Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Materials and Methods

Chemicals. [$Ni(NO_3)_2.6H_2O$] was purchased from Strem Chemicals, USA. Activated carbon support of 100 mesh particle size was purchased from Sigma Aldrich. Pure dihydroeugenol (DHE) and 4-(3-hydroxypropyl)-2-methoxyphenol (DHE-OH) were purchased from Sigma-Aldrich and used as received. Isoeugenol (i-EuOH) was obtained from TCI America. 2,6-dimethoxy-4-propylphenol (DMPP) was synthesized by catalytic hydrogenation of 4-allyl-2,6-dimethoxyphenol. In this method, 4-Allyl-2,6-dimethoxyphenol was dissolved in a suspension of Pd/C (5 wt%, 105 mg) in 15 mL MeOH (1.945 g, 10.1 mmol). The reaction mixture was placed in a stainless steel Parr reactor, pressurized with 34 bar H_2 and heated at 60 °C for 3 h. Pd/C was removed by filtration and methanol was removed *in vacuo* to obtain crude DMPP as a colorless oil. The product was further purified on a silica-gel column with a mobile phase of 17% ethyl acetate and 83% hexanes, and analyzed by ^1H NMR (Figure S7). ^1H NMR ($CDCl_3$) δ 0.94 (t, 3H, CH_3), 1.61 (m, 2H, CH_2), 2.51 (t, 2H, CH_2), 3.88 (s, 6H, OCH_3), 5.35 (s, 1H, OH), 6.40 (s, 2H, ArH).

Lignocellulosic Feedstocks. Poplar (*P. tremula* x *P. alba*, WT-717) and Birch (*Betula papyrifera,* WT) were provided by Purdue University's Department of Forestry and Natural Resources Department. Eucalyptus (*Eucalyptus grandis* x *E. urophylla,* WT) was provided by William H. Rottman, ArborGen, Inc. (Ridgeville, SC, USA).

Catalyst. Ni/C catalyst was prepared by incipient wetness impregnation method by following the procedure of Song et al.[12] In this method, 2.7 g nickel(II) hexahydrate [$Ni(NO_3)_2.6H_2O$] (Sigma Aldrich) was added into 8 mL ultrapure water in a glass vial. After stirring the Ni(II) solution for 30 minutes to ensure complete dissolution of [$Ni(NO_3)_2.6H_2O$] salt, the solution was transferred into a 10 mL burette. Then the solution was slowly dripped onto 5 g activated carbon (Sigma Aldrich, 100 mesh, lot # MKBN8769B) in a small beaker and the mixture was continuously stirred to ensure high dispersion. The mixture was air dried for 24 h and then dried at 120 ºC for 12 h. The dried sample was then reduced in a tube furnace under 100 sccm of N_2 flow at 450 ºC. This temperature was maintained for 2h and the heat ramp was 1 h. As-synthesized Ni/C catalyst contained ~11wt% Ni.

Instrumentation for Catalyst Characterization

FE-SEM analysis of the Ni/C sample was performed by using a FEI NOVA nanoSEM field emission scanning electron microscope (FEI Company, Hillsboro Oregon) equipped with ET (Everhart-Thornley) detector or the high-resolution thorough-the lens (TLD) detector operated at an accelerating voltage of 5kV. Sample for FE-SEM analysis was prepared as follows: Ni/C sample was sonicated for 10 minutes in water to achieve uniform dispersion. One drop of this solution was deposited on the round cover slip, oven died, sputter coated with Pt for 60 seconds and imaged. HRTEM images of the sample were taken on a FEI Tecnai transmission electron microscope (FEI Company, Hillsboro, OR) equipped with a LaB6 filament and ORIUS SC600B CCD camera obtained from Gatan Inc. The operating conditions of the instrument are as follows: 200 kV accelerating voltage, spot 1, 200 mm condenser aperture and 70 mm objective aperture.
For TEM analysis, Ni/C sample was first sonicated for 10 minutes in water to achieve uniform dispersion and 3µl of this solution was deposited on a 400 mesh copper grid (formvar and carbon coated). The solution was allowed to sit on the copper grid for two minutes to dry before taking

TEM images. Grazing incidence X-ray diffraction (GIXD) patterns of the Ni/C sample were recorded on a Rigaku SmartLab diffractometer using CuKα radiation. BET surface area of the Ni/C catalyst was obtained from N_2 adsorption-desorption study at 77K, conducted at Micromeritics Analytical Services facility (Norcross, GA) by using a TriStar II Plus surface area and porosity analyzer.

Biomass preparation

Biomass was first milled to pass through a 40 mesh screen using a Mini Wiley Mill (Thomas Scientific, Swedesboro, NJ), and washed consecutively with water and ethanol soxhlet using the LAP Determination of Extractives in Biomass procedure.[16] Following soxhlet extraction, the biomass was dried and evaluated using a moisture analyzer (Halogen model HB43-S, Mettler-Toledo LLC, Columbus, OH).

Determination of Lignin Content in Washed Biomass

DFRC (Derivatization Followed by Reductive Cleavage). Composition of lignin was determined by DFRC analysis as previously reported.[17] In this method, 15 mg of cell-wall samples were resuspended in 20% acetyl bromide solution, containing 4,4'-ethylidenebisphenol dissolved in acetic acid as an internal standard. The dissolved lignin solution was dried down, dissolved in 2 mL of dioxane/acetic acid/ water (5/4/1, v/v/v) and reacted with 50 mg of Zn dust for 25 minutes. The reaction products were purified with C-18 SPE columns (Supelco), and acetylated with pyridine/acetic anhydride (2/3, v/v). The lignin derivatives were analyzed by gas chromatography/flame ionization detection (GC-FID) (Model 7890A, Agilent Technologies, Santa Clara, CA) using response factors relative to the internal standard of 0.80 for *p*-coumaryl alcohol peracetate, 0.82 for coniferyl alcohol peracetate, and 0.74 for sinapyl alcohol peracetate.

ABSL. Lignin content was determined by the acetyl bromide method.[18-19] The dried samples (between 2 and 5 mg) were added to a 10-mL glass tube with 2.5 mL of 25% acetyl bromide in acetic acid. The tubes were tightly sealed with Teflon lined caps. Tubes were stirred overnight at room temperature until the wall tissue completely dissolved. The samples were transferred into 50-mL volumetric flasks containing 2 mL 2 M NaOH. The tubes were rinsed with acetic acid to complete the transfer. 0.35 mL of 0.5 M freshly prepared hydroxylamine hydrochloride was added to the volumetric flasks which were then made up to 50 mL with acetic acid and inverted several times. The absorbance of the solutions was recorded at 280 nm with UV/Vis spectrophotometer (Model DU730, Beckman Coulter, Brea, CA).

Catalysis

In a typical experiments, 1.0 g of biomass, 0.05 g or 0.1 g Ni/C, methanol (20 mL), and a glass stir bar were added to a stainless steel Parr reactor, which was subsequently sealed. The reactor was first purged with N_2 gas and then pressurized with 2 bar N_2. The mixture was heated at 200 °C for the desired reaction time and then terminated the reaction by removing the heat and cooling the reactor to room temperature. The reaction mixture was filtered to remove Ni/C and remaining solid biomass residue. The filtrate was collected and diluted in a volumetric flask. This solution was analyzed by a GC-FID as described below to quantify yield.

GC Analysis

The yield of lignin derived products were measured by analyzing the product solutions on a GC instrument (Agilent 6890N) equipped with a FID detector, autosampler and DB-5 capillary column of dimension 0.25 mm ID × 0.25 μm × 30 m. Essential parameters of GC analysis are as follows: injection volume 1.0 μL, inlet temperature 275 °C, detector temperature 275 °C and a split ratio 1:10. Initial column temperature was 50 °C (1 min) with a temperature rise at 10 °C/min up to 250 °C and then at 25 °C/min to the final temperature of 300 °C. GC peaks for all lignin derived products (DHE, DMPP, i-EuOH, Mi-EuOH and DHE-OH) were identified by retention time in comparison with authentic samples. Each peak of GC chromatogram was properly integrated and the actual concentration of each product was obtained from the pre-calibrated plot of peak area against concentrations. Mi-EuOH concentration was calculated from the calibration plot of DMPP.

Table S1. *Acetyl Bromide Soluble Lignin (ABSL) and Derivatization Followed by Reductive Cleavage (DFRC) analysis lignin composition for birch, poplar and eucalyptus.*

Biomass Type	% ABSL	Ratio of H, G and S lignin
Poplar	19	1:8.3:9.6
Birch	16	1:6.0:6.7
Eucalyptus	24	1:45:87

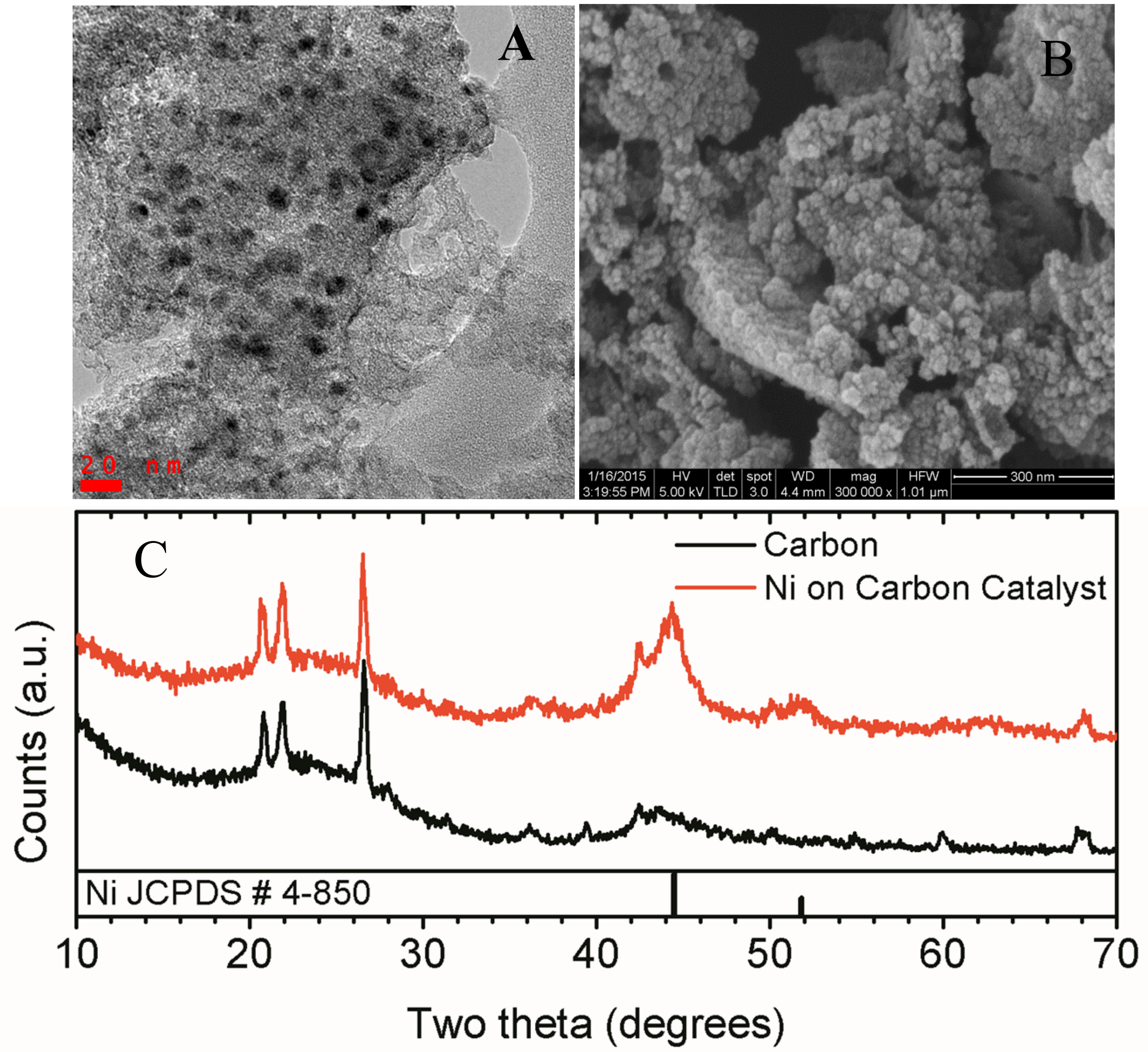

Figure S1. *HRTEM (a), FE-TEM (b) images, and GIXD profile of the Ni/C catalyst.*

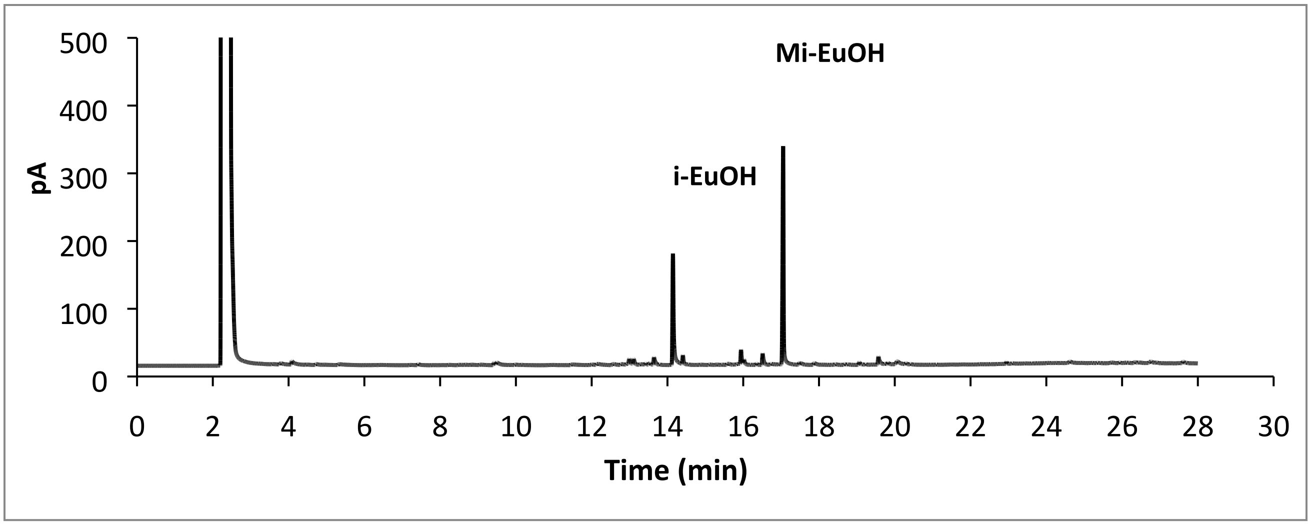

Figure S2. *GC chromatogram of lignin catalysis products obtained from birch wood using 5 wt% Ni/C.*

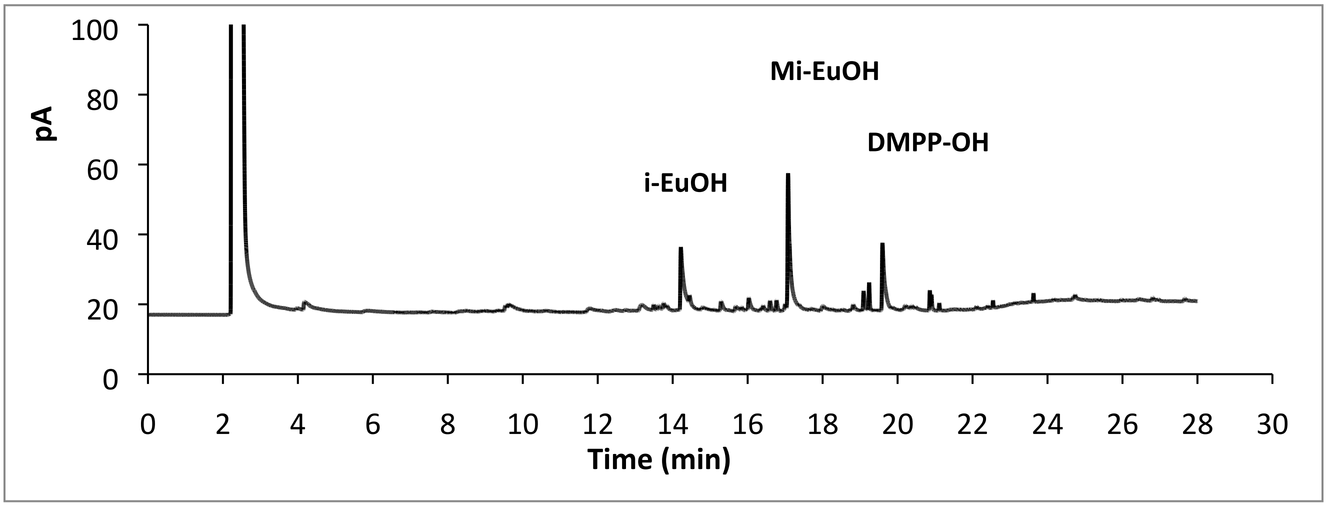

Figure S3. *GC chromatogram of lignin catalysis products obtained from poplar wood using 5 wt% Ni/C.*

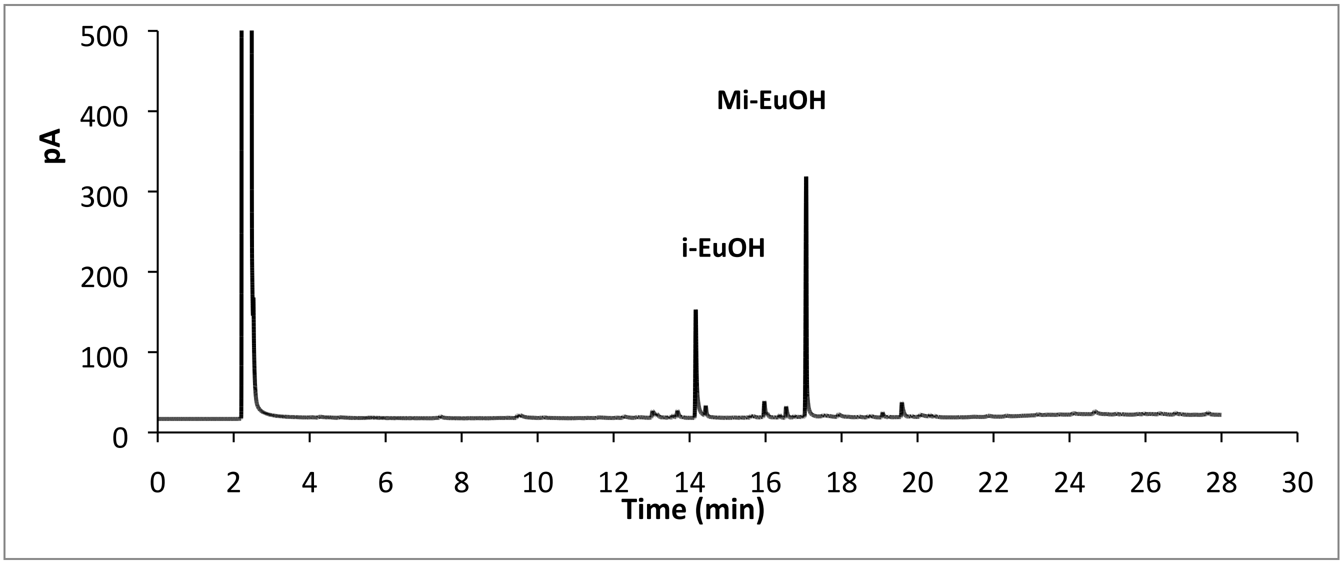

Figure S4. *GC chromatogram of lignin catalysis products obtained from eucalyptus wood using 5 wt% Ni/C.*

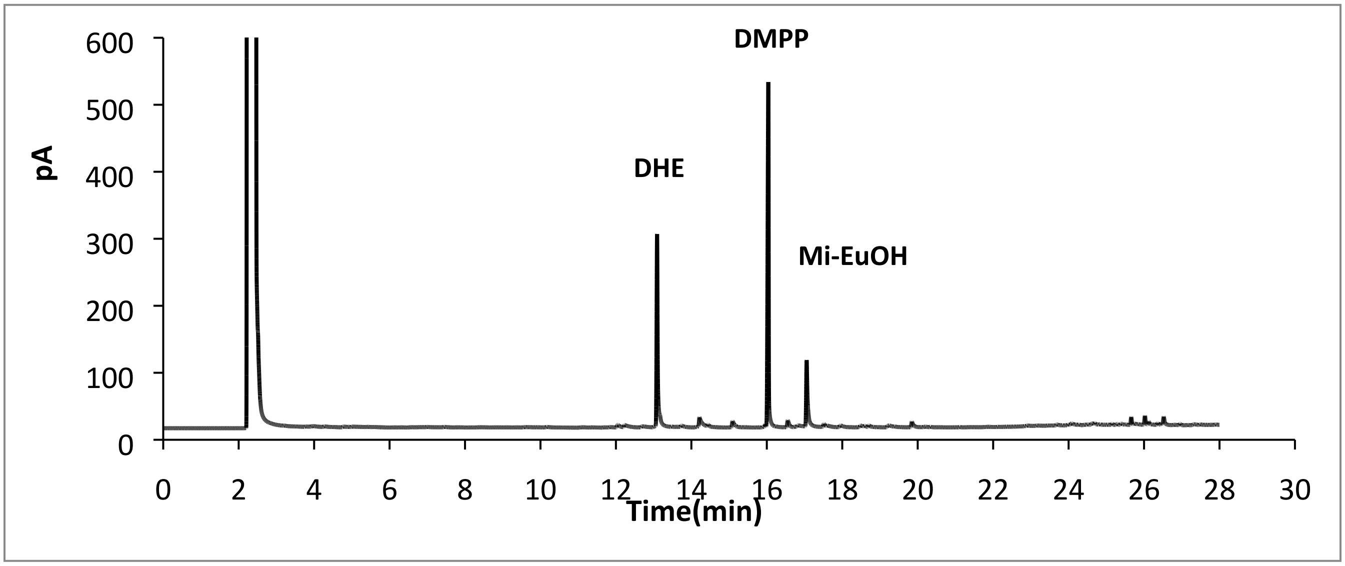

Figure S5. *GC chromatogram of lignin catalysis products obtained from birch wood using 10 wt% Ni/C.*

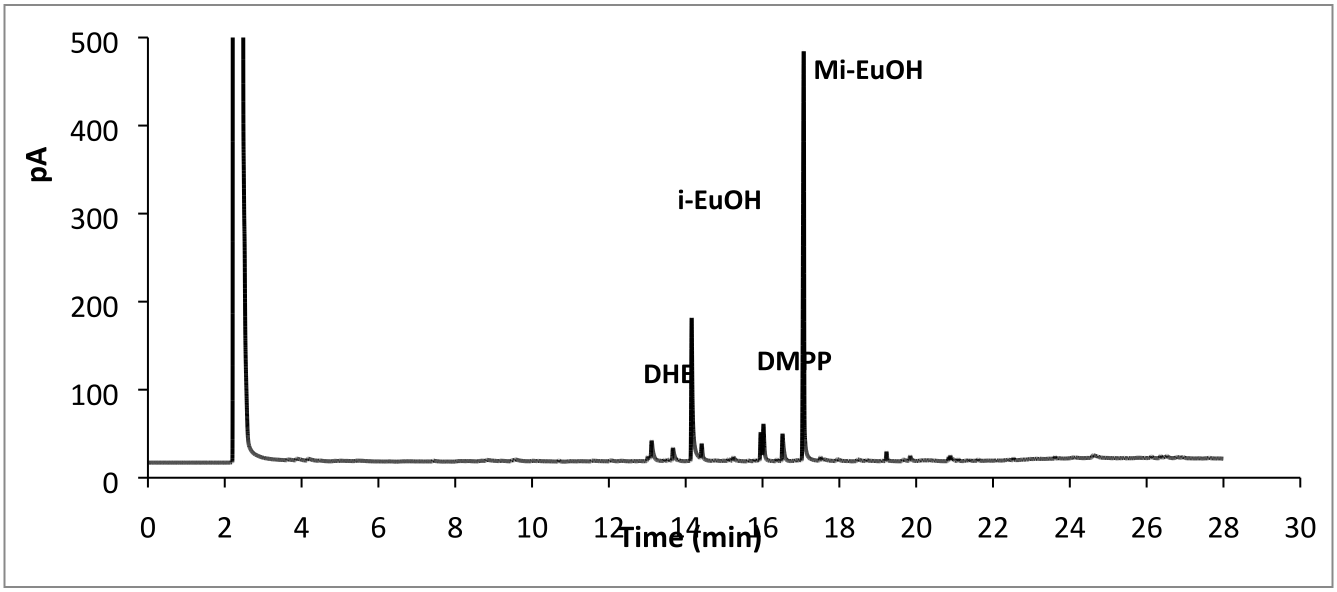

Figure S6. *GC chromatogram of lignin catalysis products obtained from poplar wood using 10 wt% Ni/C.*

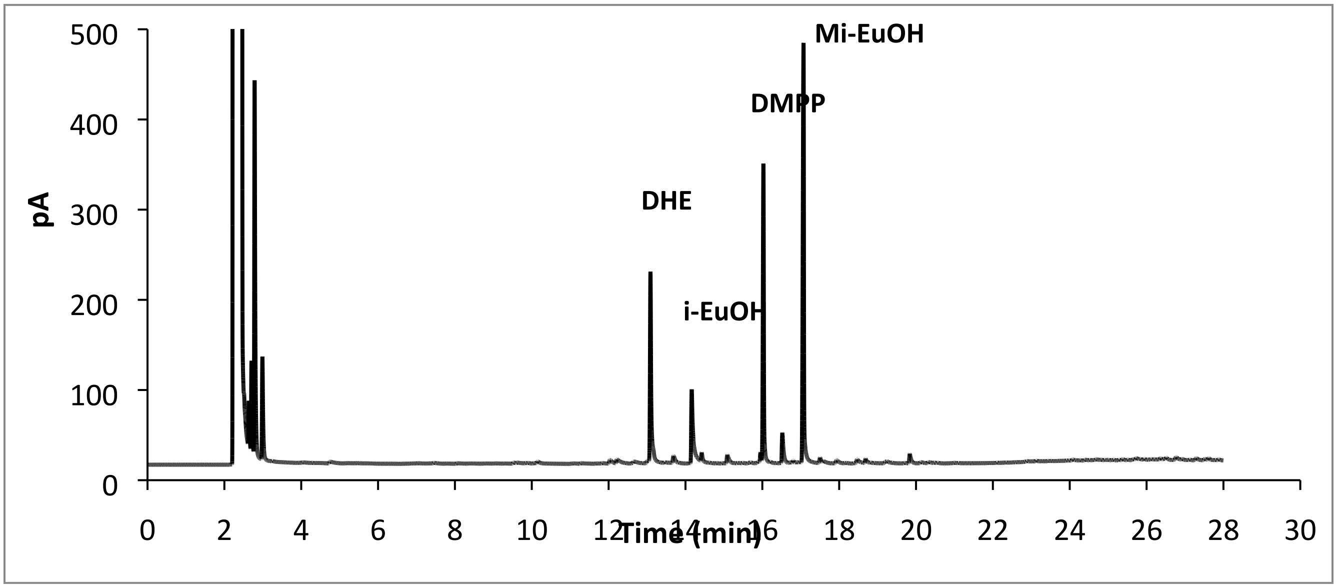

Figure S7. *GC chromatogram of lignin catalysis products obtained from eucalyptus wood using 10 wt% Ni/C.*

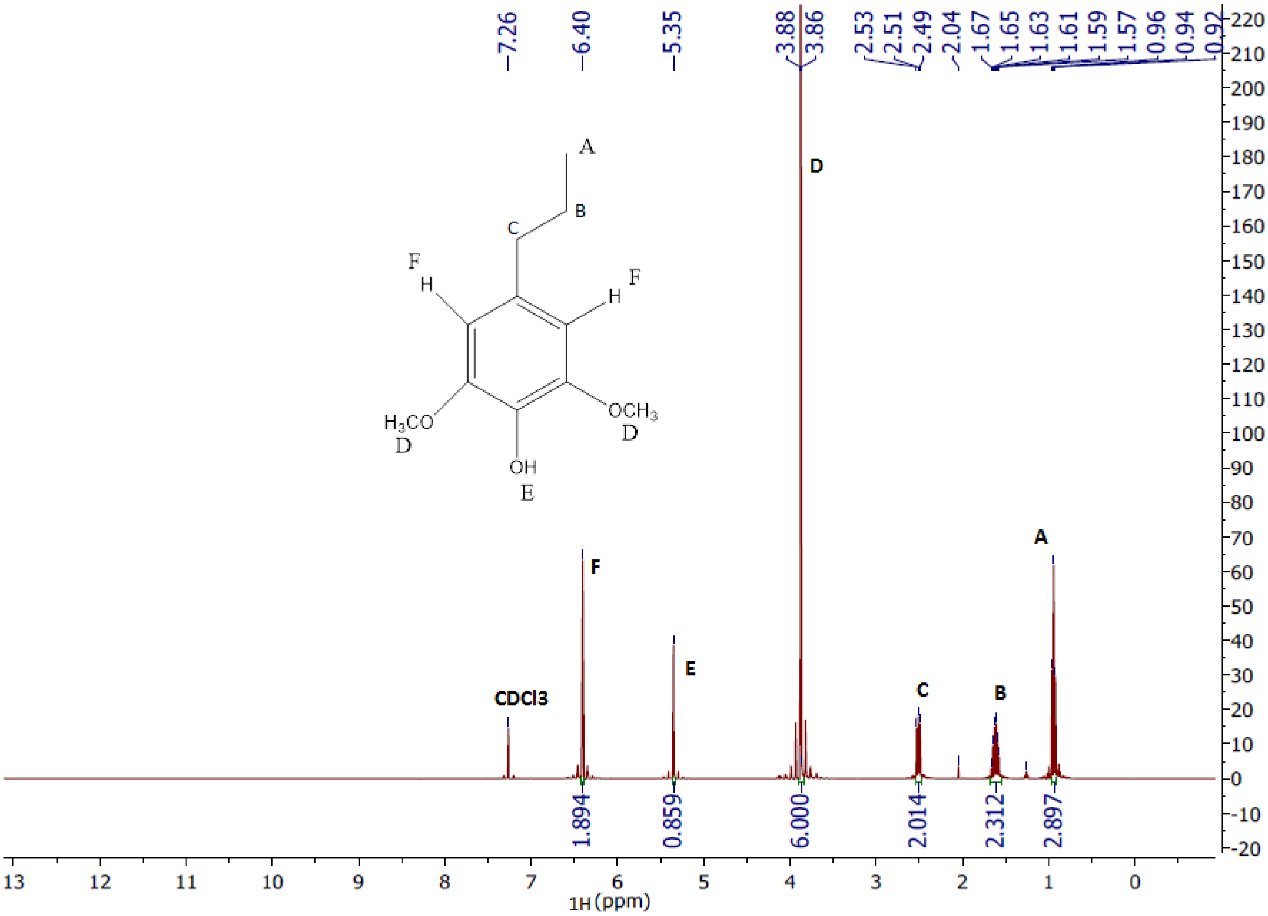

Figure S8. *^{1}H NMR spectrum of synthesized/standard DMPP.*

References for supporting information

16. A. Sluiter, R. Ruiz, C. Scarlata, J. Suiter, D. Templeton, *Determination of Extractives in Biomass* (*LAP*). NREL/TP-510-42619.

17. (a) F. Lu, J. Ralph *J. Agri. Food Chem*. **1999**, *45*, 2590. (b) J.-K. Weng, T. Akiyama, N. D. Bonawitz, X. Li, J. Ralph, C. Chapple, *Plant Cell* **2010**, *22*, 1620.

18. R. S. Fukushima, R. D. Hatfield, *J. Agric. Food Chem*. **2001**, *49*, 3133.

19. J. Ralph, T. Akiyama, H. Kim, F. Lu, P. F. Schatz, J. M. Marita, S. A. Ralph, M. S. S. Reddy, F. Chen, R. A, Dixon, *J. Biol. Chem.* **2006**, *281*, 8843.