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Ionic liquid [OMIm][OAc] directly inducing oxidation cleavage of β-O-4 bond of lignin model compounds

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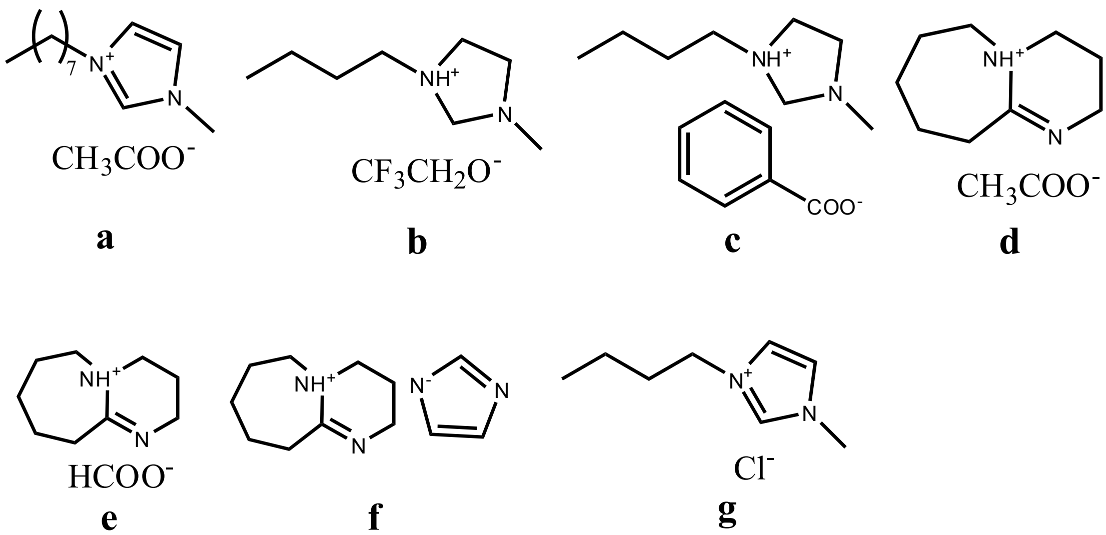


Figure S1. Structures of the ILs used. a) [OMIm][OAc], b) [BMIm][TFA], c) [BMIm][BA], d) [HDBU][OAc], e) [HDBU][HCOO], f) [HDBU][Im], g) [BMIm]Cl.

2. Materials

Tert-butanol (>99.5%), methyl tertiary butyl ether, benzoic acid, diethyl ether(A.R.), potassium acetate were obtained from Sinopharm Chemical Reagent Co., Ltd. Formic acid (98%), imidazole (98%), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO, 98%) were provided by J&K Scientific Ltd. Phenol (99%), guaiacol, potassium carbonate (K_2CO_3, 99%), 2-bromoacetophenone (99%), diphenyl ether(99%), benzyl phenyl ether (99%), 1,8-diazabicyclo [5,4,0]-7-undecene(DBU, 99%) were purchased from Alfa Aesar. Acetonitrile (CH_3CN), toluene, dichloromethane, acetic acid (AR), ethanol (99%) were obtained from the Beijing Chemical Company. Benzoylformaldehyde monohydrate, benzoylformic Acid and 4-methoxyphenol were provided by Tokyo Chemical Industry Co., Ltd. Eucalyptus sawdust was purchased from Jiangmen City Xinhui District Mu Jiang Weihua spice factory. DMSO-d_6 was bought from Beijing InnoChem Science & Technoloty Co., Ltd.. Oxygen (>99.99%), argon(>99.99%), nitrogen (>99.99%), hydrogen (>99.99%), carbon monoxide (>99.99%) and carbon dioxide (>99.99%) were provided by Beijing Analytic Instrument Company.

The ionic liquids (ILs) 1-octyl-3-methylimidazolium acetate ([OMIm][OAc], 99%), 1-butyl-3-methylimidazolium trifluoroethanol ([BMIm][TFA], 99%), 1-butyl-3-methylimidazolium benzoate ([BMIm][BA], 99%), 1-butyl-3-methylimidazolium chloride ([BMIm]Cl, 99%) were purchased from Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. All the ionic liquids were dried at 70 ^{o}C for 24 hours before used.

3. Preparation of 2-phenoxyacetophenone (1) and 2-(2-methoxyphenoxy)-1-phenylethanone (4)

1 was synthesized according to the following procedures. In the experiment, a three-neck round bottom flask equipped with a reflux condenser was charged with 5.2 g phenol (55 mmol), 13.88 g potassium carbonate (100 mmol), and 100 mL acetonitrile. The flask was heated to reflux temperature, and then 10 g of 2-bromoacetophenone (50 mmol) dissolved in 50 mL acetonitrile was added dropwisely into the flask. The mixtures were stirred for 4 hour at reflux temperature, and then it was filtered through Celite and concentrated in vacuum. The resulting solid was purified by column chromatography to obtain **1**. NMR spectra were acquired on a Bruker Advanve III-400HD spectrometer. NMR chemical shifts are reported as δ in parts per million (ppm) relative to the residual solvent signal. ^{1}H NMR ($CDCl_3$, 400MHz)[ppm] δ 8.003-8.021 (d, 2H), 7.62 (t, 1H), 7.5-7.52 (t, 2H), 7.274-7.314 (t, 2H), 6.94-7.01 (m. 3H), 5.27 (s, 2H).

2-(2-methoxyphenoxy)-1-phenylethanone (**4**), 2-phenyloxy-1-phenylethanol(**6**), and 2-(2-methoxyphenoxy)-1-phenylethanol was synthesized according to method in literature.[s1]

4. Preparation of ILs [HDBU][HCOO], [HDBU][OAc] and [HDBU][Im]

DBU of 1.495 mL (10 mmol) was dissolved in ethanol and agitated at ice water temperature. Equimolar formic acid (0.46 g) or acetate acid (0.6 g) or imidazole (0.68 g) in ethanol solution was mixed with DBU slowly. The mixture was stirred for 1h and then stopped. The ethanol was removed by reduced pressure distillation, and the final solution was dried under vacuum condition for 20 minutes, and then transferred into vacuum drying oven at 70 ^{o}C overnight. The ILs with [HCOO] or [OAc] or [Im] anions were obtained, respectively.

5. Oxidation of lignin model compounds

The oxidation reactions were conducted in a Teflon-lined stainless-steel reactor of 10 mL. In the experiment, desired amount of IL, lignin model compound or lignin, and water were added in the reactor. The air in the reactor was removed under vacuum and the reactor was placed in the preheated furnace of the desired temperature, then oxygen was charged into the reactor and the stirrer of the reactor was started. After a suitable reaction time, the reactor was cooled in the ice water, and the gas was released into a gas sample bag. Gaseous product was analysed by GC (gas chromatography) with TCD detector. Quantification of the liquid product from lignin model compounds were conducted using high performance liquid chromatography (HPLC), which was performed on a SHIMADZU LC-15C series with a UV detector (at 280 nm) and a C18 column (4.6 × 250 mm). Column temperature was 35 ^{o}C. Water/acetonitrile with gradient elution was used as the mobile phase. NMR spectra were recorded on a Bruker Advance III HD 400 MHz NMR spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer, and the samples were prepared by the KBr pellet method.

In the reusing experiment, after the oxidation reaction, diethyl ether (4×3 mL) was used to extract the product from the reaction mixture. The IL [OMIm][OAc] was washed by water (3×5 mL), and dried in vacuum at 70 ^{o}C for 24 hours. Then the IL was reused in the next run at the same reaction condition.

6. Relating results

Figure S2 shows the GC spectra of typical gas products of the reaction (Entry 1 in Table 1). The peaks were identified by standard gases. The gaseous products collected from the reactor contained hydrogen, oxygen, carbon monoxide and carbon dioxide.

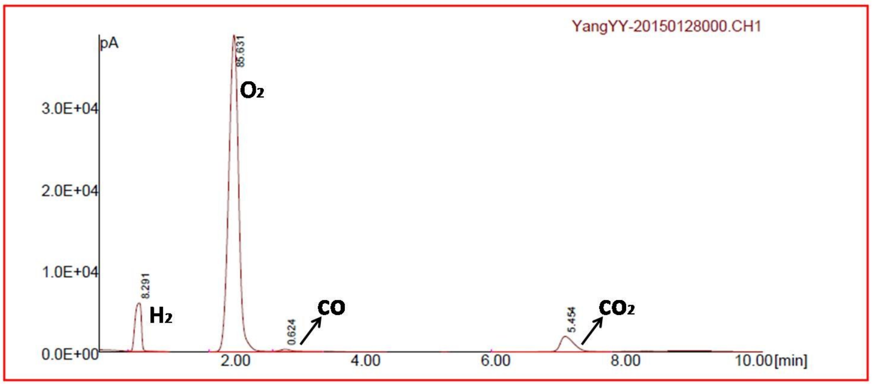


Figure S2. GC trace of the gaseous products of the reaction at the condition of entry 1 in Table 1.

Figure S3 shows the HPLC chromatogram of the reaction mixture for the oxidation of 2-phenoxyacetophenone (**1**) with a shorter reaction time (1 h). The peaks were identified by standard reagents. The results indicate that besides phenol, benzoic acid, and unreacted 2-phenoxyacetophenone, formic acid could be detected. In addition, an unknow compound was found.

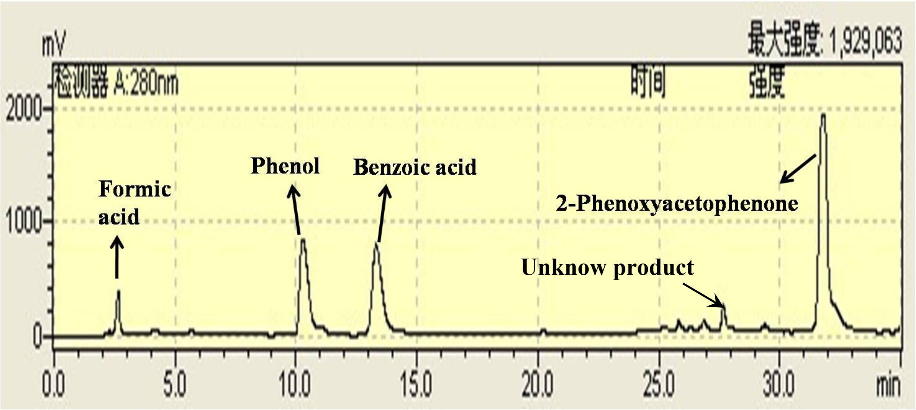
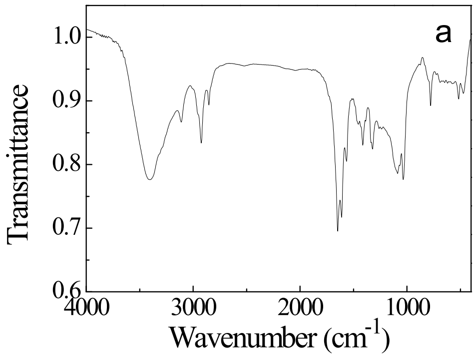


Figure S3. The HPLC chromatogram of the reaction mixture for the oxidation of 2-phenoxyacetophenone (**1**) with a reaction time of 1 h. Other condition was the same as that of entry 1 in Table 1.

We analyzed **1** and the unknow compound by the IR spectra method. From Fig S4a, a band at 1708 cm^{-1} was assigned to the absorptions of C=O group of **1**, and other bands at 1598 cm^{-1}、1582 cm^{-1}、1499 cm^{-1} and 1480 cm^{-1} belonged to vibration absorption of benzene rings. From the IR spectra of the unknow compound (Fig. S4b), two bands at 1648 cm^{-1} and 1600 cm^{-1} were found and band strengthens were similar, which showed that the unknow intermediate product contained two adjacent carbonyl groups.



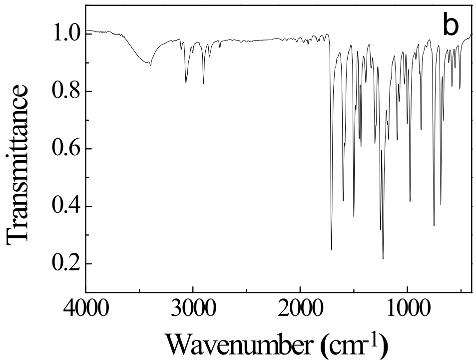
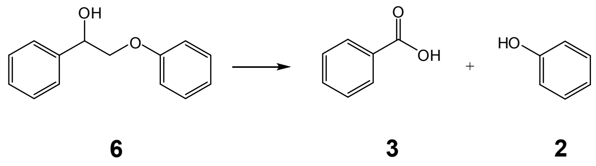


Figure S4 IR spectra of 2-phenoxyacetophenone (**a**) and unknow intermediate compound (**b**)

To verify the generality of our reaction system, another β-O-4 lignin model compound 2-phenyloxy-1-phenylethanol(**6**) were tested (Scheme S1). The compound 2-phenyloxy-1-phenethanol represents the β-O-4 linkage by the dilignol model structure. The reaction temperature increased from 110 °C to 130 °C(entry 1-3 in Table S1), both conversion and yields increased. However, the temperature increased continuously (entry 4-5 in Table S1), the yields decreased gradually. Though changing the reaction pressure (entry 6-9 in Table S1), we could see that the yields of benzoic acid and phenol were 75% and 51% with the oxygen pressure of 3 MPa, respectively. All the results revealed that our work provided a new metal-free catalysis method to cleave the C-O bond for the lignin model compound effectively.



Scheme s1 Transformation of 2-phenyloxy-1-phenylethanol

Table S1. Oxidation of lignin model compound **6** with [OMIm][OAc][a]

Entry	Temp.(℃)	Pressure(MPa)	Conversion(%)	Yield(**2**)(%)	Yield(**3**)(%)[b]
1	110	1	40	18	23
2	120	1	73	30	37
3	130	1	>99	34	42
4	150	1	>99	27	20
5	170	1	>99	22	15
6	130	2	>99	43	48
7	130	3	>99	51	75
8	130	4	>99	45	53
9	130	5	>99	42	48

a Reaction condition: 2-phenyloxy-1-phenethanol, 0.0832 g; ionic liquid, 1 g; H_2O, 25 μL; reaction time, 8 h; b Yield(**2**)= yield of phenol , Yield(**3**)= yield of benzoic acid.

The organosolv lignin was extracted from eucalyptus by dioxane using the method in the literature.[S2] By the gel permeation chromatograph (GPC) technique (Figure S5), the weight average molecular weight (Mw) of organosolv lignin measured was 88000 Da. Heteronuclear single-quantum correla-tion (HSQC) NMR spectra of organosolv lignin were measured and recorded (Figure S6). The accounting ratios of the main linkages β-O-4, β-5, β−β and β−1 in lignin were 60.2%, 7.7%, 18.2% and 13.8%, respectively. After reaction at 130 °C and the oxygen pressure of 2 MPa for 24 hours (other conditions were the same as those of entry 1 in Table 1), conversion of organosolv lignin reached 90% (0.1g organosolv lignin). We characterized the oils obtained from depolymerization of the organosolv lignin by GC-MS method. The results showed that the IL was effective for depolymerizing the organosolv lignin, and oil products included phenols and aromatic acids (Figure S7), which showed our reaction system from model compounds benefited to the depolymerisation of real lignin.

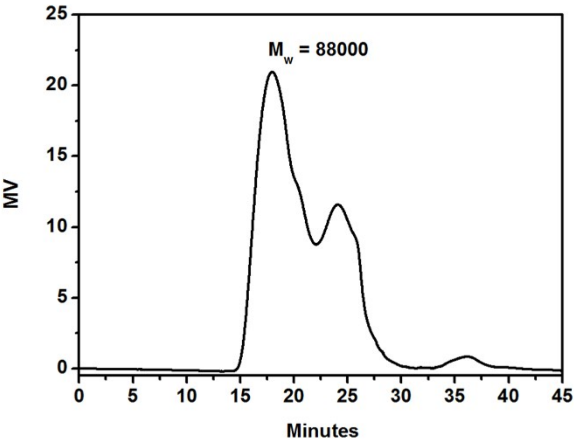


Figure S5 GPC spectra of organosolv lignin.

The gel permeation chromatograph (GPC) analysis was performance with a PL-GPC210 gel permeation chromatograph of Polymer Laboratories Co., equipped with a refractive index detector, two PLgel 10 pm MIXED-B columns (300 mm × 7.5 mm), a PLgel 10 pm guard column (50 mm × 7.5 mm) and a filter (2 pm). Calibrations were made by narrow dispersion polystyrene standards and linear polyethylene fractions. N,N-Dimethylformamide (DMF) was used as eluent and the column temperature was 50 °C. The flow rate of the eluent was 1.0 $\mathrm{mL{\bullet}min^{-1}}$.

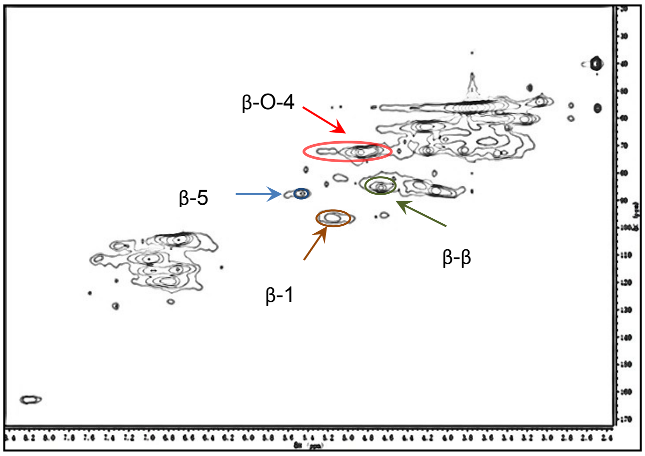


Figure S6 Heteronuclear single-quantum correlation (HSQC) spectra of organosolv lignin.

The typical semi-quantitative method to calculate the relative abundance of diagnostic structures is described as follows. Relative percentages of A–D units were estimated via a semi-quantitative analysis[S3] of the volume integral of the HSQC cross-signal by the following formula:

$I_X\% = I_X/(I_A + I_B + I_C + I_D) \times 100\%$

where I_A, I_B, I_C, and I_D are the integral values of α-position of β-O-4 (A), β-β (B), β-5(C), and β-1(D), respectively.

Two-dimensional NMR spectra were recorded at 25 °C on a Bruker AVANCE 500 MHz using a z-gradient triple resonance probe. Lignins (40 mg) were dissolved in 0.75 mL of DMSO-d_6, and spectra were recorded in HSQC experiments. The spectral widths for the HSQC spectra were 5000 Hz and 25625 Hz for the ^{1}H and ^{13}C dimensions, respectively. The number of collected complex points was 2048 for the ^{1}H-dimension with a recycle delay of 5 s. The number of transients was 64, and 256 time increments were always recorded in the ^{13}C-dimension. The J-coupling evolution delay was set to 3.2 ms. A squared cosine-bell apodization function was applied in both dimensions. Prior to Fourier transform the data matrixes were zero filled up to 1024 points in the ^{13}C-dimension. The central solvent peak was used as an internal reference (δ_H/δ_C 2.50/40.1 ppm).

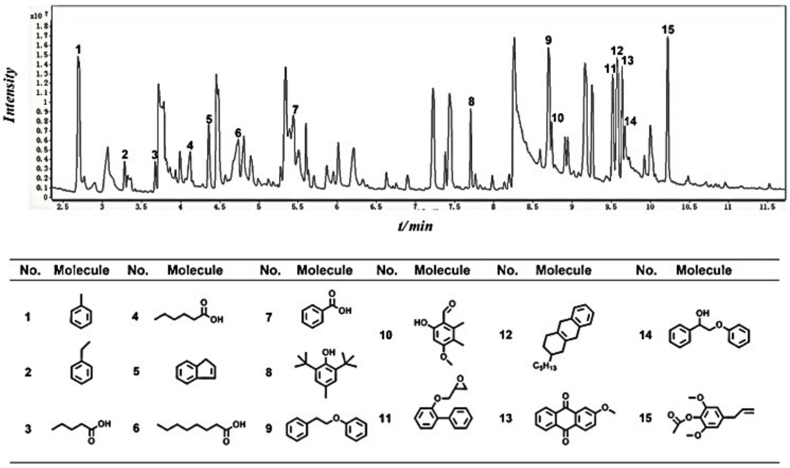


Figure S7 GC-MS spectra of the oil derived from the organosolv lignin after reaction at 130 ^{o}C and 3 MPa with a reaction time of 24 hours. Other conditions were the same as those of entry 1 in Table 1.

Further, we selected 2-(2-methoxyphenoxy)-1-phenylethanol as the reactant and analyzed the product distribution using GC-MS in the short reaction time. From the analysis data (Figure S8), we knew the chemicals like 2-(2-methoxyphenoxy)-1-phenylethanol, 2-(2-methoxyphenoxy)-1-phenylethanone, guaiacol and benzoic acid existing in our reaction system. Moreover, the composition of the gaseous products from the reactions was the same as that from 2-phenoxyacetophenone. Thus, we inferred that the transformation of 2-(2-methoxyphenoxy)-1-phenylethanol underwent to ketone first, and then proceeded via similar reaction route of 2-phenoxyacetophenone.

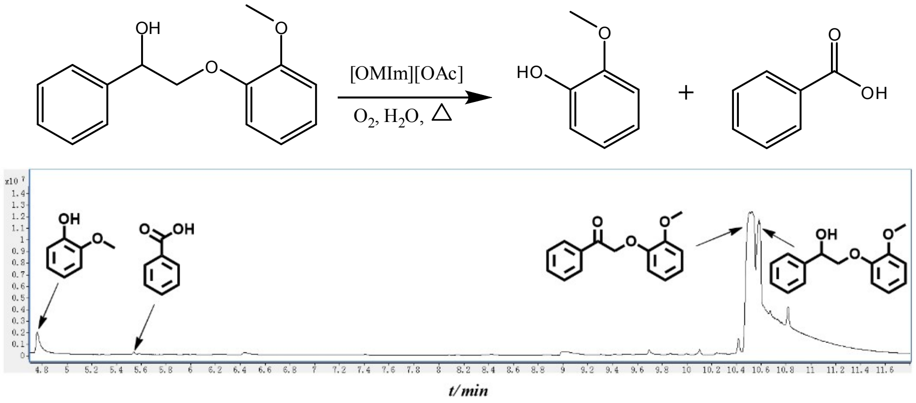


Figure S8 Transformation of 2-(2-methoxyphenoxy)-1-phenylethanol and GC analysis of products

Usually, ionic liquids with weak acid anions like acetate anion show weak alkaline property in the reaction. In the presence of alkali, the oxygen molecule can be reduced to different species like OOH radical, OH radical and HO_2^- (E. Johansson and S. Ljunggren, J. Wood Chem. Technol., 1994, 14(4), 507-525). Thus, oxygen was activated in our reaction system. After we added the free radical quenching agent 2,2,6,6-tetramethylpiperidinyloxy（TEMPO）into the reactor, we found that TEMPO had no obvious effects on conversion and the yields of products. The results showed that there were not OOH radicals and OH radicals existing in our reaction system. So, HO_2^- maybe was oxygen active intermediate.

According to the chemical structures of reactant and products, we know that the transformation of model compound **1** proceeded via the cleavage of C_α-C_β bond and C_β-O bond into phenol and benzoic acid. Under alkaline conditions, the cleavage of lignin model compound often deals with the attacking of OH^- to C-H bond between two benzene rings of model compound (H. Xu and Y. Z. Lai, J. Wood Chem. Technol., 1999, 19(1&2), 1-12). In our experiments, acetate anion of ionic liquid showed weak alkaline property. Meantime, hydrogen from C_β tends to become acidic property under the inducing role of adjacent carbonyl group. Thus, we inferred that acetate anion attacked firstly the hydrogen from C_β during the reaction process.

7. References

S1. J. M. Nichols, L. M. Bishop, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.*, 2010, 132, 12554-12555.

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S3. J. L. Wen, S. L. Sun, B. L. Xue and R. C. Sun, *Materials*, 2013, **6**, 359-391.