

Supporting information for:

**Novel biphasic DES/GVL solvent for effective biomass fractionation  
and valorization**

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**Table S1.** Sugars and other derivatives in the pretreated liquor after biphasic solvent pretreatment under different pretreatment temperatures.

| Degradation products (g/L) | Temperature (°C) |       |       |
|----------------------------|------------------|-------|-------|
|                            | 120              | 130   | 140   |
| Glucose                    | 0.35             | 0.28  | 0.13  |
| Xylose                     | 0.28             | 0.26  | 0.19  |
| Furfural                   | 3.40             | 4.49  | 3.41  |
| Lactic acid                | 0.04             | 0.08  | 0.06  |
| Formic acid                | 0.135            | 0.169 | 0.221 |
| Acetic acid                | 0.828            | 1.058 | 1.564 |
| Levulinic acid             | 0.174            | 0.155 | 0.134 |
| HMF                        | 0.139            | 0.137 | 0.154 |
| Arabinose                  | 0.011            | 0.021 | 0.031 |

**Table S2** Recovery yield and polysaccharides content of recovered lignin.

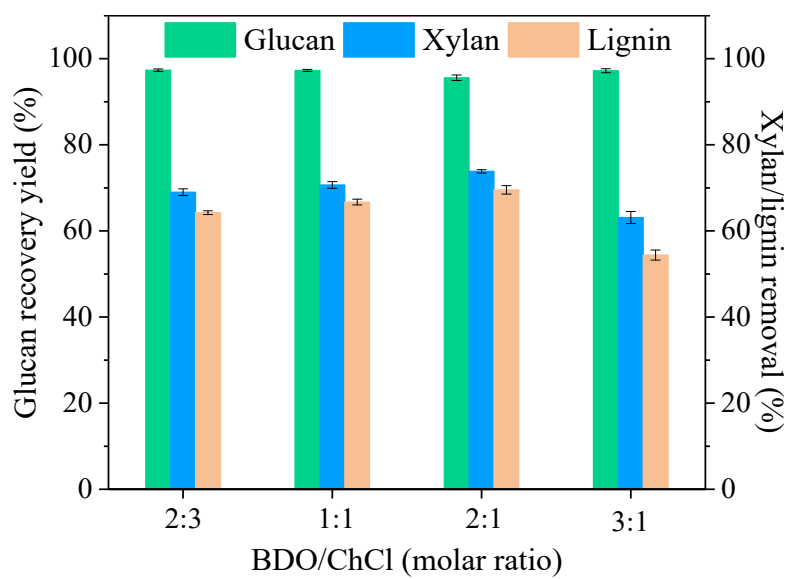
| Sample (Temp<br>(°C)/Time (min)) | Lignin recovery<br>(%) | Glucose<br>(%) | Xylose<br>(%) | Arabinose<br>(%) |
|----------------------------------|------------------------|----------------|---------------|------------------|
| L <sub>120/60</sub>              | 96.48                  | 0              | 0.05          | 0                |
| L <sub>130/60</sub>              | 95.21                  | 0              | 0.06          | 0                |
| L <sub>140/60</sub>              | 95.24                  | 0              | 0             | 0                |
| L <sub>130/30</sub>              | 98.59                  | 0.03           | 0.02          | 0                |
| L <sub>130/60</sub>              | 95.21                  | 0              | 0             | 0                |
| L <sub>130/90</sub>              | 98.29                  | 0              | 0             | 0                |

**Table S3** Lignin depolymerization and product distribution.

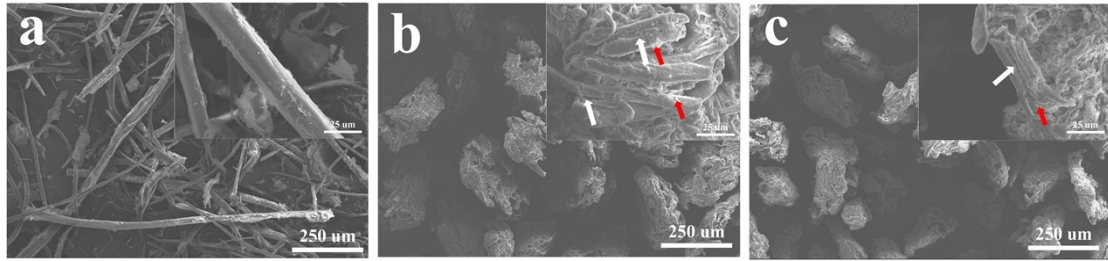
|                  | Phenolic monomer yield (%) |     |     |     |     |      | Total |
|------------------|----------------------------|-----|-----|-----|-----|------|-------|
|                  | 1                          | 2   | 3   | 4   | 5   | 6    |       |
| CEL              | 0.5                        | 8.7 | 4.3 | 6.2 | 2.1 | 10.1 | 31.9  |
| L <sub>120</sub> | 0                          | 4.1 | 3.5 | 4.2 | 1.2 | 8.9  | 21.9  |
| L <sub>130</sub> | 0                          | 0.1 | 2.5 | 0.2 | 0.1 | 0.9  | 3.8   |
| L <sub>LA</sub>  | 0                          | 0   | 0   | 0   | 0   | 0    | 0     |

**Table S4.** Quantification of CEL and Regenerated Lignin.

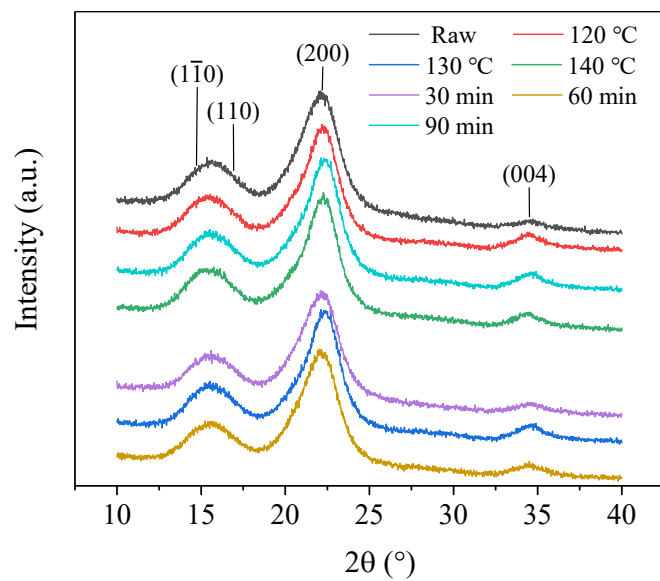
| Sample           | $\beta$ - $\beta$ (%) | $\beta$ -5 (%) | FA (%) | PCE (%) |
|------------------|-----------------------|----------------|--------|---------|
| CEL              | 4.11                  | 5.44           | 6.12   | 25.14   |
| L <sub>120</sub> | 1.94                  | 3.22           | 0      | 33.45   |
| L <sub>130</sub> | 1.85                  | 2.11           | 0      | 30.10   |
| L <sub>140</sub> | 1.53                  | 0.69           | 0      | 22.19   |



**Fig. S1.** Components variations under different BDO to ChCl molar ratios.

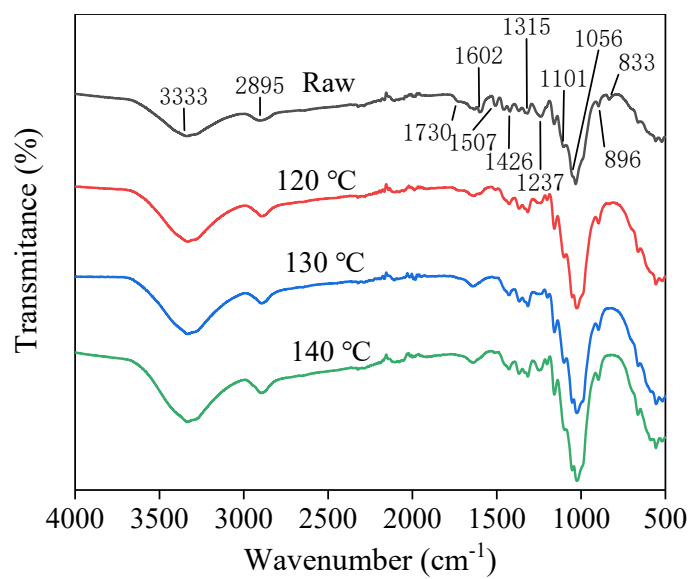


**Fig. S2.** The morphology analysis of the raw (a) and pretreated bamboo under different temperature of 120 (b) and 140 °C (c).

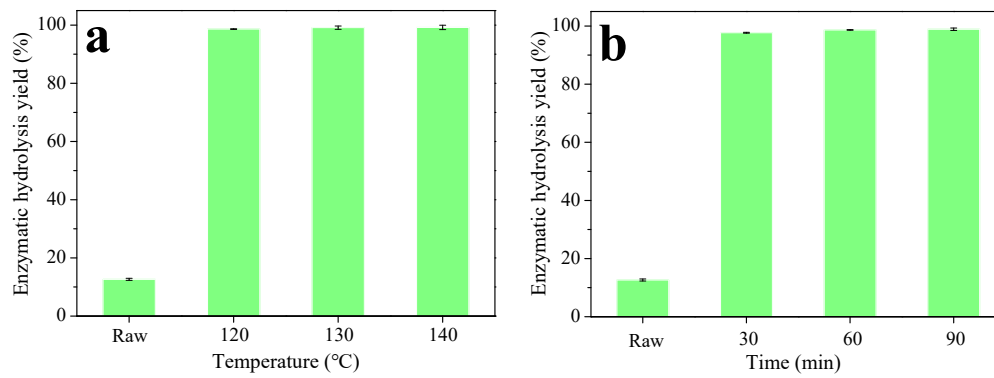


**Fig. S3.** XRD patterns of raw and pretreated samples.

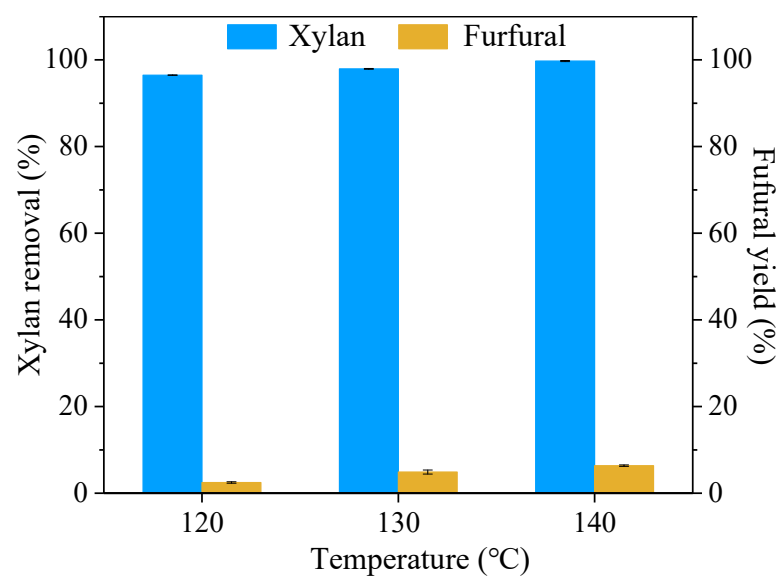




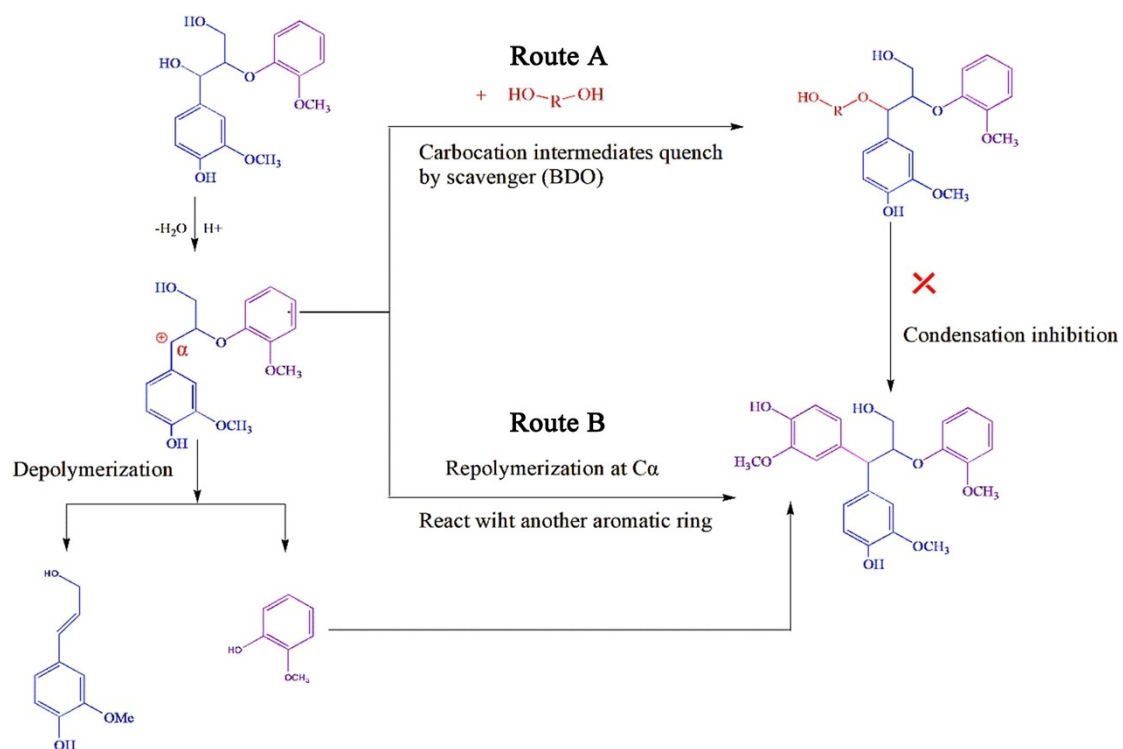
**Fig. S4.** The FTIR spectra of the raw and pretreated bamboo under different temperature.



**Fig. S5.** Glucan enzymatic saccharification yield under different pretreatment temperature for 1 h (a), and different time at 120 °C (b) with the optimal additions of the  $\text{Al}_2(\text{SO}_4)_3$  (0.15 M) and  $\text{H}_2\text{SO}_4$  (0.075 M).



**Fig. S6.** The xylan recovery and furfural yield under different temperatures under monophasic DES pretreatment.



**Fig. S7.** Lignin extraction in normal case (Route B), and the lignin protection by our 1,4-BDO DES (Route A).

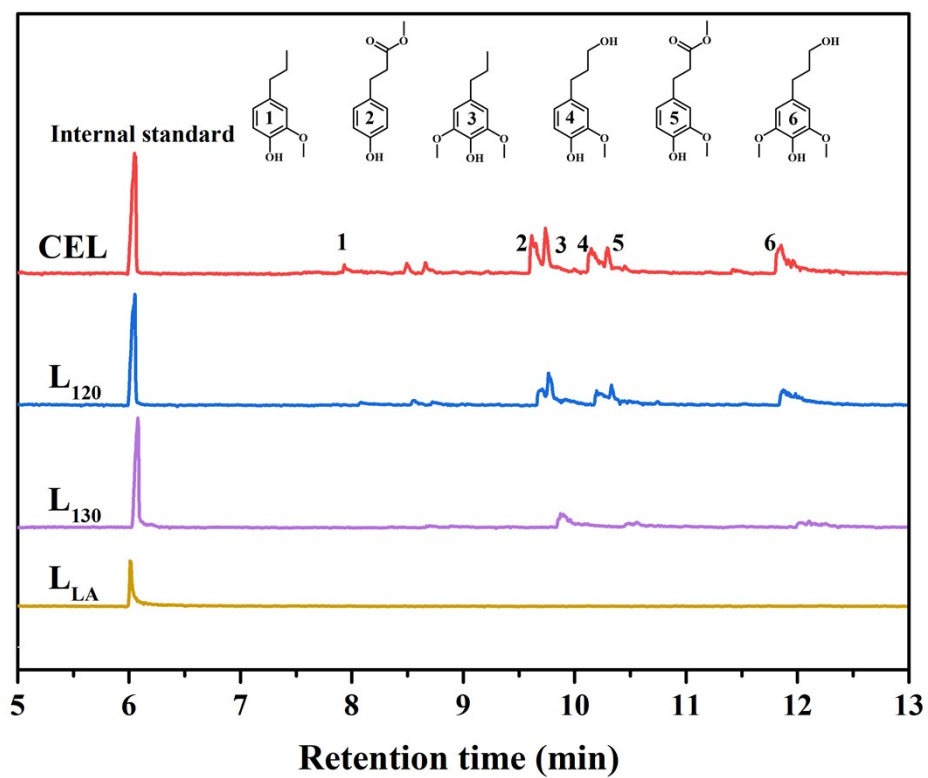


Fig. S8. GC-FID spectra of hydrogenolysis products from CEL and recovered lignins.