Electronic Supplementary Information

Lignin depolymerization (LDP) in alcohol over nickel-based catalysts via a fragmentation-hydrogenolysis process

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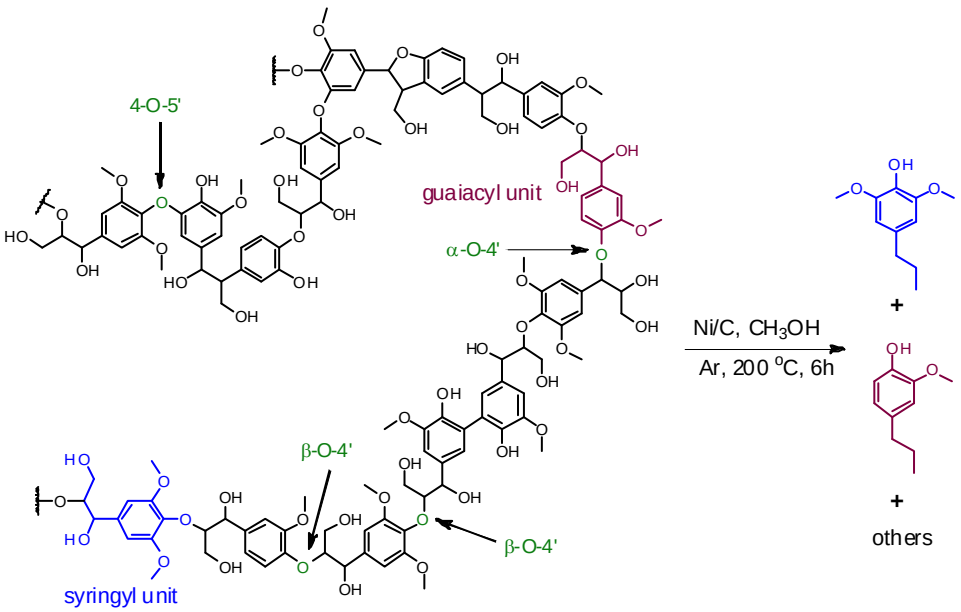
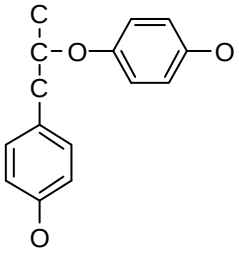
1. The typical structure of birch lignin.



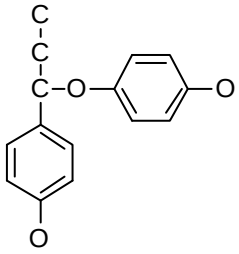
Scheme S1. Representative birch lignin structure (derived from hardwood lignin structure). Green color shows the linkage pattern of birch lignin. Blue color displays the syringyl unit and guaiacyl unit. As shown in the scheme, two hydroxyl groups attached to Cα and Cγ are removed after reaction compared with the product PSol.

2. The four basic C-O-C linkages in birch lignin

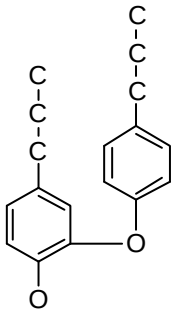
The four basic linkages in birch which can give monomeric phenols after C-O bond was cleaved. The percentage numbers indicate their distribution frequency (per 100 C9 units).



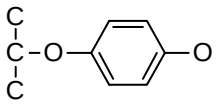
A: arylglycerol-β-aryl ether
β-O-4' 60%



B: noncyclic benzyl aryl ether
α-O-4' 6-8%



C: diphenyl ether
4-O-5' 6.5%



D: glyceraldehyde-2-aryl ether
2%

Scheme S2. The categories of ether linkages in birch lignin

A: β-O-4 (arylglycerol-β-aryl ether), accounting for 60%, B: α-O-4 (noncyclic benzyl aryl ether), accounting for 6-8%, C: 4-O-5 (diphenyl ether), accounting for 6.5%, D: glyceraldehyde-2-aryl ether, accounting for 2%. The total linkage which can release monomeric phenols is 74.5-76.5%. According to the discussion in main text, the maximum yield of lignin conversion originating from C-O bond was in the range of 56% to 59%.

3. Product analysis

(1) MS and NMR spectra of 4-propylguaiacol (product 1)

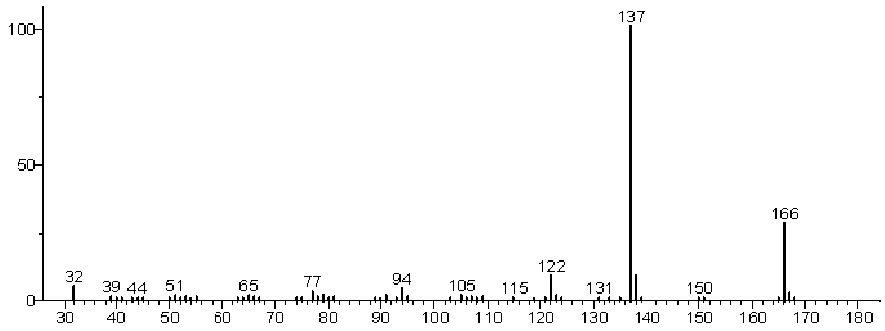


Figure S1. Mass spectrum of 4-propylguaiacol (product 1)

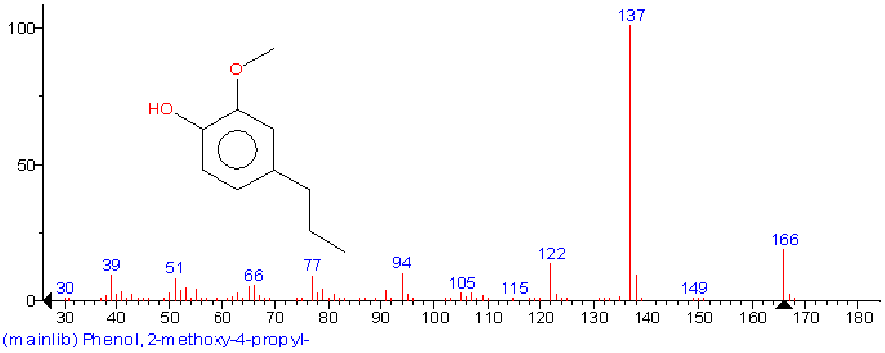


Figure S2. The standard reference mass spectrum of 4-propylguaiacol, NIST MS number 135362. (Source: NIST webbook online database.)

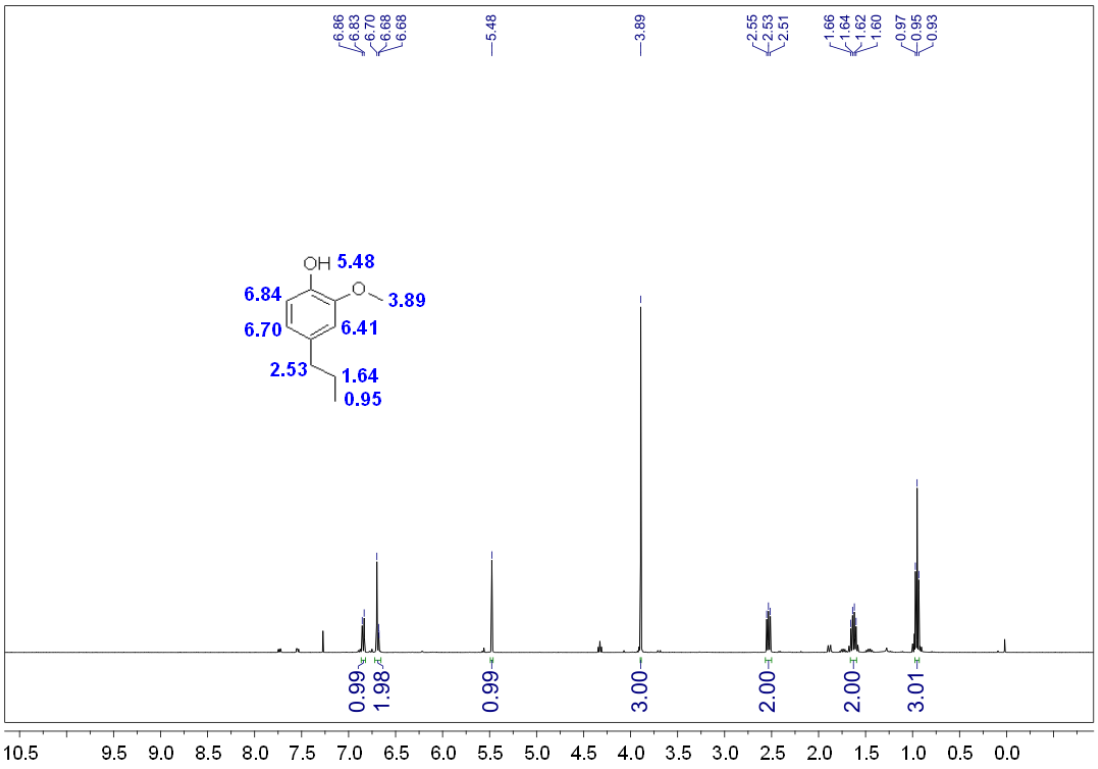


Figure S3. ^{1}H NMR spectrum of propylguaiacol (product 1 in Figure 2A). The trace amount of impurity in this spectrum is propenylguaiacol (products 3 in Figure 2A). These two products cannot be separated entirely over silica column chromatography because of their close structure and polarity.

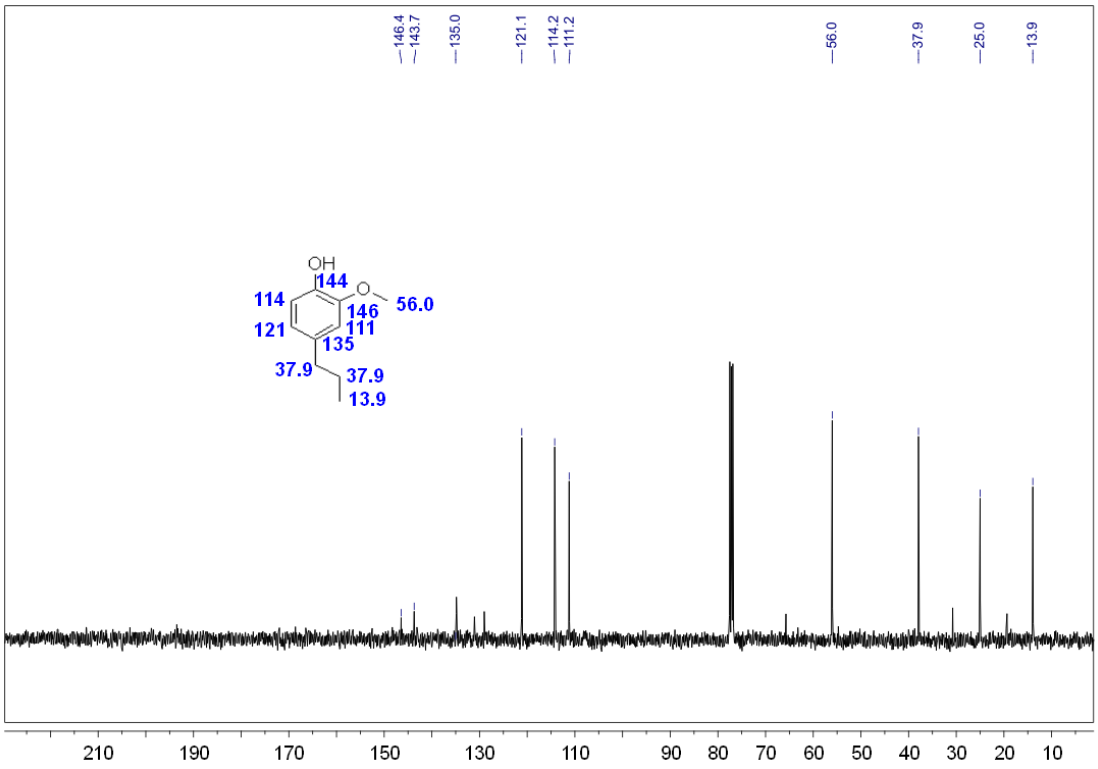


Figure S4. ^{13}C NMR spectrum of propylguaiacol (product 1). The impurity in this spectrum is propenylguaiacol.

(2) MS and NMR of 4-propylsyringol (product 2)

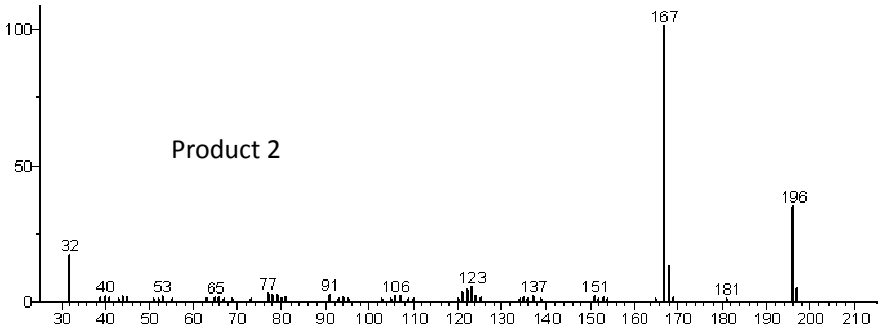


Figure S5. Mass spectrum of 4-propylsyringol (products 2). This structure was confirmed with literature.[3]

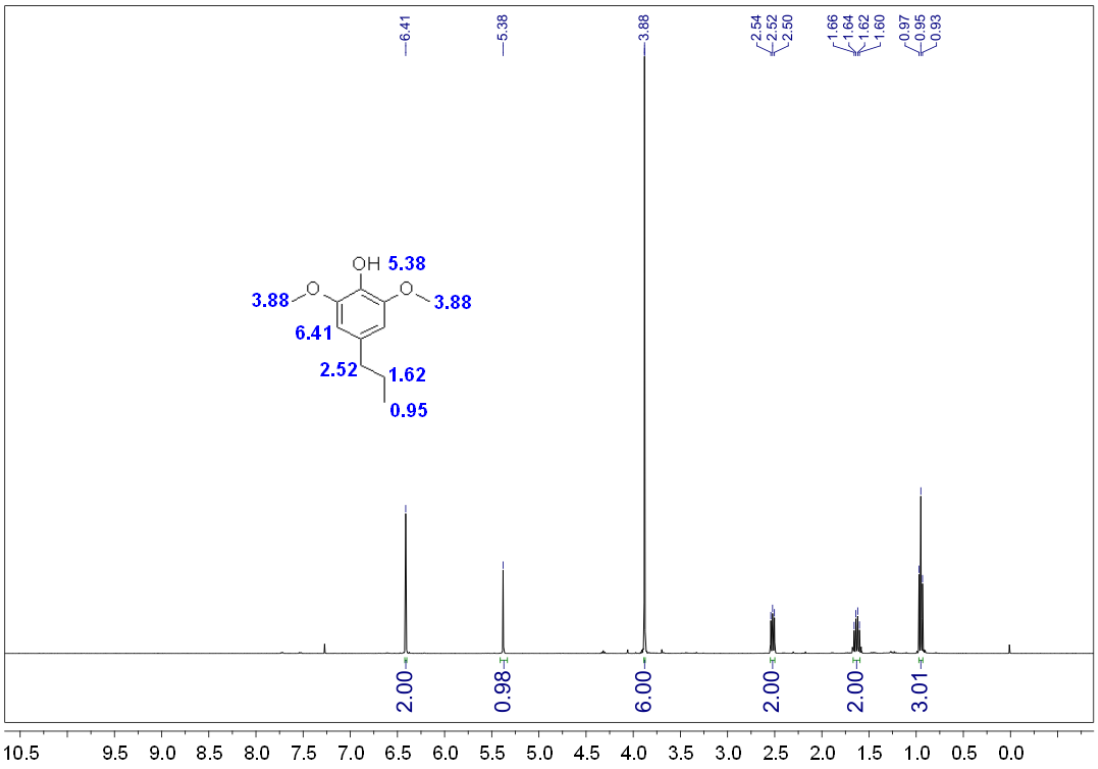


Figure S6. ^{1}H NMR spectrum of 4-propylsyringol (product 2).

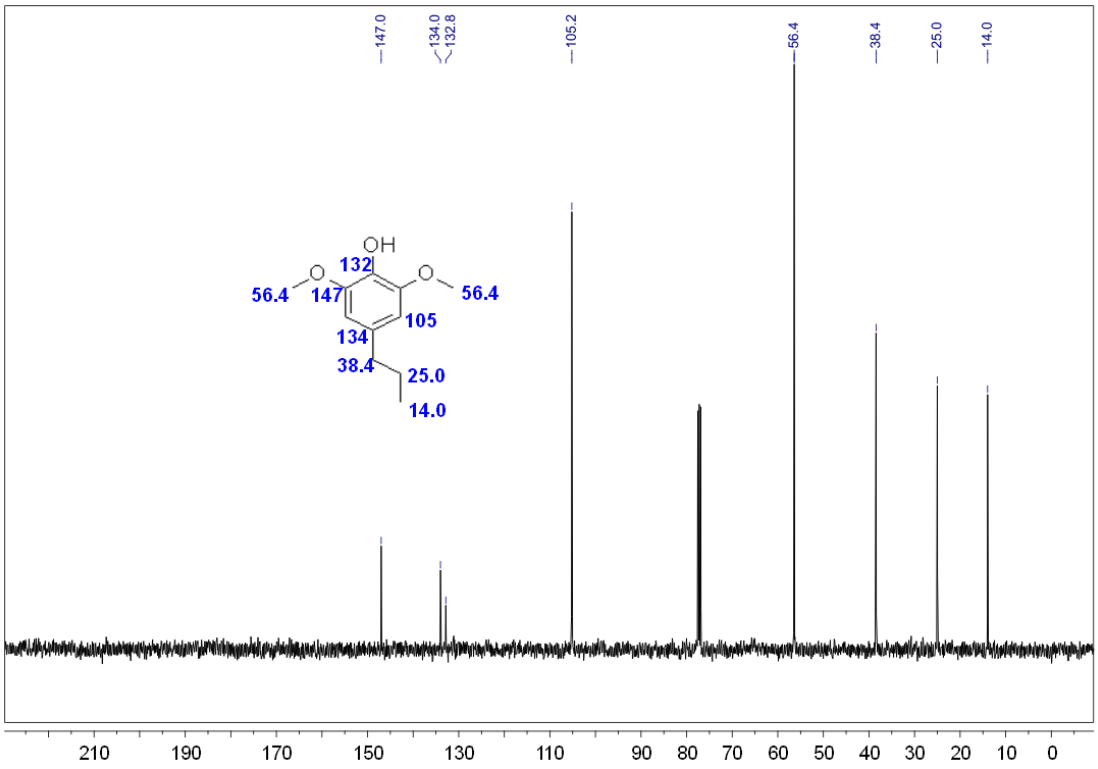


Figure S7. ^{13}C NMR spectra of product 2 (4-propylsyringol). The ^{1}H NMR and ^{13}C NMR data of product 2 were well agreed with reported literature[3].

(3) MS of product 3 (propenylguaiacol)

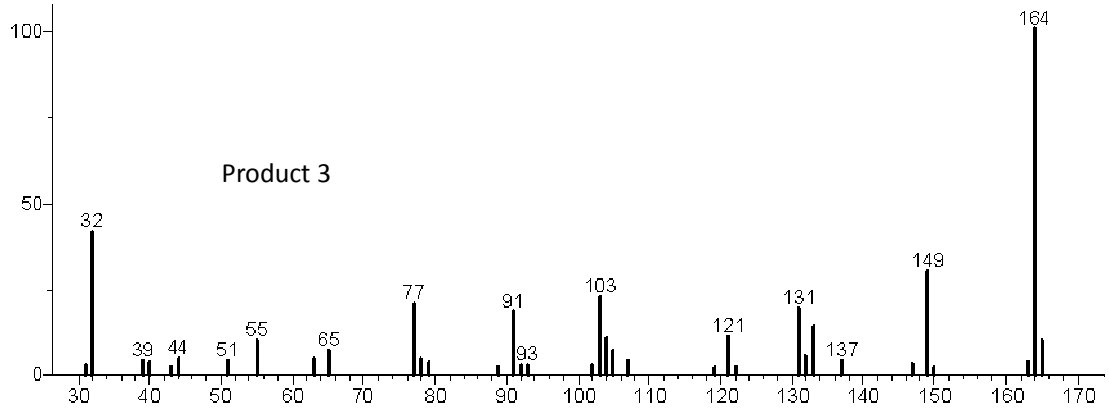


Figure S8. Mass spectra of 4-propenylsyringol (products 3). The position of double bond was confirmed by standard sample of propenylguaiacol.

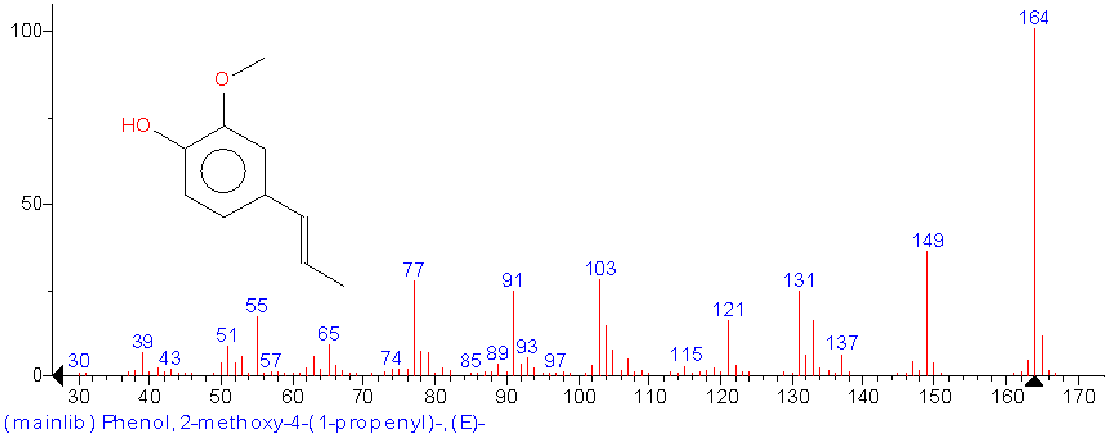


Figure S9. The standard reference mass spectrum of propenylguaiacol, NIST MS number 113236. (Source: NIST webbook online database.)

(4) MS of product dimer.

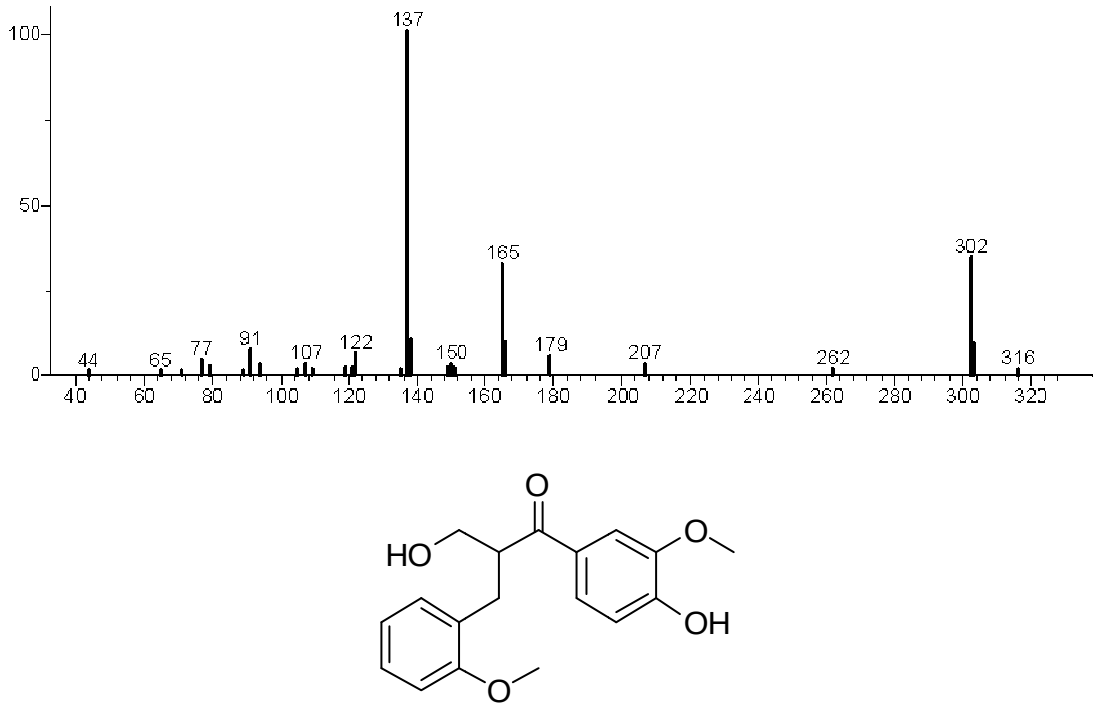


Figure S10. Mass spectra of dimer and its possible structure.

4. The fate of cellulose in LDP reaction

(1) The The possibility of microcrystal cellulose degraded under the conditions similar with LDP reaction.

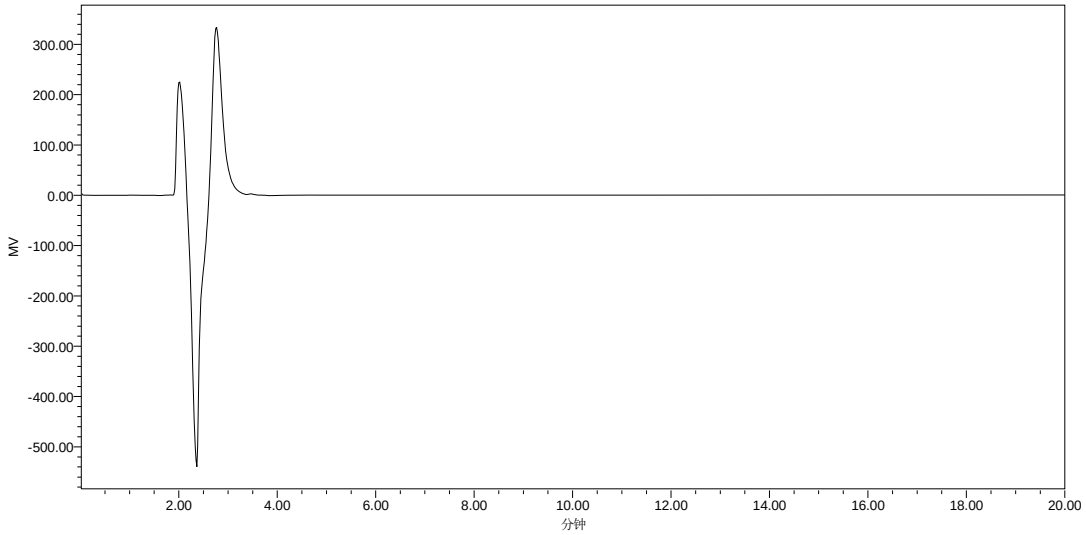


Figure S11. HPLC result of hydrogenation of cellulose under LDP conditions (microcrystalline cellulose 0.50 g, methanol 10.0 mL, Ni/C 50 mg, 200 ^{o}C, 6 h, 1atm Ar). The reaction liquid was analyzed by liquid chromatography (Waters e2695, Prevail™ Carbohydrate ES Columns (5μm, 4.6×250mm), mobile phase acetonitrile/water = 75:25(v/v), flowing rate 1.4 mL min^{-1}, column temperature 30 ^{o}C). The result showed in Figure S11. The peak before 3.5 minute is due to solvent. There is no peak present later than solvent. This result indicates that no sugar or sugar alcohol is detected.

(2) The possibility of cellobiose degraded under the conditions similar with lignin

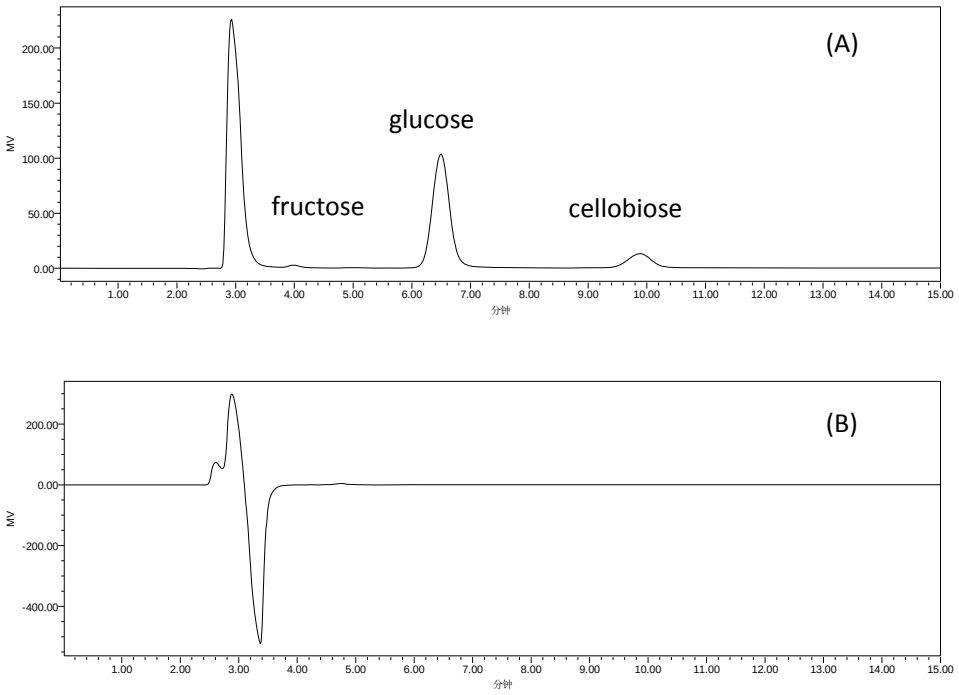


Figure S12. HPLC Retention time of standard sample of fructose, glucose and cellobiose(A), and HPLC result of hydrogenolysis of cellobiose (B) under reaction conditions. Reaction conditions: cellobiose 0.50 g, methanol 2.0 mL, Ni/C 50 mg, 200 ^{o}C, 6 h, 1atm Ar. The analysis procedure of cellobiose was the same with microcrystal cellulose.

5. The proposed fragmented lignin structure.

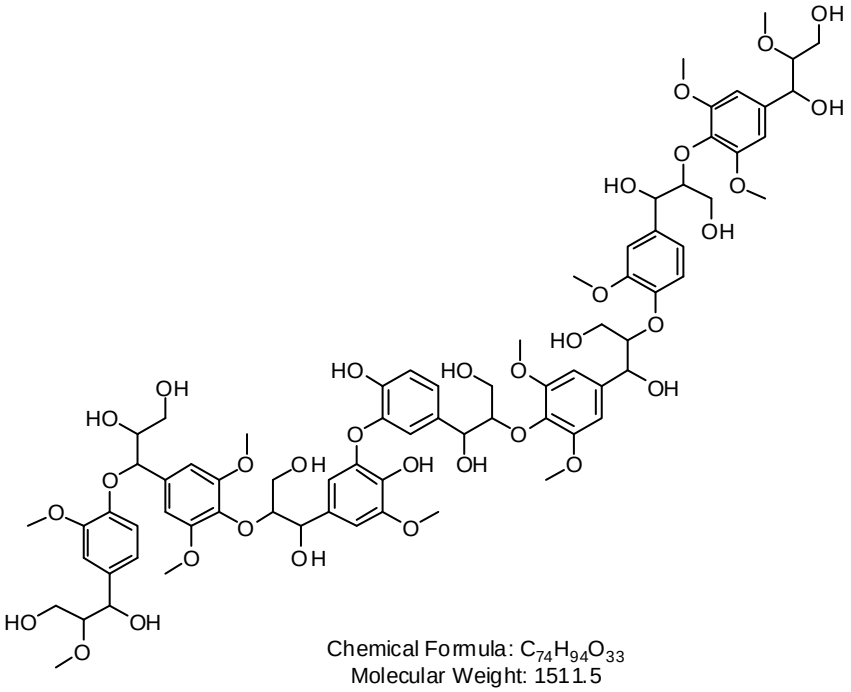
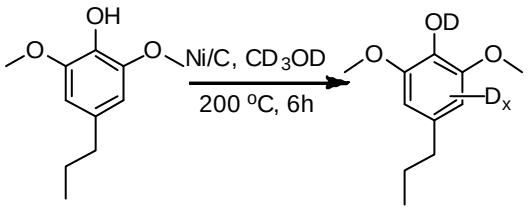


Figure S13. The proposed fragmented lignin structure with molecular weight of 1511.5.

6. Isotopic tests on mechanism of LDP into monomeric phenols

(1) 4-propylsyringol reacted with CD_3OD under LDP condition.



Scheme S3. H/D exchange reaction for 4-propylsyringol

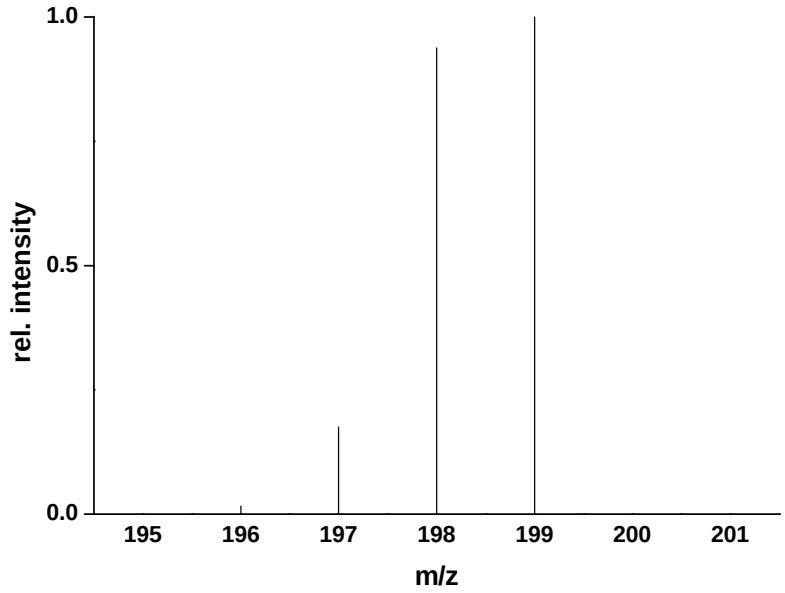


Figure S14. MS spectrum of 4-propyl-syringol from H/D exchange reaction of 4-propyl-syringol in CD_3OD (contribution of ^{13}C is subtracted).

Table S1. Isotopic distribution of deuterated 4-propylsyringol[a]

d0	d1	d2	d3
1	8	44	47

a: Determined by GC-MS. The contribution of ^{13}C was subtracted.

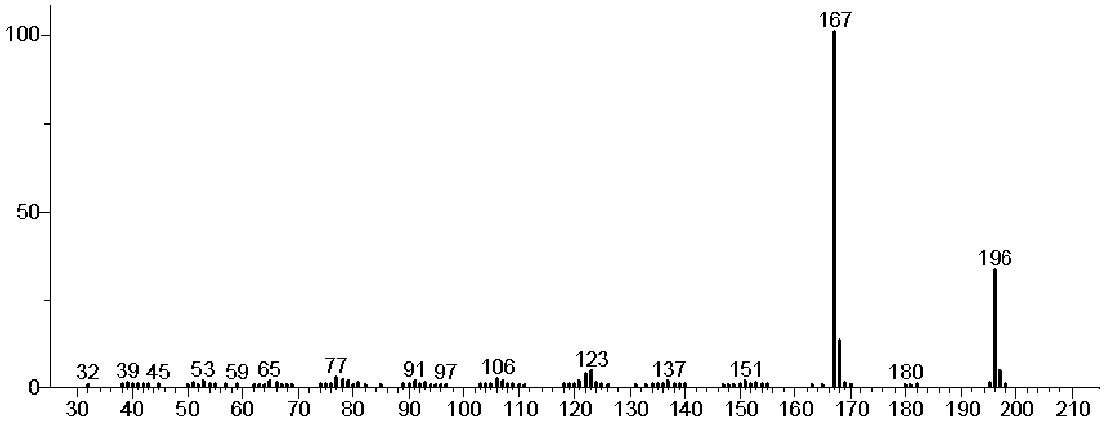


Figure S15. MS spectrum of 4-propylsyringol

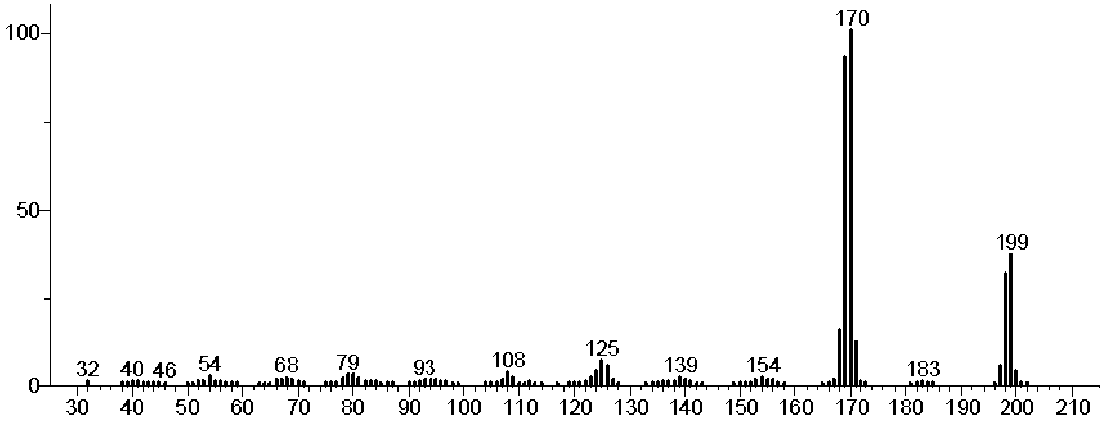


Figure S1. MS spectrum of 4-propylsyringol after H/D exchange reaction

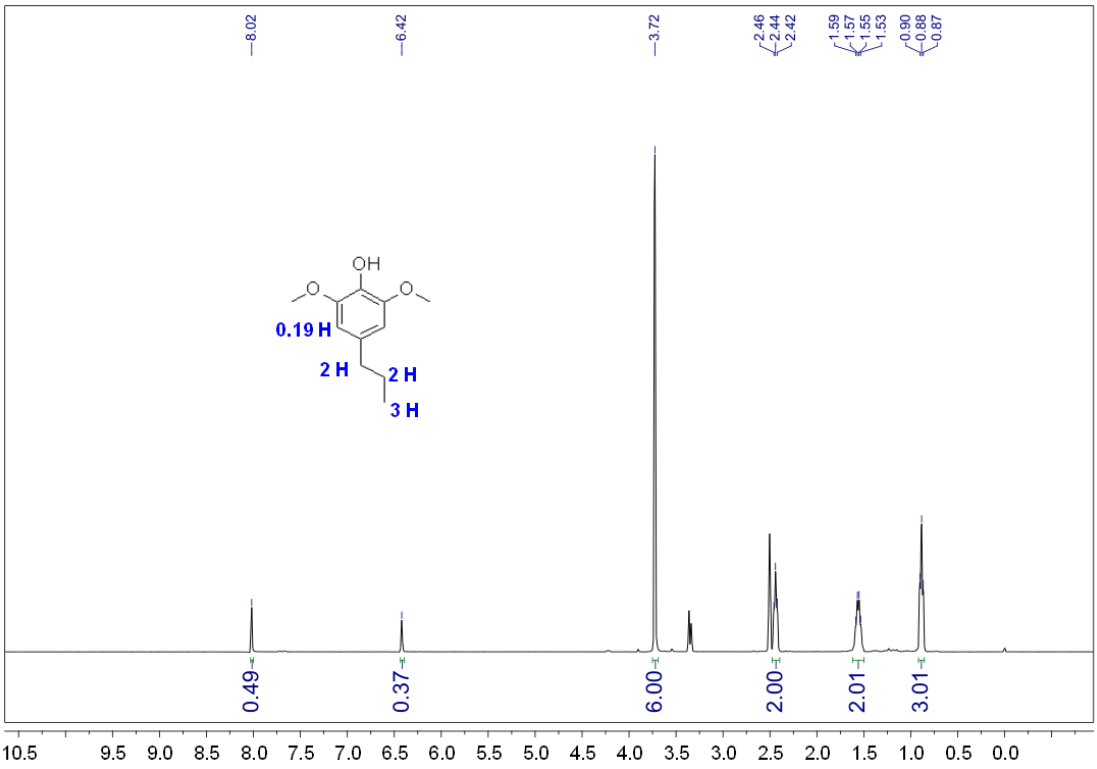
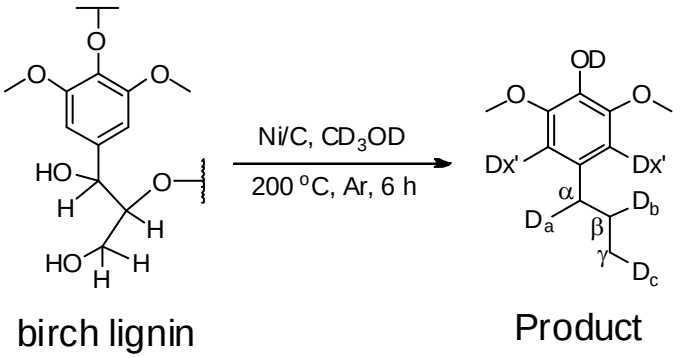


Figure S17. ^{1}H NMR of 4-propylsyringol after H/D exchange reaction.

(2) LDP reaction in CD_3OD



Scheme S4. Deuterated 4-propylsyringol obtained from the depolymerization of lignin in CD_3OD

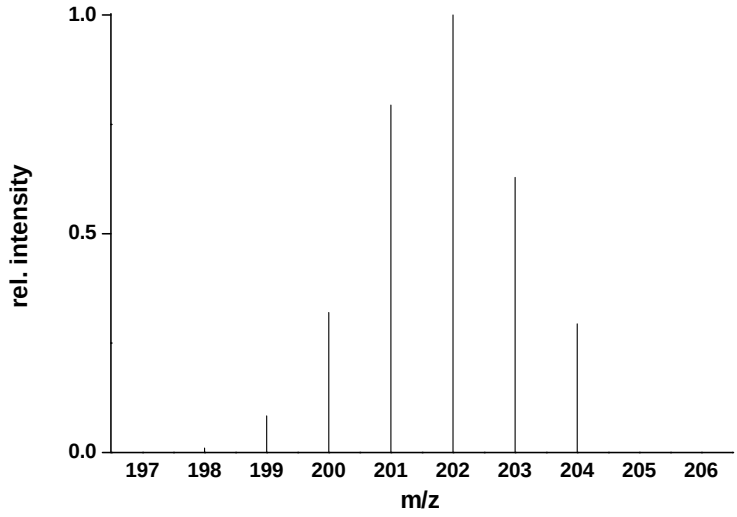


Figure S18. MS spectrum of 4-propylsyringol produced from lignin depolymerization reaction in CD_3OD (The contribution of ^{13}C isotopic natural abundance is subtracted).

Table S2. Isotopic distribution of deuterated 4-propylsyringol produced from lignin[a]

D%						
d2	d3	d4	d5	d6	d7	d8
0	3	10	25	32	20	9

a: Determined by GC-MS. The contribution of ^{13}C was subtracted.

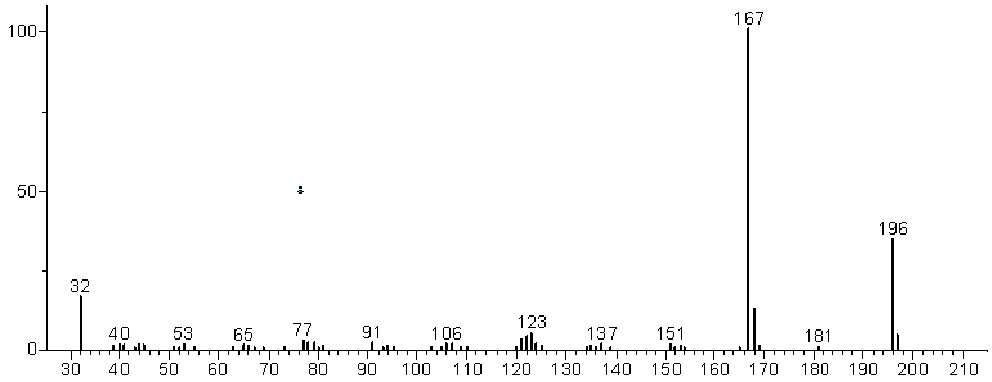


Figure S19. MS spectrum of 4-propylsyringol

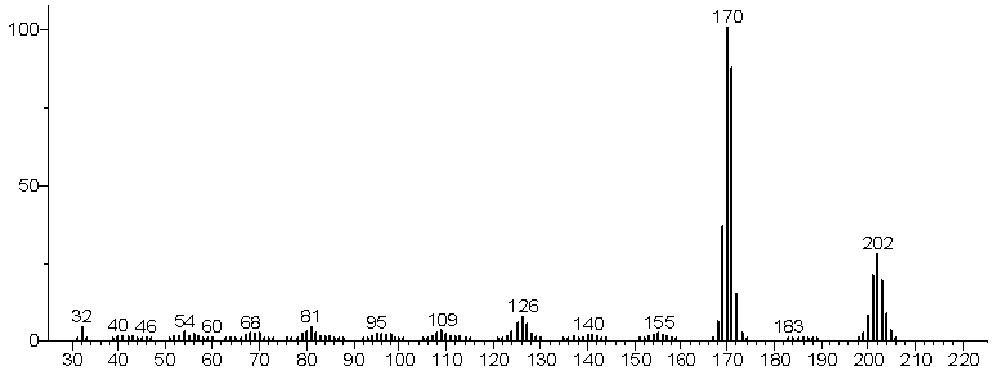


Figure S20. MS spectrum of 4-propylsyringol produced from lignin depolymerization in CD_3OD

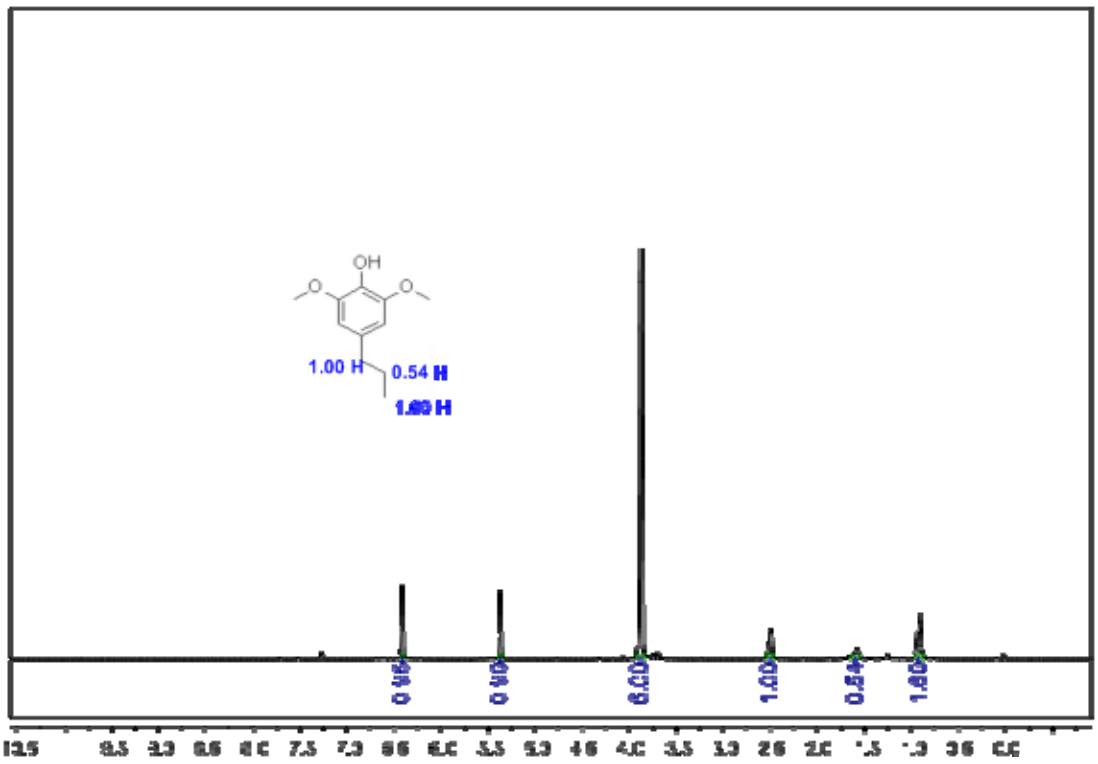


Figure S21. ^{1}H NMR of deuterated 4-propylsyringol obtained from lignin depolymerization in CD_3OD

(3) 1-phenyl-1-propanol reacted with CD_3OD over nickel catalyst under LDP conditions

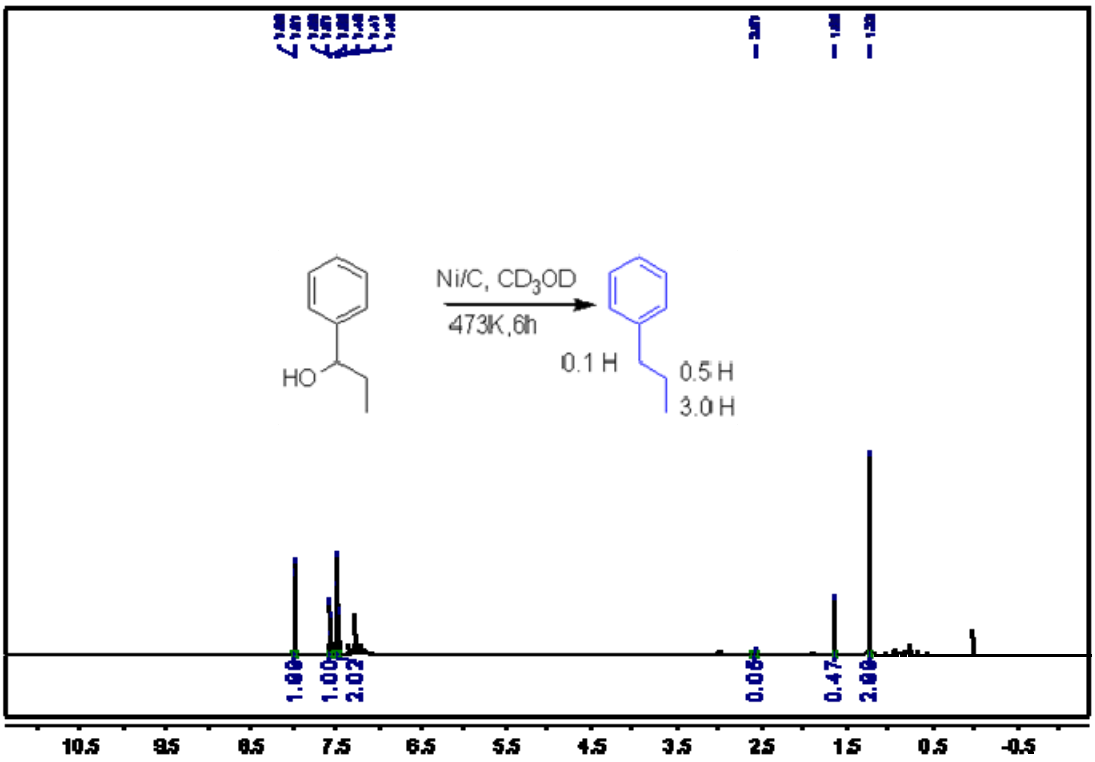


Figure S22. ^1H NMR of 1-phenyl-1-propanol, the chemical shift of different hydrogen atoms are assigned according to literature.[4]

7. Proposed mechanism of Ni-arene catalyzed C-O bonds cleavage

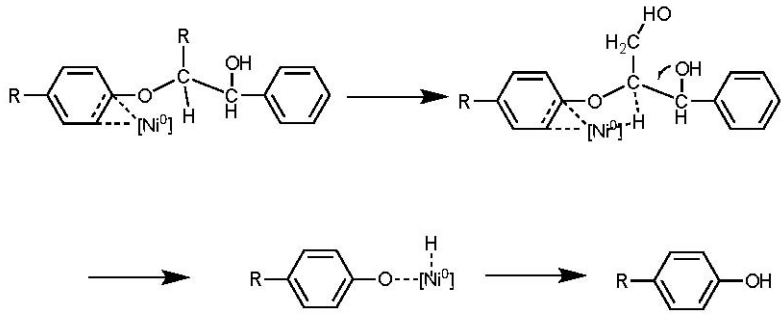


Figure S23. Proposed mechanism of Ni-arene catalyzed C-O bonds cleavage

8. The detection of hydrogen or deuterium gas in effluent gas after reaction

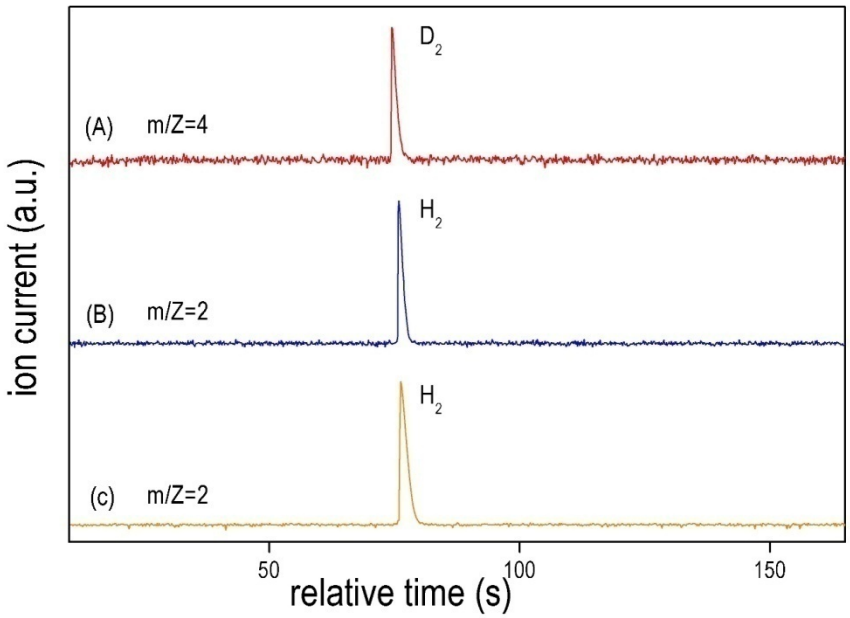


Figure S24. The detection of hydrogen or deuterium gas in (A) CD3OD, (B) ethanol, and (C) ethylene glycol.

9. Explanation of MALDI-TOF results

Principally, average molecular weights (Mn, Mw) can be determined directly from the time domain of MALDI-TOF according to the following equations:

$$Mn = \Sigma(N_i M_i) / N_i$$

$$Mw = \Sigma(N_i M_i^2) / \Sigma(N_i M_i)$$

where N_i and M_i represent signal intensity in peak area and mass for the oligomer containing i monomers, respectively. The polydispersity (PD) was determined from the ratio of Mw to Mn (5). In this study, we calculated the molecular weight (Mw and Mn) using XMASS data processing software from Bruker.

References

(1) Yu, W. Q.; Xu, J.; Ma, H.; Chen, C.; Zhao, J.; Miao, H.; Song, Q. *Catal. Commun.* **2010**, *11*, 493-497.

(2) Alberton, A. L.; Souza, M. M. V. M.; Schmal, M. *Catal. Today* **2007**, *123*, 257-264.

(3) (a)Marques, G.; Gutierrez, A.; del Rio, J. C. *J. Agric. Food. Chem.* **2007**, *55*, 1327-1336. (b)Angle, S. R.; Arnaiz, D. O. *J. Org. Chem.* **1992**, *57*, 5937-5947.

(4) Saavedra, J. Z.; Resendez, A.; Rovira, A.; Eagon, S.; Haddenham, D.; Singaram, B. *J. Org. Chem.* **2011**, *77*, 221-228.

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