

## Supporting Information

### **Metal-free and mild photo-thermal synergism in ionic liquid for lignin C<sub>α</sub>-C<sub>β</sub> bond cleavage to aldehydes**

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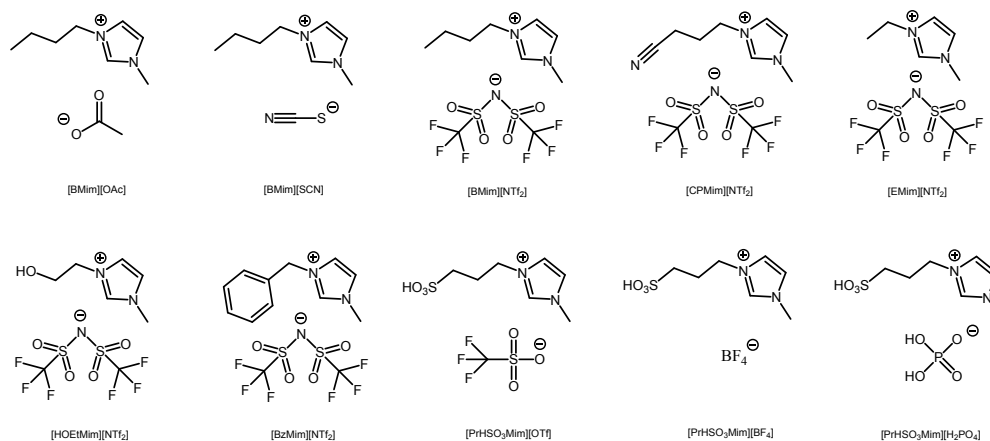
## 1. Experimental

**Materials.** The Lignin model compounds 2-phenoxy-1-phenylethanol (**1**) (97+%) was from Ark Pharm, Inc.. 2-(2-Methoxyphenoxy)-1-phenylethanol (**2**) (95%) was provided by Shanghai Bepharma Science&Technology Co.,Ltd.. Bibenzyl (**3**) (99%), benzaldehyde (99%) and phenylacetaldehyde (98%), were from Beijing InnoChem Science & Technology Co., Ltd.. Alkali lignin was provided by Green Value SA. Methyl tertiary butyl ether (MTBE) was obtained from Shanghai Aladdin Reagent Co. Ltd. phenol, phosphoric acid aqueous solution (85%) was purchased from XiLong Scientific Co., Ltd. Sulfuric acid (98%) was provided by Beijing Chemical works. Sulphonethane (98+%) was from Sinopharm Chemical Reagent Co., Ltd. The ionic liquids [BMim][OAc], [BMim][SCN], [BMim][NTf<sub>2</sub>], [EMim][NTf<sub>2</sub>], [BzMim][NTf<sub>2</sub>], [CPMim][NTf<sub>2</sub>], [HOEtMim][NTf<sub>2</sub>], [PrHSO<sub>3</sub>Mim][OTf], [PrHSO<sub>3</sub>Mim][BF<sub>4</sub>], [PrHSO<sub>3</sub>Mim][H<sub>2</sub>PO<sub>4</sub>] were provided by Qingdao Aolike New Material Technology Co., Ltd, which were dried in vacuum at 343 K for 24 h before use.

**Analytical methods.** Qualitative analysis was performed by gas chromatography mass spectrometry (GC-MS) on a SHIMADZU GCMS-QP2020 instrument with a Rtx-5MS capillary column (30m\*0.25mm). The quantitative analysis of alkali lignin degradation was conducted by the same GC-MS equipment using n-dodecane as the internal standard. The quantitative analysis of lignin model compound degradation was conducted by gas chromatography (GC) using a Shimadzu GC-2014 instrument equipped with a Rtx-5 column. FT-IR analysis was performed on a Nicolet 380 spectrometer at a 4-cm<sup>-1</sup> resolution. The heteronuclear single quantum coherence (HSQC) NMR analysis was conducted on a Bruker Avance III HD 600 MHz spectrometer at room temperature (DMSO-*d*<sub>6</sub>) with 80 mg of lignin samples dissolved in 0.5 mL of DMSO-*d*<sub>6</sub>. The detailed acquisition parameters were described in our previous work<sup>1</sup>. The electron paramagnetic resonance (EPR) measurement of free radicals was performed on the X-band EPR spectrometer (JEOL, JES FA-200). The spectra were recorded with the microwave power of 0.998 mW at the frequency of 9.05 GHz, modulation frequency of 100 kHz, modulation amplitude (or width) of 0.1 mT, time constant of 0.1s and sweep width of 15 mT.

**DFT Calculations.** The density functional theory (DFT) calculations were carried out using the Gaussian 09 program. The B3LYP/6-311+G(d,p) method was used for structure optimizations, and subsequent frequency calculations at the same level verify the optimized structures to be ground states without imaginary frequencies (NImag = 0).

## 2. Structures of the ionic liquids used



Scheme S1 Structures of the ILs used.

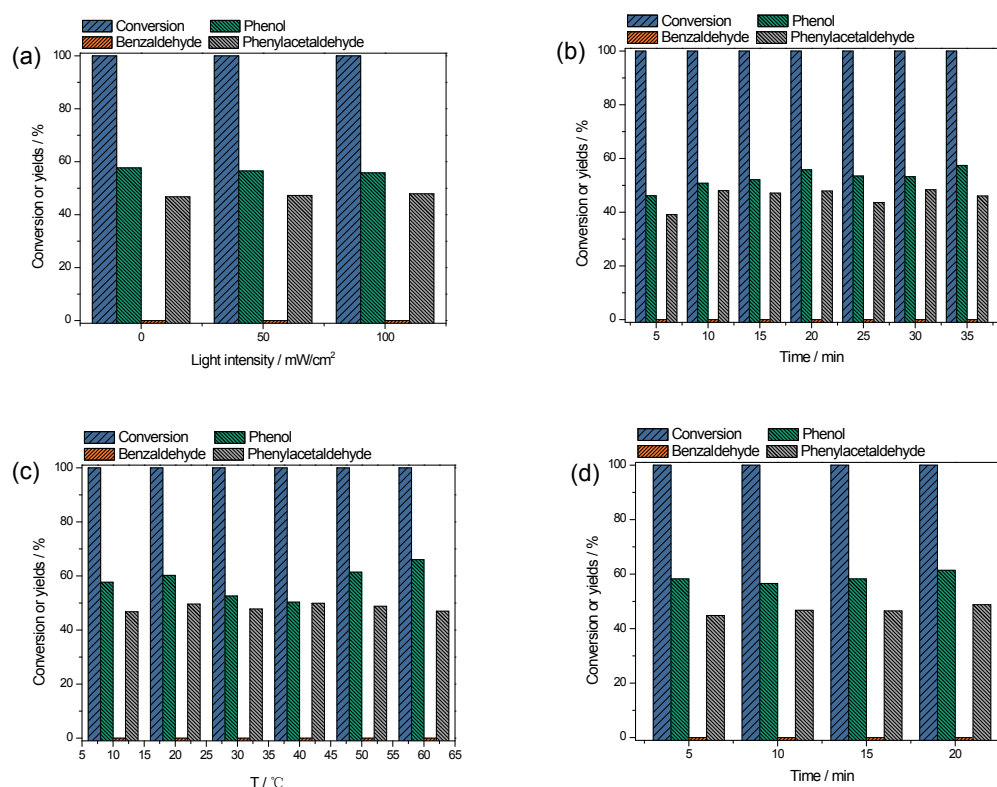
### 3. Degradation of lignin model compound 1 with TEMPO or in dark at 220 °C

**Table S1** Degradation of lignin model compound 1.

Entry	Time /s	Phenol (%)	Benzaldehyde (%)	Phenylacetaldehyde (%)
1 <sup>a</sup>	10	54.8	n.d.	49.1
2 <sup>a</sup>	30	57.5	n.d.	47.3
3 <sup>a</sup>	60	23.8	n.d.	3.7
4 <sup>b</sup>	1200	36.4	n.d.	34.0

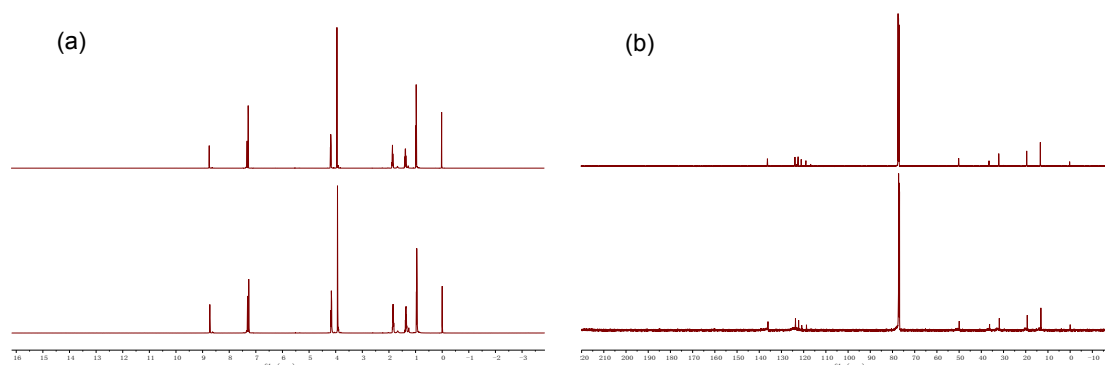
Reaction conditions: <sup>a</sup>1 5 mg, [BMim][NTf<sub>2</sub>] 250 mg, H<sub>2</sub>SO<sub>4</sub> 1 wt%, temperature 220 °C, in dark; <sup>b</sup>1 5 mg, TEMPO 1.4 wt%, [BMim][NTf<sub>2</sub>] 250 mg, H<sub>2</sub>SO<sub>4</sub> 1 wt%, temperature 50 °C, UV light (100 mW/cm<sup>2</sup>), atmosphere.

### 4. Degradation of 1 at UV light/ heating alone conditions



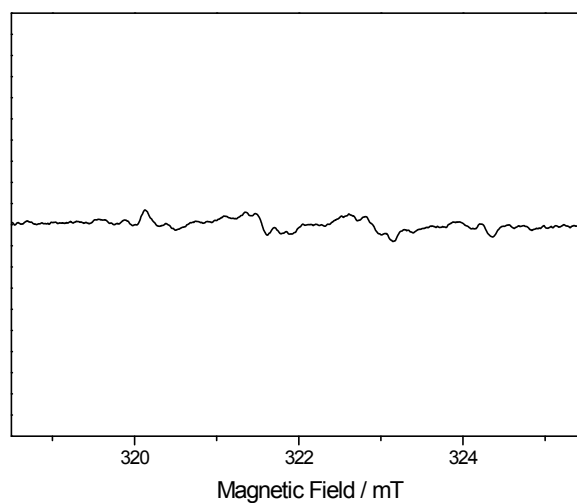
**Fig. S1** Degradation of 1 with the conditions: 1 5 mg, [BMim][NTf<sub>2</sub>] 250 mg, H<sub>2</sub>SO<sub>4</sub> 1 wt%, atmosphere, (a) temperature 10 °C, UV light (power density: 0-100 mW/cm<sup>2</sup>), reaction time 20 min; (b) temperature 10 °C, UV light (power density: 100 mW/cm<sup>2</sup>), reaction time 5-35 min; (c) temperature 10-60 °C, without UV light irradiation, reaction time 20 min; (d) temperature 50 °C, without UV light irradiation, reaction time 5-20 min.

## 5. Stability of [BMim][NTf<sub>2</sub>] under UV light and heating conditions



**Fig. S2** (a) <sup>1</sup>H NMR spectra and (b) <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> for original [BMim][NTf<sub>2</sub>] (top) and the regenerated [BMim][NTf<sub>2</sub>] (below) after reuse for 5 times.

## 6. EPR spectrum of pure [BMim][NTf<sub>2</sub>]



**Fig. S3** EPR spectrum of pure [BMim][NTf<sub>2</sub>].

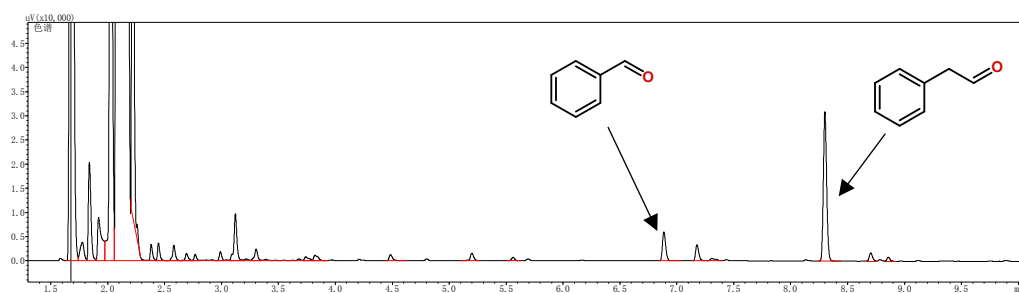
## 7. Photo-thermal degradation of **1** under various atmosphere

**Table S2** Photo-thermal degradation of **1** under various atmosphere.

Entry	Conversion	Phenol (%)	Benzaldehyde (%)	Phenylacetaldehyde (%)
1 <sup>a</sup>	100	50.3	18.0	23.4
2 <sup>b</sup>	98.9	38.2	2.1	24.6

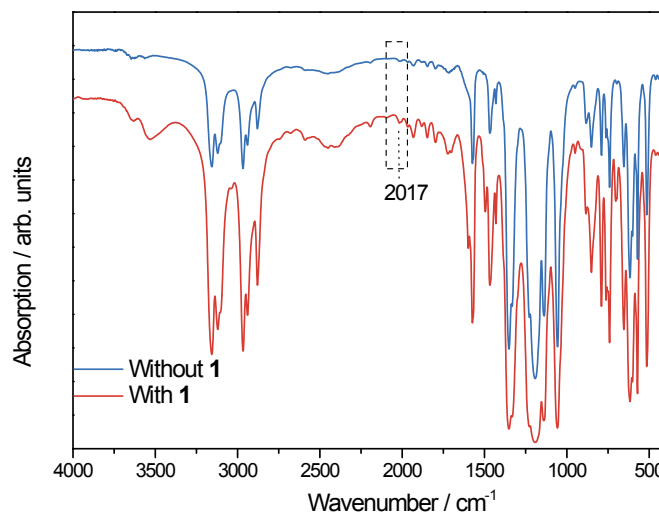
Reaction conditions: **1** 5 mg, [BMim][NTf<sub>2</sub>] 250 mg, H<sub>2</sub>SO<sub>4</sub> 1 wt%, temperature 50 °C, UV light (100 mW/cm<sup>2</sup>), reaction time 20 min, <sup>a</sup>in O<sub>2</sub> (1 atm); <sup>b</sup>in N<sub>2</sub> (1 atm).

## 8. Conversion of phenylacetaldehyde under photo-thermal conditions



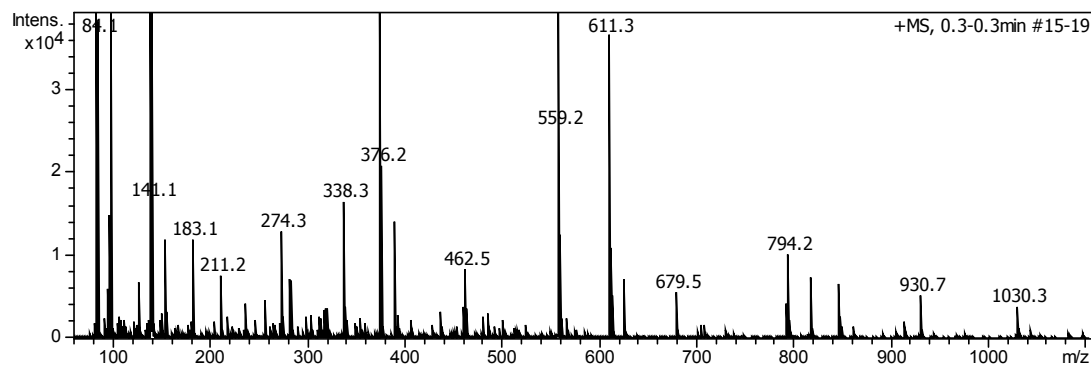
**Fig. S4** Conversion of phenylacetaldehyde under the conditions: phenylacetaldehyde 5 mg, [BMim][NTf<sub>2</sub>] 250 mg, H<sub>2</sub>SO<sub>4</sub> 1 wt%, temperature 50 °C, UV light (100 mW/cm<sup>2</sup>), reaction time 5 min, atmosphere.

## 9. Conversion of phenylacetaldehyde under photo-thermal conditions



**Fig. S5** FT-IR spectra of the 1-ILs reaction system at 50 °C under UV light irradiation (100 mW/cm<sup>2</sup>) for 20 min with and without 1.

## 10. ESI spectrum of oil products.



**Fig. S6** ESI spectrum of oil products.

## 11. Assignment of FT-IR absorption bands for alkali lignin

**Table S3** Assignment of FT-IR absorption bands for alkali lignin<sup>2-5</sup>.

Absorption bands/cm <sup>-1</sup>	Assignment
3431 (wide)	O-H stretch in aromatic and aliphatic OH groups
2940	C-H asymmetric vibration in -CH <sub>3</sub> and -CH <sub>2</sub> - groups
2849	C-H symmetrical vibration in -CH <sub>3</sub> and -CH <sub>2</sub> - groups
1612	aromatic skeletal vibrations
1515	aromatic skeletal vibrations
1463	C-H deformation combined with aromatic ring vibration
1426	aromatic skeletal vibrations
1328	syringyl ring breathing with C-O stretching
1217	guaiacyl ring breathing with C-O stretching
1155	C-O stretch in ester groups
1123	aromatic C-H in-plane deformation for syringyl type
1031	Aromatic C-H in-plane deformation for guaiacyl type and C-O deformation in primary alcohols
834	C-H out of plane deformation in the 4-hydroxyphenyl unit

### References

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