

Supplementary Information

One-pot cascade production of 2,5-diformylfuran from glucose over catalysts from renewable resources

Mei Hong,* Yuxiang Liu, Haidi Sun, Liping He, Junkai Zhu, Huixian Wang, Shifa Wang and
Licheng Li*

Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources,

International Innovation Center for Forest Chemicals and Materials, College of Chemical

Engineering, Nanjing Forestry University, Nanjing, 210037, China

E-mail: hongmei-613@njfu.edu.cn

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Section 1. Acidity Titration Characterization

The content of $-\text{SO}_3\text{H}$ group ($c_{\text{SO}_3\text{H}}$) was measured as follows: the catalyst (250 mg) was added into an aqueous solution of sodium chloride (0.05 M, 30 mL); the mixture was stirred for 1 h at room temperature under ultrasonic vibration; after centrifugation, an aqueous solution of sodium hydroxide (0.05 M) was used to titrate the supernatant solution with phenolphthalein as the indicator. Subsequently, the content of both $-\text{SO}_3\text{H}$ and $-\text{COOH}$ groups ($c_{\text{SO}_3\text{H} + \text{COOH}}$) was measured as follows: the catalyst (250 mg) was added to an aqueous solution of sodium bicarbonate (0.05 M, 30 mL); the mixture was stirred for 1 h at room temperature under ultrasonic vibration; after centrifugation, the supernatant solution was titrated by hydrochloric acid (0.05 M) using phenolphthalein as the indicator. Finally, the content of total functional groups ($c_{\text{SO}_3\text{H} + \text{COOH} + \text{OH}}$) was measured as follows: the catalyst (250 mg) was added to an aqueous solution of sodium hydroxide (0.05 M, 30 mL); the mixture was stirred for 1 h at room temperature under ultrasonic vibration; after centrifugation, the supernatant solution was titrated by hydrochloric acid (0.05 M) using phenolphthalein as the indicator. The content of every functional group was based on the average value of three parallel titrations, calculated according to the following equations:

$$c_{\text{COOH}} = c_{\text{SO}_3\text{H} + \text{COOH}} - c_{\text{SO}_3\text{H}} \quad (1)$$

$$c_{\text{OH}} = c_{\text{SO}_3\text{H} + \text{COOH} + \text{OH}} - c_{\text{SO}_3\text{H} + \text{COOH}} \quad (2)$$

Section 2. Kinetics of the reaction of glucose

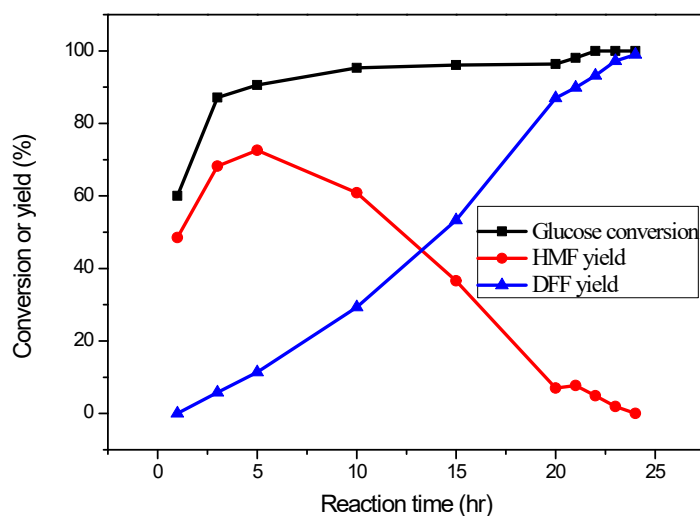


Fig. S1. Kinetics of the reaction of glucose.

Section 3. General information

All reagents were used without further purification. Fructose and DMSO were purchased from Sigma Aldrich. Sn-Mont was prepared in our laboratory. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVIII-600M spectrometers at 600 and 150 MHz. Chemical shift values are reported in ppm from tetramethylsilane as the internal standard (TMS: δ 7.26 for ^1H and δ 77.16 for ^{13}C).

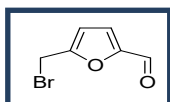
Section 4. Procedure for the synthesis of MSMFC from fructose

A solution of fructose (7 g) in DMSO (15 mL) was refluxed at 180 °C for 24 h with stirring in the presence of Sn-Mont (3 g). The reaction was monitored by quantitative HPLC analysis with an external standard. Once the highest yield of MSMFC was achieved, the reaction mixture was cooled to room temperature and filtered to separate the catalyst. Catalyst bed was washed with dichloromethane (200 mL), and further the mother liquor was washed with copious amounts of water. The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum to a small volume. The resulting concentrated solution was purified by column chromatography (15:1,

petroleum ether/ethyl acetate) to obtain brown liquid 0.85 g (14% yield).

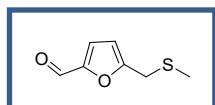
Section 5. Characterization data

5-(bromomethyl)furan-2-carbaldehyde



¹H NMR (600 MHz, CDCl₃): δ 9.60 (s, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 6.57 (d, *J* = 3.5 Hz, 1H), 4.47 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 177.6, 156.1, 152.7, 121.9, 112.0, 21.5.

5-methylsulfanylmethyl-furan-2-carbaldehyde



¹H NMR (600 MHz, CDCl₃): δ 9.50 (s, 1H), 7.15 (d, *J* = 3.54 Hz, 1H), 6.38 (d, *J* = 3.54 Hz, 1H), 3.66 (s, 2H), 2.06 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 177.2, 159.2, 152.3, 122.8, 110.3, 30.3, 15.7.

Section 6. ^1H NMR and ^{13}C NMR Spectra

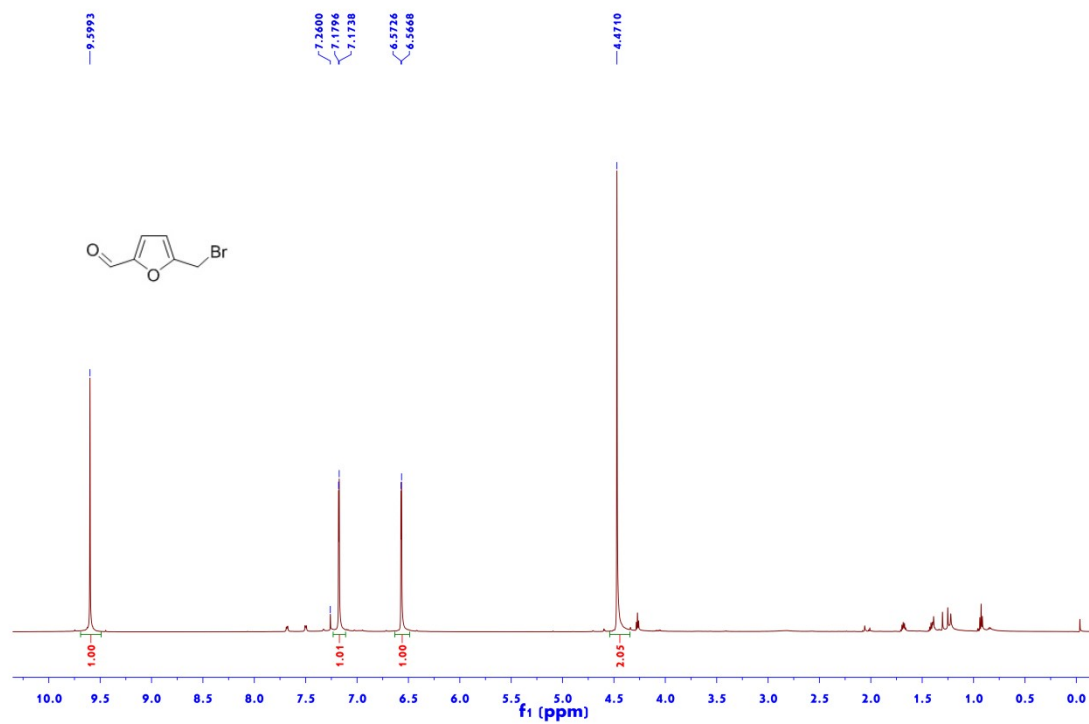


Fig. S2. ^1H NMR spectra of 5-(bromomethyl)furan-2-carbaldehyde

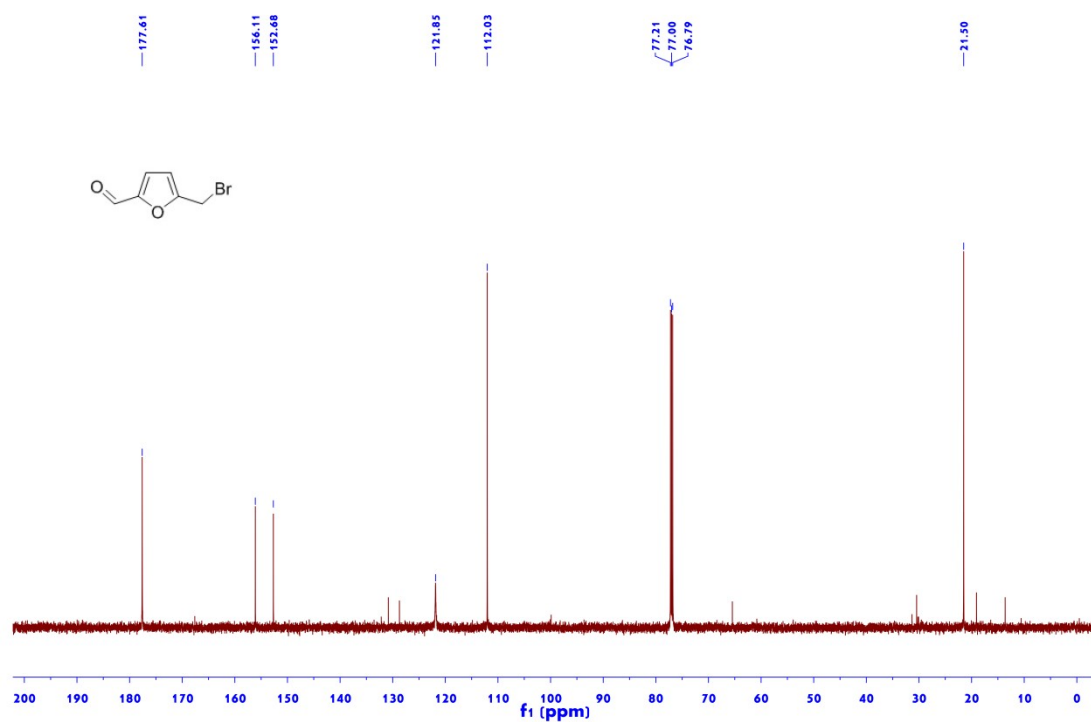


Fig. S3. ^{13}C NMR spectra of 5-(bromomethyl)furan-2-carbaldehyde

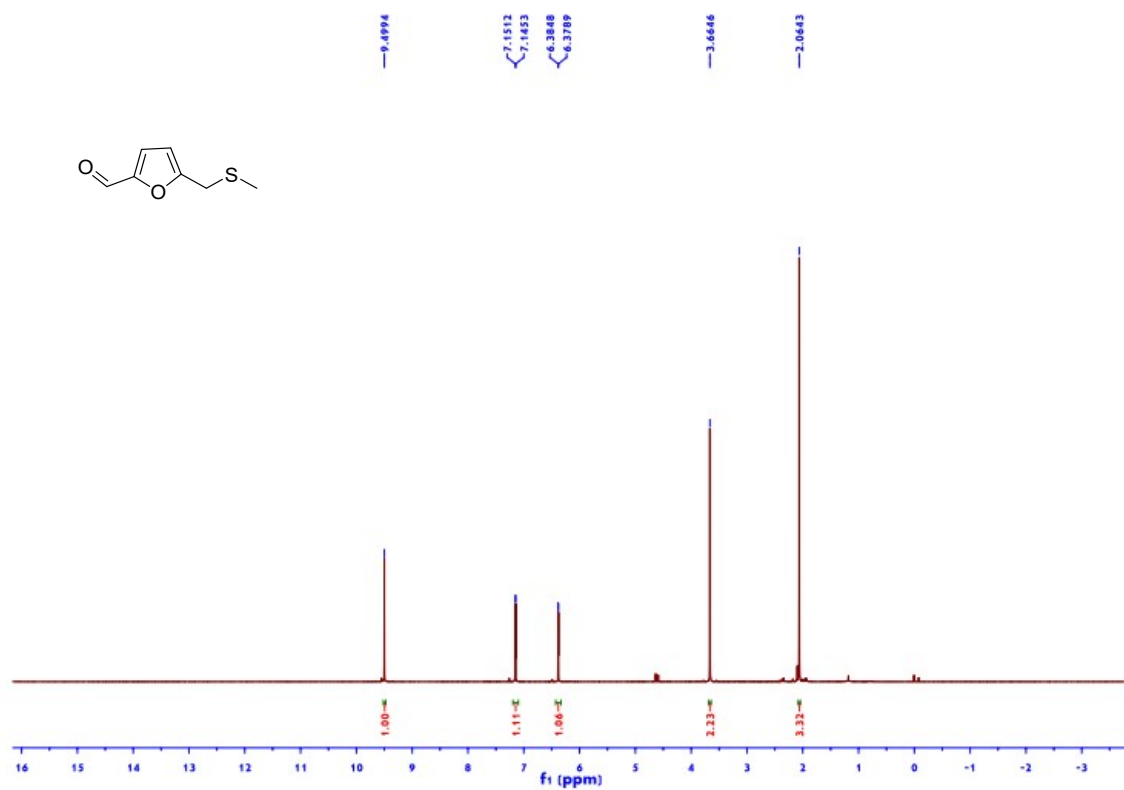


Fig. S4. ¹H NMR spectra of 5-methylsulfanylmethyl-furan-2-carbaldehyde

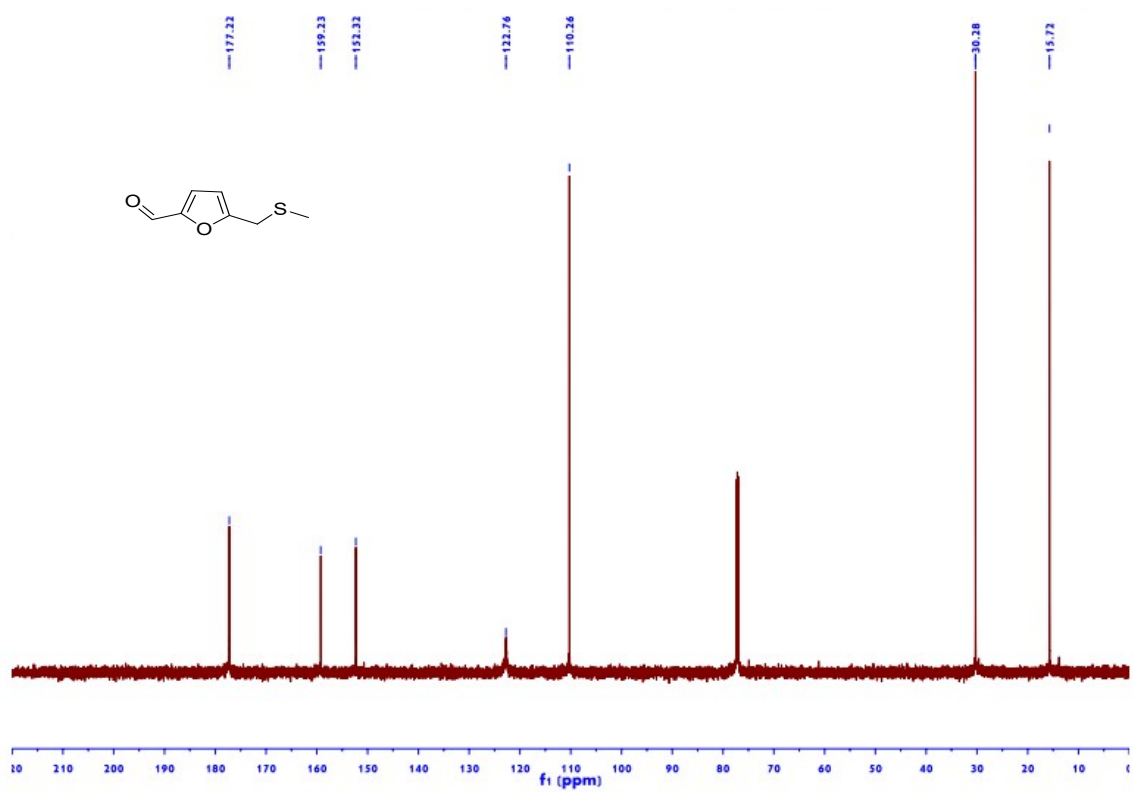


Fig. S5. ^{13}C NMR spectra of 5-methylsulfanylmethyl-furan-2-carbaldehyde

Section 7. The FE-SEM/EDS images of the catalysts after using for four runs

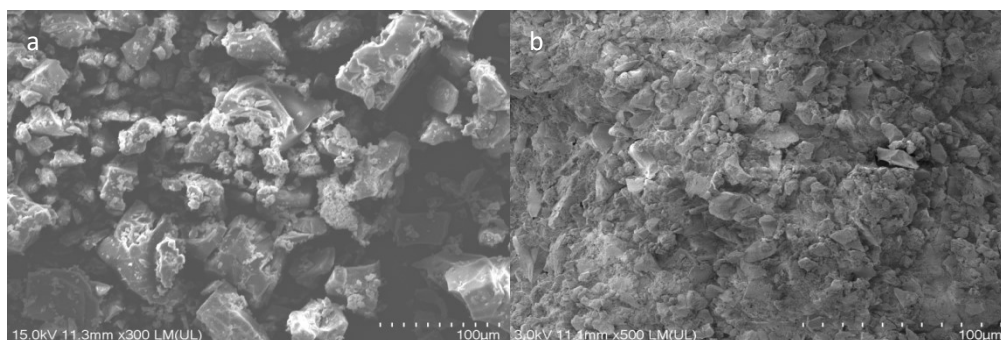


Fig. S6. The FE-SEM images of (a) $\text{Al}(\text{NO}_3)_3@\text{LH}$ and (b) $\text{Al}(\text{NO}_3)_3@\text{LH-PH}$ after using for four runs.

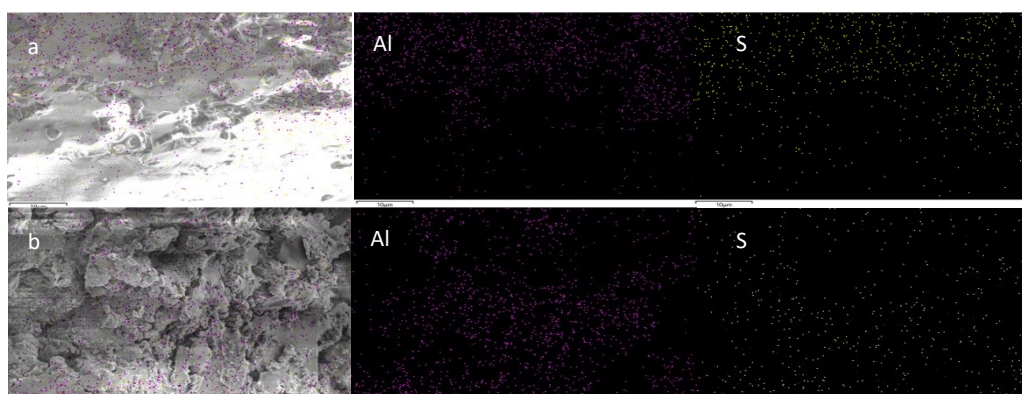


Fig. S7. EDS elemental (Al and S) mapping of (a) $\text{Al}(\text{NO}_3)_3@\text{LH}$ and (b) $\text{Al}(\text{NO}_3)_3@\text{LH-PH}$ after using for four runs.