Supporting Information for the Paper entitled

Tin-Catalyzed Conversion of Biomass-Derived Triose Sugar and Formaldehyde to (±)-α-Hydroxy-γ-Butyrolactone

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A. General Techniques

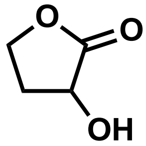
Proton (^{1}H) nuclear magnetic resonance (NMR) spectrum was recorded in $CDCl_3$ or methanol-d_4 with an AVANCE 400 spectrometer operated at 400 MHz. A Shimadzu QP5000 equipped with DB-1 column was used for GC-MS analysis. Materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., and Aldrich Inc and were used without further purification.

The reaction products were identified by ^{1}H nuclear magnetic resonance (NMR) and gas chromatography-mass spectrometry (GC-MS). The conversion and product yields were determined by ^{1}H NMR analysis.

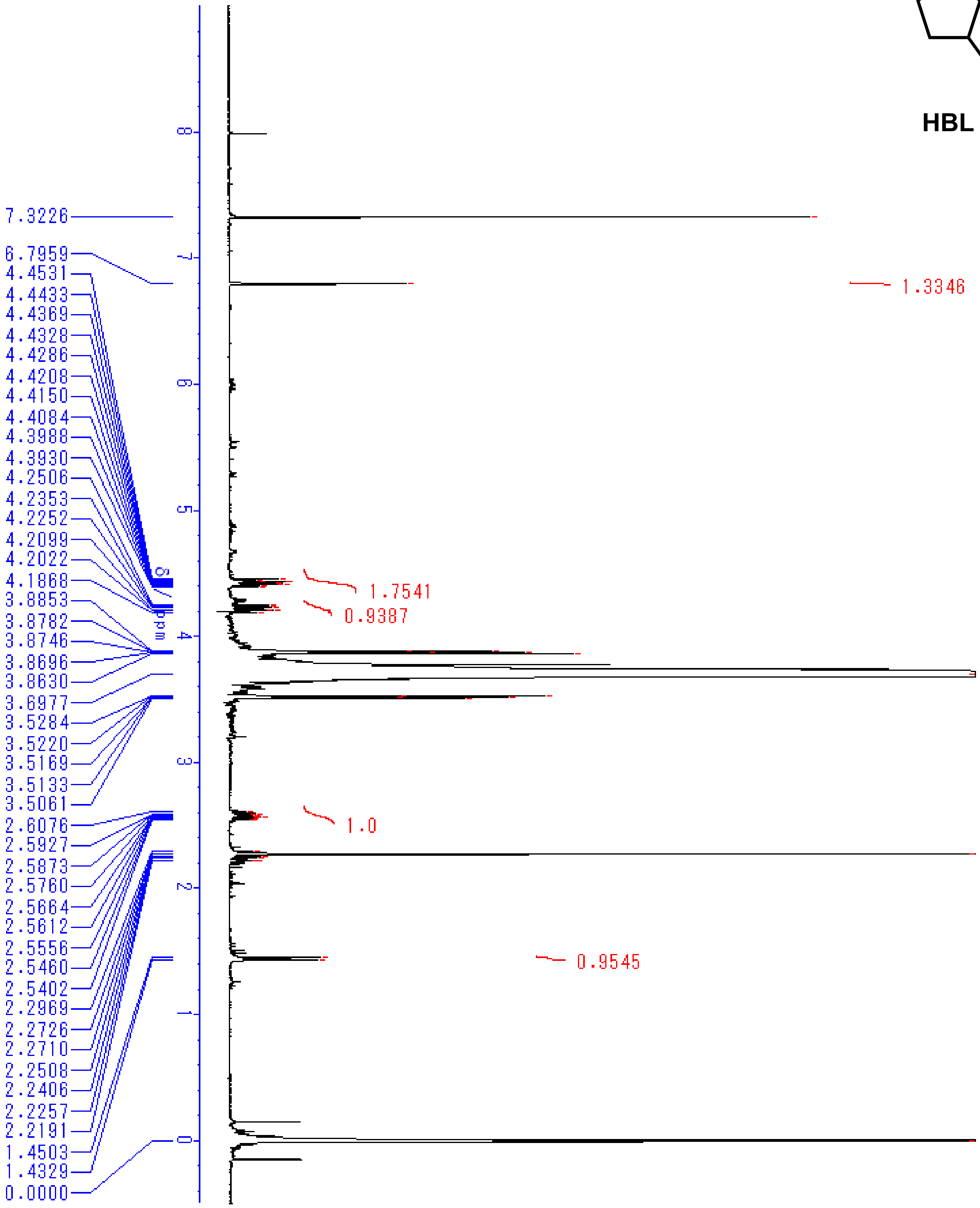
B, Typical Procesure of HBL (2)

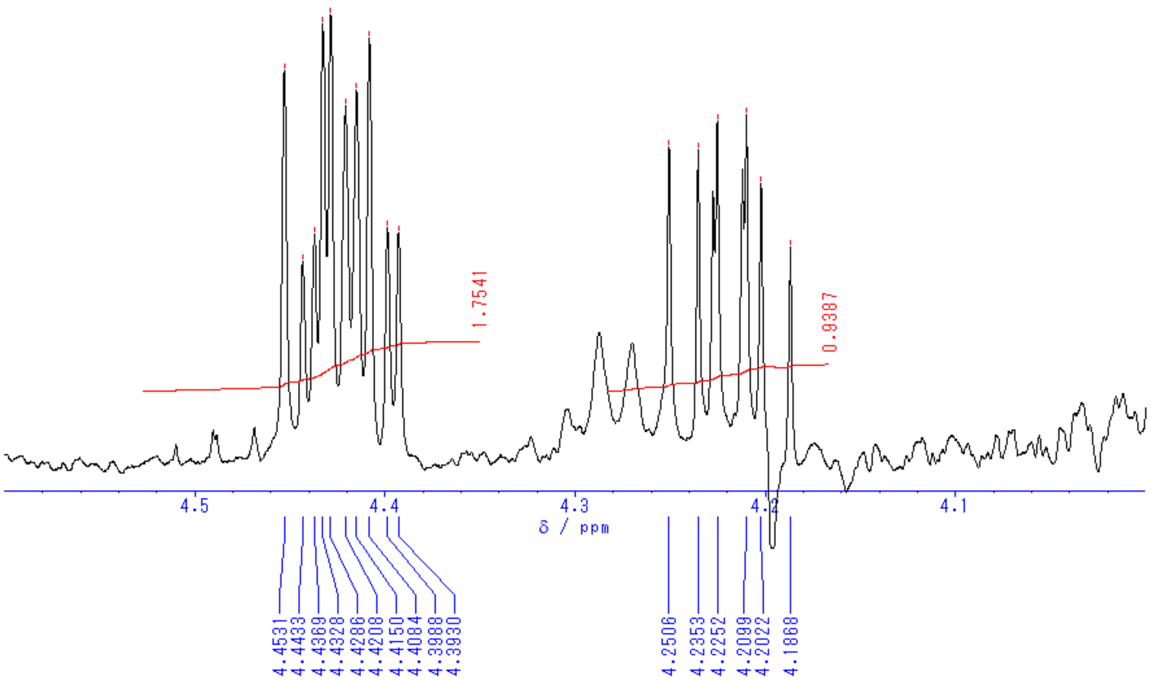
(Table 1 entry 4): A 50 cm^3 stainless-steel autoclave equipped with a magnetic bar was charged with 1,3-dihydroxyacetone (113 mg, 1.25 mmol), paraformaldehyde (39.4 mg, 1.31 mmol), 1,4-dioxane (4.0 mL), H_2O (1.11 mmol) and $SnCl_4$ (37.3 mg, 0.171 mmol) at room temperature, then filled with argon. After being stirred at 140 ^oC for 3 h under argon, reaction mixture was cooled down to room temperature, then 1,3,5-Trimethylbenzene (43.8 mg, 0.365 mmol) was used as an internal standard.

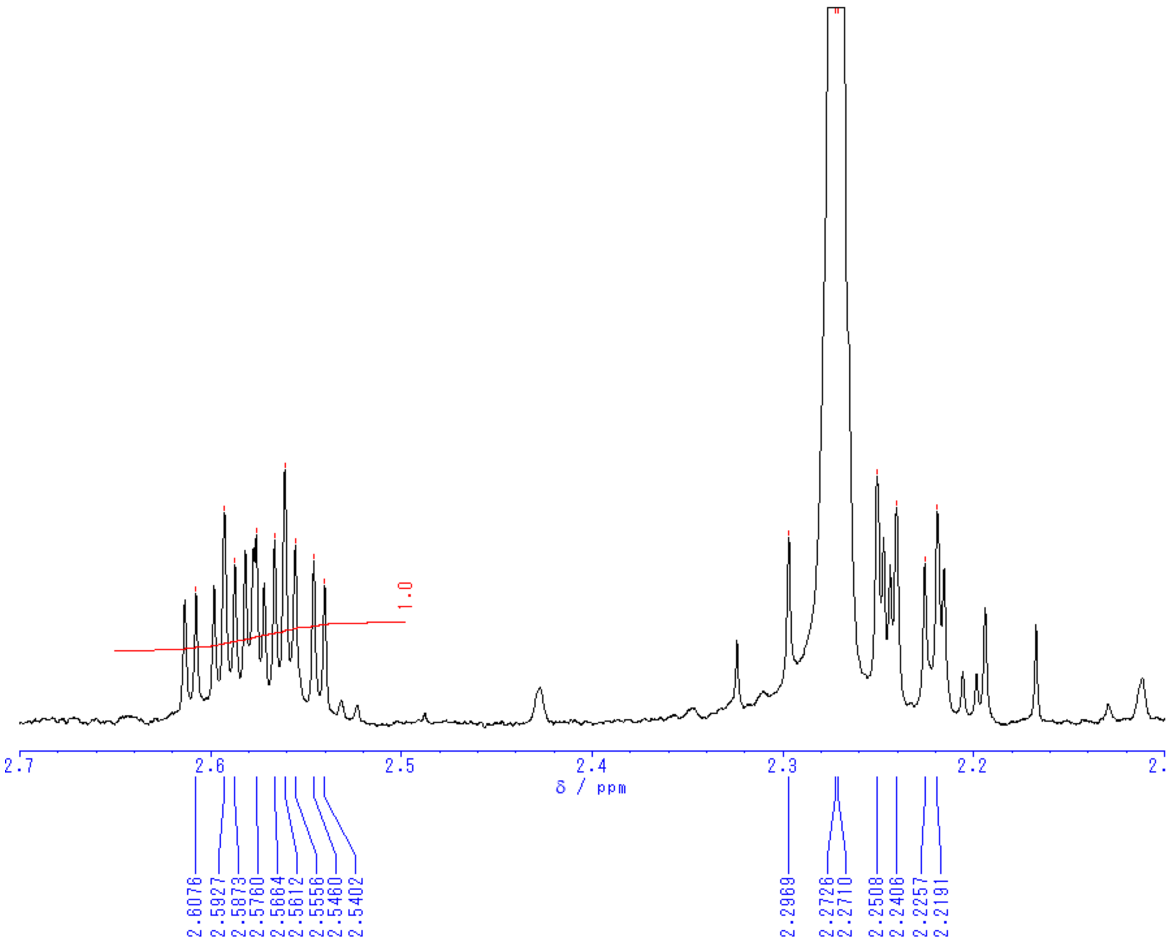
C, ^{1}H NMR chart of the reaction mixture (Table 1, entry 4)



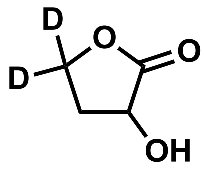
HBL (2)



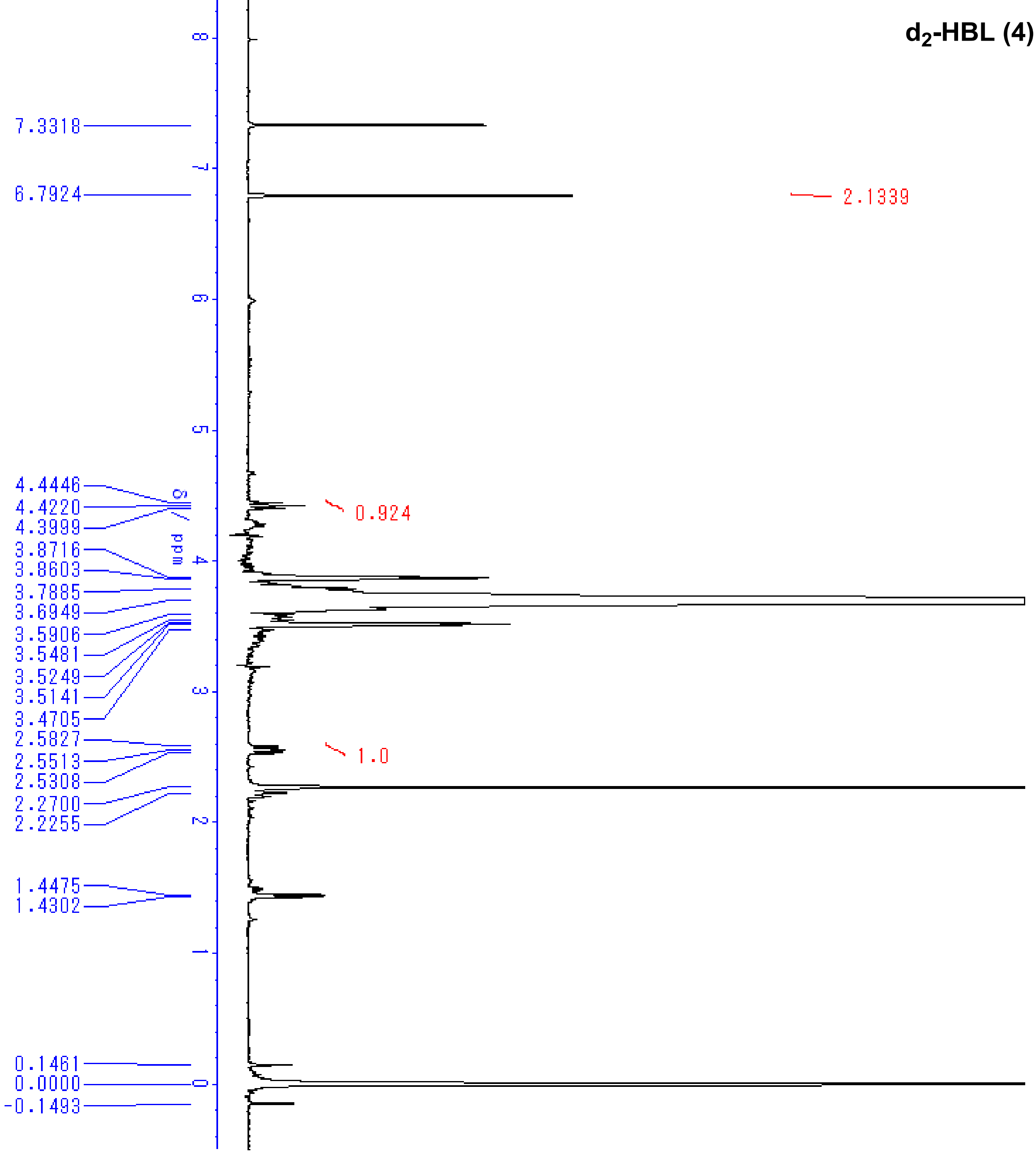

1.7541
0.9387
4.5
4.4
4.3
4.2
4.1
δ / ppm
4.4531
4.4433
4.4369
4.4328
4.4286
4.4208
4.4150
4.4084
4.3988
4.3930
4.2506
4.2353
4.2252
4.2099
4.2022
4.1868

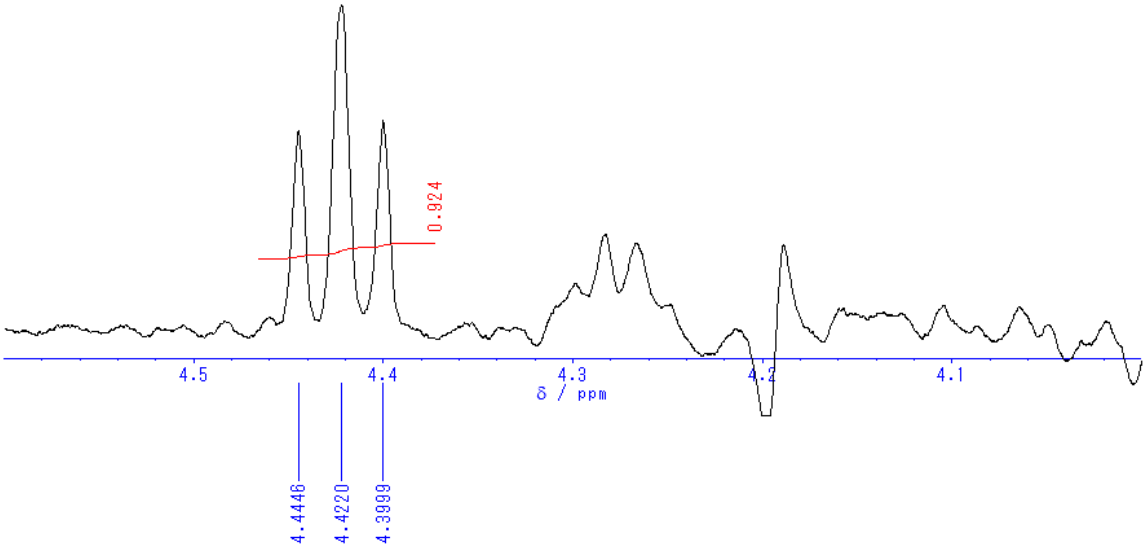

1.0
2.7
2.6
2.5
2.4
2.3
2.2
2.1
δ / ppm
2.6076
2.5927
2.5873
2.5760
2.5664
2.5612
2.5556
2.5460
2.5402
2.2969
2.2726
2.2710
2.2508
2.2406
2.2257
2.2191

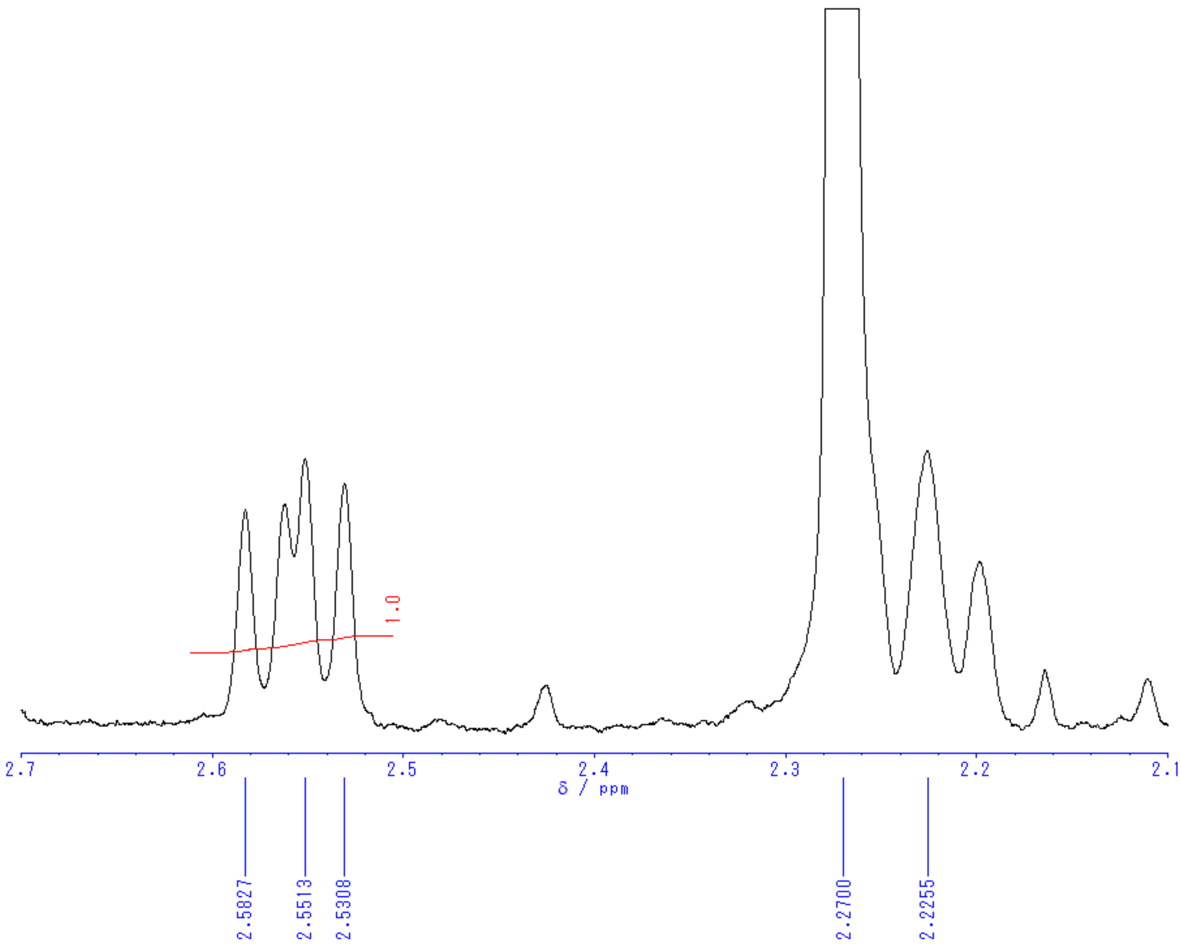
D, ^{1}H NMR chart of the reaction mixture (Scheme 1)



d$_2$-HBL (4)




0.924
4.5
4.4
4.3
4.2
4.1
δ / ppm
4.4446
4.4220
4.3999


1.0
2.7
2.6
2.5
2.4
2.3
2.2
2.1
δ / ppm
2.5827
2.5513
2.5308
2.2700
2.2255

E, The Optimization of the Reaction Consitions

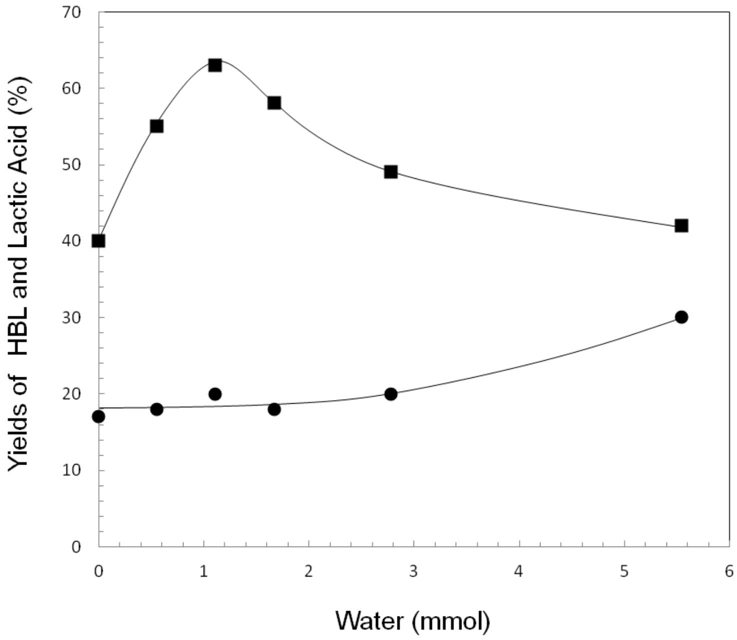


Fig. S1 The effect of the amount of water on yields of HBL (**2**) and lactic acid (**3**). ■:HBL (**2**), ●:lactic acid (**3**). Reaction conditions: DHA (**1**) (1.25 mmol), paraformaldehyde (1.31 mmol), tin (IV) chloride (0.171 mmol), 1,4-dioxane (4.0 mL), Ar, 3 h, 140 ^{o}C. Using an internal standard technique. Yield was based on **1**. The conversion of **1** was >99%.

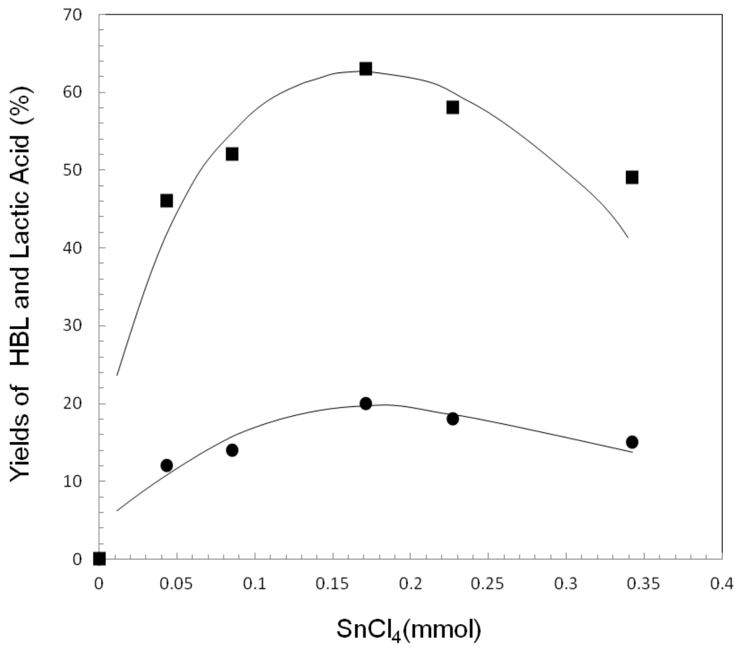


Fig. S2 The effect of the amount of $SnCl_4$ on yields of HBL (**2**) and lactic acid (**3**). ■:HBL (**2**), ●:lactic acid (**3**). Reaction conditions: DHA (**1**) (1.25 mmol), paraformaldehyde (1.31 mmol), water (0.111 mmol), 1,4-dioxane (4.0 mL), Ar, 3 h, 140 ^{o}C. Using an internal standard technique. Yield was based on **1**. The conversion of **1** was >99%.

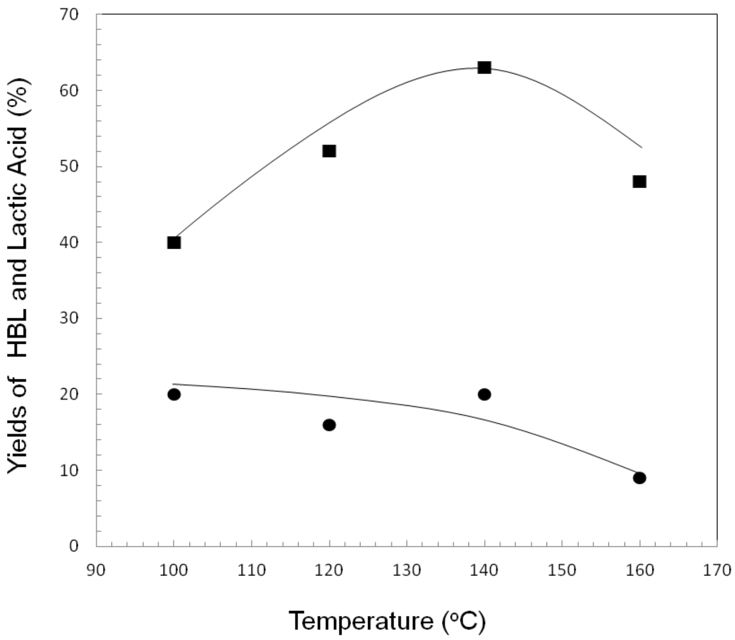


Fig. S3 The effect of the reaction temperature on yields of HBL (**2**) and lactic acid (**3**). ■:HBL (**2**), ●:lactic acid (**3**). Reaction conditions: DHA (**1**) (1.25 mmol), paraformaldehyde (1.31 mmol), tin (IV) chloride (0.171 mmol), water (0.111 mmol), 1,4-dioxane (4.0 mL), Ar, 3 h. Using an internal standard technique. Yield was based on **1**. The conversion of **1** was >99%.

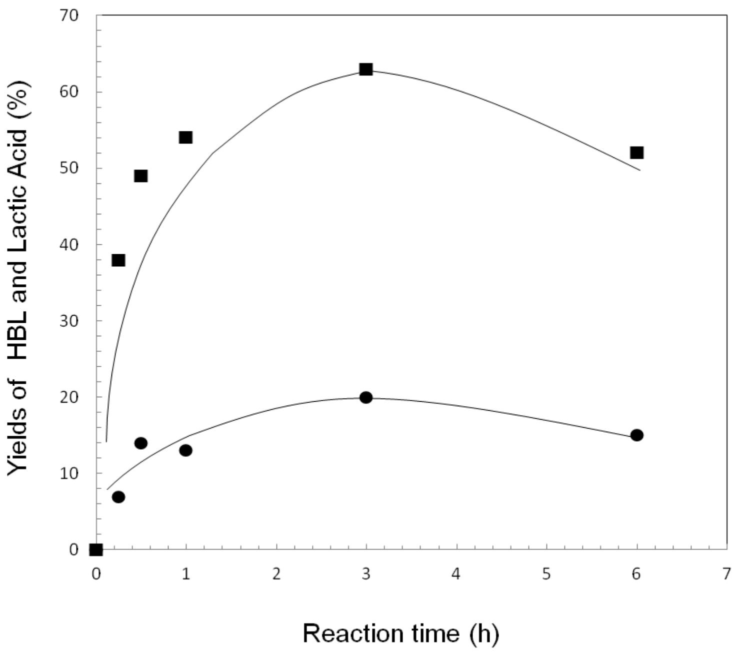


Fig. S4 The effect of the reaction time on yields of HBL (**2**) and lactic acid (**3**). ■:HBL (**2**), ●:lactic acid (**3**). Reaction conditions: DHA (**1**) (1.25 mmol), paraformaldehyde (1.31 mmol), tin (IV) chloride (0.171 mmol), water (0.111 mmol), 1,4-dioxane (4.0 mL), Ar, 140 °C. Using an internal standard technique. Yield was based on **1**. The conversion of **1** was >99%.