

## Supporting Information

For

### The production of 4-ethyltoluene via directional valorization of lignin

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- Supplementary Text
- Figures S1 to S8
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- NMR spectra

## 1. Materials and Methods

Poplar and Birch were provided by Shanxi province, China. They were cut into pieces, milled and screened in a mill (DFT-200A, Shanghai) to obtain a 20–40 mesh fraction.  $\gamma$ -valerolactone (GVL), 1,4-dioxane, propionaldehyde and cyclohexane were provided by Beijing InnoChem Science & Technology Co., Ltd. Anisole, benzene, toluene, ethylbenzene, 4-ethyltoluene, chlorobenzene, n-decane, phenol, dihydroconiferyl alcohol, 4-(3-hydroxypropyl)-2,6-dimethoxyphenol and methyl cinnamate were purchased from J&K scientific Ltd. LiI, LiBF<sub>4</sub>, HCl, CH<sub>3</sub>COONa, CH<sub>3</sub>COOH, H<sub>2</sub>SO<sub>4</sub> were purchased from J&K scientific Ltd. RhCl<sub>3</sub>, PdCl<sub>2</sub>, RuCl<sub>3</sub>, NiCl<sub>2</sub>, CoCl<sub>2</sub>, Rh(CO)<sub>4</sub>Cl<sub>2</sub> and Deuterated DMSO were purchased from Energy Chemical. Liquid-state cellulase (100 FPU/mL) were supplied by Novozymes, Beijing, China. All the chemicals were used as received.

## 2. Preparation of lignin

### 2.1 Preparation of double enzymatic mild lignin (DEL)

DEL was prepared according to the method reported with minor modification.<sup>S1</sup> Poplar sawdust was undergone two consecutive ball-milling and excessive amounts cellulase (50 FPU/g substrates) hydrolysis. The ball-milling process was performed in a planetary ball mill (FritschGMBH, Idar-Oberstein, Germany). Poplar sawdust was milled for 6 h and then dried at 60 °C in an oven for overnight. The ball-milled poplar powder (10g) was suspended in acetate buffer (0.05 mM, 250 mL, pH 4.8) with loading of 5.0 mL of Novozyme Celluclast (500 FPU). The reaction mixture was incubated at 50 °C in a rotary shaker (150 rpm) for 72 h. After enzymatic hydrolysis, the mixture was centrifuged. The residue lignin was washed extensively with hot acidic water and then freeze-dried. The dried residue lignin was undergone ball-milling again and cellulase hydrolysis under same conditions.

### 2.2 Preparation of GVL-lignin

GVL-lignin was prepared in 500 mL high-pressure and corrosion-resistant stirred batch reactor (Beijing Century Sen Long Instruments Company, Beijing, China) according to the method reported with minor modification.<sup>S2</sup> Birch powder (25g) was added to 80 wt %  $\gamma$ -valerolactone (400 g) and 100 mM H<sub>2</sub>SO<sub>4</sub>. Then the batch reactor was heated to 120 °C with stirring (800 rpm). After 30 min, the reactor was cooled by flowing water through the external heating jacket. The suspension was filtrated and diluted 5 times with water to precipitate and regenerate crude lignin. The crude lignin was centrifuged, washed for several times, and finally freeze-dried, the GVL-lignin was obtained.

### 2.3 Preparation of PA-lignin

PA-lignin was prepared in 500 mL high-pressure and corrosion-resistant stirred batch reactor (Beijing Century Sen Long Instruments Company, Beijing, China) according to the method reported with minor modification.<sup>S3</sup> 40 g Birch or Poplar sawdust were mixed with 360 mL 1,4-dioxane, 25.2 mL water, 16.8 mL HCl solution

(37%) and 38 mL propionaldehyde solution. Then the reactor was heated to 80 °C with stirring (800 rpm). After stirring for 150 min, the suspension was filtrated and washed with 1,4-dioxane. Then the filtrate was evaporated at 45 °C under reduced pressure. The concentrated filtrate was slowly dropped into 10-fold volume of acidic water (pH=2.0) to precipitate crude lignin. The crude lignin was collected by filtration and dried under vacuum.

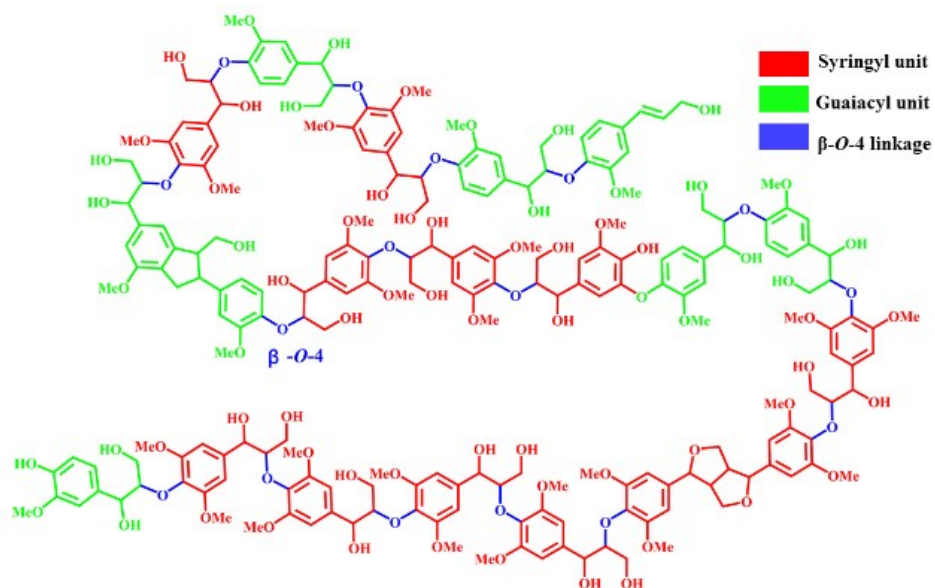
#### 2.4 Organosol lignin (OL) extraction process

Organosol lignin was prepared according to the method reported with minor modification.<sup>S4</sup> The preparation of organosol lignin was carried out in a 1000 mL Parr reactor (Parr Instrument Company, USA). Poplar powder (50 g) was added to 70% isopropanol/water solution (500 mL). Then the batch reactor was heated to 220 °C with stirring (1000 rpm) for 1 h. Then the reactor was immersed into an ice water bath to quench the reaction. The suspension was filtrated and poured into 10-fold volume of acidic water (pH=2.0). After being centrifuged and freeze-dried, organosol lignin was obtained.

### 3 Reaction procedures for producing 4-ethyltoluene.

The reaction was performed in a 15 mL Teflon-lined stainless-steel reactor equipped with a magnetic stirrer. In a typical experiment, 200 mg lignin, 268 mg LiI, 94 mg LiBF<sub>4</sub>, 10 mg RhCl<sub>3</sub>·n H<sub>2</sub>O and 2 mL toluene were loaded into the reactor. The reactor was sealed and purged with CO to remove the air at room temperature. CO was charged into the reactor to the desired pressure. Then the reactor was placed in a furnace with a stirring speed of 500 rpm at desired temperature controlled by a PID temperature controller (model SX/A-1, Beijing Tianchen Electronic Company). After the reaction, the reactor was cooled in an ice-water bath and the residual gas was released slowly and collected in a gasbag. The gaseous sample was analyzed by GC (Agilent 4890D) equipped with a TCD detector and a packed column (Carbon molecular sieve TDX-01, 1 m in length and 3 mm in diameter) using argon as the carrier gas. A known amount of n-dodecane as the internal standard was added into the reactor and stirred vigorously for 5 min. After that, the liquid reaction mixture was centrifuged, the supernatant liquid was collected for qualitative analysis using a GC-MS (Agilent 5977A, HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and quantitative analysis using GC (Agilent 7890) equipped with a flame ionization detector (FID) and the same HP-5MS capillary column. The yields of ethylbenzene and 4-ethyltoluene were calculated from the GC data. As lignin is reactant, the residue solid was washed with deionized water, then dried in vacuum at 60 °C for 48 h over P<sub>2</sub>O<sub>5</sub> desiccant and characterized by 2D-HSQC NMR in DMSO-*d*<sub>6</sub> (Bruker Advance III 600).<sup>S5</sup>

## 4. Results and discussion



**Figure S1.** Schematic representation of a typical broadleaf lignin structure.<sup>S6</sup>

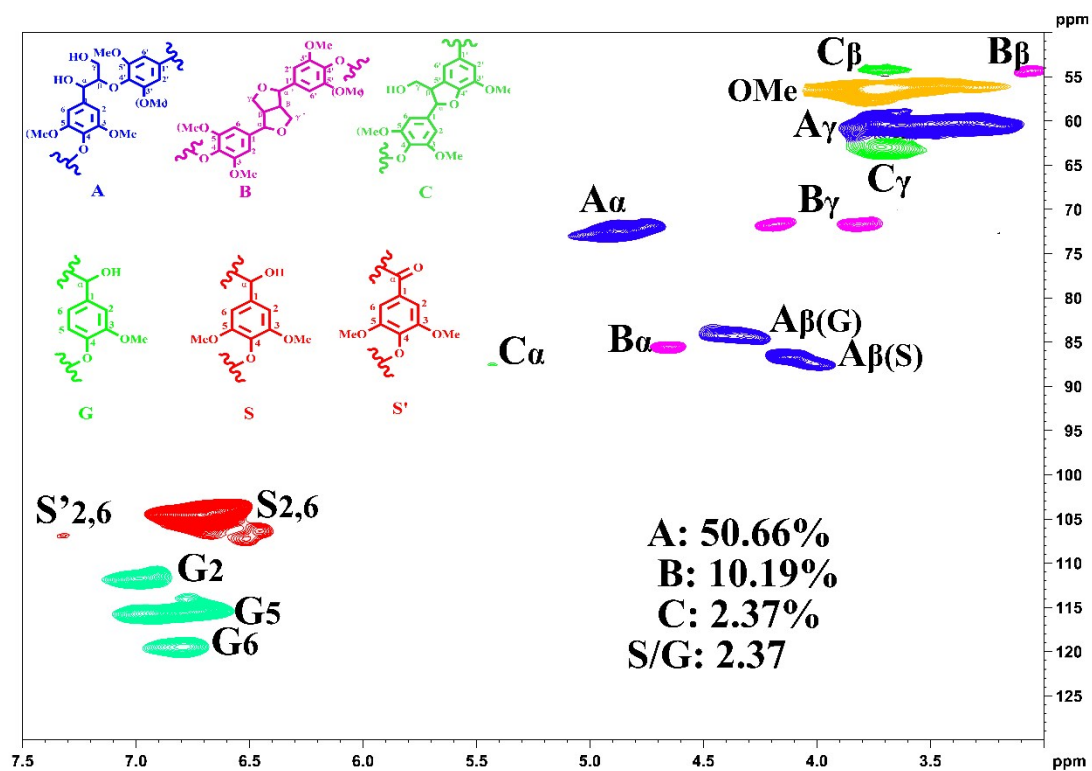
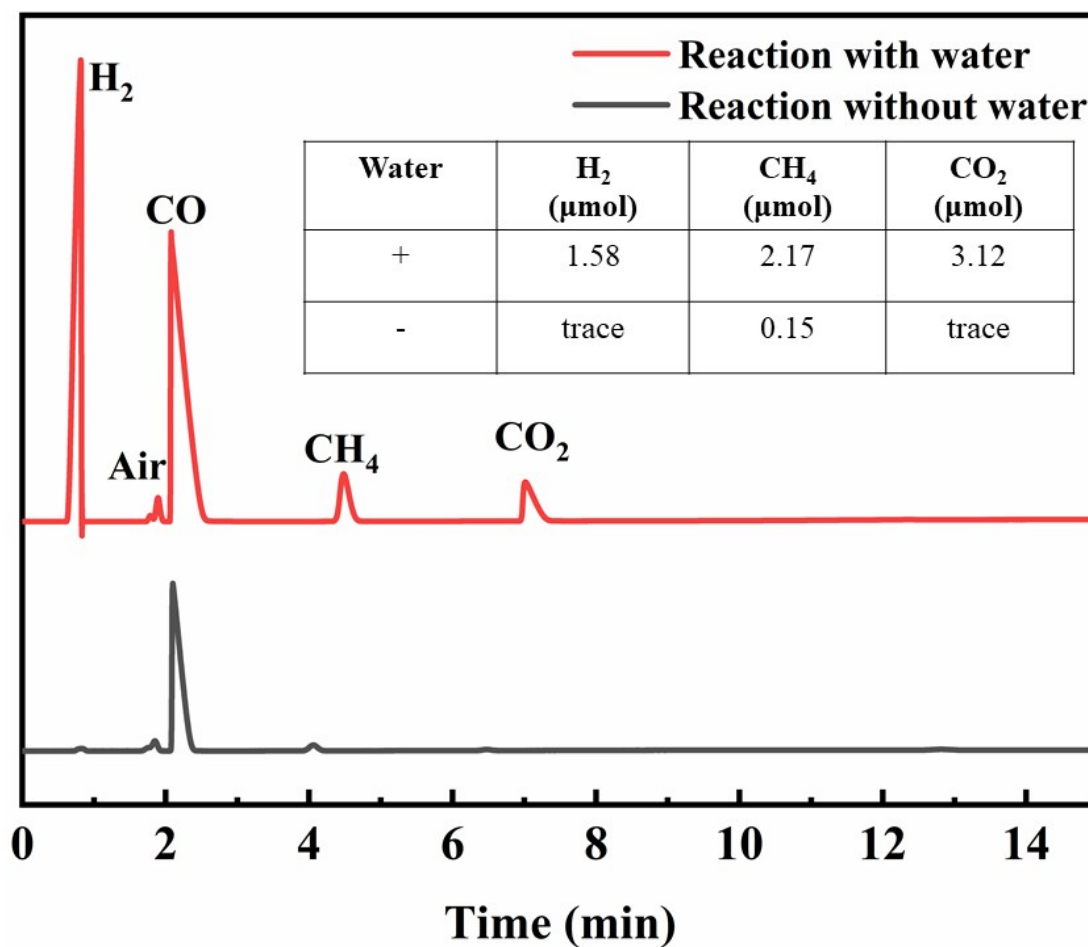
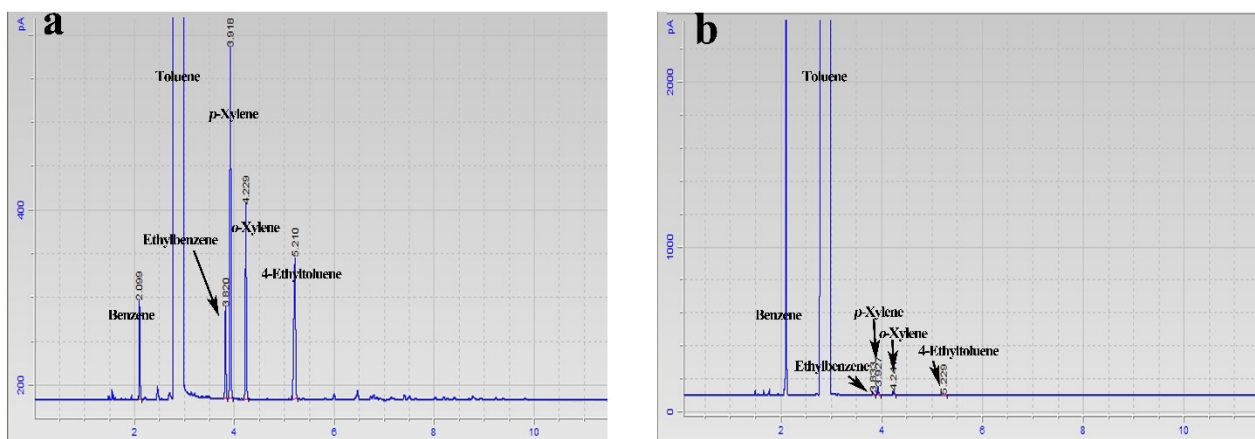


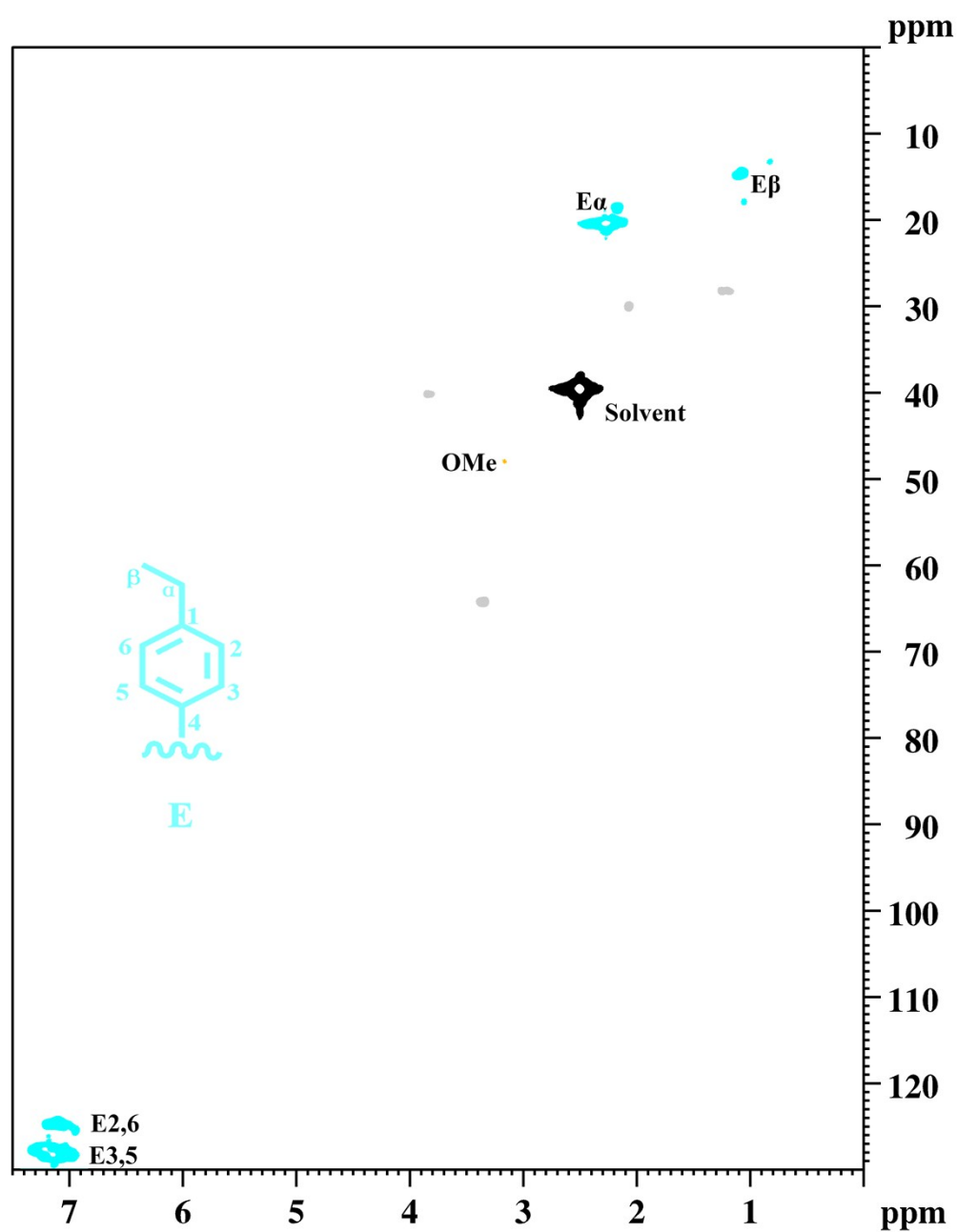
Figure S2. 2D-HSQC-NMR spectra of DEL from Birch in DMSO- $d_6$



**Figure S3** The GC trace of the gaseous sample after lignin transformation (Reaction condition see Table 1, entries 1 and 12). (+: added 0.1 g water; -: without water)

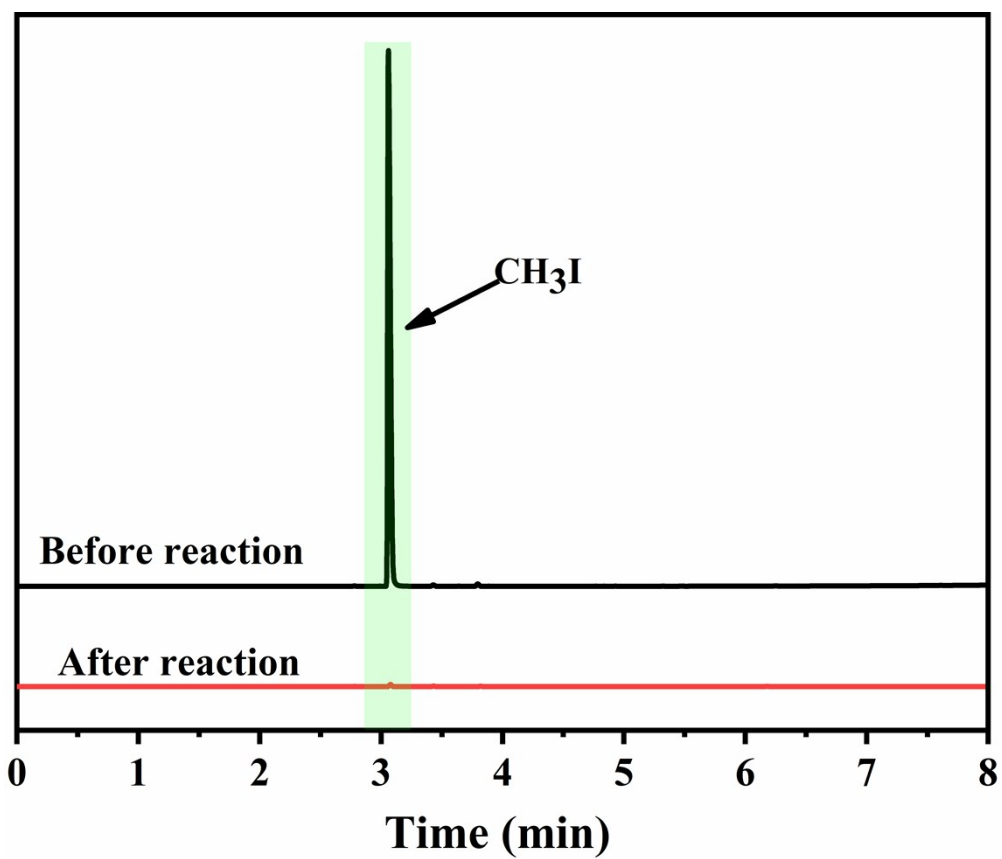


**Figure S4.** The GC traces of the products: (a) **Reaction conditions:** 200 mg DEL, 268 mg LiI, 94 mg LiBF<sub>4</sub>, 10 mg RhCl<sub>3</sub>·nH<sub>2</sub>O, 220 °C, CO 4 MPa, 72 h; (b) **Reaction conditions:** 200 mg DEL, 94 mg LiBF<sub>4</sub>, 10 mg RhCl<sub>3</sub>·nH<sub>2</sub>O, 220 °C, CO 4 MPa, 72 h;

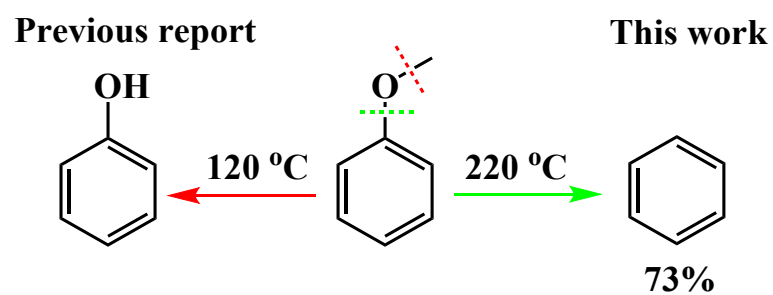


**Figure S5.** The full 2D-HSQC NMR spectra of the DEL after reaction. Reaction conditions: 200 mg DEL, 268 mg LiI, 94 mg  $\text{LiBF}_4$ , 10 mg  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ , 220  $^\circ\text{C}$ ,  $\text{CO}$  4 MPa, 72 h.

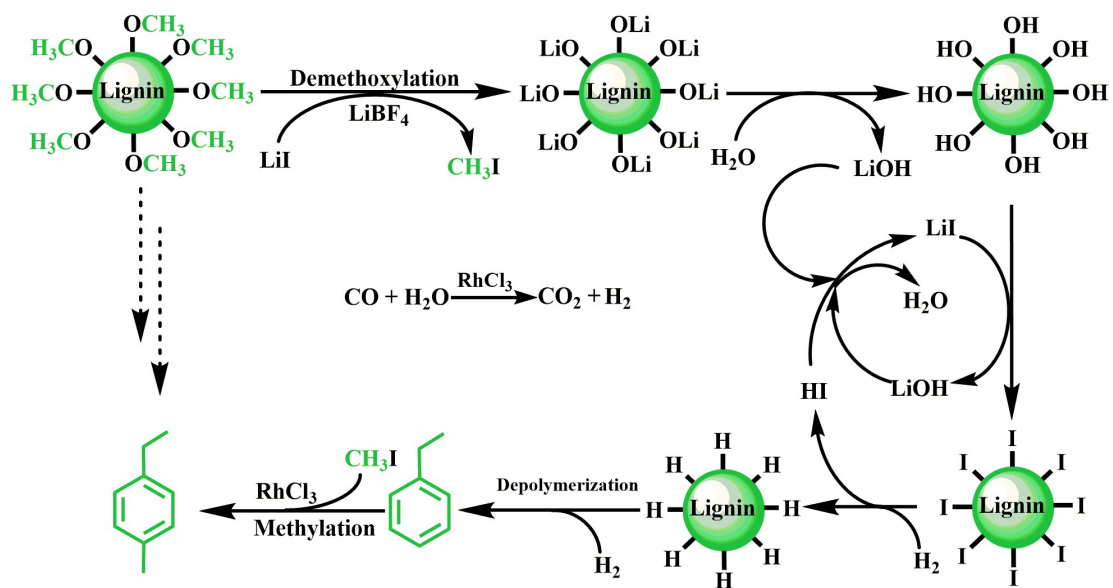




**Figure S6.** The HS-GC-FID chromatogram of methoxy group in DEL before and after reaction.



**Figure S7.** The reaction of anisole to produce phenol and benzene. Reaction conditions: 1 mmol anisole, 0.01 g RhCl<sub>3</sub>, 2 mmol LiI, 1.5 ml HMinBF<sub>4</sub>, 4 MPa CO, 15 mmol H<sub>2</sub>O, 120 °C, 12h (left); 1 mmol anisole, 0.01 g RhCl<sub>3</sub>, 268 mg LiI, 94 mg LiBF<sub>4</sub>, 0.6 mg water, 2 ml toluene, 4 MPa CO, 220 °C, 24h (right).



**Figure S8.** Possible reaction mechanism of lignin transformation into 4-ethyltoluene with  $\text{RhCl}_3$ - $\text{LiI}$ - $\text{LiBF}_4$  catalytic system.

**Table S1** Results for the utilization of methoxy group in different catalytic system <sup>a</sup>

Entry	Solvent	Catalyst	Yield (mmol)			Utilization of methoxy (wt%) <sup>b</sup>
			benzene	<i>o</i> -xylene	<i>p</i> -xylene	
1	toluene	RhCl <sub>3</sub>	0.8	0.8	1.9	94.2
2	toluene	PdCl <sub>2</sub>	0.1	0.2	0.5	29.0
3	toluene	RuCl <sub>3</sub>	0.2	0.1	0.3	11.2
4	toluene	NiCl <sub>2</sub>	trace	trace	trace	0.9
5	toluene	CoCl <sub>3</sub>	trace	trace	trace	0.8
6	toluene	- <sup>c</sup>	trace	trace	trace	0.2
7	toluene	Rh <sub>2</sub> (CO) <sub>4</sub> Cl <sub>2</sub>	0.3	0.9	1.3	94.8
10 <sup>d</sup>	toluene	RhCl <sub>3</sub>	0.8	0.8	1.9	88.6
11 <sup>d</sup>	toluene	Rh <sub>2</sub> (CO) <sub>4</sub> Cl <sub>2</sub>	0.3	0.9	1.3	94.8
12 <sup>e</sup>	toluene	RhCl <sub>3</sub>	0.4	1.0	1.3	94.7
13 <sup>f</sup>	toluene	RhCl <sub>3</sub>	0.8	1.1	1.6	97.8
14	benzene	RhCl <sub>3</sub>	-	-	-	28.3 <sup>g</sup>
15	chlorobenzene	RhCl <sub>3</sub>	-	-	-	1.2
16	<i>n</i> -decane	RhCl <sub>3</sub>	-	-	-	0.2
17	cyclohexane	RhCl <sub>3</sub>	-	-	-	0.4
18 <sup>h</sup>	toluene	RhCl <sub>3</sub>	2.8	1.7	1.1	-

<sup>a</sup> Reaction condition: 200 mg DEL, 268 mg LiI, 94 mg LiBF<sub>4</sub>, 10 mg RhCl<sub>3</sub>, 0.6 mg water, 2 mL extra dry toluene, 220 °C, CO 4 MPa, 72 h; <sup>b</sup> Utilization of methoxy (wt%)=( $n_{4\text{-ethyltoluene}}+n_{o\text{-xylene}}+n_{p\text{-xylene}}-n_{\text{benzene}}$ )\*31/ $m_{\text{methyl group in lignin}}$ , the content of methoxy group in DEL was 32.9 wt%; <sup>c</sup> without catalyst; <sup>d</sup> without water; <sup>e</sup> adding 0.1 ml H<sub>2</sub>O; <sup>f</sup> adding 0.5 ml H<sub>2</sub>O; <sup>g</sup> the utilization of methoxy is based on the amount of methyl group in 4-ethyltoluene and toluene. Utilization of methoxy (wt%)=( $n_{4\text{-ethyltoluene}}+n_{\text{toluene}}$ )\*31/ $m_{\text{methyl group in lignin}}$ ; <sup>h</sup> without lignin.

**Table S2** The effect of reaction time on the utilization of methoxy group <sup>a</sup>

Entry	Time (h)	Yield (mmol)			Utilization of methoxy (wt%)
		benzene	<i>o</i> -xylene	<i>p</i> -xylene	
1	6	0.5	0.2	0.5	9.0
2	12	0.6	0.3	0.8	21.8
3	18	0.7	0.4	1.0	34.6
4	24	0.7	0.4	1.5	56.3
5	30	0.7	0.6	1.6	71.5
6	36	0.8	0.7	1.8	82.8
7	42	0.8	0.7	1.8	85.0
8	48	0.8	0.8	1.9	89.1
9	54	0.9	0.8	1.9	89.0
10	60	0.9	0.8	1.9	91.3
11	66	0.9	0.8	1.9	91.5
12	72	0.8	0.8	1.9	94.2

<sup>a</sup> Reaction condition: 200 mg DEL, 268 mg LiI, 94 mg LiBF<sub>4</sub>, 10 mg RhCl<sub>3</sub>, 0.6 mg water, 2 mL extra dry toluene, 220 °C, CO 4 MPa, 72 h, the amount of methoxy group in DEL is 32.90 wt%; <sup>b</sup>; Utilization of methoxy (wt%)=(n<sub>4-ethyltoluene</sub>+n<sub>o-xylene</sub>+n<sub>p-xylene</sub>-n<sub>benzene</sub>)\*31/m<sub>methyl group in lignin</sub>.

**Table S3** The effect of the temperature on the utilization of methoxy group <sup>a</sup>

Entry	Temperature (°C)	Yield (mmol)			Utilization of methoxy (wt%) <sup>b</sup>
		benzene	<i>o</i> -xylene	<i>p</i> -xylene	
1	160	-	-	-	-
2	180	0.4	0.6	1.3	34.7
3	200	0.8	0.8	1.9	68.9
4	220	0.8	0.8	1.9	94.2
5	240	0.1	0.1	0.2	96.2

<sup>a</sup> Reaction condition: 200 mg DEL, 268 mg LiI, 94 mg LiBF<sub>4</sub>, 10 mg RhCl<sub>3</sub>, 0.6 mg water, 2 mL extra dry toluene, 220 °C, CO 4 MPa, 72 h, the amount of methoxy group in DEL is 32.90 wt%;

<sup>b</sup>; Utilization of methoxy (wt%)=(*n*<sub>4-ethyltoluene</sub>+*n*<sub>*o*-xylene</sub>+*n*<sub>*p*-xylene</sub>-*n*<sub>benzene</sub>)\*31/*m*<sub>methyl group in lignin</sub>.

**Table S4** The effect of RhCl<sub>3</sub> dosage on the utilization of methoxy group <sup>a</sup>

Entry	RhCl <sub>3</sub> (mg)	Yield (mmol)			Utilization of methoxy (wt%) <sup>b</sup>
		benzene	<i>o</i> -xylene	<i>p</i> -xylene	
1	0	0.1	0.1	0.1	6.8
2	5	0.6	0.5	1.0	72.8
3	10	0.8	0.8	1.9	94.2
4	15	0.8	0.7	2.0	97.0

<sup>a</sup> Reaction condition: 200 mg DEL, 268 mg LiI, 94 mg LiBF<sub>4</sub>, 10 mg RhCl<sub>3</sub>, 0.6 mg water, 2 mL extra dry toluene, 220 °C, CO 4 MPa, 72 h, the amount of methoxy group in DEL is 32.90 wt%; <sup>b</sup>; Utilization of methoxy (wt%)=(n<sub>4-ethyltoluene</sub>+n<sub>*o*-xylene</sub>+n<sub>*p*-xylene</sub>-n<sub>benzene</sub>)\*31/m<sub>methyl group in lignin</sub>.

**Table S5** The effect of LiI dosage on the utilization of methoxy group <sup>a</sup>

Entry	LiI (mg)	Yield (mmol)			Utilization of methoxy (wt%) <sup>b</sup>
		benzene	<i>o</i> -xylene	<i>p</i> -xylene	
1	0	4.3	0.2	0.4	-
2	134	1.2	0.6	1.7	54.9
3	268	0.8	0.8	1.9	94.2
4	402	0.8	0.8	2.0	97.0

<sup>a</sup>Reaction condition: 200 mg DEL, 94 mgLiBF<sub>4</sub>, 10 mg RhCl<sub>3</sub>, 0.6 mg water, 2 mL extra dry toluene, 220 °C, CO 4 MPa, 72 h, the amount of methoxy group in DEL is 32.90 wt%; <sup>b</sup> Utilization of methoxy (wt%)=(n<sub>4-ethyltoluene</sub>+n<sub>*o*-xylene</sub>+n<sub>*p*-xylene</sub>-n<sub>benzene</sub>)\*31/m<sub>methyl group in lignin</sub>

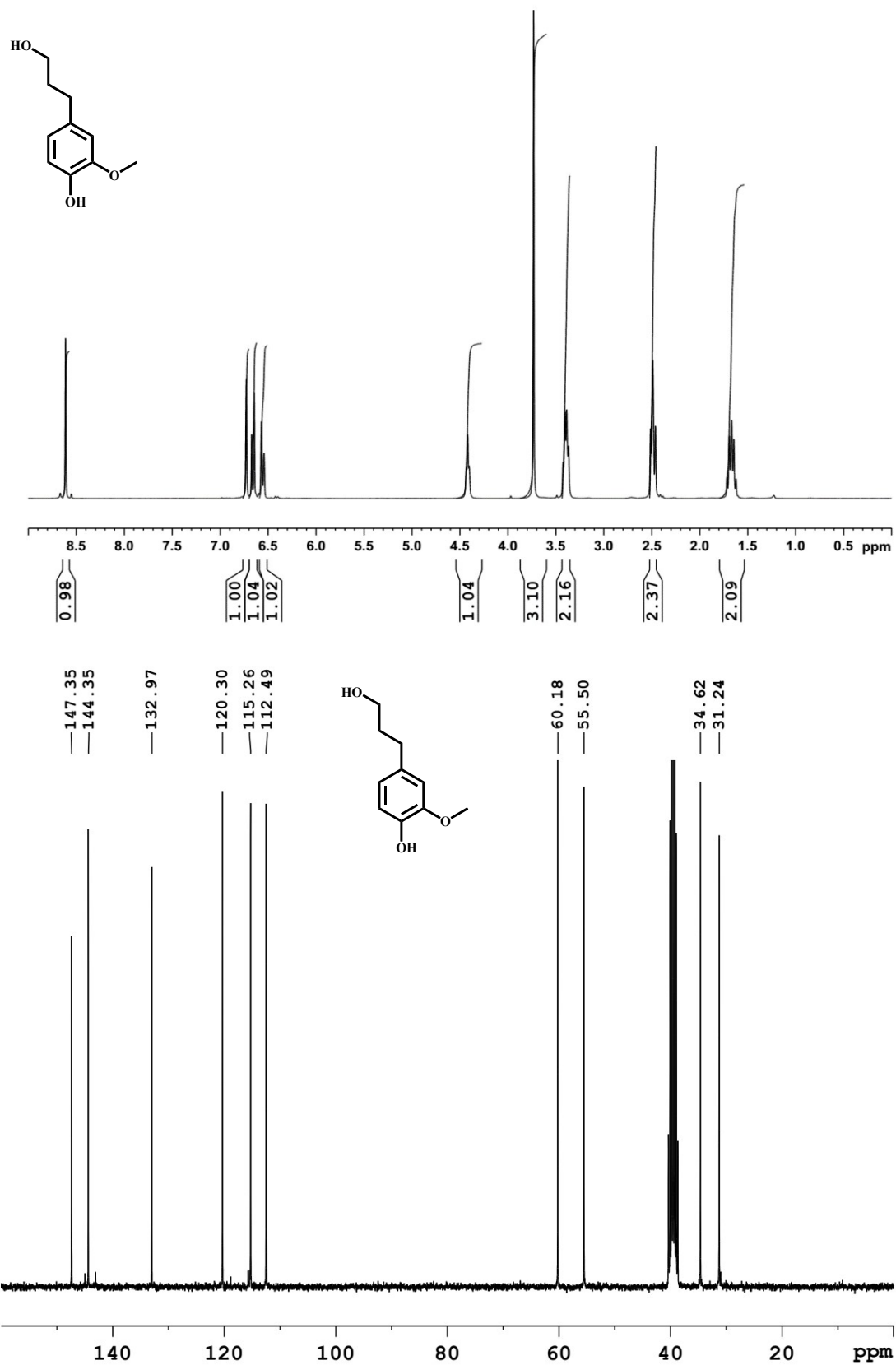


**Table S6** Production of 4-ethyltoluene (ET) and ethylbenzene (EB) from different substrates<sup>a</sup>

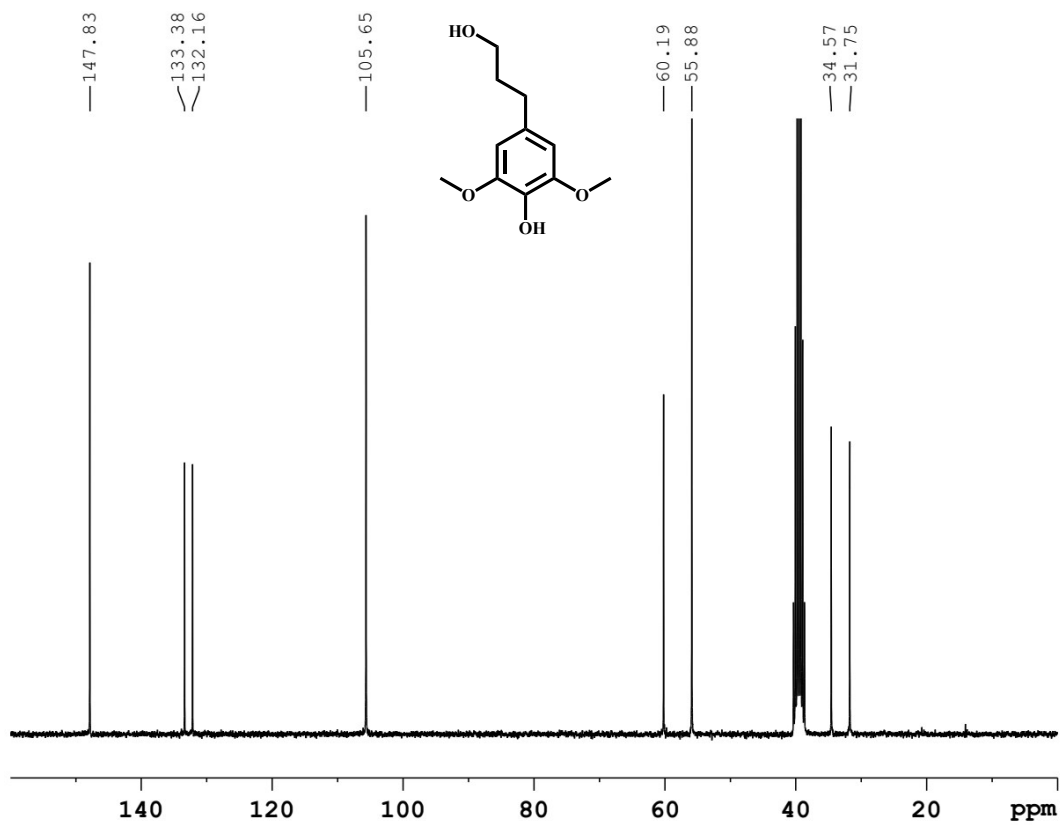
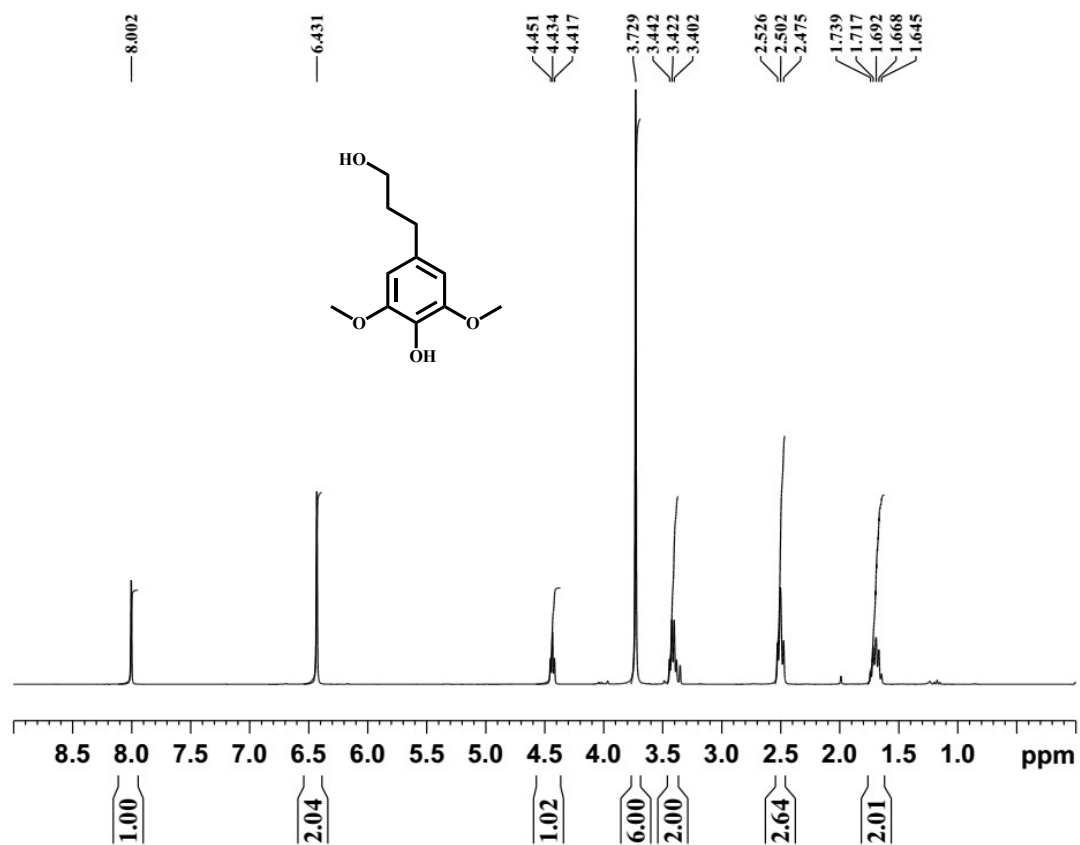
Substrate	Content (wt %)		n(ET): n(EB)	Total content (wt %)
	ET <sup>b</sup>	EB <sup>b</sup>		
DEL	7.2	1.0	7.2:1	8.2
GVL-lignin	9.5	3.6	2.5:1	13.1
PA-lignin <sup>c</sup>	6.5	0.3	21.7:1	6.8
OL	5.0	0.9	5.6:1	5.9
PA-Lignin <sup>d</sup>	4.4	0.6	7.3:1	5.0
Poplar <sup>e</sup>	5.2	2.8	1.9:1	7.9

<sup>a</sup> Reaction Condition: 200 mg substance, 268 mg LiI, 94 mgLiBF<sub>4</sub>, 10 mg RhCl<sub>3</sub>.nH<sub>2</sub>O, 0.6 mg water, 2 mL extra dry toluene, 220 °C, CO 4 MPa, 72 h; <sup>b</sup> EB represent ethylbenzene, ET represent 4-ethyltoluene; <sup>c</sup> PA-lignin was prepared from poplar; <sup>d</sup> PA-lignin was prepared from red birch; <sup>e</sup> The yield of products was based on the weight of lignin in poplar.

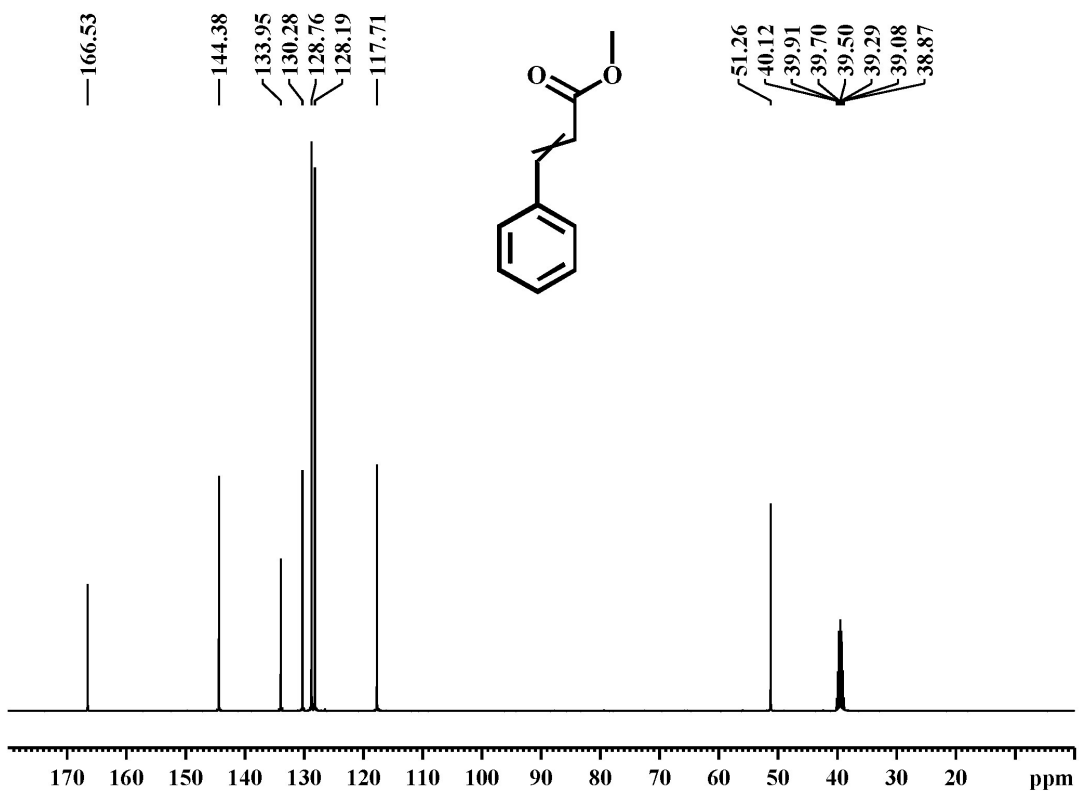
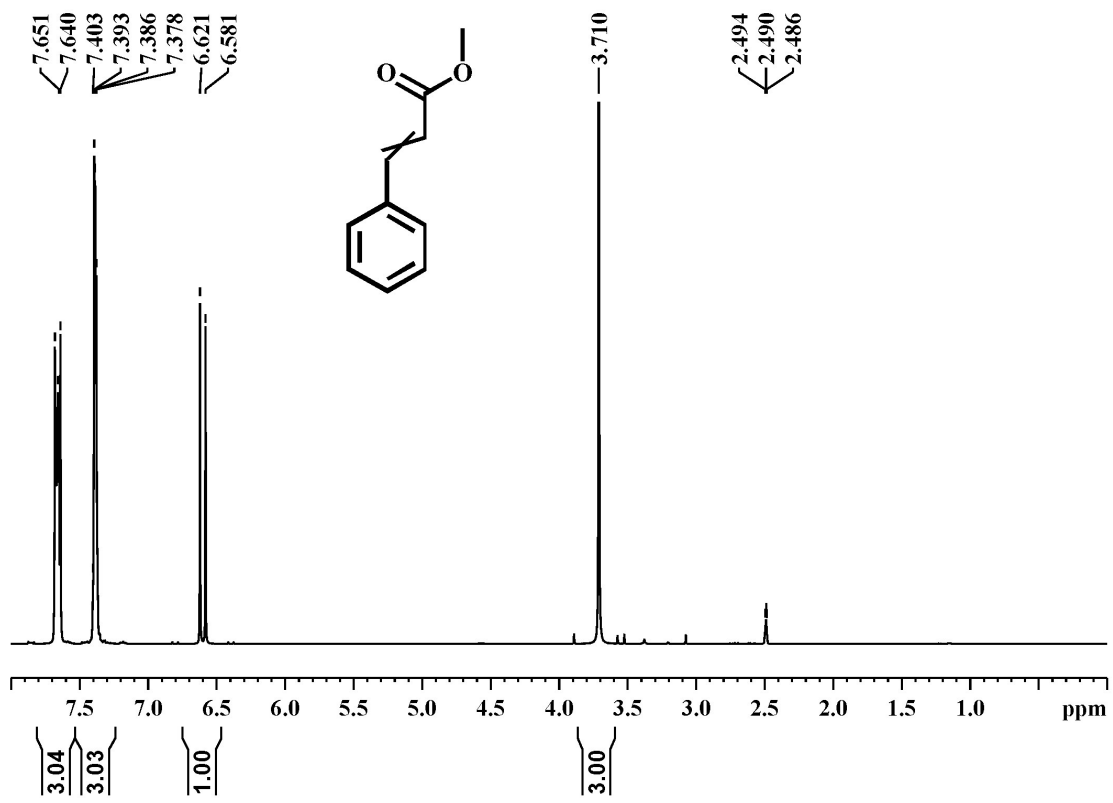
# NMR spectra



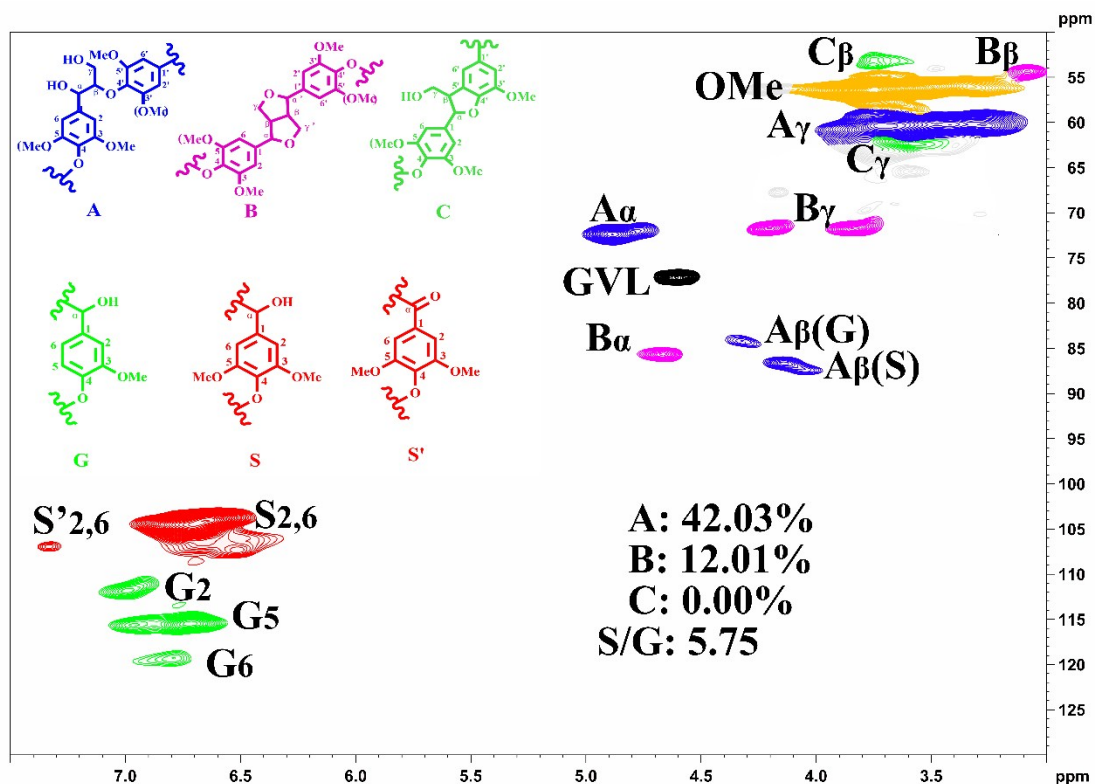
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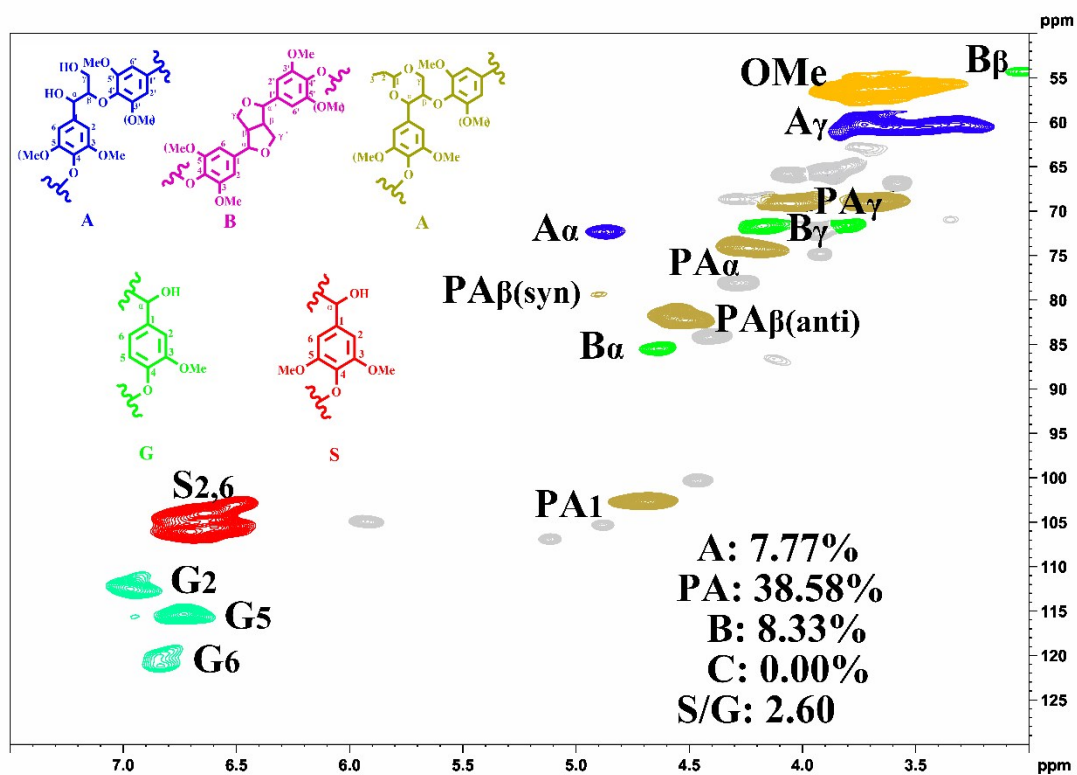
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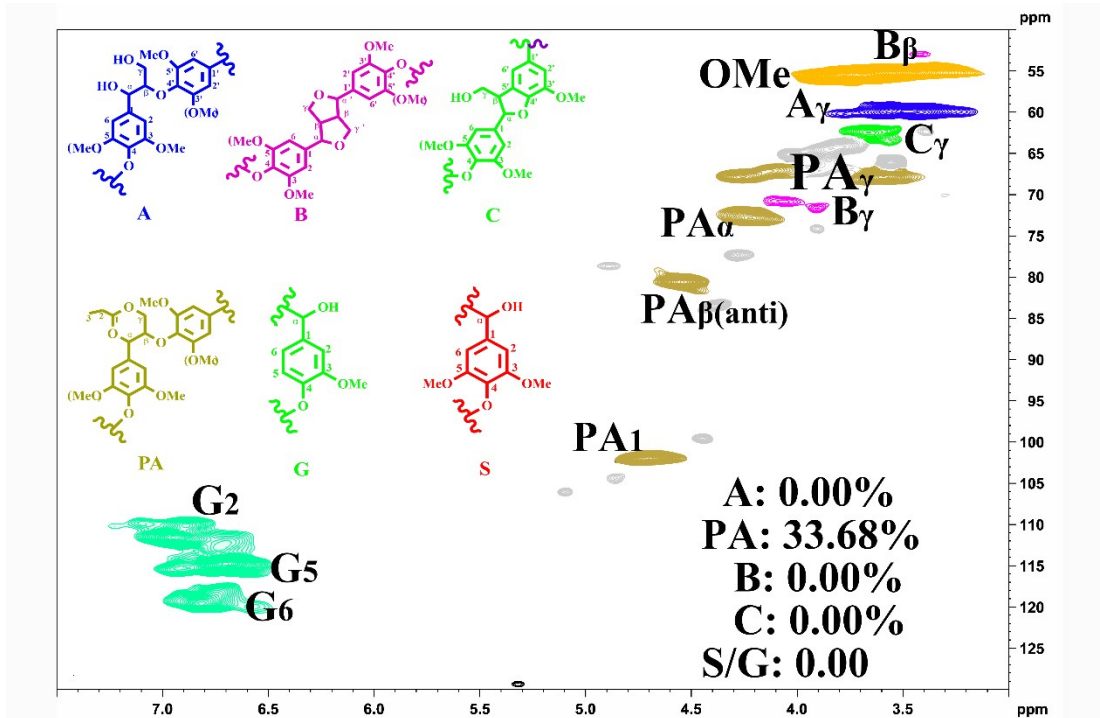
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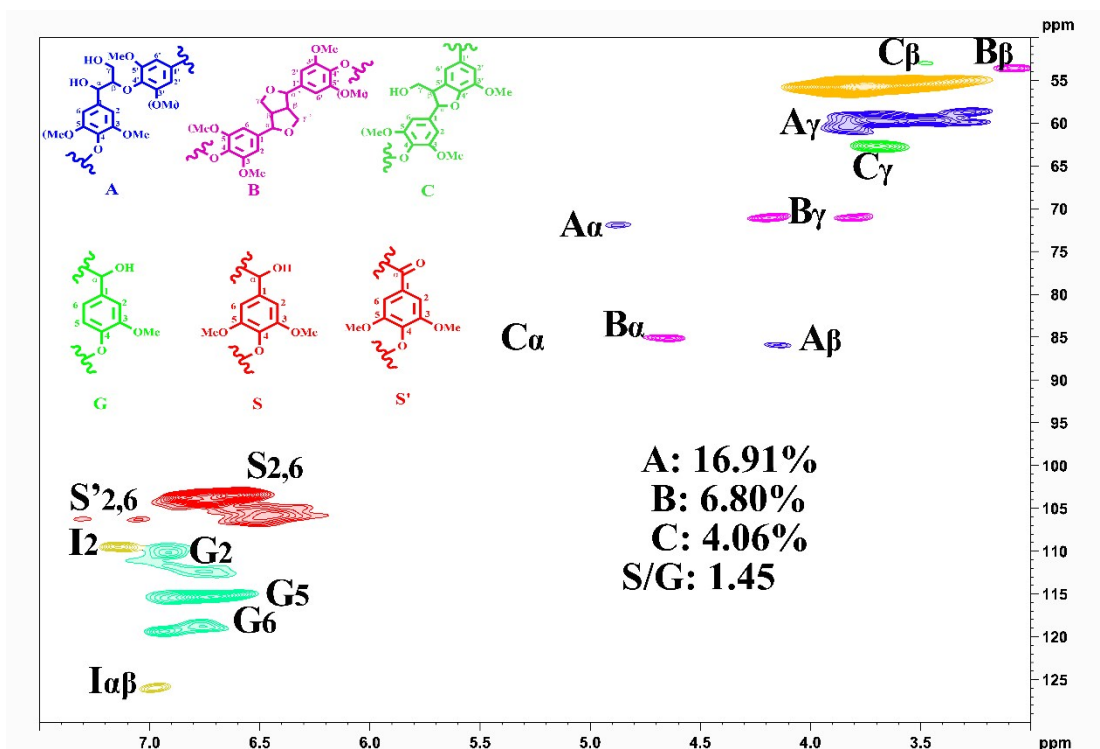
2D-HSQC-NMR spectra of GVL-lignin from Birch in DMSO- $d_6$



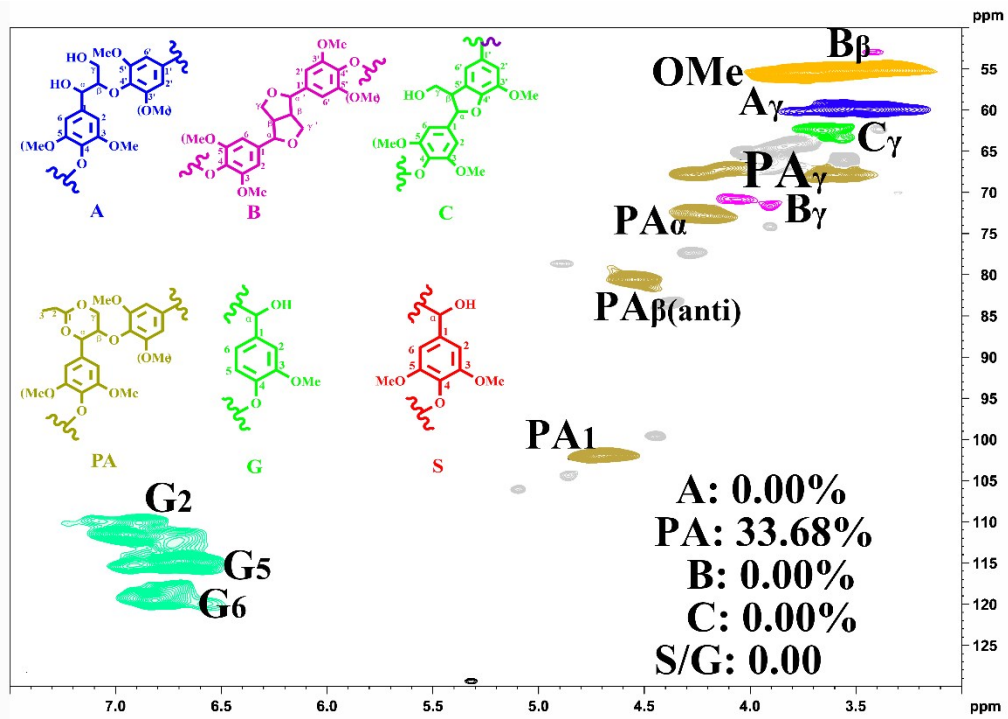
2D-HSQC-NMR spectra of PA-lignin from Birch in DMSO- $d_6$



2D-HSQC-NMR spectra of PA lignin from poplar in DMSO- $d_6$



2D-HSQC-NMR spectra of OL from Eucalyptus in DMSO- $d_6$



2D-HSQC-NMR spectra of PA-lignin from poplar in DMSO- $d_6$

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