Electronic Supplementary Information

(1) Materials

All chemicals were used as received. Sodium lignosulfonate is purchased from ABCR GmbH & Co. KG (ABCR AB137729). Ethylene glycol, cyclohexane, and all metal salts were purchased from Tianjin Kemel Chemical Reagent Co. Ltd. The Pd/AC, Pt/AC, Ru/AC, and MgO were purchased from Aladdin Chemical Reagent Corporation. Hβ, NaY, and ZSM-5 were purchased from Nankai University catalyst Co., Ltd. MCM-41 and SBA-15 was obtained from Changchun Jilin University High-tech. Co., Ltd. Activated carbon (80–100 mesh) was purchased from Beijing Guanghua Timber Mill.

(2) Catalyst preparation procedure

The nickel catalysts were prepared by incipient wetness impregnation method. Typically, nickel nitrate salt ($Ni(NO_3)_2{\cdot}6H_2O$, 16.5139 g) was added into distilled water (48 mL) under stirring to obtain a transparent solution. Then, activated carbon (30 g) was added into the solution at room temperature. The sample was covered by culture dish to maintain surface incipient wetness through 24 h. The sample was then dried at 393 K for overnight. The dried sample was reduced in a horizontal furnace in H_2 flow (30 mL min^{-1}). The reduction temperature reached 673 K in 60 min and was maintained for 2 h. The zeolite-supported catalysts were reduced at 823 K for 2 h. The metal loading for each nickel and copper based catalysts is 10% wt. The loading amount of Pd/AC, Ru/AC, and Pt/AC is 5% wt. The procedure for the preparation of binary metal catalysts were similar to the nickel catalysts, and the loading of second metal composition was 1 wt % of support.

(3) Synthesis of phenolic β-O-4 lignin model compound

The lignin model compound guaiacyl glycerol-β-guaiacyl ether (GGGE) was prepared from acetovanillone through a multistep synthesis route, using a reported procedure with minor modification [1].

Briefly, acetovanillone (1.992 g) was dissolved in EtOH (50 mL), into which the $CuBr_2$ ethanol solution (4.467 g $CuBr_2$ in 50 mL EtOH) was added. The reaction was monitored by TLC. The product of **1a** was purified over silica column. Guaiacol was added dropwisely to sodium ethylate solution (50 mL) to prepare **1b**. Then **1a** and **1b** were mixed in DMF (35 mL). The mixture was placed in an ice bath after stirring for several minutes. The pH value of the solution was adjusted with diluted HCl to 3 and the solution was extracted with $CHCl_3$ for several times. The organic layer was dried by $MgSO_4$, and filtered. The solvent was removed by evaporation under reduced pressure to give viscous oil, which was further purified over column silica gel using benzene/ethyl acetate (3:1). The obtained **2a** was dissolved in EtOH (30 mL), followed by adding formaldehyde (30 mL) and K_2CO_3 (1.7g). The solution was stirred at 323 K for 2 h. Diluted HCl was added to adjust the pH to 3 and the solution was extracted with $CHCl_3$, the organic layer was dried over $MgSO_4$, filtered, evaporated under reduced pressure and purified on silica column to obtained **3a**. $NaBH_4$ (0.17g, 45 mmol) was added to a solution of **3a** (4.8 g, 17.8 mmol) in NaOH solution (0.1mol L^{-1},100 mL). The reaction mixture was stirred at room temperature overnight and then the pH of the mixture was adjusted to 3 by diluted HCl. The mixture was washed by distilled water, extracted with $CHCl_3$, dried over $MgSO_4$, filtered, and concentrated under vacuum. The resulted oil was purified over silica column and crystallized in ethyl ether.

^1H NMR and ^{13}C NMR spectra are similar with literatures [2].

^1H NMR (d6-DMSO) δ7.15~6.84 (m,7H, aromatic H), 5.65 (d,1H, Ar-OH), 4.97(d, 1H, $C_\alpha H$), 4.0 (m, 1H, $C_\beta H$), 3.92 (s, 3H, OCH_3), 3.90 (s,3H, OCH_3), 3.66~3.50 (m, 2H, $C\gamma H_2O$), 3.49 (d, 1H, $C_\alpha OH$), 2.72 (m, 1H, $C_\gamma OH$); ^{13}C NMR (d6-DMSO) δ150.3, 149.0, 147.6, 146.5, 133.6, 121.6, 121.3, 120.4, 119.6, 113.2, 112.0, 110.5, 85.0 (threo C_β),84.4 (erythro C_β), 72.3 (threo C_α), 71.6 (erythro C_α), 60.7 (threo C_γ), 60.6 (erythro C_γ), 56.2 (threo $ArOCH_3$), 56.0 (erythro $ArOCH_3$);

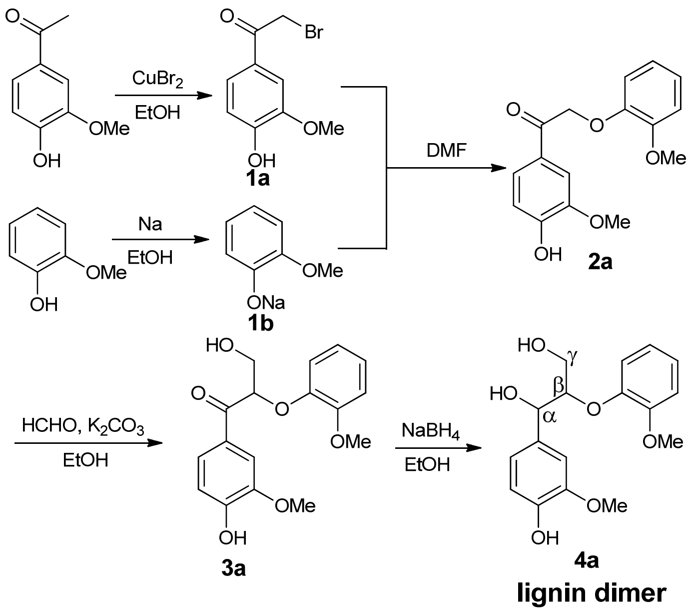


Figure S1 Synthetic route of lignin model compound, guaiacyl glycerol-β-guaiacyl ether (GGGE)

(4) Catalytic reaction

In a typical run, sodium lignosulfonate (2.00 g) was dissolved in ethylene glycol (120 mL) to give a brown transparent solution. The solution combined with catalyst was transferred into a 600-mL autoclave (Parr instruments). The reactor was sealed and purged with H_2 several times in order to replace air. When the desired temperature (473 K) was achieved, H_2 gas was charged to 5 MPa and the stirring speed was set at 1000 r.p.m. The reaction was stopped after a certain time. The reactor was cooled down to room temperature before sampling and analyzing.

(5) Product extraction

The liquid sample was centrifuged, and then transferred to a funnel (500 mL), followed by sequential extracting with cyclohexane for five times (1 × 160 mL, 4×120 mL, totally 640 mL). The solvent was removed in a rotary evaporator under reduced pressure at 323 K. The finial products was dissolved in ethanol (5 mL) and then injection into GC to determine the selectivity of products.

(6) Products analysis

The product was analyzed by Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (30m×0.25mm×0.32mm) and a flame ionization detector (FID). The temperature of the column was initially kept at 373 K for 2 min, and the column temperature was then increased at a rate of 20 K min^{-1} to 523 K. The quantification of products was performed on GC-MS system (Agilent 6890 N GC/5973 MS detector) using helium as carrier gas under split model (60:1). Typically, the inject amount is 1 μL) with an autosampler. The temperature program of GC-MS was same to GC used.

The amount of guaiacol in lignosulfonate was analysed using UV spectroscopy. The absorption spectra of lignosulfonate were recorded by a UV/VIS spectrophotometer (UV-2550, Shimadzu) with a slit width of 1 cm. The characteristic absorption of lignosulfonate is 276 nm. The amount of guaiacol in lignosulfonate was calculated using an established guaiacol standard curve (Figure S2). Typically, precisely sampling 0.50 mL reaction liquid was diluted by 1000 times with ethylene glycol.

(7) Definition of the conversion and product selectivity

$$\text{Conversion of lignosulfonate} = \left(1 - \frac{\text{the amount of unreacted lignosulfonate}}{\text{the added lignosulfonate}}\right) \times 100\%$$

$$\text{Selectivity of product } (\mathrm{P}i) = \frac{\text{the integrated GC peak area of product } (\mathrm{P}i)}{\text{the sum up integrated GC peak area of total detected product} (\Sigma \mathrm{P}i)} \times 100\%$$

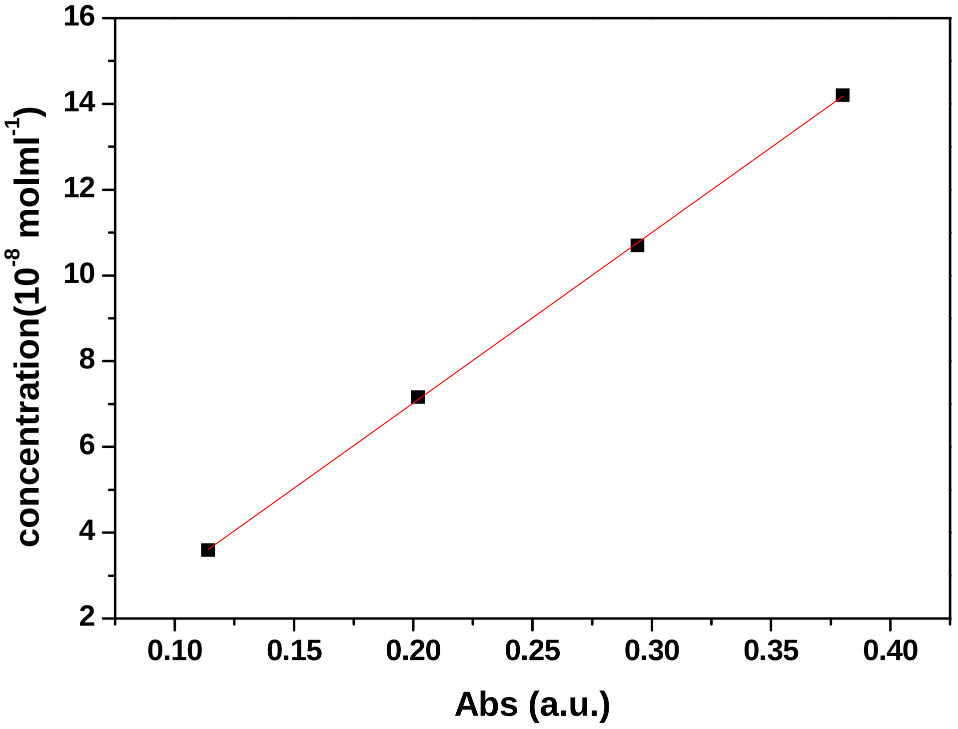


Figure S2 Guaiacol standard curve to determin the amount of aromatic rings in lignosulfonate. Regression equation is y=39.74*x-0392, R=0.9998. y and x is representation of the guaiacol concentration and its absorption at 276 nm respectively.

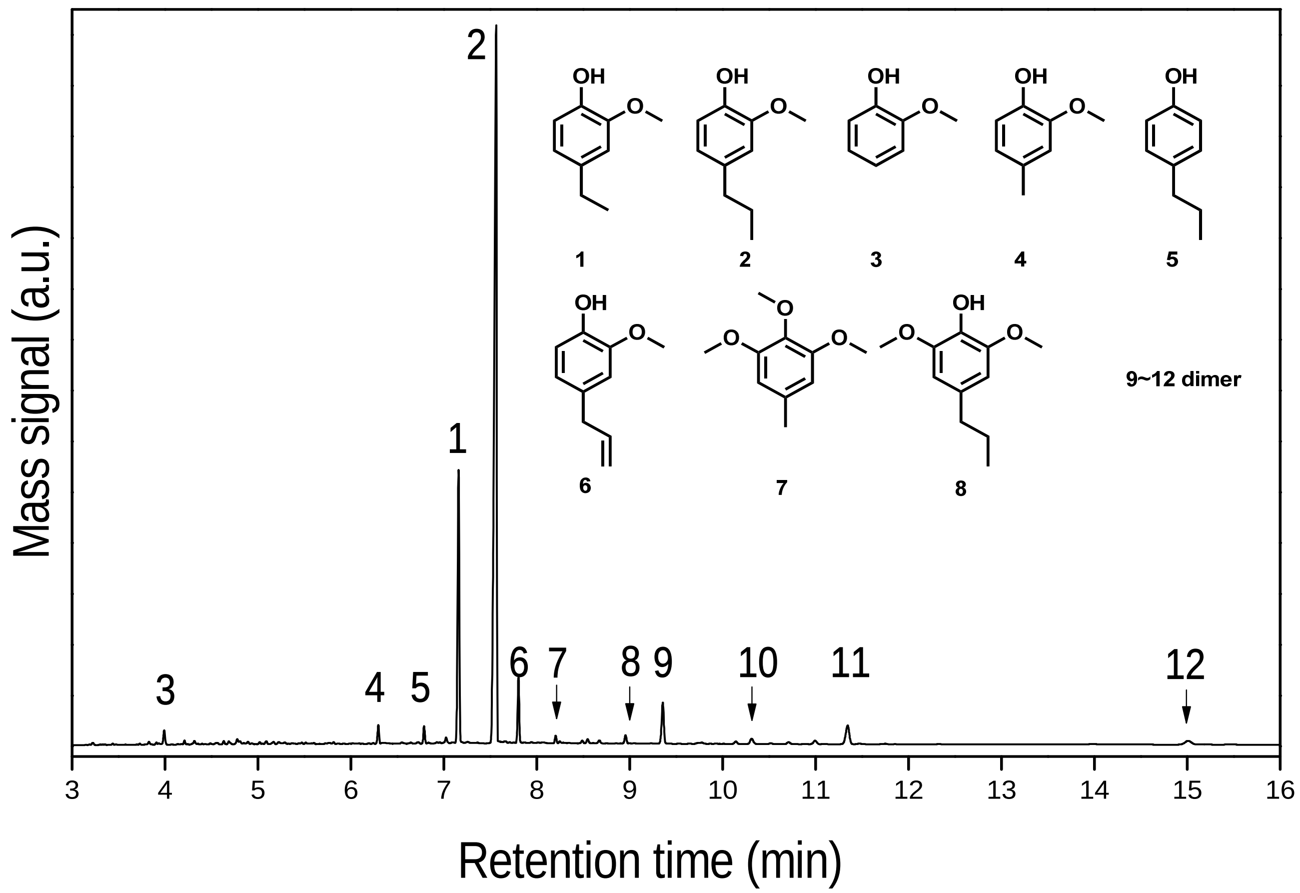


Figure S3 Spectrum of gas chromatography of a reaction mixture (entry 9, Table 1). Inset graphics depict the structures of detected products. Their mass spectra and reference mass spectra are given in **ESI**.

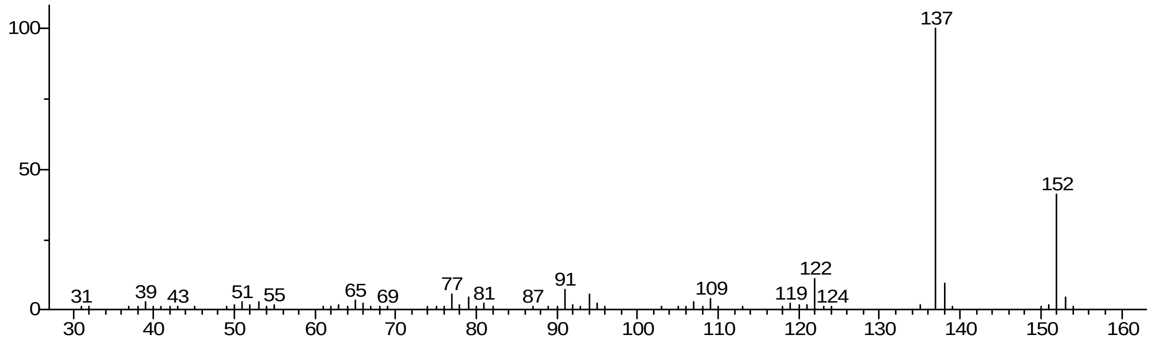
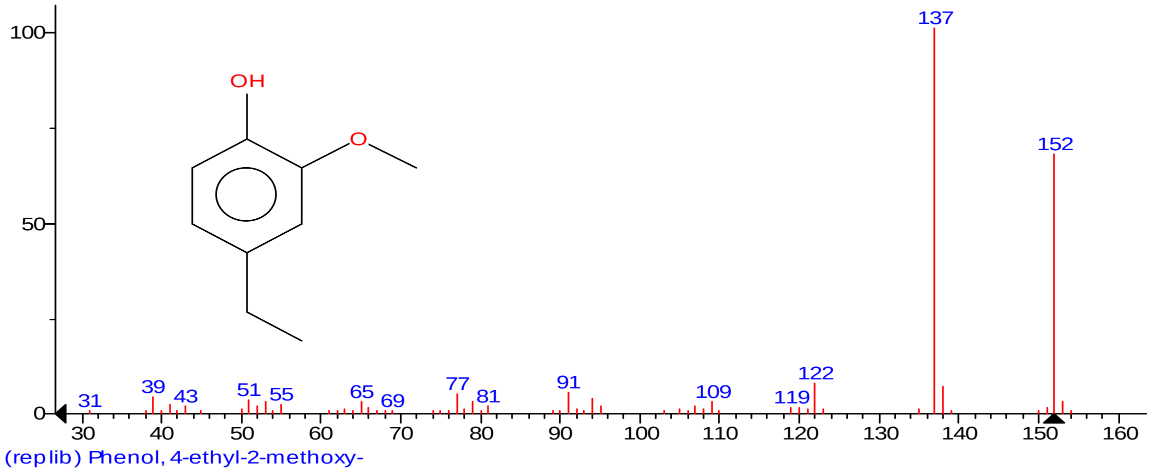


Figure S4 Mass spectrum of major product 1 (4-ethyl-guaiacol)



5 Figure S5 The standard reference mass spectrum of 4-ethyl-guaiacol, NIST MS number 135148. (Source: NIST webbook online database.)

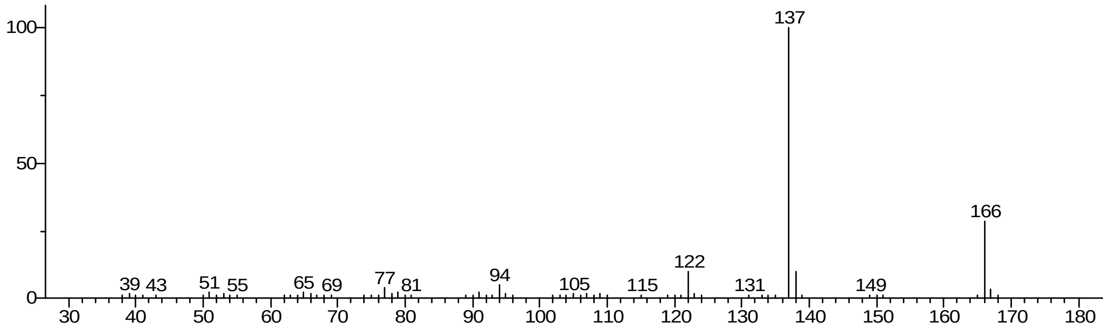


Figure S6 Mass spectrum of major product 2 (4-propyl-guaiacol)

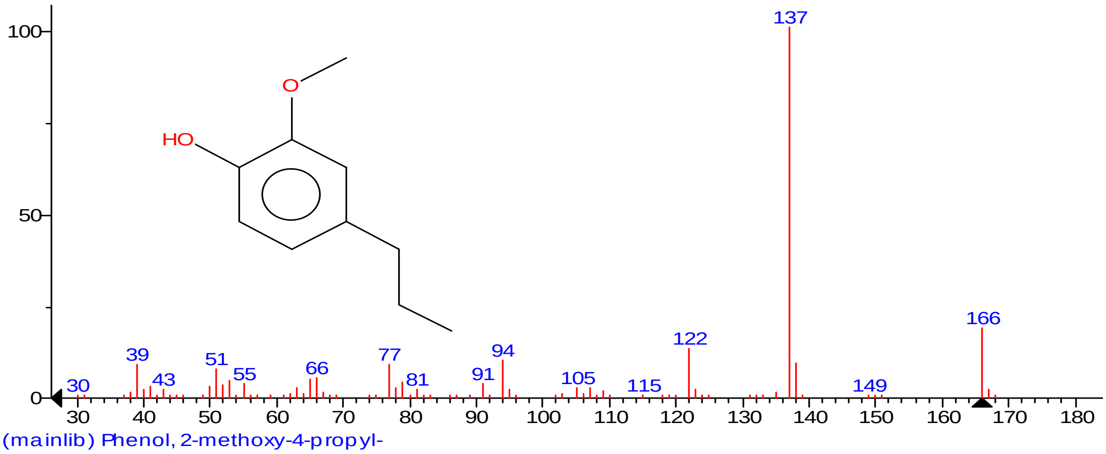


Figure S7 The standard reference mass spectrum of 4-propyl-guaiacol, NIST MS number 135362.
5 (Source: NIST webbook online database.)

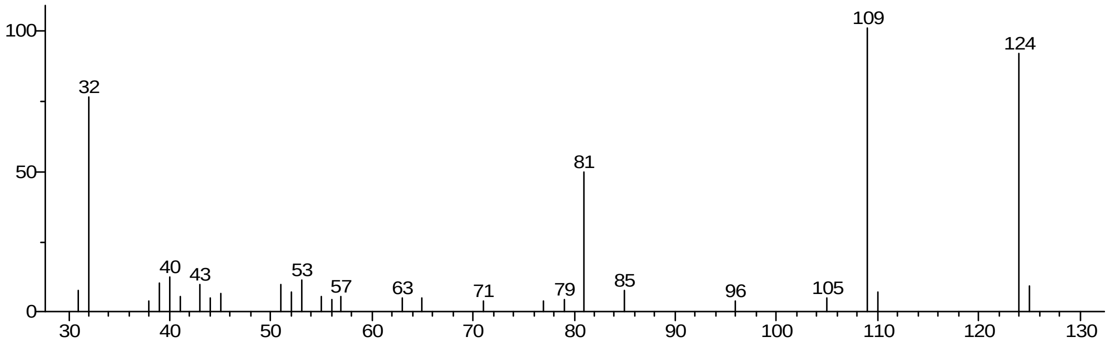


Figure S8 Mass spectrum of product 3 (guaiacol)

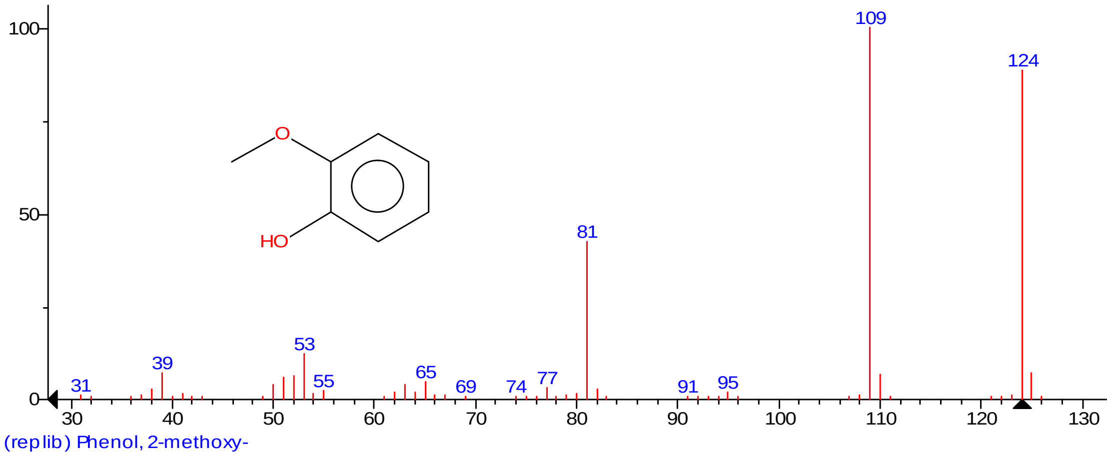


Figure S9 The standard reference mass spectrum of guaiacol, NIST MS number 291437. (Source: NIST webbook online database.)

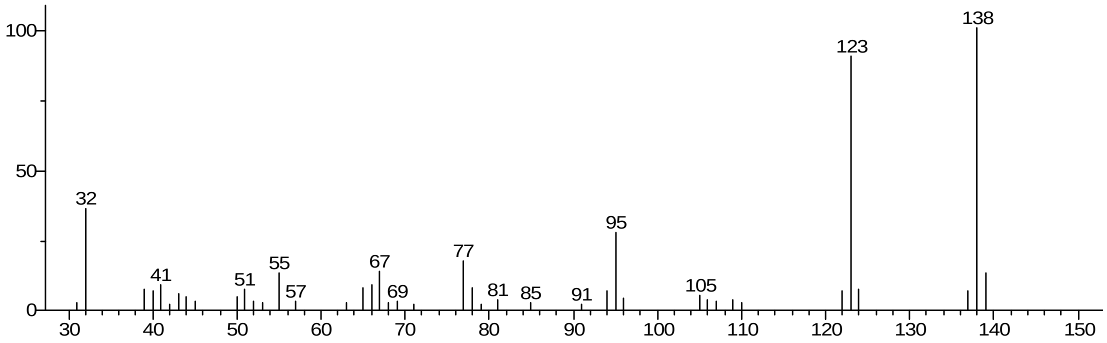


Figure S10 Mass spectrum of product 4 (4-methyl-guaiacol)

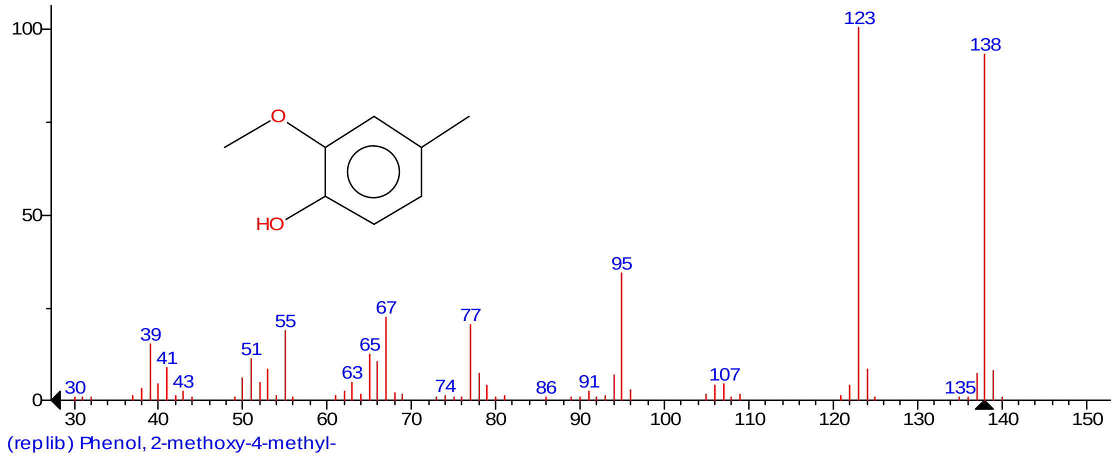


Figure S11 The standard reference mass spectrum of 4-methyl-guaiacol, NIST MS number 233910. (Source: NIST webbook online database.)

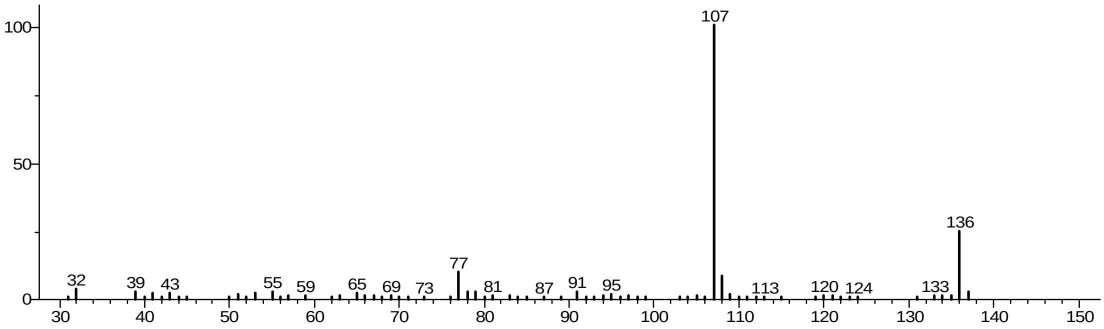


Figure S12 Mass spectrum of product 5 (4-propyl-phenol)

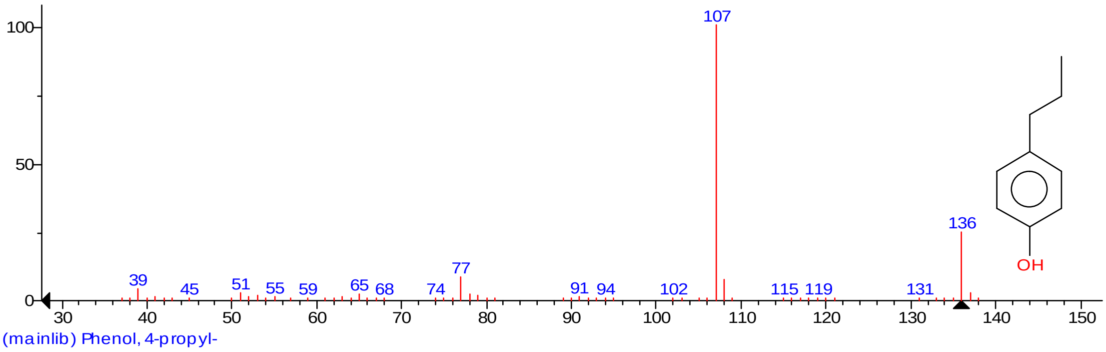


Figure S13 The standard reference mass spectrum of 4-propyl-phenol, NIST MS number 229180. (Source: NIST webbook online database.)

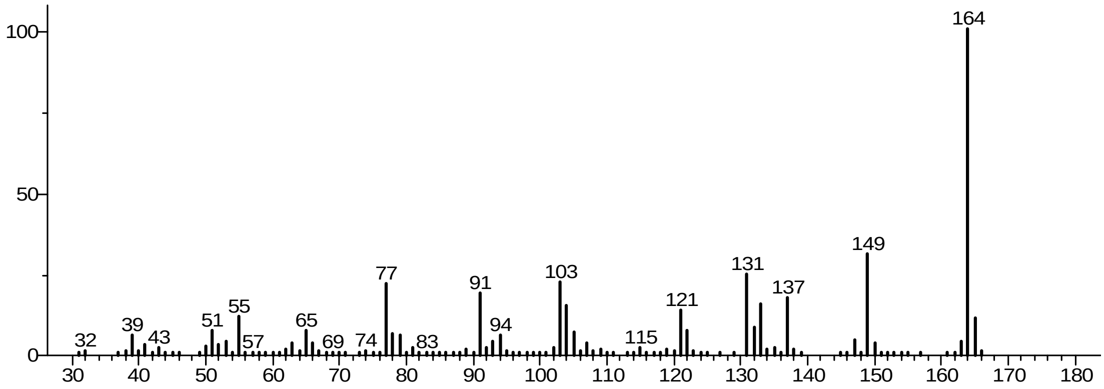


Figure S14 Mass spectrum of product 6 (4-allyl-guaiacol)

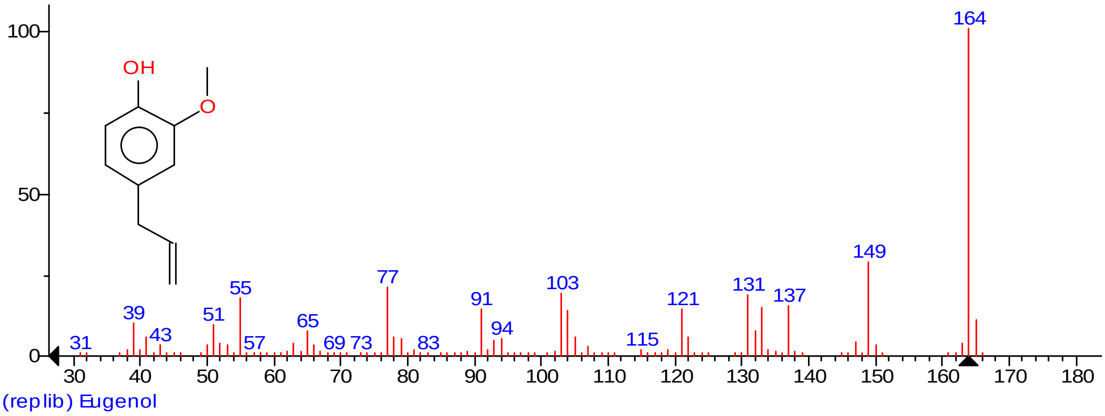


Figure S15 The standard reference mass spectrum of 4-allyl-guaiacol, NIST MS number 291519. (Source: NIST webbook online database.)

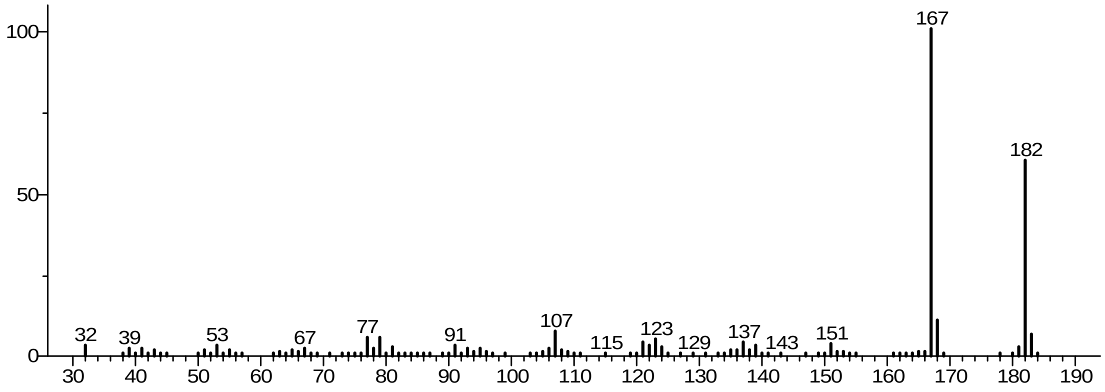


Figure S16 Mass spectrum of product 7 (1,2,3-trimethoxy-5-methyl-benzene)

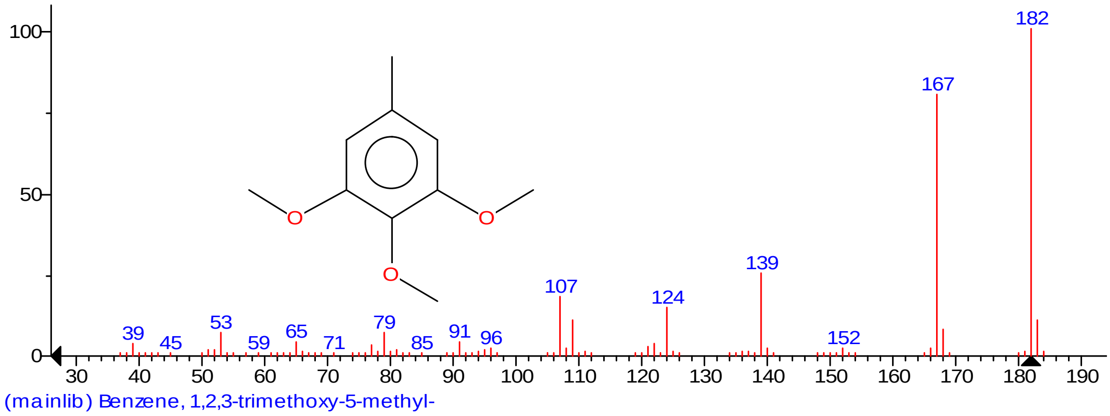


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Figure S17 The standard reference mass spectrum of 1,2,3-trimethoxy-5-methyl-benzene, NIST MS number 236982. (Source: NIST webbook online database.)

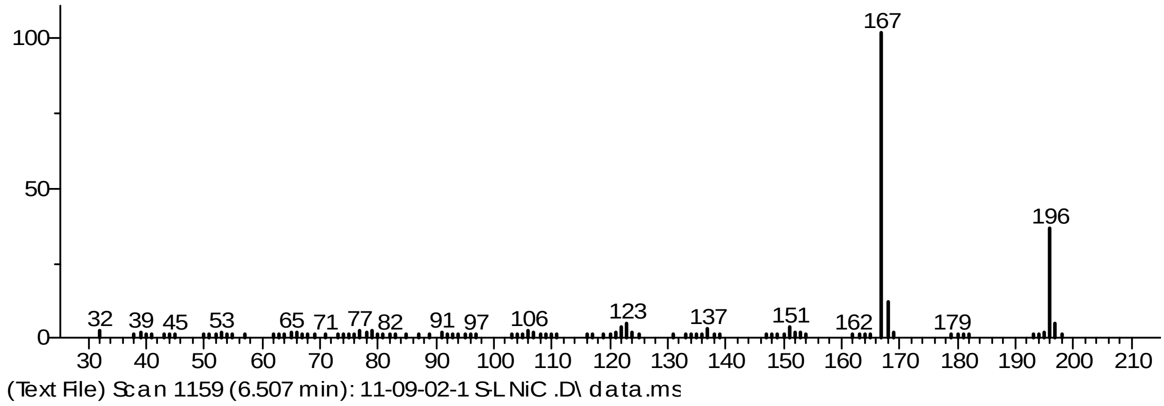

Figure S18 Mass spectrum of product 8 (4-propyl-syringol), and its structure was documented with mass fragments[3].

Dimer of hydrogenolysis lignosulfonate

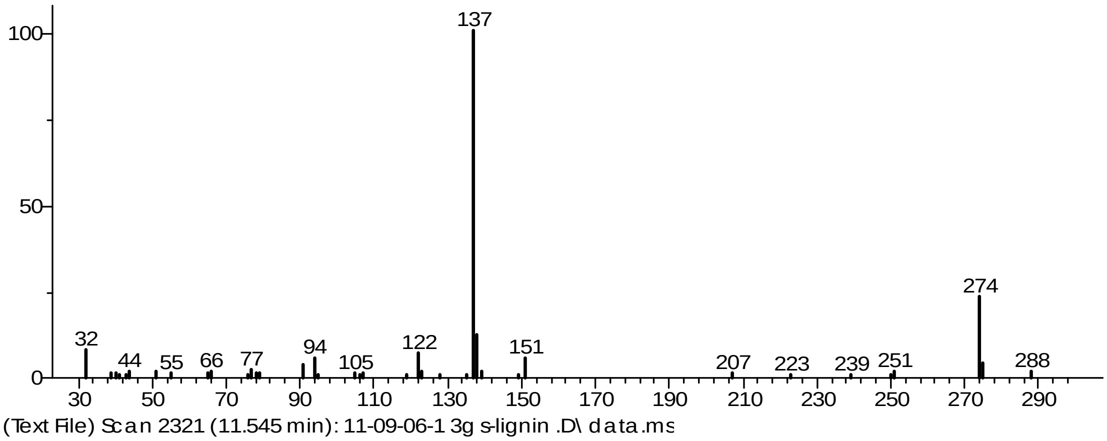

Figure S19 Mass spectrum of product 9 (dimer, 1,2-diguaiacylethane), The mass fragments were assigned according to literature [4].

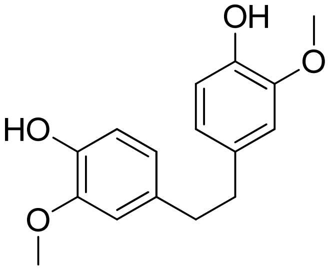

Figure S20 Structure of product 9.

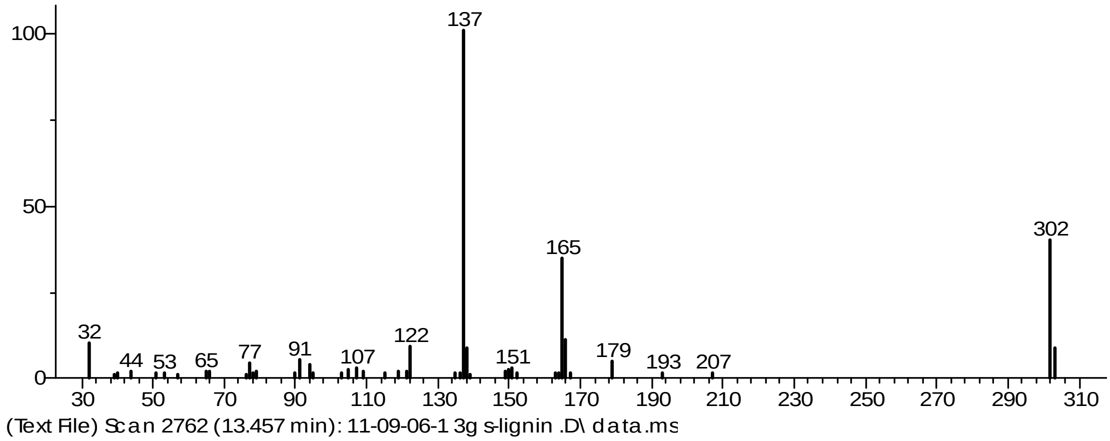

Figure S21 Mass spectrum of product 10 (dimer, 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-1-propanone).

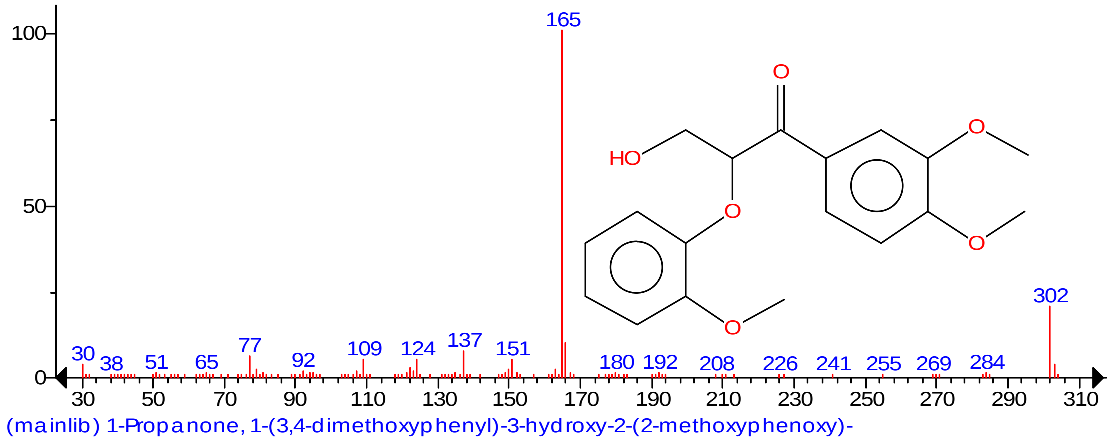

Figure S22 The reference mass spectrum of 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-1-propanone).

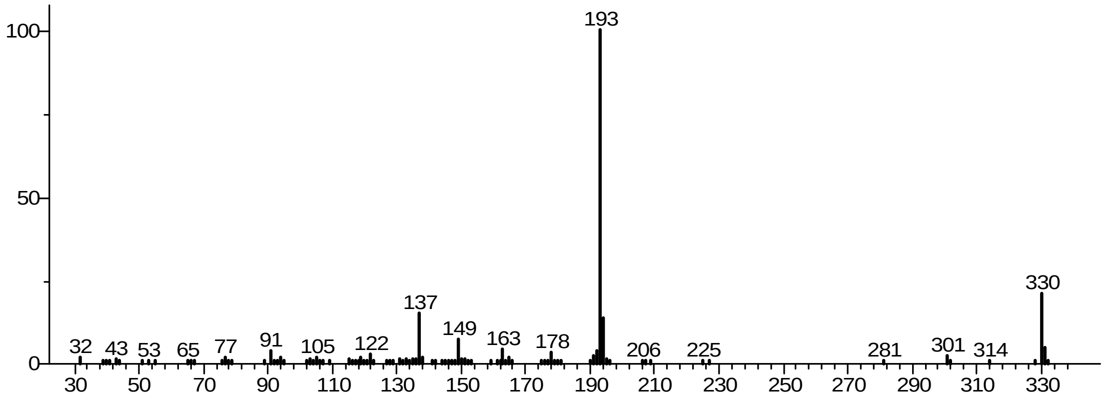

Figure S23 Mass spectrum of product 11 (dimer, the probable structure was listed in Fig. S25).

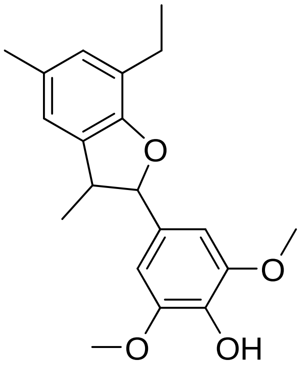

Figure S24 The probable structure of dimer 11.

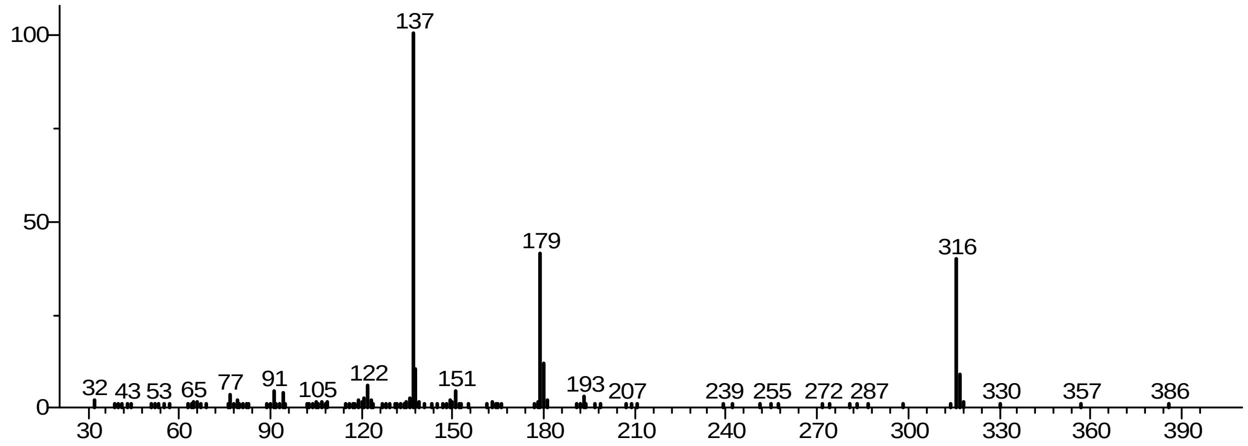

Figure S25 Mass spectrum of product 11 (dimer).

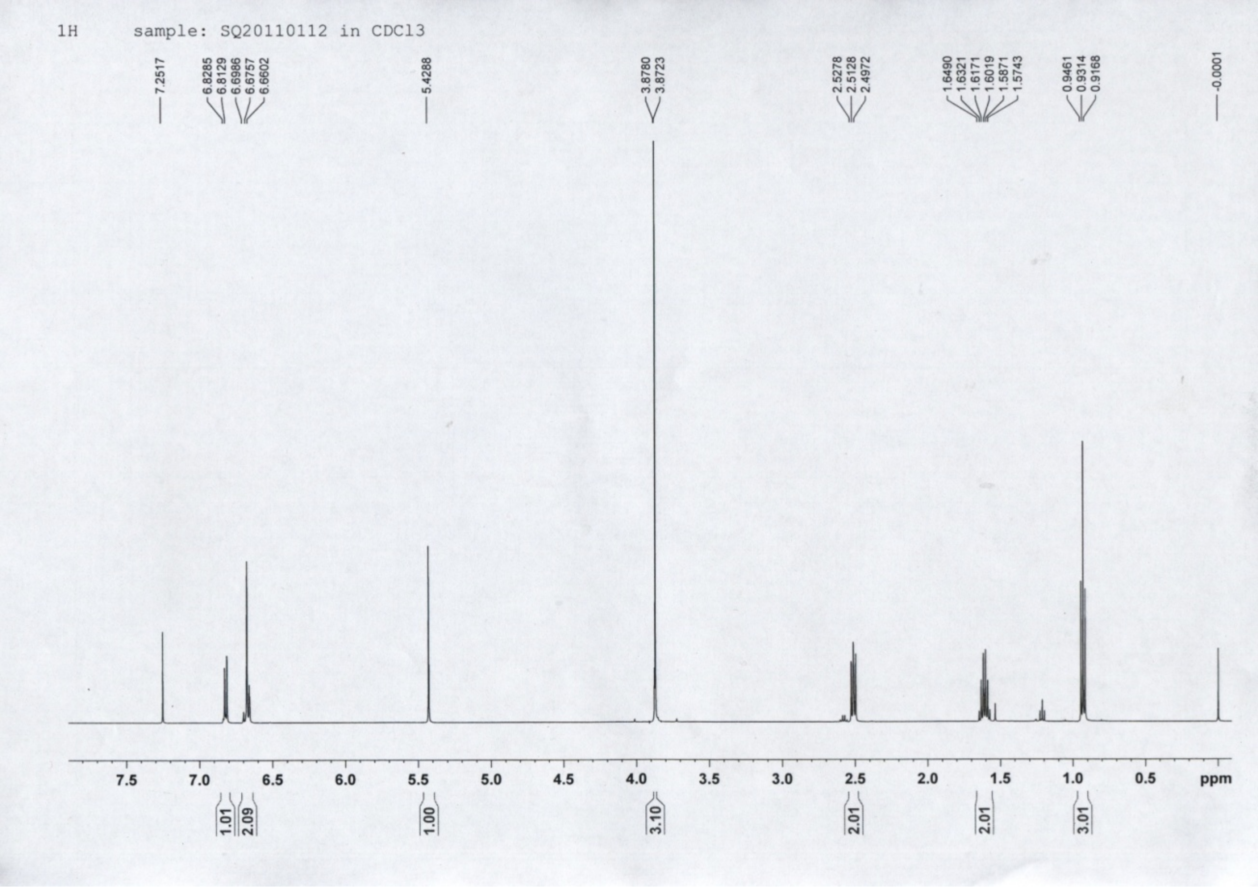

Figure S26 ^{1}H NMR of 2-Methoxy-4-(n-propyl) phenol.

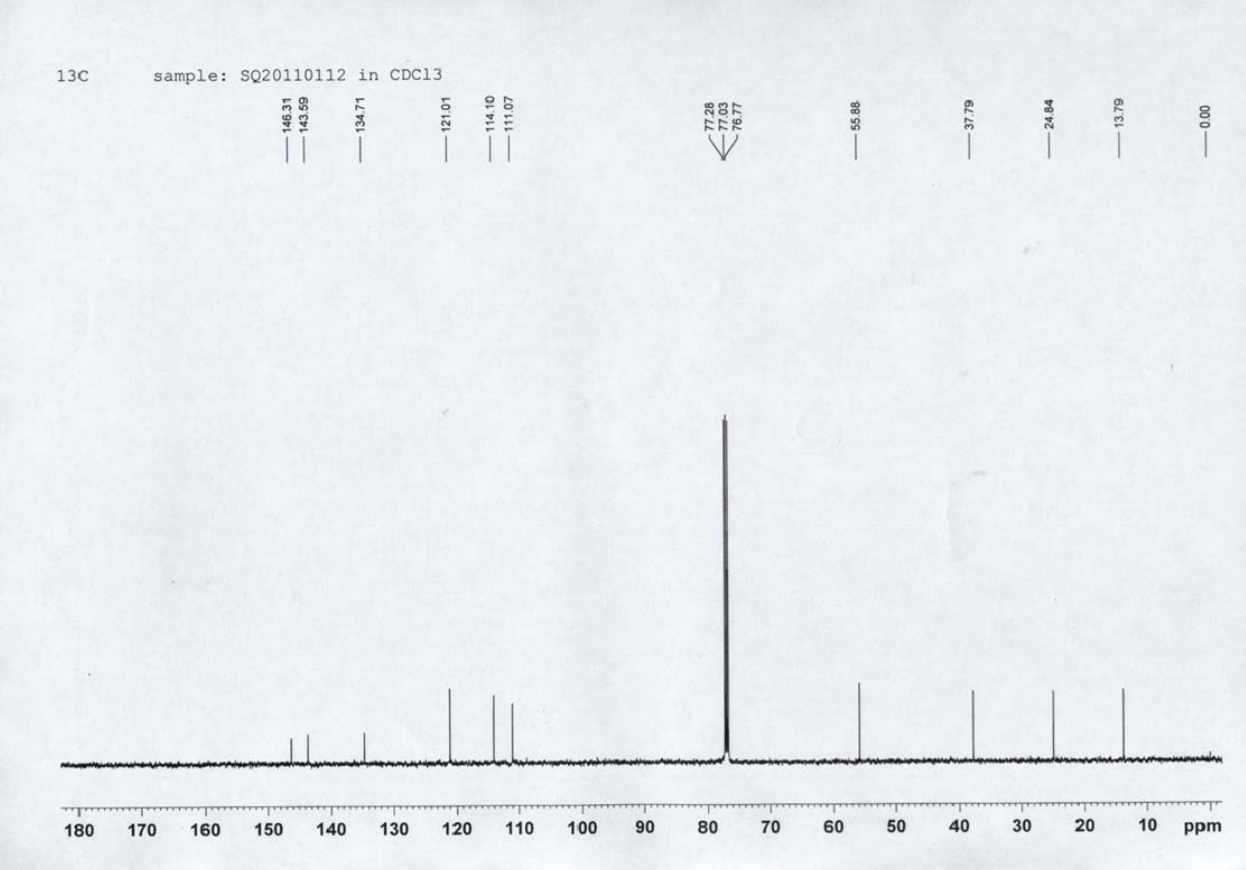

Figure S27 ^{13}C-NMR of 2-Methoxy-4-(n-propyl) phenol.

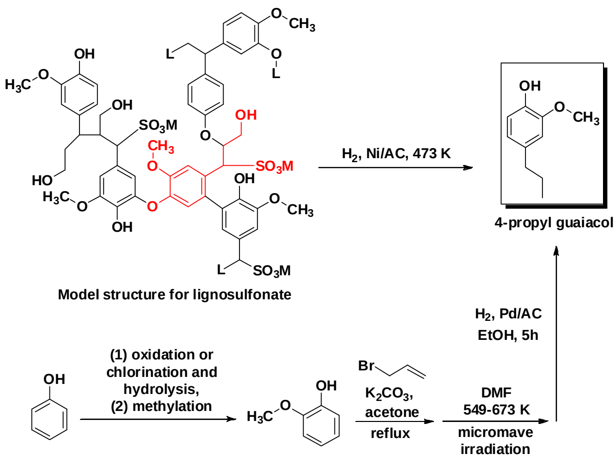

Figure S28 A representative example of direct and cost-effective synthesis of 4-propyl guaiacol (PA) through catalytic hydrogenolysis of lignosulfonate vis synthetic organic routes starting from petroleum-based molecules.

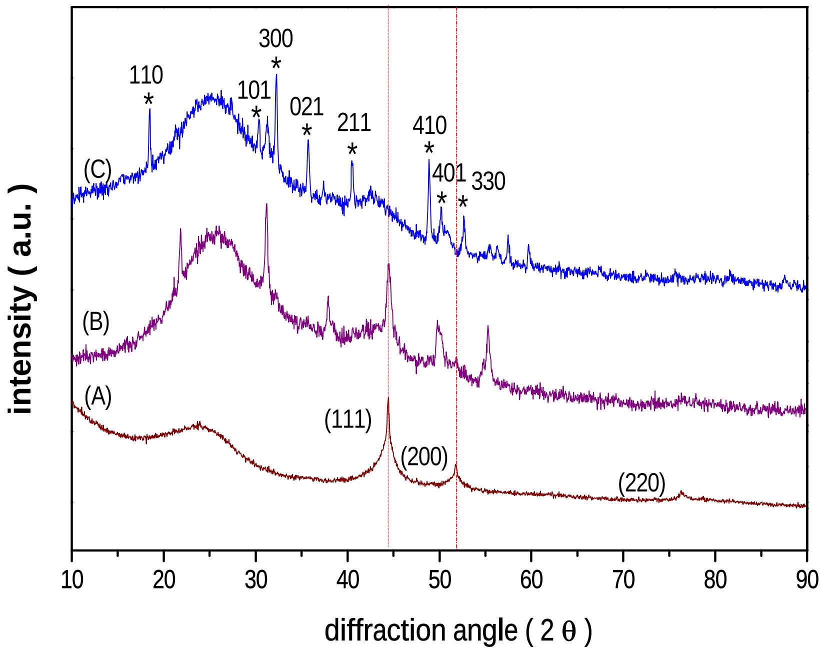

Figure S29. XRD spectra of fresh Ni/AC (A), reacted Ni/AC with lignosulfonate in ethylene glycol (EG) under 5MPa H_2 (B), and reacted Ni/AC with lignosulfonate in water under 5MPa H_2 (C). The 5 fresh Ni/AC catalyst indicates the nickel (0) metal phase, showing characteristic diffraction peaks at (111), (200) and (220). Treatment of the catalyst in EG generates a mixture of Ni and nickel sulfide. Treatment of the catalyst in water leads to the disappearance of nickel (0) metal and the generation of nickel sulfide.

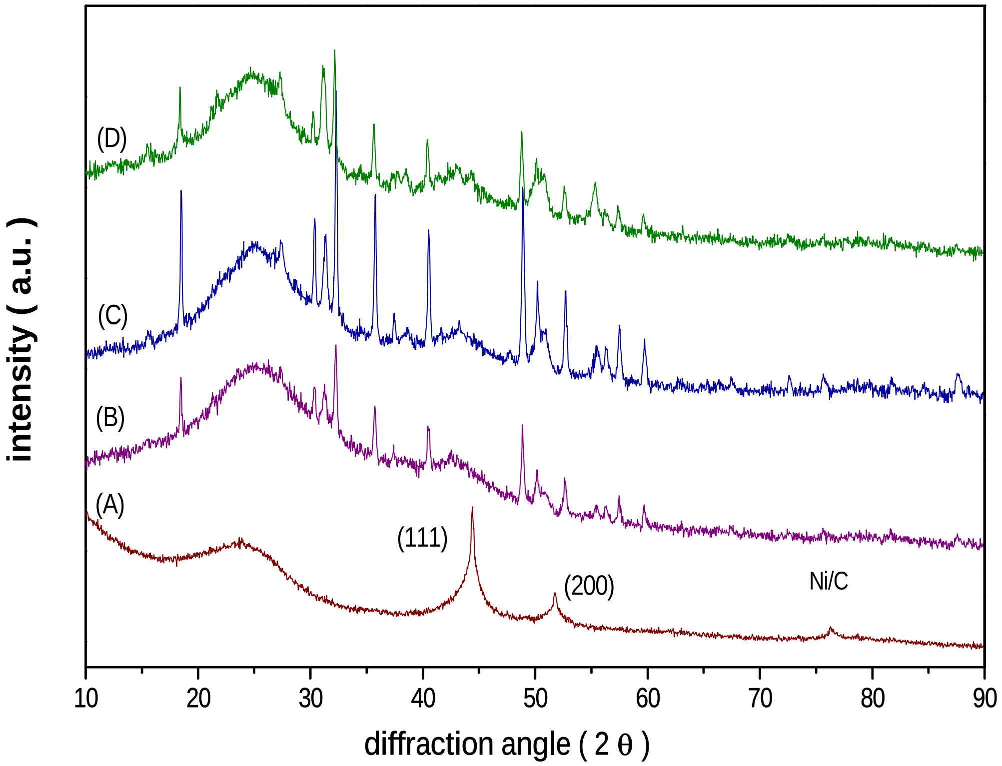

Figure S30 Testing the reducibility of poisoned Ni/AC catalysts by LS in EG under hydrogen and nitrogen atmosphere, respectively. (A) Fresh catalyst of Ni/AC. (B) Treating Ni/AC with 40% lignosulfonate in water. Typical nickel sulfides were formed. (C) Treating the sample (B) in EG under nitrogen at 473 K. No reduction of nickel sulfide was observed. (D) Treating the sample (B) in EG under hydrogen at 473 K. Intensity of diffracted peaks attributed to nickel sulfide greatly decreased. Nickel phase was not clearly observed in XRD characterization, suggesting that reduced nickel is finely dispersed on catalyst support, which is blind to X-ray diffraction.

Figure S 31 Detection of evoluted gas from a reaction with Pd/C as catalyst. The left image is the orignial 1 mol L^{-1} Pb(AC)$_2$ solution. The right image is the reacted Pb(AC)$_2$ solution. The reaction indicates that there is no H_2S coming out of the reaction system.

Figure S32 The images of reacted catalyst. The left image is Pd/AC, and the middle image is Pt/AC, 5 the right image is Ni/AC.

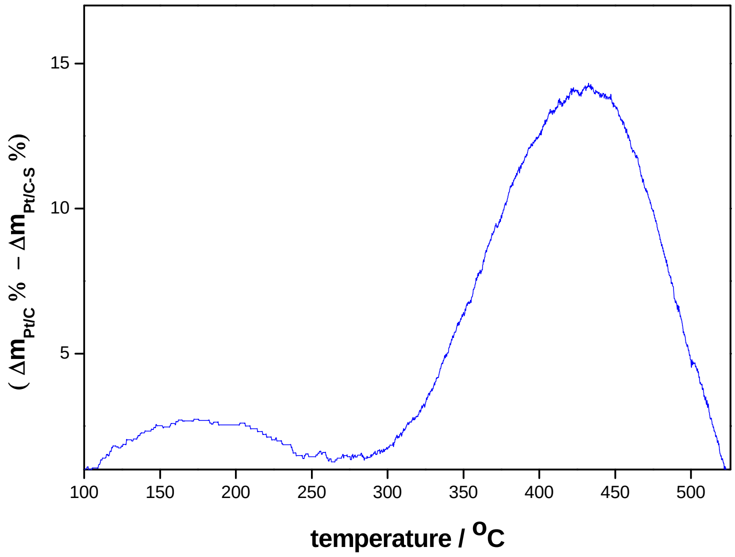

Figure S 33 Weight loss percentage of used Pt/AC catalyst. The Y axis defined as Y= (weight loss of fresh Pt/AC- weight loss of used Pt/AC)/initial weight of fresh Pt/AC. as depicted in Fig S 34, the Pt/C catalyst have serious coke problem during hydrogenolysis lignosulfonate.

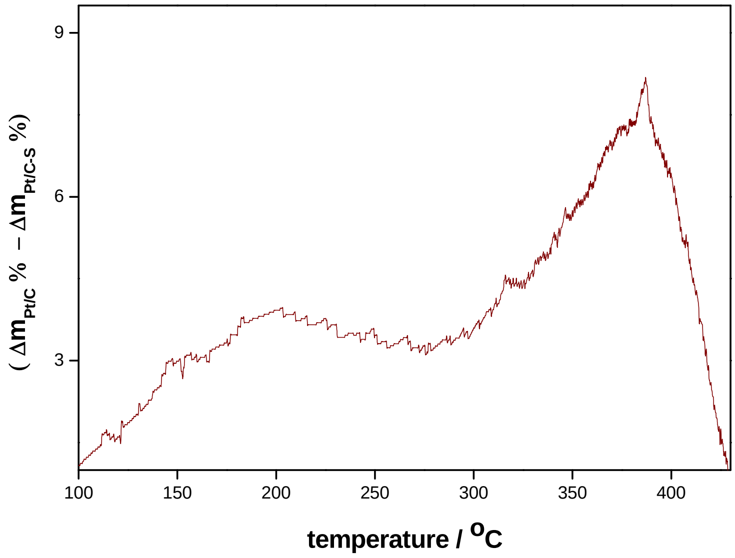

Figure S 34 Weight loss percentage of used Pt/AC catalyst. The Y axis defined as Y= (weight loss of fresh Pd/C- weight loss of used Pd/C)/initial weight of fresh Pd/AC.

Reference

[1] a) S. K. Badamali, R. Luque, J. H. Clark, S. W. Breeden, *Catal. Commun.* **2011**, *12*, 993-995; b) C. Crestini, M. DAuria, *Tetrahedron* **1997**, *53*, 7877-7888.

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

[4] M. D. Guillén, M. L. Ibargoitia, *J. Sci. Food. Agric.* **1999**, *79*, 1889-1903.