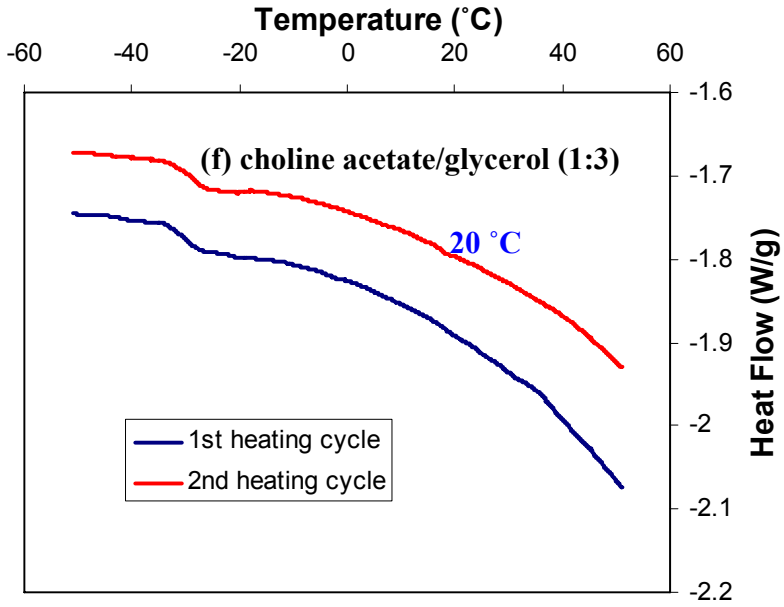
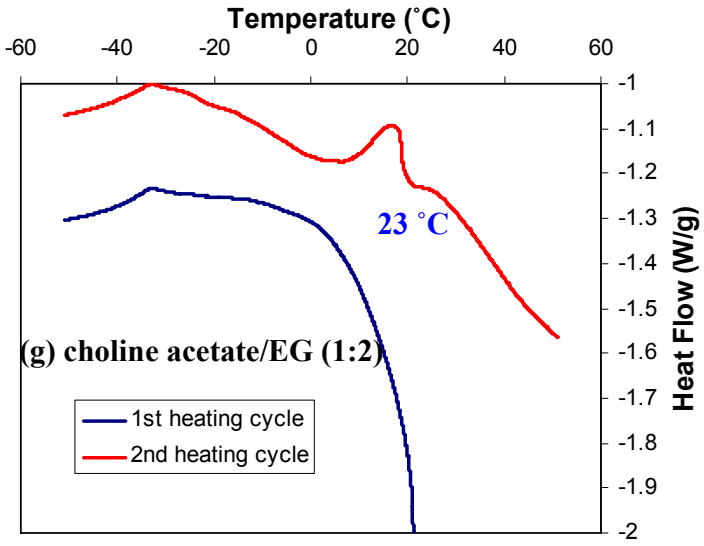
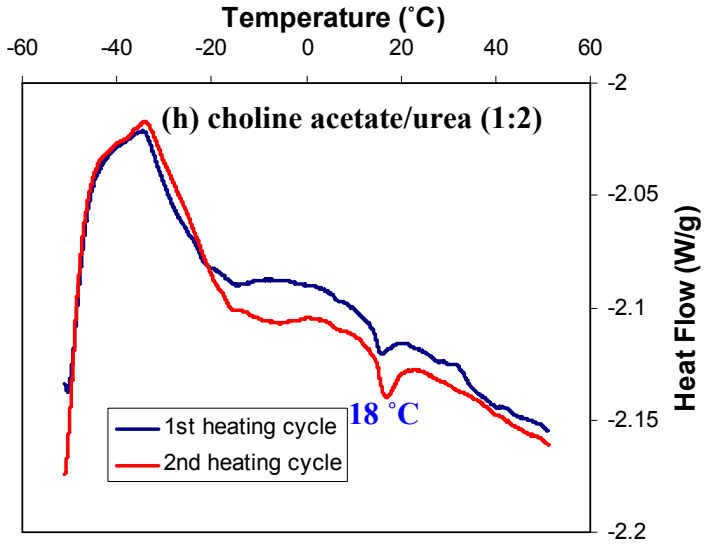

Temperature (˚C)
-60
-40
-20
0
20
40
60
(c) choline acetate/glycerol (1:1.25)
14 ˚C
1st heating cycle
2nd heating cycle
-1.36
-1.38
-1.4
-1.42
-1.44
-1.46
-1.48
-1.5
Heat Flow (W/g)


Temperature (˚C)
-60
-40
-20
0
20
40
60
(d) choline acetate/glycerol (1:1.5)
13 ˚C
1st heating cycle
2nd heating cycle
-1.2
-1.22
-1.24
-1.26
-1.28
-1.3
-1.32
-1.34
-1.36
-1.38
-1.4
Heat Flow (W/g)


Temperature (˚C)
-60
-40
-20
0
20
40
60
(e) choline acetate/glycerol (1:2)
1st heating cycle
2nd heating cycle
23 ˚C
-1.5
-1.55
-1.6
-1.65
-1.7
-1.75
Heat Flow (W/g)


Temperature (˚C)
-60
-40
-20
0
20
40
60
(f) choline acetate/glycerol (1:3)
20 ˚C
1st heating cycle
2nd heating cycle
-1.6
-1.7
-1.8
-1.9
-2
-2.1
-2.2
Heat Flow (W/g)


Temperature (˚C)
-60
-40
-20
0
20
40
60
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
-1.7
-1.8
-1.9
-2
Heat Flow (W/g)
23 ˚C
(g) choline acetate/EG (1:2)
1st heating cycle
2nd heating cycle


Temperature (˚C)
-60
-40
-20
0
20
40
60
-2
-2.05
-2.1
-2.15
-2.2
Heat Flow (W/g)
(h) choline acetate/urea (1:2)
18 ˚C
1st heating cycle
2nd heating cycle

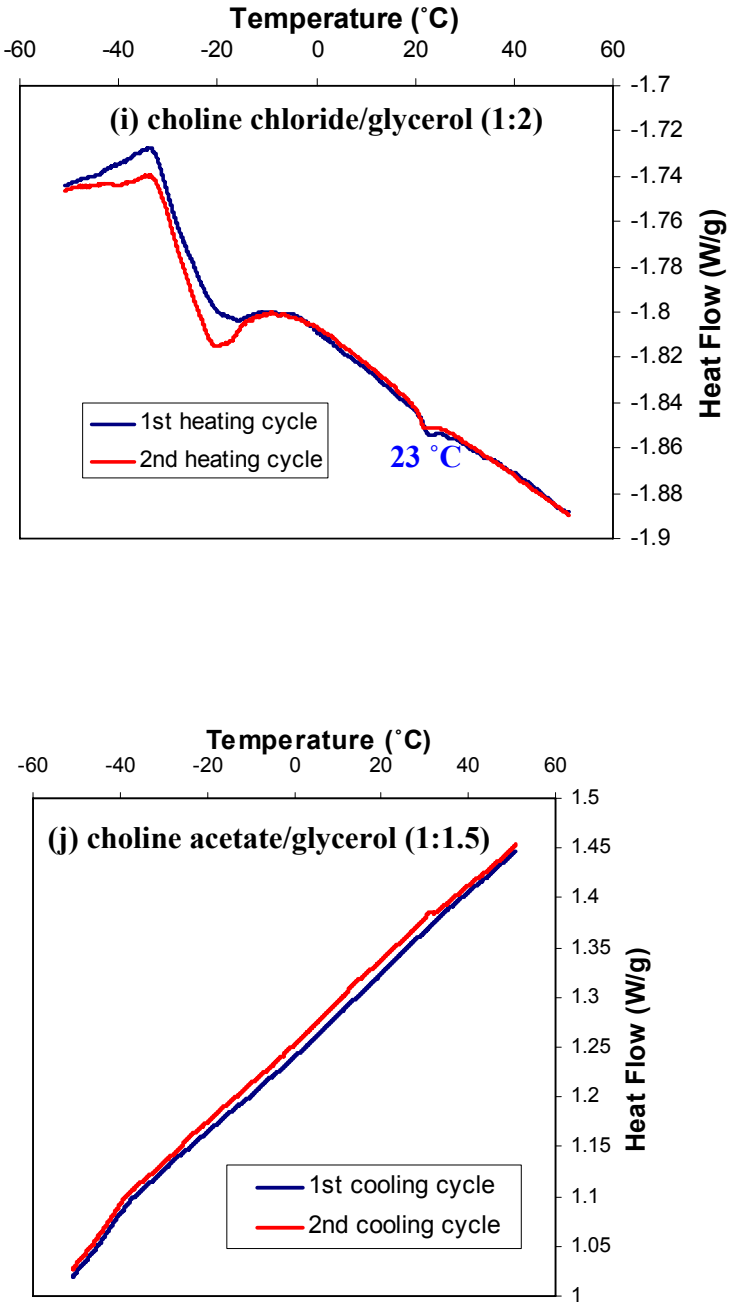


Fig. S1 DSC heating (a-i) and cooling (j) curves of ionic mixtures.

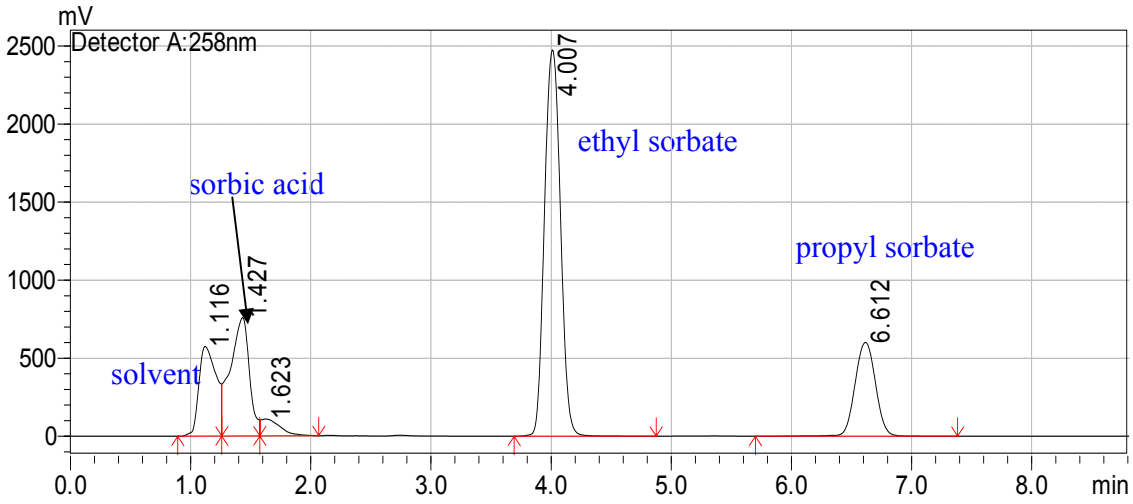


Fig. S2 A representative HPLC chromatograph of enzymatic transesterification of ethyl sorbate and 1-propanol [conditions: 1.0 mL choline acetate/glycerol (1:2), 5 mM ethyl sorbate, 0.67 M 1-propanol, 20 mg Novozym 435, 1 vol% water, 50 ˚C, and reaction time 30 min].

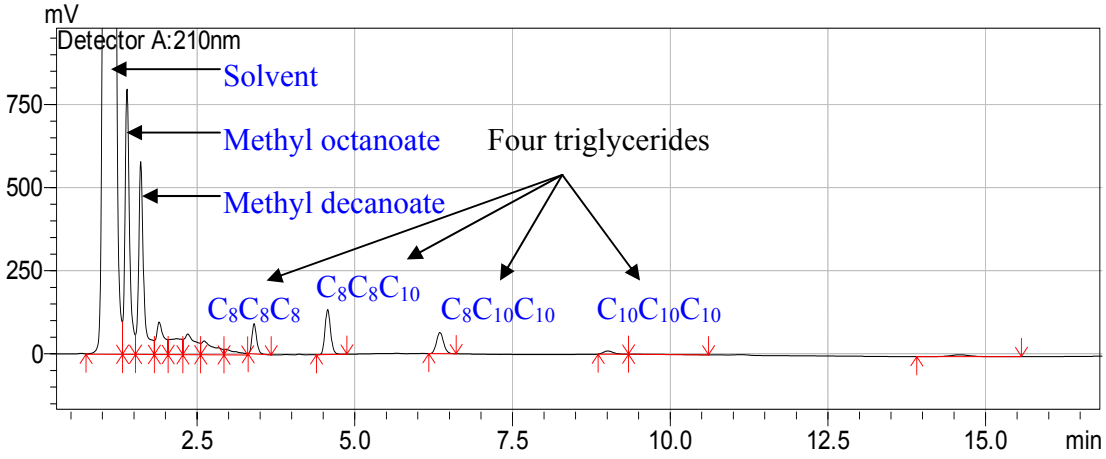


Fig. S3 A representative HPLC chromatograph of enzymatic conversion of Miglyol oil [reaction conditions: 1.0 mL choline acetate/glycerol (1:1.5), 0.11 g Miglyol oil, 200 µL methanol, 30 mg Novozym 435, 1 vol% water, and 50 ˚C].

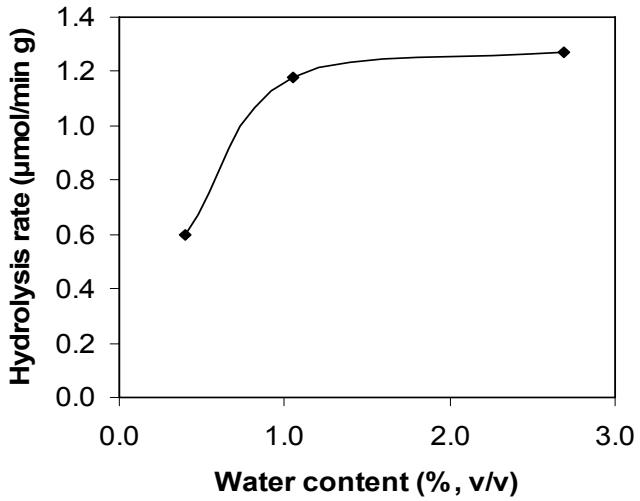
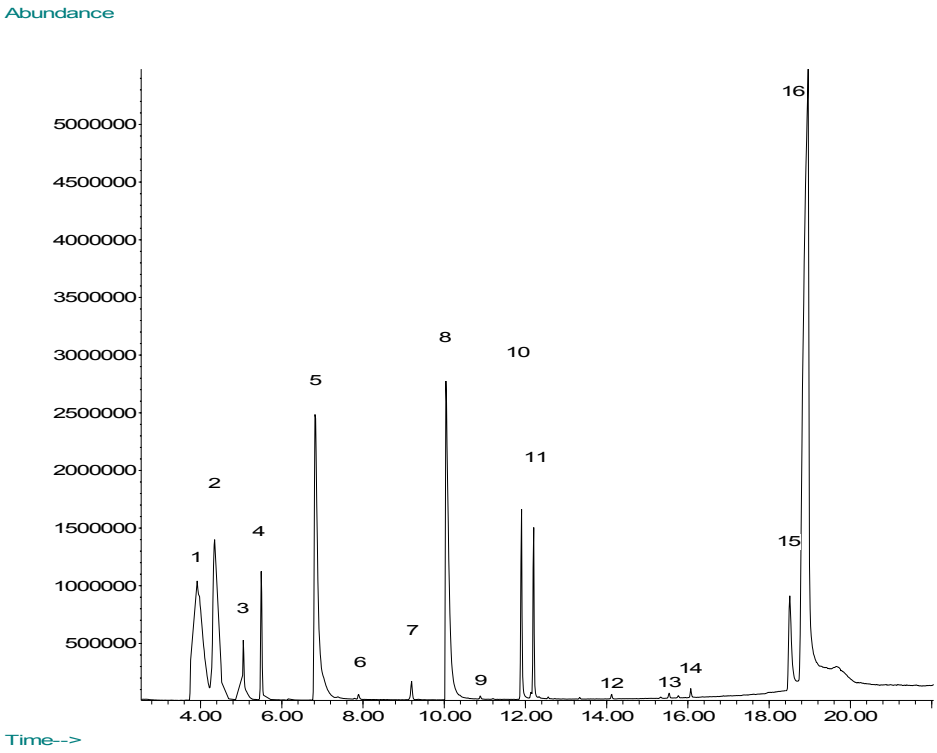


Fig. S4 Hydrolysis rate of ethyl sorbate in *t*-butanol (conditions: 1.0 mL *t*-butanol, 5 mM ethyl sorbate, various amounts of water, 20 mg Novozym 435, and 50 ˚C).



1. **Trimethylamine and ethylene oxide (shoulder peak)**
2. **Methyl acetate**
3. **Propyl acetate** and acetone (shoulder peak)
4. **1-Propanol**
5. ***N*,*N*-Dimethyl-2-aminoethanol**
6. Dimethylaminoethanol acetate
7. Ethylene glycol monovinyl ether
8. **Acetic acid**
9. Ethyl sorbate
10. ***N*,*N*-Dimethyl-2-isopropoxyethylamine**
11. **2-Hydroxyethyl acetate**
12. 3-Methoxy-1,2-propanediol
13. Methyltriglycol acetate
14. Higher MW homolog of peak #10
15. **Glycerol acetate**
16. **Glycerol**

Fig. S5 GC-MS total ion chromatogram (TIC) of the reaction mixture of transesterification between ethyl sorbate and 1-propanol [conditions: 1.0 mL choline acetate/glycerol (1:1.5), 5 mM ethyl sorbate, 0.67 M 1-propanol, 20 mg Novozym 435, 1 vol% water, 50 ˚C, and reaction time 1 h. At the end of reaction, 2.0 mL methanol was added to dissolve the reaction mixture. After centrifugation to settle the enzyme, the clear supernatant was collected for GC-MS analysis]

Interpretation of GC-MS data: Major GC-MS peaks include #1, 2, 3, 4, 5, 8, 10, 11, 15 and 16. Choline acetate is a non-volatile compound. During the GC separation, this quaternary ammonium salt is decomposed into several major compounds including trimethylamine (peak #1), *N*,*N*-dimethyl-2-aminoethanol (peak #5), and acetic acid (peak #8). These decomposed compounds further reacted under GC conditions to form peak #2, 3, 6, 13, and 15. The reactant (ethyl sorbate) was shown as a small peak #9 because its initial concentration was low (5 mM),

and after dilution with methanol, its concentration was below 1.7 mM). The products (propyl sorbate and sorbic acid) were not shown as major peaks in Fig S4 due to their very low concentrations, but was clearly observed in HPLC analysis due to their high molar extinction coefficients (such as the representative chromatograph in Fig S2). Some other peaks may be attributed to those compounds possibly migrated from Novozym® 435[1] and their reactions with other compounds.

References

1 H. Zhao, Z. Song, *Biochem. Eng. J.,* 2010, **49**, 113-118.