Supporting information

Is oxidation-reduction a real robust strategy for lignin conversion? A comparative study on lignin and model compounds

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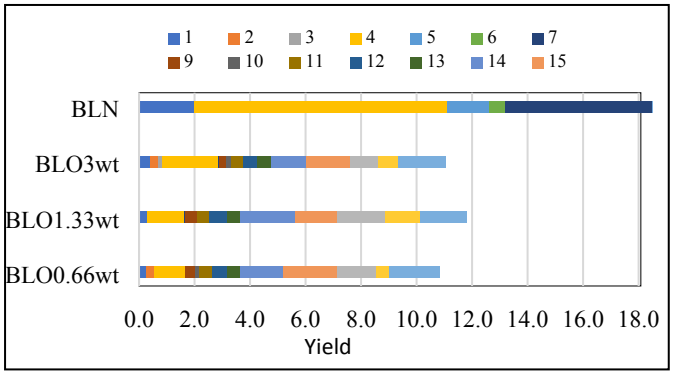
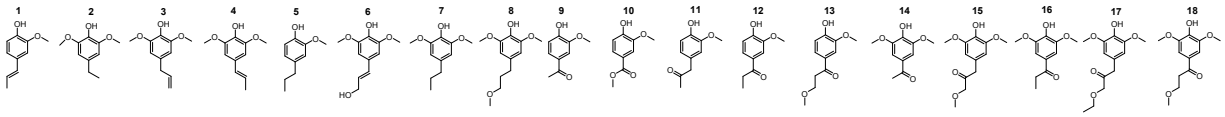
1. Supporting Figures & Tables

Chart S1. Bar chart of depolymerization results and GC-FID spectrum of lignin oil for various lignins and the corresponding forms of lignin$^{\alpha\text{-}OX}$ over W_2C/AC.



Lignin [a]	Total oil (mg)	Lignin residue (mg)	Mass balance %
BLN	55	40	95%
BLO^{3WT}	36	44	80%
BLO$^{1.33WT}$	39	45	84%
BLO$^{0.66WT}$	40	50	90%

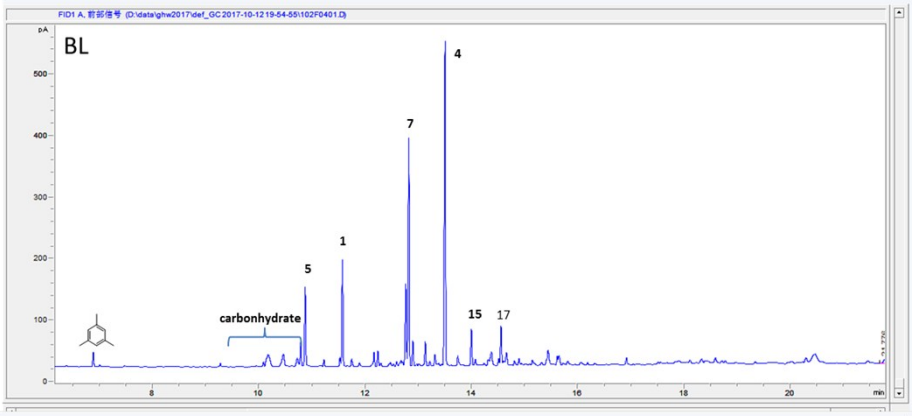
[a] To clarify, Beech lignin (BL), Beech lignin oxidation with 0.66 wt eqv. DDQ (BLO$^{0.66WT}$), Beech lignin oxidation with 1.33 wt eqv. DDQ (BLO$^{1.33WT}$), Beech lignin oxidation with 3 wt eqv. DDQ (BLO^{3WT}). Reaction conditions: substrate: 100 mg, 30% W_2C/AC: 100 mg, methanol: 30 ml, 200 °C, 6 h, 1 MPa H_2 (R.T.)

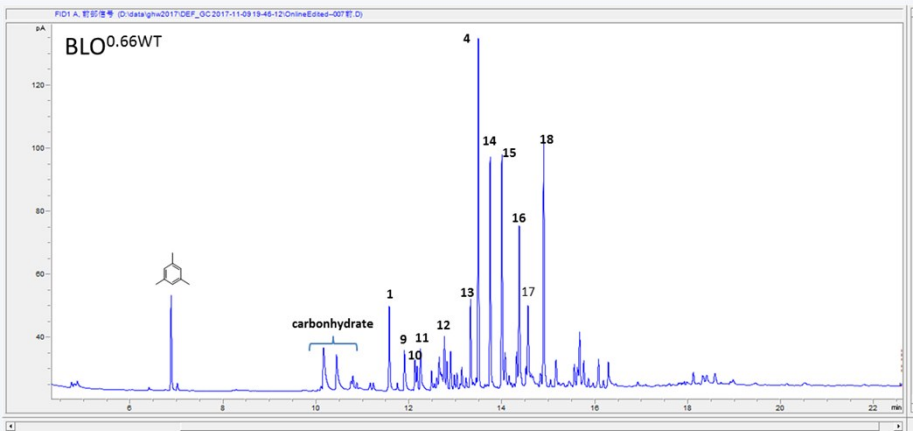


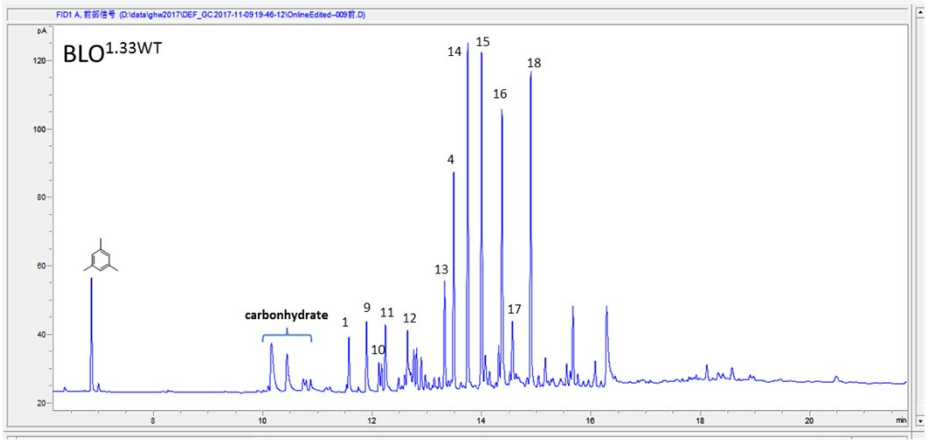
As for the mass balance, it's quite difficult to separate the lignin residue from the catalyst (as our catalysts were activated carbon (AC) supported catalysts and the lignin residue would get stuck in the porous AC), but we tried our best to calculate the lignin residue through the following method:

we first separated the catalysts (with lignin residue stuck inside) and reaction mixture through filtration after reaction. After drying the catalysts (with lignin residue), we calculated the weight of lignin residue through subtracting the catalysts we added. The amount of lignin oil was calculated through vacuuming down the reaction mixture. As shown in Chart S1, the mass balance was not great for all the lignins because of the operation error or some unforeseen issue existed during the operation process.

GC-FID Spectrum of lignin oil after reaction







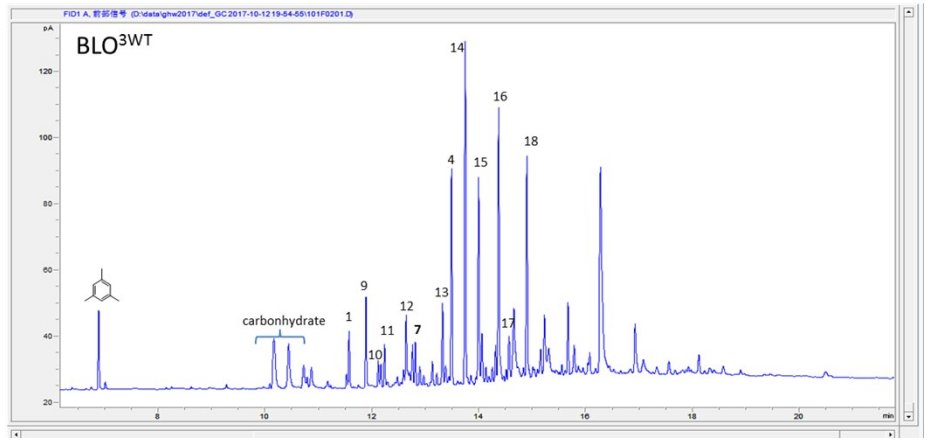
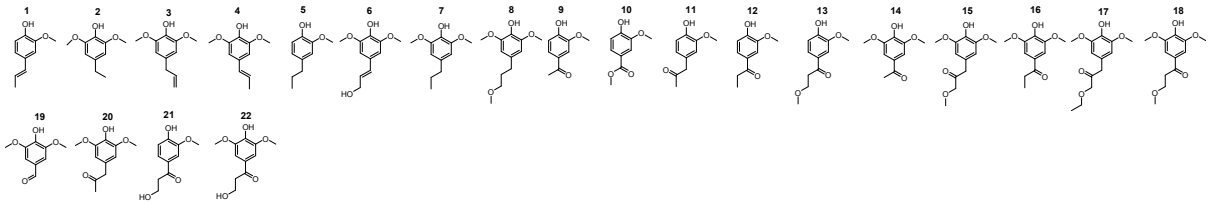


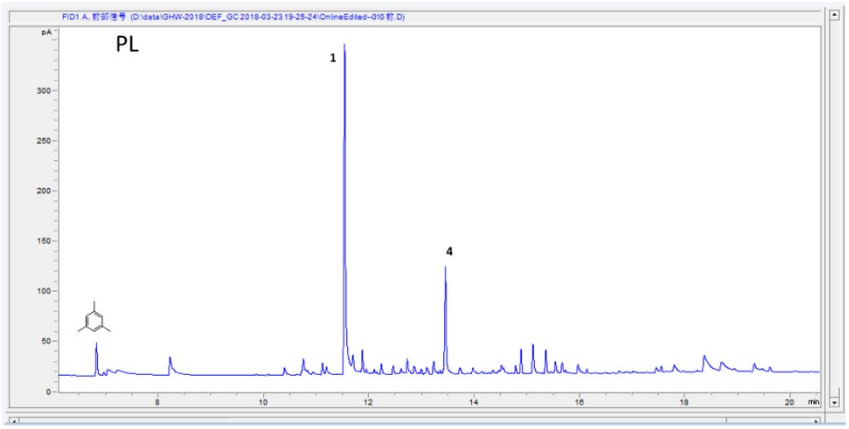
Table S1. Catalytic hydrogenolysis of various lignins and the corresponding forms of lignin$^{\alpha\text{-}OX}$ over W_2C/AC.

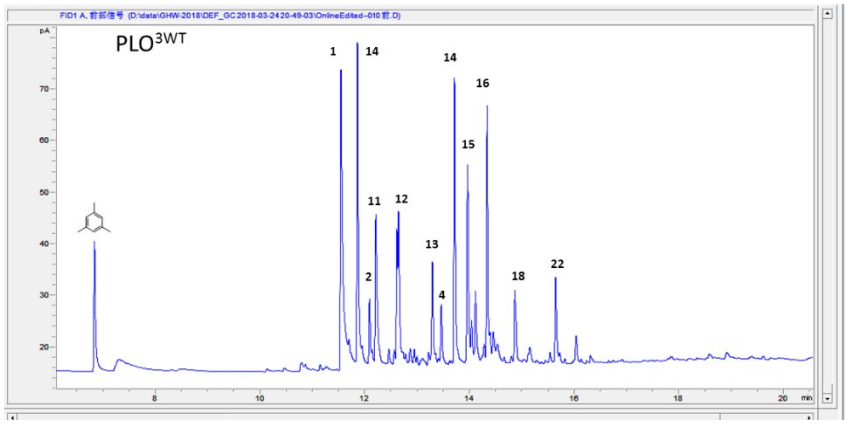
Numbered products	Lignin^{OX}			Lignin		
	BLO^{3WT}	PLO^{3WT}	BiL^{3WT}	BL	PL	BiL
1	0.3	1.3	0.0	2.0	4.8	0.5
2	0.0	0.0	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0	0.2	0.2
4	1.4	0.2	0.3	9.1	2.0	3.2
5	0.0	0.0	0.0	1.5	0.8	0.2
6	0.0	0.0	0.0	0.6	0.0	0.0
7	0.0	0.1	0.0	5.3	0.6	0.3
8	0.0	0.0	0.0	0.0	0.0	0.0
Total aryl-aromatics	1.7	1.6	0.3	18.5	8.4	4.4
9	0.5	1.1	0.1	0.0	0.3	0.0
10	0.0	0.3	0.1	0.0	0.0	0.0
11	0.4	0.8	0.4	0.0	0.4	0.3
12	0.7	0.7	0.5	0.0	0.3	0.0
13	0.5	0.4	0.3	0.0	0.0	0.0
14	2.0	1.0	1.0	0.0	0.2	0.0
15	1.5	1.0	1.4	0.0	0.2	0.7
16	1.7	0.9	0.8	0.0	0.0	0.2
17	1.2	0.1	0.2	0.0	0.2	1.1
18	1.7	0.4	0.5	0.0	0.0	0.5
19	0.0	0.0	0.0	0.0	0.4	0.2
20	0.0	0.2	0.2	0.0	0.0	0.0
21	0.0	0.3	0.2	0.0	0.0	0.0
22	0.0	0.0	0.0	0.0	0.0	0.2
Total carbonyl-containing aromatics	10.2	7.2	5.7	0.0	2.0	3.2
YTM	11.8	8.7	5.8	18.5	10.2	7.4
YTO	35.6	44.1	47.5	39.5	66.2	51.7

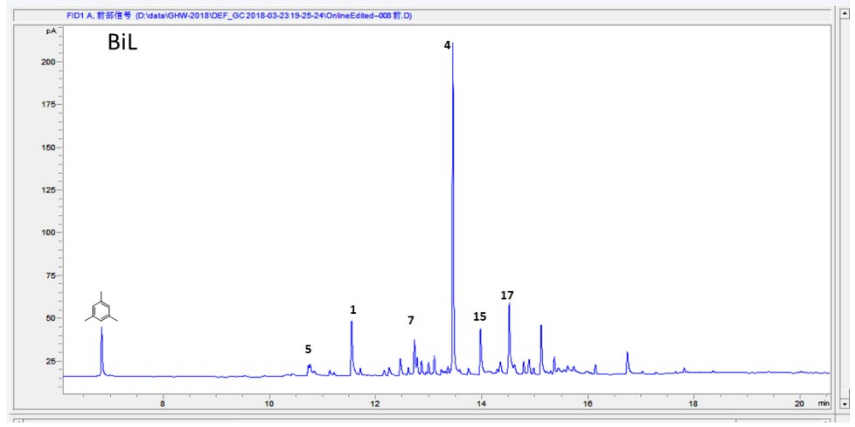


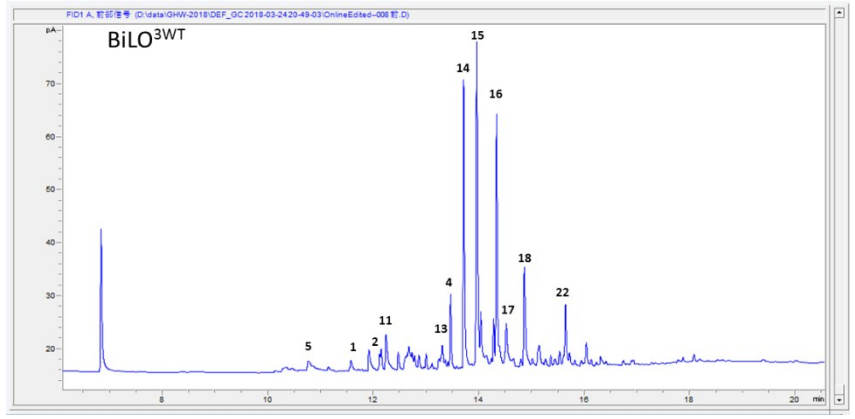
Reaction conditions: substrate: 100 mg, 30% W_2C/AC: 100 mg, methanol: 30 mL, 200 °C, 6 h, 1 MPa H_2 (R.T.)

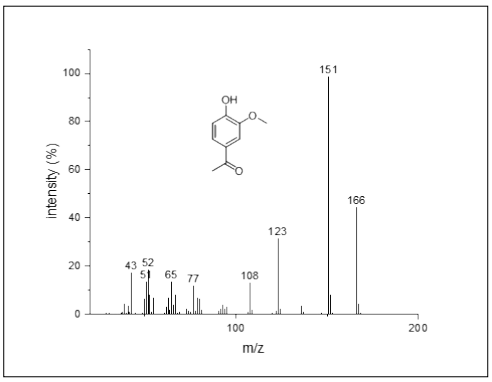
GC-FID Spectrum of lignin oil after reaction







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m/z
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O
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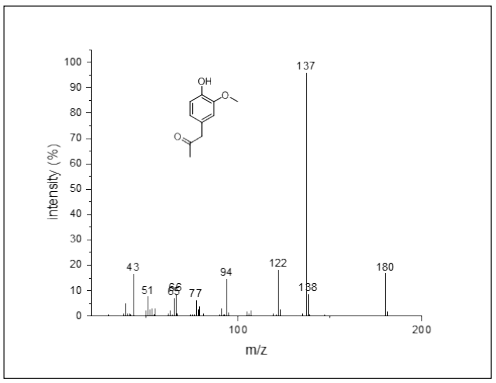
166
123
43
52
51
65
77
108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m/z
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O
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94
122
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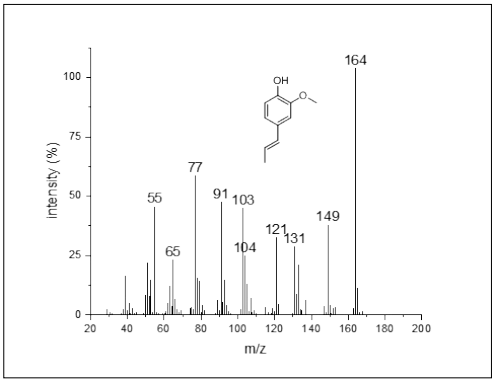
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m/z
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104
121
131
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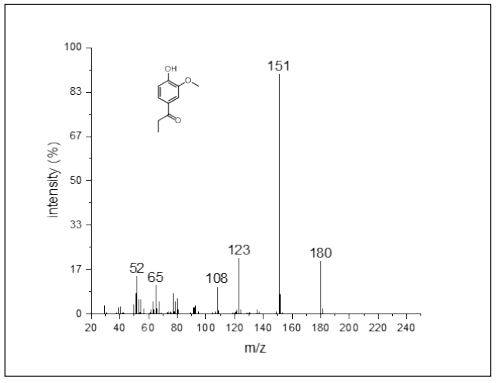
intensity (%)
m/z
OH
O
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52
65
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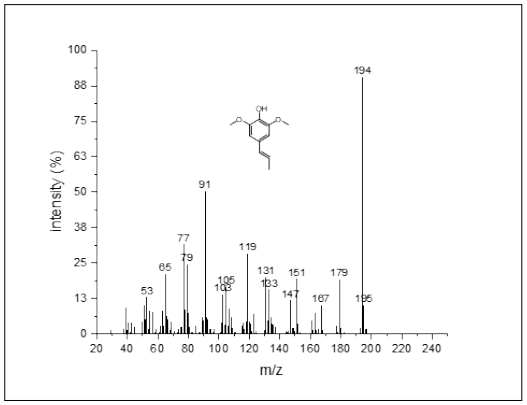
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m/z
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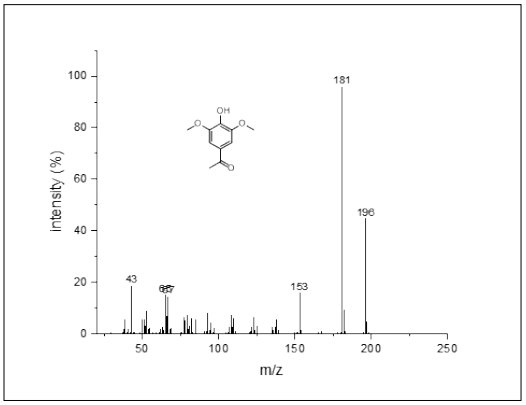

intensity (%)
m/z
OH
O
181
196
43
153

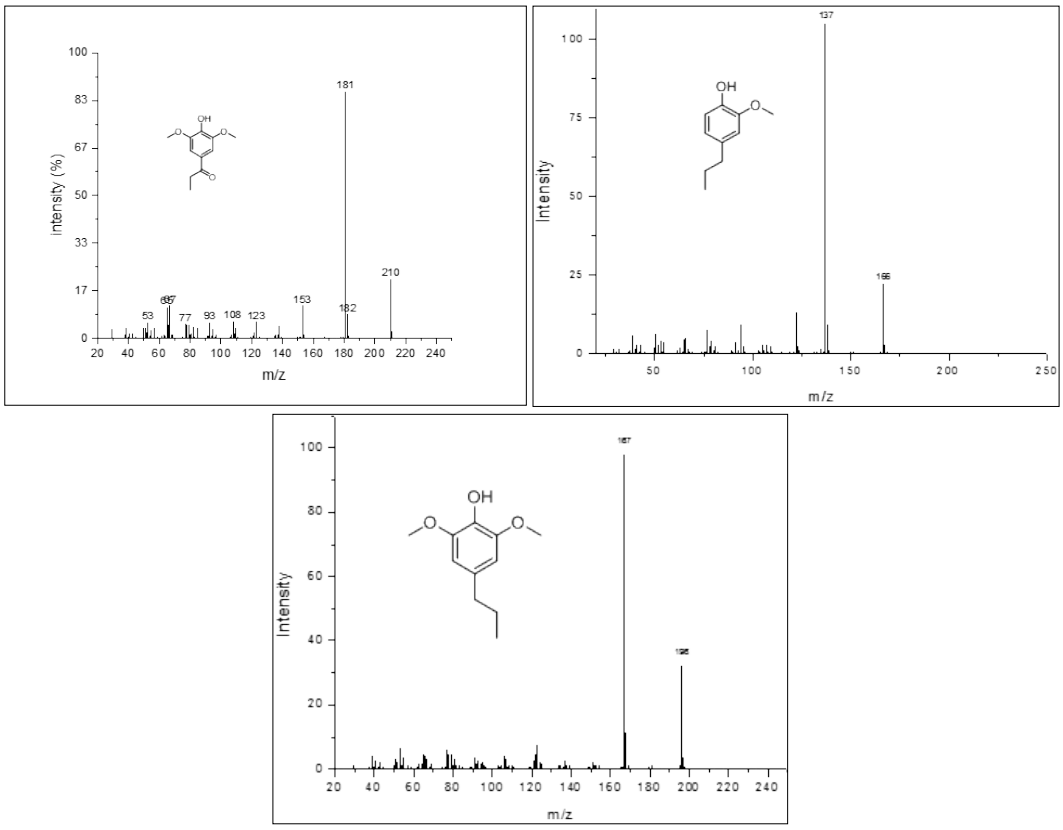
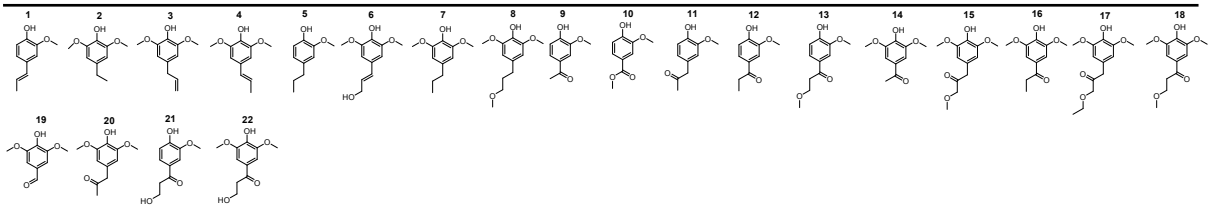


Figure S1. Identification of monomers from lignin and lignin$^{\alpha\text{-}OX}$.

Table S2. Further study of BLO^{3WT} and BL under mild conditions over W_2C/AC.

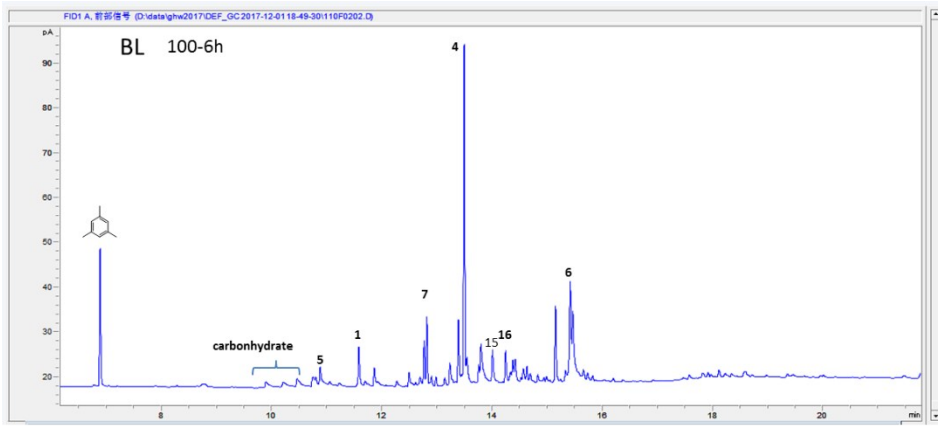
Numbered	BL^{3WT}				BL			
Products	100 6h	100 24h	150 6h	200 6h	100 6h	100 24h	150 6h	200 6h
1	0.0	0.0	0.0	0.3	0.2	0.5	0.7	2.0
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4	0.0	0.2	0.4	1.4	1.3	3.7	3.8	9.1
5	0.0	0.0	0.0	0.0	0.1	0.3	0.3	1.5
6	0.0	0.0	0.0	0.0	0.4	0.0	0.3	0.6
7	0.3	0.0	0.0	0.0	0.2	0.9	1.2	5.3
8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total aryl-aromatics	0.3	0.2	0.4	1.7	2.2	5.4	6.3	18.5
9	0.0	0.0	0.0	0.5	0.1	0.0	0.0	0.0
10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
11	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0
12	0.0	0.4	0.4	0.7	0.0	0.0	0.0	0.0
13	0.0	0.0	0.3	0.5	0.0	0.0	0.0	0.0
14	0.0	0.0	0.2	2.0	0.0	0.0	0.0	0.0
15	0.0	0.0	0.0	1.5	0.0	0.0	0.0	0.0
16	0.2	0.3	0.5	1.7	0.2	0.2	0.3	0.0
17	0.5	0.2	0.0	1.2	0.0	0.3	0.7	0.0
18	0.0	0.2	0.0	1.7	0.0	0.0	0.0	0.0
19	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.0
20	0.3	0.3	0.3	0.0	0.2	0.1	0.4	0.0
21	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
22	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total carbonyl-containing aromatics	1.0	1.4	1.7	10.2	0.5	0.8	1.6	0.0
YTM	1.4	1.5	2.1	11.8	2.6	6.1	8.0	18.5
YTO	38.5	38.4	37.5	35.6	27.8	42.5	45.9	39.5

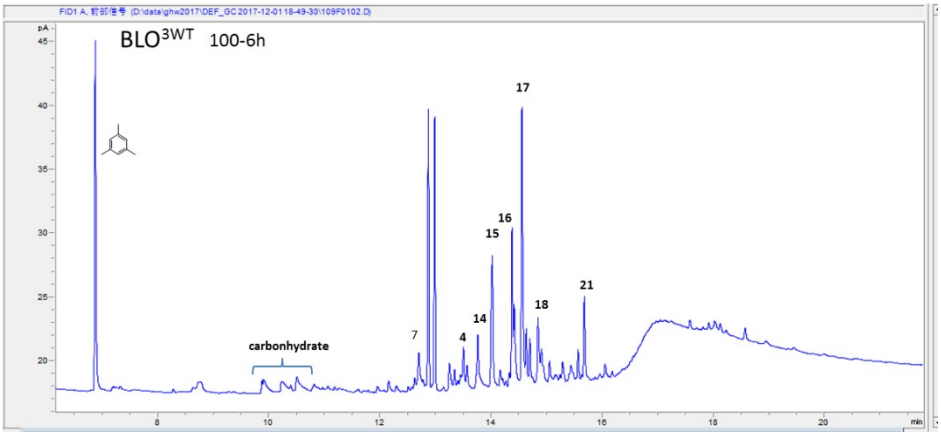


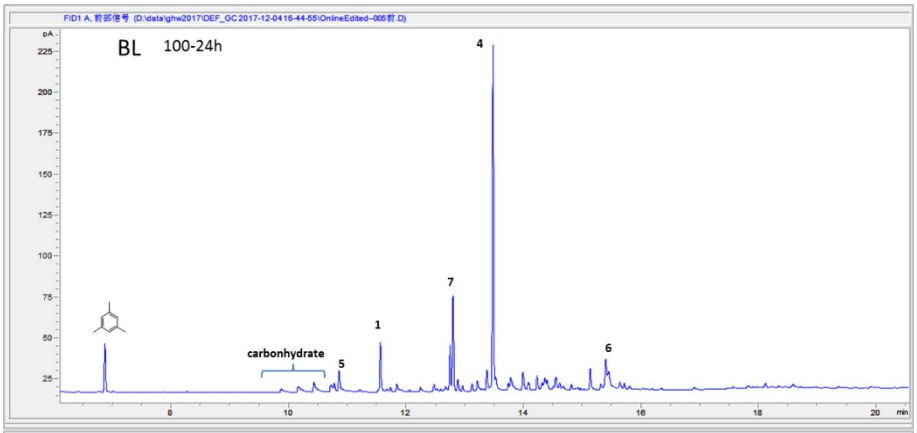
[a]100 mg 30% W_2C/AC was used under 200 6 h condition

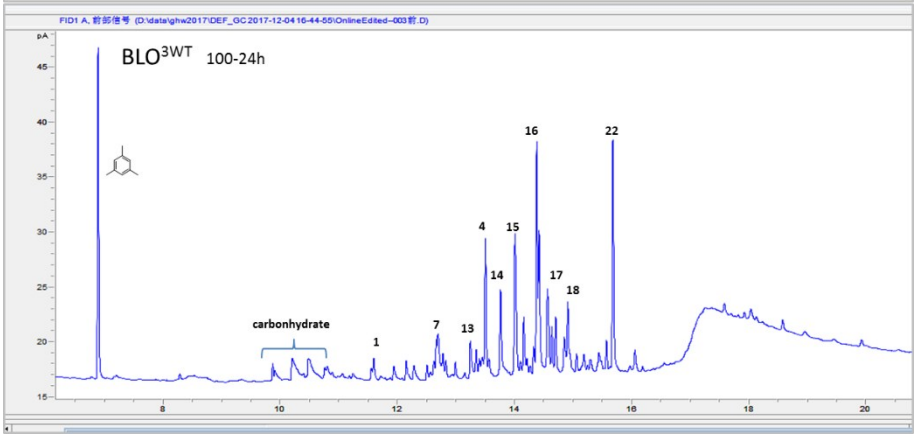
Reaction conditions: substrate: 100 mg, 30% W_2C/AC: 100 mg, methanol: 30 mL, 100/150/200 °C, 6/24 h, 1 MPa H_2 (R.T.)

GC-FID Spectrum of lignin oil after reaction









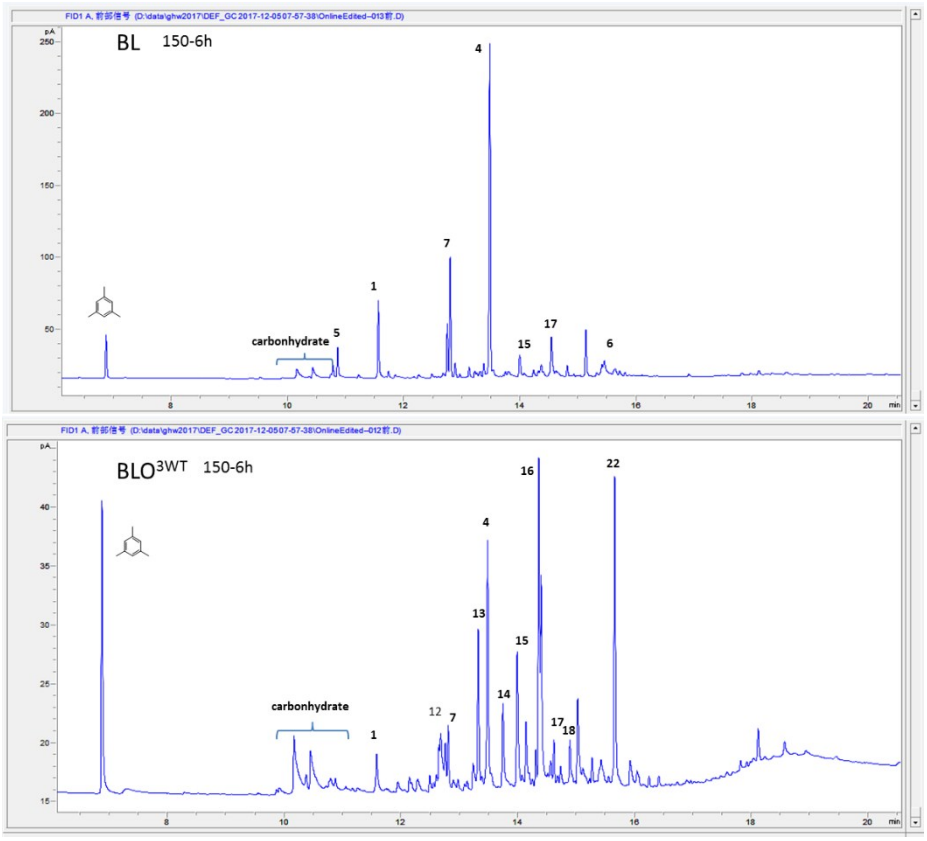
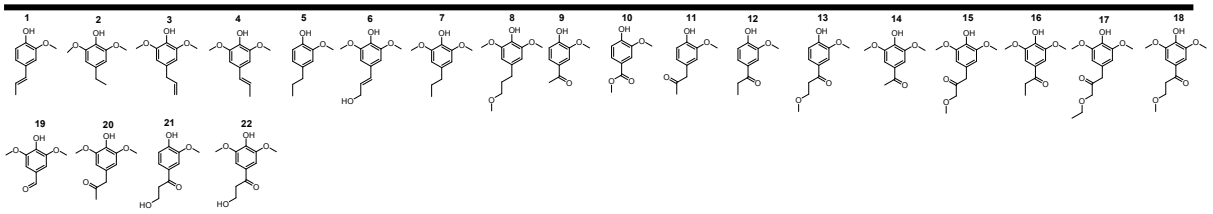
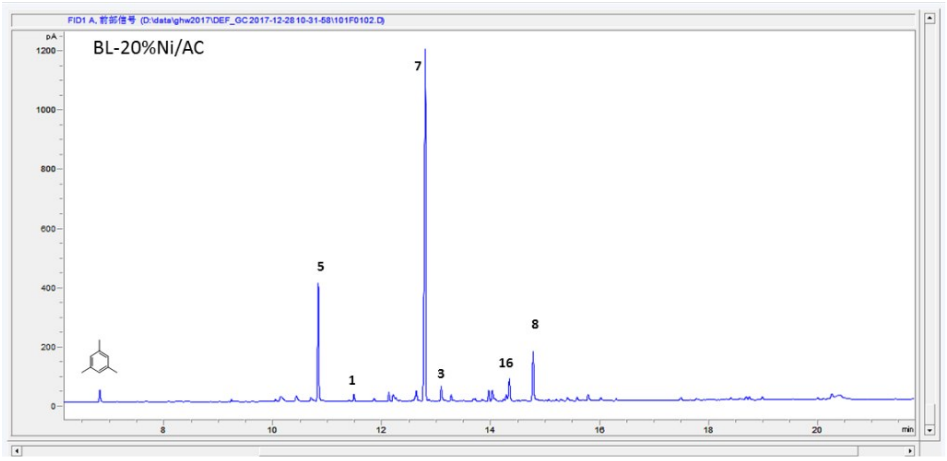

BL 150-6h
carbonhydrate
1
4
5
6
7
15
17
BLO3WT 150-6h
carbonhydrate
1
4
7
12
13
14
15
16
17
18
22

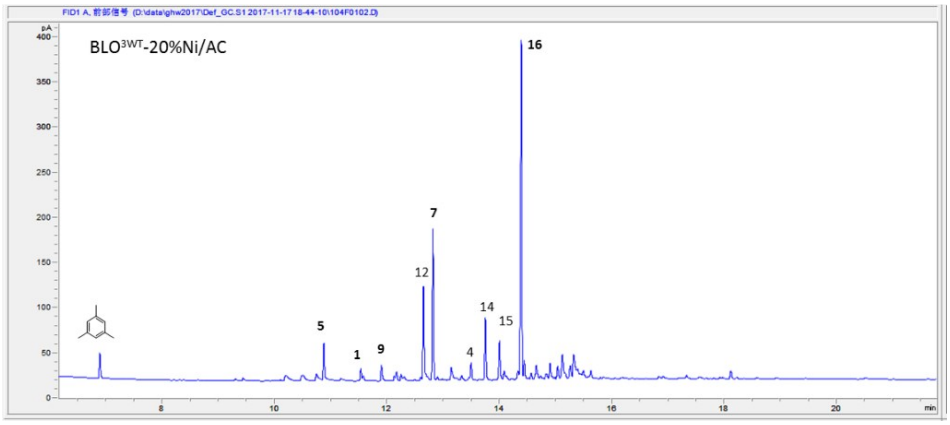
Table S3. Depolymerization results of BL and BLO^{3WT} over various catalysts.

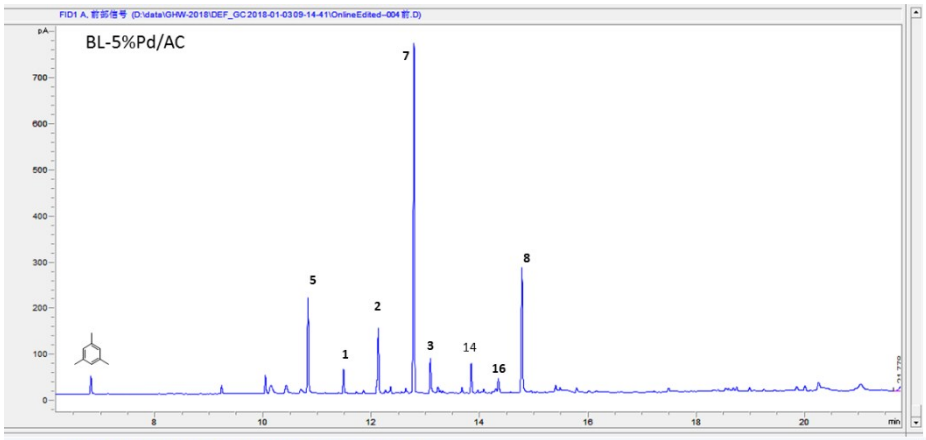
Numbered	BL				BLO^{3WT}			
Products	20%Ni/AC	5%Pd/AC	5%Pt/AC	5%Rh/AC	20%Ni/AC	5%Pd/AC	5%Pt/AC	5%Rh/AC
1	0.3	0.0	0.4	0.3	0.1	1.3	1.2	0.8
2	0.5	2.2	1.8	1.7	0.3	1.6	1.9	0.8
3	0.6	1.0	0.4	0.8	0.2	1.1	0.1	0.1
4	0.0	0.0	0.1	0.0	0.4	0.2	1.0	0.3
5	3.7	2.1	2.8	2.4	0.5	0.7	0.3	0.4
6	0.3	0.0	0.4	0.3	0.3	0.0	0.4	0.3
7	16.0	9.3	11.6	11.0	2.2	1.0	1.1	1.5
8	2.9	4.2	1.8	3.2	0.0	4.2	1.8	0.3
Total aryl-aromatics	24.3	18.8	19.3	19.7	4.0	10.1	7.8	4.5
9	0.1	0.0	0.0	0.1	0.3	0.4	0.2	0.2
10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
11	0.0	0.0	0.4	0.4	0.3	0.3	0.3	0.0
12	0.8	0.0	0.4	0.7	1.7	0.5	1.2	1.2
13	0.0	0.0	0.0	0.2	0.2	0.1	0.0	0.0
14	0.2	0.9	0.2	0.5	1.1	0.1	0.6	0.6
15	0.6	0.1	0.5	0.7	0.0	0.7	1.0	0.9
16	1.2	0.5	0.7	1.9	6.6	0.4	0.1	5.0
17	0.0	0.0	0.0	0.5	0.2	0.0	0.1	0.0
18	0.0	0.3	0.0	0.0	0.0	0.2	0.2	0.3
19	0.4	0.3	0.0	0.7	0.0	0.0	0.0	0.0
20	0.6	0.1	0.0	0.0	0.8	0.2	0.0	0.0
21	0.4	0.2	0.0	0.0	0.0	0.3	0.0	0.0
22	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total carbonyl-containing aromatics	4.3	2.4	2.2	5.7	11.2	3.2	3.7	8.2
YTM	28.3	21.2	21.2	25.3	15.3	13.2	11.6	12.6
YTO	65.2	73.0	73.2	80.6	44.7	67.8	67.0	62.5

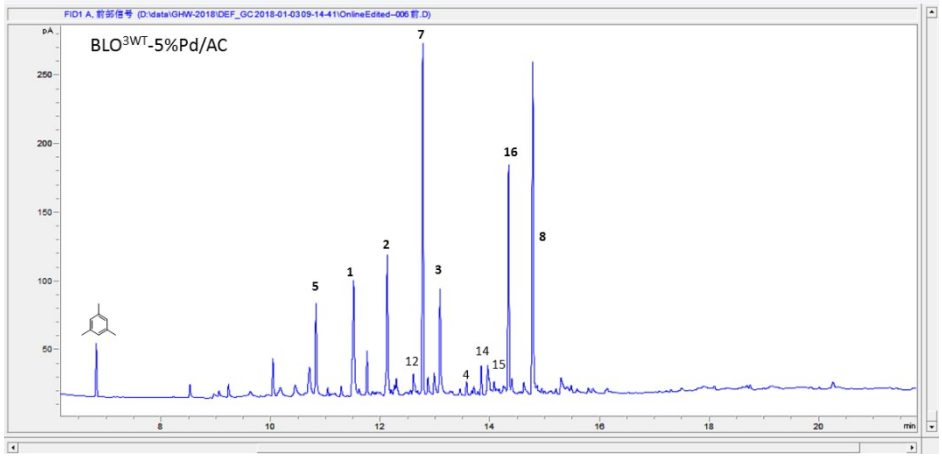


Reaction conditions: substrate: 100 mg, catalyst: 100 mg, methanol: 30 mL, 200 °C, 6 h, 1 MPa H_2 (R.T.)

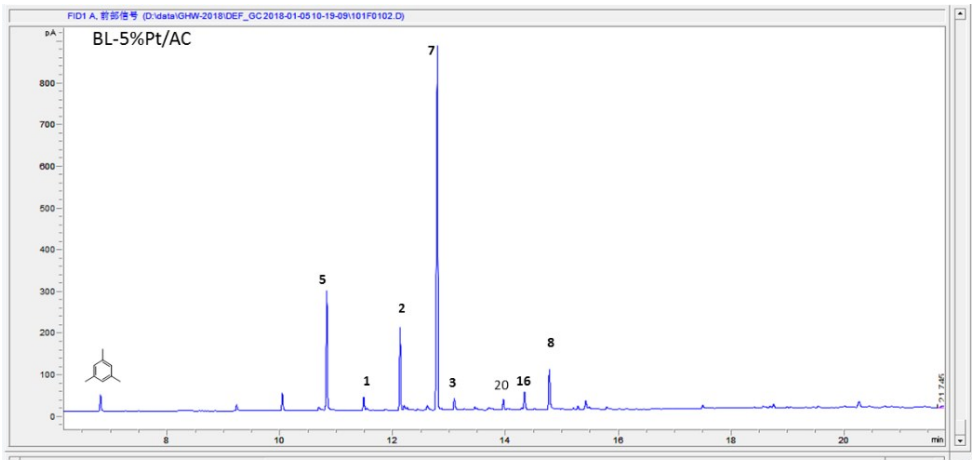








GC-FID Spectrum of lignin oil after reaction


BL-5%Pt/AC
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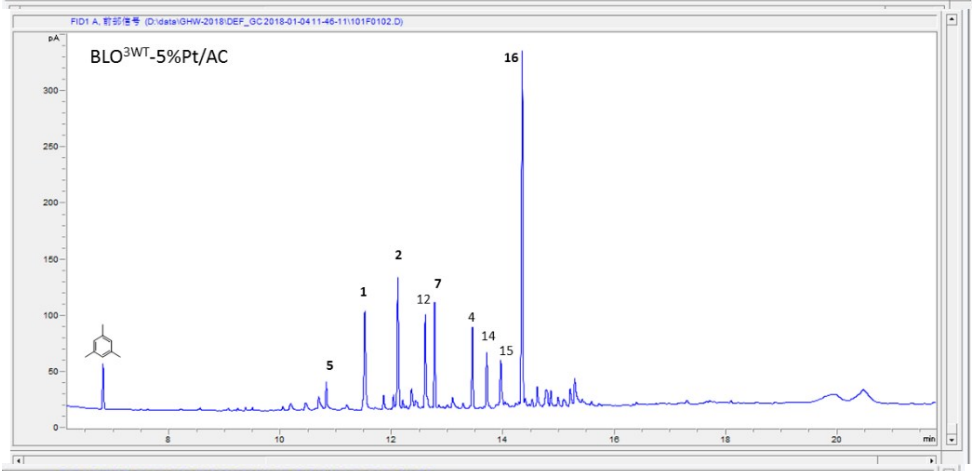
5
2
8
1
3
20
16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1
7
12
4
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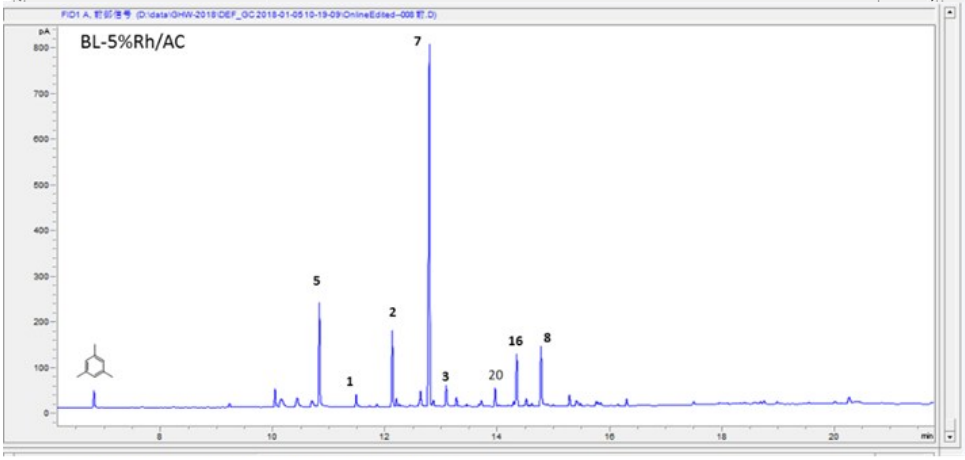
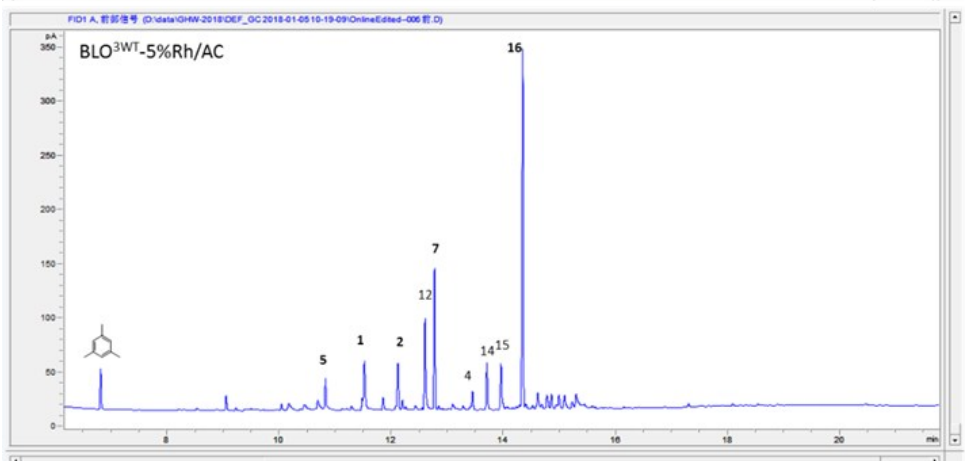
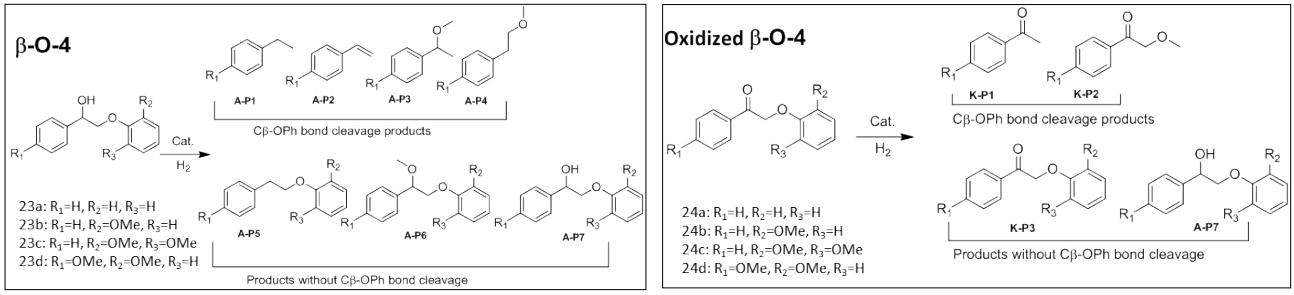
15
5


BL-5%Rh/AC
7
5
2
16
8
1
3
20


BLO3WT-5%Rh/AC
16
7
12
1
2
5
14
15
4



Linkage type	Sub.	Conversion %	Yield (%) of C-O cleavage products					Yield (%) of products without C-O cleavage			
			A-P1	A-P2	A-P3	A-P4	Total	A-P5	A-P6	A-P7	Total
β-O-4	23a	42	0	6	0	0	6	6	0	58	64
	23b	100	9	36	17	5	67	4	4	0	8
	23c	100	6	37	20	4	67	0	4	0	4
	23d	95	14	7	7	20	48	0	0	5	5
			K-P1	K-P2			Total	K-P3	A-P7		Total
Oxidized β-O-4	24a	61	32	4			36	39	9		48
	24b	100	95	5			100	0	0		0
	24c	100	99	5			100	0	0		0
	24d	100	88	0			88	0	6		6

Chart S2. Hydrogenolysis activity comparison of **i)** β-O-4 model compounds and **ii)** Oxidized β-O-4 over W_2C/AC.

Notes: reaction conditions: substrate: 100 mg, 30% W_2C/AC: 100 mg, methanol: 30 mL, 220 °C, 2 h, 1 MPa H_2 (R.T.)

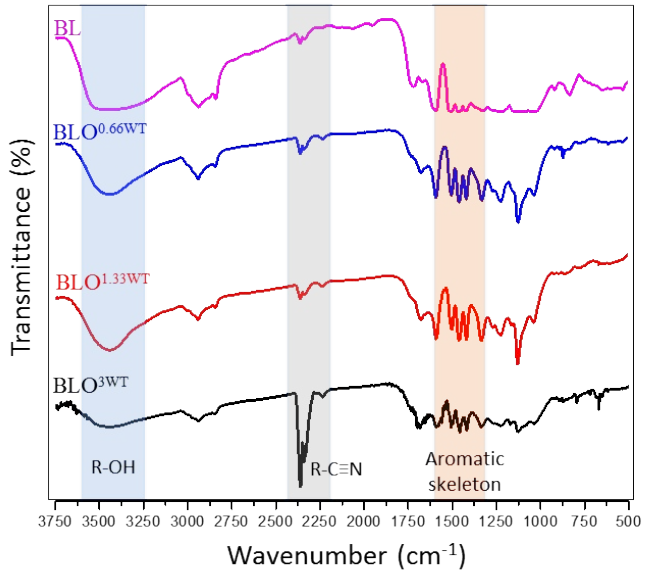


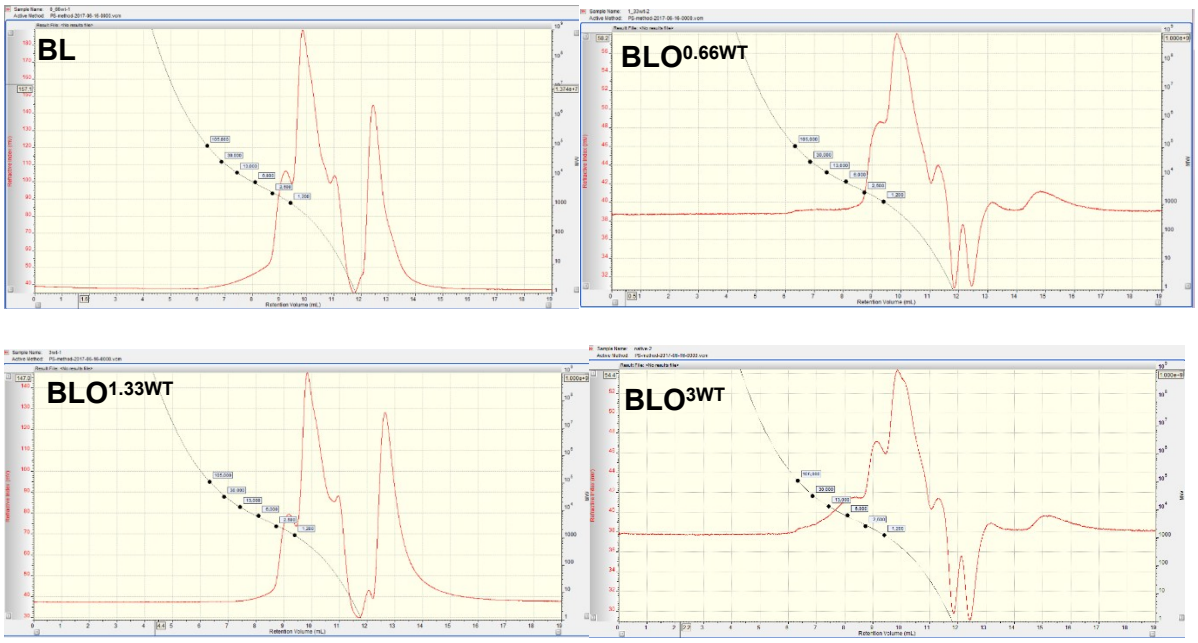
Figure S2. Full FT-IR spectra of BL and BLOs.

As shown in **Figure S2**, all the samples exhibited similar aromatic skeleton (~1500 cm^{-1}, light orange) as the proof of lignin structure.[1] R-OH (~ 3500 cm^{-1}, light blue) was also observed in both BLOs and BL as the existence of both aliphatic alcohol and phenolic alcohol. Moreover, R-C ≡ N (~2375 cm^{-1}, light grey) was detected in all lignin samples, and BLO^{3WT} showed stronger intensity of R-C ≡ N as the existence of DDQ residue, which agreed with the elemental analysis where BLO^{3WT} contained 2.83% of **N** comparing to 0.03%, 1.05% and 1.72% of **N** in BL, $BLO^{0.66WT}$ and $BLO^{1.33WT}$ separately (**Table S4**).

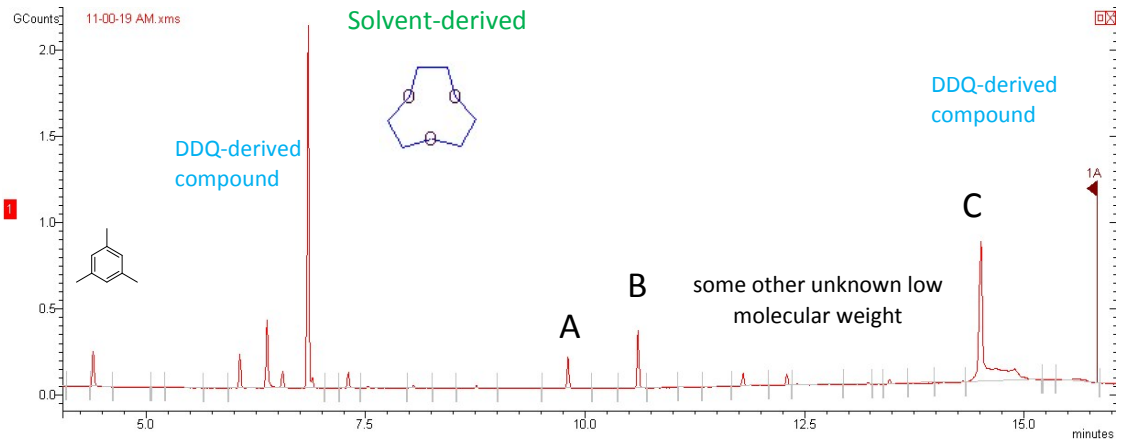
Table S4. Elemental analysis results of various lignin and the corresponding forms of lignin$^{\alpha\text{-}OX}$.

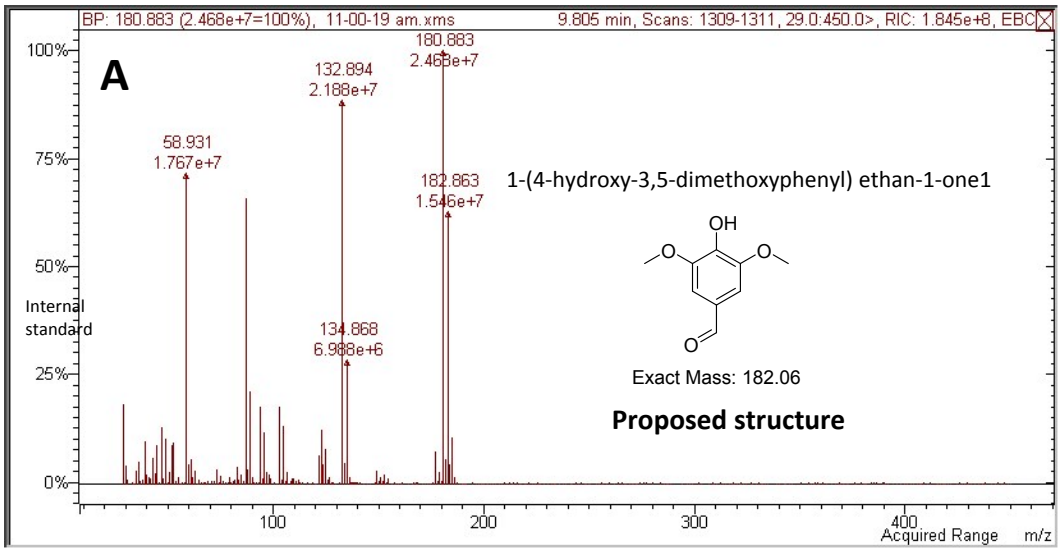
Elements \ Lignin	BL	BLO $^{0.66wt}$	BLO $^{1.33wt}$	BLO^{3wt}
C [%]	73.15	56.73	55.03	54.16
H [%]	6.76	4.69	4.24	3.73
O [%]	20.06	37.54	39.01	39.28
N [%]	0.03	1.05	1.72	2.83
S [%]	0.00	0.00	0.00	0.00
C/H	10.82	12.11	12.97	14.54

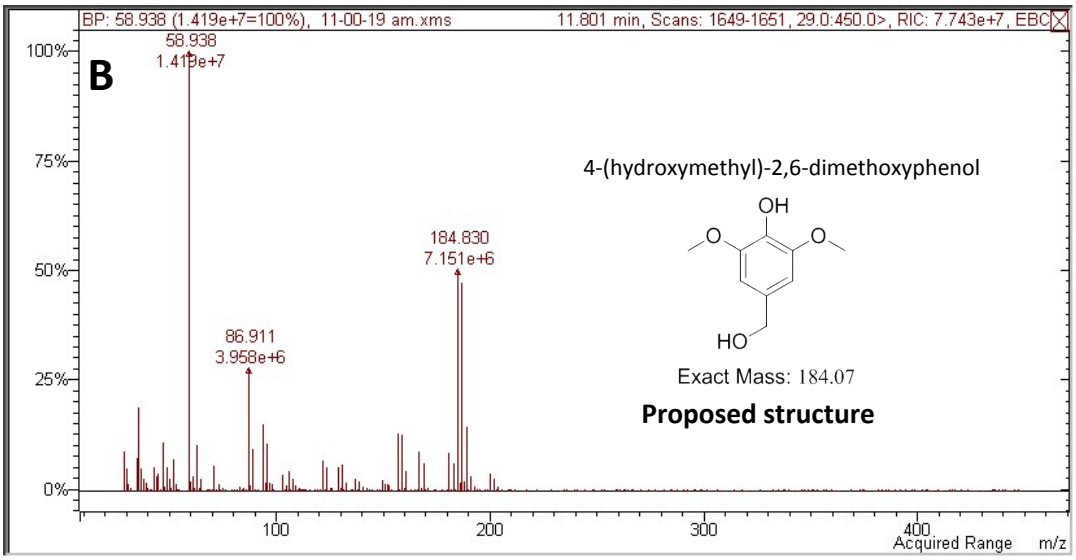
To examine the elemental components of BL and, elemental analysis was undertaken. From Table S4, we observed notable decrease of **C** in BLOs, arranging from 54.16% to 56.73 in BLOs, comparing with 73.15% in BL. Similar trend was observed in the percentage of **H**, in which 6.76 % was detected in BL comparing with 3.73% in BLO^{3WT} as the dehydrogenation during oxidation procedure. In terms of C/H ratio, although not dramatic but still nonnegligible difference (10.82 for BL and 14.54 for BLO^{3WT}) can be seen, implying a slight change of BLOs structure. Trace **N** was detected in BL, making up 0.03% of the total components, while more (as many as 2.83 %) was observed in BLO^{3WT} which originated from DDQ or DDQ-H_2 residue.[12] No **S** was detected in any kinds of lignin.



Figures S3. Weight-(Mw) and number-average (Mn) molecular weight of lignin by GPC analysis.


GCounts
11-00-19 AM.xms
Solvent-derived
DDQ-derived compound
DDQ-derived compound
A
B
C
some other unknown low molecular weight
1A
minutes


BP: 180.883 (2.468e+7=100%), 11-00-19 am.xms
9.805 min, Scans: 1309-1311, 29.0:450.0>, RIC: 1.845e+8, EBC
A
180.883
2.468e+7
132.894
2.188e+7
58.931
1.767e+7
182.863
1.546e+7
134.868
6.988e+6
Internal standard
1-(4-hydroxy-3,5-dimethoxyphenyl) ethan-1-one1
Exact Mass: 182.06
Proposed structure
Acquired Range
m/z


BP: 58.938 (1.419e+7=100%), 11-00-19 am.xms
11.801 min, Scans: 1649-1651, 29.0:450.0>, RIC: 7.743e+7, EBC
B
58.938
1.419e+7
184.830
7.151e+6
86.911
3.958e+6
4-(hydroxymethyl)-2,6-dimethoxyphenol
Exact Mass: 184.07
Proposed structure
Acquired Range
m/z

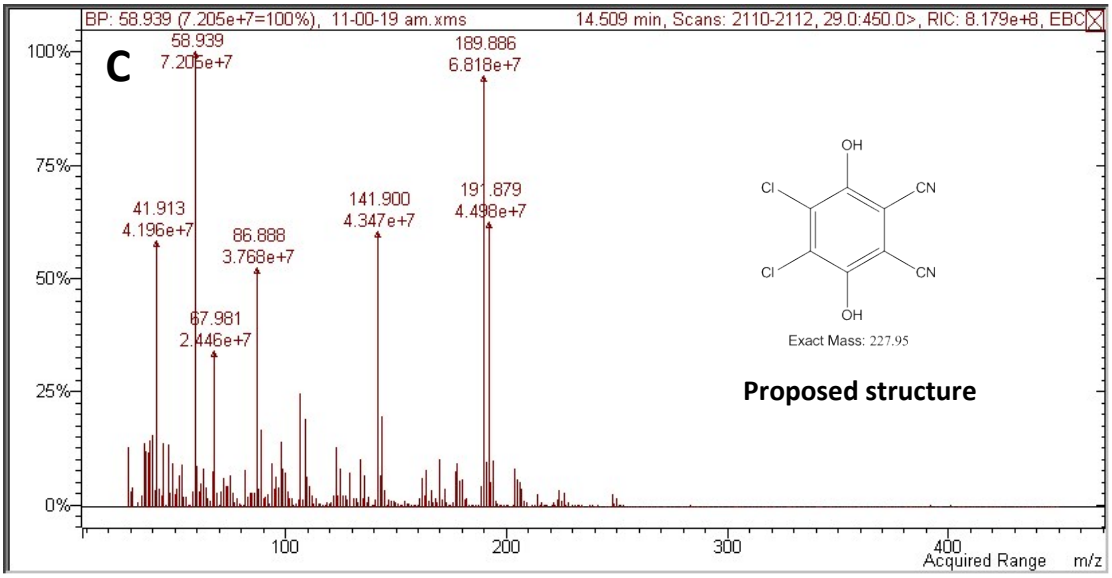
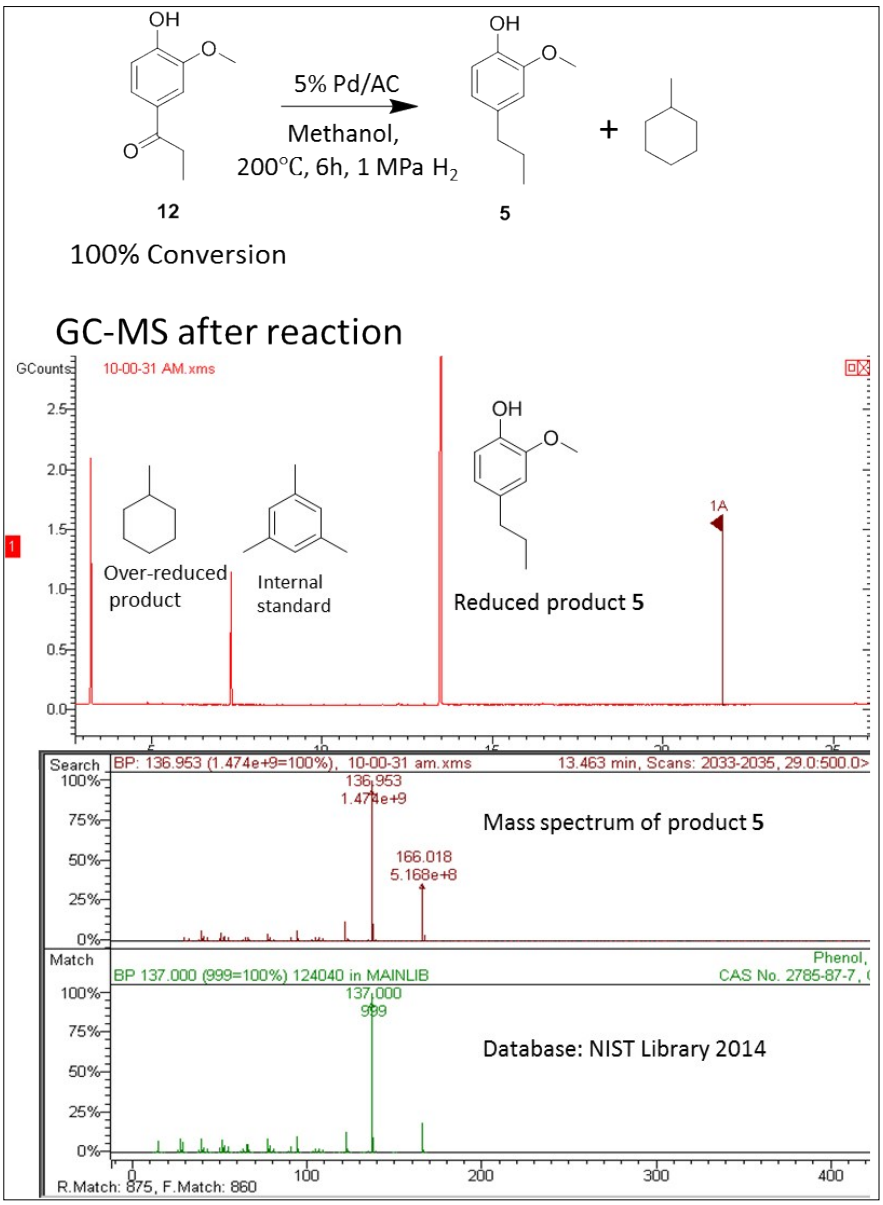


Figure S4. GC-MS analysis of compounds released during oxidation progress.



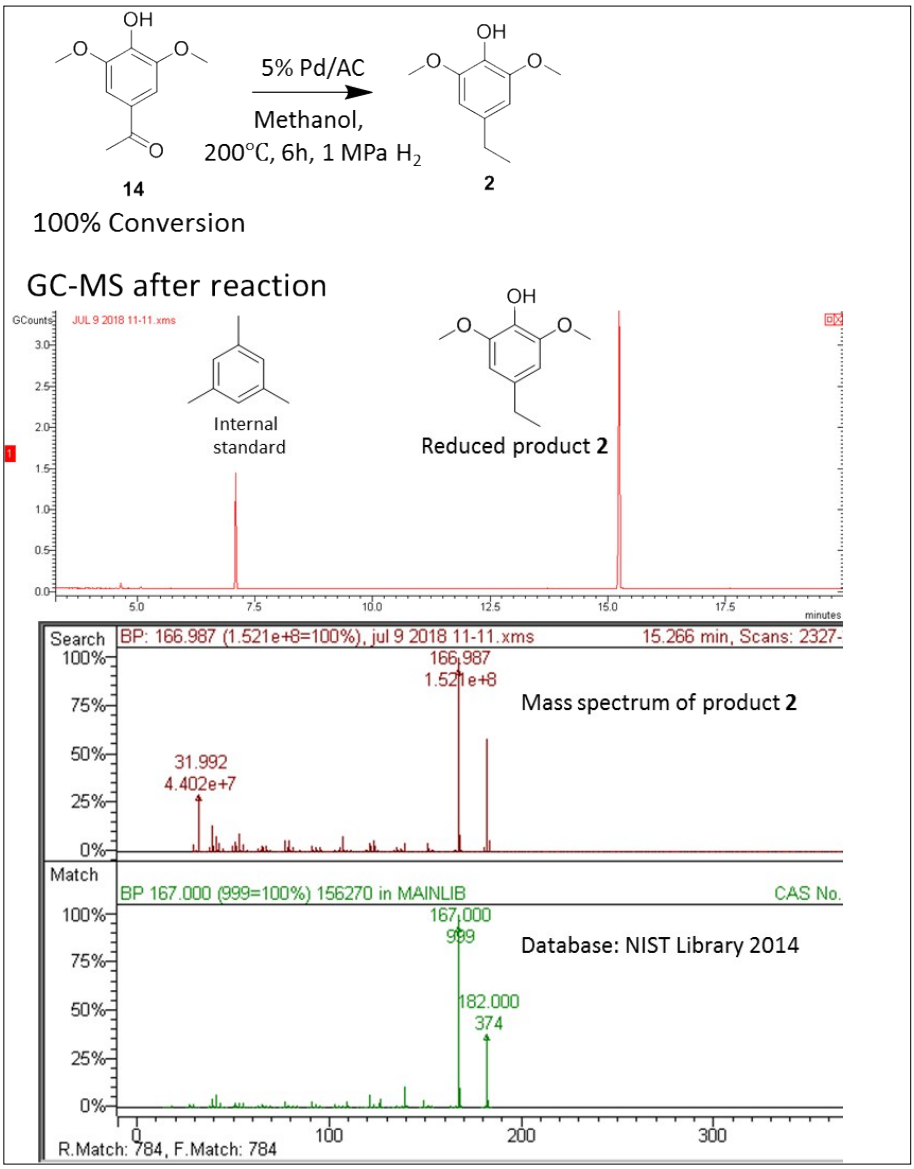
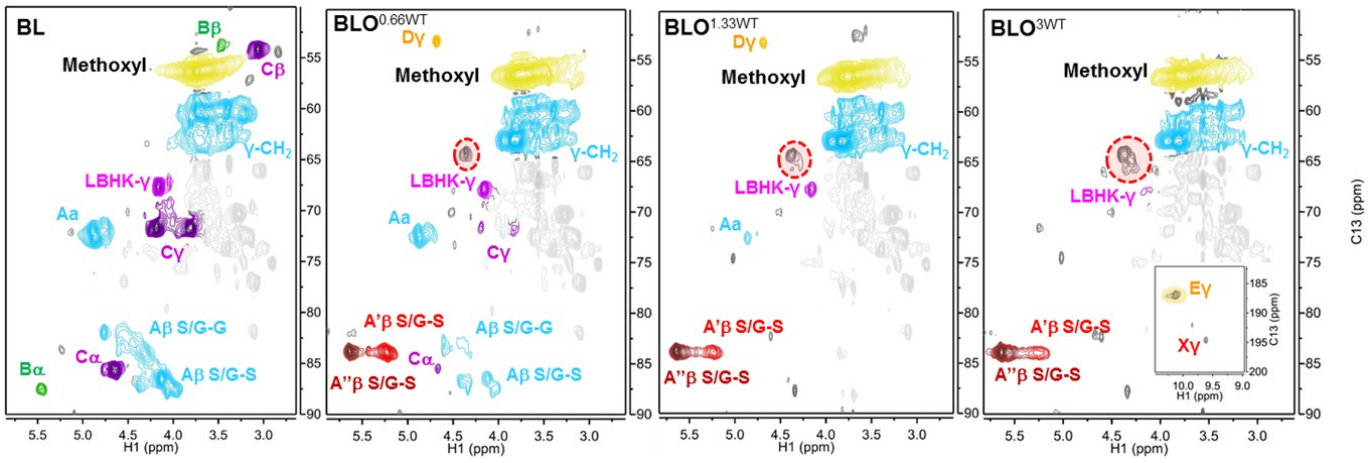


Figure S5. Proof study of the reduction of carbonyl-containing aromatic products （**12** to **5** & **14** to **2**） over 5% Pd/AC.



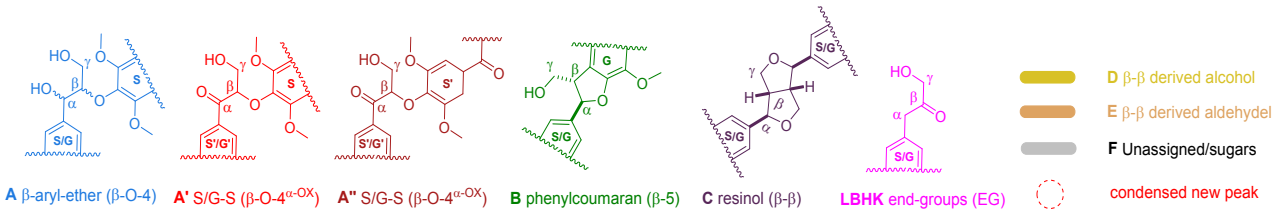


Figure S6. 2D HSQC NMR spectrum of BL and BLOs (prepared under different oxidative pretreatments with DDQ).[2]

Please note that these data are repeated 2D-HSQC-NMR spectrum in order to revisit unknown signals which were overlooked in our previous study[2] in Chem. Sci., 2018, 9, 702–711. Therefore, the discussion on the NMR in the present work and the previous study are totally different and the data are not the same.

2. References

1. (a) Liu, Y.; Hu, T.; Wu, Z.; Zeng, G.; Huang, D.; Shen, Y.; He, X.; Lai, M.; He, Y., *Environ Sci Pollut Res Int* **2014,** *21* (24), 14004; (b) Liu, Q.; Wang, S.; Zheng, Y.; Luo, Z.; Cen, K., *J. Anal. Appl. Pyrol.* **2008,** *82* (1), 170; (c) Guo, H.; Zhang, B.; Qi, Z.; Li, C.; Ji, J.; Dai, T.; Wang, A.; Zhang, T., *ChemSusChem.* **2017,** *10* (3), 523; (d) Derkacheva, O.; Sukhov, D., *Macromol. Symp.* **2008,** *265* (1), 61; (e) Faix, O., *Holzforschung.***1991,** *45* (s1), 21.

2. Guo, H.; Miles-Barrett, Daniel M.; Neal, A. R.; Zhang, T.; Li, C.; Westwood, N. J., *Chem. Sci.* **2018,** *9* (3), 702.