

## Electronic Supplementary Material for

### One-pot producing diethyl maleate *via* catalytic conversion of raw lignocellulosic biomass

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<b>Experimental section</b>	S3
<b>Table S1</b> The standard equations of model compounds	S7
<b>Fig. S1</b> The volatile products in the reaction mixture detected by GC-MS	S7
<b>Table S2</b> The detail volatile products in the reaction mixture detected by GC-MS	S8
<b>Table S3</b> Selective conversion of bagasse into DEM	S9
<b>Table S4</b> The acidic properties of [BSmim]CuPW <sub>12</sub> O <sub>40</sub> and CuHPW <sub>12</sub> O <sub>40</sub>	S10
<b>Fig. S2</b> HAADF-STEM and EDS mapping images of catalysts	S10
<b>Fig. S3</b> The H <sub>2</sub> -TPR analysis of [BSmim]CuPW <sub>12</sub> O <sub>40</sub> and CuHPW <sub>12</sub> O <sub>40</sub>	S11
<b>Fig. S4</b> Effect of catalyst dosage on the bagasse conversion	S12

<b>Fig. S5</b> Effect of reaction time on the conversion of bagasse at 140 °C	S12
<b>Fig. S6</b> Effect of reaction time on the conversion of bagasse at 150 °C	S13
<b>Fig. S7</b> Effect of reaction time on the conversion of bagasse at 160 °C	S13
<b>Fig. S8</b> Effect of reaction time on the conversion of bagasse at 170 °C	S14
<b>Fig. S9</b> Recycle performances of [BSmim]CuPW <sub>12</sub> O <sub>40</sub> catalyst	S15
<b>Table S5</b> The recycle performances of [BSmim]CuPW <sub>12</sub> O <sub>40</sub> catalyst	S15
<b>Fig. S10</b> <sup>1</sup> H-NMR spectra of [BSmim]CuPW <sub>12</sub> O <sub>40</sub> catalyst	S16
<b>Fig. S11</b> <sup>13</sup> C-NMR spectra of [BSmim]CuPW <sub>12</sub> O <sub>40</sub> catalyst	S17
<b>Fig. S12</b> FT-IR spectra of [BSmim]CuPW <sub>12</sub> O <sub>40</sub> catalyst	S18
<b>Fig. S13</b> Thermogravimetric curves of POM-IL in the range of 40-650 °C	S19
<b>Table S6</b> Selective conversion of various lignocellulose to DEM	S20
<b>Table S7</b> The elemental analysis of lignocellulose	S21
<b>Table S8</b> The carbon yield of DEM from various lignocellulose	S21
<b>Fig. S14</b> The conversion of bagasse lignin to DEM in this process	S22
<b>Fig. S15</b> The conversion of <i>p</i> -hydroxybenzaldehyde to DEM in this process	S22
<b>Fig. S16</b> The conversion of vanillin to DEM in this process	S23
<b>Fig. S17</b> The conversion of syringaldehyde to DEM in this process	S23
<b>Fig. S18</b> The conversion of microcrystalline cellulose to DEM in this process	S24
<b>Fig. S19</b> The conversion of α-cellulose to DEM in this process	S24
<b>Fig. S20</b> The conversion of glucose to DEM in this process	S25
<b>Fig. S21</b> The conversion of xylose to DEM in this process	S25
<b>Fig. S22</b> The conversion of HMF to DEM in this process	S26

<b>Fig. S23</b> The conversion of furfural to DEM in this process	S26
<b>Fig. S24</b> The conversion of levulinic acid to DEM in this process	S27
<b>Notes and references</b>	S28

## 1. Experimental section

### 1.1 Materials

1,4-butane sultone (analytical grade) was purchased from Acros (Belgium). *N*-methylimidazole,  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 5\text{H}_2\text{O}$ ,  $\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2\cdot\text{H}_2\text{O}$ ,  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ , and  $\text{Na}_2\text{CO}_3$  were all purchased from Guangzhou Jinhuada Chemical Reagents Factory Co., Ltd and used without further purification. Lignocellulose model compounds, such as glucose, xylose, HMF, maleic acid, succinic acid and levulinic acid were all purchased from J&K. Bagasse lignin was extracted from raw lignocellulose (bagasse, 10.0 g) using 150 mL 80% v/v aqueous ethanol solution (containing 1.0 g of 98% sulfuric acid) at 120 °C for 4 h following the literature procedure.<sup>1</sup> The preparation of polyoxometalate ionic liquids (IL) were according to our previous report.<sup>2</sup>

### 1.2 Procedure for catalytic conversion of lignocellulose/model compounds and products separation

In general, 0.1 g of raw lignocellulose, 0.4 mmol of IL [BSmim]CuPW<sub>12</sub>O<sub>40</sub> catalyst (1.26 g) and 10 mL of ethanol were added in a 100 mL stainless autoclave (Lanzhou Jiatexing Industry and trade co., Ltd). The reactor was sealed, purged five times with O<sub>2</sub>, and filled to pressure of 1.0 MPa, and then was put into an oil bath preheated to the required reaction temperature and kept for designed time, while being agitated by magnetic stir at 500 rpm. After that, the reactor was quenched by ice water. The liquid and solid mixture were removed and collected after washing the reactor by ethanol for three times (5 mL × 3), then centrifuged and separated. The liquid mixture was diluted to a fixed volume of 50 mL with the addition of dimethyl phthalate as internal standard for qualitative and quantitative analysis by Gas Chromatography-Mass Spectrometer (GC-MS). The residual biomass after reaction was obtained by washing the solid mixture (5 mL × 3 of water) and drying in a vacuum for calculating the conversion of lignocellulose. Then the water phase was evaporated under a vacuum at 45 °C for recovery the IL catalyst and dried in a vacuum.

In comparative and controlling experiments, a series of lignocellulose model compounds (biomass components, monolignols, derivatives and potential molecular fragments from biomass) were tested under the same procedures as that for raw lignocellulosic biomass, *i.e.*, 0.1 g of model compound, 0.4 mmol of [BSmim]CuPW<sub>12</sub>O<sub>40</sub> catalyst and 10 mL of ethanol solvent, the conversion of cellulose and lignin were determined by the above procedures and our previous report

respectively.<sup>2</sup> Furthermore, the water phase products, such as sugars, furfurals and levulinic acid were tested by High Performance Liquid Chromatography (HPLC) and Gas Chromatography with flame ionization detector (GC-FID).

In a typical procedure of glucose isomerization, 1.0 mmol of glucose, 0.1 mmol of [BSmim]CuPW<sub>12</sub>O<sub>40</sub>/ CuHPW<sub>12</sub>O<sub>40</sub> catalyst and 10 mL of ethanol were mixed in a Teflon-lined stainless-steel autoclave. The reactor was first purged with N<sub>2</sub> for five times to displace the air and then heated to the designated temperature under stirring at 500 rpm (90-100 °C for 1 h and 110-130 °C for 0.5 h). After reaction, the mixture was cooled down to room temperature. The resulting liquid was diluted to 50 mL with water for qualitative and quantitative analysis using HPLC. The determination was performed on Hi-Plex column with a refractive index detector (RID). The column temperature was set to 65 °C and the detector temperature was 50 °C. And ultrapure water was employed as mobile phase with the flow rate of 0.6 mL min<sup>-1</sup>.

The yield and selectivity of products were calculated according to the equation (1) and (2).

$$\text{Yield (mg g}^{-1}\text{)} = \frac{W_P}{W_F} \quad \text{Eq.1}$$

$$\text{Selectivity (\%)} = \frac{W_P}{W_T} \times 100\% \quad \text{Eq.2}$$

W<sub>F</sub>: the weight of feed lignocellulose/model compound (g); W<sub>P</sub>: the weight of volatile products, which was determined by GC-FID (mg); W<sub>T</sub>: the weight of total volatile products (mg).

### 1.3 Catalyst and Product analysis

Experimental section and data analysis of XAS characterization. Cu K-edge XAS measurements were carried out at BL14W1 beamline station of Shanghai Synchrotron Radiation Facility (SSRF). XAS data were collected in fluorescence mode by using a Lytle detector. XAS data processing was conducted by following the standard analysis procedures. S02 was determined from Cu foil and was fixed when fitting the samples. Fitting range:  $3.0 \leq k (\text{\AA}^{-1}) \leq 12.0$  and  $1.0 \leq R (\text{\AA}) \leq 2.3$ . Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) was performed with a micromeritics Autochem II 2920 (Micromeritics, USA) with a thermal conductivity detector (TCD). About 100 mg samples were loaded and pretreated at 100°C in Ar for one hour, then cooled down to 50 °C and kept at this temperature with the flow rate of 30 mL min<sup>-1</sup> 10% H<sub>2</sub>/Ar for another 2 h. After that, the samples were heated

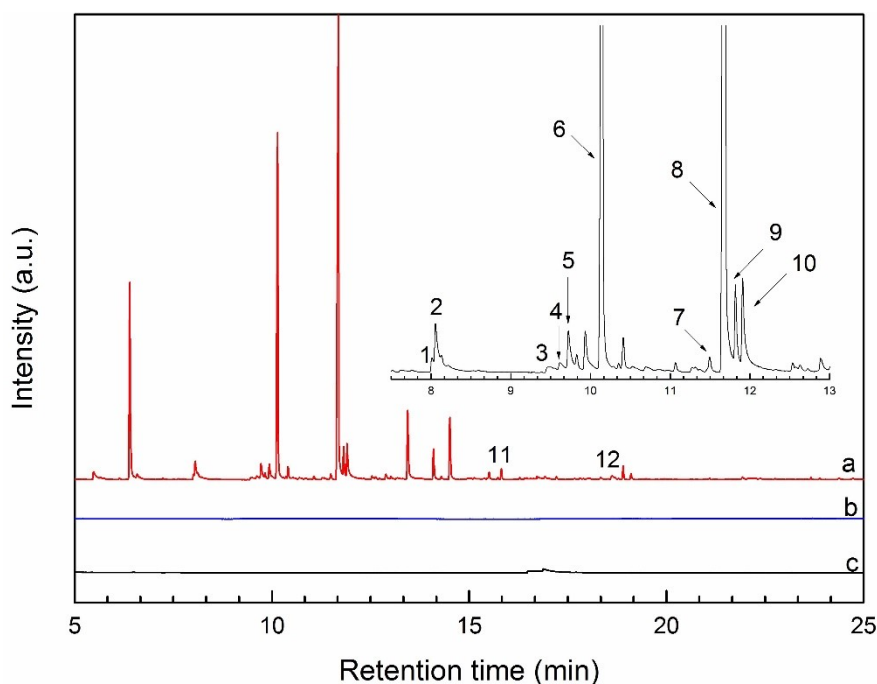
from 50 to 800 °C at the rate of 20 °C min<sup>-1</sup> and held at 800 °C for 10 min. The Pyridine-FTIR analysis of catalysts were carried out at Bruker Tensor 27. Firstly, the samples were dried at 100°C in the vacuum drying oven for 12 h, then treated in the *in-situ* infrared cell at 10<sup>-3</sup> Pa, 300 °C for 4 h and cooled down to room temperature. Secondly, the samples were loaded in the pyridine atmosphere for 0.5 h and desorption for another 0.5 h. Finally, the cell was heated to 150 °C with the rate of 10 °C min<sup>-1</sup> and kept for 1 h. The scanning range was from 1400 to 1700 cm<sup>-1</sup> with the resolution of 4 cm<sup>-1</sup>. High-angle annular dark-field scanning TEM (HAADF-STEM) and energy-dispersed spectroscopy (EDS) mapping data were acquired with a JEOL JEM-2100F electron microscope operated at 200 kV, equipped with an Oxford instruments energy-dispersive X-ray spectroscopy attachment (EDS, Oxford Inca energy X-max N 80T). <sup>1</sup>H-Nuclear magnetic resonance (<sup>1</sup>H-NMR) and <sup>13</sup>C-NMR spectra of fresh and recovered catalysts after carefully washed by ethyl acetate were taken on a Bruker AV-400 spectrometer using DMSO-*d*<sub>6</sub> as solvent. The Fourier transform infrared spectroscopy (FT-IR) of catalysts were obtained on a Bruker 27 FT-IR spectrometer in the range of 400-4000 cm<sup>-1</sup> using KBr as testing background. The thermogravimetrically property (TG) of catalysts were conducted on NETZSCH STA449C from 40 to 650 °C with the heating rate of 10 °C min<sup>-1</sup>.

The volatile products were identified by GC-MS (Agilent 5977A, GC-MS apparatus with capillary column, HP-5 MS 5% phenyl Methyl silox; 30 m × 250 μm × 0.25 μm) based on an Agilent MS library. The initial oven temperature was 50 °C (hold for 3 min), and then it was programmed to 280 °C with the rate of 8 °C min<sup>-1</sup> and hold for another 5 mins. And the quantitative analysis of these products were achieved by an Agilent 7890B Gas chromatography with a flame ionization detector (GC-FID). The same chromatography column and temperature program as the GC-MS analysis were used. And the non-volatile products and sugars were diluted with water and determined by HPLC (An Agilent 1200 equipped a RID detector and an HPX-87H column (300 × 7.8 mm, 9 μm)). Analysis was done at 65 °C, using 5 mM H<sub>2</sub>SO<sub>4</sub> eluent at 0.6 mL min<sup>-1</sup> of flow rate. The standard curves of glucose, xylose, HMF, maleic acid, succinic acid and levulinic acid were also prepared (0.1-10 mg mL<sup>-1</sup>, Table S1). and only trace amount of maleic acid and levulinic acid were detected in the mixture.

**Table S1** The standard equations of model compounds

Entry	Sample	Standard equations	R <sup>2</sup>
1	Glucose	Y=290308.2X + 6726.0	0.99978
2	Xylose	Y=269432.6X + 5719.0	0.99997
3	HMF	Y=337865.85X + 12422.2	0.99976
4	Maleic acid	Y=275490.8X + 10721	0.99977
5	Succinic acid	Y=203587.8X + 5880.7	0.99993
6	Levulinic acid	Y=201220.3X + 16783.0	0.99968

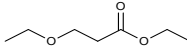
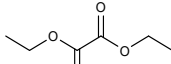
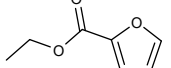
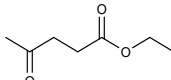
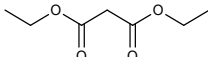
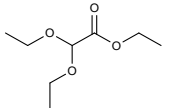
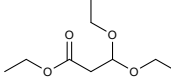
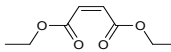
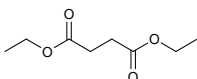
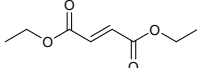
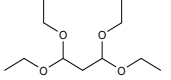
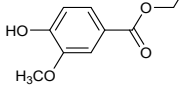
Y: peak area of HPLC; X: the concentration of products (mg mL<sup>-1</sup>).



**Fig. S1** The volatile products in the reaction mixture detected by GC-MS.

Reaction conditions: (a) 0.1 g bagasse, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 4 h, 1 MPa O<sub>2</sub>; (b) 0.1 g bagasse, 10 mL ethanol, 170 °C, 4 h, 1 MPa O<sub>2</sub>; (c) 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 4 h, 1 MPa O<sub>2</sub>.

**Table S2** The detail volatile products in the reaction mixture detected by GC-MS

Entry	Retention time (min)	Compounds	Structure	Formula	Molecular weight (g mol <sup>-1</sup> )
1	8.01	Ethyl 3-ethoxypropionate		C <sub>7</sub> H <sub>14</sub> O <sub>3</sub>	146
2	8.05	Diethyl oxalate		C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	146
3	9.41	Ethyl 3-furoate		C <sub>7</sub> H <sub>8</sub> O <sub>3</sub>	140
4	9.62	Ethyl levulinate		C <sub>7</sub> H <sub>12</sub> O <sub>3</sub>	144
5	9.72	Diethyl malonate		C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>	160
6	10.14	Ethyl diethoxyacetate		C <sub>8</sub> H <sub>16</sub> O <sub>4</sub>	176
7	11.49	Ethyl 3,3-diethoxypropionate		C <sub>9</sub> H <sub>18</sub> O <sub>4</sub>	190
8	11.69	Diethyl maleate		C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>	172
9	11.82	Diethyl succinate		C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>	174
10	11.91	Diethyl fumarate		C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>	172
11	15.82	1,1,3,3-tetraethoxypropane		C <sub>11</sub> H <sub>24</sub> O <sub>4</sub>	220
12	18.62	Ethyl vanillate		C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	196

Reaction condition: 0.1 g bagasse, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 4 h, 1 MPa O<sub>2</sub>.



**Table S3** Selective conversion of bagasse into DEM

Entry	Substrate	Catalyst	Conversion (%)	Yield (mg g <sup>-1</sup> )													DEM selectivity (%)
				1	2	3	4	5	6	7	8	9	10	11	12	Total	
1	Bagasse	— <sup>a</sup>	19.3	—	—	—	—	—	—	—	—	—	—	—	0.2	0.2	0
2	Bagasse	[BSmim]HSO <sub>4</sub>	80.4	7.0	6.9	8.0	1.4	6.0	3.3	3.8	6.6	52.8	3.5	4.6	—	103.9	6.7
3	Bagasse	[BSmim]Na <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	86.0	17.3	6.9	—	—	21.5	—	15.8	—	23.4	3.6	—	3.2	91.7	18.9
4	Bagasse	[BSmim]CuPW <sub>12</sub> O <sub>40</sub>	96.7	219.8	13.1	19.7	1.4	7.1	2.0	2.2	6.3	87.7	1.7	2.7	3.2	366.9	59.9
5	Bagasse	[BSmim]Na <sub>2</sub> PW <sub>12</sub> O <sub>40</sub> / CuSO <sub>4</sub>	97.8	88.6	6.5	6.5	—	34.1	0.8	2.8	4.8	91.6	2.8	1.6	2.7	242.8	36.5
6 <sup>b</sup>	Bagasse	CuSO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub>	88.4	6.2	—	—	—	16.5	—	—	—	40.9	1.8	—	2.3	67.7	9.2
7	Bagasse	CuHPW <sub>12</sub> O <sub>40</sub>	97.2	114.5	7.2	14.6	—	—	1.9	—	2.5	74.1	1.2	2.9	1.9	220.8	51.9
8	Microcrystalline cellulose	[BSmim]CuPW <sub>12</sub> O <sub>40</sub>	100	167.5	12.6	15.8	1.8	15.6	4.0	7.6	5.7	112.5	2.6	2.7	—	348.3	48.1
9	Microcrystalline cellulose	CuHPW <sub>12</sub> O <sub>40</sub>	100	134.4	4.3	19.0	—	—	5.0	—	—	—	24.2	—	—	186.9	71.9
10	α-cellulose	[BSmim]CuPW <sub>12</sub> O <sub>40</sub>	85.0	156.1	12.9	15.2	0.9	14.3	3.4	7.8	4.9	111.1	2.7	3.0	—	332.3	47.0
11	α-cellulose	CuHPW <sub>12</sub> O <sub>40</sub>	93.4	121.9	3.4	14.3	—	—	2.8	—	—	34.2	—	—	—	176.6	69.0
12	Glucose	[BSmim]CuPW <sub>12</sub> O <sub>40</sub>	100	189.6	13.9	23.8	—	14.7	3.0	3.1	3.6	114.4	2.8	3.7	—	372.6	50.9
13	Glucose	CuHPW <sub>12</sub> O <sub>40</sub>	100	145.9	2.4	17.5	—	—	—	—	—	12.6	34.4	—	—	212.8	68.6
14	Xylose	[BSmim]CuPW <sub>12</sub> O <sub>40</sub>	100	213.9	14.4	25.5	—	6.9	—	—	3.6	117.9	3.0	4.0	—	389.2	55.0
15	Xylose	CuHPW <sub>12</sub> O <sub>40</sub>	100	171.9	4.5	17.7	—	—	1.5	—	—	22.6	24.5	—	—	242.7	70.8

Reaction condition: 0.1 g bagasse, 0.4 mmol catalyst, 10 mL 100% ethanol, 170 °C, 4 h, 1 MPa O<sub>2</sub>; <sup>a</sup> —: not added or detected; <sup>b</sup> 0.4 mmol CuSO<sub>4</sub> and 0.2 mmol H<sub>2</sub>SO<sub>4</sub>. **1:** Diethyl maleate;

**2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl 3-ethoxypropionate; **5:** Diethyl oxalate; **6:** Ethyl 3-furoate; **7:** Ethyl levulinate; **8:** Diethyl malonate; **9:** Ethyl diethoxyacetate; **10:** Ethyl

3,3-diethoxypropionate;

**11:**

1,1,3,3-tetraethoxypropane;

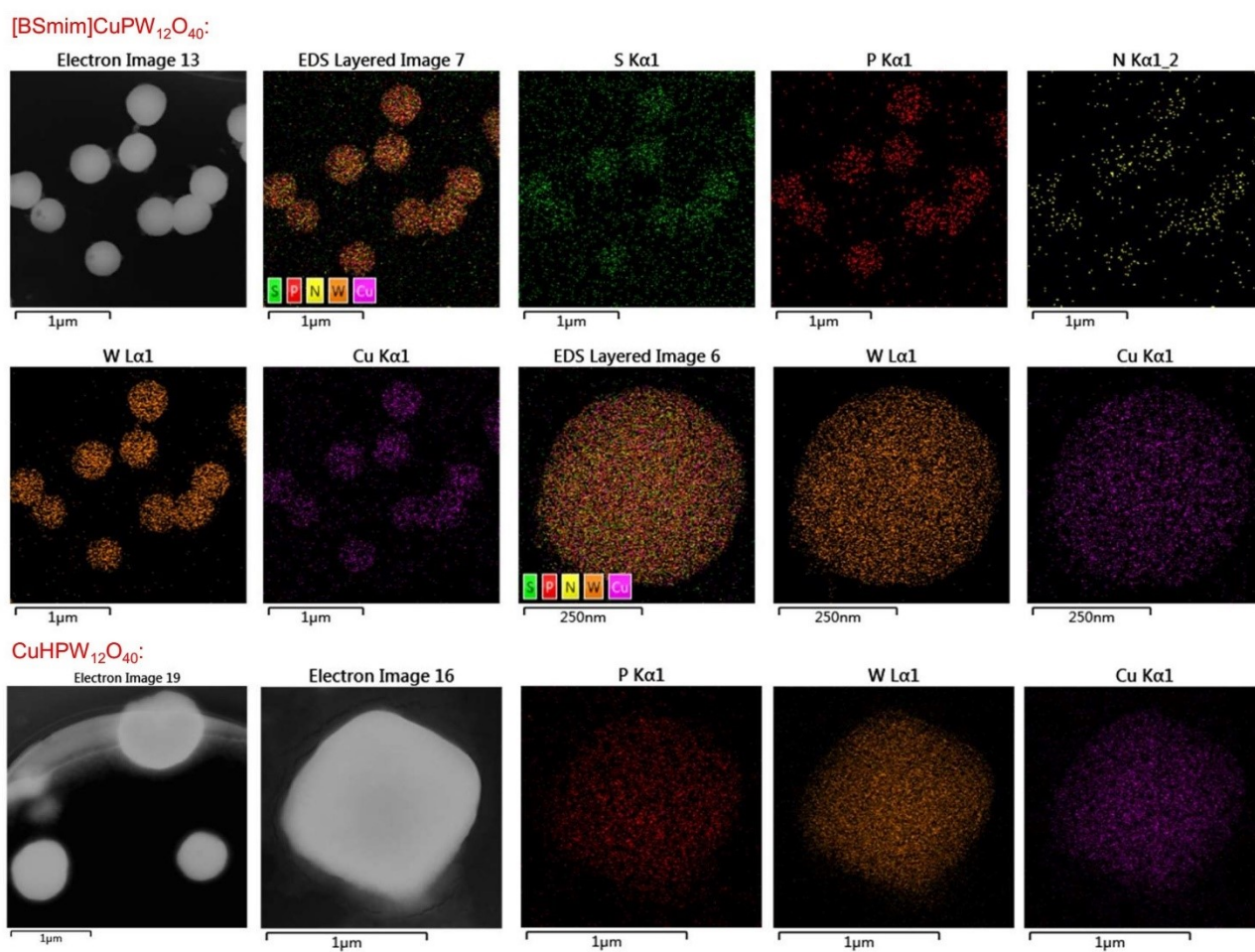
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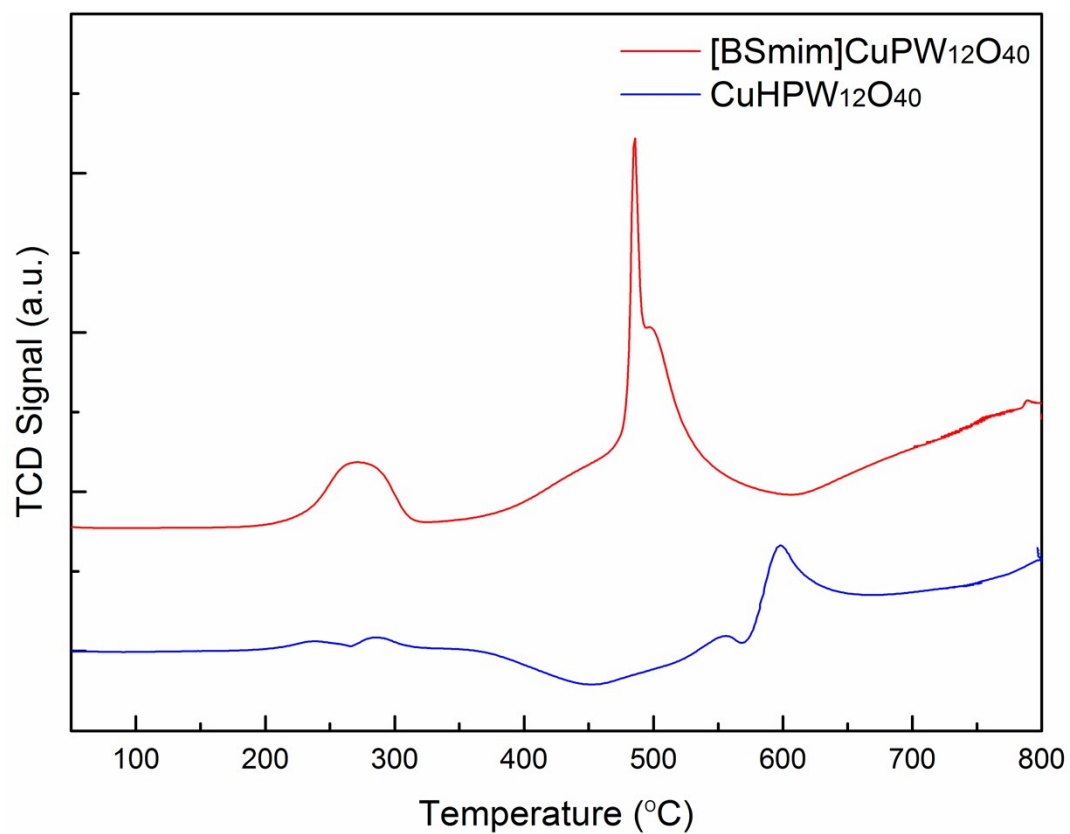
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vanillate.

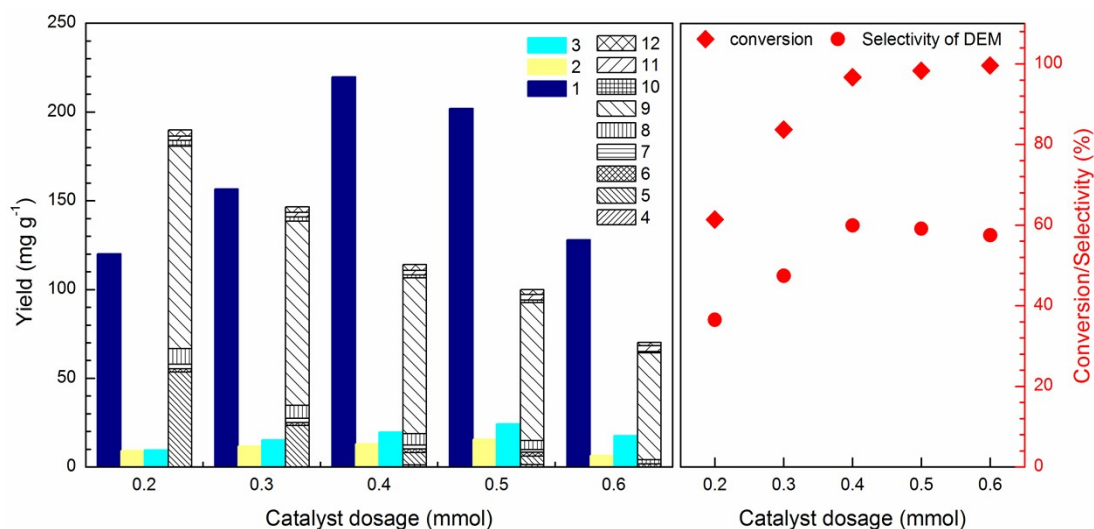
**Table S4** The acidic properties of [BSmim]CuPW<sub>12</sub>O<sub>40</sub> and CuHPW<sub>12</sub>O<sub>40</sub>

Entry	Catalyst	Acid sites ( $\mu\text{mol g}^{-1}$ ) <sup>a</sup>			
		B	L	Total	B/L
1	[BSmim]CuPW <sub>12</sub> O <sub>40</sub>	12.36	38.22	50.58	0.32
2	CuHPW <sub>12</sub> O <sub>40</sub>	19.83	52.44	72.27	0.38

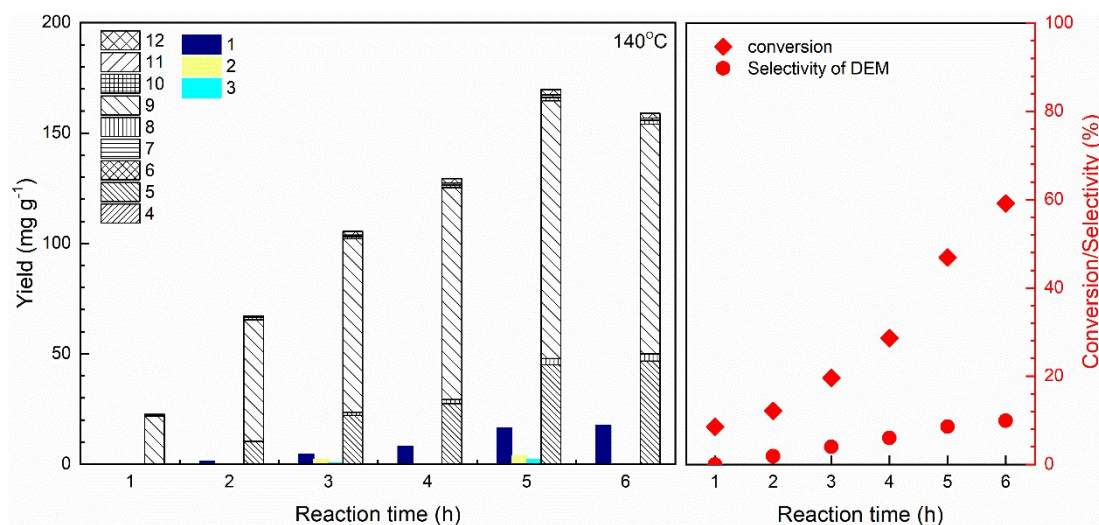
<sup>a</sup> B: Brønsted acid; L: Lewis acid.**Fig. S2** HAADF-STEM and EDS mapping images of catalysts.



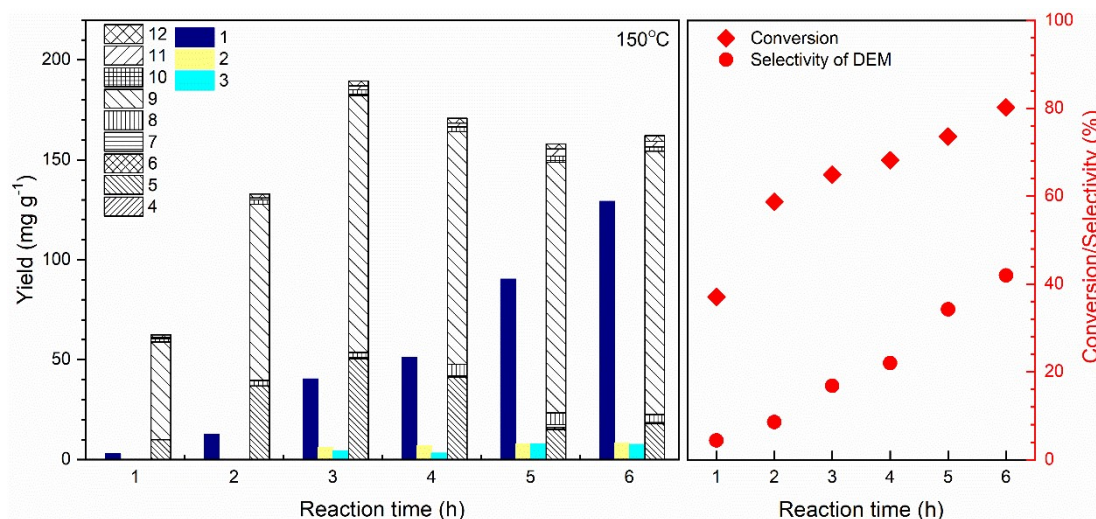
**Fig. S3** The H<sub>2</sub>-TPR analysis of [BSmim]CuPW<sub>12</sub>O<sub>40</sub> and CuHPW<sub>12</sub>O<sub>40</sub>.



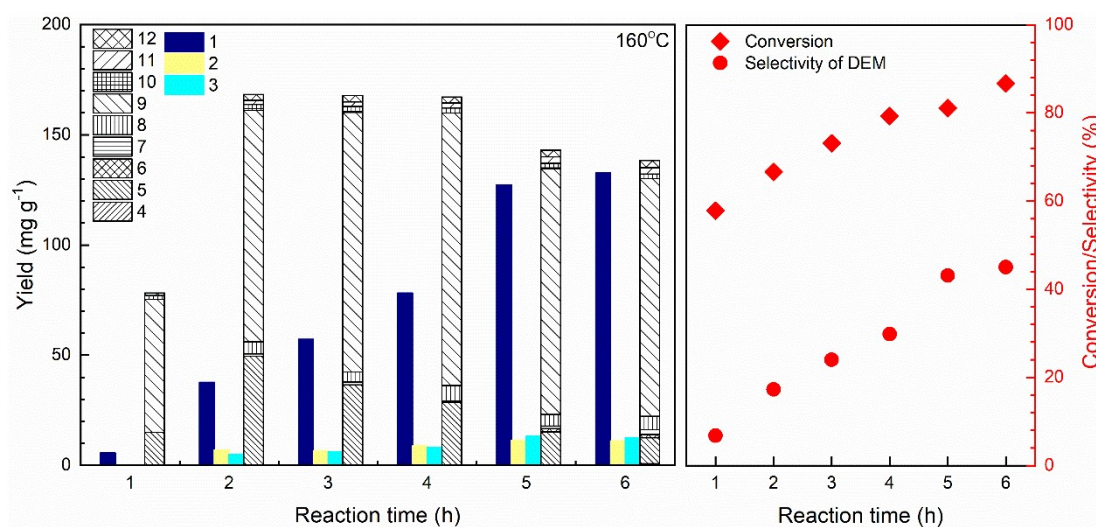
**Fig. S4** Effect of catalyst dosage on the bagasse conversion. Reaction conditions: 0.1 g bagasse, [BSmim]CuPW<sub>12</sub>O<sub>40</sub> as catalyst, 10 mL ethanol, 170 °C, 4 h, 1 MPa O<sub>2</sub>; **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl 3-ethoxypropionate; **5**: Diethyl oxalate; **6**: Ethyl 3-furoate; **7**: Ethyl levulinate; **8**: Diethyl malonate; **9**: Ethyl diethoxyacetate; **10**: Ethyl 3,3-diethoxypropionate; **11**: 1,1,3,3-tetraethoxypropane; **12**: Ethyl vanillate.



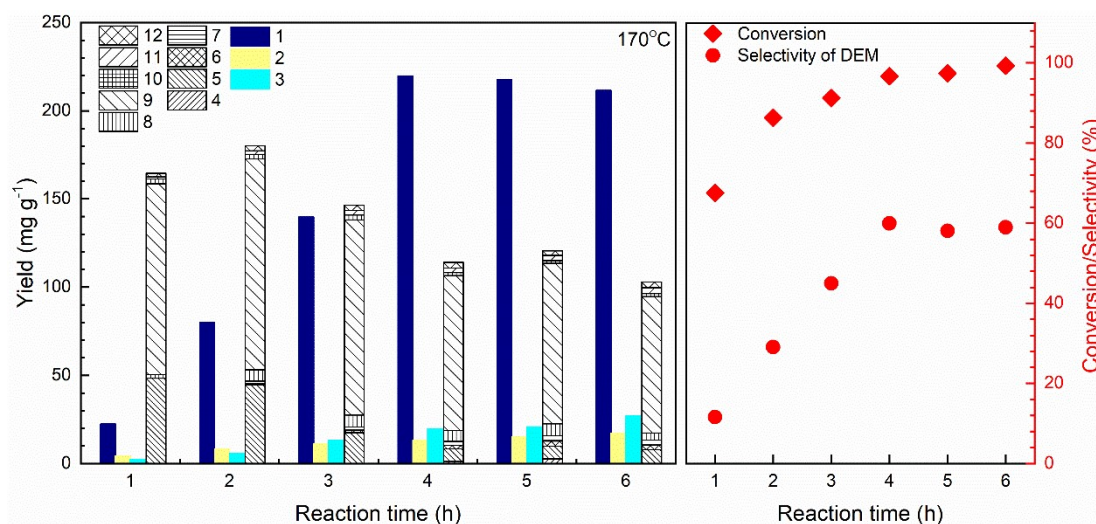
**Fig. S5** Effect of reaction time on the conversion of bagasse at 140 °C. Reaction condition: 0.1 g bagasse, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 1 MPa O<sub>2</sub>; **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl 3-ethoxypropionate; **5**: Diethyl oxalate; **6**: Ethyl 3-furoate; **7**: Ethyl levulinate; **8**: Diethyl malonate; **9**: Ethyl diethoxyacetate; **10**: Ethyl 3,3-diethoxypropionate; **11**: 1,1,3,3-tetraethoxypropane; **12**: Ethyl vanillate.



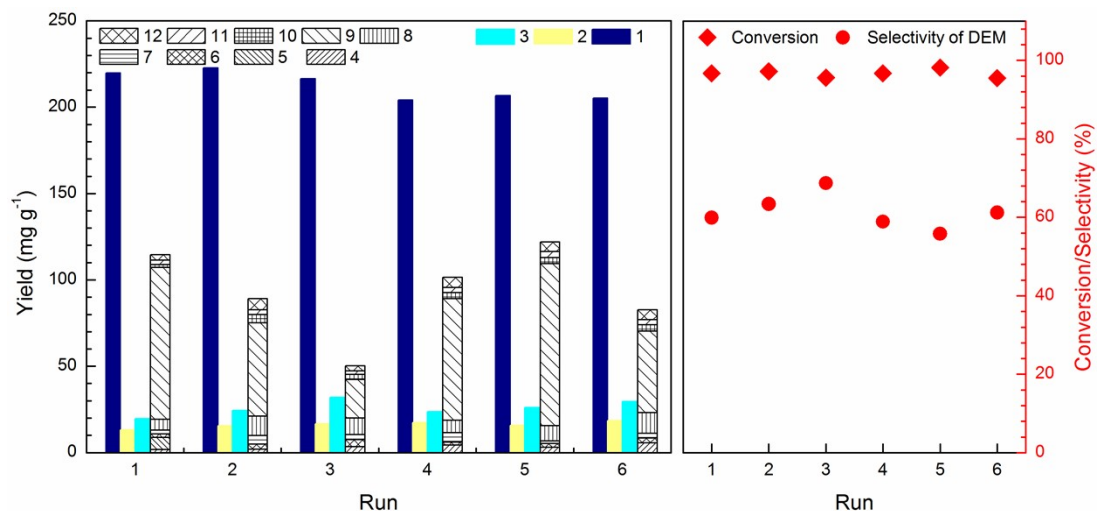
**Fig. S6** Effect of reaction time on the conversion of bagasse at 150 °C. Reaction condition: 0.1 g bagasse, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 1 MPa O<sub>2</sub>; **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl 3-ethoxypropionate; **5**: Diethyl oxalate; **6**: Ethyl 3-furoate; **7**: Ethyl levulinate; **8**: Diethyl malonate; **9**: Ethyl diethoxyacetate; **10**: Ethyl 3,3-diethoxypropionate; **11**: 1,1,3,3-tetraethoxypropane; **12**: Ethyl vanillate.



**Fig. S7** Effect of reaction time on the conversion of bagasse at 160 °C. Reaction condition: 0.1 g bagasse, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 1 MPa O<sub>2</sub>; **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl 3-ethoxypropionate; **5**: Diethyl oxalate; **6**: Ethyl 3-furoate; **7**: Ethyl levulinate; **8**: Diethyl malonate; **9**: Ethyl diethoxyacetate; **10**: Ethyl 3,3-diethoxypropionate; **11**: 1,1,3,3-tetraethoxypropane; **12**: Ethyl vanillate.



**Fig. S8** Effect of reaction time on the conversion of bagasse at 170 °C. Reaction condition: 0.1 g bagasse, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 1 MPa O<sub>2</sub>; **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl 3-ethoxypropionate; **5**: Diethyl oxalate; **6**: Ethyl 3-furoate; **7**: Ethyl levulinate; **8**: Diethyl malonate; **9**: Ethyl diethoxyacetate; **10**: Ethyl 3,3-diethoxypropionate; **11**: 1,1,3,3-tetraethoxypropane; **12**: Ethyl vanillate.



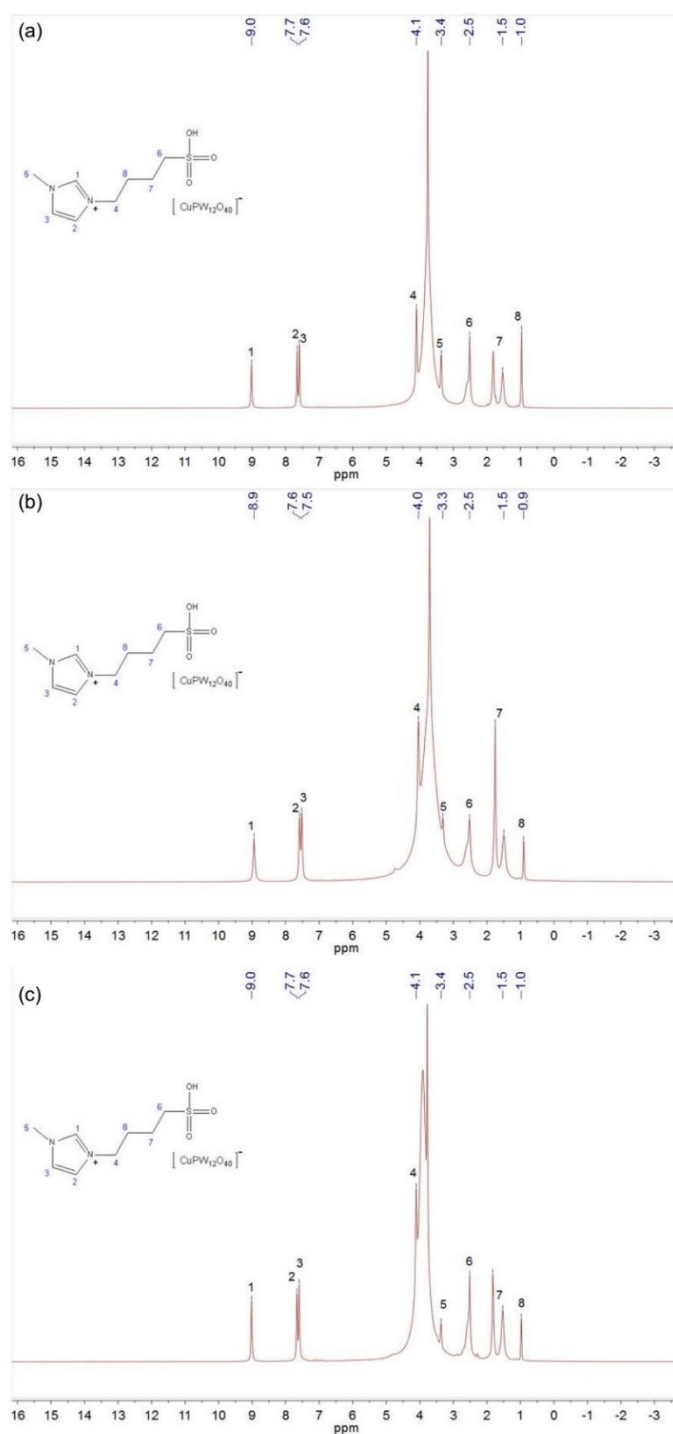
**Fig. S9** Recycle performances of [BSmim]CuPW<sub>12</sub>O<sub>40</sub> catalyst. Reaction condition: 0.1 g bagasse, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 4 h, 1 MPa O<sub>2</sub>; **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl 3-ethoxypropionate; **5**: Diethyl oxalate; **6**: Ethyl 3-furoate; **7**: Ethyl levulinate; **8**: Diethyl malonate; **9**: Ethyl diethoxyacetate; **10**: Ethyl 3,3-diethoxypropionate; **11**: 1,1,3,3-tetraethoxypropane; **12**: Ethyl vanillate.

**Table S5** The recycle performances of [BSmim]CuPW<sub>12</sub>O<sub>40</sub> catalyst

Run	DEM yield (mg g <sup>-1</sup> )	TON
1	219.8	3.2
2	222.7	3.2
3	216.6	3.1
4	204.1	3.0
5	206.8	3.0
6	205.3	3.0

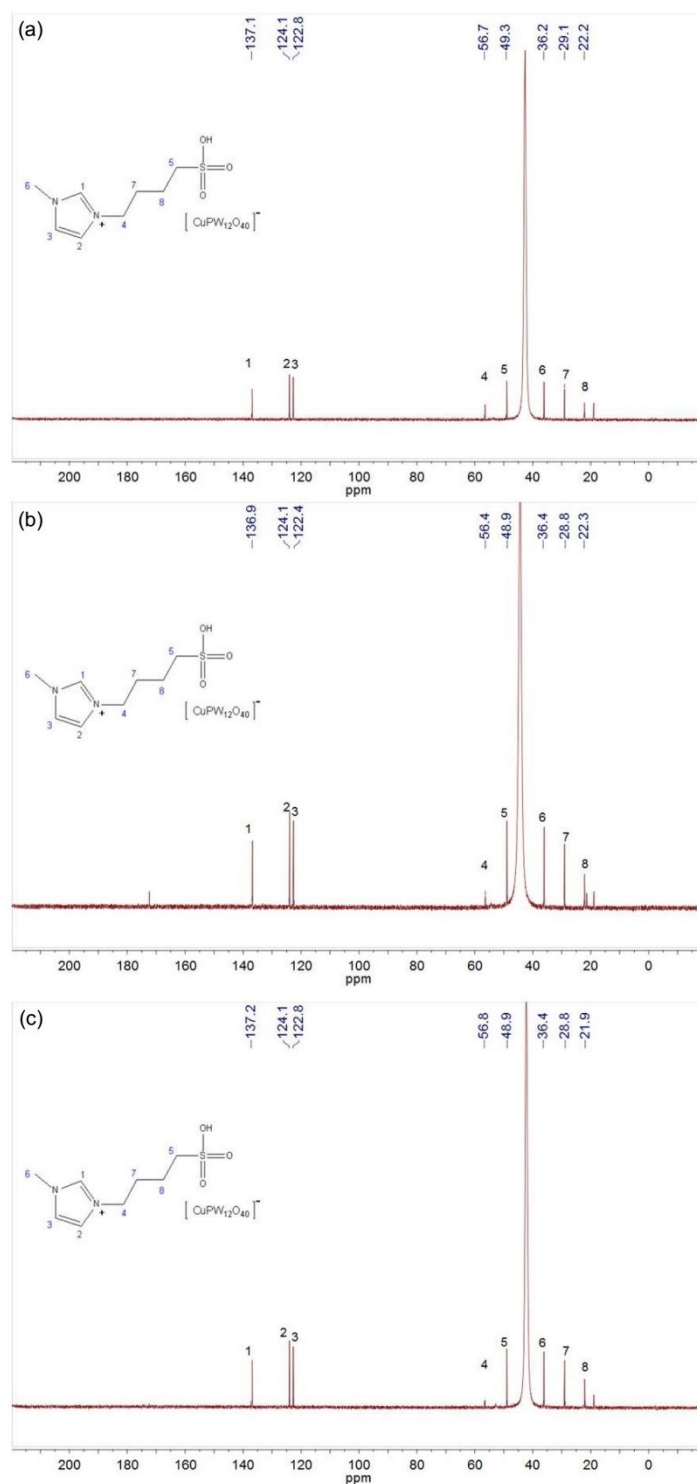
TON = n(DEM)/n(catalyst), M(DEM) = 172.18 g mol<sup>-1</sup>, Reaction condition: 0.1 g bagasse, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 4 h, 1 MPa O<sub>2</sub>.

# $^1\text{H}$ -NMR and $^{13}\text{C}$ -NMR spectra



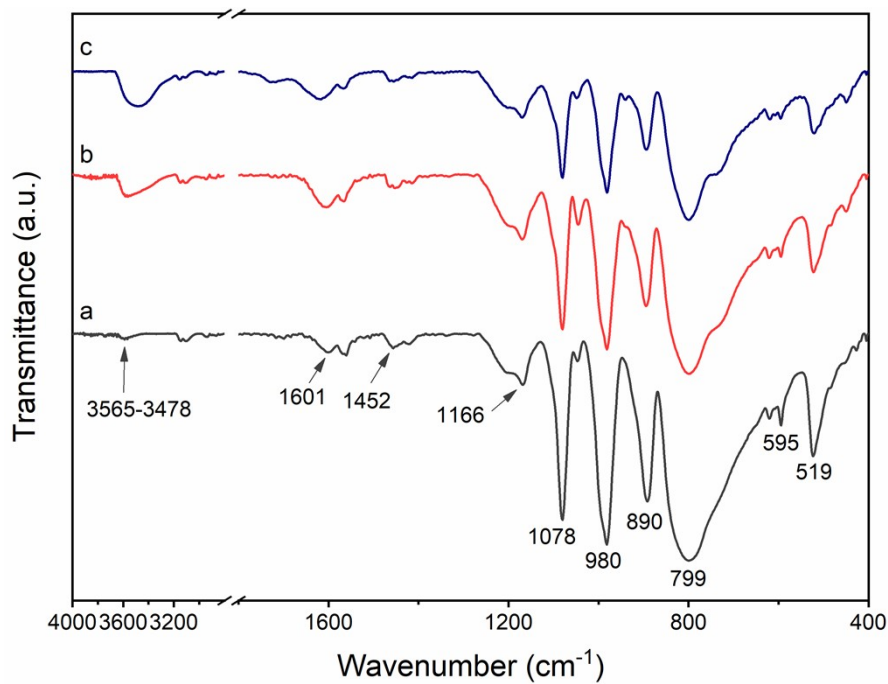
**Fig. S10**  $^1\text{H}$ -NMR spectra of [BSmim] $\text{CuPW}_{12}\text{O}_{40}$  catalyst. (a) fresh catalyst; (b) recovered catalyst from blank reaction: 0.4 mmol of catalyst, 10 mL of ethanol, 10 MPa  $\text{O}_2$ , 170  $^\circ\text{C}$ , 4 h; (c) recovered catalyst from bagasse conversion: 0.1 g of bagasse, 0.4 mmol of catalyst, 10 mL of ethanol, 10 MPa  $\text{O}_2$ , 170  $^\circ\text{C}$ , 4 h.





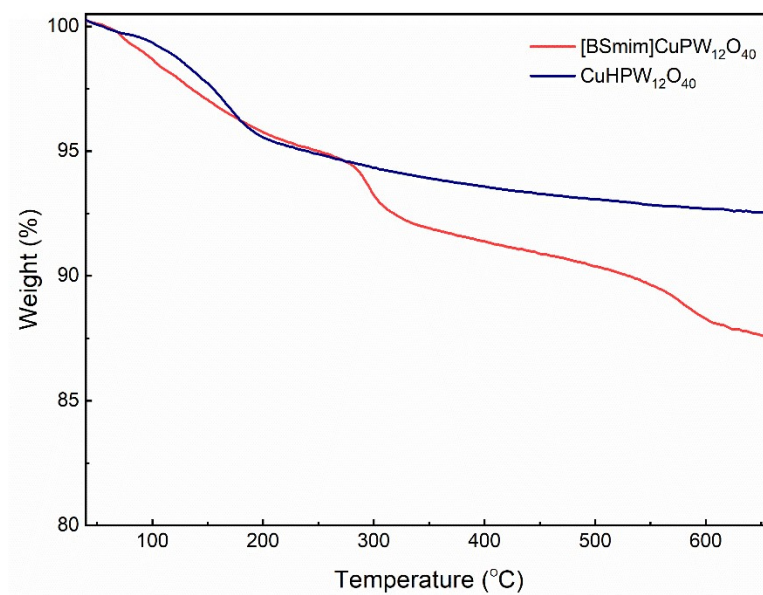
**Fig. S11**  $^{13}\text{C}$ -NMR spectra of [BSmim] $\text{CuPW}_{12}\text{O}_{40}$  catalyst. (a) fresh catalyst; (b) recovered catalyst from blank reaction: 0.4 mmol of catalyst, 10 mL of ethanol, 10 MPa  $\text{O}_2$ , 170  $^\circ\text{C}$ , 4 h; (c) recovered catalyst from bagasse conversion: 0.1 g of bagasse, 0.4 mmol of catalyst, 10 mL of ethanol, 10 MPa  $\text{O}_2$ , 170  $^\circ\text{C}$ , 4 h.

FT-IR:



**Fig. S12** FT-IR spectra of [BSmim]CuPW<sub>12</sub>O<sub>40</sub> catalyst. (a) fresh catalyst; (b) recovered catalyst from blank reaction: 0.4 mmol of catalyst, 10 mL of ethanol, 10 MPa O<sub>2</sub>, 170 °C, 4 h; (c) recovered catalyst from bagasse conversion: 0.1 g of bagasse, 0.4 mmol of catalyst, 10 mL of ethanol, 10 MPa O<sub>2</sub>, 170 °C, 4 h.

TG:



**Fig. S13** Thermogravimetric curves of POM-IL in the range of 40-650 °C.

**Table S6** Selective conversion of various lignocellulose to DEM

Entry	Lignocellulose	Conversion (%)	Yield (mg g <sup>-1</sup> )												DEM selectivity (%)	
			1	2	3	4	5	6	7	8	9	10	11	12		Total
1	Corn stalk	93.8	329.6	20.0	48.2	2.1	— <sup>a</sup>	—	—	8.4	53.2	3.6	3.9	—	469.0	70.3
2	Corn cob	95.4	312.3	19.3	37.3	1.5	—	2.8	—	3.7	62.4	2.5	3.6	—	445.4	70.1
3	Rice straw	99.3	307.0	17.6	33.1	1.2	—	—	3.0	3.9	56.5	3.0	3.8	—	429.1	71.5
4	Sawdust	98.2	295.7	15.6	31.7	—	—	—	—	4.0	30.9	3.2	4.0	7.2	392.3	75.4
5	Tapioca	97.5	255.2	16.2	21.8	6.0	—	1.9	3.2	10.9	100.1	3.5	3.2	7.0	429.0	59.5
6	Bagasse	96.7	219.8	13.1	19.7	1.4	7.1	2.0	2.2	6.3	87.7	1.7	2.7	3.2	366.9	59.9
7	Pine	97.8	208.5	26.1	21.2	—	—	2.0	—	9.3	78.6	3.5	4.0	5.1	358.3	58.2
8	Wheat straw	94.3	201.7	16.4	21.6	1.0	—	2.3	1.5	4.8	94.3	3.1	4.0	—	350.7	57.5

Reaction condition: 0.1 g raw lignocellulose, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 4 h, 1 MPa O<sub>2</sub>; <sup>a</sup> —: not detected; **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl 3-ethoxypropionate; **5**: Diethyl oxalate; **6**: Ethyl 3-furoate; **7**: Ethyl levulinate; **8**: Diethyl malonate; **9**: Ethyl diethoxyacetate; **10**: Ethyl 3,3-diethoxypropionate; **11**: 1,1,3,3-tetraethoxypropane; **12**: Ethyl vanillate.

**Table S7** The elemental analysis of lignocellulose

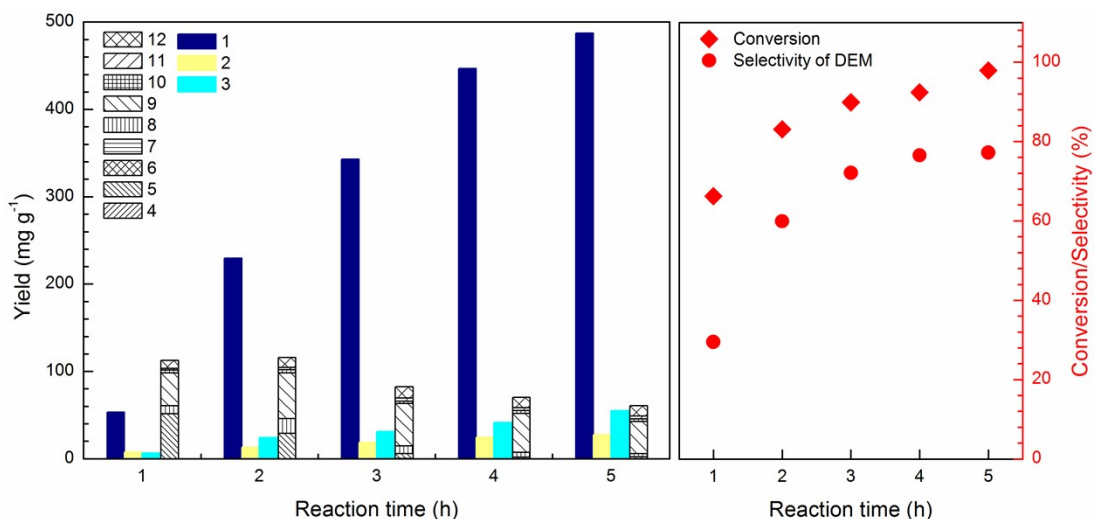
Entry	Lignocellulose	Element analysis (%) <sup>a</sup>				
		C	H	O	N	S
1	Corn stalk	44.23	5.951	48.893	0.613	0.313
2	Corn cob	43.06	6.177	49.675	0.612	0.476
3	Rice straw	37.21	5.652	56.184	0.727	0.227
4	Sawdust	44.99	6.109	47.595	0.470	0.836
5	Tapioca	44.45	6.107	48.438	0.711	0.294
6	Bagasse	43.00	6.254	49.786	0.584	0.376
7	Pine	44.89	6.218	48.312	0.385	0.195
8	Wheat straw	40.93	6.119	51.735	0.955	0.261

<sup>a</sup> The oxygen content = (100-C-H-N-S)%

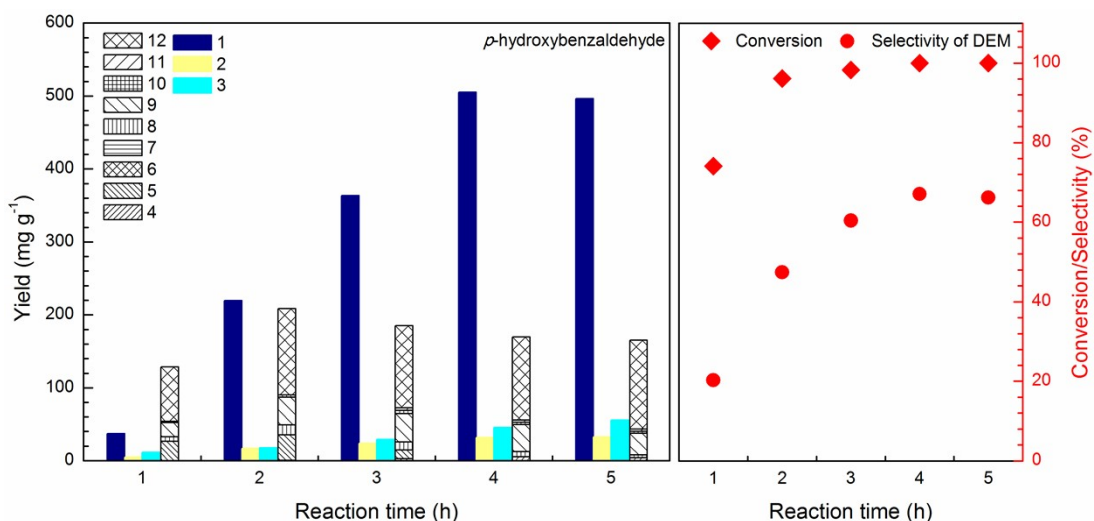
**Table S8** The carbon yield of DEM from various lignocellulose

Entry	Lignocellulose	Theory value of DEM (mg g <sup>-1</sup> ) <sup>a</sup>	DEM yield (mg g <sup>-1</sup> )	Carbon yield of DEM (%)
1	Corn stalk	1584.9	329.6	20.8
2	Corn cob	1543	312.3	20.2
3	Rice straw	1333.4	307	23.0
4	Sawdust	1612.1	295.7	18.3
5	Tapioca	1592.8	255.2	16.0
6	Bagasse	1540.8	219.8	14.3
7	Pine	1608.6	208.5	13.0
8	Wheat straw	1466.7	201.7	13.8

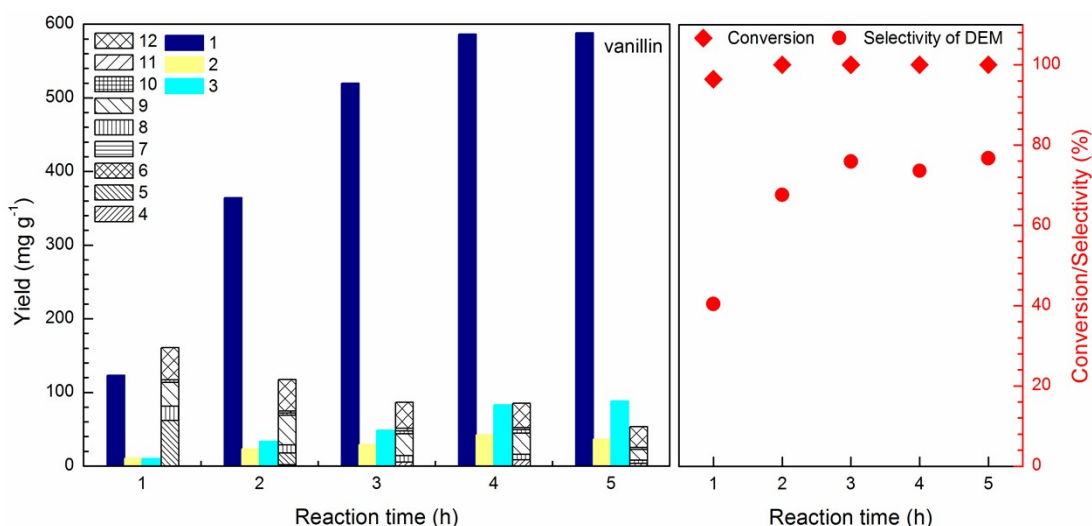
<sup>a</sup>: theory value of DEM = Mass of lignocellulose × Carbon content/Atomic mass of carbon (12)/DEM carbon number (4) × DEM molecular weight (172 g/mol) × 1000 (mg/g)



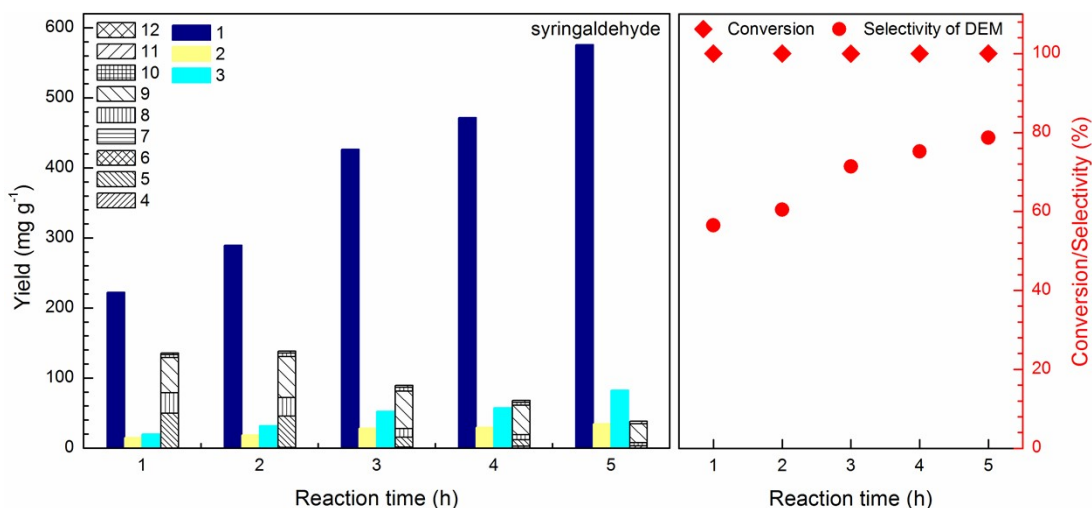
**Fig. S14** The conversion of bagasse lignin to DEM in this process. Reaction conditions: 0.1 g bagasse lignin, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl 3-ethoxypropionate; **5:** Diethyl oxalate; **6:** Ethyl 3-furoate; **7:** Ethyl levulinate; **8:** Diethyl malonate; **9:** Ethyl diethoxyacetate; **10:** Ethyl 3,3-diethoxypropionate; **11:** 1,1,3,3-tetraethoxypropane; **12:** Ethyl vanillate.



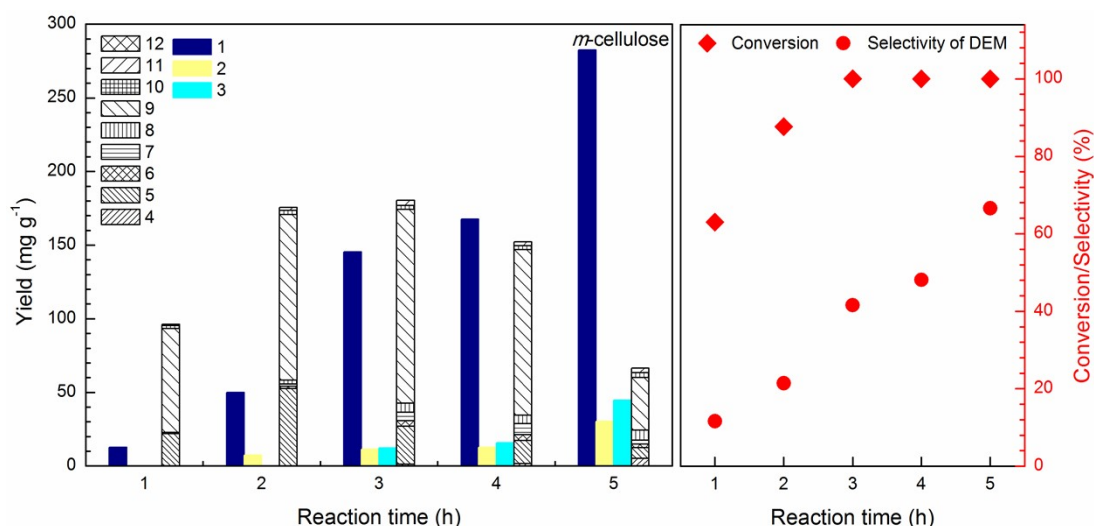
**Fig. S15** The conversion of *p*-hydroxybenzaldehyde to DEM in this process. Reaction conditions: 0.1 g *p*-hydroxybenzaldehyde, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl 3-ethoxypropionate; **5:** Diethyl oxalate; **6:** Ethyl 3-furoate; **7:** Ethyl levulinate; **8:** Diethyl malonate; **9:** Ethyl diethoxyacetate; **10:** Ethyl 3,3-diethoxypropionate; **11:** 1,1,3,3-tetraethoxypropane; **12:** ethyl paraben.



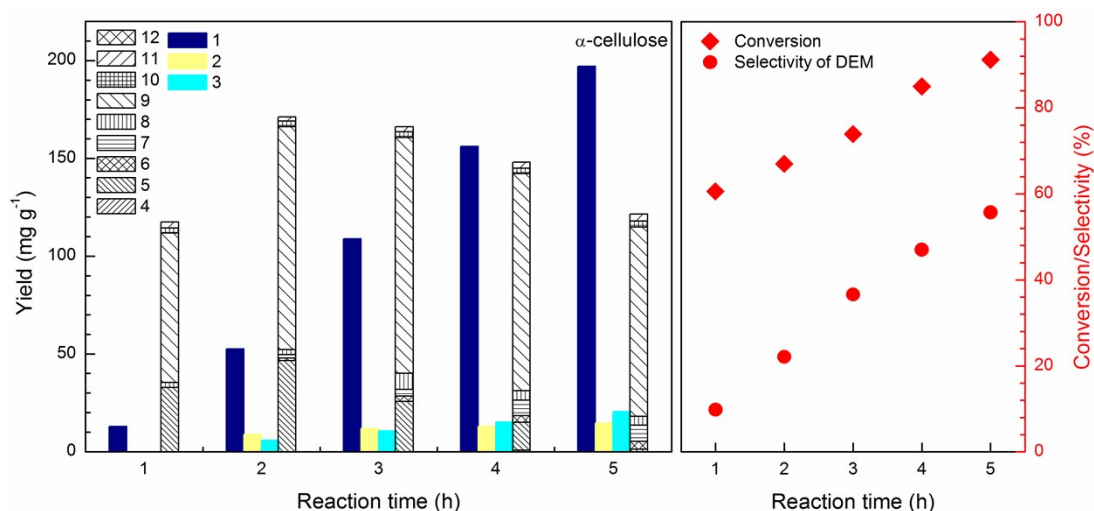
**Fig. S16** The conversion of vanillin to DEM in this process. Reaction conditions: 0.1 g vanillin, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl 3-ethoxypropionate; **5**: Diethyl oxalate; **6**: Ethyl 3-furoate; **7**: Ethyl levulinate; **8**: Diethyl malonate; **9**: Ethyl diethoxyacetate; **10**: Ethyl 3,3-diethoxypropionate; **11**: 1,1,3,3-tetraethoxypropane; **12**: Ethyl vanillate.



**Fig. S17** The conversion of syringaldehyde to DEM in this process. Reaction conditions: 0.1 g syringaldehyde, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl 3-ethoxypropionate; **5**: Diethyl oxalate; **6**: Ethyl 3-furoate; **7**: Ethyl levulinate; **8**: Diethyl malonate; **9**: Ethyl diethoxyacetate; **10**: Ethyl 3,3-diethoxypropionate; **11**: 1,1,3,3-tetraethoxypropane; **12**: Ethyl vanillate.

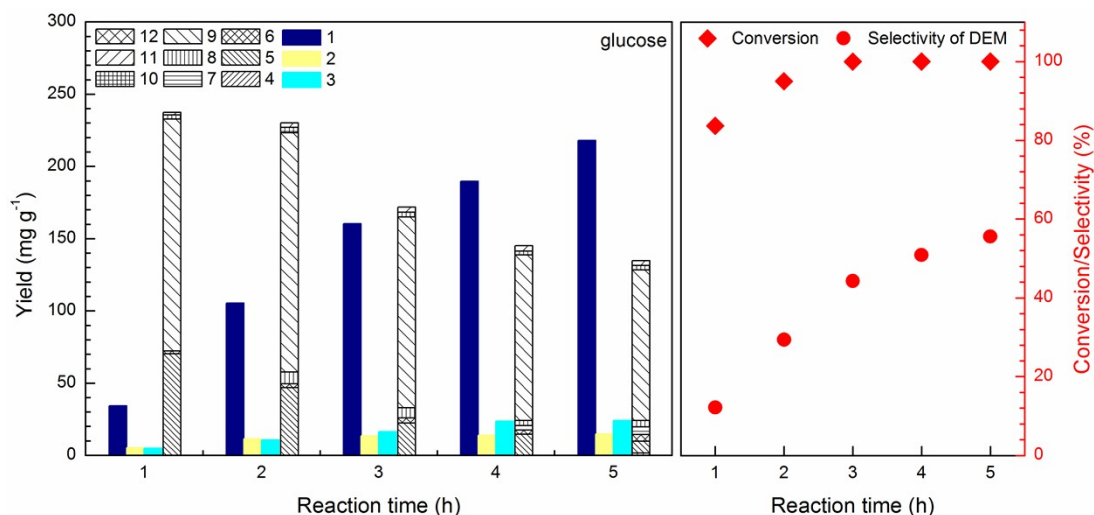


**Fig. S18** The conversion of microcrystalline cellulose to DEM in this process. Reaction conditions: 0.1 g microcrystalline cellulose, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl 3-ethoxypropionate; **5:** Diethyl oxalate; **6:** Ethyl 3-furoate; **7:** Ethyl levulinate; **8:** Diethyl malonate; **9:** Ethyl diethoxyacetate; **10:** Ethyl 3,3-diethoxypropionate; **11:** 1,1,3,3-tetraethoxypropane; **12:** Ethyl vanillate.

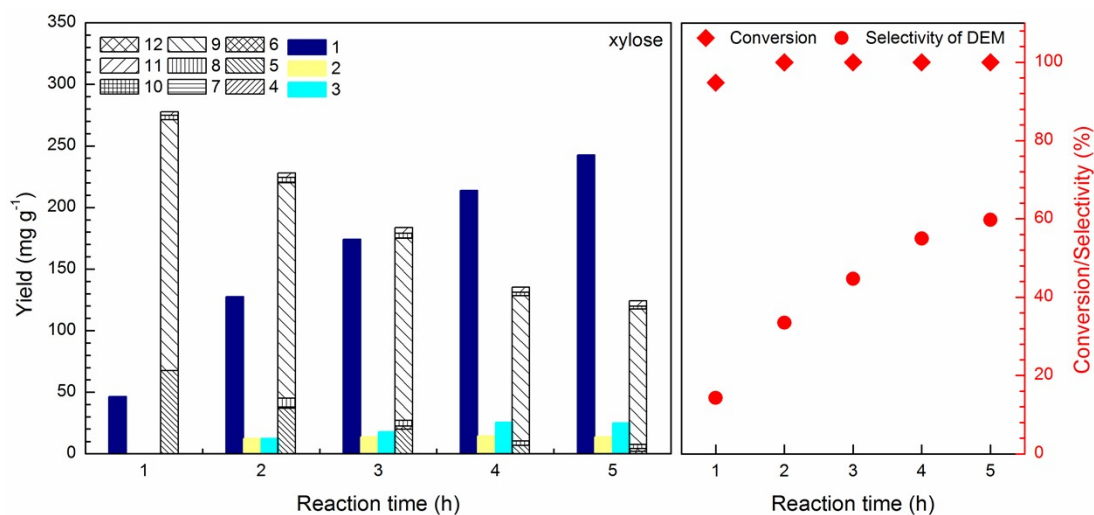


**Fig. S19** The conversion of  $\alpha$ -cellulose to DEM in this process. Reaction conditions: 0.1 g  $\alpha$ -cellulose, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl 3-ethoxypropionate; **5:** Diethyl oxalate; **6:** Ethyl 3-furoate; **7:** Ethyl levulinate; **8:** Diethyl malonate; **9:** Ethyl diethoxyacetate; **10:** Ethyl 3,3-diethoxypropionate; **11:** 1,1,3,3-tetraethoxypropane; **12:** Ethyl vanillate.

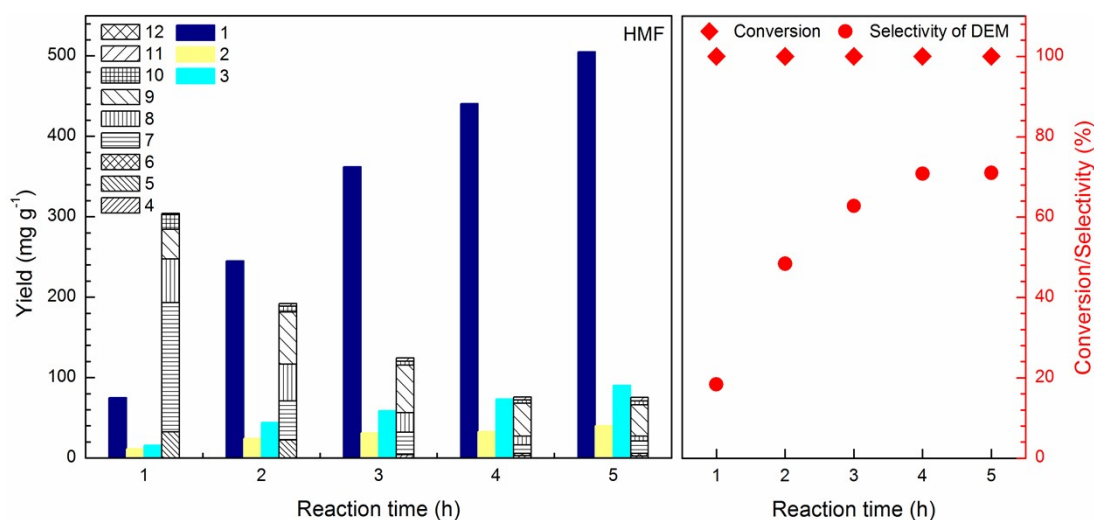




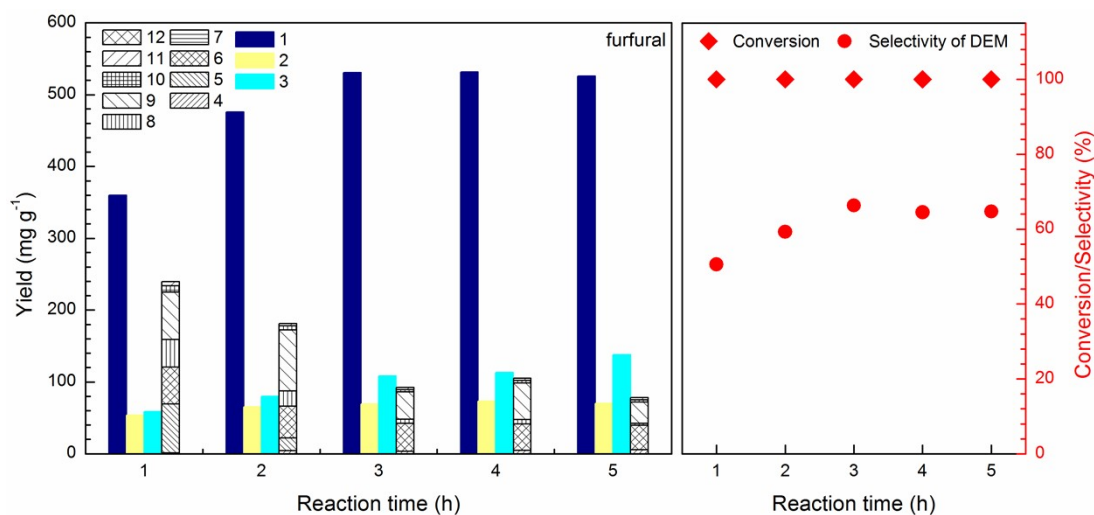
**Fig. S20** The conversion of glucose to DEM in this process. Reaction conditions: 0.1 g glucose, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl 3-ethoxypropionate; **5:** Diethyl oxalate; **6:** Ethyl 3-furoate; **7:** Ethyl levulinate; **8:** Diethyl malonate; **9:** Ethyl diethoxyacetate; **10:** Ethyl 3,3-diethoxypropionate; **11:** 1,1,3,3-tetraethoxypropane; **12:** Ethyl vanillate.



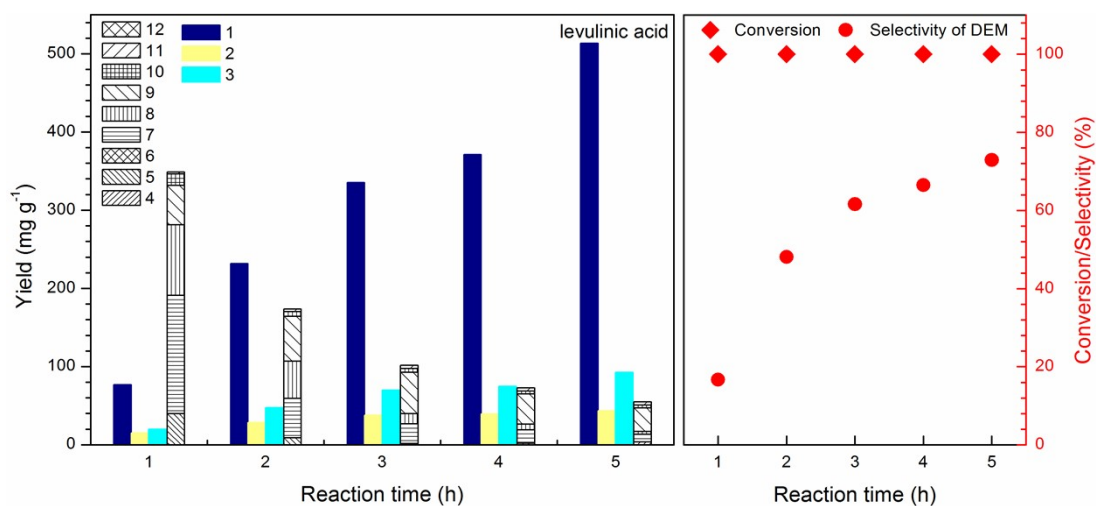
**Fig. S21** The conversion of xylose to DEM in this process. Reaction conditions: 0.1 g xylose, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl 3-ethoxypropionate; **5:** Diethyl oxalate; **6:** Ethyl 3-furoate; **7:** Ethyl levulinate; **8:** Diethyl malonate; **9:** Ethyl diethoxyacetate; **10:** Ethyl 3,3-diethoxypropionate; **11:** 1,1,3,3-tetraethoxypropane; **12:** Ethyl vanillate.



**Fig. S22** The conversion of HMF to DEM in this process. Reaction conditions: 0.1 g HMF, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl 3-ethoxypropionate; **5:** Diethyl oxalate; **6:** Ethyl 3-furoate; **7:** Ethyl levulinate; **8:** Diethyl malonate; **9:** Ethyl diethoxyacetate; **10:** Ethyl 3,3-diethoxypropionate; **11:** 1,1,3,3-tetraethoxypropane; **12:** Ethyl vanillate.



**Fig. S23** The conversion of furfural to DEM in this process. Reaction conditions: 0.1 g furfural, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl 3-ethoxypropionate; **5:** Diethyl oxalate; **6:** Ethyl 3-furoate; **7:** Ethyl levulinate; **8:** Diethyl malonate; **9:** Ethyl diethoxyacetate; **10:** Ethyl 3,3-diethoxypropionate; **11:** 1,1,3,3-tetraethoxypropane; **12:** Ethyl vanillate.



**Fig. S24** The conversion of levulinic acid to DEM in this process. Reaction conditions: 0.1 g levulinic acid, 0.4 mmol [BSmim]CuPW<sub>12</sub>O<sub>40</sub>, 10 mL ethanol, 170 °C, 1 MPa O<sub>2</sub>. **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl 3-ethoxypropionate; **5**: Diethyl oxalate; **6**: Ethyl 3-furoate; **7**: Ethyl levulinate; **8**: Diethyl malonate; **9**: Ethyl diethoxyacetate; **10**: Ethyl 3,3-diethoxypropionate; **11**: 1,1,3,3-tetraethoxypropane; **12**: Ethyl vanillate.

## Notes and references

1. J. Long, X. Li, B. Guo, L. Wang, and N. Zhang, *Catal. Today*, 2013, **200**, 99-105.
2. Z. Cai, J. Long, Y. Li, L. Ye, B. Yin, L. J. France, J. Dong, L. Zheng, H. He, S. Liu, S. C. E. Tsang, and X. Li, *Chem*, 2019, **5**, 2365-2377.