

Supporting information

High efficient lignin depolymerization via effective inhibition of condensation during polyoxometalate mediated oxidation

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S1. Regeneration of polyoxometalate

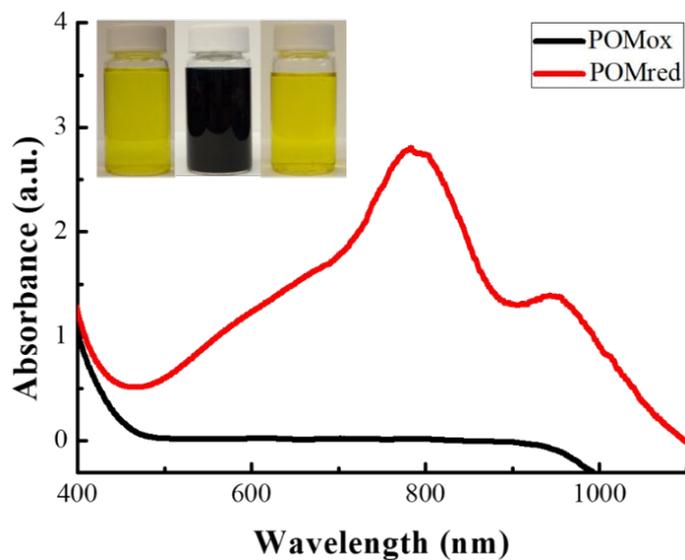
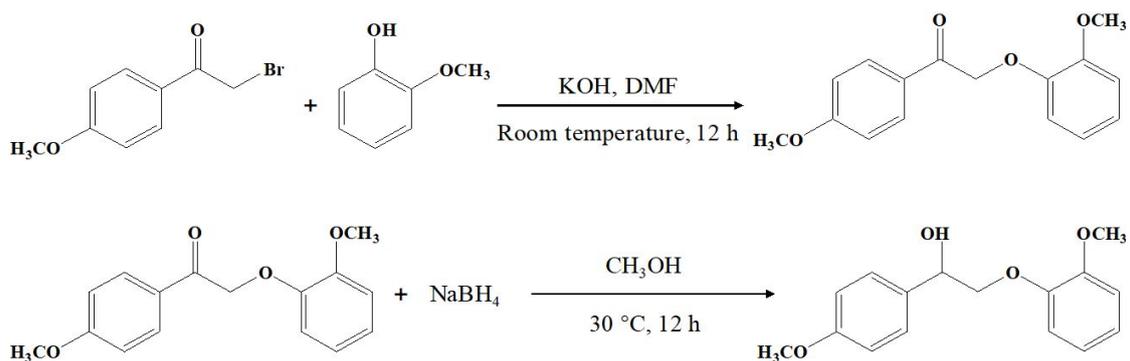


Fig. S1 UV-vis absorbance spectra of POM_{ox} and H-POM_{red} solution, and the insert digital photograph of the original POM_{ox} (left), H-POM_{red} (middle), re-oxidation POM_{ox} (right).

S2. Lignin model compounds synthesis and their characterization



To synthesize 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanone, 2-Bromo-4'-methoxyacetophenone (1.7 g), Guaiacol (1.1 g) and potassium hydroxide (0.5 g) were dissolved in 35 mL DMF(dimethylformamide) and stirred at room temperature for 12 h. After reaction, the reaction mixture was poured into water and extracted with 2V

ethyl ether for 3 times. After drying of ethyl ether phase with sodium sulfate, 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanone was recrystallized from ethanol. Then the products were analyzed by GC-MS and $^1\text{H-NMR}$.

To synthesize 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol, a solution of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanone (0.49 g) in methanol (20 mL) was treated with sodium borohydride (0.07 g) and stirred 12 h. A saturated solution of ammonium sulphate (20 mL) followed by chloroform (20 mL) was added to the reaction mixture. The organic layer was separated, and washed with water for three times. Organic phase was dried with sodium sulfate, then the organic solvent was removed via rotary evaporators to obtain residual products. Finally, the residual products were recrystallized from ethanol to obtain pure 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanol. The final products were analyzed by GC-MS and $^1\text{H-NMR}$.

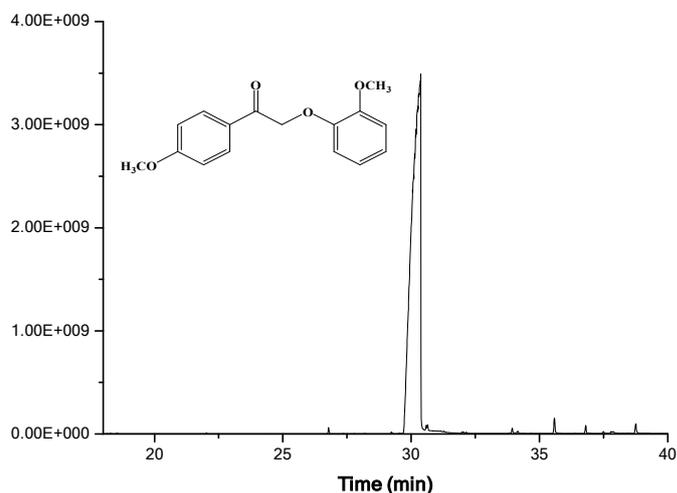


Fig. S2 GC-MS pattern of the 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanone (β -O-4-K).

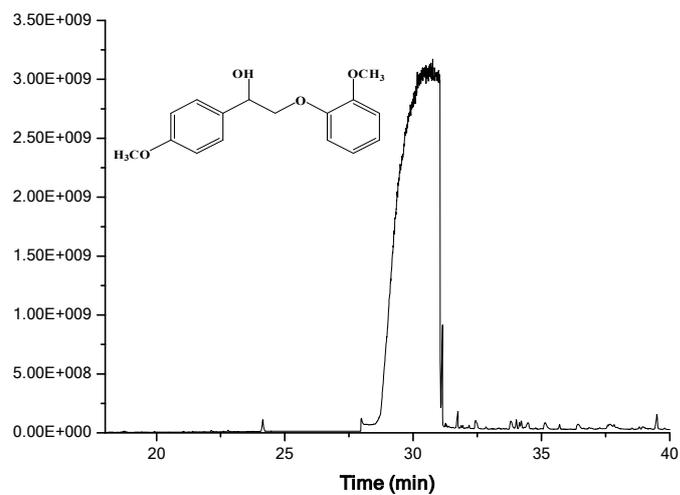


Fig. S3 GC-MS pattern of the 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanol (β -O-4-A).

$^1\text{H-NMR}$ (700 MHz, DMSO- d_6) δ = 8.03-7.99 (m, 2H), 7.09-6.81 (m, 6H), 5.45 (s, 2H),
3.86 (s, 3H), 3.78 (s, 3H).

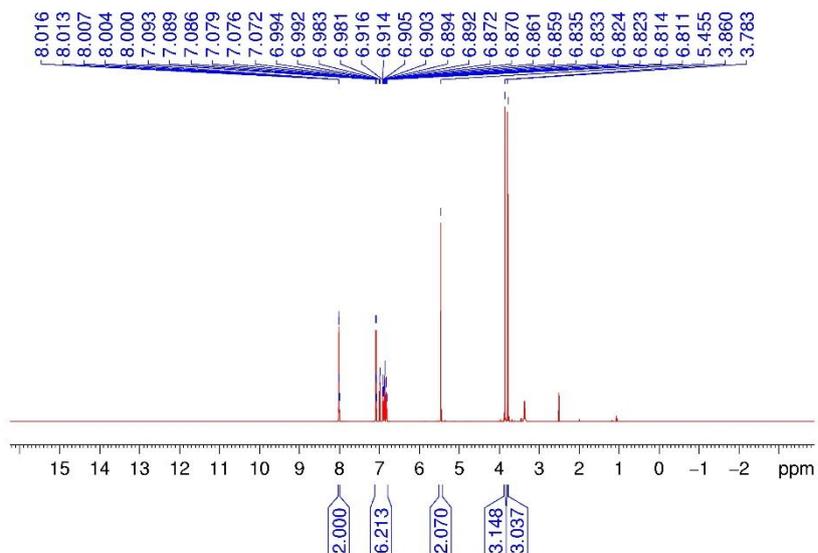


Fig. S4 $^1\text{H-NMR}$ pattern of the 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanone ($\beta\text{-O-4-K}$).

$^1\text{H-NMR}$ (700 MHz, DMSO- d_6) δ = 7.37 (t, 2H), 7.37-6.84 (m, 6H), 5.49 (t, 1H), 4.87 (dd, 1H), 3.95 (ddd, 2H), 3.74 (t, 6H).

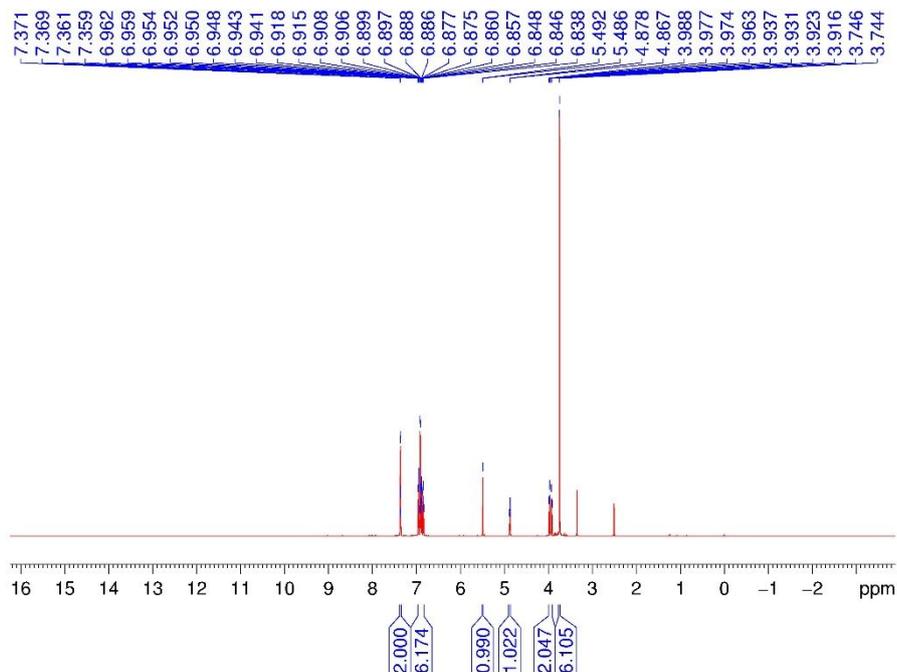
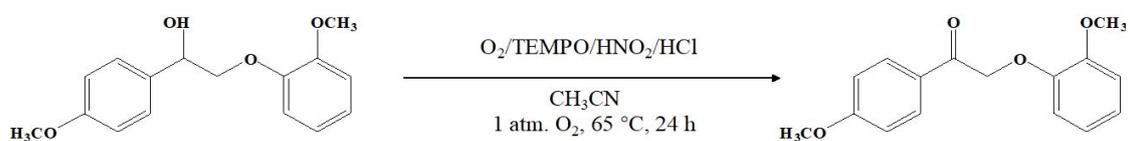


Fig. S5 $^1\text{H-NMR}$ pattern of the 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanol (β -O-4-A).

S3. Selective oxidation of lignin model compounds



To a 50 mL bottle, 200 mg of lignin model compounds (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanol (β -O-4-A)) and 6 mg TEMPO were added. 10 mL acetonitrile (containing 100 μL H₂O), 6 μL of hydrochloric acid (37%) in 1.5 mL acetonitrile and 9 μL of nitric acid (67%) in 1.5 mL acetonitrile were injected respectively. The reaction mixture was stirred at 65 °C with 1 atm. O₂ for 24 h.

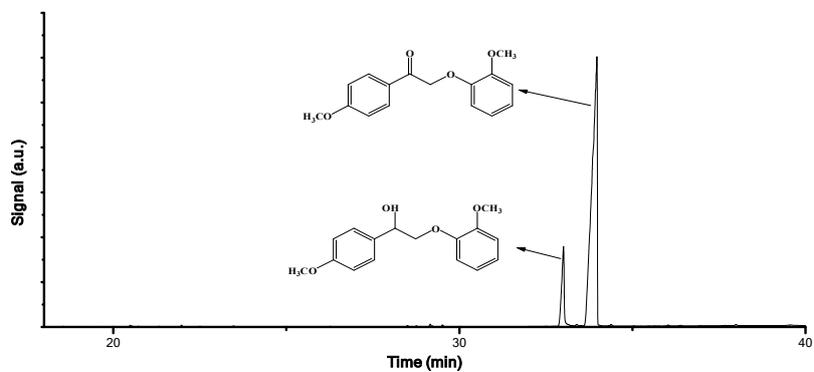


Fig. S6 GC-FID pattern of products derived from selective oxidation of lignin model compounds

Table S1 Products derived from selective oxidation of lignin model compounds

Compound	Structure	Retention time (min)	Area	Content (%)
M1		33.972	3.1610	88%
M2		33.009	0.4403	12%

S4. 2D-NMR spectra of raw lignin

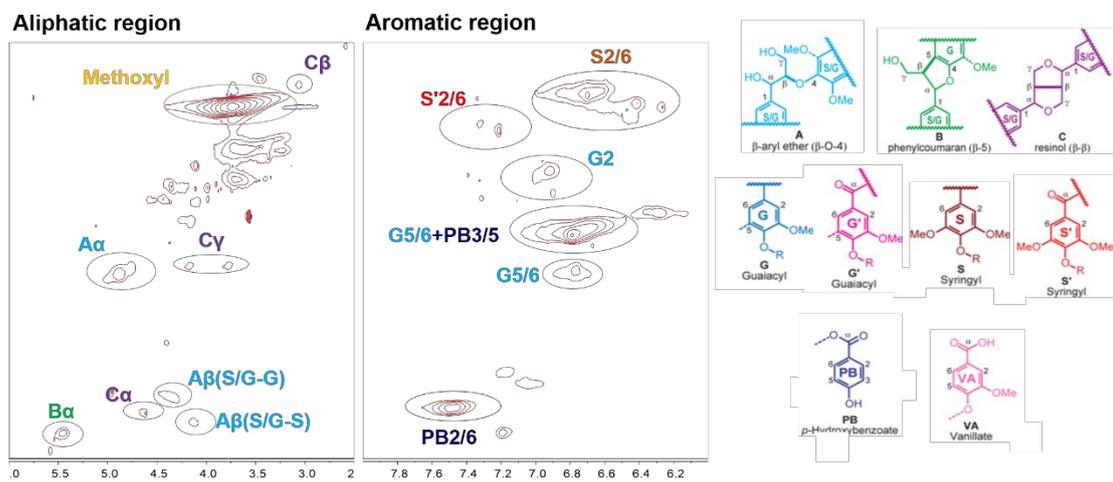


Fig. S7 Aliphatic regions and aromatic regions of the raw lignin obtained with (HSQC) NMR. And the main structures presented in the raw lignin.

S5. Composition of lignin oil and gas products

S5.1 Gas products analysis

Table S2 Analysis of the gas phase under vary conditions.

Entry	Blocking Ca-OH	Gas	Gas pressure (bar)	Solvent	Temperature (°C)	Time (h)	Gas products composition (Vol %)		Gas products yield ^a (C %)
							CO ₂	CO	
1	Without	O ₂	10	Methanol/Water (18 mL/2 mL)	150	4	2.68	0.30	11.64
2	Without	N ₂	10	Methanol/Water (10 mL/10 mL)	150	4	0.3	0.02	1.25
3	Without	Air	Atmospheric pressure	Water (20 mL)	150	4	0.27	0.02	1.13
4	Without	N ₂	Atmospheric pressure	Methanol/Water (18 mL/2 mL)	150	4	0.24	0.02	1.01
5	Without	O ₂	10	Methanol/Water (18 mL/2 mL)	150	4	2.01	0.16	16.70
6	Without	O ₂	10	Methanol/Water (18 mL/2 mL)	150	4	2.00	0.16	16.68
7	With	O ₂	10	Methanol/Water (18 mL/2 mL)	150	2	2.52	0.18	10.53
8	With	O ₂	10	Methanol/Water (18 mL/2 mL)	150	4	3.47	0.48	15.41
9	With	O ₂	10	Methanol/Water (18 mL/2 mL)	150	6	5.01	0.56	21.71
10	With	O ₂	10	Methanol/Water (18 mL/2 mL)	150	8	6.55	0.64	28.03
11	With	O ₂	10	Methanol/Water (18 mL/2 mL)	100	4	2.12	0.11	7.11

S5.2 Possible formation processes of aliphatic compounds

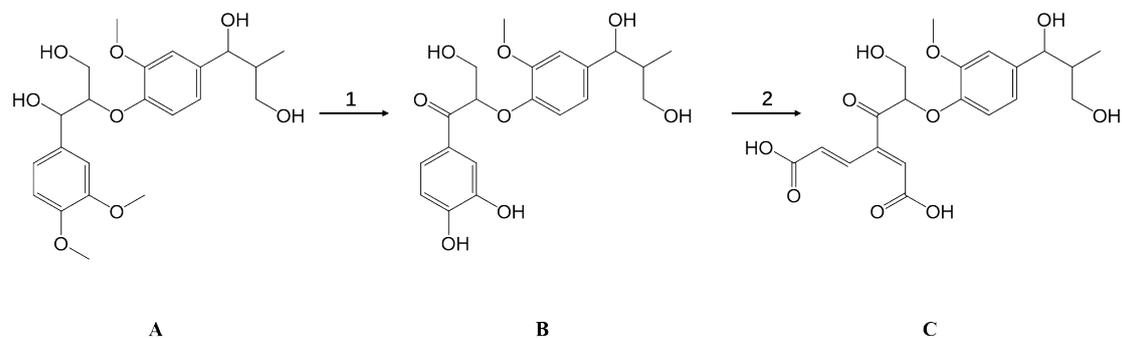


Fig. S8 scheme representing 1) oxidation, depolymerization, and demethylation and 2) ring opening, leading to unsaturated aliphatic and hydroxylated carboxylic acid containing structure C^[1].

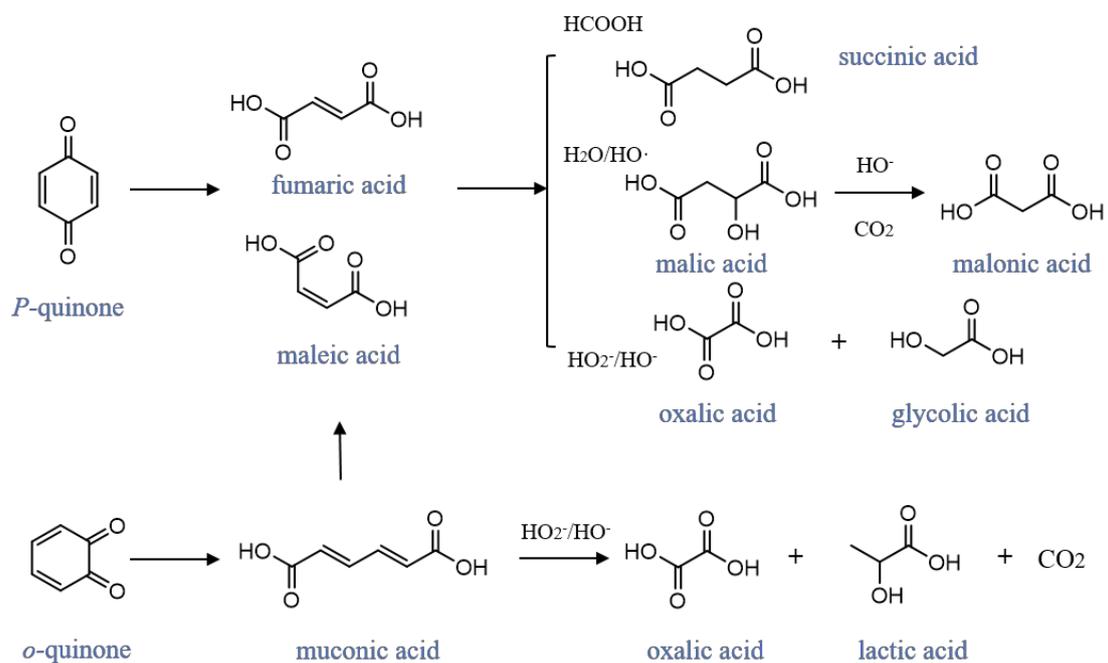


Fig. S9 Proposed reaction pathways for the production of unsaturated aliphatic carboxylic acid^[2].

S5.3 GPC analysis of lignin oil and raw lignin

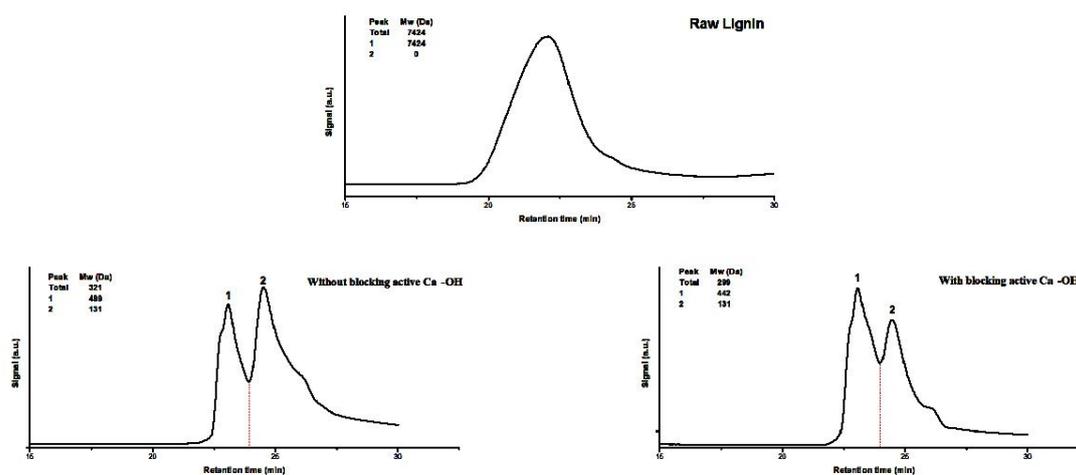


Fig. S10 GPC analysis of lignin and lignin oil obtained from the depolymerization of the lignin with and without blocking active C_{α} -OH.

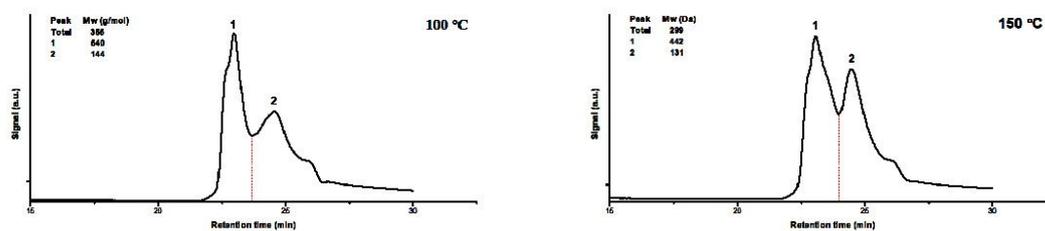


Fig. S10 GPC analysis of the lignin oil obtained from the depolymerization of the lignin with vary temperatures 100°C, 150°C.

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- [2] R. Ma, M. Guo, Prof., #x, D. X. Zhang, *Chemsuschem* **2014**, *7*, 412-415.