

## Supporting Information

### ***In situ* trapping of enol intermediates with alcohol during acid-catalysed de-polymerisation of lignin in a non-polar solvent**

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## Experimental Section

**General procedure** All chemicals were purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan). *Eucalyptus globulus* and Japanese cedar wood were procured from Nippon Paper Industries Co., Ltd (Tokyo, Japan). The wood chips were ground to 1.5  $\phi$  mesh size and used for experiments without the removal of extractives. The water contents of the woods were 9% (Japanese wood) and 6% (*E. globulus*). For use in reactions with dry wood, the wood particles were dried in *vacuo* at 70 °C for 1 h before use.

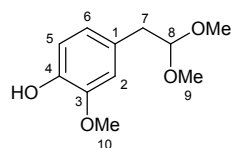
<sup>1</sup>H-, <sup>13</sup>C-, HSQC- and HMBC-NMR spectra were recorded in CDCl<sub>3</sub> in the presence of tetramethylsilane (TMS) as the internal standard using an ESC-400 (JEOL Ltd, Tokyo, Japan) and Agilent NMR System 500 MHz (Agilent Technologies, CA, USA) machines. Gel permeation chromatography (GPC) analysis was performed with a Waters Alliance HPLC system (Waters Corporation, MA, USA), equipped with a Waters RI detector (2414); the samples were resolved at 40 °C over three TSKgel SuperMultiporeHZ-M columns (4.6 mm i.d.  $\times$  15 cm) connected in tandem along with a guard column. Analytes were eluted using THF as a mobile phase (0.35 mL min<sup>-1</sup>). Number average molecular weight (*M<sub>n</sub>*) and weight average molecular weight (*M<sub>w</sub>*) distributions were calibrated using Shodex polystyrene standards (Showa Denko K. K., Tokyo, Japan). Gas chromatography/mass spectrometry (GC/MS) analysis was performed with Agilent 5975B GC/MS system (Agilent Technologies, CA, USA), equipped with a HP-5MS column (15 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film thickness; Agilent Technologies, CA, USA). The GC oven temperature was maintained at 50 °C for the initial 5 min. Subsequently, it was programmed to increase to 300 °C at a heating rate of 10 °C min<sup>-1</sup> and then maintained at 300 °C for the final 13 min. Helium (1.0 mL min<sup>-1</sup>) was used as the carrier gas. The mass spectrometer was operated in the electron impact ionization mode at 70 eV over a mass/charge (*m/z*) scan range from 40 *m/z* to 600 *m/z*. The split ratio was 1:30, and the ion source temperature was set at 230 °C. Microwave heating was performed in a 20 mL glass vial using Initiator+ (Biotage AB, Uppsala Sweden).

### Acid catalyzed depolymerization of wood in toluene/methanol.

An aliquot (0.7 mL) of methanolic H<sub>2</sub>SO<sub>4</sub> (1% H<sub>2</sub>SO<sub>4</sub> in methanol) was added to a solution of toluene (12 mL), methanol (2.3 mL) and wood particles (Japanese cedar or *E. globulus*, 1.5  $\phi$ , 1.0 g) in a 20 mL microwave reaction vial at room temperature. After securing the cap, the vial was heated at 140 °C–170 °C for 10–25 min. The vial was cooled to room temperature. On the addition of distilled water (10 mL), a white precipitate was observed. The residue was removed by filtration, and the filtrate was extracted with toluene (3 times). The extracts were combined and washed with brine in a separatory funnel, dried over MgSO<sub>4</sub> and evaporated to obtain a low molecular mass lignin fraction with reddish brown colour. After the measurement of total yield, yields of degradation products from lignin and cellulose were determined by <sup>1</sup>H NMR using 1,1,2,2-tetrachloroethane and CDCl<sub>3</sub> as an internal standard and solvent, respectively. The yields of the products were calculated by quantitative NMR (qNMR), i.e. by integrating peaks corresponding to specific protons in the characterized products in relation to that present in the internal standard. Methoxymethylfurfural (MMF)<sup>1</sup>, levoglucosenone<sup>2</sup> and levulinic acid methyl ester<sup>3</sup> were

identified by comparison with data reported previously. Lignin monomers **2a**, **2b**, **4a** and **4b** were characterized by NMR ( $^1\text{H}$ -,  $^{13}\text{C}$ -, HMQC and HMBC) and GC-MS analysis after purification by column chromatography. Specific proton peaks used in the determination of product yields were located at  $\delta_{\text{H}}$  (ppm) 9.51 (1H, s, CHO; for MMF), 5.00 (1 H, dd,  $J = 4.8$  Hz, C=CHCH; for levoglucosenone), 2.75 (2 H, t,  $J = 6.4$  Hz,  $\text{CH}_2$ ; for levulinic acid methyl ester), 2.84 (2 H, d,  $J = 5.6$  Hz, CH; for homovanillyl aldehyde dimethylacetal (**2a**)), 6.48 (2 H, s, Ph; for homosyringaldehyde dimethylacetal (**2b**)), 2.10 (3 H, s,  $\text{CH}_3$ ; for 1-(4-hydroxy-3-methoxyphenyl)-1-methoxypropan-2-one (**4a**)) and 2.11 (3 H, s,  $\text{CH}_3$ ; for 1-(4-hydroxy-3,5-dimethoxyphenyl)-1-methoxypropan-2-one (**4b**)). The yield of lignin oligomers was determined by the ratio of total yield and lignin monomer.

### Homovanillyl aldehyde dimethyl acetal (**2a**)



Compound **2a**;  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ) 2.84 (2 H, d,  $J = 5.6$  Hz, 7-H), 3.35 (6 H, s, 9-H), 3.88 (3 H, s, 10-H), 4.50 (1 H, t,  $J = 5.6$  Hz, 8-H), 5.52 (1 H, s, OH), 6.73 (1 H, dd,  $J = 2.0$  and 8.1 Hz, 6-H), 6.76 (1 H, d,  $J = 2.0$  Hz, 2-H) and 6.84 (1 H, d,  $J = 8.1$  Hz, 5-H);  $\delta_{\text{C}}$  (125 MHz;  $\text{CDCl}_3$ ) 39.4 (C-7), 53.5 (C-9), 55.9 (C-10), 105.6 (C-8), 112.0 (C-2), 114.2 (C-5), 122.1 (C-6), 128.9 (C-1), 144.2 (C-4) and 146.3 (C-3); MS (EI, 70 eV)  $m/z$  212 ( $\text{M}^+$ , 4%), 180 (31), 137 (30), 133 (41) and 75 (100).

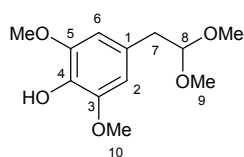
### $^1\text{H}$ -/ $^{13}\text{C}$ -NMR Data and correlations observed for **2a**

C.	$\delta_{\text{C}}$ (ppm)	H	$\delta_{\text{H}}$ (ppm)	HSQC	HMBC
1	128.9	1	-		5-H, 8-H, 7-H
2	112.0	2	6.76, d, $J = 2.0$ Hz	2-H	6-H, 7-H
3	146.3	3	-		5-H, 2-H, 10-H, OH
4	144.2	4	-		5-H, 2-H, 6-H, OH
5	114.2	5	6.84, d, $J = 8.1$ Hz	5-H	OH
6	122.1	6	6.73, dd, $J = 2.0, 8.1$ Hz	6-H	2-H, 7-H
7	39.4	7	2.84, d, $J = 5.6$ Hz	7-H	2-H, 6-H
8	105.6	8	4.50, t, $J = 5.6$ Hz	8-H	7-H, 9-H
9	53.5	9	3.35, s	9-H	8-H
10	55.9	10	3.88, s	10-H	

<sup>1</sup> N. Yoshida, N. Kasuya, N. Haga, K. Fukuda, *Polymer Journal*, 2008, **40**, 1164–1169

Homosyringaldehyde dimethylacetal (**2b**)  
 R. M. Sarobe, I. Fernández, R. A. Spurrillo, M. Á. Sierra, A. G. Suárez, *Org. Lett.*, 2008, **10** (16), 3389–3392

<sup>3</sup> R. I. Khusnutdinov, A. R. Baiguzina, A. A. Smirnov, R. R. Mukminov, U. M. Dzhemilev, *Russ. J. Appl. Chem.*, 2007, **80**(10), 1687–1690

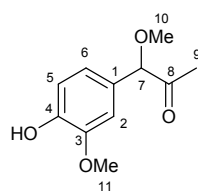


Compound **2b**;  $\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ) 2.83 (2 H, d,  $J = 5.6$  Hz, 7-H), 3.35 (6 H, s, 9-H), 3.85 (6 H, s, 10-H), 4.52 (1 H, t,  $J = 5.6$  Hz, 8-H), 5.69 (1 H, s, OH) and 6.48 (2 H, s, 2-H and 6-H);  $\delta_{\text{C}}$  (125 MHz;  $\text{CDCl}_3$ ) 39.8 (C-7), 53.4 (C-9), 56.3 (C-10), 105.6 (C-8), 106.3 (C-2, C-6), 128.0 (C-1), 133.5 (C-4), and 147.0 (C-3, C-5); MS (EI, 70 eV)  $m/z$  (%): 242 ( $\text{M}^+$ , 13%), 211 (12), 167 (15) and 75 (100).

### $^1\text{H}/^{13}\text{C}$ -NMR Data and correlations observed for **2b**

C.	$\delta_{\text{C}}$ (ppm)	H	$\delta_{\text{H}}$ (ppm)	HSQC	HMBC
1	128.0	1	-		2-H
2, 6	106.3	2, 6	6.48, s	2-H, 6-H	2-H, 6-H, 7-H
3, 5	147.0	3, 5	-		2-H, 10-H, OH
4	133.5	4	-		2-H
7	39.8	7	2.83, d, $J = 5.6$ Hz	7-H	2-H, 8-H
8	105.6	8	4.52, t, $J = 5.6$ Hz	8-H	9-H
9	53.4	9	3.35, s	9-H	8-H
10	56.3	10	3.85, s	10-H	

### 1-(4-Hydroxy-3-methoxyphenyl)-1-methoxypropan-2-one (**4a**)



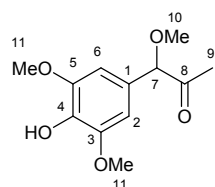
$\delta_{\text{H}}$  (500 MHz;  $\text{CDCl}_3$ ) 2.10 (3 H, s, 9-H), 3.36 (3 H, s, 10-H), 3.87 (3 H, s, 11-H), 4.59 (1 H, s, 7-H), 5.81 (1 H, s, OH), 6.84 (1 H,  $J = 2.0$  Hz, 2-H) and 6.90 (2 H, m, H-5 and H-6);  $\delta_{\text{C}}$  (125 MHz;  $\text{CDCl}_3$ ) 25.3 (C-9), 56.0 (C-11), 57.0 (C-10), 89.1 (C-7), 109.0 (C-2), 114.6 (C-5), 120.7 (C-6), 127.5 (C-1), 146.2 (C-4), 147.1 (C-3) and 206.6 (C-8); MS (EI, 70 eV)  $m/z$  210 ( $\text{M}^+$ , 1%), 168 (10), 167 (100), 152 (25), 151 (19) and 137 (6).

### $^1\text{H}/^{13}\text{C}$ -NMR Data and correlations observed for **4a**

C	$^{13}\text{C}$ NMR $\delta$	H	$^1\text{H}$ NMR $\delta$ (ppm)	HMQC	HMBC
1	127.5	1	-		H-7
2	109.0	2	6.84, d, $J = 2.0$ Hz	H-2	H-7
3	147.1	3	-		H-5, H-2, H-11, OH
4	146.2	4	-		H-2, OH
5	114.6	5	6.90, m	H-5	OH

6	120.7	6	6.90, m	H-6	H-7
7	89.1	7	4.59, s	H-7	H-9, H-10
8	206.6	8	-		H-7, H-9
9	25.3	9	2.10, s	H-9	
10	57.0	10	3.36, s	H-10	H-7
11	56.0	11	3.87, s	H-11	

### 1-(4-Hydroxy-3,5-dimethoxyphenyl)-1-methoxypropan-2-one (4b)



$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ )  $\delta$  ppm 2.11 (3H, s, H-9), 3.38 (3H, s, H-10), 3.89 (6H, s, H-11), 4.57 (1H, s, H-7), 5.71 (1H, s, OH), 6.61 (2H, s, H-2, H-6)  $^{13}\text{C}$  NMR (125MHz;  $\text{CDCl}_3$ )  $\delta$  ppm 25.1 (C-9), 56.4 (C-11), 57.1 (C-10), 89.3 (C-7), 103.8 (C-1, C-6), 126.8 (C-1), 135.2 (C-4), 147.5 (C-3, C-5), 206.5 (C-3, C-5), MS (EI, 70 eV)  $m/z$  198 (11%), 197 (100), 182 (24), 181 (10) and 167 (6).

### $^1\text{H}/^{13}\text{C}$ -NMR Data and correlations observed for 4b

C	$^{13}\text{C}$ NMR $\delta$	H	$^1\text{H}$ NMR $\delta$ (ppm)	HMQC	HMBC
1	126.8	1	-		H-2, H-6, H-7
2, 6	103.8	2, 6	6.61, s	H-2, H-6	H-7
3, 5	147.5	3, 5	-		H-2, H-6, H-11, OH
4	135.2	4	-		H-2, H-6, OH
7	89.3	7	4.57, s	H-7	H-2, H-6, H-9, H-10
8	206.5	8	-		H-7, H-9
9	25.1	9	2.11, s	H-9	H-7
10	57.1	10	3.38, s	H-10	H-7
11	56.4	11	3.89, s	H-11	