Supplementary Information for

An uncondensed lignin depolymerized in the solid state and isolated from lignocellulosic biomass: A mechanistic study

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**Figure S2.** Reverse-phase HPLC analysis of the catalytic cleavage of the $\beta$–O–4-aryl ether bond of model GG in LiBr trihydrate without acid (A) and with 10 mM HCl (B) for 60 min. Note: HK monomer was not quantitatively analyzed due to its poor stability.

**Figure S3.** GC-MS identification of the low molecular weight products of GG reaction in NLBTH (A) and ALBTH (B). Reaction conditions: A, 100 °C for 240 min without acid; B, 100 °C for 20 min with 10 mM HCl.

**Figure S4.** GPC chromatograms of the GG condensation products in the NLBTH (top) and ALBTH (middle). Note: The samples after NMR analysis were precipitated into acidic water for GPC analysis.

**Figure S5.** HSQC-TOCSY NMR spectra of GG reaction products in LiBr trihydrate reaction at 100 °C with 10 mM HCl for 10 min (A) and without acid (B) for 240 min.

**Figure S6.** The detailed reaction pathways of the proposed reactions.

**Figure S7.** The condensation between monomeric models. A. Reaction of TMBA in NLBTH at 100 °C for 30 min; B. Reaction of TMBA with excess GA in ALBTH at 100 °C for 30 min; and C. Reaction of TMBA with excess CS in ALBTH at 100 °C for 30 min.

**Table S1.** Lignin (Klason) content and ALBTH lignin yield of different biomass

**Table S2.** Hydrogenolysis of ALBTH and Klason lignins isolated from poplar and native lignin in poplar
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guaiacyl; **H**, *p*-hydroxyphenyl; **pCA**, *p*-coumarate; **FA**, ferulate; **pBA**, *p*-hydroxybenzoate; **T**, tricin

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### Table S1. Lignin (Klason) contents and ALBTH lignin yields of different biomass

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Klason lignin (% on biomass)</th>
<th>ALBTH lignin yield (% on biomass)</th>
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<tbody>
<tr>
<td></td>
<td>30 min</td>
<td>120 min</td>
</tr>
<tr>
<td>Poplar</td>
<td>22.2±0.4</td>
<td>20.7±0.2</td>
</tr>
<tr>
<td>Aspen</td>
<td>22.0±0.0</td>
<td>20.5±0.2</td>
</tr>
<tr>
<td>Eucalyptus</td>
<td>28.4±0.4</td>
<td>26.1±0.0</td>
</tr>
<tr>
<td>Douglas fir</td>
<td>25.9±0.0</td>
<td>24.0±0.2</td>
</tr>
<tr>
<td>Corn stover</td>
<td>12.8±0.1</td>
<td>13.8±0.1</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>17.5±0.2</td>
<td>17.1±0.1</td>
</tr>
</tbody>
</table>


Note: The ALBTH reactions were conducted at 110 °C in 60% LiBr with 40 mM HCl.

### Table S2. Hydrogenolysis of ALBTH and Klason lignins isolated from poplar and native lignin in poplar

<table>
<thead>
<tr>
<th></th>
<th>ALBTH lignin</th>
<th>Klason lignin</th>
<th>Raw poplar</th>
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<tbody>
<tr>
<td>Lignin oil yield (%)</td>
<td>96.0</td>
<td>29.6</td>
<td>93.1⁴</td>
</tr>
<tr>
<td>Insoluble residue yield (%)</td>
<td>4.3</td>
<td>63.7</td>
<td>63.3</td>
</tr>
</tbody>
</table>

Note: ⁴. Lignin oil yield from raw poplar was calculated based on the lignin content in poplar (20.7%, by the ALBTH method). Hydrogenolysis conditions: ALBTH and Klason lignins (0.20 g each) from poplar and poplar powder (0.95 g, containing ~0.20 g lignin) were hydrogenolyzed using a Pd/C catalyst (0.04 g) in methanol (25 mL) with 40 bar H₂ at 220 °C for 6 h.