SUPLEMENTARY INFORMATION for

Catalytic Conversion of Biomass Derivatives to Lactic Acid with Increased Selectivity in Aqueous Tin(II) Chloride/Choline Chloride System

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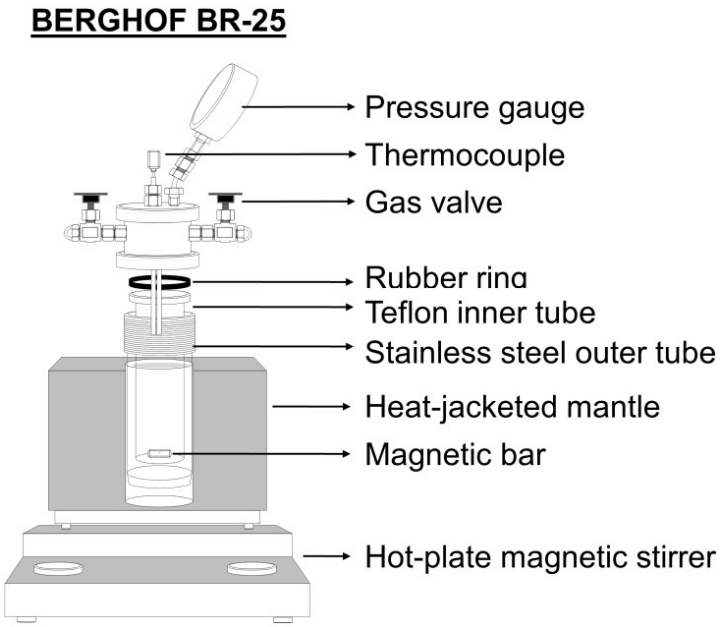


Fig. S1. Schematic of autoclave reactor used in this study.

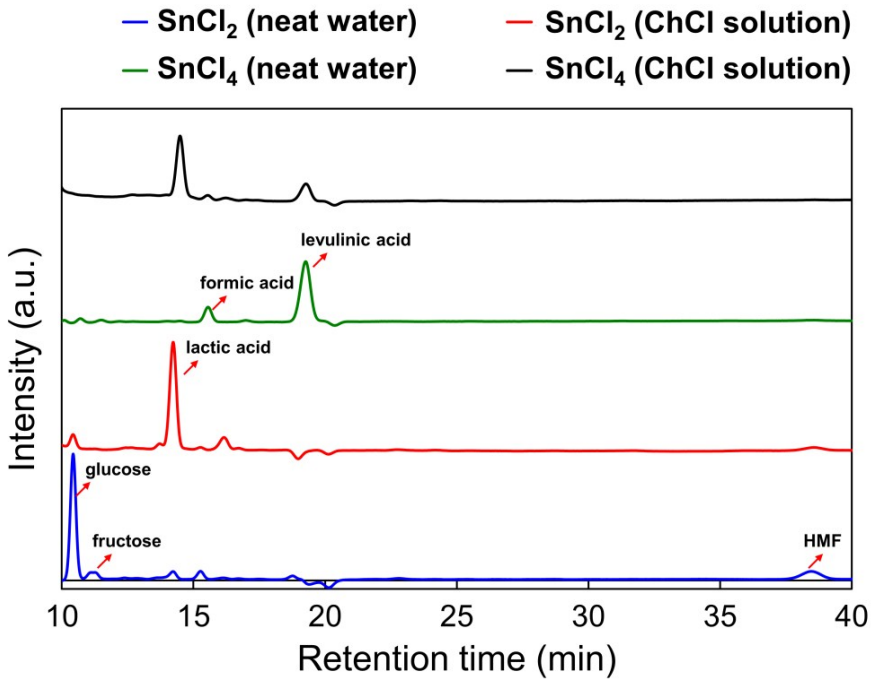


Fig. S2. Typical HPLC spectrum of products from the catalytic system with $SnCl_2$ or $SnCl_4$ in neat water or ChCl aqueous solution

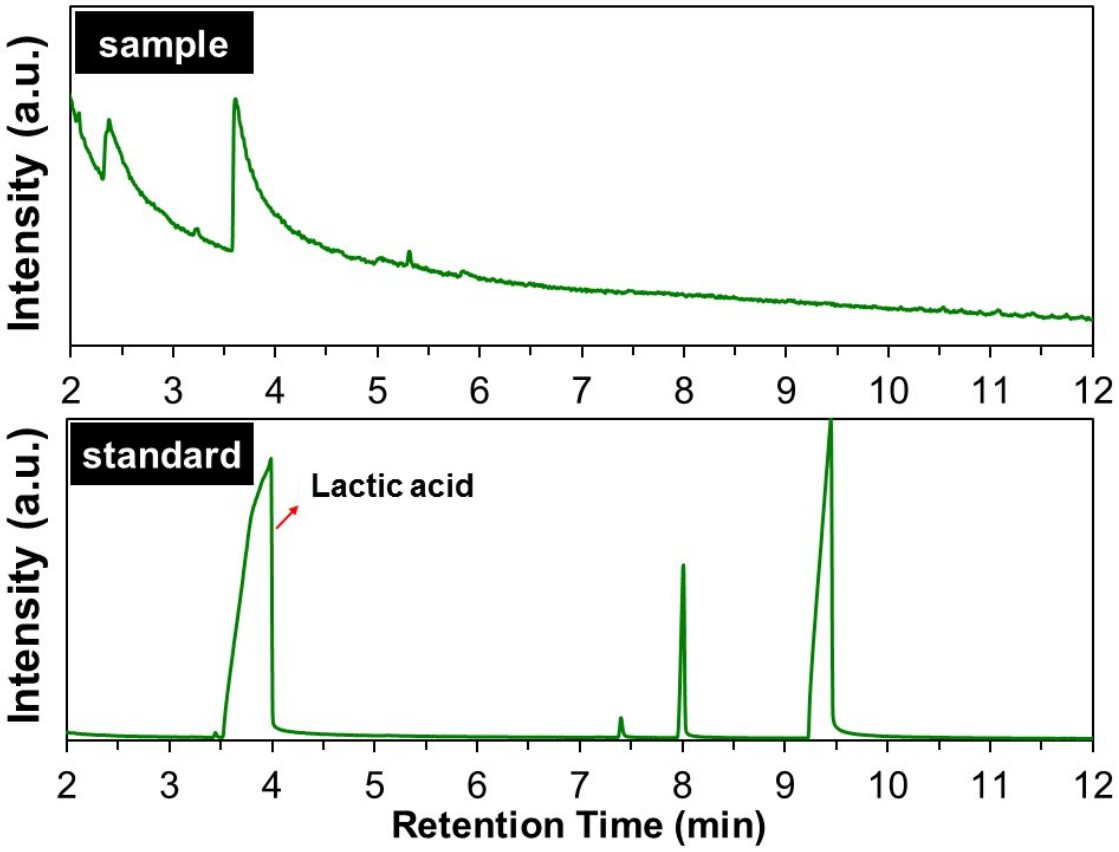


Fig. S3. GC-MS spectra of purified LacA product and the standard. Identification of compounds is based on the built-in NIST spectra library of GC-MS.

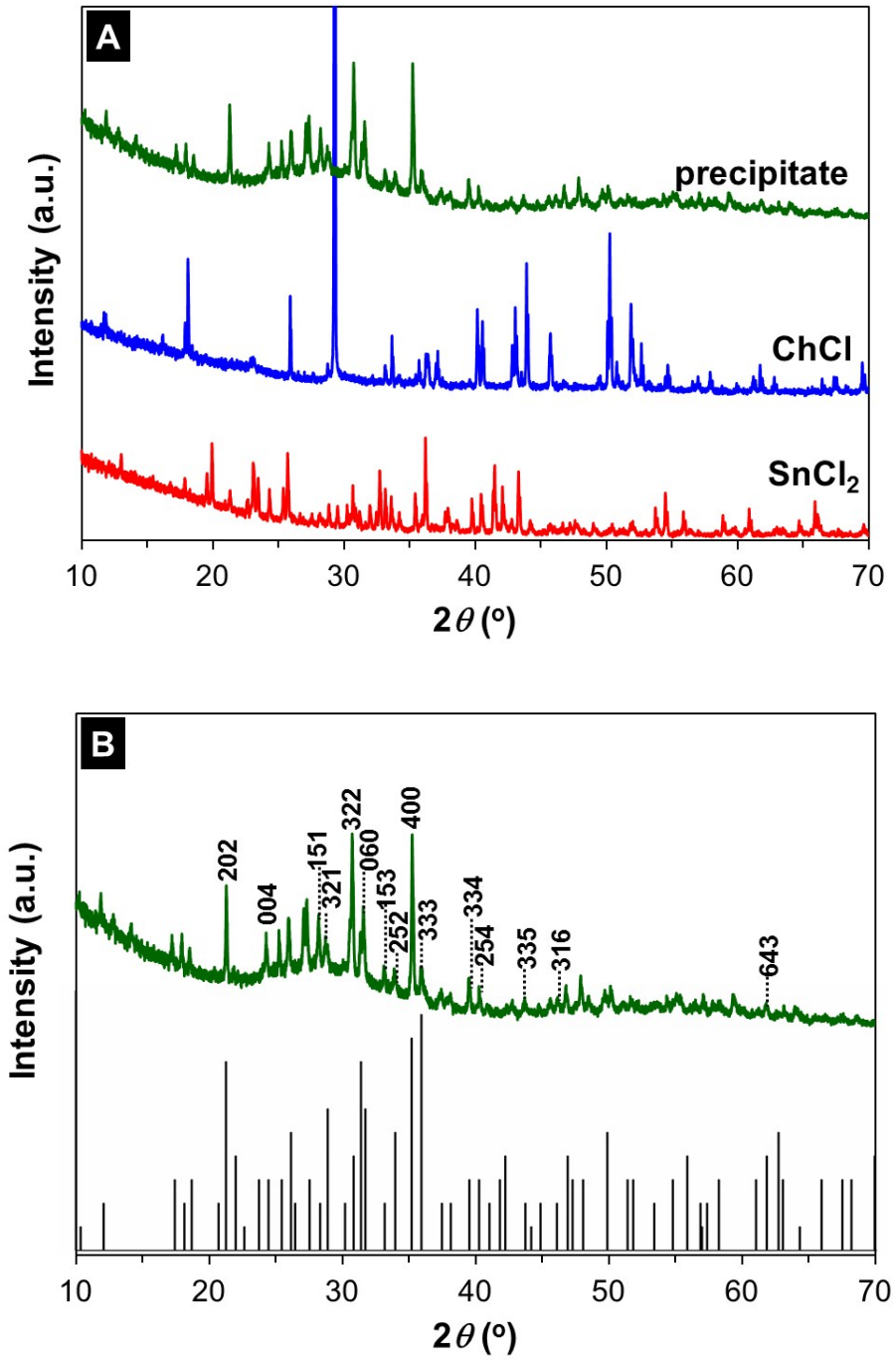


Fig. S4. X-ray diffractogram of the solid materials obtained in neat water compared with $SnCl_2$, crystalline ChCl (A) and the database of tin(hydro)oxide chloride (00-015-0676) (B).[1]

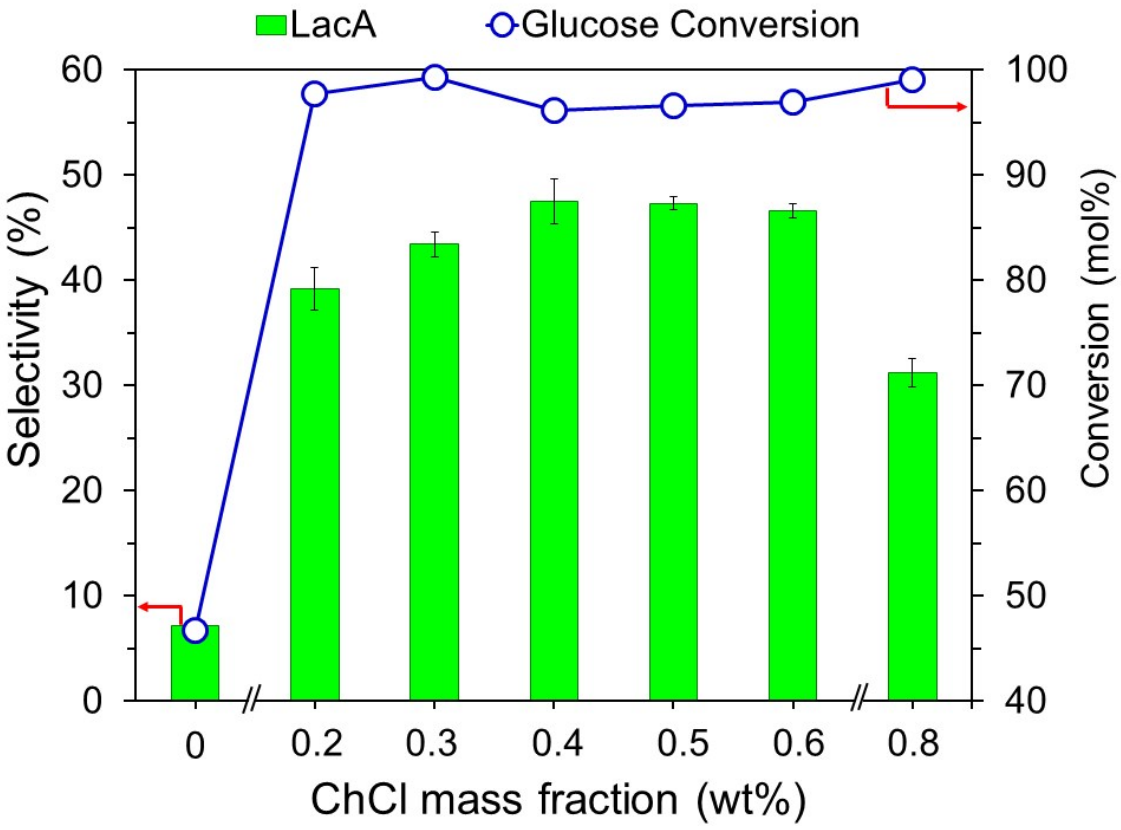


Fig. S5. Effect of ChCl mass fraction on the selectivity of reaction. Reaction conditions: 155 ^{o}C, 90 min, 2.0wt% Glucose, 0.9wt% $SnCl_2$ and 10 g ChCl aqueous solution.

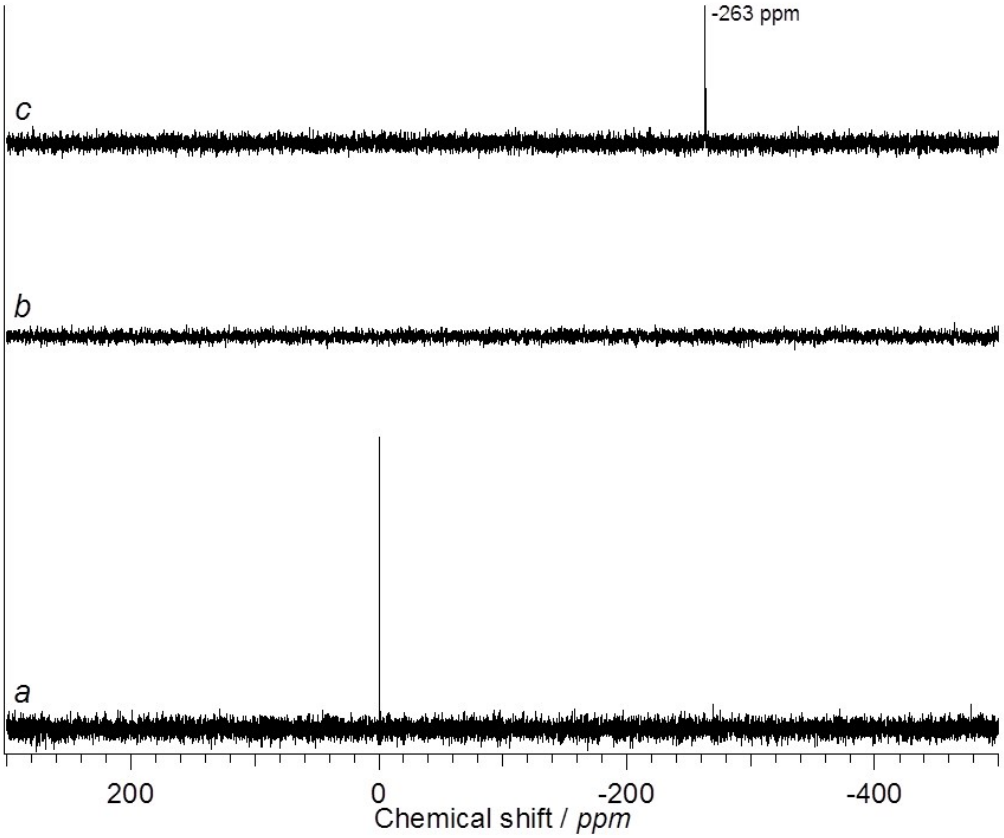


Fig. S6. ^{119}Sn spectra of (a) 1% Me_4Sn in $CDCl_3$ (standard), (b) 0.1 M $SnCl_2$ in methanol-d_4 and (c) 3.3wt% $SnCl_2$ solution in 50wt%ChCl/D_2O.

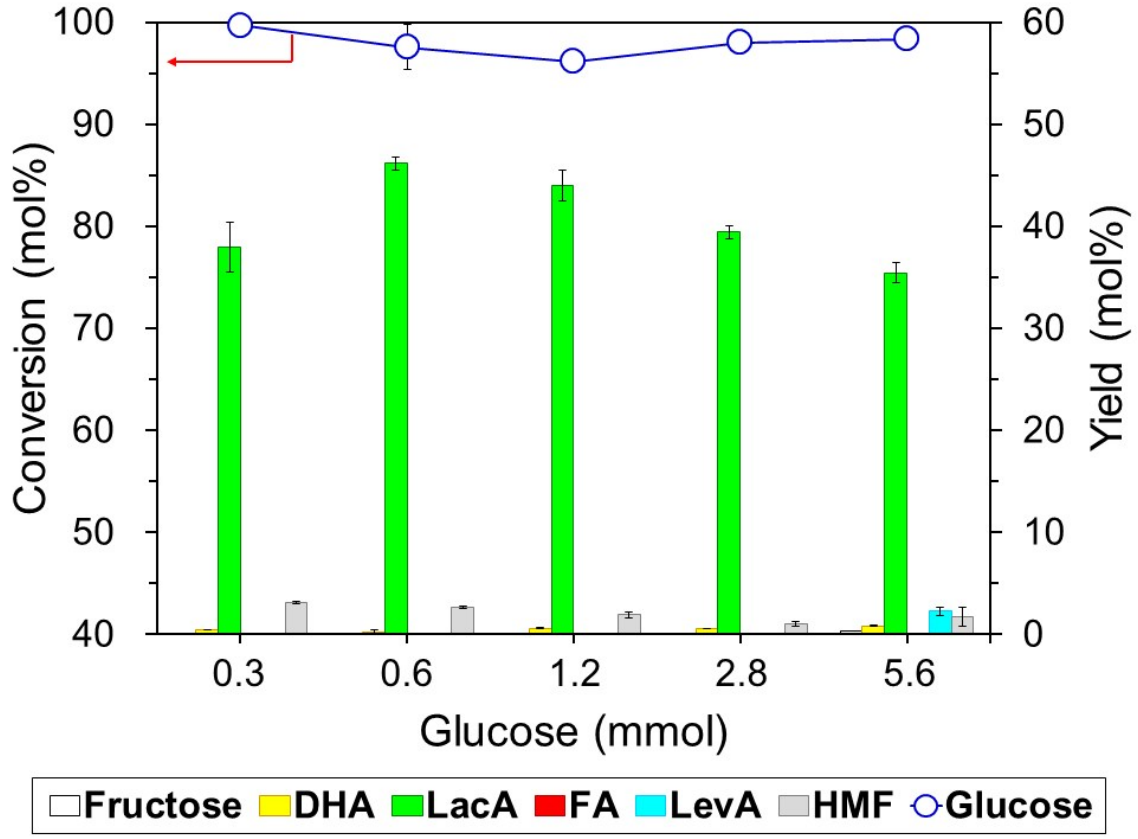


Fig. S7. Effect of initial glucose concentration in the solution on the catalytic performance of $SnCl_2$. Reaction conditions: 155 °C, 90 min, 1.8 wt% $SnCl_2$ and 10 g ChCl aqueous solution (40 wt%)

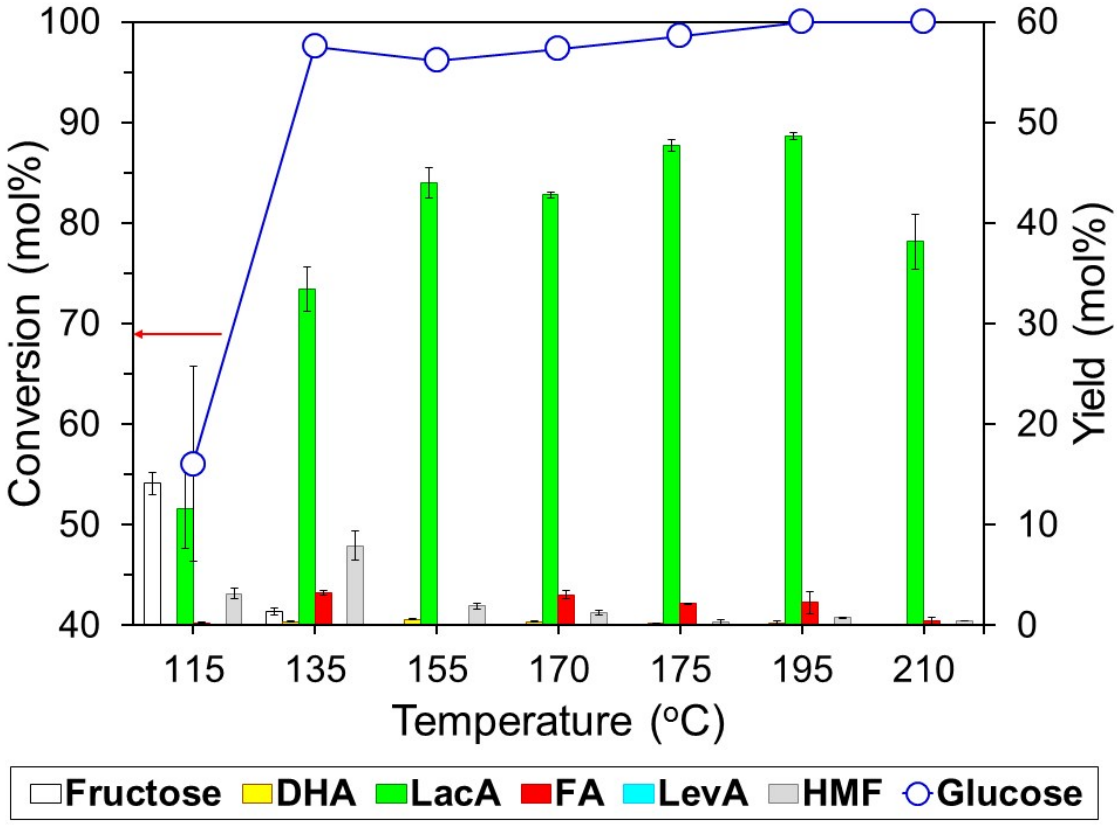


Fig. S8. Effect of reaction temperature on the yield of LacA and glucose conversion. Reaction conditions: 90 min, 2.0 wt% glucose, 0.9 wt% $SnCl_2$ and 10 g ChCl aqueous solution (40 wt%).

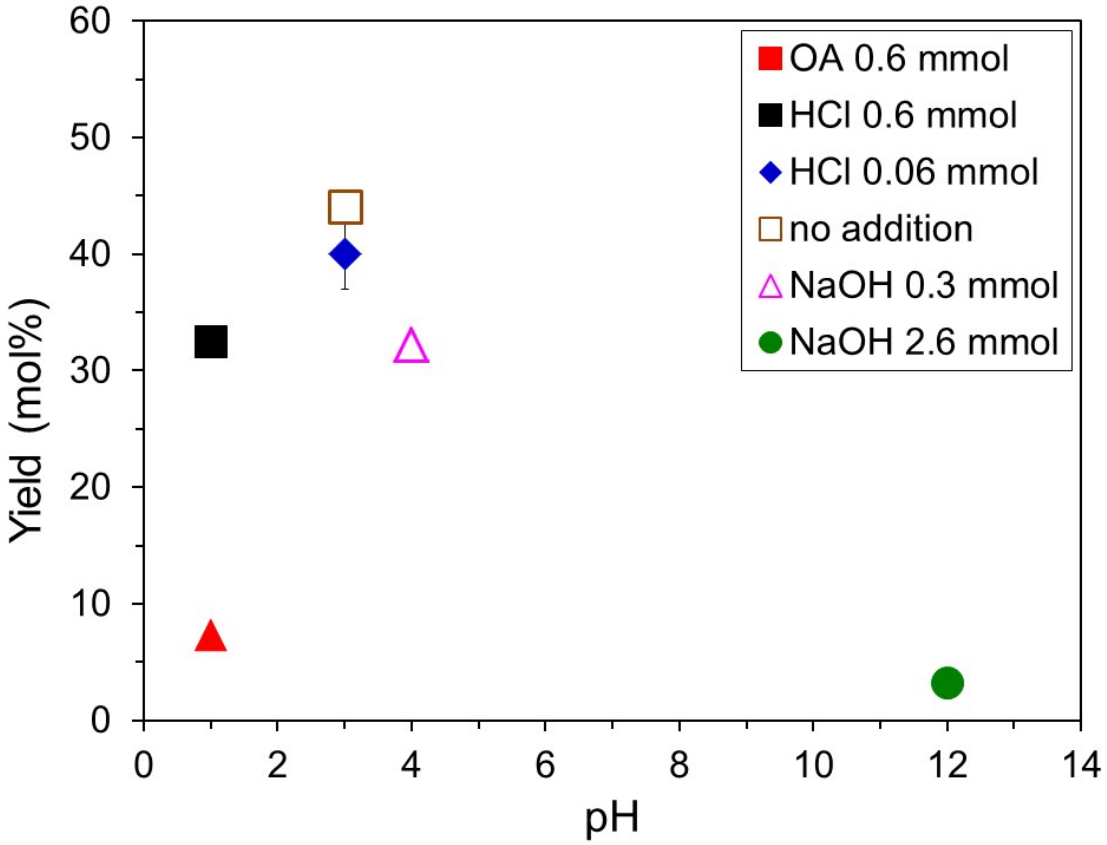


Fig. S9. Effect of pH value on the yield of LacA. Reaction conditions: 155 °C, 90 min, 2.0 wt% glucose, 0.9 wt% $SnCl_2$ and 10 g ChCl aqueous solution (40 wt%)

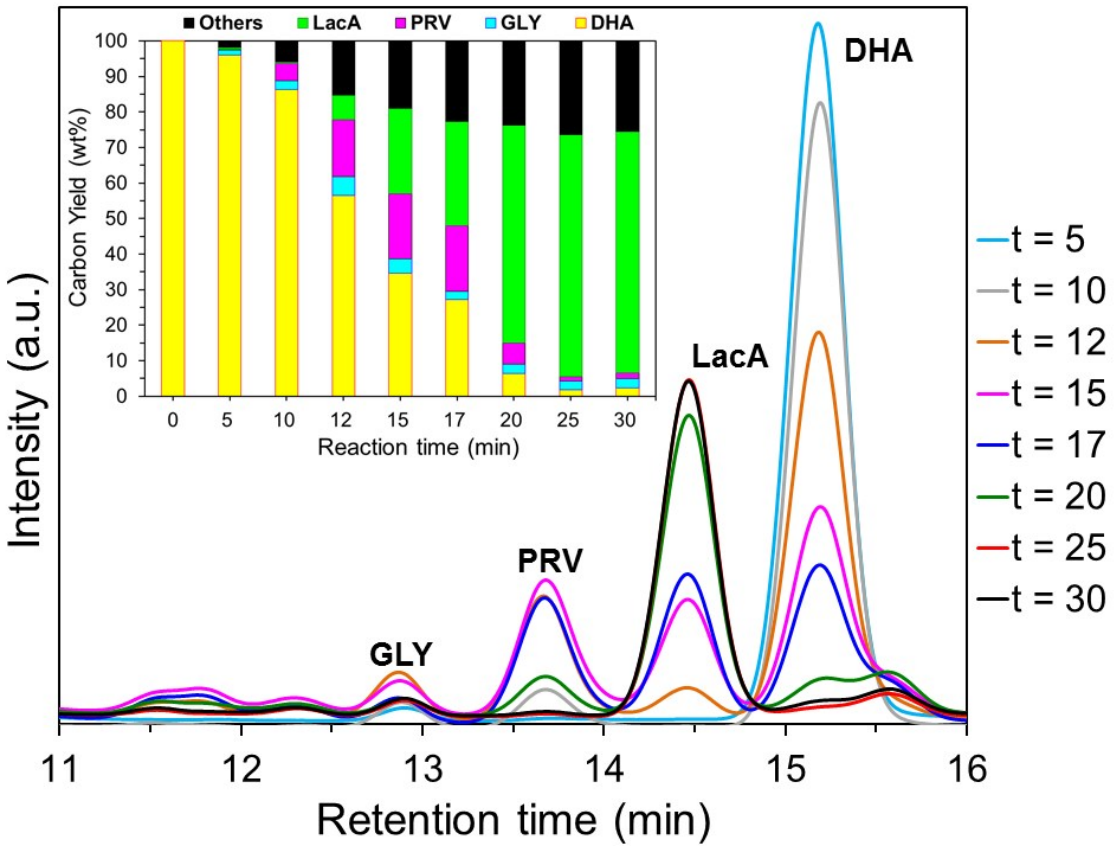


Fig. S10. Evolution of the products from DHA conversion in neat water at 110 °C during reaction time (t, minutes). GLY, PRV, LacA and DHA are the abbreviations of glyceraldehyde, pyruvaldehyde, lactic acid and dihydroxyacetone, respectively.

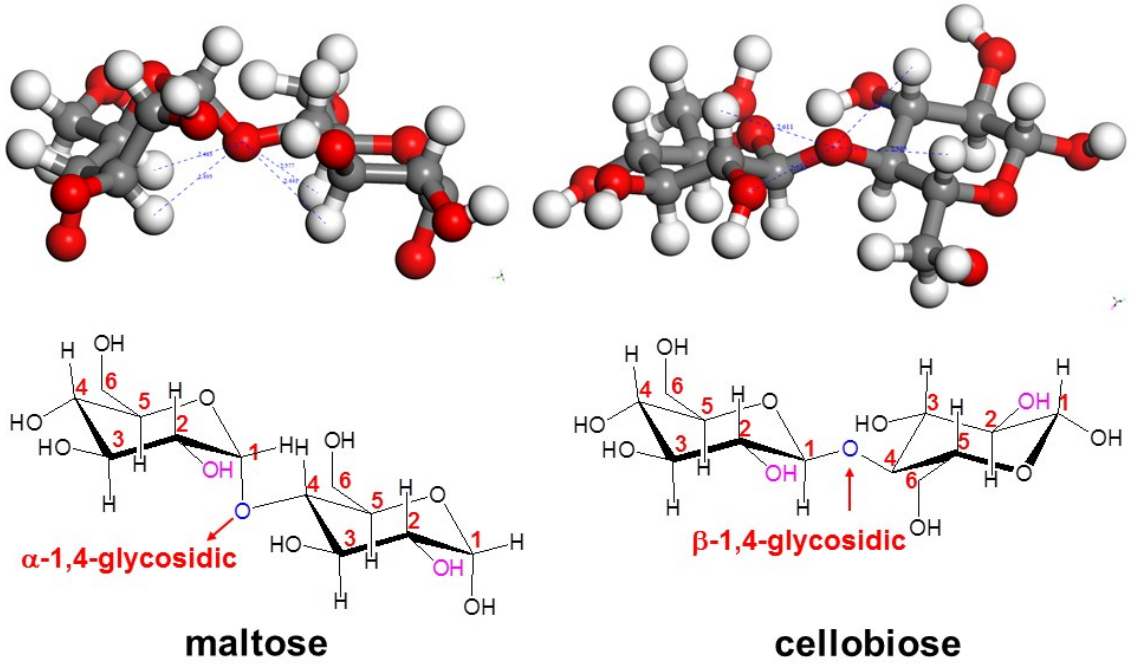


Fig. S11. The different configurations of 1,4-glycosidic bonding in maltose and cellobiose. The blue dashed lines show the possible steric hindrance around glycosidic bonding of dissacharides with the closest neighbor atoms, *i.e.* four hydrogen atoms in maltose and three hydrogen atoms with one oxygen atom of hydroxyl in cellobiose. Due to the larger atom size of oxygen compared with hydrogen, the β-1,4-glycosidic linkage of cellobiose should have more steric (blockage) hindrance than the α-1,4-glycosidic linkage of maltose.

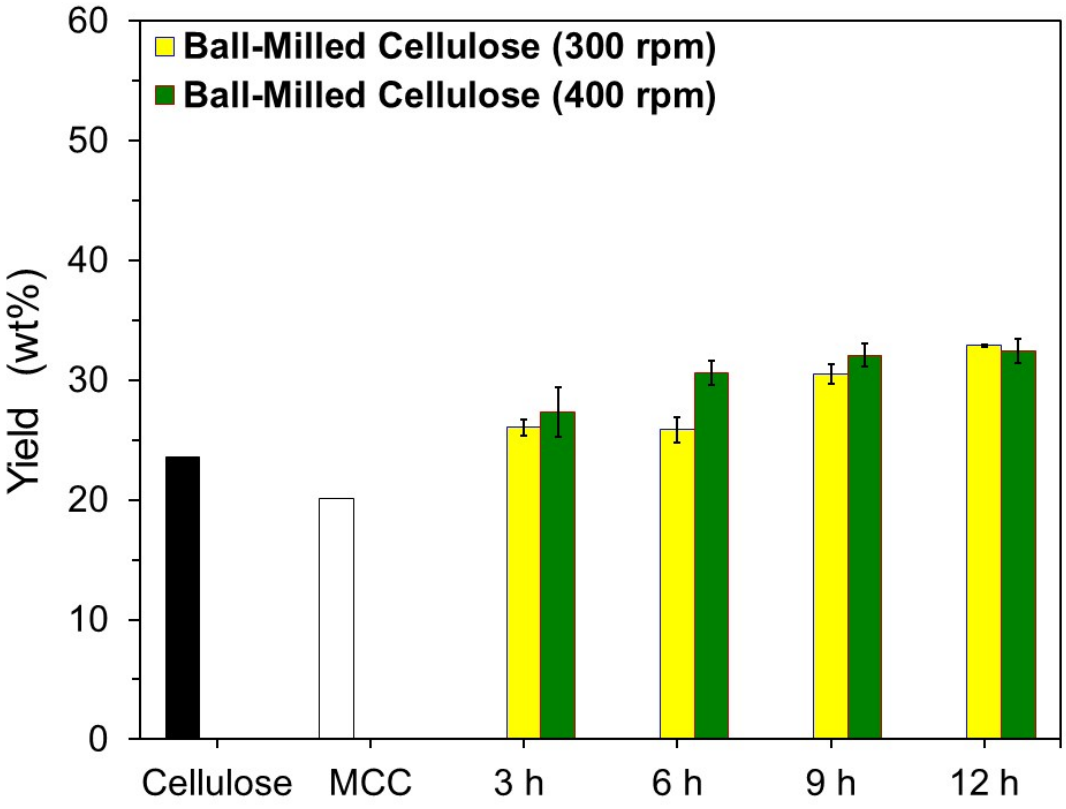


Fig. S12. Yields of LacA from untreated-cellulose, microcrystalline cellulose (MCC) and ball-milled cellulose. Reaction conditions: T = 190±5 °C, t = 90 min, 1.9wt% of glucose, 1.2wt% of $SnCl_2$ and 10 g of ChCl aqueous solution (50wt%).

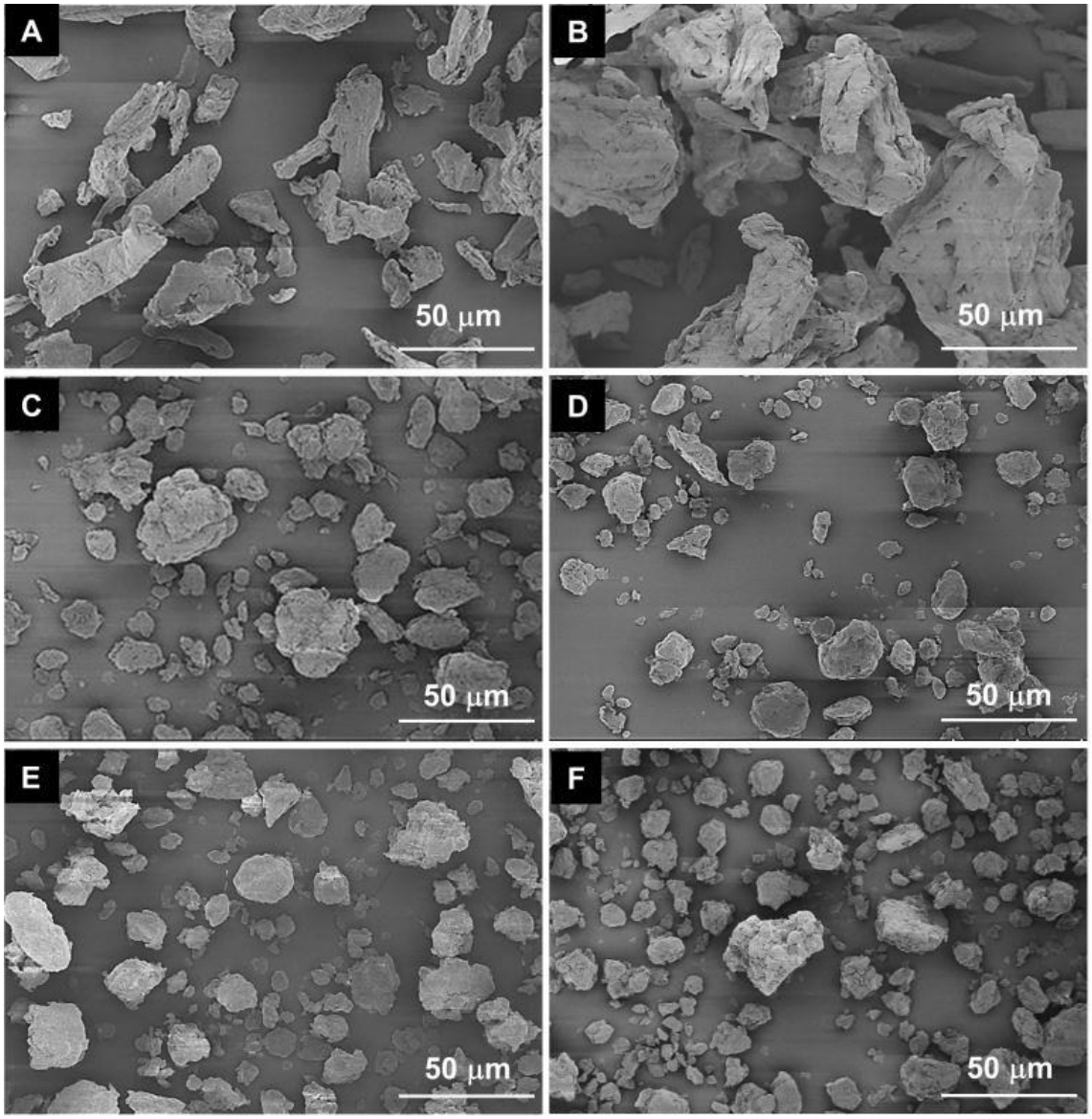


Fig. S13. Scanning electron image (SEM) of commercial cellulose (A), microcrystalline cellulose (B) and ball-milled cellulose (BMC) with various ball-milling conditions (BMC-300rpm-3h (C); BMC-400rpm-3h (D); BMC-400rpm-12h (D)).

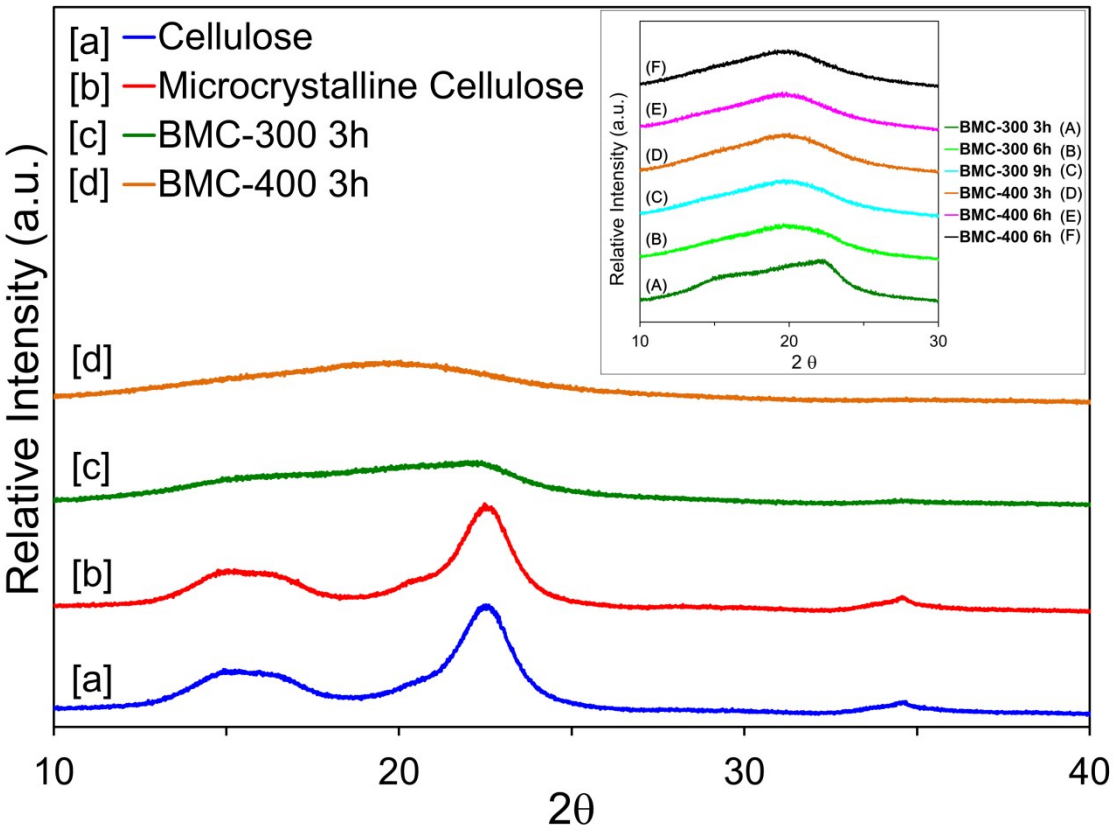


Fig. S14. XRD patterns of commercial cellulose (a), microcrystalline cellulose (b) and ball-milled cellulose (BMC) with various milling conditions (c, d). Inset figure shows the effect of milling condition on the crystallinity of cellulose.

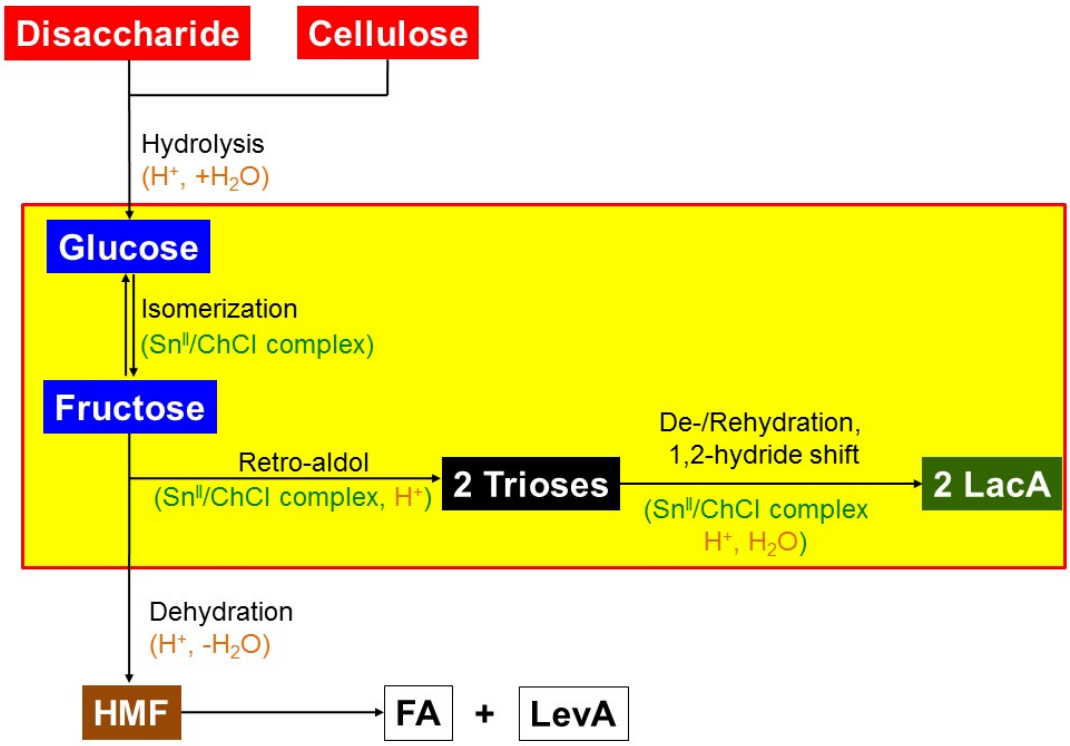


Fig. S15. The simplified reaction routes for carbohydrates transformation to LacA in ChCl aqueous solution by using $SnCl_2$ as the catalyst.

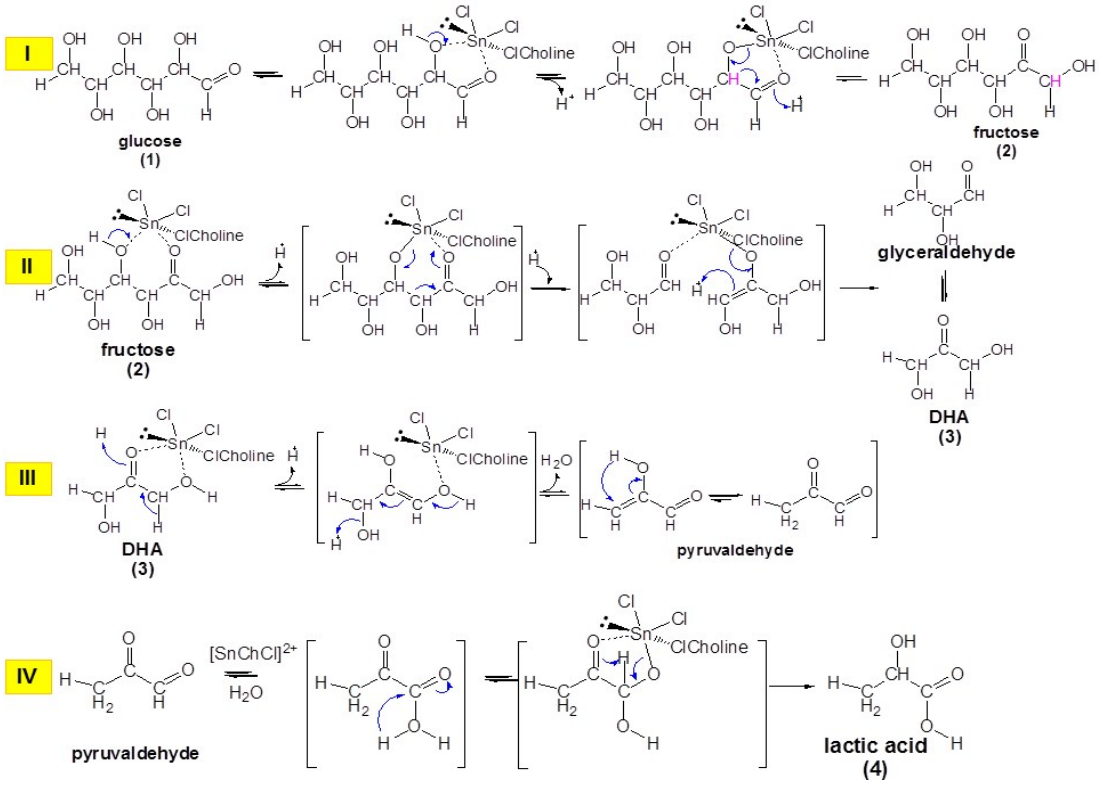


Fig. S16. The proposed reaction mechanism of LacA synthesis from glucose with $SnCl_2$/ChCl complex as the catalyst in the aqueous solution.

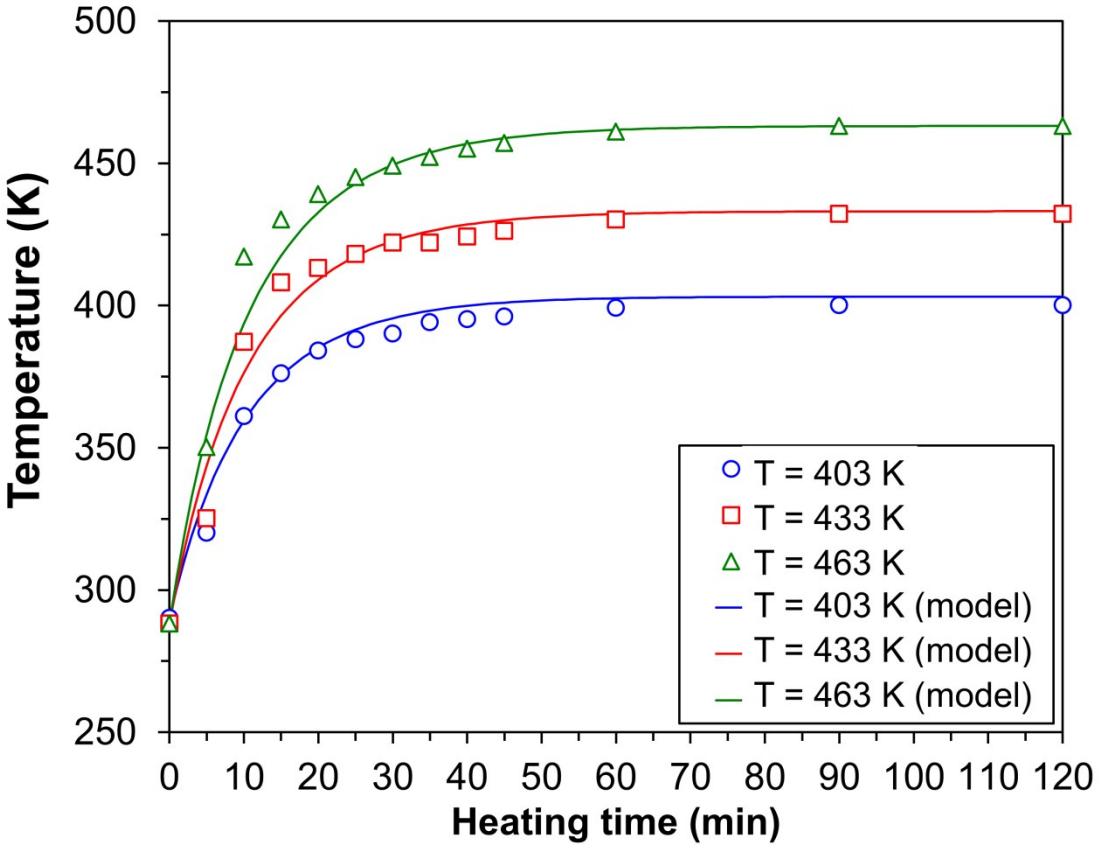


Fig. S17. The temperature profiles inside the reactor during experiment.

Table S1. Experimental design for the optimization of LacA synthesis from glucose in 50 wt% ChCl aqueous solution by using central composite design (CCD)

Run	Glucose Loading Amount	Catalyst Loading Amount	Glucose Loading Amount	Catalyst Loading Amount	Conversion	Yield
	Coded Unit		Uncoded Unit			
			(g)	(g)	(mol%)	(mol%)
1	-1	-1	0.184	0.080	100.00	38.75
2	1	-1	0.194	0.080	100.00	41.89
3	-1	1	0.184	0.150	100.00	44.04
4	1	1	0.194	0.150	97.11	36.48
5	-1.41	0	0.182	0.115	100.00	38.56
6	1.41	0	0.196	0.115	99.87	37.34
7	0	-1.41	0.189	0.066	98.59	44.59
8	0	1.41	0.189	0.164	100.00	38.46
9	0	0	0.189	0.115	100.00	46.35
10	0	0	0.189	0.115	99.84	47.66
11	0	0	0.189	0.115	100.00	47.94
12	0	0	0.189	0.115	96.79	47.70
13	0	0	0.189	0.115	100.00	46.40

The analysis was performed using uncoded units.

Estimated Regression Coefficients for Yield

Term	Coef	SE Coef	T	P
Constant	-6700	744.4	-9.000	0.000
Glucose	69521	7833.3	8.875	0.000
Catalyst	3365	743.1	4.529	0.003
Glucose*Glucose	-179675	20687.5	-8.685	0.000
Catalyst*Catalyst	-2208	422.2	-5.229	0.001
Glucose*Catalyst	-15286	3897.4	-3.922	0.006

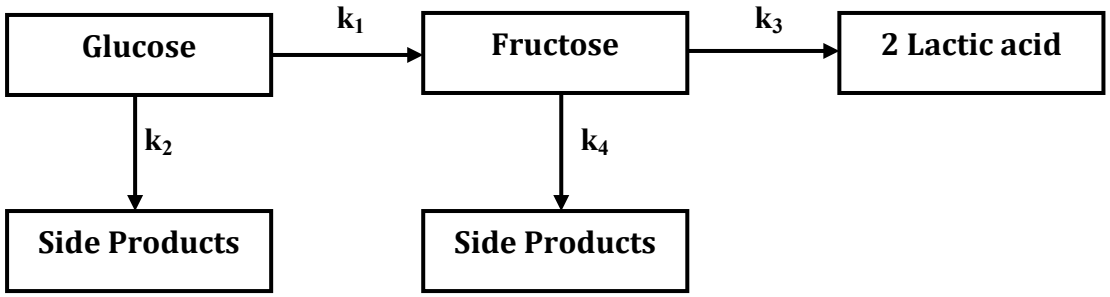
S = 1.364 R-Sq = 94.3% R-Sq(adj) = 90.21%

X-ray Crystallography

The colorless block crystals of [Choline][$SnCl_3$] were obtained by cooling the solution of $SnCl_2$ (0.35 g) dissolved in a 10 g of 50 wt% Choline chloride/water solution to 5°C. Diffraction measurements were carried out on a R-AXIS RAPID II diffractometor with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Structural analyses were performed by using Yadokari-XG for Windows.[2] The structure was solved and refined by SIR-2014 and SHELXL-2017, respectively.[3, 4] The tin, chlorine, oxygen, nitrogen, and carbon atoms were refined anisotropically. The hydrogen atoms of the choline cation were located using riding models. CCDC 1851698 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Kinetic Study

A simplified diagram scheme of LacA formation mechanism in a ChCl aquoues solution by using $SnCl_2$ as the catalyst can be described as follows:



Here, DHA is not included in the scheme due to its rapid consumption in the reaction. The isomerization of glucose to fructose is assumed as one side reaction since only trace amount of glucose was detected from fructose conversion. Meanwhile, the formations of other products such as HMF, FA, LevA and carbonaceous chemicals are also included and termed as the side products. Therefore, the reaction rate for each reaction can be defined as follows:

$$R_1 = k_1 * C_{glucose}^{p} \quad (1)$$

$$R_2 = k_2 * C_{glucose}^{q} \quad (2)$$

$$R_3 = k_3 * C_{fructose}^{r} \quad (3)$$

$$R_4 = k_4 * C_{fructose}^{s} \quad (4)$$

where p, q, r, and s are order of reactions. Meanwhile, k is reaction rate constant which is defined by using modified Arhenius equation [5]:

$$k_i = A_i e^{\left[-\frac{E_{a,i}}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right)\right]} \quad (5)$$

where A_i, $E_{a,i}$, R, T and T_r are pre-exponential factor, activation energy, gas constant (8.314 J mol^{-1}, K^{-1}) reaction temperature and the reference temperature (130 ^oC), respectively, in SI units.

Hence, the distribution profile of each component during reaction can be represented as follows:

$$\frac{dC_{glucose}}{dt} = -(R_1 + R_2) \quad (6)$$

$$\frac{dC_{fructose}}{dt} = R_1 - (R_3 + R_4) \quad (7)$$

$$\frac{dC_{lactic\ acid}}{dt} = 2\,R_3 \quad (8)$$

Here, the temperature distribution profile inside the reactor can be modeled using heat balance equation [6] and the results presented in Fig. S17:

$$\frac{dT}{dt} = \left[h * (T_m - T)\right] * \left[\frac{1}{\left(T\frac{dC_{p,mix}}{dT}\right) + C_{p,mix}}\right] \quad (9)$$

where T_m, T and h are the maximum temperature, reaction temperature and heat rate constant, respectively.

Heat capacities of pure components and their mixtures can be written as [7]:

$$C_{p,i} = a_i + b_i T + c_i T^2 + d_i T^{-2} \quad (10)$$

$$C_{p,mix} = \sum_i x_i * C_{p,i}\ ; i = 1, 2, 3, \ldots \quad (11)$$

where a, b, c, and d are heat parameters of choline chloride, glucose and water referred to our previous work[5]. The kinetic parameters such as reaction order, reaction constant, activation energy and heat transfer coefficient are determined simultaneously by the minimization of the errors between all experimental data and the model by using

MATLAB. The results are presented in Table S2 and the main reactions of this model showed good quality (R^2 >90%).

Table S2. Kinetic parameters of LacA synthesis from glucose using $SnCl_2$ catalyst in the ChCl aqueous solution.

Pre-exponential factor		**Activation energy** [kJ mol^{-1}]		**Reaction order**	
A_1 [M^{1-p} min^{-1}]	0.09	$E_{a,1}$	140.76	p	0.95
A_2 [M^{1-q} min^{-1}]	0.19	$E_{a,2}$	92.99	q	1.33
A_3 [M^{1-r} min^{-1}]	0.33	$E_{a,3}$	145.02	r	0.94
A_4 [M^{1-s} min^{-1}]	0.13	$E_{a,4}$	140.93	s	0.92
were determined at T_r = 130 ^oC					

References

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