Supporting Information For

Selectively catalytic transformation of lignin with guaiacol as the only liquid

product

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EXPERIMENTAL PROCEDURES

Synthesis of Lignin Model Compounds

The lignin model compounds (a, b) were prepared following previously reported procedures, as shown in Scheme 1 ⁵⁰.

¹H NMR of lignin model compound a (400 MHz, DMSO-*d*₆): δ 7.55 – 6.77 (m, 11H), 5.51 (d, J = 4.6 Hz, 1H), 5.06 (d, J = 4.7 Hz, 3H), 4.86 (q, J = 5.2 Hz, 1H), 4.65 (p, J = 6.2 Hz, 1H), 3.99 (ddd, J = 28.8, 12.3, 5.8 Hz, 2H), 3.79 (s, 6H), 1.30 (d, J = 6.4 Hz, 3H).

¹H NMR of lignin model compound b (400 MHz, DMSO-*d*₆): δ 7.37 (ddd, J = 26.7, 18.4, 7.2 Hz, 5H), 7.07 – 6.92 (m, 2H), 6.87 (d, J = 8.0 Hz, 1H), 6.64 (s, 2H), 5.18 – 4.98 (m, 4H), 4.81 – 4.70 (m, 1H), 4.70 – 4.55 (m, 1H), 3.91 (dd, J = 10.0, 4.6 Hz, 1H), 3.86 – 3.80 (m, 1H), 3.75 (d, J = 5.8 Hz, 9H), 1.31 (d, J = 6.4 Hz, 3H).



Supplementary Scheme 1. Synthesis of lignin model compounds.



Fig. S1. (A) The GC and MS spectra of the reaction mixture after lignin transformation (Reaction condition, see Table 1, entry 9); (B) The GC trace of the gaseous sample after lignin transformation (Reaction condition, see Table 1, entry 9); (C) The HPLC traces of the liquid mixture after the reaction and guaiacol standard sample. (Reaction condition, see Table 1, entry 9); (D) and (E) The 2D-HSQC NMR spectra of the reaction mixture in deuterated methanol (methanol- d_4) after reaction.

Reaction conditions: 50 mg organosolv lignin, 20 mg La(OTf)₃, 4 mL deuterated methanol (methanol- d_4), 10 µL water, 270 °C, 0.1 MPa Ar, 24 h.



Fig. S2. The GC graphics of gaseous(A) and liquid (B) samples after lignin model compound a transformation.

Reaction conditions: 50 mg lignin model compound a, 20 mg La(OTf)₃, 4 mL methanol, 10 μ L water, 270 °C, 0.1 MPa Ar, 24 h.



Fig. S3. The GC trace of the gaseous sample after 4-ethylguaiacol transformation. Reaction conditions: 50 mg 4-ethylguaiacol, 20 mg La(OTf)₃, 4 mL methanol, 10 μ L water, 270 °C, 0.1 MPa Ar, 24 h.



Fig. S4. Transformation route of lignin model compound a in the ethanol/water.

Reaction conditions: 50 mg lignin model compound a, 20 mg La(OTf)₃, 4 mL ethanol, 10 μ L water, 270 °C, 0.1 MPa Ar, 24 h.



Fig. S5. (A) Transformation route of lignin model compound b. Reaction conditions: 50 mg lignin model compound b, 20 mg La(OTf)₃, 4 mL methanol, 10 μ L water, 270 °C, 0.1 MPa Ar, 24 h; (B) Transformation route of 2,6-dimethoxy-4-methylphenol. Reaction conditions: 20 mg 2,6-dimethoxy-4-methylphenol, 50 mg La(OTf)₃, 4 mL methanol, 10 μ L water, 270 °C, 0.1 MPa Ar, 24 h.



Fig. S6. The GC trace of gaseous (A) and liquid (B) samples after lignin model compound b transformation.

Reaction conditions: 50 mg lignin model compound b, 20 mg La(OTf)₃, 4 mL methanol, 10 μ L water, 270 °C, 0.1 MPa Ar, 24 h.



Fig. S7. (A) The HPLC traces of the liquid mixture after the scale up reaction and guaiacol standard sample. (B) The GC trace of the gaseous sample after the reaction.
Reaction condition: 1.50 g organosolv lignin, 600 mg La(OTf)₃, 120 mL methanol, 0.3 mL water, 270 °C, 0.1 MPa Ar, 24 h.



Fig. S8. The 2D-HSQC NMR spectrum of the reaction mixture after the scale-up reaction. Reaction condition: 1.50 g organosolv lignin, 600 mg La(OTf)₃, 120 mL methanol, 0.3 mL water, 270 °C, 0.1 MPa Ar, 24 h.

	(_{H3} C	COT OCH3		∧ _{ОСН3} + м	esidual solid	
		Lignin	Gua	iacol		
Entry	Cataly Catalyst	vtic system* methanol/water (mL/mL)	Tem. (°C)	Catalyst (mg)	Guaiacol yield (wt. %) ^b	Molar Yield (mol%) °
1	La(OTf) ₃	2.0/2.0	270	20	3.0	4.8
2	La(OTf) ₃	2.4/1.6	270	20	5.1	8.2
3	La(OTf) ₃	3.2/0.8	270	20	11.6	18.7
4	La(OTf) ₃	3.6/0.4	270	20	17.6	28.4
5	La(OTf) ₃	3.8/0.2	270	20	20.5	33.0
6	$La(OTf)_3$	4.0/0.01	270	0	0.3	0.5
7	$La(OTf)_3$	4.0/0.01	270	5	5.3	8.5
8	La(OTf) ₃	4.0/0.01	270	10	13.5	21.7
9	$La(OTf)_3$	4.0/0.01	270	15	20.6	33.2
10	$La(OTf)_3$	4.0/0.01	270	20	22.5	36.2

Table S1 Transformation of lignin under different reaction conditions ^a

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^a Reaction conditions: 50 mg organosolv lignin, 24 h, 0.1 MPa Ar, 500 rpm. ^b Guaiacol yield is calculated based on the mass of lignin. ^c The calculation of molar yield was estimated as follow:

$$n_{benzene\ ring\ in\ lignin} = \frac{m_{lignin}}{M_{hypothesis}} \times (n_S + n_G)$$
(S1)

Molar yield (mol%) =
$$\frac{n_{guaiacol}}{n_{benzene ring in lignin}} \times 100$$

(S2)

In the equations S1 and S2:

n_{benzene ring in lignin} (mol): the mole number of benzene ring in lignin;

m_{lignin} (g): the amount of lignin used in this work;

M_{hypothesis} (g/mol): the hypothesis molecular weight.

For example, the S/G ratio in the organosolv lignin is determined as 1.45:1 according to the 2D-HSQC NMR. Based on this result, we hypothesized that lignin was composed of 1.45*n S units and n G units. To simplify, 4-(3-hydroxypropyl)-2,6-dimethoxyphenol represented S units and 4-(3-hydroxypropyl)-2-methoxyphenol represented G units. So the $M_{hypothesis}$ (g/mol) is (1.45*n*Mw(4-(3-hydroxypropyl)-2,6-dimethoxyphenol)+n*Mw(4-(3-hydroxypropyl)-2,6-dimethoxyphenol)), namely 489.635*n (g/mol);

 n_S and n_G (mol): the hypothesis mole number of S units and n G units. For example, in the organosolv lignin, n_S is 1.45*n (mol) and n_G is n (mol);

n_{guaiacol} (mol): the mole number of the guaiacol obtained from this work.

Under optimal conditions (Entry 10, the same as Table 1, entry 9 in main text), the yields of guaiacol and residue solid are 22.5% and 72.1%, respectively, which suggested that nearly all of the lignin was transformed into guaiacol and the solid residue.

Lignin samples	S	:	G	:	FA	:	Н	:	PCE
Organosolv lignin from hardwood	1.45	:	1.00	:	0	:	0	:	0
EMAL-p	0	:	1.00	:	0	:	0	:	0
EMAL-b	1.35	:	1.00	:	0.02	:	0.10	:	0.68

Table S2 The ratio of S/G/FA/H/PCE in various lignins^a

^a S:G:FA:H:PCE= 0.5 I(S_{2,6}):I(G₂): I(FA₂): 0.5I(H_{2,6}):0.5 I(PCE_{2,6}). S: syringyl units, G: guaiacyl units; FA: ferulates; H: *p*-hydroxyphenyl units; PCE: *p*-coumarates













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