## Supplementary Information for

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

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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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Route I. Acid catalyzed formation of benzyl cation



Route II. LiBr trihydrate catalyzed formation of benzyl cation

$$\begin{array}{c} L^{*}_{D} & \overset{OH}{\longrightarrow} \\ H^{*}_{D} & \overset{O$$

Route III. Formation of  $\beta$ -cation via an enol ether intermediate

Route IV. Formation of  $\beta$ -cation via hydride shift

Route V. Acid catalyzed formation of benzodioxane



Route VI. LiBr trihydrate catalyzed formation of phenyl-dihydrobenzofuran

Route VII. LiBr trihydrate/acid catalyzed formation of diphenylmethane



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**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.

Biomass(% on biomass) $30 \text{ min}$ $120 \text{ min}$ Poplar $22.2\pm0.4$ $20.7\pm0.2$ $21.0\pm0.2$ Aspen $22.0\pm0.0$ $20.5\pm0.2$ $20.4\pm0.1$ Eucalyptus $28.4\pm0.4$ $26.1\pm0.0$ $26.8\pm0.0$	Biomass	
Poplar22.2±0.420.7±0.221.0±0.2Aspen22.0±0.020.5±0.220.4±0.1Eucalyptus28.4±0.426.1±0.026.8±0.0		
Aspen $22.0\pm0.0$ $20.5\pm0.2$ $20.4\pm0.1$ Eucalyptus $28.4\pm0.4$ $26.1\pm0.0$ $26.8\pm0.0$	Poplar	
Eucalyptus 28 4+0 4 26 1+0 0 26 8+0 0	Aspen	
	Eucalyptus	
Douglas fir 25.9±0.0 24.0±0.2 24.4±0.3	Douglas fir	
Corn stover 12.8±0.1 13.8±0.1 14.2±0.3	Corn stover	
Switchgrass 17.5±0.2 17.1±0.1 17.6±0.3	Switchgrass	

Table S1. Lignin (Klason) contents and ALBTH lignin yields of different biomass<sup>1</sup>

1. N. Li, X. Pan and J. Alexander, Green Chemistry, 2016, 18, 5367-5376.

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

	ALBTH lignin	Klason lignin	Raw poplar
Lignin oil yield (%)	96.0	29.6	93.1ª
Insoluble residue yield (%)	4.3	63.7	63.3

Note: a. 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  $H_2$  at 220 °C for 6 h.