

SUPPLEMENTAL INFORMATION

Selective production of diethyl maleate *via* oxidative cleavage of lignin aromatic unit

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I. Materials and Methods

Materials. Tetrahydrofuran (THF, HPLC grade), *N*-methyl imidazole, 1, 4-butane sulfonate, dealkaline lignin and the model compounds were purchased from J&K Chemical Co., Ltd. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$, MnCO_3 , Na_2CO_3 , $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and CoCO_3 were purchased from Guangzhou Guanghua Chemical Reagents Factory Co., Ltd. All materials and reagents are analytical grade and were used as received. Organosolv lignins were extracted from raw biomass (10.0 g) using 150 mL 80% v/v aqueous ethanol solution (containing 1.0 g 98% sulfuric acid) at 393 K for 4 h according to our previous literature.¹ The contents of H, G and S structural units of these lignin were measured by quantitative ^{13}C -NMR method as presented in previous studies.^{2,3}

Table S1. The structural unit contents of different lignin.

Lignin	Structural unit content (%)		
	H	G	S
Wheat stalk	29.9	32.8	37.3
Corn	13.5	47.2	39.3
Bagasse	14.8	45.6	39.6
Pine	0	81.9	18.1
Rice straw	22.2	37.8	40.0
Dealkaline	0	82.3	17.7

Preparation and characterization of polyoxometalate ionic liquids (POM-ILs).

According to the reported procedures,⁴ *N*-methyl imidazole and equimolar 1, 4-butane sulfonate were mixed and stirred magnetically at 313 K for 24 h. Then the white solid (denoted as [BSmim]) was washed with diethyl ether three times for removal of the unreacted materials and was dried in a vacuum.

Metal carbonate was dispersed in 20 mL deionized water (containing 10 mmol transition metal ion) and added dropwise to a 20 mL aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$ (10 mmol). Then the solution was stirred at room temperature for 6.0 h. The $\text{MHPW}_{12}\text{O}_{40}$ (M= Na, Mn, Co, Ni and Cu) was obtained after

removing water and drying in a vacuum at 353 K for 24 h.⁵ After that, equimolar MHPW₁₂O₄₀ aqueous solution was added dropwise to above prepared white solid (BSmim). The mixture was stirred at room temperature for another 24 h. After solvent removal and drying in a vacuum at 353 K for 24 h,⁶ the polyoxometalate ILs [BSmim]MPW₁₂O₄₀ were obtained.

¹H-nuclear magnetic resonance (¹H-NMR) and ¹³C-NMR spectra of POM-IL were performed on a Bruker AV-400 spectrometer using D₂O and DMSO-*d*₆ as solvent, respectively. Fourier transform infrared spectrometry (FT-IR) spectra were obtained by Bruker Tensor 27 FT-IR spectrophotometer (the range of 400-4000 cm⁻¹, KBr pelleting method). The thermal stability of IL was analyzed by thermogravimetry (TG, NETZSCH STA449C, the oven temperature was ramped up from 313 to 923 K at 10 K min⁻¹). The elemental contents of P, W, Cu, Ni, Co, Mn and Na were analyzed on an Agilent 7700 Series ICP-MS apparatus. X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX-3A Auto X-ray diffractometer with Cu K α radiation (λ = 1.5418 Å). Intensity data were collected over a 2 θ range of 5-80° with a step of 0.01°. Hydrogen temperature-programmed reduction (H₂-TPR) was performed with a Micromeritics Autochem II instrument (Micromeritics, USA), equipped with a thermal conductivity detector (TCD). Approximately 100 mg of catalysts sample was loaded in a U-shape quartz reactor, pre-treated at 100 °C (20 °C min⁻¹) in Ar for 1 h, then cooled to 50 °C and held at this temperature in flowing 10% H₂/Ar (30 mL min⁻¹) for 2 h. The sample was heated from 50 to 800 °C at the rate of 20 °C min⁻¹ under 10% H₂/Ar (30 mL min⁻¹) and kept at this temperature for 10 min.

General procedure for catalytic oxidation of lignin and model compound.

In a typical process, 0.25 g lignin, 0.9 mmol POM-IL catalyst and 20 mL 100% ethanol were charged in a 100 mL stainless autoclave (Andorra MED1220, Premex Co. Ltd., Switzerland). After air purging with pure oxygen five times and pressurizing to 0.8 MPa, the reactor was heated from room temperature to the designated temperature for the desired time. Then, it was cooled down to room

temperature by ice water bath. The reaction mixture was removed and the reactor was washed with anhydrous ethanol (3×5.0 mL). IL catalyst could be precipitated at room temperature and used for the next run after drying (extra fresh catalyst was added for the system loss). Afterwards, the liquid mixture was then diluted by ethanol to 50 mL for qualitative and quantitative analysis, while dimethyl phthalate was used as the internal standard. Otherwise, when the ethanol aqueous solution was used, the mixture after reaction was rotary evaporated under reduced pressure for solvent recovery, followed by an intensive esterification reaction with 10 mL anhydrous ethanol at 373 K for 2 h. After that, it was diluted by ethanol to 50 mL as well. Volatile products were qualitative and quantitative analyzed *via* gas chromatography mass spectrometry (GC-MS) and gas chromatography-flame ionization detector (GC-FID). The residual lignin can be obtained through a simple precipitation process. For example, for the recovery of organosolv lignin, 60 mL deionized water was added into 20 mL above reaction mixture, then the precipitated solid was centrifugation and drying until constant weight. For the recovery of dealkaline lignin, the mixture after reaction was first acidified to pH=2 with an 1.0 mol L^{-1} HCl solution, and then the same procedure as that of above organosolv lignin was conducted.

In the atmosphere investigation, for a one-stage process, a mixture of nitrogen and oxygen with various molar ratios was used and the depolymerization of lignin was conducted at 433 K for 5.0 h. For a typical two-stage process, the lignin was first depolymerized at above mentioned condition. When the mixture was cooled down to room temperature, an extra 0.8 MPa nitrogen or oxygen was purged into, and then the reaction was heated to 433 K for 1.0 or 2.0 h. The product separation and analysis procedure were also indifferent with that for the general process in this study. In comparative and control experiments, a series of model compounds (monolignols and potential intermediate products) were tested under the same procedures as that for lignin (i.e., 0.25 g model compound, 0.9 mmol POM-IL catalyst and 20 mL 100% ethanol solvent). Triplicate experiments were conducted and the data

shown in this study is the average.

The conversion of lignin/model compound, the yield and selectivity of products were calculated according to Eq. 1 to 4, respectively.

$$\text{Conversion(\%)} = \left(1 - \frac{W_R}{W_F}\right) \times 100\% \quad \text{Eq.1}$$

$$\text{Yield}(\text{mg g}^{-1}) = \frac{W_P}{W_F} \quad \text{Eq.2}$$

$$\text{Selectivity of DEM (\%)} = \frac{W_D}{W_P} \times 100\% \quad \text{Eq.3}$$

$$\text{Selectivity of C}_4 \text{ ester (\%)} = \frac{W_E}{W_P} \times 100\% \quad \text{Eq.4}$$

W_R : the weight of regenerated lignin (g); W_F : the weight of feed lignin/model compound (g); W_P : the weight of total volatile products determined by GC-FID (mg); W_D : the weight of DEM (mg); W_E : the weight of C₄ ester including DEM, diethyl succinate, diethyl fumarate, diethyl malate.

Product analysis. The reaction products were identified by GC-MS based on an Agilent library (Agilent 7890B/5977A GC-MS apparatus). The capillary column of HP-5 MS (5% phenyl Methyl silox, 30 m×250 μm×0.25 μm) was used for chemical separation. The oven temperature was programmed from 323 (held for 3 min) to 553 K (held for another 5 min) with the rate of 8 K min⁻¹. The quantitative analysis of these products was conducted on an Agilent 7890B GC with a flame ionization detector (GC-FID) using the same chromatography column and temperature program as the GC-MS analysis. Dimethyl phthalate was selected as the internal standard compound.

Gel permeation chromatography (GPC) analysis of the original and regenerated lignin was carried out on an Agilent 1260 HPLC apparatus with a differential refraction detector (RID). THF was used as eluent at a flow rate of 1 mL min⁻¹ with the polystyrene standards for the molecular weight calibration curve measurement. FT-IR spectra were obtained by Bruker Tensor 27 FT-IR spectrophotometer (the

range of 400-4000 cm^{-1} , KBr pelleting method). ^{13}C -NMR and heteronuclear single quantum (HSQC) spectra were performed on a Bruker ABANCE III HD 600 spectrometer using $\text{DMSO-}d_6$ as solvent. The elemental analysis was characterized by vario EL III element analyzer and oxygen content was based on the assumption that the residue only contains C, H, N, S, and O.

The carbon balance, C_9 unit utilization efficiency and TON were calculated according to Eq.5 to Eq.10, respectively.

$$\text{Carbon yield of oligomer (\%)} = \frac{W_o \times C_o}{W_F \times C_F} \times 100\% \quad \text{Eq.5}$$

$$\text{Carbon yield of volatile products (\%)} = \frac{W_P \times C_P}{W_F \times C_F} \times 100\% \quad \text{Eq.6}$$

$$N_{\text{C}_9} \text{ (mmol)} = \frac{W_F \times C_C}{M_C \times 9} \times 1000 \text{ mmol / mol} \quad \text{Eq.7}$$

$$N_{\text{DEM}} \text{ (mmol)} = \frac{Y_{\text{DEM}} \times W_F}{M_{\text{DEM}}} \quad \text{Eq.8}$$

$$\text{C}_9 \text{ unit utilization efficiency (\%)} = \frac{N_{\text{DEM}}}{N_{\text{C}_9}} \times 100\% \quad \text{Eq.9}$$

$$\text{TON} = \frac{N_{\text{C}_9-\text{DEM}}}{N_{\text{catalyst}}} \times 100\% \quad \text{Eq.10}$$

W_o : the weight of oligomer (g); C_o : the carbon content of oligomer determined by element analysis (%); W_F : the weight of feed lignin (g); C_F : the carbon content of raw bagasse lignin; W_P : the weight of volatile products determined by GC-FID; C_P : the carbon content of volatile products = carbon obtained from lignin/molecular weight; N_{C_9} : the content of C_9 unit in lignin (mmol); C_C : the content of Carbon based on the elemental analysis (%); M_C : the mass number of carbon, 12 g mol^{-1} ; Y_{DEM} : the yield of DEM determined by GC-FID (mg g^{-1}); M_{DEM} : the molecular mass of DEM, 172 g mol^{-1} ; $N_{\text{C}_9-\text{DEM}}$: the C_9 unit transformed into DEM (mmol); N_{catalyst} : the catalyst used in this process (mmol).

II. Characterization of polyoxometalate ionic liquid catalysts

¹³C-NMR, ¹H-NMR, FT-IR and TG analysis of POM-ILs

[BSmim]CuPW₁₂O₄₀.^a ¹H-NMR (400 MHz, D₂O): δ ppm 8.71 (s, 1H), 7.59-7.54 (m, 2H), 4.37 (m, 2H), 4.07 (s, 3H), 3.05 (m, 2H), 2.14 (m, 2H), 1.84 (m, 2H). ¹³C-NMR (400 MHz, DMSO-*d*₆): δ ppm 135.51, 123.25, 121.82, 49.82, 48.47, 35.35, 27.78, 20.70. FT-IR (KBr): ν (cm⁻¹) 3562, 3490, 3153, 2938, 1971, 1606, 1448, 1169, 1076, 976, 890, 789, 596, 518. Onset decomposition temperature: 572.4 K.

[BSmim]NiPW₁₂O₄₀. ¹H-NMR (400 MHz, D₂O): δ ppm 8.70 (s, 1H), 7.61-7.56 (m, 2H), 4.39 (m, 2H), 4.11 (s, 3H), 3.08 (m, 2H), 2.17 (m, 2H), 1.86 (m, 2H). ¹³C-NMR (400 MHz, DMSO-*d*₆): δ ppm 134.57, 122.13, 120.75, 48.83, 47.30, 34.29, 26.80, 19.78. FT-IR (KBr): ν (cm⁻¹) 3554, 3440, 3203, 2945, 1971, 1621, 1448, 1162, 1076, 970, 904, 789, 603, 518. Onset decomposition temperature: 592.5 K.

[BSmim]CoPW₁₂O₄₀. ¹H-NMR (400 MHz, D₂O): δ ppm 8.36 (s, 1H), 7.29 (s, 1H), 7.23 (s, 1H), 4.11 (m, 2H), 3.77 (s, 3H), 2.85 (m, 2H), 1.90 (m, 2H), 1.56 (m, 2H). ¹³C-NMR (400 MHz, DMSO-*d*₆): δ ppm 136.33, 123.81, 122.44, 51.16, 48.94, 35.98, 28.56, 21.58. FT-IR (KBr): ν (cm⁻¹) 3504, 3368, 3218, 2945, 1971, 1621, 1456, 1162, 1076, 983, 897, 789, 610, 518. Onset decomposition temperature: 566.2 K.

[BSmim]MnPW₁₂O₄₀. ¹H-NMR (400 MHz, D₂O): δ ppm 8.62 (s, 1H), 7.39-7.33 (m, 2H), 4.14 (m, 2H), 3.78 (s, 3H), 2.84 (m, 2H), 1.91 (m, 2H), 1.63 (m, 2H). ¹³C-NMR (400 MHz, DMSO-*d*₆): δ ppm 135.73, 123.33, 121.95, 49.21, 48.49, 35.66, 28.08, 21.03. FT-IR (KBr): ν (cm⁻¹) 3447, 3354, 3153, 2953, 1971, 1621, 1456, 1169, 1084, 983, 897, 783, 603, 510. Onset decomposition temperature: 607.9 K.

[BSmim]Na₂PW₁₂O₄₀. ¹H NMR (400 MHz, D₂O): δ ppm 8.71 (s, 1H), 7.59 (s, 1H), 7.54 (s, 1H), 4.37 (t, *J* = 7.0 Hz, 2H), 4.07 (s, 3H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.17-2.09 (m, 2H), 1.85-1.77 (m, 2H). ¹³C-NMR (400 MHz, DMSO-*d*₆): δ ppm 136.21, 123.83, 122.43, 50.39, 49.01, 35.98, 28.46, 21.41. FT-IR (KBr): ν (cm⁻¹) 3525, 3419, 3160, 2945, 1978, 1628, 1442, 1162, 1076, 976, 897, 783, 603, 518.

Onset decomposition temperature: 563.1 K.

Recovered [BSmim]CuPW₁₂O₄₀. ¹H-NMR (400 MHz, D₂O): δ ppm 8.72 (s, 1H), 7.55 (m, 2H), 4.37 (m, 2H), 4.06 (s, 3H), 3.05 (m, 2H), 2.14 (m, 2H), 1.83 (m, 2H). ¹³C-NMR (400 MHz, DMSO-*d*₆): δ ppm 136.23, 123.83, 122.44, 50.49, 49.00, 35.98, 28.47, 21.42. FT-IR (KBr): ν (cm⁻¹) 3568, 3483, 3160, 2960, 1978, 1606, 1448, 1162, 1076, 983, 890, 789, 603, 518. Onset decomposition temperature: 569.0 K.

Notes: [BSmim] represents the Methyl-3-(butyl-4-sulfonate) imidazolium cation.

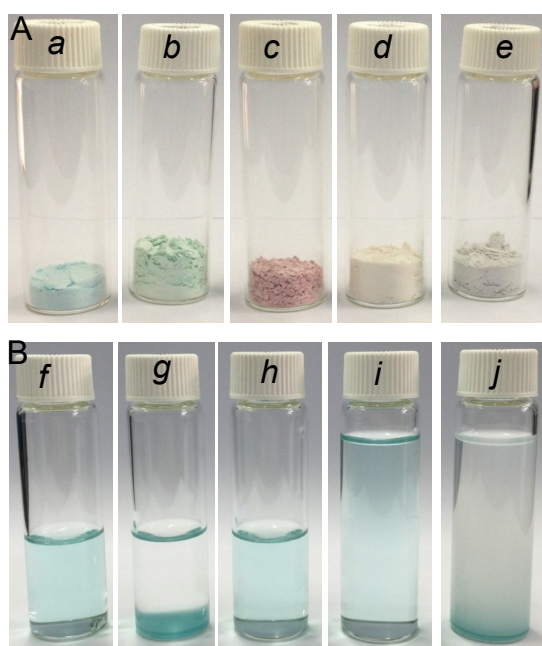


Figure S1. The ILs [BSmim]MPW₁₂O₄₀ (from *a* to *e*, M= Cu, Ni, Co, Mn, and Na) (A) and the solubility of CuHPW₁₂O₄₀ and [BSmim]CuPW₁₂O₄₀ (B). (*f*): 0.5 g CuHPW₁₂O₄₀ in 5 mL 80% ethanol-water solvent at room temperature. (*g*): mixture of 0.5 g [BSmim]CuPW₁₂O₄₀ and 5 mL 80% ethanol-water solvent at room temperature. (*h*) *g* at 80 °C; (*i*) added 5 mL of ethanol to *f*. (*j*): added 5 mL of ethanol to *h*.

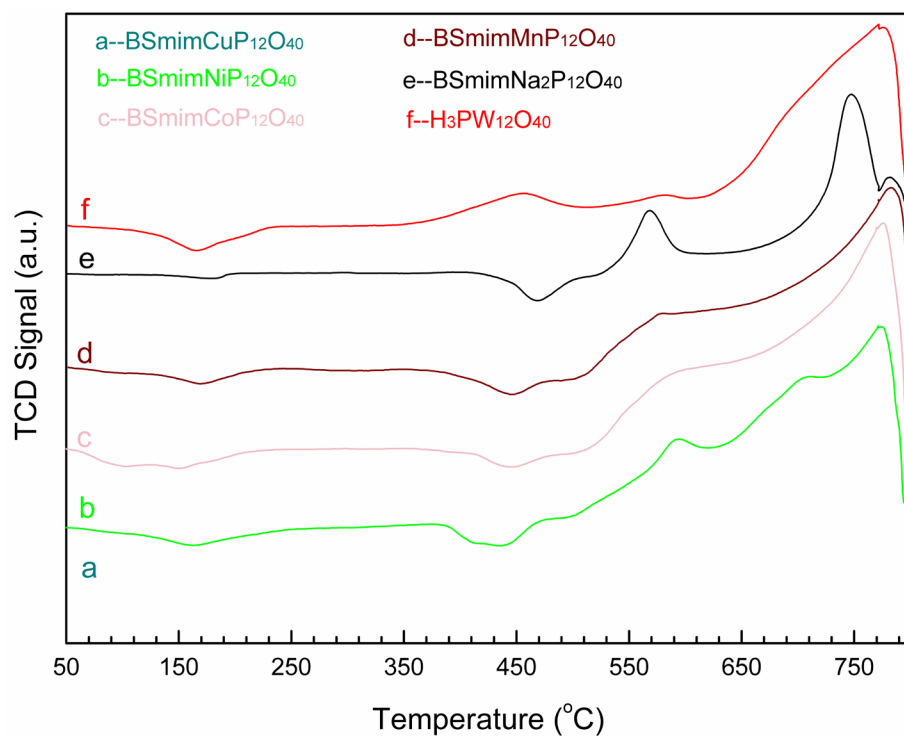


Figure S2. Temperature programmed reduction (TPR) data of the POM-ILs showing their reduction from 160°C

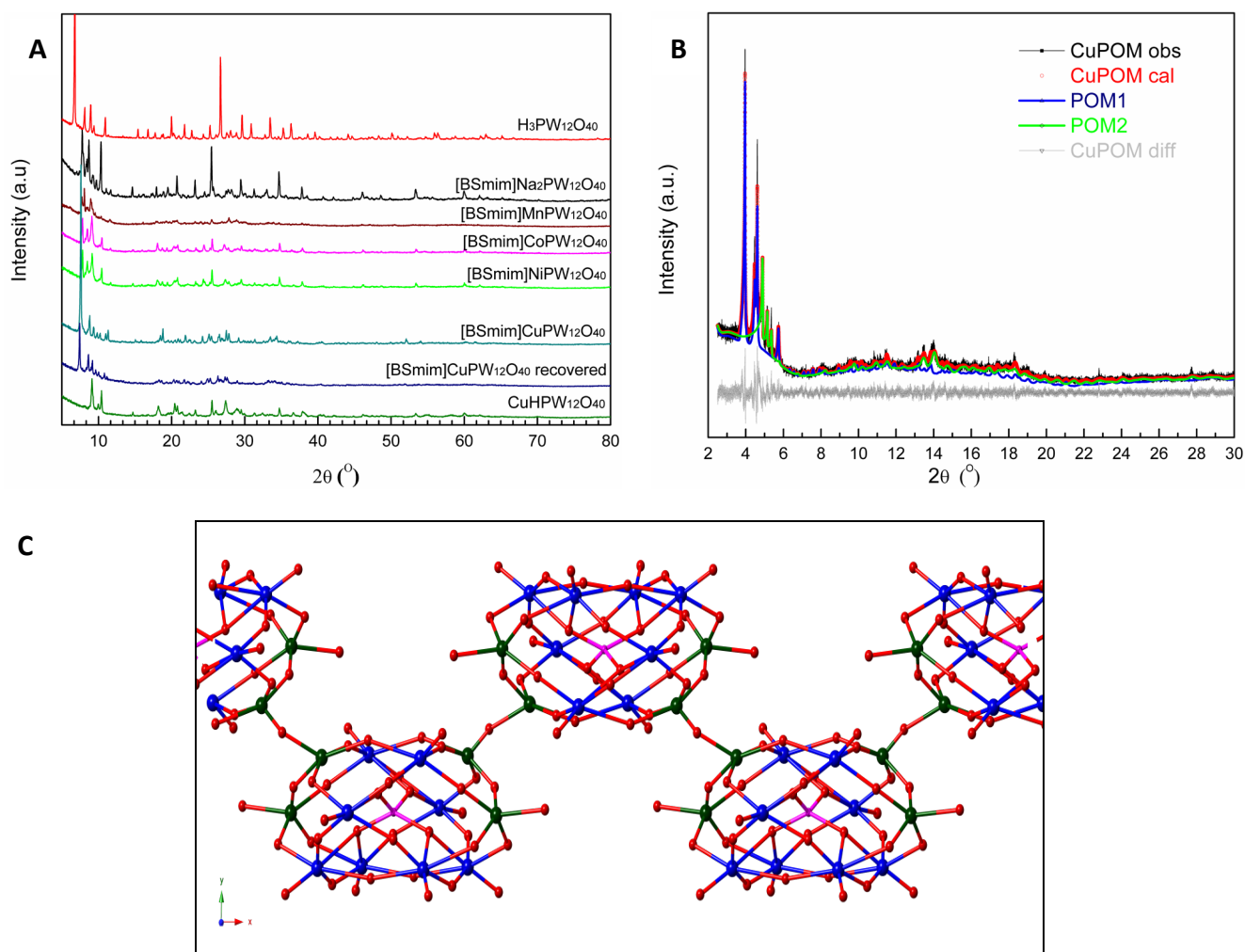


Figure S3. XRD patterns of POM-IL catalysts and synchrotron PXRD refinement and the structure of CuPOM. (A) XRD patterns of IL catalysts. (B) Comparison of the experiment data (black line) and Le Bail profile refinement (red circle). Red circle is the sum of the phase 1(CuPOM1) blue line and the phase 2 (CuPOM2) green line and the difference between them (grey line) from $2.5 \sim 30^\circ$. (C) The structure of CuPOM is obtained by transforming the space group *Pcca* to *Pncn* using winGX software, which was based on the Le Bail profile refinement data. The framework of CuPOM is using the ball-stick mode, framework O: red, W^{VI} : blue, $(\text{W/Cu})^{\text{V}}$: green, P: pink. (Unit cell parameters illustrate in Supplementary Table S2)

High resolution Synchrotron PXRD data were collected on Beamline I11, Diamond Light Source, UK. Detailed description of the beamline can be found elsewhere.⁷ The energy of the incident X-ray

beam was set at 15 keV. The wavelength and the 2 θ zero point correction were refined using a diffraction pattern obtained from a high quality silicon powder (SRM640c). Unit cell parameters of samples Cu-POM1 and Cu-POM2 obtained from powder diffraction data which was based on a Le Bail profile refinement using the TOPAS and summarized in Supplementary **Table S2**. The *Pncn* structure of the CuPOM was deduced from the *Pcca* space group transformed through the matrix using $\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$ WinGX software.

Table S2. Crystallographic data and details of the CuPOM sample.

Samples	Cu-POM1	Cu-POM2
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pncn</i>	<i>Pncn</i>
Chemical formula	$[\text{P}(\text{W}/\text{Cu})^{\text{V}}_4\text{W}^{\text{VI}}_8\text{O}_{39}]^{\text{n-}} \cdot \text{n} (\text{O}_2/\text{H}_2\text{O})$	$[\text{P}(\text{W}/\text{Cu})^{\text{V}}_4\text{W}^{\text{VI}}_8\text{O}_{39}]^{\text{n-}} \cdot \text{n} (\text{O}_2/\text{H}_2\text{O})$
2 θ range refinement (°)	2.5 – 30	
Detector	Multi-analyser crystals	
Refinement methods	Rietveld refinement	
<i>a</i> (Å)	20.48624(9)	17.61397(4)
<i>b</i> (Å)	14.40534(9)	11.46489(5)
<i>c</i> (Å)	16.48389(1)	15.19459(7)
<i>V</i> (Å ³)	4856.1(1)	3068.1 (1)
<i>R</i> _{wp} / <i>R</i> _p / <i>R</i> _{exp} (%)	9.975/7.861/6.605	
Wavelength (Å)	0.825255 (2)	
2 θ Zero point (°)	-0.0001 (2)	
Gof χ^2	1.510	

Table S3. The detailed parameters Rietveld refinement of POM-IL

Species	Atom	X	Y	Z	SOF	$B_{eq}(\text{\AA}^2)$
CU-POM1/2	site P1	0	0.4457	0.25	1	2
	site W1	0.2467	0.4503	0.3217	1	2
	site W2	0.1126	0.4413	0.0953	1	2
	site W3	0.0729	0.5802	0.3617	1	2
	site W4	-0.0606	0.3122	0.1352	1	2
	site W5	0.1816	0.5794	0.2128	1	2
	site W6	0.1764	0.3123	0.2041	1	2
	site O1	0.0863	0.4926	0.2749	1	2
	site O2	0.0392	0.3988	0.1955	1	2
	site O3	0.1124	0.2879	0.2824	1	2
	site O4	0.0526	0.6029	0.1784	1	2
	site O7	0.0013	0.5058	0.0967	1	2
	site O8	0.1606	0.3848	0.3646	1	2
	site O9	0.1442	0.6214	0.2923	1	2
	site O10	0.0655	0.2699	0.1595	1	2
	site O11	0.2769	0.5237	0.2598	1	2
	site O12	0.1992	0.3682	0.127	1	2
	site O13	0.1955	0.5232	0.3757	1	2
	site O14	0.0148	0.3686	0.0753	1	2
	site O15	0.3633	0.4354	0.3536	1	2
	site O16	0.1686	0.4567	0.0216	1	2
	site O17	0.0856	0.6408	0.4208	1	2
	site O18	-0.1119	0.2507	0.0859	1	2
	site O19	0.258	0.641	0.1791	1	2
	site O20	0.2729	0.2521	0.1968	1	2
	site O5	0.1821	0.5061	0.1497	1	2
	site O6	0.2422	0.3856	0.2522	1	2
O atoms of water	O	0.32482	-0.15407	1.36937	5.78(6)	2
For CuPOM-1	O	0.73191	-0.27770	-0.50310	1.96(6)	2
	O	0.30770	1.18390	-1.05108	12.56(7)	2
	O	-0.72126	1.16347	0.48646	7.09(6)	2

Table S4. M K-edge and W L₃-edge EXAFS curve fitting parameters of [BSmim]MPW₁₂O₄₀ (M = Mn, Co, Ni, Cu).

Table S4a. Mn K-edge and W L₃-edge EXAFS curve Fitting parameters.^a

sample	Shell	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0 (eV)	<i>R</i> , %
MnO ₂ ^b	Mn–O	6	1.90	0.005	4.3	0.01
[BSmim]MnPW ₁₂ O ₄₀ ^c	Mn–O	6.0	2.16	0.007	8.7	0.01
	W–O1	1.0	1.70	0.001	1.4	0.03
	W–O2	3.9	1.90	0.004		
	W–O3	1.0	2.41	0.011		
[BSmim]MnPW ₁₂ O ₄₀ _H ₂ ^c	Mn–O	5.6	2.15	0.007	8.9	0.01
	W–O1	0.9	1.71	0.001	2.5	0.05
	W–O2	4.1	1.91	0.004		
	W–O3	1.0	2.43	0.011		

^a *N*, coordination number; *R*, distance between absorber and backscatter atoms; σ^2 , Debye–Waller factor to account for both thermal and structural disorders; ΔE_0 , inner potential correction; *R* factor (%) indicates the goodness of the fit. Error bounds (accuracies) that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as $N \pm 20\%$; $R \pm 1\%$; $\sigma^2 \pm 20\%$; $\Delta E_0 \pm 20\%$. S_0^2 were determined from MnO₂ and WO₃ standard fitting and fixed. Bold numbers indicate fixed coordination number (*N*) according to the crystal structure. O1, O2, and O3 represent the first, second, and third nearest neighbor coordination O atoms. ^b Fitting range: $2.0 \leq k \text{ (}/\text{\AA)} \leq 12.6$ and $1.0 \leq R \text{ (}\text{\AA)} \leq 2.0$. ^c Mn K-edge fitting range: $2.5 \leq k \text{ (}/\text{\AA)} \leq 12.0$ and $1.0 \leq R \text{ (}\text{\AA)} \leq 2.4$; W L₃-edge fitting range: $2.5 \leq k \text{ (}/\text{\AA)} \leq 14.5$ and $1.0 \leq R \text{ (}\text{\AA)} \leq 2.4$.

Table S4b. Co K-edge and W L₃-edge EXAFS curve fitting parameters.^a

sample	Shell	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0 (eV)	<i>R</i> , %
Co bulk ^b	Co–Co	12	2.49	0.008	0.7	0.01
CoO ^c	Co–O	6	2.12	0.009	-9.9	1.0
	Co–Co	12	3.01	0.009		
[BSmim]CoPW ₁₂ O ₄₀ ^d	Co–O	6.0	2.08	0.006	-3.1	0.01
	W–O1	1.0	1.70	0.001	3.0	0.09
	W–O2	3.9	1.91	0.004		
	W–O3	1.0	2.42	0.011		
[BSmim]CoPW ₁₂ O ₄₀ _H ₂ ^d	Co–O	5.8	2.08	0.006	-3.3	0.01
	W–O1	0.8	1.71	0.001	4.7	0.05
	W–O2	3.8	1.91	0.004		
	W–O3	1.0	2.44	0.011		

^a *N*, coordination number; *R*, distance between absorber and backscatter atoms; σ^2 , Debye–Waller factor to account for both thermal and structural disorders; ΔE_0 , inner potential correction; *R* factor (%) indicates the goodness of the fit. Error bounds (accuracies) that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as $N \pm 20\%$; $R \pm 1\%$; $\sigma^2 \pm 20\%$; $\Delta E_0 \pm 20\%$. S_0^2 were determined from CoO and WO₃ standard fitting and fixed. Bold numbers indicate fixed coordination number (*N*) according to the crystal structure. O1, O2, and O3 represent the first, second, and third nearest neighbor coordination O atoms. ^b Fitting range: $3.2 \leq k$ (1/Å) ≤ 14.0 and $1.4 \leq R$ (Å) ≤ 2.7 . ^cFitting range: $3.2 \leq k$ (1/Å) ≤ 14.5 and $1.0 \leq R$ (Å) ≤ 3.2 . ^dCo K-edge fitting range: $3.2 \leq k$ (1/Å) ≤ 11.9 and $1.0 \leq R$ (Å) ≤ 2.4 ; W L₃-edge: fitting range: $2.5 \leq k$ (1/Å) ≤ 14.5 and $1.0 \leq R$ (Å) ≤ 2.4 .

Table S4c. Ni K-edge and W L₃-edge EXAFS curve fitting parameters.^a

sample	Shell	<i>N</i>	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0 (eV)	<i>R</i> , %
Ni bulk ^b	Ni-Ni	12	2.48	0.008	0.7	0.01
NiO ^c	Ni-O	6	2.08	0.005	1.8	0.01
	Ni-Ni	12	2.95	0.006		
[BSmim]NiPW ₁₂ O ₄₀ ^d	Ni-O	5.9	2.04	0.007	-10.9	0.01
	W-O1	1.0	1.70	0.001	3.2	0.07
	W-O2	3.9	1.91	0.004		
	W-O3	1.0	2.49	0.011		
[BSmim]NiPW ₁₂ O ₄₀ _H ₂ ^d	Ni-O	5.7	2.03	0.007	-11.9	0.2
	W-O1	1.0	1.72	0.002	5.1	0.08
	W-O2	3.8	1.92	0.004		
	W-O3	0.5	2.44	0.011		

^a *N*, coordination number; *R*, distance between absorber and backscatter atoms; σ^2 , Debye–Waller factor to account for both thermal and structural disorders; ΔE_0 , inner potential correction; *R* factor (%) indicates the goodness of the fit. Error bounds (accuracies) that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as $N \pm 20\%$; $R \pm 1\%$; $\sigma^2 \pm 20\%$; $\Delta E_0 \pm 20\%$. S_0^2 were determined from NiO and WO₃ standard fitting and fixed. Bold numbers indicate fixed coordination number (*N*) according to the crystal structure. O1, O2, and O3 represent the first, second, and third nearest neighbor coordination O atoms. ^b Fitting range: $3.9 \leq k$ (1/Å) ≤ 13.9 and $1.6 \leq R$ (Å) ≤ 2.6 . ^c Fitting range: $3.7 \leq k$ (1/Å) ≤ 14.5 and $1.0 \leq R$ (Å) ≤ 3.2 . ^d Ni K-edge fitting range: $3.2 \leq k$ (1/Å) ≤ 11.9 and $1.0 \leq R$ (Å) ≤ 2.4 ; W L₃-edge fitting range: $2.5 \leq k$ (1/Å) ≤ 14.5 and $1.0 \leq R$ (Å) ≤ 2.4 .

Table S4d. Cu K-edge and W L₃-edge EXAFS curve fitting parameters.^a

sample	Shell	<i>N</i> ^a	<i>R</i> (Å)	σ^2 (Å ²)	ΔE_0 (eV)	<i>R</i> , %
Cu bulk ^b	Cu–Cu	12	2.54	0.008	1.0	0.01
Cu ₂ O ^c	Cu–O	2	1.86	0.003	4.0	0.04
CuO ^c	Cu–O	4	1.96	0.005	2.1	0.01
[BSmim]CuPW ₁₂ O ₄₀ ^d	Cu–O1	4.6	1.96	0.005	3.6	0.01
	Cu–O2	1.0	2.26	0.010		
	W–O1	1.0	1.70	0.001	3.2	0.07
	W–O2	4.0	1.91	0.004		
	W–O3	1.0	2.49	0.011		
[BSmim]CuPW ₁₂ O ₄₀ _H ₂ ^d	Cu–O1	4.0	1.96	0.005	2.5	0.05
	Cu–O2	1.0	2.21	0.010		
	W–O1	1.0	1.71	0.001	3.3	0.14
	W–O2	3.6	1.91	0.004		
	W–O3	0.8	2.49	0.011		

^a *N*, coordination number; *R*, distance between absorber and backscatter atoms; σ^2 , Debye–Waller factor to account for both thermal and structural disorders; ΔE_0 , inner potential correction; *R* factor (%) indicates the goodness of the fit. Error bounds (accuracies) that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as $N \pm 20\%$; $R \pm 1\%$; $\sigma^2 \pm 20\%$; $\Delta E_0 \pm 20\%$. S_0^2 were determined from CuO and WO₃ standard fitting and fixed. Bold numbers indicate fixed coordination number (*N*) according to the crystal structure. O1, O2, and O3 represent the first, second, and third nearest neighbor coordination O atoms. ^b Fitting range: $2.5 \leq k (\text{\AA}^{-1}) \leq 12.5$ and $1.6 \leq R (\text{\AA}) \leq 2.8$. ^cFitting range: $2.5 \leq k (\text{\AA}^{-1}) \leq 12.5$ and $1.0 \leq R (\text{\AA}) \leq 2.0$. ^dCu K-edge fitting range: $2.9 \leq k (\text{\AA}^{-1}) \leq 12.5$ and $1.0 \leq R (\text{\AA}) \leq 2.6$; W L₃-edge fitting range: $2.5 \leq k (\text{\AA}^{-1}) \leq 14.5$ and $1.0 \leq R (\text{\AA}) \leq 2.4$.

To understand the coordination environment and chemical states of M/W in POM-ILs, X-ray absorption fine structure spectra were collected at 1W1B beamline of Beijing Synchrotron Radiation source in China in fluorescence mode using a Si (111) double crystal monochromator under ambient condition. The incident and fluorescence X-ray intensities were detected by standard ionization chambers and Lytle-type detectors, respectively. The EXAFS raw data were then background-subtracted, normalized and Fourier transformed by the standard procedures with the

ATHENA program;⁶ least-squares curve fitting analysis of the EXAFS $\chi(k)$ data was carried out using the ARTEMIS program.

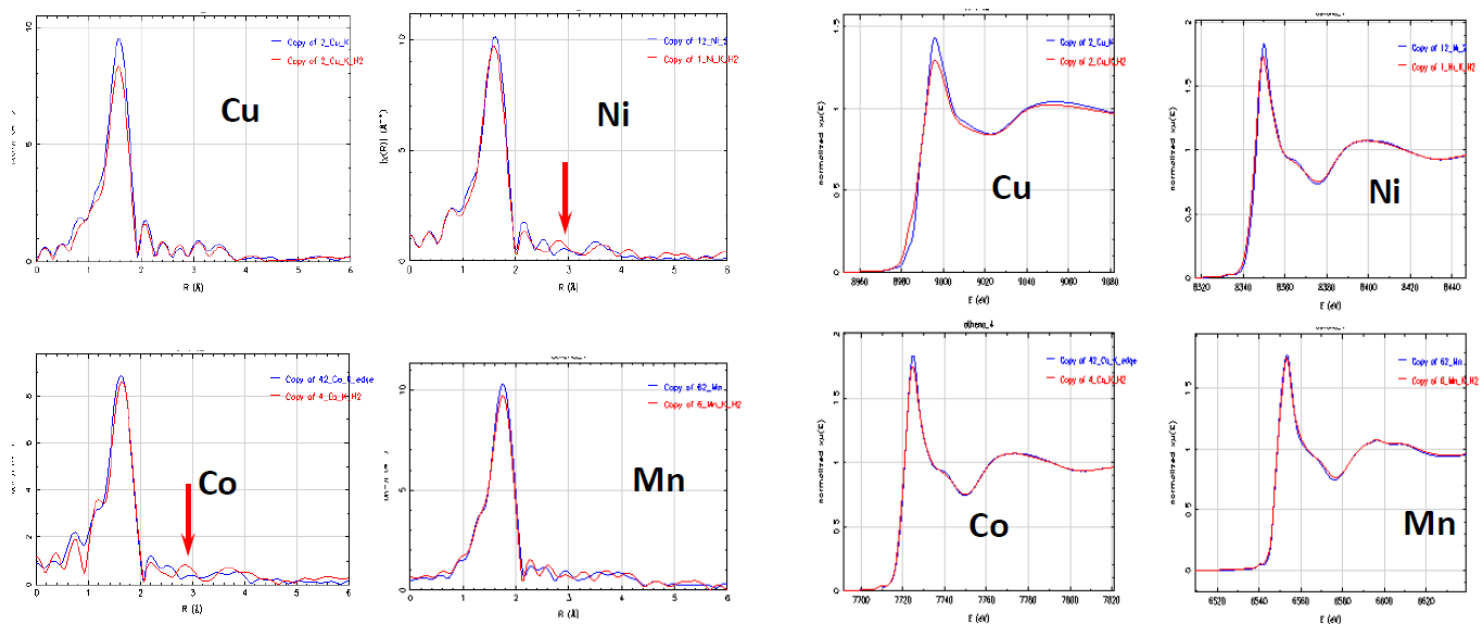


Figure S4a. EXAFS and XANES analyses of POM-ILs

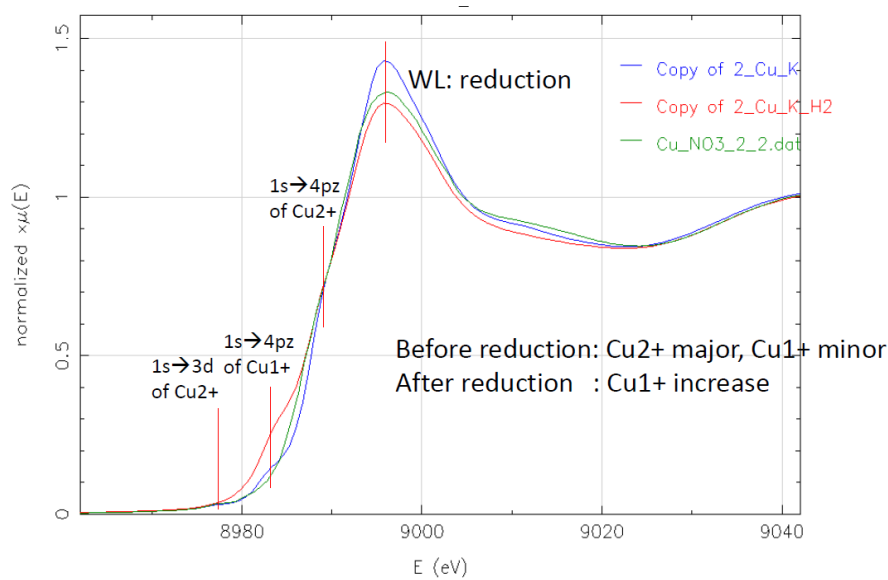


Figure S4b. XANES analyses of [BSmim]CuPW₁₂O₄₀

Table S5. ICP-MS analysis of POM-ILs.^a

IL catalyst	Element	Concentration (mg L ⁻¹) ^b	Analysis 1 (mg L ⁻¹)	Analysis 2 (mg L ⁻¹)	Average (mg L ⁻¹)	Error (%)
[BSmim]CuPW ₁₂ O ₄₀	Cu	6.06	5.97	5.88	5.93	2.15
	P	3.18	3.21	3.15	3.18	0.06
	W	20.93	20.16	19.98	20.07	4.11
[BSmim]NiPW ₁₂ O ₄₀	Ni	5.60	5.34	5.40	5.37	4.11
	P	3.23	3.20	3.27	3.24	0.28
	W	20.96	20.76	20.84	20.80	0.76
[BSmim]CoPW ₁₂ O ₄₀	Co	5.69	5.35	5.47	5.41	4.92
	P	3.20	3.21	3.23	3.22	0.77
	W	20.95	20.79	20.81	20.80	0.72
[BSmim]MnPW ₁₂ O ₄₀	Mn	5.22	5.11	5.09	5.10	2.30
	P	3.17	3.20	3.19	3.20	0.69
	W	20.98	20.14	20.28	20.21	3.67
[BSmim]Na ₂ PW ₁₂ O ₄₀	Na	4.39	4.15	4.21	4.18	4.78
	P	3.20	3.26	3.19	3.23	0.80
	W	21.05	19.98	19.87	19.93	5.32

^a The concentration of IL catalyst is 300 mgL⁻¹ for Cu, Co, Mn, Ni, Na and P, and is 30 mgL⁻¹ for

W; ^b Theoretical value.

III. The selective oxidation of lignin and model compounds

Table S6. Selective oxidation of bagasse lignin over various catalysts.

Entry	Catalysts	Conv. (%)	Yield (mg g ⁻¹)											DEM selectivity ^a	Average molar mass of regenerated lignin		
			1	2	3	4	5	6	7	8	9	10	total	(%)	<i>M_w</i>	<i>M_n</i>	D
1	None	48.2	— ^b	—	—	—	—	1.1	2.0	3.4	5.7	2.5	14.7	0	1643	990	1.66
2	[BSmim]HSO ₄	82.4	6.5	4.4	4.1	0.9	—	10.0	1.8	17.9	2.5	—	48.1	13.5	688	375	1.83
3	[BSmim]Na ₂ PW ₁₂ O ₄₀	81.3	53.6	3.7	2.5	—	—	1.6	7.7	—	—	—	69.1	77.6	999	688	1.45
4	[BSmim]MnPW ₁₂ O ₄₀	80.9	87.7	12.5	4.0	3.4	7.1	—	15.6	—	—	—	130.3	67.3	949	663	1.43
5	[BSmim]CoPW ₁₂ O ₄₀	80.6	93.3	6.8	4.1	1.4	7.3	7.6	26.0	—	—	—	146.5	63.7	933	652	1.43
6	[BSmim]NiPW ₁₂ O ₄₀	84.3	100.4	5.1	7.3	3.2	8.1	11.2	27.1	—	3.9	—	166.3	60.4	920	647	1.42
7	[BSmim]CuPW ₁₂ O ₄₀	90.7	153.6	4.8	12.0	5.8	16.9	25.2	31.7	—	9.1	—	259.1	59.3	786	613	1.28
8 ^c	[Bmim]CuPW ₁₂ O ₄₀	80.8	11.0	1.7	2.1	1.9	1.4	13.7	1.8	9.7	2.9	—	46.2	23.8	1132	846	1.34
9 ^d	H ₂ SO ₄ /CuSO ₄	86.8	16.5	0.9	1.6	1.8	11.4	12.0	10.7	10.2	9.4	—	74.5	22.1	898	648	1.39
10 ^e	[BSmim]Na ₂ PW ₁₂ O ₄₀ /CuSO ₄	90.0	100.9	3.1	5.9	1.3	15.2	17.9	16.7	—	1.6	—	162.6	62.1	886	682	1.30
11 ^f	[BSmim]CuPW ₁₂ O ₄₀	31.3	—	—	—	—	—	—	—	—	—	—	78.6	0	954	726	1.31

Reaction conditions: 0.25 g bagasse lignin, 0.9 mmol catalyst, 20 mL of 80% ethanol-water, 0.8 MPa O₂, 433 K, 5 h. ^a the selectivity of DEM is based on the volatile product determined by GC-MS; ^b not added or detected; ^c After removed the solvents, then 10 mL ethanol and 0.45 mmol H₂SO₄ were added at 373 K for 2 h; ^d 0.45 mmol H₂SO₄/0.9 mmol CuSO₄; ^e 0.9 mmol [BSmim]Na₂PW₁₂O₄₀/(0.9 mmol) CuSO₄. ^f 0.8 MPa N₂, volatile products: guaiacol (1.6 mg g⁻¹), phenol (2.7 mg g⁻¹), 4-ethylguaiacol (5.3 mg g⁻¹), 4-ethylphenol (54.1 mg g⁻¹), 5-methyl-2-isopropylphenol (4.2 mg g⁻¹), 2,6-dimethoxyphenol (3.6 mg g⁻¹), 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl) ethanone (7.1 mg g⁻¹). **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Diethyl malate; **5**: Ethyl ethoxyacetate; **6**: Ethyl 4-hydroxybenzoate; **7**: Ethyl vanillate; **8**: 4-Hydroxybenzaldehyde; **9**: Vanillin; **10**: Syringaldehyde. Original bagasse lignin with the *M_w*, *M_n* and D values of 2698, 1156 and 2.33, respectively, see [Table S13](#), $D=M_w/M_n$.

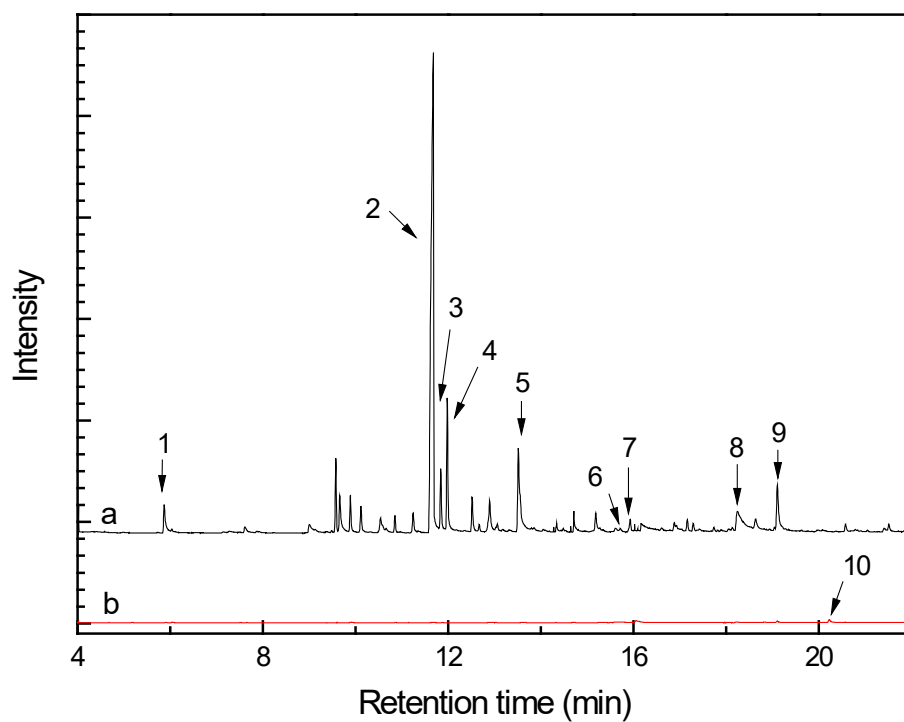
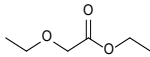
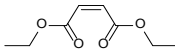
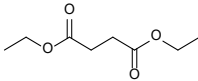
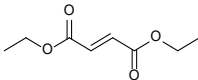
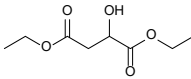
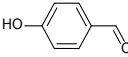
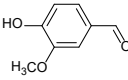
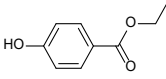
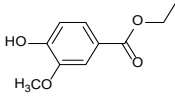
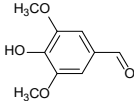


Figure S5. GC-MS analysis of the volatile products with (a) and without (b) [BSmim]CuPW₁₂O₄₀.

Reaction conditions: 0.25 g bagasse lignin, 0.9 mmol [BSmim]CuPW₁₂O₄₀ catalyst, 20 mL 80% ethanol-water, 433 K, 5 h, 0.8 MPa O₂.

Table S7. The volatile products detected by GC-MS.

Entry	Retention time (min)	Products	Structure	Formula	Molecular weight (g mol ⁻¹)
1	5.94	Ethyl ethoxyacetate		C ₆ H ₁₂ O ₃	132
2	11.68	Diethyl maleate		C ₈ H ₁₂ O ₄	172
3	12.03	Diethyl succinate		C ₈ H ₁₄ O ₄	174
4	12.95	Diethyl fumarate		C ₈ H ₁₂ O ₄	172
5	13.58	Diethyl malate		C ₈ H ₁₄ O ₅	190
6	15.80	4-hydroxybenzaldehyde		C ₇ H ₆ O ₂	122
7	16.08	Vanillin		C ₈ H ₈ O ₃	152
8	18.23	Ethyl 4-hydroxybenzoate		C ₉ H ₁₀ O ₃	166
9	19.15	Ethyl vanillate		C ₁₀ H ₁₂ O ₄	196
10	20.26	Syringaldehyde		C ₉ H ₁₀ O ₄	182

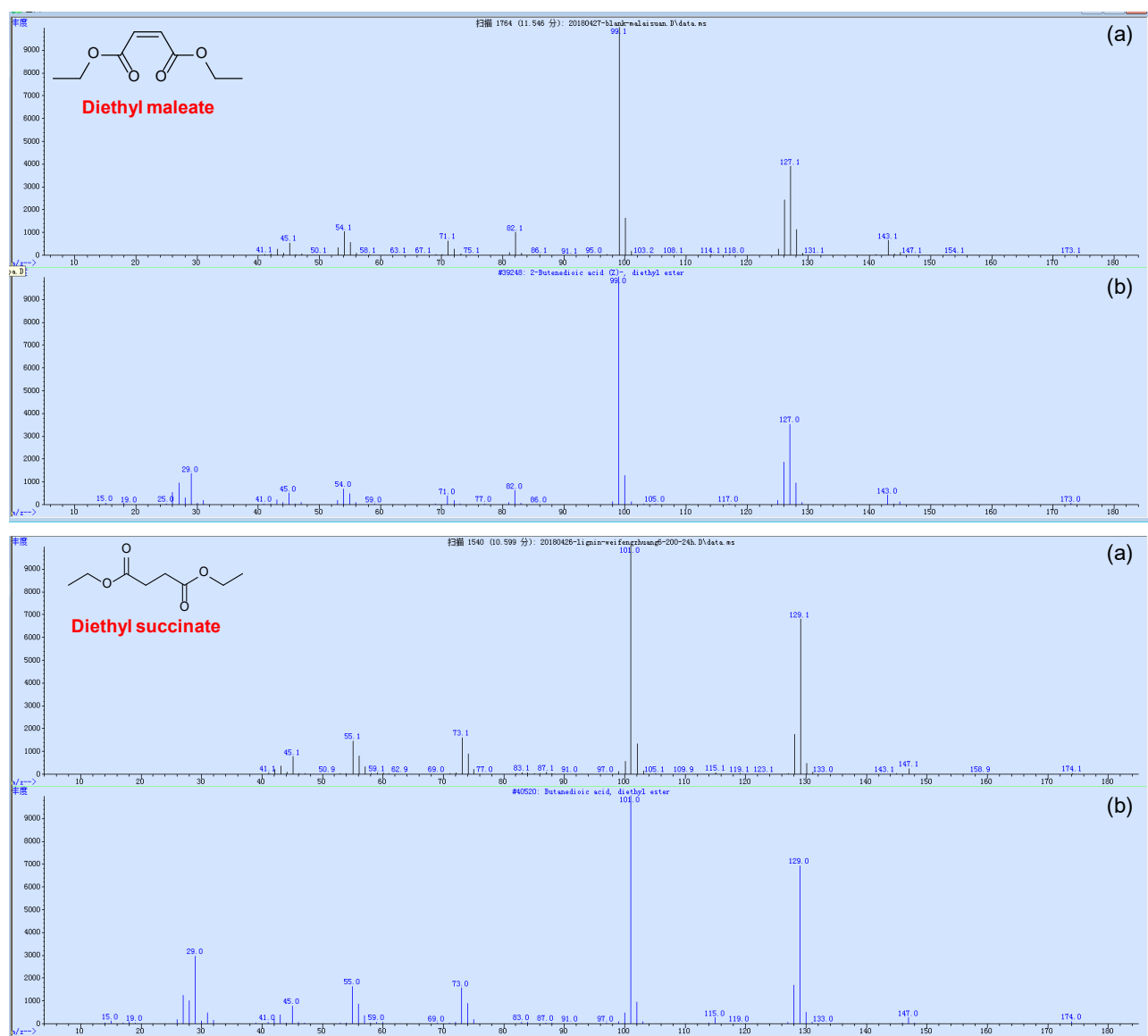


Figure S6a. The MS spectra of C4 esters produced in this process. ^a: the data from the reaction mixture; ^b: the data from MS library.

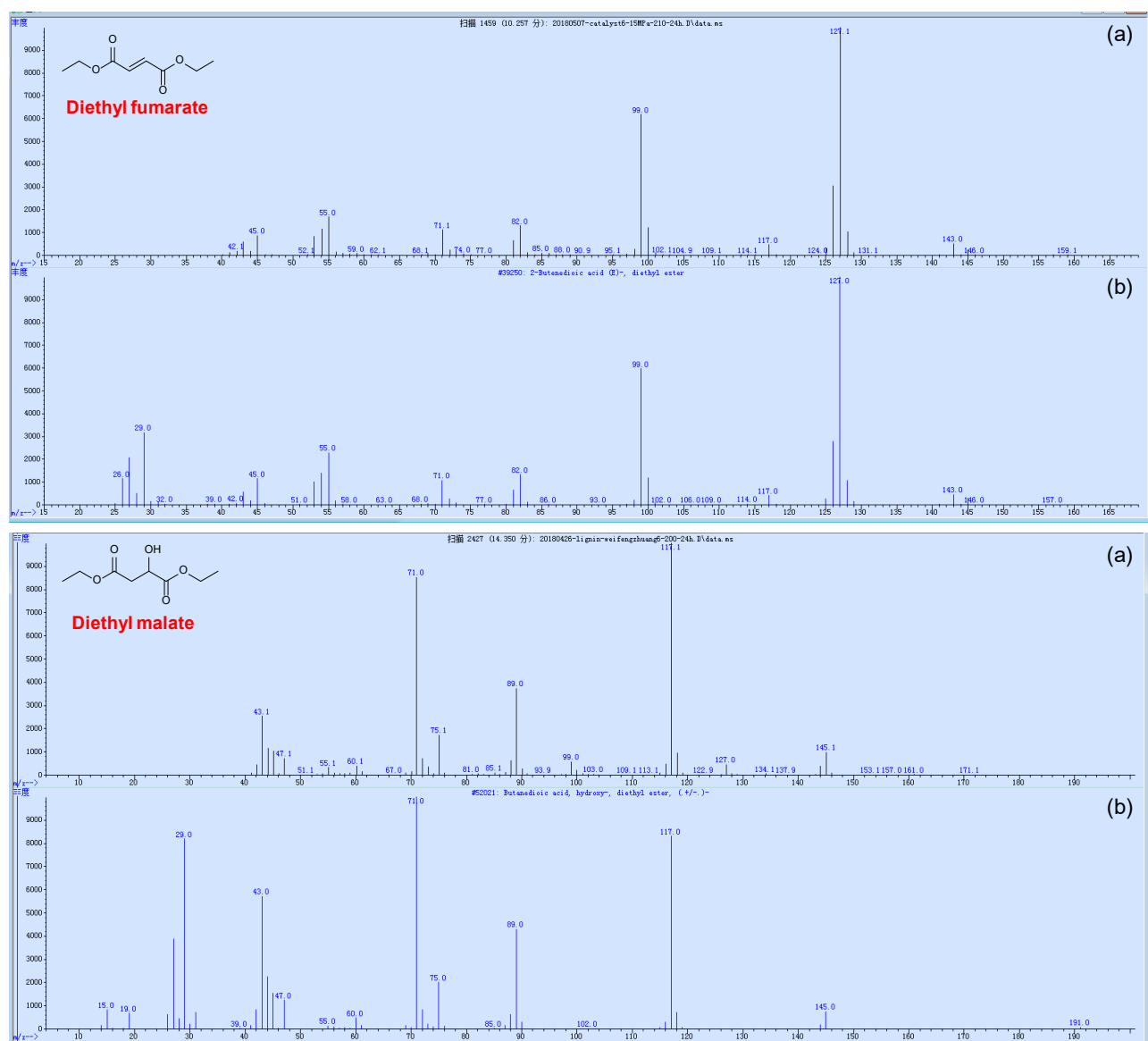


Figure S6b. The MS spectra of C4 esters produced in this process. ^a: the data from the reaction mixture; ^b: the data from MS library.

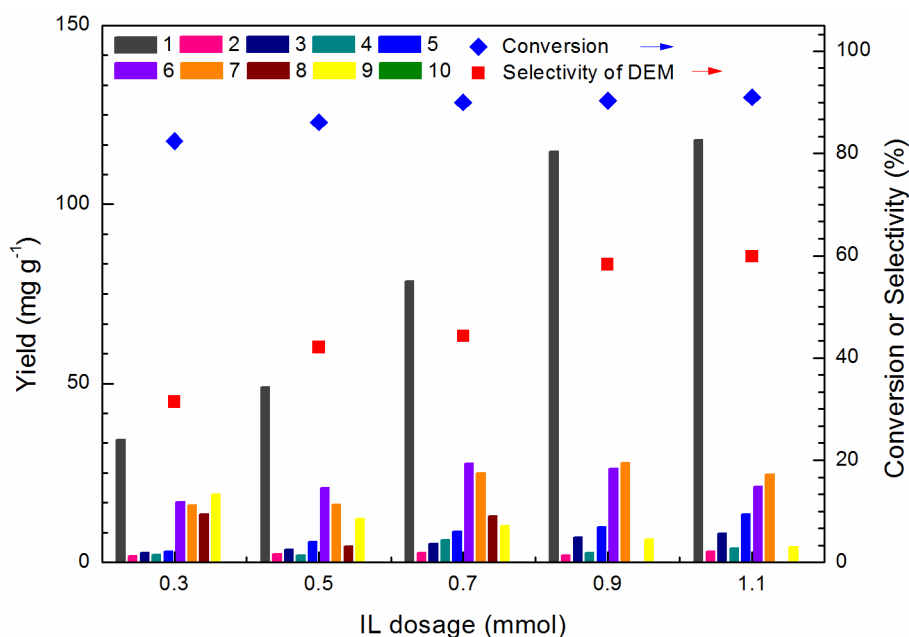


Figure S7. Effect of POM-IL catalysts dosage on the oxidation of lignin.

Reaction condition: 0.25 g bagasse lignin, [BSmim]CuPW₁₂O₄₀ as catalyst, 20 mL 80% ethanol-water, 433 K, 3 h, 0.8 MPa O₂. 1: Diethyl maleate; 2: Diethyl succinate; 3: Diethyl fumarate; 4: Diethyl malate; 5: Ethyl ethoxyacetate; 6: Ethyl 4-hydroxybenzoate; 7: Ethyl vanillate; 8: 4-Hydroxybenzaldehyde; 9: Vanillin; 10: Syringaldehyde.

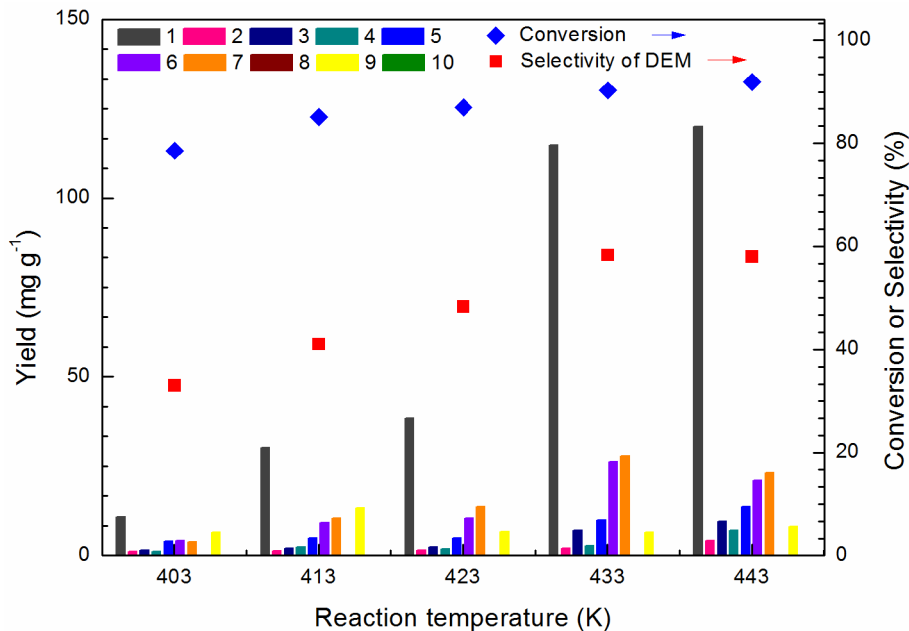


Figure S8. Effect of reaction temperature on the oxidation of lignin.

Reaction condition: 0.25 g bagasse lignin, 0.9 mmol [BSmim]CuPW₁₂O₄₀, 20 mL 80% ethanol-water, 3 h, 0.8 MPa O₂. 1: Diethyl maleate; 2: Diethyl succinate; 3: Diethyl fumarate; 4: Diethyl malate; 5: Ethyl ethoxyacetate; 6: Ethyl 4-hydroxybenzoate; 7: Ethyl vanillate; 8: 4-Hydroxybenzaldehyde; 9: Vanillin; 10: Syringaldehyde.

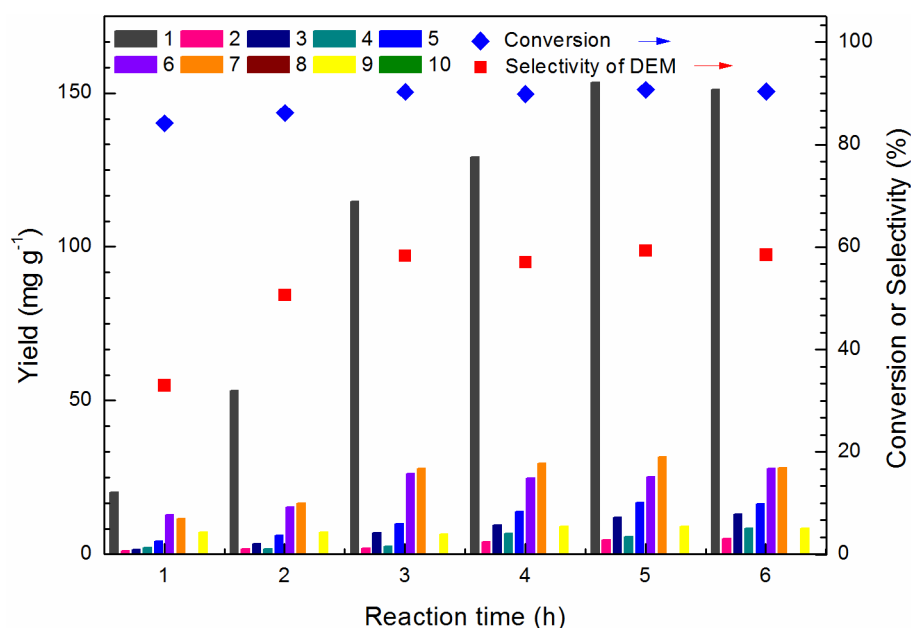


Figure S9. Effect of reaction time on the oxidation of lignin.

Reaction condition: 0.25 g bagasse lignin, 0.9 mmol [BSmim]CuPW₁₂O₄₀, 20 mL 80% ethanol-water, 433 K, 0.8 MPa O₂. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Diethyl malate; **5:** Ethyl ethoxyacetate; **6:** Ethyl 4-hydroxybenzoate; **7:** Ethyl vanillate; **8:** 4-Hydroxybenzaldehyde; **9:** Vanillin; **10:** Syringaldehyde.

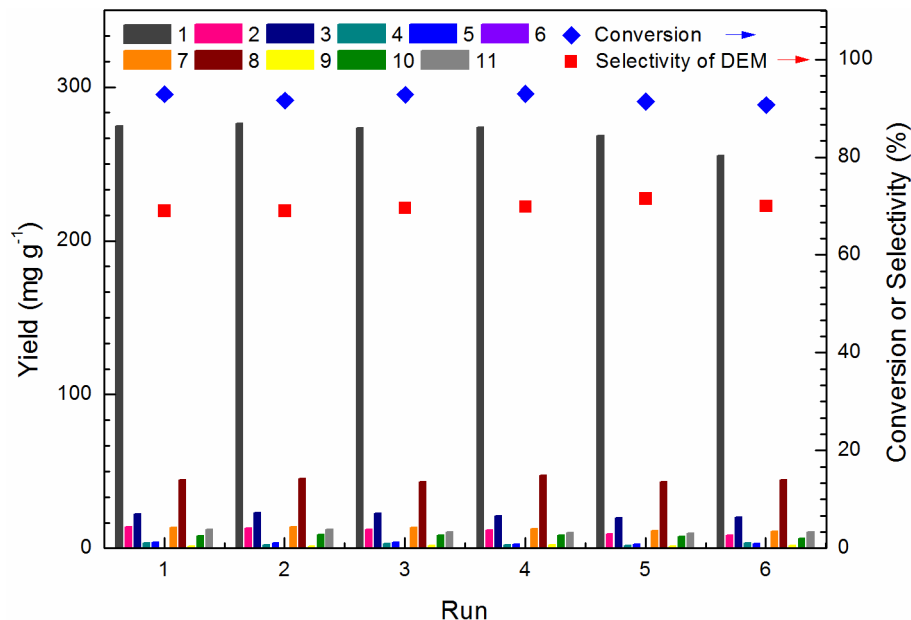


Figure S10. Recycle performances of IL [BSmim]CuPW₁₂O₄₀ catalyst.

Reaction conditions: 0.25 g bagasse lignin, 0.9 mmol [BSmim]CuPW₁₂O₄₀, 20 mL 100% ethanol, 433 K, 5 h, 0.8 MPa O₂. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl ethoxyacetate; **5:** Ethyl 3-ethoxypropionate; **6:** Diethyl oxalate; **7:** Diethyl malonate; **8:** Ethyl diethoxyacetate; **9:** Ethyl 3,3-diethoxypropionate; **10:** Ethyl 4-hydroxybenzoate; **11:** Ethyl vanillate.

Table S8. Selective oxidation of bagasse lignin in different aqueous ethanol.

Entry	Ethanol concentration (%)	Conversion (%)	Yield (mg g ⁻¹)															DEM selectivity (%)
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	Total	
1	0	29.3	1.7	2.7	2.0	1.9	— ^a	—	—	—	—	—	—	—	—	—	8.3	20.5
2	20	46.8	16.6	2.6	7.3	9.5	—	4.2	1.1	8.4	4.2	—	—	—	—	—	53.9	30.8
3	40	84.4	61.0	8.0	16.6	25.6	8.3	—	—	—	—	—	—	—	—	—	119.5	51.0
4	60	87.3	83.1	12.5	16.3	23.1	0.9	16.5	5.1	19.5	11.3	—	0.3	—	—	—	188.6	44.1
5	80	90.7	153.6	4.8	12.0	5.8	16.9	25.2	31.7	—	9.1	—	—	—	—	—	259.1	59.3
6	100	92.9	274.7	13.8	22.4	—	3.4	8.3	12.1	—	—	—	3.9	13.8	44.4	1.6	398.4	69.0
7 ^b	40	100	152.9	—	163.5	179.3	—	—	—	—	—	—	—	—	—	—	495.7	30.8
8 ^b	80	100	416.3	—	41.3	31.3	—	—	—	—	—	—	—	—	—	—	488.9	85.1
9 ^b	100	100	1111.5	—	—	—	—	—	—	—	—	—	—	—	—	—	1111.5	100.0

Reaction conditions: 0.25 g bagasse lignin, 0.9 mmol [BSmim]CuPW₁₂O₄₀ catalyst, 20 mL ethanol-water, 433 K, 5 h, 0.8 MPa O₂. ^a not detected. ^b 0.25 g of maleic acid as substrate. **1**: Diethyl maleate.

2: Diethyl succinate. **3**: Diethyl fumarate. **4**: Diethyl malate. **5**: Ethyl ethoxyacetate. **6**: Ethyl 4-hydroxybenzoate. **7**: Ethyl vanillate. **8**: 4-Hydroxybenzaldehyde. **9**: Vanillin. **10**: Syringaldehyde. **11**:

Ethyl 3-ethoxypropionate. **12**: Diethyl malonate. **13**: Ethyl diethoxyacetate. **14**: Ethyl 3,3-diethoxypropionate.

Table S9. The elemental analysis of lignin before and after the reaction.

Entry	Material	Element content (%)				
		C	H	O ^[a]	N	S
1	Raw bagasse lignin	59.59	6.42	33.12	0.40	0.47
2	Oligomer	42.97	4.42	52.53	0.08	0.00
3	Regenerated lignin	43.11	4.27	52.31	0.31	0.00

Reaction condition: 0.25 g bagasse lignin, 0.9 mmol [BSmim]CuPW₁₂O₄₀, 20 mL 100% ethanol, 433 K, 5 h, 0.8 MPa O₂. ^a Oxygen content (%) = (100 – C – H – N – S)%; raw bagasse lignin :C₉H_{11.65}O_{3.75}N_{0.05}S_{0.02} (180.99 g/mol)

Table S10. The selective oxidation of bagasse lignin.

Entry	Atmosphere/time(h)		Conv. (%)	Yield (mg g ⁻¹) ^a												DEM Sel. (%)
	1 st run	2 nd run ^b		1	2	3	4	5	6	7	8	9	10	11	Total	
1	0.8 MPa O ₂ /5.0	—	92.9	274.7	13.8	22.4	—	3.4	13.8	3.9	44.4	1.6	8.3	12.1	398.4	69.0
2	0.8 MPa O ₂ /5.0	0.8 MPa N ₂ /1.0	91.4	281.6	13.8	23.3	8.3	9.6	18.2	5.3	8.2	4.1	20.2	12.2	404.8	69.6
3	0.8 MPa O ₂ /5.0	0.8 MPa O ₂ /1.0	96.5	483.8	21.0	47.5	13.3	10.0	24.1	5.7	10.1	4.3	15.4	9.3	644.5	75.1
4	0.8 MPa O ₂ /5.0	0.8 MPa O ₂ /2.0	100	522.3	30.3	56.1	22.5	9.6	23.5	5.3	9.8	3.9	—	—	683.3	76.4
5	0.2MPa N ₂ -0.8 MPa O ₂ /5.0	—	94.2	348.6	17.3	32.7	12.0	10.1	20.1	4.2	9.3	4.6	16.2	11.2	486.3	71.7
6	0.4MPa N ₂ -0.8 MPa O ₂ /5.0	—	94.2	350.1	18.7	31.2	13.2	11.3	20.2	4.7	10.1	5.2	18.7	12.4	495.8	70.6
7	0.2MPa N ₂ -1.0 MPa O ₂ /5.0	—	94.4	357.2	18.1	33.6	14.1	10.9	19.8	5.3	9.7	5.8	19.3	13.1	506.9	70.5

Reaction conditions: 0.25 g bagasse lignin, 0.9 mmol BSmimCuPW₁₂O₄₀ catalyst, 20 mL 100% ethanol, 433 K. ^a **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Diethyl malate; **5**: Ethyl ethoxyacetate; **6**: Diethyl malonate; **7**: Ethyl 3-ethoxypropionate; **8**: Ethyl diethoxyacetate; **9**: Ethyl 3,3-diethoxypropionate; **10**: Ethyl 4-hydroxybenzoate; **11**: Ethyl vanillate. ^b change in conversion and product distribution after re-testing the obtained product mixture from 1st run by injecting additional gas into the autoclave (2nd run) for the time specified.

Table S11. Gaseous composition before and after reaction.

Entry	Before/after reaction (vol. %)			
	O ₂	N ₂	CO ₂	CO
1 ^a	94.1/79.5	5.9/16.1	-/4.4	-/-
2 ^b	78.6/65.5	21.4/28.9	-/4.9	-/0.7
3 ^c	65.9/51.3	34.1/44.2	-/3.7	-/0.8
4 ^d	83.2/73.3	16.8/21.9	-/4.1	-/0.7

Reaction conditions: 0.25 g bagasse lignin, 0.9 mmol BSmimCuPW₁₂O₄₀ catalyst, 20 mL ethanol, 433 K, 5h. ^a 0.8 MPa O₂; ^b

0.2MPa N₂ and 0.8 MPa O₂; ^c 0.4 MPa N₂ and 0.8 MPa O₂; ^d 0.2 MPa N₂ and 1.0 MPa O₂.

Table S12. The molar content changes of gaseous fraction.

Entry	Before/after reaction(mmol)		
	O ₂	CO ₂	CO
1 ^a	25.4/15.7	-/1.17	-/0.17
2 ^b	25.5/15.3	-/1.11	-/0.24
3 ^c	32.2/21.8	-/1.22	-/0.21

Reaction conditions: 0.25 g bagasse lignin, 0.9 mmol BSmimCuPW₁₂O₄₀ catalyst, 20 mL ethanol, 433 K, 5h. ^a 0.2MPa N₂ and

0.8 MPa O₂; ^b 0.4 MPa N₂ and 0.8 MPa O₂; ^c 0.2 MPa N₂ and 1.0 MPa O₂.

Table S13. Average molecular weight of raw lignin.

Sample	M_w (g mol ⁻¹)	M_n (g mol ⁻¹)	D ^a
Rice stalk lignin	3319	2170	1.53
Wheat stalk lignin	3094	1693	1.83
Pine lignin	2984	1338	2.23
Bagasse lignin	2698	1156	2.33
Corn stalk lignin	2090	1170	1.79
Dealkaline lignin ^b	17029	15613	1.09

^a D= M_w/M_n . ^b the acetylated dealkaline lignin.

Table S14. The oxidative ring cleavage of various lignin feedstocks.

Entry	Lignin resource	Yield (mg g ⁻¹)												Selectivity of
		1	2	3	4	5	6	7	8	9	10	11	Total	DEM (%)
1	Wheat stalk	404.8	26.6	35.0	5.0	— ^a	—	18.0	50.3	3.9	—	13.1	556.7	72.7
2	Corn stalk	308.7	15.9	22.9	3.5	—	13.4	12.2	46.1	1.9	7.9	8.7	441.2	70.0
3	Bagasse	274.7	13.8	22.4	3.4	3.9	—	13.8	44.4	1.6	8.3	12.1	398.4	69.0
4	Pine	255.2	19.4	32.0	2.4	—	—	5.9	25.5	2.8	—	18.3	361.5	70.6
5	Rice straw	254.3	15.8	18.3	3.1	3.3	17.0	13.3	46.6	2.6	—	8.4	382.7	66.4
6	Dealkaline	210.6	13.7	24.6	—	3.3	—	3.8	20.6	2.4	—	17.9	296.9	70.9

Reaction conditions: 0.25 g lignin, 0.9 mmol [BSmim]CuPW₁₂O₄₀, 20 mL 100% ethanol, 433 K, 5 h, 0.8 MPa O₂. ^a not detected. **1**: Diethyl maleate; **2**: Diethyl succinate; **3**: Diethyl fumarate; **4**: Ethyl ethoxyacetate; **5**: Ethyl 3-ethoxypropionate; **6**: Diethyl oxalate; **7**: Diethyl malonate; **8**: Ethyl diethoxyacetate; **9**: Ethyl 3,3-diethoxypropionate; **10**: Ethyl 4-hydroxybenzoate; **11**: Ethyl vanillate.

Table S15. Assignment of FT-IR spectra.

Wave numbers (cm ⁻¹)	The attributions of the main absorptions
3,443	OH stretching
2,941	C-H stretching in methyl and methylene groups
2,859	-CH ₂ -symmetry stretching in methyl and methylene groups
1,702	C=O stretching in unconjugated ketones, carbonyls and in ester groups
1,608	Aromatic skeleton and C=O (S>G, G condensed>G etherified)
1,509	Aromatic skeleton (G>S)
1,467	C-H deformation (asymmetric CH ₃ and CH ₂)
1,426	Aromatic skeletal vibrations combined with C-H in plane deformations
1,368	C-H stretching of side groups (CH ₃)
1,327	S unit plus G unit condensed (G unit bound via position 5)
1,274	G ring and C=O stretching
1,233	C-C, C-O and C=O stretching
1,129	typical of S unit
1,087	secondary alcohol and aliphatic ether
1040	C-O of primary alcohol, Guaiacyl C-H
988	C-O valence vibration
894	C-H bending in aromatic skeleton
831	C-H out plane deformation

S: syringyl unit. G: guaiacyl unit

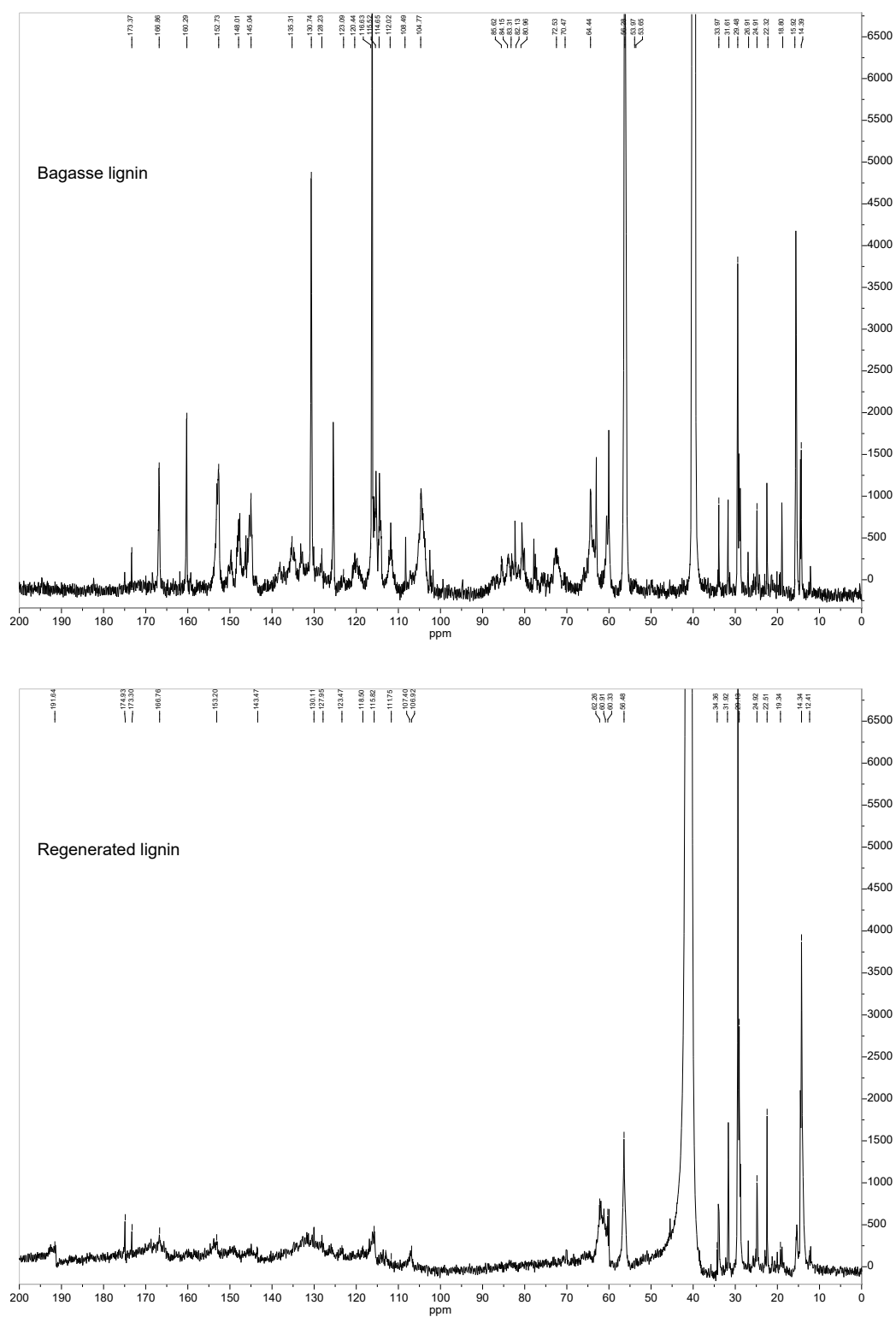
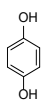
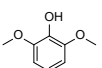
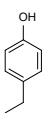
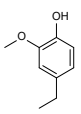
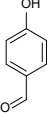
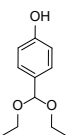
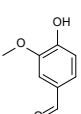
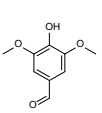
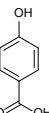
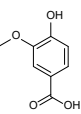
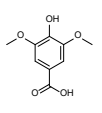


Figure S11. ^{13}C -NMR spectra of original and regenerated bagasse lignin

Table S16. The oxidation of model compounds over [BSmim]CuPW₁₂O₄₀.

Entr y	Substrates	Conversion (%)	Yield (mg g ⁻¹) ^a											DEM selectivity (%)
			1	2	3	4	5	6	7	8	9	10	Total	
1		100	176.7	16.9	20.6	3.5	—	7.7	23.9	2.5	—	—	251.8	70.2
2		100	442.4	27.1	32.6	6.8	18.1	9.9	40.4	4.4	—	—	581.7	76.1
3		100	446.5	28.0	36.2	6.9	17.5	11.5	38.7	2.9	—	—	588.2	75.9
4		100	205.2	14.7	15.4	4.5	30.3	15.0	33.3	3.2	—	—	321.6	63.8
5		100	257.3	12.9	21.7	4.9	25.8	21.3	41.8	2.4	—	—	388.1	66.3
6		100	228.2	13.3	14.1	5.0	23.0	14.1	35.6	3.4	—	—	336.7	67.8
7		100	368.4	19.7	24.1	5.0	14.6	14.1	51.7	4.8	—	—	502.4	73.3
8		86.0	243.9	16.1	21.8	3.8	15.8	8.0	29.8	2.9	108.0	—	450.1	54.2
9		86.2	315.1	15.8	18.4	9.2	30.0	6.3	9.2	2.9	—	—	490.2 ^b	64.3
10		100	357.8	14.6	16.2	3.9	21.5	13.7	37.4	3.2	—	48.6	516.9	69.2
11		100	360.5	13.7	21.8	4.6	36.5	24.1	48.1	2.3	—	—	511.6	70.5
12		100	8.2	—	—	—	—	—	—	—	944.7	—	952.9	0.9
13		100	114.8	5.8	6.1	1.3	9.6	8.7	24.8	2.4	—	457.2	630.7	18.2
14		100	223.2	12.9	31.6	4.2	25.4	31.5	66.1	3.0	—	—	397.9	56.1

15		3.5	5.1	—	—	—	—	—	—	—	—	—	5.1	100.0
16		63.0	102.5	3.0	4.6	2.0	11.8	0.6	21.1	2.0	—	—	147.6	69.4
17		100	36.6	—	—	—	—	—	—	—	—	—	48.7 ^c	75.2
	(4-O-5)													
18		91.7	27.5	—	—	20.7	—	—	—	—	—	—	902.8 ^d	3.0
	(α -O-4)													
19		0.0	—	—	—	—	—	—	—	—	—	—	—	—
	(5-5)													
20		100	30.4	0.8	—	—	—	—	—	—	—	—	529.5	5.7
	(β -1)													

Reaction conditions: 0.25 g model compound, 0.9 mmol [BSmim]CuPW₁₂O₄₀ catalyst, 20 mL 100% ethanol, 433 K, 5 h, 0.8 MPa O₂. ^a not detected;

^b including 83.3 mg g⁻¹ of other volatile products; ^c propanedioic acid, diethyl ester: 12.1 mg g⁻¹; ^d benzoic acid, ethyl ester: 839.9 mg g⁻¹, benzoic acid: 14.7 mg g⁻¹; ^e benzene, 1-methoxy-4-methyl-: 10.6 mg g⁻¹; benzene, 1-ethyl-4-methoxy-: 6.6 mg g⁻¹; benzenemethanol, 4-methoxy-, formate: 19.3 mg g⁻¹; benzaldehyde, 4-methoxy-: 50.1 mg g⁻¹; benzoic acid, 4-methoxy-, ethyl ester: 396.3 mg g⁻¹; benzoic acid, 4-methoxy-, 4-ethylphenyl ester: 15.4 mg g⁻¹. **1:** Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate; **4:** Ethyl ethoxyacetate; **5:** Diethyl oxalate; **6:** Diethyl malonate; **7:**

Ethyl diethoxyacetate; **8:** Ethyl 3,3-diethoxypropionate; **9:** Ethyl 4-hydroxybenzoate; **10:** Ethyl vanillate.

Plausible pathway for lignin depolymerization and oxidative ring cleavage

Based on above mentioned process of lignin oxidative ring cleavage, product distribution and typical lignin depolymerization product oxidation, a plausible pathway for this efficient depolymerization of lignin and DEM formation from the renewable lignin is proposed in the context of literature (Figure S12).⁸⁻¹² For the DEM production, the lignin (**1**) is firstly dehydrated under strong acidic condition to form vinyl ether (**2**)¹¹ in adjacent to the β -aryl ether bond probably via benzylic carbocation formation. Without catalyst, the reactive carbocation may attack electron-rich lignin aromatic rings leading to C-C formation (Shuai et al. used formaldehyde to block this reactive species during hydrogenolysis of lignin to produce improved yields of monomers).¹³⁻¹⁵ However, we show that in the intimate contact of Cu^{2+} polyoxometalate in air, this ether reacts with superoxo species from the Cu active site (see Cu catalyst elucidation in next section) to produce a dioxetane intermediate (**3**). Subsequently, the C–C and O–O bond cleavage of compound **4** occurs to afford ester (**5**) and aldehyde (**6**). It should be emphasized here that the initial aromatic aldehydes and glycolic acid which is produced by the above-mentioned intermediates can be directly detected by gas chromatography mass spectrometry (GC-MS) in form of esters (Table S7).

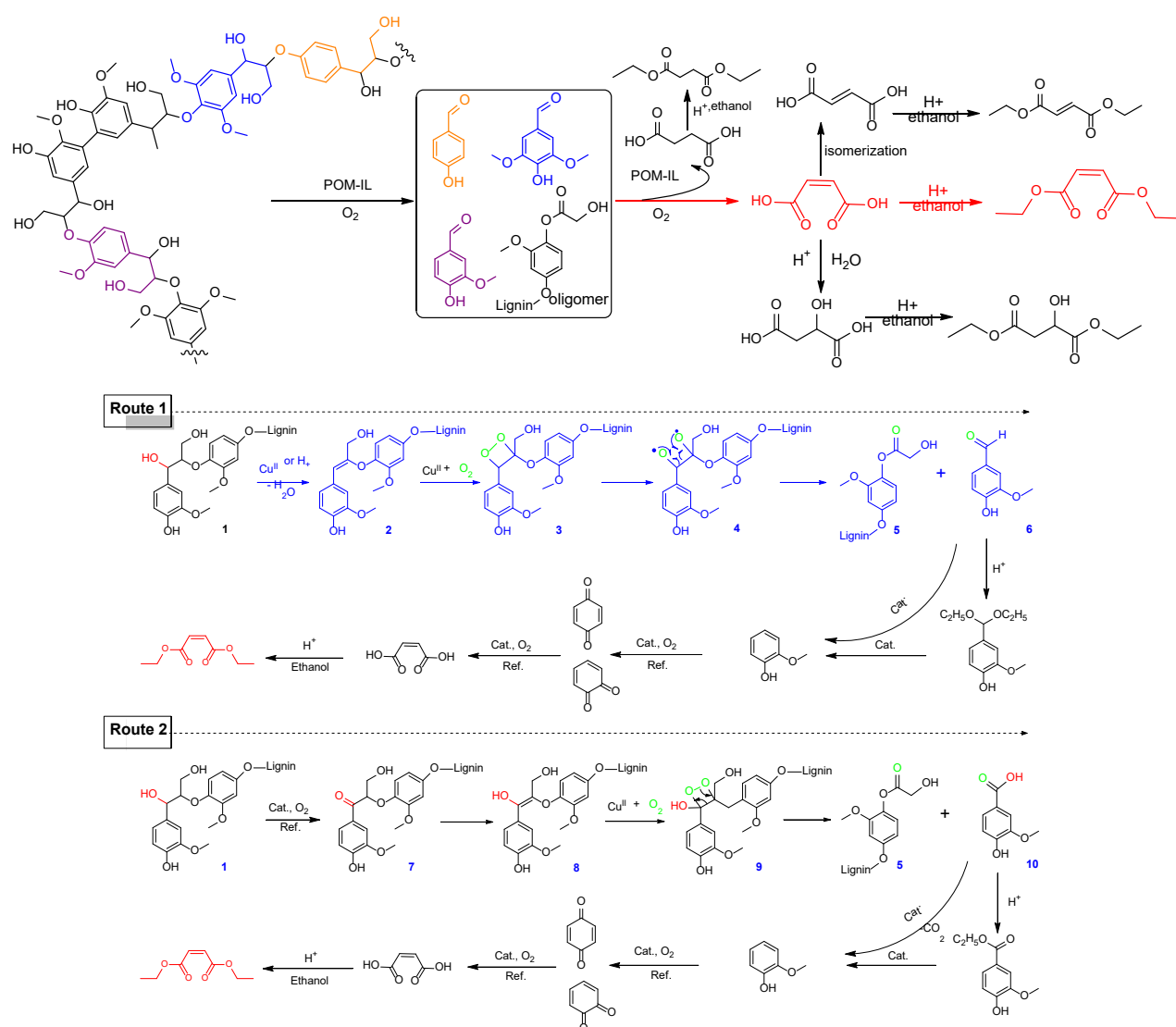
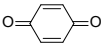
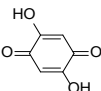
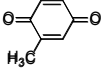
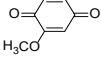
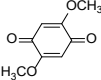
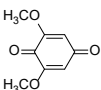
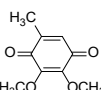


Figure S12. Proposed pathway for the lignin depolymerization and oxidative ring cleavage to DEM.

Then, extensively acetalization of aldehyde (6) in ethanol occurs with 4-(diethoxymethyl)-2-methoxyphenol as the product. This compound can be easily oxidized to benzoquinones, the main intermediate for maleic acid production in the phenol oxidation technology, after a series continuous process of oxidation and demethoxylation.^{10, 16, 17} Further, the quinones are converted to maleic acid *via* ring cleavage.¹⁸ Finally, the product of stable DEM is achieved by the rapid esterification of maleic acid in ethanol without much side reactions. On the other hand, lignin (1) can also be initially oxidized to ketones (7), which undergoes Keto-enol tautomerism step (this process can be confirmed by above HSQC, FT-IR, and ¹³C-NMR characterization of the original and regenerated lignin as shown in Figure 3 and Figure S11) to form the vinyl ether (8). The compound (8) is then

transformed to ester (**5**) and carboxylic acid (**10**) through intermediate **9** via a similar C-C bond and O-O bond cleavage as that of chemical (**3**).^{9, 12, 19} Simultaneously, the carboxylic acid (**10**) is esterified with ethanol. Both the carboxylic acid and ester would be decarboxylated²⁰ as anticipated over the POM-IL catalyst. The decarboxylation product is then oxidized to benzoquinones, which finally gives the target product of DEM through the same oxidation and esterification process as that of aldehyde (**6**). To support this cleavage pathway, oxidation of quinones is investigated. As shown in Table S17, the intermediates could be converted efficiently with 100% conversion in the ethanol, giving DEM selectivity of higher than 70% for each run.

Table S17. Selective oxidation of typical model compounds.

Entry	Substrates	Conversion (%)	Yield (mg g ⁻¹) ^a									DEM selectivity (%)
			1	2	3	4	5	6	7	8	total	
1		100	447.2	26.4	32.4	6.4	18.3	10.8	37.9	2.7	582.1	76.8
2		100	377.3	19.7	23.2	7.5	25.2	12.7	36.3	—	501.9	75.2
3		100	585.4	29.6	43.0	7.3	—	14.0	40.3	2.4	722.0	81.1
4		100	412.5	24.3	31.2	6.3	25.6	15.6	44.1	2.8	562.4	73.3
5		100	389.5	20.2	27.2	5.7	14.5	9.7	31.7	2.4	500.9	77.8
6		100	356.2	21.6	34.8	5.8	22.1	13.1	43.1	2.2	498.9	71.4
7		100	451.5	21.2	37.9	5.3	10.2	11.9	44.3	2.5	584.8	77.2

Reaction conditions: 0.25 g substrate, 0.9 mmol [BSmim]CuPW₁₂O₄₀, 20 mL 100% ethanol, 433 K, 5 h, 0.8 MPa O₂. ^a not detected.

1: Diethyl maleate; **2:** Diethyl succinate; **3:** Diethyl fumarate **4:** Ethyl ethoxyacetate; **5:** Diethyl oxalate; **6:** Diethyl malonate; **7:**

Ethyl diethoxyacetate; **8:** Ethyl 3,3-diethoxypropionate.

Potential Separation of DEM

The DEM can be separated using common chromatographic techniques with the mixture of *n*-hexane and petroleum ether as the eluent in laboratory. For industrial scale, it can also be separated using rectification on the basis of the boiling point difference of these products, and there are many patents published about the maleic acid ester recovery and purification (patent list: process for the recovery of dialkyl succinate or dialkyl maleate (WO2016174388A1), process for the production of dimethyl maleate (EP1678117B1), process for the preparation of dimethyl maleate (US4827022A), dimethyl maleate purification method (CN106187775A)).

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