Electronic Supplementary Information

Cleavage of Lignin C-O Bonds over a Heterogeneous Rhenium Catalyst through Hydrogen Transfer Reactions

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General

Instruments

All lignin model compounds β-hydroxy ether substrates were prepared as described in the literature.[1] d^5-pyridine, and d^6-DMSO is purchased from Arcos Organics were used without further purification. Elemental analysis of dissolved catalyst was accomplished using a Thermo iCAP Model 6300 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). IR spectra were recorded on an Bruker Equinox 55 spectrometer. The molecular weights of lignin and residues were analyzed with a gel permeation chromatograph (Viscotek TDAmax) in tetrahydrofuran. Acetylation was performed using acetic anhydride and pyridine at room temperature for 48 h. The molecular weights were calibrated using polystyrene standards. NMR spectra were recorded on a Bruker Avance DPX-400 and Bruker AVAVCE III HD 700MHz spectrometer at room temperature, and solvent peak was used as internal reference. The 2D ^{13}C-^{1}H HSQC experiment was acquired using standard Bruker pulse sequence 'hsqcetgpsp 2.2' (phase sensitive gradient –enhanced 2D heteronuclear single quantum coherence (HSQC). The 50 mg lignin was dissolved in 0.5 mL 4:1 d^6-DMSO: d^5-Pyridine. Nitrogen adsorption-desorption measurements were performed at −196 ^oC with a Micromeritics ASAP2010 instrument. Gas chromatography-mass spectroscopy (GC-MS) was performed on Varian 450GC-320 MS with FID detector and HP-5 capillary column. Catalytic runs were monitored by Agilent 7890 with HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) using mesitylene as internal standard and the gases were collected and analyzed by GC-TCD. Temperature programmed reduction of hydrogen (H_2-TPR-MS) were conducted on a MicromeriticsAutoChem II 2920 chemisorber. The results were recorded by Mass spectrum. In TPR measurement, the samples were pretreated in Ar for 1h to remove adsorbed water, and then cooled to -80 ^oC, until baseline is stable, the gas flow was switched to 10% H_2/Ar and the sample was heated from room temperature to 900 ^oC with a temperature ramp of 10 ^oC/min. The amount of H_2 consumption was monitored by a thermal conductivity detector (TCD), while a cold trap (a mixture of isopropanol and liquid nitrogen) was placed to remove generated water.

Matrix assisted Laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) was carried out to check the oil molecular weight distribution in absciex TOF-5800. A 15 g/L solution of DHB (2,5-dihydroxylbenzoic acid) in methanol was used as matrix. The analyses were developed in negative mode. X-ray absorption fine structure (XAFS) spectra at Re L_3-edge were recorded at the 14W beamline of Shanghai Synchrotron Radiation Facility (SSRF) in China. The beam line employs a double Si (111)-crystal monochromator for energy selection with a resolution better than 2×10^{-4}. The catalyst was transferred to glove box without exposure to air before measurement. Re powder, commercial ReO_2, Re_2O_7 and NH_4ReO_4 were used as reference samples. The collected data were processed by Athena software package.

Catalyst preparation

The MO_x/AC (AC, NORIT, M = Re, W, V, Mo) catalysts were prepared by impregnating the AC with an aqueous solution of NH_4ReO_4, $(NH_4)_6H_2W_{12}O_{40} \cdot H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and NH_4VO_3. After drying at 110 ^oC for 12h, the MO_x/AC was calcined in nitrogen at 500 ^oC for 3 h. The loading amount Re, W, Mo and V was 1.18%, 0.72%, 0.63%, 0.40%, respectively, which is determined by ICP-AES.

Activity test

Lignin extraction procedure: All the lignin samples were prepared using a procedure previously described in the literature.[2] The poplar and wheat straw (20 mesh) were extracted with toluene-methanol (2:1) at 110 °C for 5 h in a Soxhlet apparatus before treatment. The extracted free powder (10 g) was transferred to a 400 mL stirred reactor and refluxed at 100 °C for 2 h, during which time the hemicellulose hydrolysis was catalyzed by 1.0 N H_2SO_4. The reaction mixture after hydrolysis was vacuum-filtered to obtain a solid residue and a filtrate containing the acid-soluble lignin and sugars. The lignin fraction in the filtrate was precipitated at pH 1.5 over 24 h at 20 °C, then filtered, washed with pH 2.0 H_2SO_4 solvent and air dried. The residue was delignified with ethanol-water (60/40, v/v) in 400 mL 1.0 N H_2SO_4 at 75 °C for another 2 h. After filtration, the filtrate was evaporated at 40 °C in a rotary vacuum evaporator to remove ethanol, the lignin from the black liquor was precipitated at pH 1.5 over 24 h at 20 °C, filtered, washed with water and air dried, obtaining 0.5 g organosolv poplar lignin (5 wt% based on woody powder), and 0.4 g organosolv wheat lignin (4 wt% based on woody powder).

General procedure for ReO_x/AC catalyzed lignin model compounds: The catalytic reaction was performed in a Parr autoclave (Parr, 75 mL). Typically, the model compound (0.41 mmol), catalyst (1.6 mol% Re), the standard mesitylene (18 mg) and isopropanol (15 mL) were placed to the autoclave (Parr, 75 mL) and flushed by N_2 for several times. The reaction vessel was conducted at 200 °C with 100 psi N_2 and stirred (800 rpm) for 3 h. After reaction, the gases were collected and the liquid phase was analyzed by gas chromatography with a flame ionization detector (GC-FID) employing the mesitylene as an internal standard (HP-5 column, 30 m × 0.32 mm × 0.25 μm). For recycling experiment, after reaction, the solution was filtrated, then the catalyst was dried at 60 ^{o}C within 5 h for next use.

Quantify the mass of lignin oil after reaction: The catalytic conversion of lignin material was carried out in a stainless-steel autoclave (Parr, 75 mL) with an initial N_2 pressure of 100 psi and 200 ^{o}C for 8 h. Typically, lignin (100 mg), ReO_x/AC (1.6 mol% Re), and isopropanol (15 mL) were charged in the autoclave and stirred at rate of 800 rpm. After reaction, the reaction mixture was cooled to room temperature and was filtered. The gases were collected in a gas bag. The solid residue was washed with isopropanol and was dried at 50 ^{o}C under vacuum for 2D-HSQC-NMR characterization. The liquid was vacuumed at 30 °C to afford a liquid oil. Noting that lignin does not dissolve in ethyl acetate, ethyl acetate was added (3×15 mL) in the oil to extract the low molecular aromatic products. The extraction liquid was collected, then evaporated at 30 °C to remove solvent, affording a 54.0% yield of oil products from organosolv poplar lignin (OPL) and a 50.2% yield from organosolv wheat lignin (OWL). The liquid oil was then diluted to 2 mL with isopropanol, the monomer products in liquid oil were analyzed by HP 5973 GC–MS (HP-5 column, 30 m × 0.32 mm × 0.25 μm) and quantified by GC-FID using an internal standard method (standard: mesitylene). The molecular weight distribution of the liquid oil was analyzed by Matrix assisted laser desorption/ionization time-of-flight mass spectrometry.

For recycling experiment of catalytic OPL reaction: after reaction, the solution was filtrated. The organic solution was evaporated at 35 ^{o}C to remove isopropanol. And the solid including the catalyst and residue was dried for next use. The fresh OPL and isopropanol was directly added into the autoclave for next recycle. The quantify and qualitative of the oil products was determined by above mentioned method.

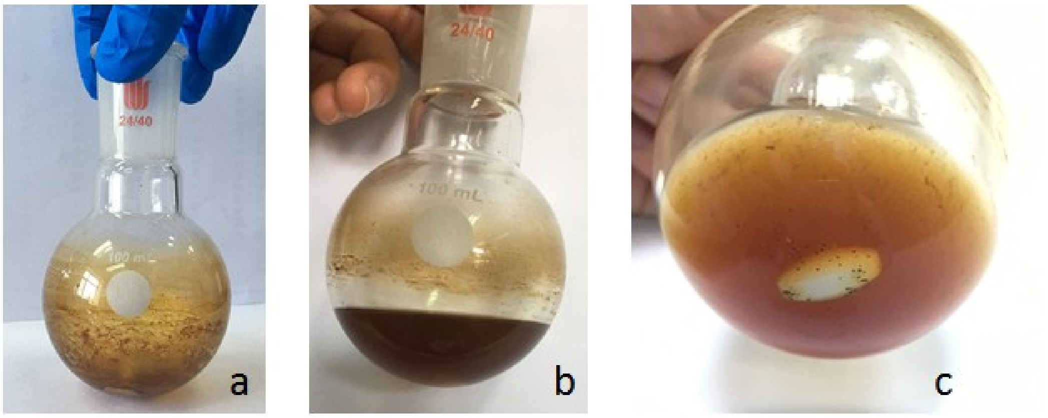


Figure S1 (a) the oil products after evaporation of the solvent; (b) after adding the ethyl acetate; (c) lignin precipitate in the ethyl acetate solution.

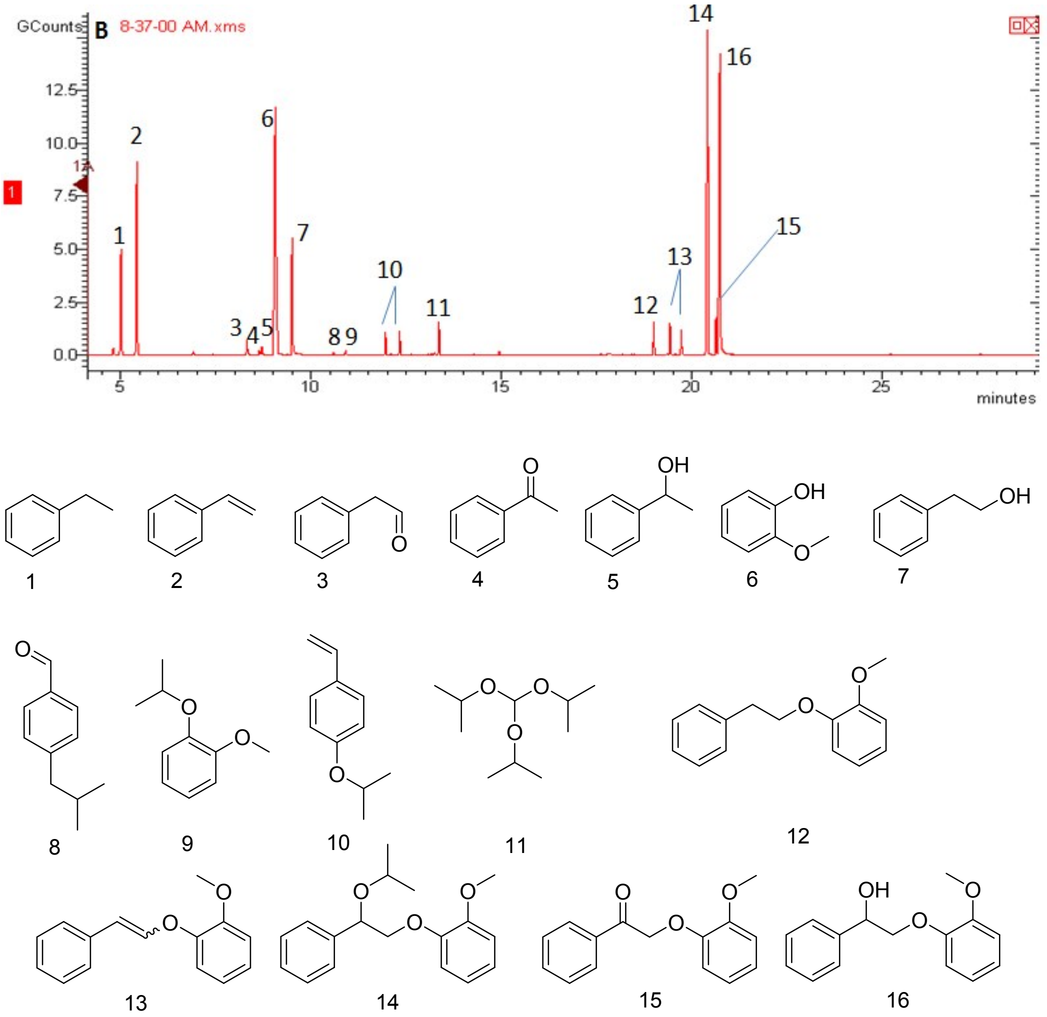
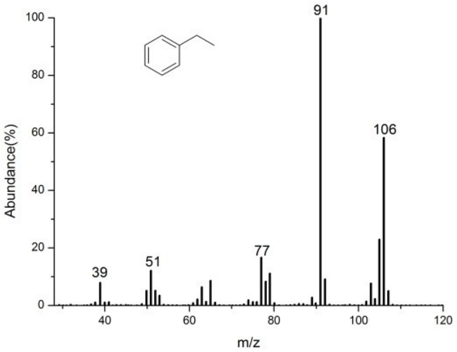
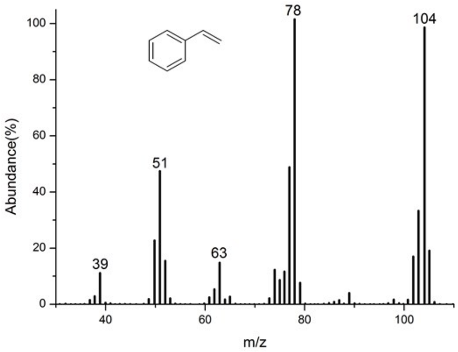
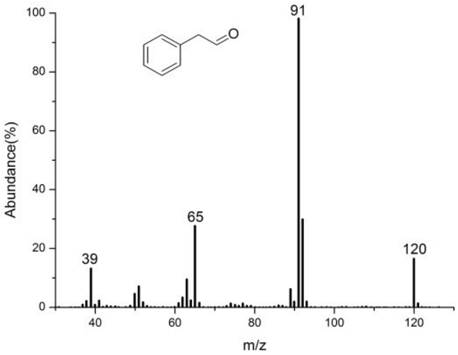


Figure S2 GC-MS spectrum and identification of compounds of the reaction mixture for the conversion of model compound **1** catalyzed by active carbon.



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65
39
120
Abundance(%)
m/z
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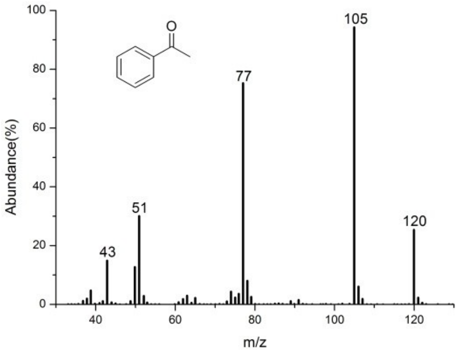
40
60
80
100
120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m/z
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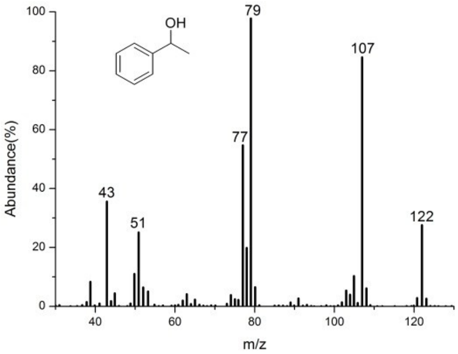
60
80
100
120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77
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Abundance(%)
m/z
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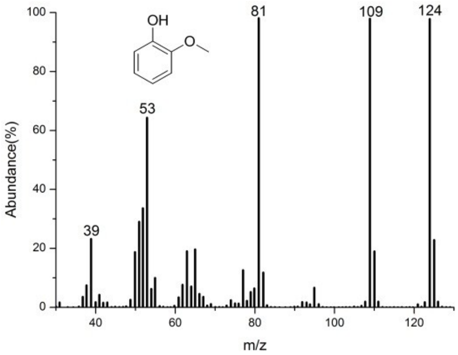
80
100
120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Abundance(%)
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60
80
100
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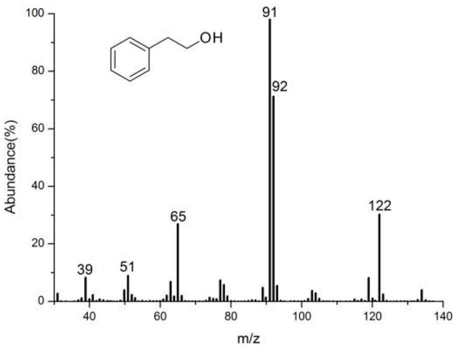
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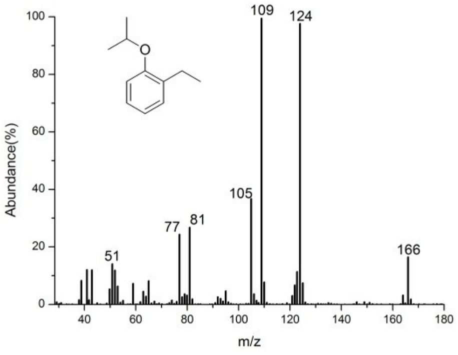
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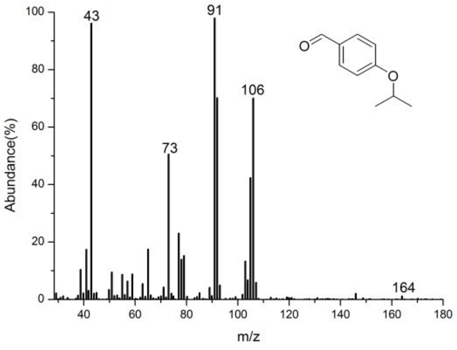
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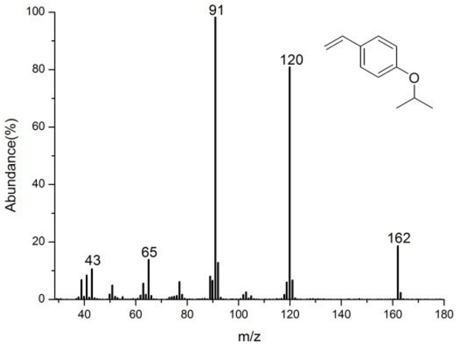
120
140
160
180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Abundance(%)
m/z
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40
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120
140
160
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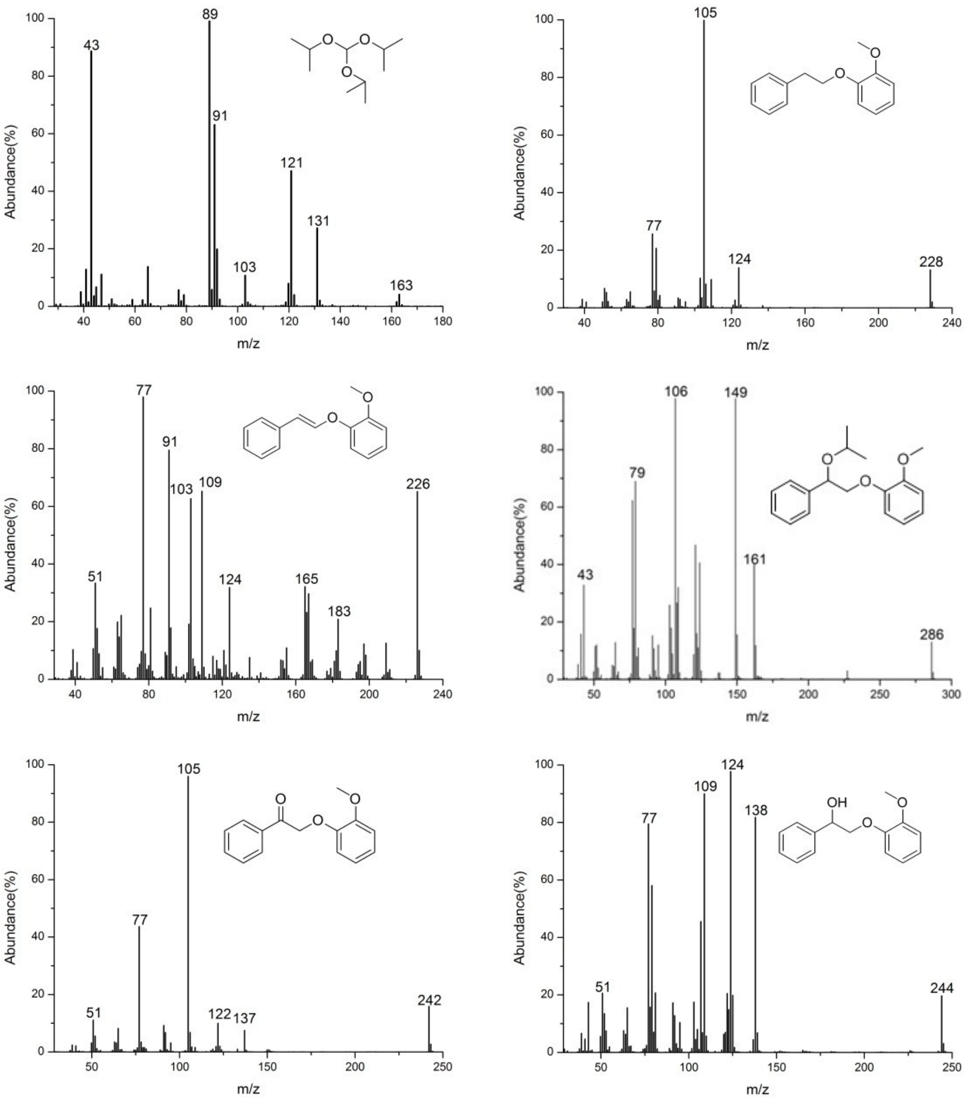


Figure S3. GC-MS spectra of various products

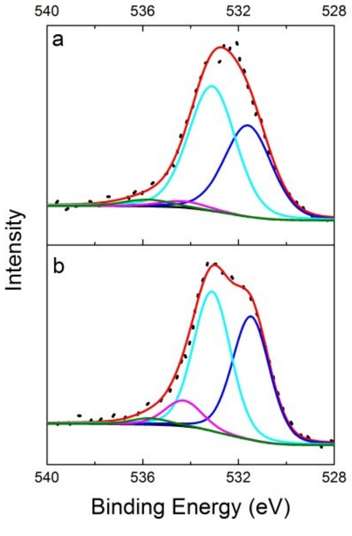


Figure S4 XPS patterns of O1S for the active carbon (a: fresh carbon, b: carbon after boiling with HNO_3 (activate carbon-AC))。

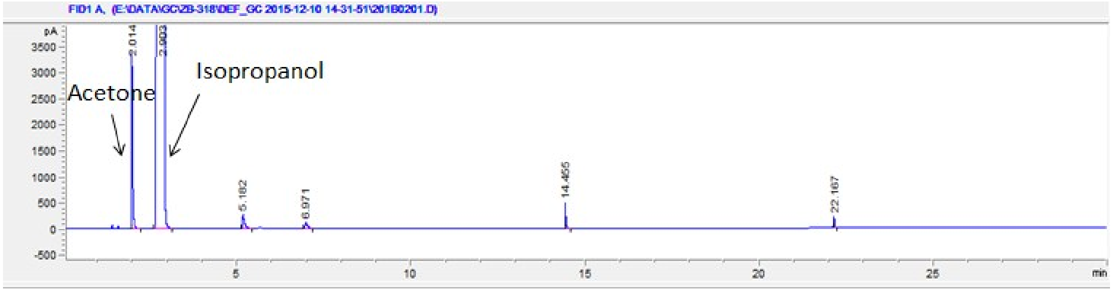


Figure S5. Acetone detected by GC-FID.

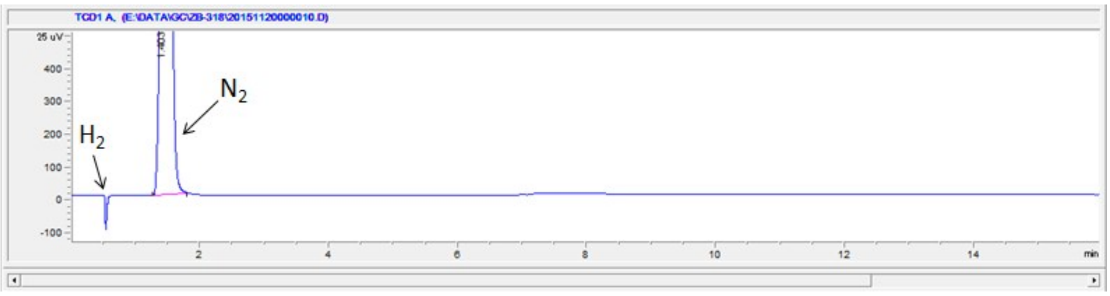


Figure S6. Gases analyzed by GC-TCD.

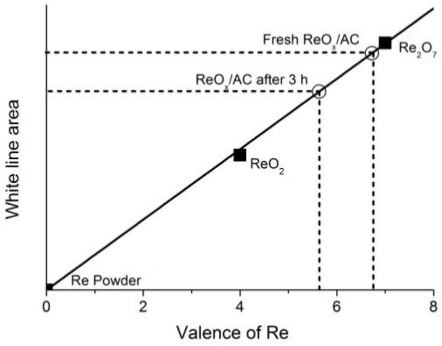
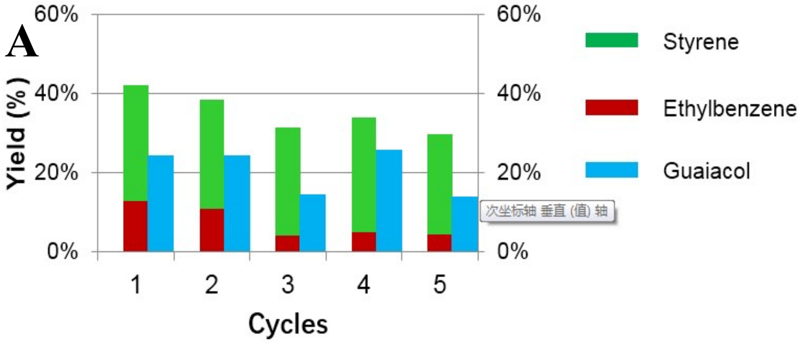


Figure S7 Relation between white line area and valence of Re



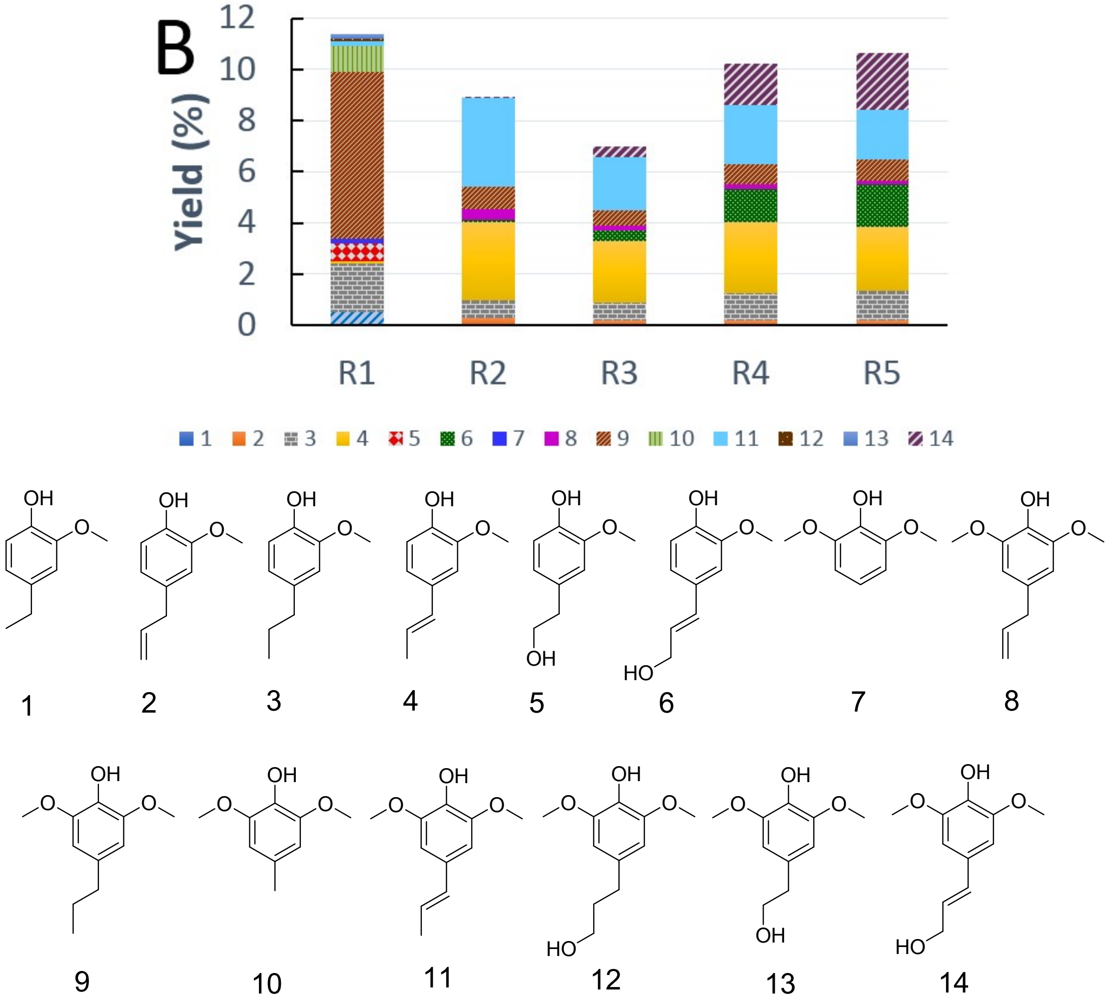


Figure S8. (A) Recycling test in the conversion of lignin model compound **1** over ReO_x/AC. Condition: 2-(2-methoxyphenoxy)-1-phenylethanol (100 mg), ReO_x/AC (1.18 wt% Re, 1.58 mol% Re), ^{i}PrOH (15 mL) and mesitylene (18 mg) were charged in a stainless-steel autoclave (Parr, 75 mL) with an initial N_2 pressure of 100 psi at 160 ^{o}C for 3 h; (B) Recycling test in the depolymerization of organsolv poplar lignin (OPL) over ReO_x/AC. Condition: OPL = 100 mg, ReO_x/AC (1.18 wt% Re, 1.6 mol% Re), ^{i}PrOH (15 mL) were charged in a stainless-steel autoclave (Parr, 75 mL) with an initial N_2 pressure of 100 psi at 100 ^{o}C for 8 h.

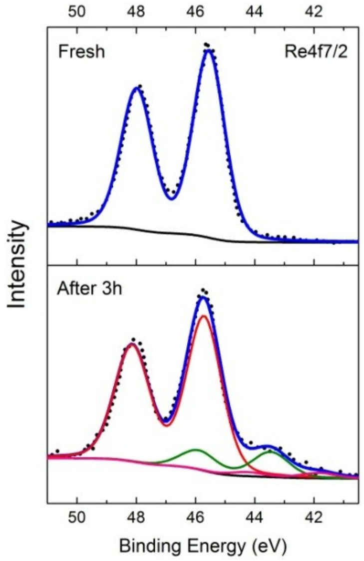
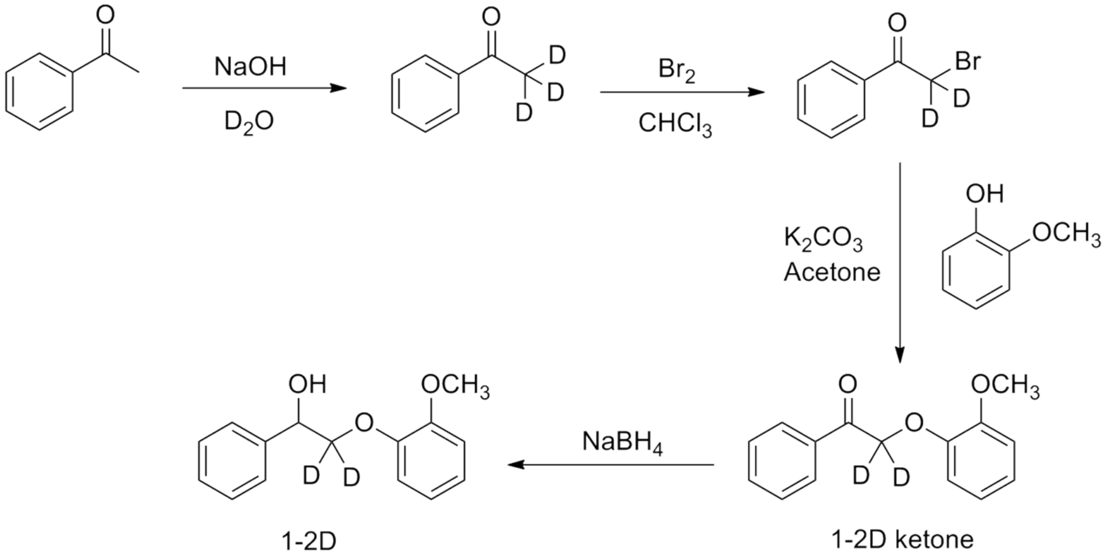


Figure S9 XPS patterns of Re4f for the catalyst before and after reaction in air.

Isotopic labeling

Synthesis of deuterium labeling of 2-(2-methoxyphenoxy)-1-phenylethanol (1-2D)

The synthesis of deuteium labeling of 2-(2-methoxyphenoxy)-1-phenylethanol was done in analogy to a method reported literatures.[1,3]



Scheme S1. Synthesis pathway of 2-(2-methoxyphenoxy)-1-phenylethanol (1-2D)

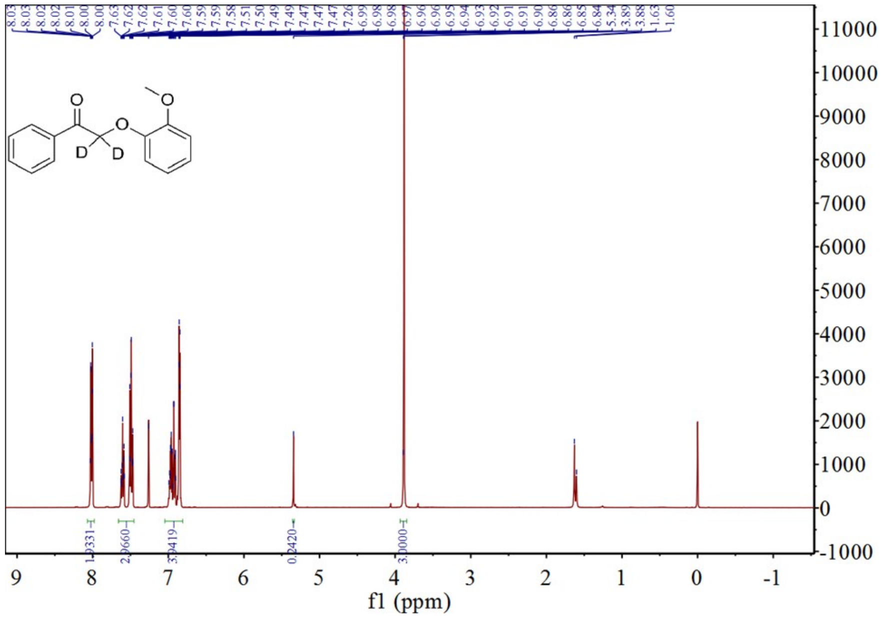


Figure S10 NMR spectra of 1-2D ketone

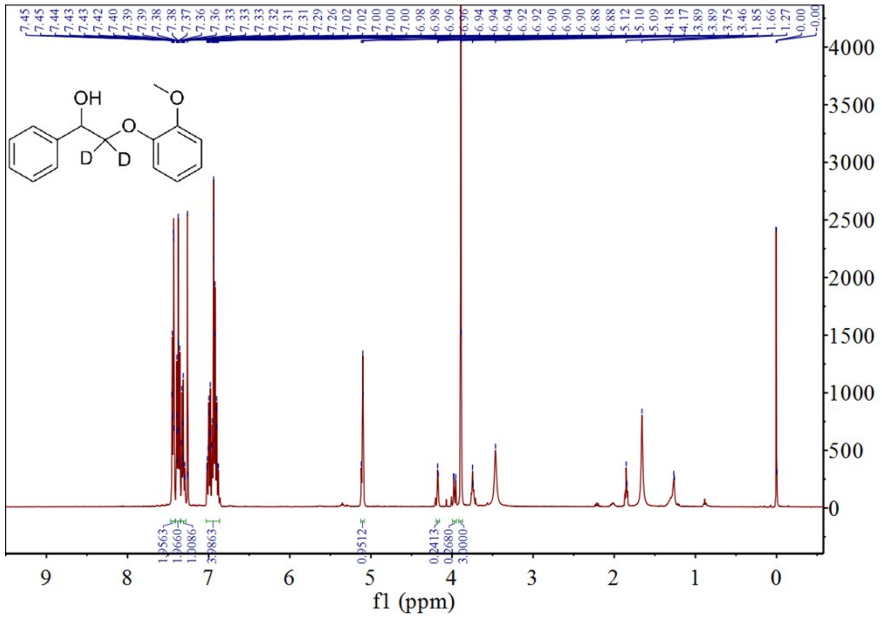
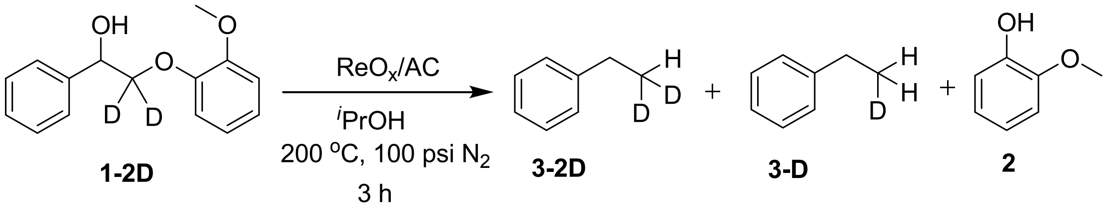


Figure S11 NMR spectra of **1-2D**

Conversion of deuterium labeling of 2-(2-methoxyphenoxy)-1-phenylethanol (1-2D)



Scheme S2. Conversion of **1-2D** over ReO$_x$/AC in dry ^{i}PrOH at 200 ^{o}C for 3 h

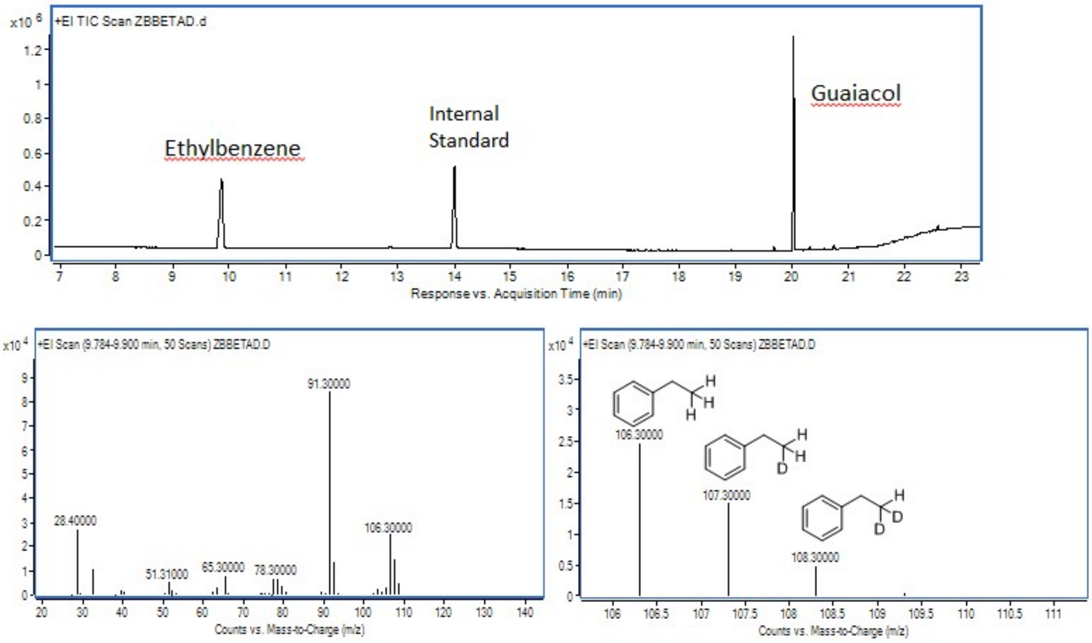


Figure S12 MS spectra of **1-2D** reaction solution.

The labeling substrate **1** PhCHOHCD$_2$OPhOCH$_3$ we used in the labeling experiment is 75%D according to the NMR results (Figure S6.2). The labeling D on the C2 position is somewhat sensitive to moisture, and D is easily exchanged by H when meeting H$_2$O. MS spectrum showed that ethylbenzene was the major product. This is because that one part of ethylbenzene was produced from 25% unlabeled substrate, and other ethylbenzene was from PhCH$_2$CH$_2$D and PHCH$_2$CHD$_2$ that exchanged by H due to the presence of water from dehydration reaction. Nevertheless, the isotopically-labeling experiment proved that both dehydration and hydrogenolysis occurred owing to the formation of dehydration product **3-D** and hydrogenolysis product **3-2D**.

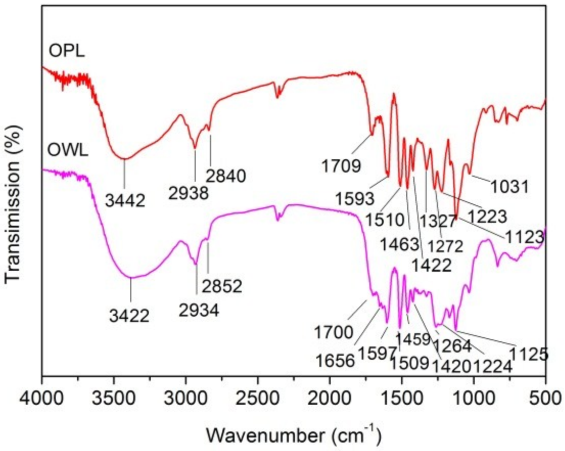


Figure S13 FTIR spectra of OPL and OWL

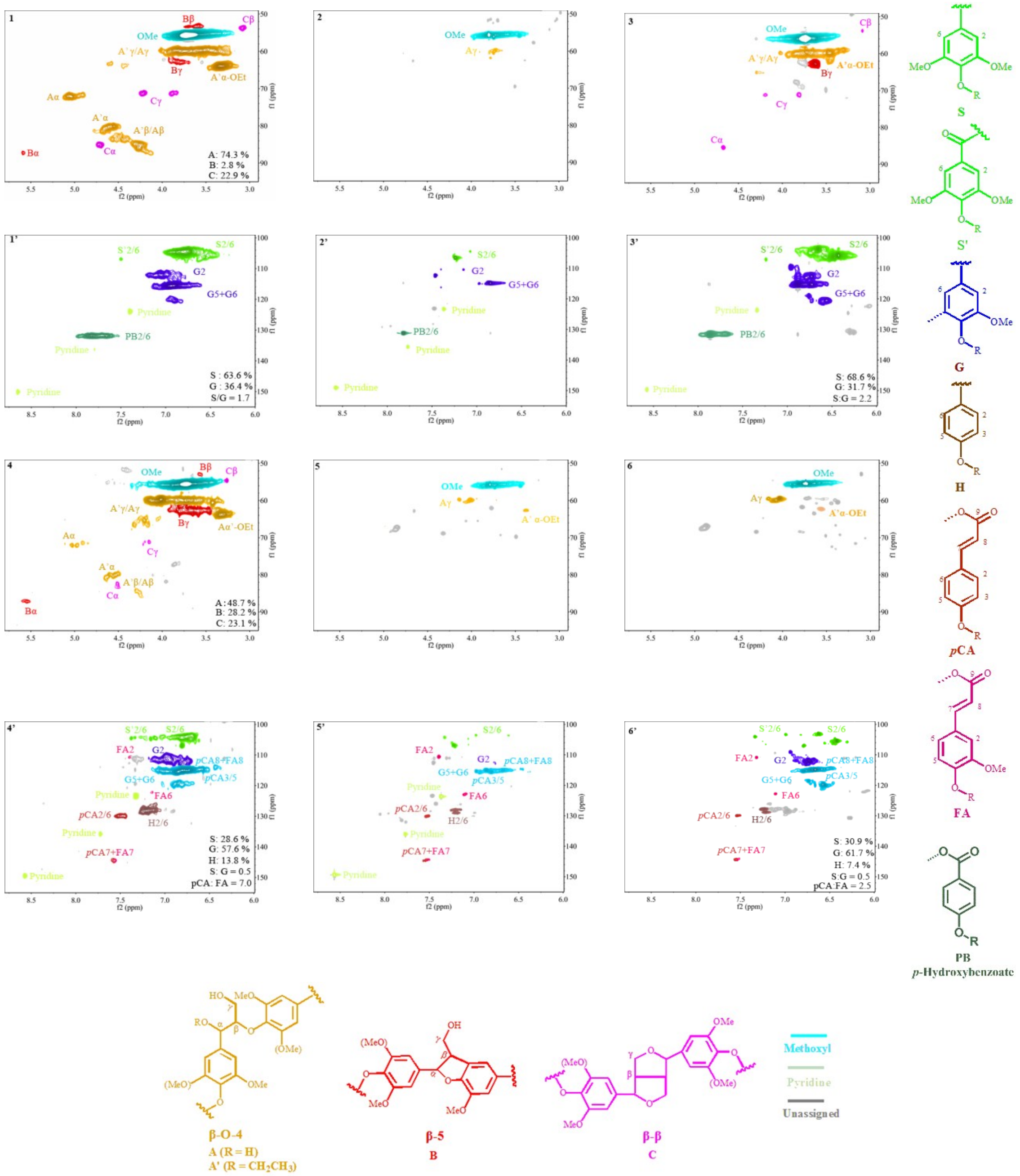
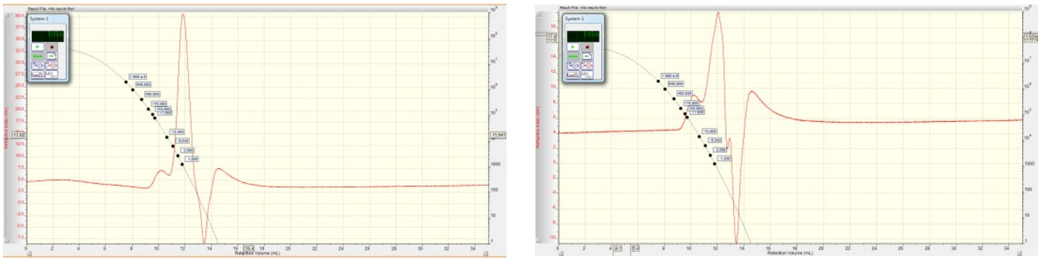
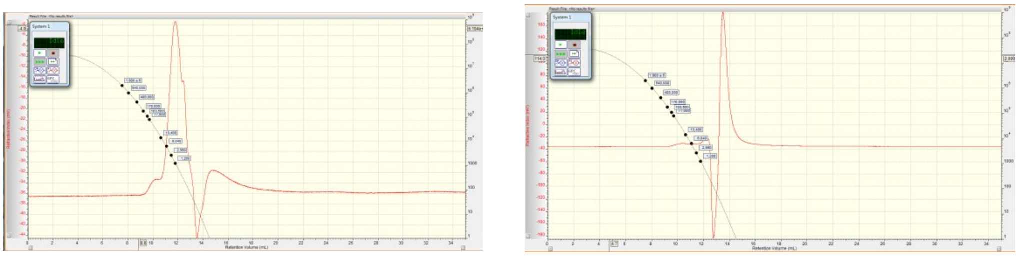


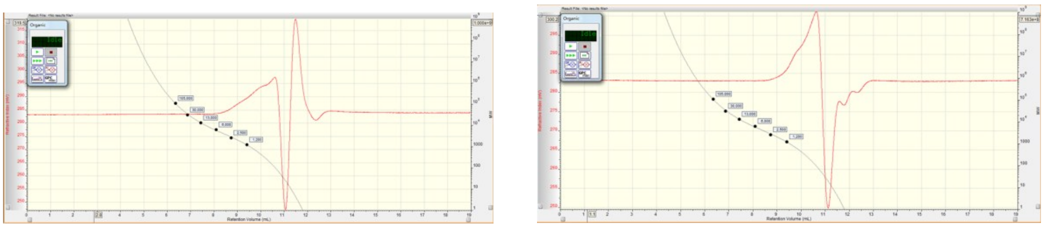
Figure S14 2D-HSQC-NMR spectra of various lignin. (**1 and 1'**) isolated organosolv poplar lignin (OPL); (**2 and 2'**) the residue after catalytic OPL reaction; (**3 and 3'**) the oil production after catalytic OPL reaction; (**4 and 4**') isolated organosolv wheat straw lignin (OWL); (**5 and 5'**) the residue after catalytic OWL reaction; (**6 and 6'**) the oil production after catalytic OWL reaction. **1**-**5** are dissolved in 4:1 DMSO-d^6:pyridine-d^5; and **6** are dissolved in DMSO-d^6.



OPL OPL-Residue



OWL OWL-Residue



OPL Oil Wheat Oil

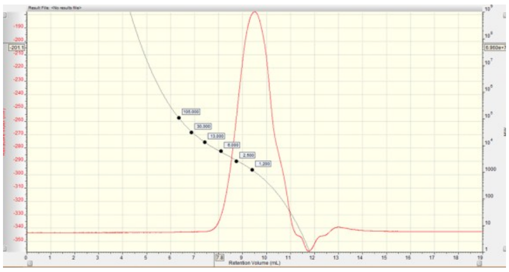


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Figure 15 GPC spectra of lignin and lignin oil

To look insight into the change of the structure before and after reaction, measuring the volume integrals of various cross peaks in 2D HSQC NMR spectra were performed according to reported literatures methods.[4] Volume integration (linkages/100 C9 units) allows for estimation of the differences in interunit linkage composition. It suggested that the signals of substructure **A** and **B** were obvious vanished for OPL and OWL oils. The **C** linkage remained for OPL oil. We therefore speculated that **B** and **C** likely did not give rise to monomers directly during this catalytic process although their signals obviously decreased after reaction, probably due to the change or modification of the structure in such a complicated process. The different conversion performance of the two lignins (OPL, OWL) could attribute to the structural variations of the different biomass resources.

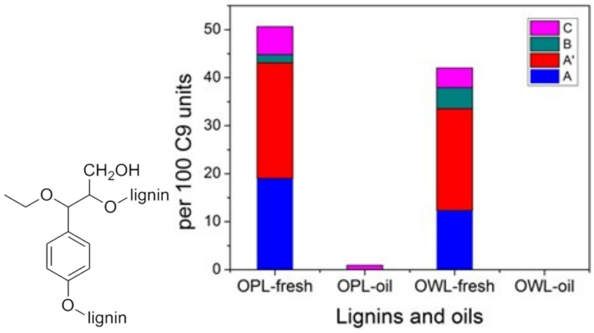


Figure S16 (left) **A'** structure-nucleophilic addition of ethanol, (right) **A**, **B** and **C** linkages per 100 C9 units in various lignins and oils.

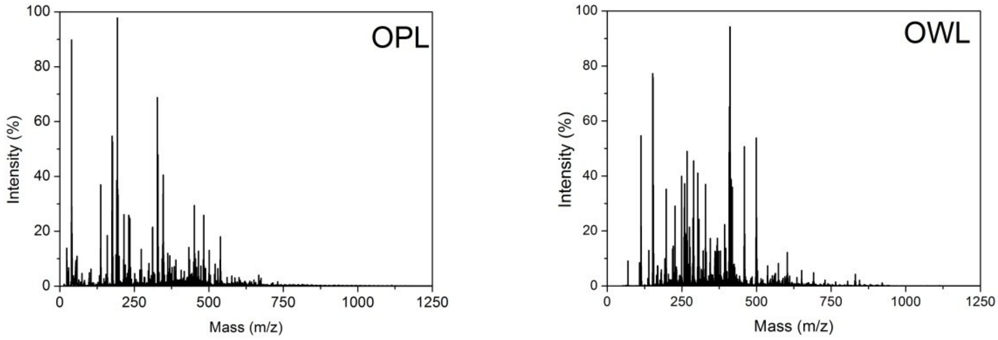
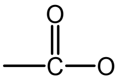


Figure S17 Expanded MALDI-TOF oil analyses of OPL and OWL.

Table S1. The assignment of the XPS peaks shown in **Figure S4**

Element	Peak assignment	C		AC	
		Binding energy (eV)	Content (%)	Binding energy (eV)	Content (%)
O 1s	C=O (quinones)	531.6	39.9	531.5	41.9
	C-O (phenols)	533.1	54.5	533.1	47.3
		534.3	2.7	534.3	8.7
	Adsorbed H_2O	535.8	2.9	535.7	2.1

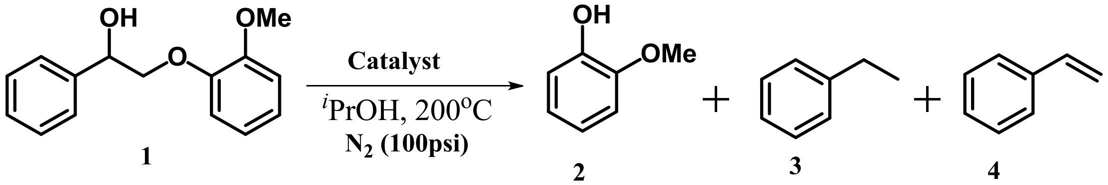


Table S2 Cleavage of C-O bonds in lignin model compound **1** over various catalysts.[a]

Entry	Cat.	Conv. [%][b]	Yield [%][b]			
			2	**3**	**4**	**3+4**
1	NH_4ReO_4	4.4	--	2.2	1.9	4.1
2	Re_2O_7	10.2	0	3.0	1.9	4.9
3	Re_2O_7+AC	45.7	33.3	20.6	8.8	29.4

[a] Reaction condition: compound **1** (100 mg, 0.41 mmol), 1.6 Re mol %, ^{i}PrOH = 15mL, T = 200 °C, t = 3h, P= 100 psi(N_2), AC = activate carbon.

[b] Conversion and yields were determined by GC-FID with mesitylene as an internal standard.

Table S3. Cleavage of C-O bond in compound **1** over various rhenium oxide[a]

Entry	Cat.	Conv. [%][b]	Yield [%][b]			
			2	**3**	**4**	**3+4**
1	NH_4ReO_4	4.4	0	2.2	1.9	4.1
2	Re_2O_7	10.2	0	3.0	1.9	4.9
3	$N(Bu)_4ReO_4$	--	--	--	--	-
4	ReO_3	--	--	--	--	--
5	ReO_2	--	--	--	--	--

[a] Reaction condition: compound 1 (100 mg), 1.58 Re mol %, ^{i}PrOH = 15 mL, T = 200 °C, t = 3 h, P = 100 psi (N_2).

Table S4 The assignment of the XPS peaks shown in **Figure 1** in the article.

Entry	Species	BE [eV]	Content [%]
1	$Re^{VI\text{-}VII}$	45.8	35.4
2	Re^{V}	43.5	46.7
3	Re^{III}	41.8	10.7
4	Re^{II}	41.0	7.2

Table S5 The assignment of the XPS peaks shown in **Figure S9**.

Entry	Species	BE [eV]	Content [%]
1	$Re^{VI\text{-}VII}$	45.8	82.3
2	Re^{V}	43.6	13.1
3	$Re^{0\text{-}IV}$	41.8	4.5

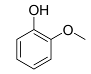
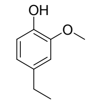
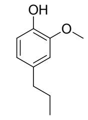
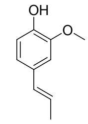
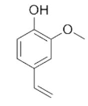
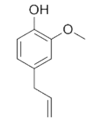
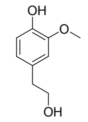
Table S6 Band assignment of FTIR spectra

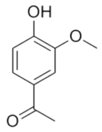
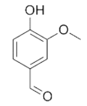
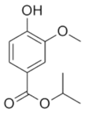
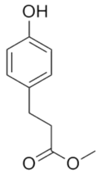
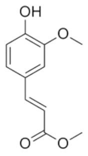
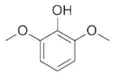
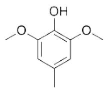
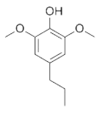
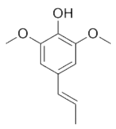
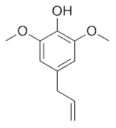
OPL	OWL	Band Assignment
3442	3422	O-H Stretching
2938	2934	C-H stretch in methyl and methylene groups
2840	2852	C-H stretch in methyl and methylene groups
1709	1700	C=O stretch in unconj. Ketones, carbonyl and ester groups
	1656	C=O stretch in conjugated p-subst. aryl ketones
1593	1597	Aromatic skeletal vibration (S>G) plus C=O stretching
1510	1509	Aromatic skeletal vibrations (G>S)
1463	1459	C-H asymmetric deformations in methyl and methylene groups
1422	1420	Aromatic skeletal vibrations combined with C-H in plane deformations
1327	1329	S ring breathing + G ring substituted in position 5
1272	1264	G ring breathing and C=O stretching
1223	1224	C-C plus C-O plus C=O stretching
1123	1125	Syringyl ring breathing
1031	1032	Aromatic C-H in-plane deformations in G units plus C-O deformations in primary alcohols
916		Aromatic C-H out of plane deformation

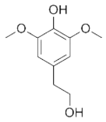
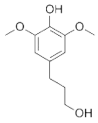
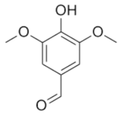
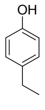
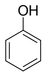
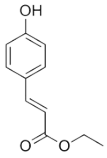
Table S7 GPC analysis of acetylated lignin and corresponding residue after catalytic reaction.

	Lignin	M_w	M_n	M_w/M_n
1	OPL	1707	847	2.02
2	OPL-Residue	897	629	1.35
3	OPL-Oil	710	264	2.69
4	OWL	2403	1083	2.22
5	OWL-Residue	897	629	1.43
6	OWL-Oil	618	249	2.48

Table S8 Identification and quantification of products obtained from the depolymerization of OPL and OWL.[a]

Monomer name	Structural formula	Unit type	Yield [wt%][b]				
			Blank-OPL[c]	OPL(AC)[d]	OPL	OWL(AC)[d]	OWL
Guaiacol		G	--	--	--	--	0.1
Guaiacylethane		G	--	--	0.5	0.1	0.6
Guaiacylpropane		G	0.1	0.1	1.9	--	0.8
Guaiacylpropene		G	0.2	0.2	0.1	0.1	0.5
p-Vinylguaiacol		G	--	--	--	--	0.1
5-allylguaiacol		G	0.2	0.1	--	--	--
Guaiacylethanol		G	--	--	0.7	--	0.3

Acetoguaiacone		G	0.2	--	--	--	--
p-Vanillin		G	0.4	--	--	--	--
isopropyl 4-hydroxy-3-methoxybenzoate		G	0.2	--	--	--	--
methyl 3-(4-hydroxyphenyl)propanoate		H	--	--	--	0.2	0.4
methyl 3-(4-hydroxy-3-methoxyphenyl)acrylate		G	--	--	--	0.4	0.5
2,6-Dimethylphenol		S	--	--	0.2	--	--
4-Methylsyringol		S	--	--	1.0	--	--
4-Propylsyringol		S	--	2.0	6.5	0.2	1.1
4-Allylsringol		S	0.1	--	0.2	0.2	0.3
2,6-Dimethoxy-4-allylphenol		S	0.5	0.2	--	--	--

4-(2-hydroxyethyl)-2,6-dimethoxyphenol		S	--	--	0.1	--	--
Dihydrosyringenin		S	--	--	0.2	--	--
Syringic aldehyde		S	0.3	--	--	--	--
4-Ethylphenol		H	--	--	--	--	0.4
Phenol		H	--	--	--	--	--
ethyl 3-(4-hydroxyphenyl)acrylate		H	--	--	--	--	0.2
Total monomers			2.2	2.6	11.4	1.2	5.3
Oil yield			30.2	36.0	54.0	34.0	50.2
Monomer in Oil [wt%]			7.3	7.2	21.1	3.5	10.6

[a] Reaction condition: a stainless-steel autoclave (Parr, 75 mL) was charged with lignin (100 mg), ReO$_x$/AC catalyst (1.6 mol% Re), and isopropanol (15 mL) with an initial N$_2$ pressure of 100 psi and reacting at 200 ^{o}C for 8 h. [b] The yield of aromatics were determined by GC-FID with an internal standard. [c] Reaction condition for Blank-OPL: stainless-steel autoclave (Parr, 75 mL) was charged with OPL (100 mg), and isopropanol (15 mL) with an initial N$_2$ pressure of 100 psi and reacting at 200 ^{o}C for 8 h. [d] Reaction condition for OPL (AC) and OWL (AC): stainless-steel autoclave (Parr, 75 mL) was charged with OPL or OWL(100 mg), AC (100 mg), isopropanol (15 mL) with an initial N$_2$ pressure of 100 psi and reacting at 200 ^{o}C for 8 h.

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