

Supporting Information for

Fragmentation of Lignin Samples with Commercial Pd/C under Ambient Pressure of Hydrogen

Fang Gao, Jonathan D. Webb, Hagit Sorek, David E. Wemmer and John F. Hartwig*

Department of Chemistry, University of California, Berkeley, California 94720-1460, United States

E-mail: jhartwig@berkeley.edu

Table of Contents

General experimental details	S4
Characterizations of resinol and phenylcoumaran model compounds	S7
General procedure for fragmentation of lignin model compounds without hydrogen	S7
Competition experiment: fragmentation of a 1:1 mixture of 2-phenoxy-1-phenylethan-1-ol and 2-(2-methoxyphenoxy)-1-phenylethan-1-one catalyzed by Pd/C (Eq 4)	S11
Time profile analysis: fragmentation of 2-phenoxy-1-phenylpropane-1,3-diol catalyzed by Pd/C catalyst (Figure 1)	S12
Figure S1. HSQC spectra of the aromatic regions of lignin samples isolated from <i>M. Giganteus</i> through ethanol-, acetone-, and dioxane-solvolysis	S13
The procedure for Pd/C catalyzed fragmentation of the isolated acetone-solv lignin sample from <i>M. Giganteus</i> under hydrogen free conditions	S13
Figure S2. HSQC spectrum of the degradation product of acetone-solv lignin with Pd/C without added H ₂ in comparison to the acetone-solv lignin from <i>M. Giganteus</i> (aromatic region)	S15
The procedure for hydrogenative treatment of dioxanesolv lignin samples from <i>M. Giganteus</i>	S15
The procedure for Pd/C catalyzed fragmentation of this pretreated dioxanesolv lignin sample under hydrogen free conditions (Scheme 3)	S16

Figure S3. HSQC spectra of the degraded material after fragmentation treatment in comparison with the hydrogenatively treated acetonesolv lignin (aliphatic region)	S17
General procedure for fragmentation of lignin samples catalyzed by Pd/C under an atmospheric pressure of hydrogen	S17
Procedure for the fragmentation of synthetic lignin catalyzed by Pd/C under an atmospheric pressure of hydrogen (Scheme 4)	S19
Figure S4. HSQC spectrum of synthetic lignin and the linkage analysis	S20
Figure S5. HSQC spectra of the degraded synthetic lignin and of the material obtained from the control experiment (aliphatic and oxygenated region)	S21
Figure S6. HSQC spectra of the degraded synthetic lignin and of the material obtained from the control experiment (aromatic region)	S23
The procedure for Pd/C catalyzed fragmentation of acetonesolv lignin under an atmospheric pressure of hydrogen (Figure 2 and Entry 1, Table 2)	S23
Figure S7. GPC traces of 1) acetonesolv lignin, 2) material obtained from the control experiment, 3) degraded acetonesolv lignin after the fragmentation reaction and 4) overlay with degraded material from fragmentation of hydrogenatively treated acetonesolv lignin under hydrogen free condition	S24
Table S1. Screening of the BASF heterogeneous catalyst kit for fragmentation of acetonesolv lignin under 15 psi of H ₂	S25
The procedure for fragmentation of ethanolsolv lignin catalyzed by Pd/C under an atmospheric pressure of hydrogen (Figure 2 and Entry 2, Table 2)	S25
Figure S8. HSQC spectra of the degraded ethanolsolv lignin in comparison with the material obtained from the control experiment (aliphatic region)	S26
Figure S9. GPC graphs of 1) ethanolsolv lignin, 2) material obtained from the control experiment and 3) degraded ethanolsolv lignin after the fragmentation reaction	S27
The procedure for Pd/C catalyzed fragmentation of dioxanesolv lignin under an atmospheric pressure of hydrogen (Figure 2 and Entry 3, Table 2)	S27
Figure S10. GPC trace of 1) dioxanesolv lignin, 2) material obtained from the control	

experiment and 3) degraded dioxanesolv lignin after the fragmentation reaction	S28
The procedure for Pd/C catalyzed fragmentation of dioxanesolv pine lignin under an atmospheric pressure of hydrogen (Figure 2 and Entry 4, Table 2)	S28
Figure S11. HSQC spectra of the degraded dioxanesolv pine lignin in comparison with the material obtained from the control experiment (aromatic region)	S29
Figure S12. GPC graphs of 1) material obtained from the control experiment and 2) degraded dioxanesolv pine lignin	S30
Scheme S1. Fragmentation of the phenylcoumarin model compound with and without 15 psi of hydrogen	S30
Scheme S2. Fragmentation of the resinol model compound with and without 15 psi of hydrogen	S31
General procedure for the gram-scale catalytic fragmentation of lignin samples under an atmospheric pressure of hydrogen with reduced loading of Pd/C	S32
Figure S13. GPC graphs of gram-scale fragmentations of 1) acetonesolv lignin, 2) ethanolsolv lignin, 3) dioxanesolv lignin and 4) dioxanesolv pine lignin	S33
Table S2. Viscosity measurement of dioxansolv lignin blended with various amount of dioxane at 22 and 50 °C	S34
Table S3. Viscosity measurement of dioxansolv lignin blended with various renewable solvents	S34
¹ H and ¹³ C NMR spectrum	S35
References	S39

General experimental details

Equipment and methods

All air-sensitive manipulations were conducted in a nitrogen-filled glovebox or by standard Schlenk technique under nitrogen. All glassware was heated in an oven and cooled under an inert atmosphere prior to use.

GC analyses were obtained on an Agilent 7890 Gas Chromatograph equipped with an HP-5 30 m x 0.20 mm ID x 0.33 μ m capillary column (Agilent) and an FID detector.

The following GC oven temperature programs were used: A) 100 °C hold for 3 min, ramp 40 °C/min to a final temperature of 300 °C, and hold for 2.5 min; B) 35 °C hold for 2 min, ramp 45 °C/min to a final temperature of 300 °C, and hold for 2 min. Helium was used as a carrier gas, with a constant column flow of 5.6 ml/min (program A) or 6.6 ml/min (program B). The injector temperature was held at 250 °C (program A) or 300 °C (program B). All GC-yields were obtained by establishing response factors of authentic samples either from commercial sources or chemical synthesis.

GC-MS analyses were obtained on an Agilent 6890-N Gas Chromatograph equipped with an HP-5 30 m x 0.25 mm x 0.25 μ m capillary column (Agilent). The GC was directly interfaced to an Agilent 5973 mass selective detector (EI, 70 eV). The following GC oven temperature programs were used: A) 50 °C hold for 2 min, ramp 40 °C/min to a final temperature of 300 °C, and hold for 2 min; B) 100 °C hold for 3 min, ramp 40 °C/min to a final temperature of 300 °C, and hold for 2.5 min. Helium was used as a carrier gas, with a constant column flow of 1 ml/min. The injector temperature was held constant at 250 °C.

The NMR spectra were acquired on a Bruker Avance 600-MHz spectrometer equipped with a CPTXI cryoprobe. Lignin and degraded products were dissolved in deuterated dimethyl sulfoxide (DMSO-*d*₆); the solvent peak was used as an internal reference (δ_C 39.5, δ_H 2.49 ppm). ¹³C-¹H HSQC experiments had the following parameters: acquired from 12 to 0 ppm in F2 (1H) by using 2048 data points for an acquisition time (AQ) of 143 ms, 210-0 ppm in F1 (13C) by using 256 increments (F1 acquisition time 4.0 ms) of 48 scans with a 1 s interscan delay (D1). Squared cosine-bell apodization function was applied in both dimensions. HSQC cross-peaks were assigned by combining the results

and comparing them with the literature.¹ A semi-quantitative analysis of the HSQC cross-peak intensities was performed in the aliphatic oxygenated region, interunit linkages were estimated from C α –H α correlations and the relative abundance of side chains involved in interunit linkages was calculated (with respect to total side chains). Volume integration of peaks in HSQC plots was accomplished using Bruker's TopSpin 3.0 software. Other Bruker implementations of 2D NMR experiments were used for structural elucidation and assignment authentication.

Molecular weight was analyzed by gel permeation chromatography (GPC). Lignin samples were dissolved in tetrahydrofuran (THF, 1 mg/mL) and analyzed on a GPC 50 Plus system (Agilent Technologies, Santa Clara, CA, USA) with a UV detector and autosampler. All lignins prepared in this study were soluble in THF at 1 mg/mL. The columns used were a series of two 300 mm \times 7.5 mm i.d., 3 μ m, MesoPore, with a 50 mm \times 7.5 mm i.d. guard column of the same material (Agilent Technologies). Samples were eluted at 30 °C with 1 mL/min THF and detected at 280 nm. The system was calibrated using polystyrene samples (EasiVial PS-L) in the range of Mp 38 640–162 Da (Agilent Technologies). Molecular weight at peak top (Mp), number-averaged molecular weight (Mn), weight-averaged molecular weight (Mw), and polydispersity (Mw/Mn) were determined by the Cirrus software (Agilent Technologies).

Viscosity was measured with the LVDV-II+P model viscometer from Brookfield Engineering Laboratories Inc, which was equipped with a SC4-15 spindle and a SCA-7R(P) sample chamber (3.7 cm³ in volume). Samples of at least 3.5 mL in volume were transferred into the chamber with a measuring pipette. Viscosity values were directly recorded from the display panel after the spindle was steadily rotating at the chosen rpm (50-200 rpm for the measurement performed in this study); the % torque values were kept above 10 for all measurements.

Solvents and reagents

Ni/C (3 wt % of Ni metal) was prepared according to the literature procedure² and stored at –30 °C in a glovebox before use. Ni/SiO₂/Al₂O₃ (20 wt % of Ni metal) was purchased from Aldrich, stored in a glovebox and used as received. Pd/C (10 wt % of Pd metal) was purchased from Aldrich, stored in a glovebox and used as received. Pd/Al₂O₃ (10 wt % of

Pd metal) and Pd/BaSO₄ (10 wt % of Pd metal) were purchased from Aldrich, stored in a glovebox and used as received. Ru/C (5 wt % of Ru metal) and Ru/Al₂O₃ (5 wt % of Ru metal) were purchased from Aldrich, stored in a glovebox and used as received. Rh/C (5 wt % of Rh metal) was purchased from Aldrich, stored in a glovebox and used as received. Pt/C (10 wt % of Pt metal) and Pt/Al₂O₃ (5.0 wt % of Pt metal) were purchased from Aldrich, stored in a glovebox and used as received. The BASF heterogeneous catalyst kit was purchased from Strem (catalog number 96-6717), stored in a glovebox and used as received. Anhydrous *m*-xylene was purchased from Aldrich and used as received. Anhydrous 1,4-dioxane was purchased from Acros and used as received. Both solvents were stored and used under a nitrogen atmosphere in a glovebox. 2-methyltetrahydrofuran (reagent grade) and γ -valerolactone (reagent grade) were purchased from Aldrich and used as received. Phenol (reagent grade) was purchased from Fisher and used as received. Acetophenone (analytical standard) was purchased from Aldrich and used as received. Ethylbenzene (analytical standard) was purchased from Aldrich and used as received. Propiophenone (analytical standard) was purchased from Aldrich and used as received. Guaiacol (natural, >99%) was purchased from Aldrich and used as received. 1,2-Dimethoxy-4-ethylbenzene (>95%) was purchased from Combi-blocks and used as received. 1,2-Dimethoxy-4-propylbenzene was purchased from Oakwood products and used as received. 4-Ethylguaiacol (analytical standard) was purchased from Aldrich and used as received. 4-Ethylphenol (analytical standard) was purchased from Aldrich and used as received. 2-Methoxy-4-propylphenol (>99%) was purchased from Aldrich and used as received. 4-(3-Hydroxypropyl)-2,6-dimethoxyphenol was purchased from Ark Pharm and used as received. Dihydroconiferyl alcohol (95%) was purchased from Combi-blocks and used as received. Hydrogen (industrial grade, 99.95%) was purchased from Praxair and was used as received. 2-Phenoxy-1-phenylethan-1-one (>97%) was purchased from TCI-America and used as received. 2-Phenoxy-1-phenylethan-1-ol and 2-(2-methoxyphenoxy)-1-phenylethan-1-ol were prepared according to the previously reported procedure.³ 2-Phenoxy-1-phenylpropane-1,3-diol was prepared according to the previously reported procedure.⁴ 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol was prepared according to the previously reported procedure.⁵ 1-(4-Hydroxy-3-methoxyphenyl)-2-(2-

methoxyphenoxy)propane-1,3-diol was prepared according to the previously reported procedure.⁶ 1,4-Bis(4-methoxyphenyl)tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan (**resinol model compound**) was prepared by adapting a synthetic sequence described in a previous publication.⁷ (2-(4-Methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)methanol (**phenylcoumaran model compound**) was prepared by adapting a synthetic sequence described in a previous publication.⁸ The synthetic lignin was obtained from the M. C. Chang group at UC Berkeley and prepared by a procedure adapted from a previous publication.⁹ Organosolv lignins derived from *M. Giganteus* and pine trees were obtained from the analytical lab headed by Stefan Bauer at the Energy Biosciences Institute of UC Berkeley; the preparation of these lignin samples was described in a previous publication, and the characterizations with 2D NMR and GPC experiments of these samples were provided in this study.¹⁰

Characterizations of resinol and phenylcoumaran model compounds

Phenylcoumaran model compound: (2-(4-Methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)methanol. ¹H NMR (300 MHz, Chloroform-*d*) δ : 7.49–7.29 (m, 4H), 7.22 (ddd, *J* = 7.7, 4.4, 1.3 Hz, 2H), 7.05–6.88 (m, 2H), 5.63 (d, *J* = 6.0 Hz, 1H), 4.00–3.84 (m, 2H), 3.71 (d, *J* = 1.2 Hz, 3H), 3.57 (q, *J* = 5.9 Hz, 1H), 2.10 (s, 1H); ¹³C NMR (125 MHz, Chloroform-*d*) δ : 159.9, 141.7, 129.0, 128.6, 127.9, 126.3, 125.5, 124.5, 120.7, 109.6, 86.6, 66.9, 64.4, 53.5; HRMS (ESI) calc'd (M+H) 257.1172, found 257.1197.

Resinol model compound: 1,4-Bis(4-methoxyphenyl)tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan. ¹H NMR (300 MHz, Chloroform-*d*) δ : 7.36–7.25 (m, 4H), 6.98–6.86 (m, 4H), 4.78 (d, *J* = 4.0 Hz, 2H), 4.35–4.18 (m, 2H), 3.89 (dd, *J* = 9.2, 3.5 Hz, 2H), 3.82 (s, 6H), 3.18–3.05 (m, 2H); ¹³C NMR (125 MHz, Chloroform-*d*) δ : 159.1, 133.0, 127.3, 113.8, 85.6, 71.6, 55.2, 54.1; HRMS (ESI) calc'd (M+H) 327.1591, found 327.1573.

General procedure for fragmentation of lignin model compounds without hydrogen

Reactions were conducted in 4 ml glass vials equipped with Teflon-lined screw caps and Teflon-coated magnetic stir bars (3 mm x 8 mm; supplied by Fisher Scientific). The

reaction vessels were heated in an oil bath; the reaction temperature refers to the temperature of the oil bath. The stirring rate was kept constant at 900 rpm (Magnetic stirrer IKA Ceramag Midi; the stir rate dial was set to 7.5).

In a glovebox, a 4 ml glass vial equipped with a Teflon-coated magnetic stir bar was charged with a heterogeneous metal catalyst (5.0-20 mol%), a lignin model compound (0.300 mmol) and a magnetic stir bar. Then, a solution of dodecane (10~25 mg, internal standard for GC) in 1.2 mL *m*-xylene or *p*-cymene/dioxane (1:1 mixture) was added, and the mixture was stirred for 1 min. The vial was sealed with a Teflon-lined screw cap and removed from the glovebox. The vessel was heated in an oil bath at the designated temperature between 120°C and 200 °C for the designated time. The resulting dark black mixture was cooled to room temperature, diluted with ether or ethyl acetate (1 ml), and passed through a short plug of Celite (2 cm in length) to remove black solid materials. The resulting clear solution was then subjected to GC and GC/MS analyses. The products have all been reported previously and were identified by comparison of the mass spectra and retention times of the products by GC/MS and GC with those of authentic compounds that are commercially available or were synthesized.

Fragmentation of 2-phenoxy-1-phenylethan-1-ol catalyzed by Ni/C (Table 1, Entry 1)

The reaction was conducted according to the General Procedure with Ni/C (3.0 wt%, 29.3 mg, 1.50×10^{-2} mmol, 5.0 mol%), 2-phenoxy-1-phenylethan-1-ol (64.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 16 h. GC analysis of the reaction mixture showed that no product formed and <2% of the substrate had converted.

Fragmentation of 2-phenoxy-1-phenylethan-1-ol catalyzed by Ni/Al₂O₃/SiO₂ (Table 1, Entry 2)

The reaction was conducted according to the General Procedure with Ni/Al₂O₃/SiO₂ (20.0 wt%, 17.6 mg, 6.00×10^{-2} mmol, 20.0 mol%), 2-phenoxy-1-phenylethan-1-ol (64.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 16 h. Analysis of the reaction mixture by GC showed that phenol (4%) and acetophenone (10%) formed.

Fragmentation of 2-phenoxy-1-phenylethan-1-ol catalyzed by Pd/C (Table 1, Entry 3)

The reaction was conducted according to the General Procedure with Pd/C (10.0 wt%, 16.0 mg, 1.50×10^{-2} mmol, 5.0 mol%), 2-phenoxy-1-phenylethan-1-ol (64.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 16 h. Analysis of the reaction mixture by GC showed that phenol (94%), acetophenone (93%) and 2-phenoxy-1-phenylethan-1-one (4%) formed.

Fragmentation of 2-phenoxy-1-phenylethan-1-ol catalyzed by Pd/Al₂O₃ (Table 1, Entry 4)

The reaction was conducted according to the General Procedure with Pd/Al₂O₃ (10.0 wt%, 16.0 mg, 1.50×10^{-2} mmol, 5.0 mol%), 2-phenoxy-1-phenylethan-1-ol (64.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 16 h. Analysis of the reaction mixture by GC showed that phenol (83%), acetophenone (87%) and 2-phenoxy-1-phenylethan-1-one (2%) formed.

Fragmentation of 2-phenoxy-1-phenylethan-1-ol catalyzed by Pd/BaSO₄ (Table 1, Entry 5)

The reaction was conducted according to the General Procedure with Pd/BaSO₄ (10.0 wt%, 32.0 mg, 3.00×10^{-2} mmol, 10.0 mol%), 2-phenoxy-1-phenylethan-1-ol (64.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 16 h. Analysis of the reaction mixture by GC showed that 2-phenoxy-1-phenylethan-1-one (4%) formed

Fragmentation of 2-phenoxy-1-phenylethan-1-ol catalyzed by Ru/C catalyst (Table 1, Entry 6)

The reaction was conducted according to the General Procedure with Ru/C (5.0 wt%, 60.6 mg, 3.00×10^{-2} mmol, 10.0 mol%), 2-phenoxy-1-phenylethan-1-ol (64.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 16 h. Analysis of the reaction mixture by GC showed that phenol (17%), acetophenone (15%) and 2-phenoxy-1-phenylethan-1-one (15%) formed.

Fragmentation of 2-phenoxy-1-phenylethan-1-ol catalyzed by Ru/Al₂O₃ catalyst

(Table 1, Entry 7)

The reaction was conducted according to the General Procedure with Ru/Al₂O₃ (5.0 wt%, 60.6 mg, 3.00x10⁻² mmol, 10.0 mol%), 2-phenoxy-1-phenylethan-1-ol (64.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 16 h. Analysis of the reaction mixture by GC showed that phenol (10%), acetophenone (10%) and 2-phenoxy-1-phenylethan-1-one (11%) formed

Fragmentation of 2-phenoxy-1-phenylethan-1-ol catalyzed by Rh/C catalyst (Table 1, Entry 8)

The reaction was conducted according to the General Procedure with Rh/C (5.0 wt%, 61.7 mg, 3.00x10⁻² mmol, 10.0 mol%), 2-phenoxy-1-phenylethan-1-ol (64.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 16 h. Analysis of the reaction mixture by GC showed that phenol (15%), acetophenone (11%) and 2-phenoxy-1-phenylethan-1-one (15%) formed.

Fragmentation of 2-phenoxy-1-phenylethan-1-ol catalyzed by Pt/Al₂O₃ catalyst (Table 1, Entry 9)

The reaction was conducted according to the General Procedure with Pt/Al₂O₃ (5.0 wt%, 117 mg, 3.00x10⁻² mmol, 10.0 mol%), 2-phenoxy-1-phenylethan-1-ol (64.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 16 h. Analysis of the reaction mixture by GC showed that phenol (63%), acetophenone (82%) and 2-phenoxy-1-phenylethan-1-one (8%) formed.

Fragmentation of 2-phenoxy-1-phenylethan-1-ol catalyzed by Pt/C catalyst (Table 1, Entry 10)

The reaction was conducted according to the General Procedure with Pt/C (10.0 wt%, 58.5 mg, 3.00x10⁻² mmol, 10.0 mol%), 2-phenoxy-1-phenylethan-1-ol (64.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 16 h. Analysis of the reaction mixture by GC showed that phenol (44%), acetophenone (45%) and 2-phenoxy-1-phenylethan-1-one (12%) formed.

Fragmentation of 2-phenoxy-1-phenylpropane-1,3-diol catalyzed by Pd/C catalyst (Eq 1)

The reaction was conducted according to the General Procedure with Pd/C (10.0 wt%, 16.0 mg, 1.50×10^{-2} mmol, 5.0 mol%), 2-phenoxy-1-phenylpropane-1,3-diol (73.3 mg, 0.300 mmol), dodecane (internal standard for GC) and *p*-cymene/dioxane (1:1 mixture, 1.2 ml) at 200 °C for 24 h. Analysis of the reaction mixture by GC showed that ethylbenzene (7%), phenol (88%), acetophenone (70%) and propiophenone (18%) formed.

Fragmentation of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol catalyzed by Pd/C catalyst (Eq 2)

The reaction was conducted according to the General Procedure with Pd/C (10.0 wt%, 16.0 mg, 1.50×10^{-2} mmol, 5.0 mol%), 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (100 mg, 0.300 mmol), dodecane (internal standard for GC) and *p*-cymene/dioxane (1:1 mixture, 1.2 ml) at 200 °C for 24 h. Analysis of the reaction mixture by GC showed that 1,2-dimethoxy-4-ethylbenzene (65%), guaiacol (90%), 1,2-dimethoxy-4-propylbenzene (trace) and small quantity of unidentified higher molecular weight products formed.

Fragmentation of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol catalyzed by Pd/C catalyst (Eq 3)

The reaction was conducted according to the General Procedure with Pd/C (10.0 wt%, 16.0 mg, 1.50×10^{-2} mmol, 5.0 mol%), 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (96.1 mg, 0.300 mmol), dodecane (internal standard for GC) in a combination of *p*-cymene and dioxane (1:1 mixture, 1.2 ml) at 200 °C for 24 h. Analysis of the reaction mixture by GC showed that 4-ethylguaiacol (45%), guaiacol (67%), 4-(3-hydroxy-2-(2-methoxyphenoxy)propyl)-2-methoxyphenol (15%) and small quantity of unidentified higher molecular weight products formed.

Competition experiment: fragmentation of a 1:1 mixture of 2-phenoxy-1-phenylethan-1-ol and 2-(2-methoxyphenoxy)-1-phenylethan-1-one catalyzed by Pd/C catalyst (Eq 4)

The reaction was conducted according to the General Procedure with Pd/C (10.0 wt%,

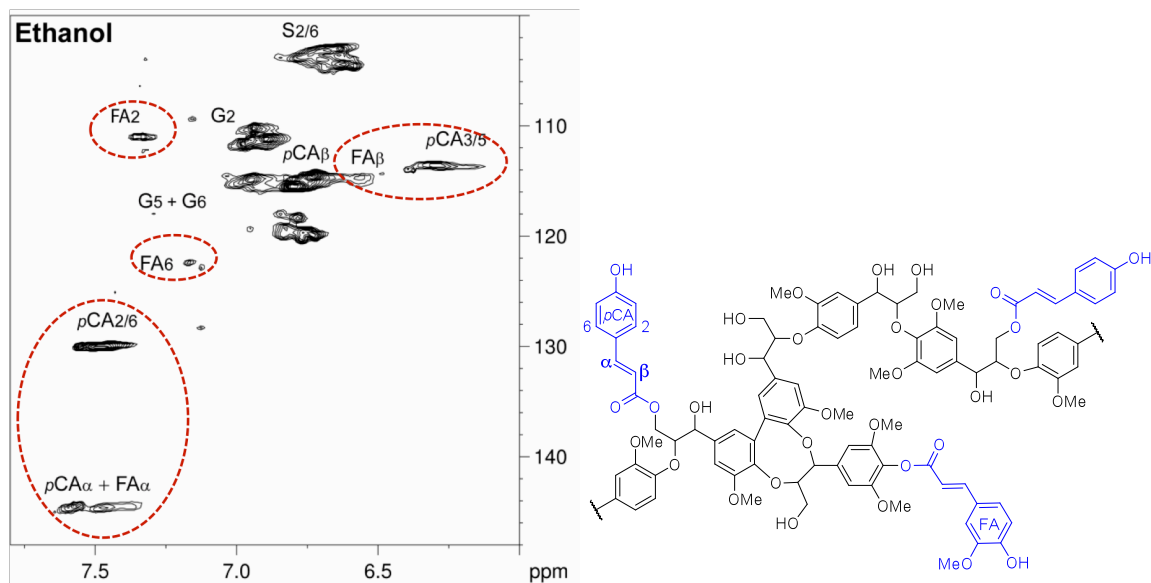
16.0 mg, 1.50×10^{-2} mmol, 5.0 mol%), 2-phenoxy-1-phenylethan-1-ol (32.1 mg, 0.150 mmol), 2-(2-methoxyphenoxy)-1-phenylethan-1-one (36.3 mg, 0.150 mmol), dodecane (internal standard for GC) and *m*-xylene (1.2 ml) at 120 °C for 4 h. Analysis of the reaction mixture by GC showed that guaiacol (92%), phenol (6%), acetophenone (103%), 2-(2-methoxyphenoxy)-1-phenylethan-1-ol (5%) and 2-phenoxy-1-phenylethan-1-one (88%) formed at 94% conversion of 2-(2-methoxyphenoxy)-1-phenylethan-1-one and 98% conversion of 2-phenoxy-1-phenylethan-1-ol.

Time profile analysis: fragmentation of 2-phenoxy-1-phenylpropane-1,3-diol catalyzed by Pd/C catalyst (Figure 1)

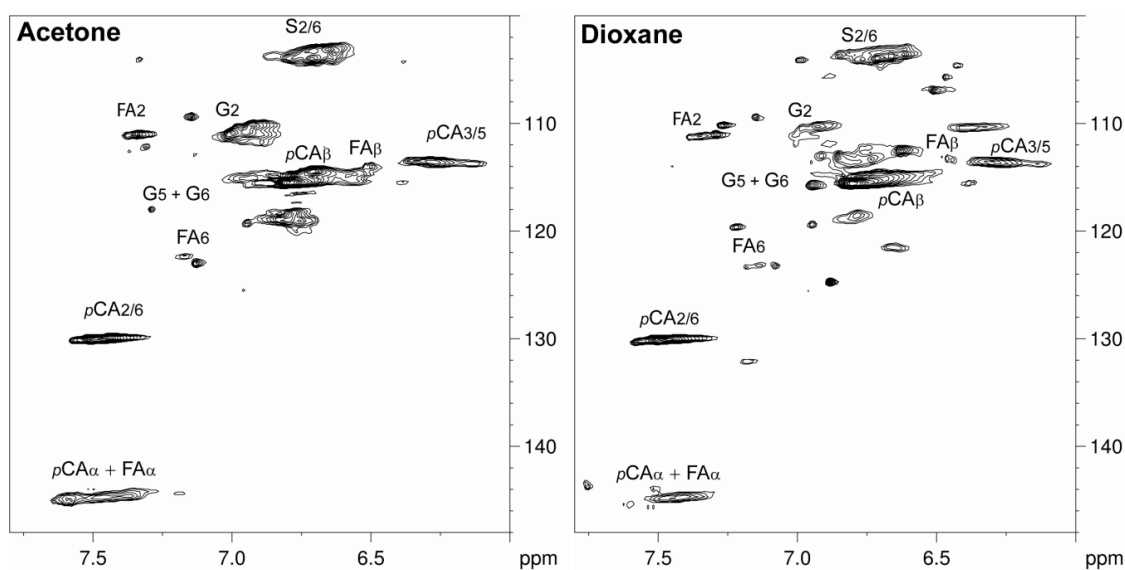
The reaction was conducted according to the General Procedure with Pd/C (10.0 wt%, 16.0 mg, 1.50×10^{-2} mmol, 5.0 mol%), 2-phenoxy-1-phenylpropane-1,3-diol (73.2 mg, 0.300 mmol), dodecane (internal standard for GC) and *p*-cymene/dioxane (1:1 mixture, 1.2 ml) at 200 °C for 8 h. Small aliquots of the reaction mixture were removed after 5 min, 15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h, and the samples were analyzed by GC. The amount of identified products was plotted against time to reveal the progress of this fragmentation reaction within the first 8 h of the reaction time. For the detailed discussion, please see the main text.

HSQC spectra of the aromatic regions of isolated lignin samples from *M. Giganteus* through organosolvolytic (with ethanol, acetone and dioxane).

The full analysis of these lignin samples through 2D NMR was disclosed previously.¹⁰



P-hydroxycinnamates units (P-CA and FA) in Ethanol-solv Miscanthus G. lignin



P-CA and FA units in Acetone & Dioxane-solv M. Giganteus lignin

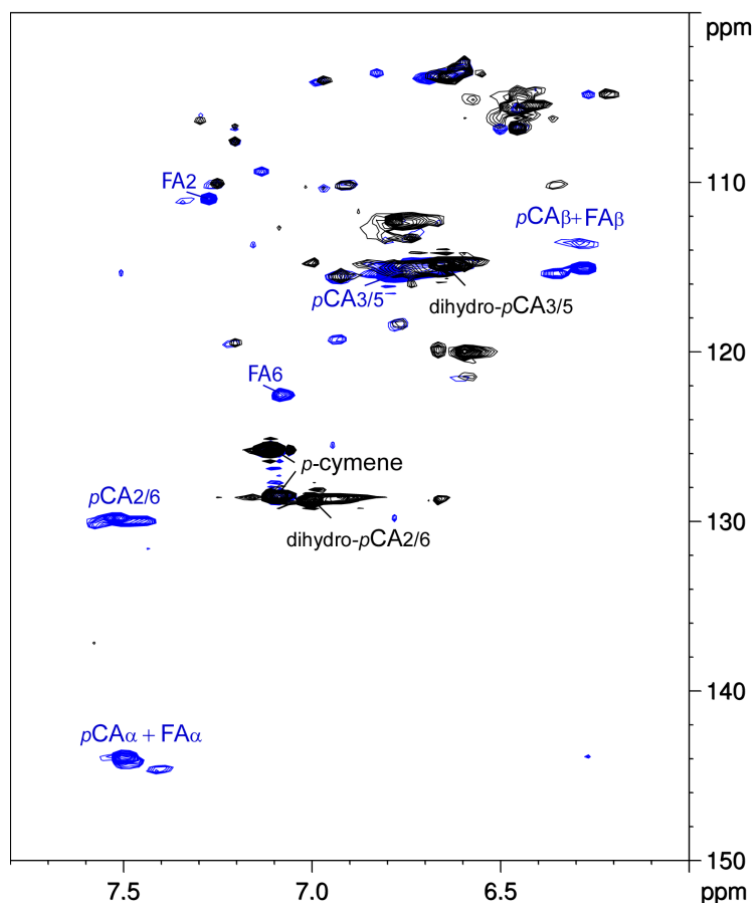
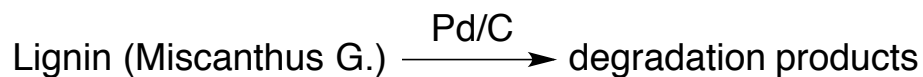
Figure S1. HSQC spectra of the aromatic regions of lignin samples isolated from *M. Giganteus* through ethanol-, acetone-, and dioxane-solvolysis

The procedure for Pd/C catalyzed fragmentation of the isolated acetone-solv lignin sample from *M. Giganteus* under hydrogen free conditions

In a glovebox, a 15 ml glass tube (~10 cm long X 1.0 cm in diameter) equipped with a

Teflon-coated magnetic stir bar was charged with Pd/C (10.0 wt%, 63.9 mg, 6.00×10^{-2} mmol, 20.0 mol%), the acetone-soluble lignin (59.4 mg, 0.300 mmol) and a magnetic stir bar. Then, 1.2 mL dioxane was added, and the mixture was stirred for 5 min to dissolve the lignin sample. The tube was sealed with the Teflon-lined screw cap and removed from the glovebox. The vessel was heated in an oil bath at 200 °C for 24 h. The resulting dark black mixture was cooled to room temperature, diluted with additional amount of dioxane (1 mL), and passed through a short plug of Celite (2 cm in length) to remove black solid materials. Additional portions of dioxane (3 x 1.0 mL) were used to wash the Celite, and the filtrates were combined to give a brown clear solution. Volatile materials were evaporated under vacuum, and the resulting dark black residual was subjected to high vacuum (<50 torr) for at least 24 h to remove remaining volatile compounds to generate a dark brown oily film (55.7 mg, 94% yield of recovery). The dark brown material was characterized by HSQC experiment.

A control experiment was conducted exactly as described above except for the exclusion of the Pd/C catalyst in the reaction. A dark brown solid was obtained (57.6 mg, 97% yield of recovery) and analyzed by HSQC experiment. The data were used for comparison purposes.



Double bonds disappeared after treatment with Pd/C without added H₂

Figure S2. HSQC spectrum of the degradation product of acetone-solv lignin with Pd/C without added H₂ in comparison to the acetone-solv lignin from *M. Giganteus* (aromatic region)

The procedure for hydrogenative treatment of dioxanesolv lignin samples from *M. Giganteus*

In a glovebox, a 50 mL round bottom flask equipped with a stir bar was charged with 10 wt % Pd/C (106 mg, 0.100 mmol, 1.0 mol%) and dioxanesolv lignin (1.98 g, ~10.0 mmol). The flask was sealed with a septum and removed from the glovebox. The vessel was attached to a manifold, and the reaction atmosphere was switched to hydrogen by

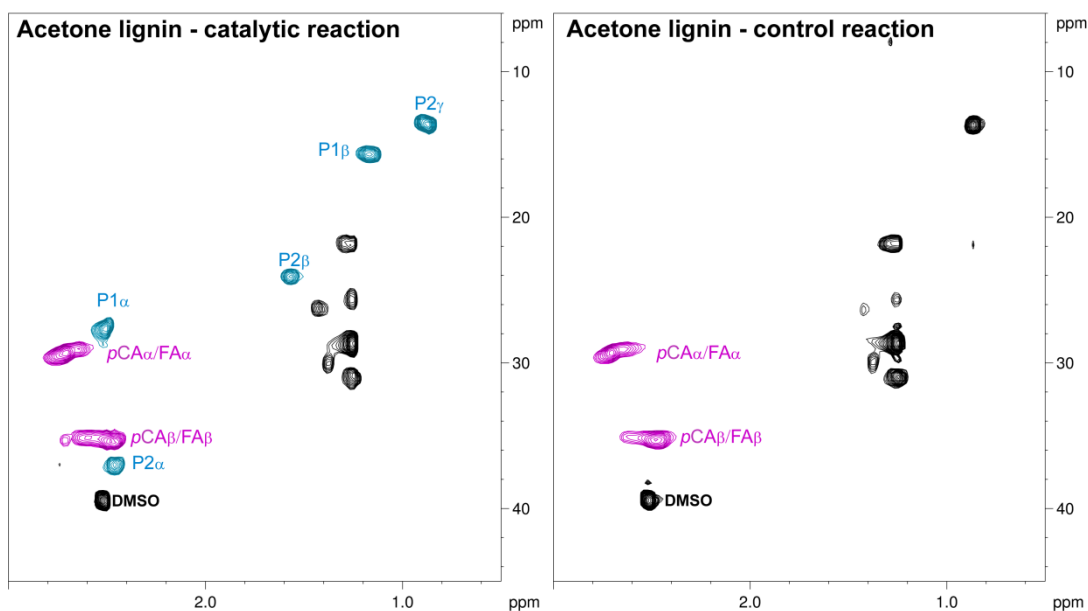
three vacuum/H₂ refill cycles. After that, dioxane (20.0 mL) was introduced via a syringe. The reaction mixture was allowed to stir under one atmosphere of hydrogen (with a H₂ balloon) at 22 °C for 4 h. The black suspension was then exposed to air and passed through a plug of Celite, and the Celite containing the residue was eluted with additional dioxane (3 x 10.0 mL). Low boiling solvents in the combined organic filtrate were evaporated under vacuum. The residue was further subjected to high vacuum (<50 torr) for at least 24 h, resulting in a dark brown solid (1.93 g, 97% yield of recovery). The material was characterized by HSQC and GPC experiments, and used in the following fragmentation study.

The procedure for Pd/C catalyzed fragmentation of the reduced acetonesolv lignin sample under hydrogen free conditions (Scheme 3)

In a glovebox, a 15 ml glass tube (~10 cm long X 1.0 cm in diameter) equipped with a Teflon-coated magnetic stir bar was charged with Pd/C (10.0 wt%, 63.9 mg, 6.00x10⁻² mmol, 20.0 mol%), the acetonesolv lignin pretreated with hydrogen as described in the previous procedure (59.4 mg, 0.300 mmol) and a magnetic stir bar. Then, 1.2 mL dioxane was added, and the mixture was stirred for 5 min to dissolve the lignin sample. The tube was sealed with the Teflon-lined screw cap and removed from the glovebox. The vessel was heated in an oil bath at 200 °C for 24 h. The resulting dark black mixture was cooled to room temperature, diluted with additional amount of dioxane (1 ml), and passed through a short plug of Celite (2 cm in length) to remove black solid materials. Additional portions of dioxane (3 x 1.0 mL) were used to wash the Celite, and the filtrates were combined to give a brown clear solution. Volatile materials were evaporated under vacuum, and the resulting dark black residual was subjected to high vacuum (<50 torr) for at least 24 h to remove remaining volatile compounds to generate a dark brown oily film (50.5 mg, 85% yield of recovery). The dark brown material was characterized by HSQC and GPC experiments.

A control experiment was conducted exactly as described above except for the exclusion of the Pd/C catalyst in the reaction. A dark brown solid was obtained (58.4 mg, 98% yield of recovery) and analyzed by HSQC and GPC experiments. The data were used for

comparison purposes (cf. Scheme 3 in the main text).



Signals for alkyl chains in the aliphatic region resulting from lignin degradation catalyzed by Pd/C

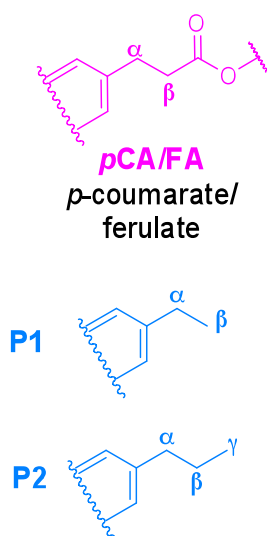


Figure S3. HSQC spectra of the degraded material and the starting hydrogenatively treated acetonesolv lignin (aliphatic region)

General procedure for the Pd/C catalyzed fragmentation of lignin samples under 1 atm of hydrogen

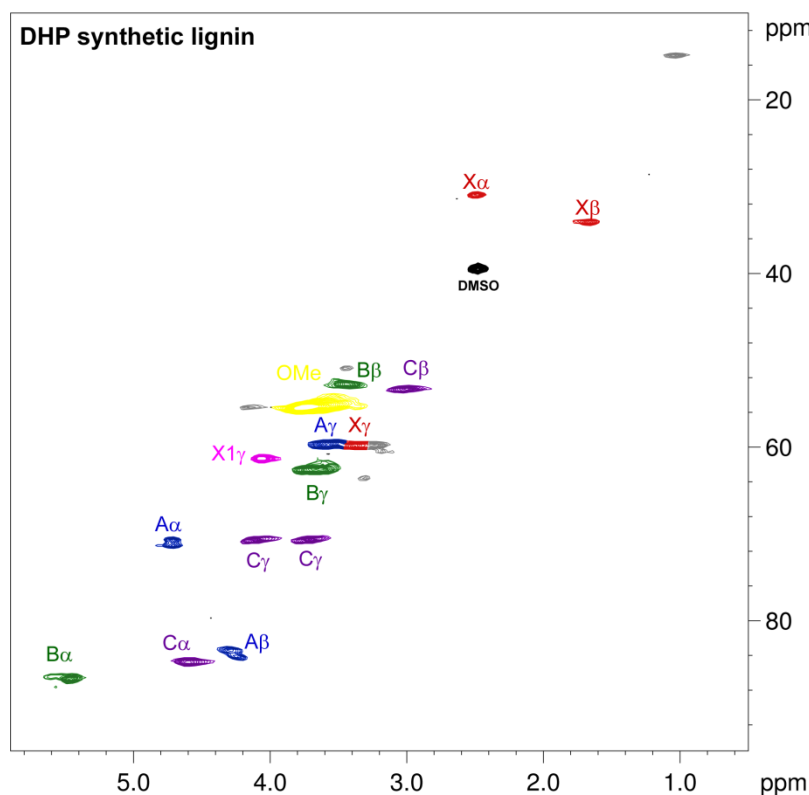
Reactions were conducted in 15 ml glass Schlenk vessels (made from glass tubes with an outer diameter of 16 mm; the volume of the vessels is 13.1-14.8 ml) equipped with Teflon screw valves and Teflon-coated magnetic stir bars (3 mm x 10 mm; supplied by Fisher Scientific). The reported pressure of hydrogen was measured at room temperature, and the pressure refers to the reading from the gauge of the gas cylinder. The reaction vessels were heated in an oil bath; the reaction temperature refers to the temperature of the oil bath. The stirring rate was kept constant at 900 rpm (Magnetic stirrer IKA Ceramag Midi; the stir rate dial was set to 7.5).

In a glovebox, a 15 ml Schlenk vessel equipped with a Teflon screw valve was charged with 10 wt% Pd/C (63.9 mg, 6.00×10^{-2} mmol of pure palladium, 20.0 mol%), a lignin sample (~60.0 mg, 0.300 mmol) and a magnetic stir bar. Then, dioxane (1.2 ml) was added, and the mixture was stirred for 5 min to dissolve the lignin. The Schlenk vessel was sealed with the Teflon screw valve and removed from the glovebox. The reaction mixture was degassed via two cycles of freeze-pump-thaw, and the vessel was pressurized with 1 bar (15 psi) of hydrogen at room temperature. The vessel was sealed with the Teflon valve and heated in an oil bath at 200 °C for 24 h. The resulting dark black mixture was cooled to room temperature, diluted with additional dioxane (1.0 ml), and passed through a short plug of Celite (2 cm in length) to remove black solid materials. Additional portions of dioxane (3 x 1.0 mL) were used to wash the Celite, and the filtrates were combined to give a clear dark brown solution. A small aliquot (100 μ L) of the resulting solution was removed and subjected to treatment with excess N,O-bis(trimethylsilyl)trifluoroacetamide (10 equivalents vs. substrate) at 65 °C for one hour. The silylation of phenols and alcohols give products with narrow peaks in the GC and GC-MS traces for these mono-lignols, as reported previously.¹⁰ The products have all been reported previously and were identified by comparison of the mass spectra and retention times of the products by GC/MS and GC with those of authentic compounds obtained commercially or synthesized. The volatile materials were evaporated under vacuum, and the resulting dark black residue was subjected to high vacuum (<50 torr) for at least 24 h to remove remaining volatile compounds. This procedure generated a dark brown oily film (67-79% yield of recovery). The dark brown material was further characterized by HSQC and GPC experiments.

The procedure for Pd/C catalyzed fragmentation of the synthetic lignin under an atmospheric pressure of hydrogen (Scheme 4)

The reaction was conducted according to the general procedure with Pd/C (63.9 mg, 6.00×10^{-2} mmol, 20.0 mol%), synthetic lignin (59.4 mg, 0.300 mmol), dioxane (1.2 ml) and H₂ (15 psi) at 200 °C for 24 h. The resulting dark brown oily film (31.4 mg, 53% yield of recovery) was analyzed by HSQC and GPC.

A control experiment was conducted exactly as described above except for the exclusion of the Pd/C catalyst in the reaction. A dark brown solid was obtained (57.7 mg, 97% yield of recovery). This solid was analyzed by HSQC and GPC experiments, and the data were used for comparison purposes (cf. Scheme 4 in the main text).



Major linkages identified from synthetic lignin sample

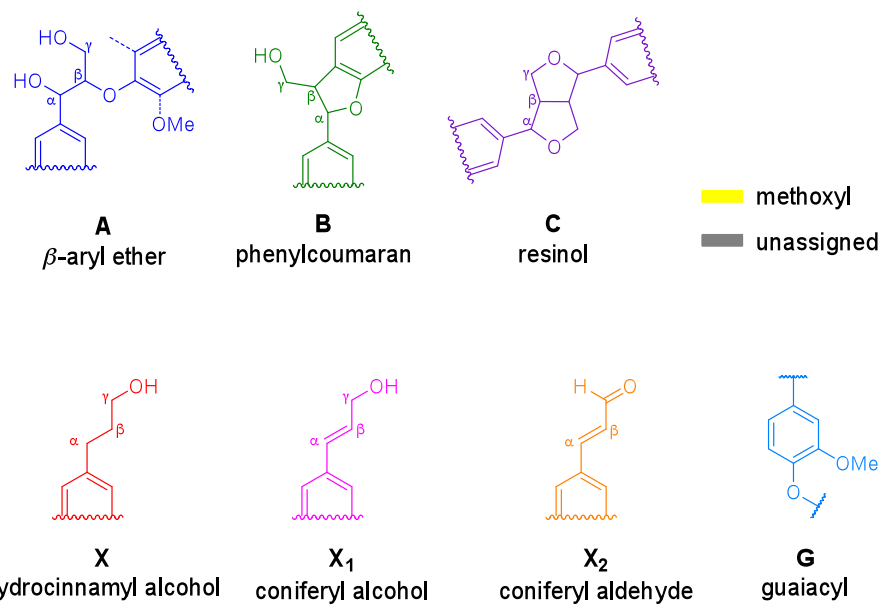
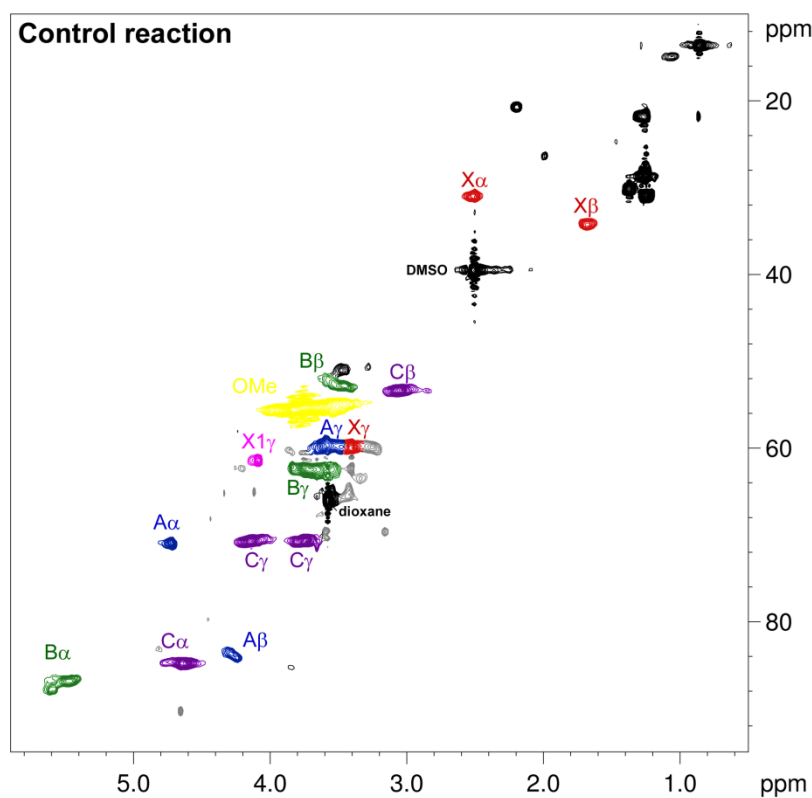
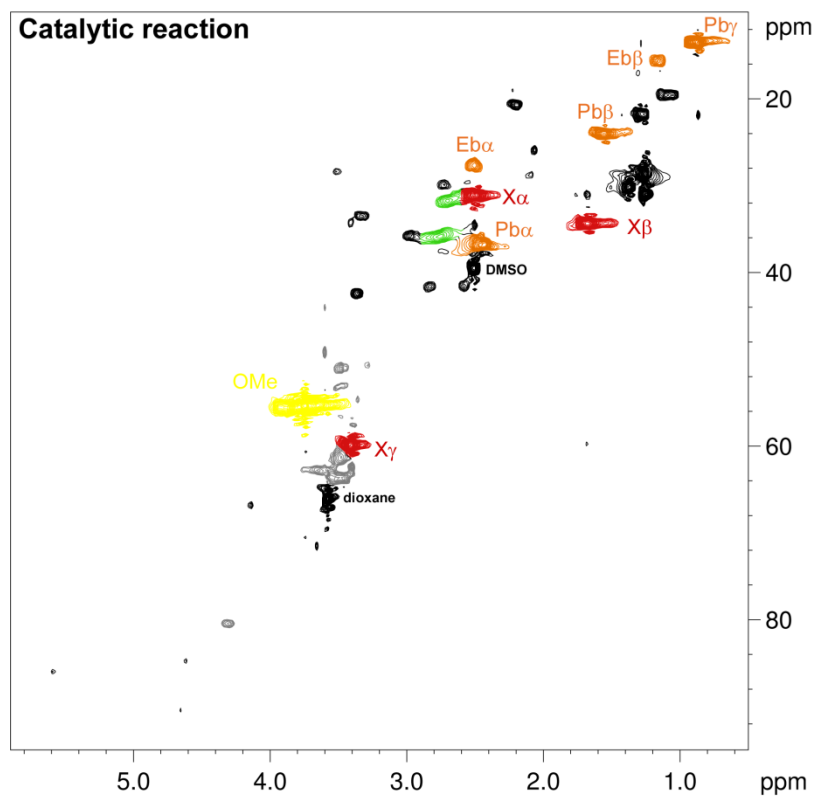


Figure S4. HSQC spectrum of the synthetic lignin and linkage analysis





Major aliphatic products formed:

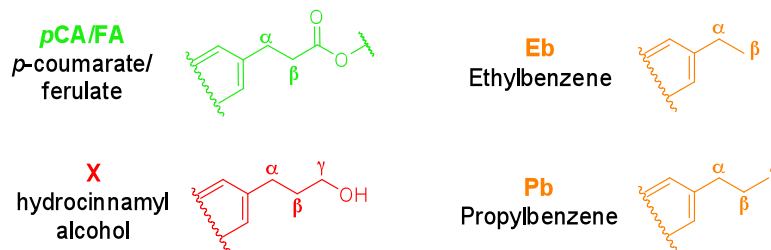
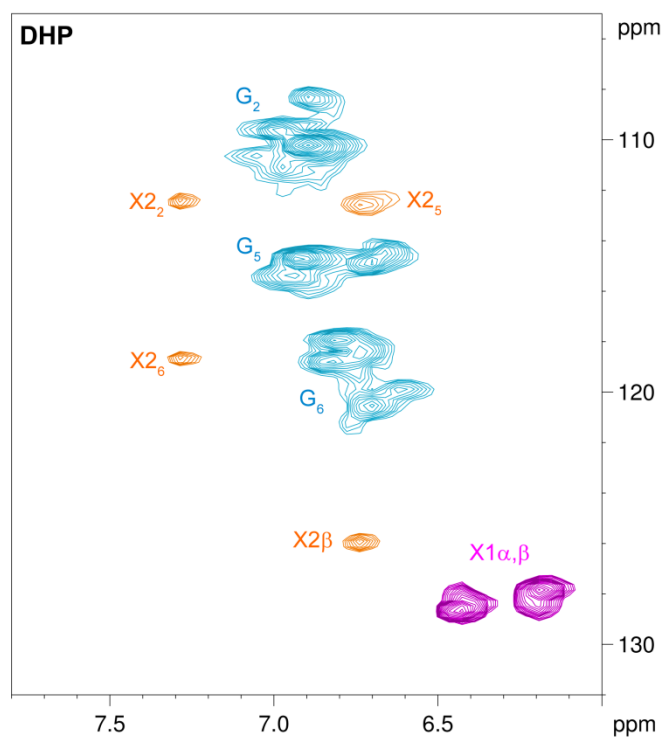
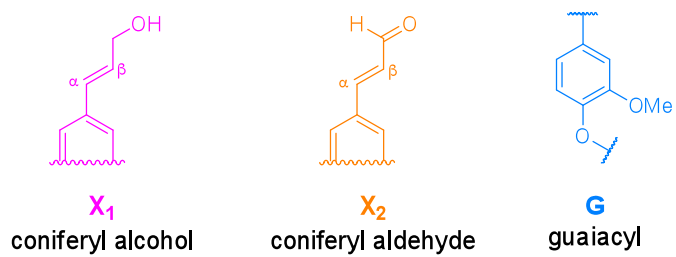
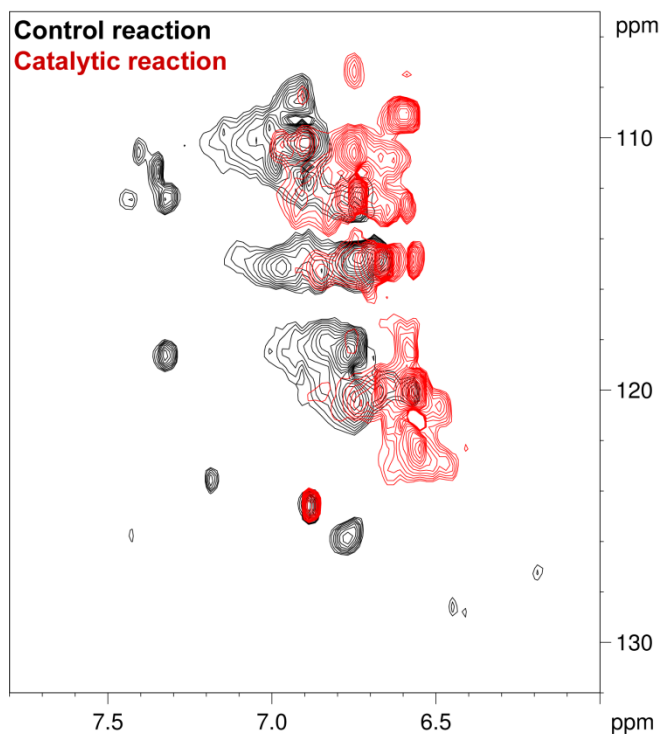


Figure S5. HSQC spectra of the degraded material after fragmentation and of the material obtained from the control experiment (aliphatic and oxygenated region)



Peak assignment for the aromatic region:





In the catalytic reaction, the aromatic protons resonate at higher field, corresponding to the reduction of the double bonds revealed in the previous graph

Figure S6. HSQC spectra of the degraded material and of the material obtained from the control experiment (aromatic region)

The procedure for Pd/C catalyzed fragmentation of acetonesolv lignin under an atmospheric pressure of hydrogen (Figure 2 and Entry 1, Table 2)

The reaction was conducted according to the general procedure with Pd/C (63.9 mg, 6.00×10^{-2} mmol, 20.0 mol%), acetonesolv lignin (59.4 mg, 0.300 mmol), dioxane (1.2 ml) and H₂ (15 psi) at 200 °C for 24 h. The resulting dark brown oily film (39.8 mg, 67% yield of recovery) was analyzed by HSQC and GPC. GC analysis of the aliquot obtained from the reaction mixture showed that 4-ethylphenol **19** (0.65 mg), 4-ethylguaiaicol **14** (2.21 mg), 2-methoxy-4-propylphenol **21** (1.19 mg), 4-ethyl-2,6-dimethoxyphenol **20** (2.58 mg), 2,6-dimethoxy-4-propylphenol **22** (1.39 mg), dihydroconiferyl alcohol **23** (0.44 mg), and 4-(3-hydroxypropyl)-2,6-dimethoxyphenol **24** (0.51 mg) formed in a combined yield of 15.1 wt%.

A control experiment was conducted exactly as described above except for the exclusion of the Pd/C catalyst in the reaction. A dark brown solid was obtained (55.5 mg, 93% yield of recovery). This solid was analyzed by HSQC and GPC, and the data were used for comparison purposes (cf. Figure 2 in the main text).

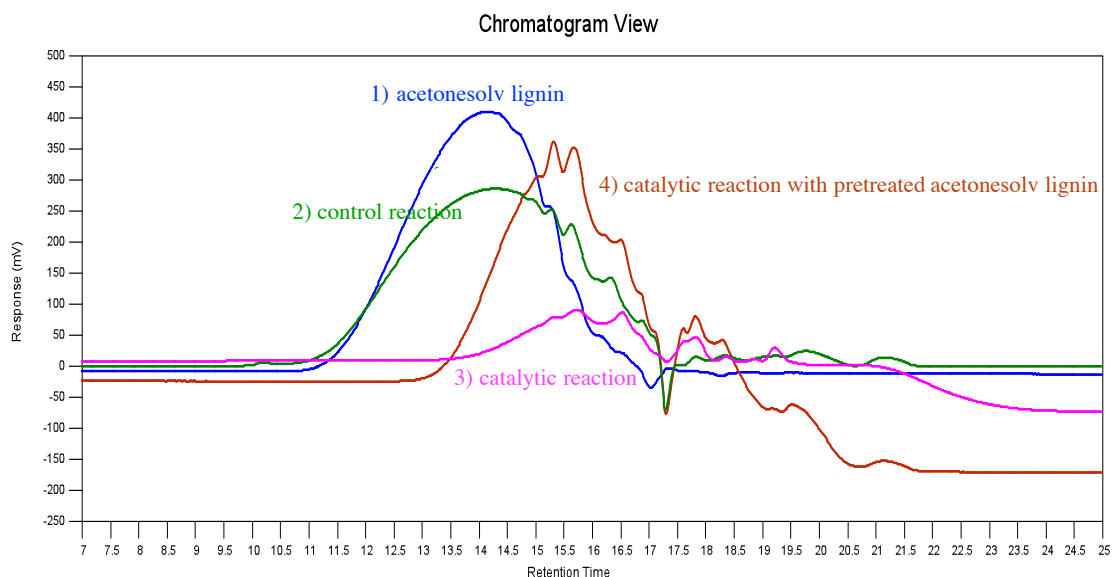


Figure S7. GPC graphs of 1) acetonesolv lignin, 2) material obtained from the control experiment, 3) degraded acetonesolv lignin after fragmentation and 4) overlay with degraded material from the fragmentation of hydrogenatively treated acetonesolv lignin under the hydrogen free condition.

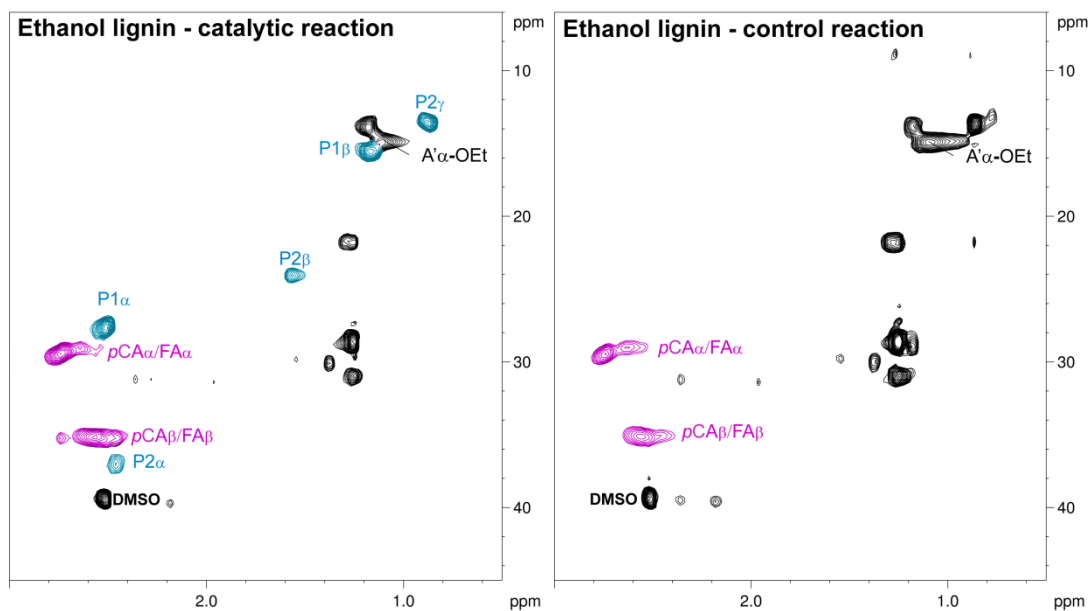
Table S1. Screening of the BASF heterogeneous catalyst kit for fragmentation of acetonesolv lignin under 15 psi of H₂

Entry	Catalyst	Yield wt %	Ratio of 14 : 21	Ratio of 20 : 22	G : S ratio
1	10 wt% Pd/C, reduced, dry powder	15.1	1.9 : 1.0	1.9 : 1.0	1.0 : 1.2
2	5wt% Pd/alumina, reduced, dry powder	<5	--	1.0 : 1.0	--
3	5wt% Pd/C, reduced, dry powder	13.5	1.9 : 1.0	1.0 : 1.4	1.1 : 1.0
4	10wt% Pd/C, wet reduced paste	<5	--	1.0 : 1.0	--
5	20wt% Pd/C, wet unreduced paste	<1	--	--	--
6	5wt% Pd on peat C, wet reduced paste	12.3	1.0 : 1.0	1.0 : 2.0	1.0 : 2.0
7	10wt% Pd on wood C, wet reduced paste	11.6	1.0 : 1.4	1.0 : 3.0	1.0 : 1.0
8	5wt% Ru/C, wet reduced paste	3.5	3.0 : 1.0	5.2 : 1.0	1.0 : 2.8
9	5wt% Pt/C, wet reduced paste	10.8	1.0 : 2.0	1.0 : 6.9	1.2 : 1.0
10	5wt% Pt/C, reduced, dry powder	11.1	1.0 : 2.4	1.0 : 5.3	1.1 : 1.0

The procedure for fragmentation of ethanolsolv lignin catalyzed by Pd/C under an atmospheric pressure of hydrogen (Figure 2 and Entry 2, Table 2)

The reaction was conducted according to the general procedure with Pd/C (63.9 mg, 6.00×10^{-2} mmol, 20.0 mol%), ethanolsolv lignin (59.4 mg, 0.300 mmol), dioxane (1.2 ml) and H₂ (15 psi) at 200 °C for 24 h. The resulting dark brown oily film (43.6 mg, 73% yield of recovery) was analyzed by HSQC and GPC experiments. GC analysis of the aliquot obtained from the reaction mixture showed that 4-ethylphenol **19** (0.57 mg), 4-ethylguaiaicol **14** (2.13 mg), 2-methoxy-4-propylphenol **21** (0.51 mg), 4-ethyl-2,6-dimethoxyphenol **20** (2.61 mg), 2,6-dimethoxy-4-propylphenol **22** (0.63 mg), dihydroconiferyl alcohol **23** (0.33 mg), and 4-(3-hydroxypropyl)-2,6-dimethoxyphenol **24** (0.38 mg) formed in combined yield of 12.0 wt%.

A control experiment was conducted exactly as described above, except for the exclusion of Pd/C catalyst in the reaction. A dark brown solid was obtained (58.2 mg, 98% yield of recovery). The solid was analyzed by HSQC and GPC, and the data were used for comparison purposes (cf. Figure 2 in the main text).



New formation of alkyl chains in the aliphatic region

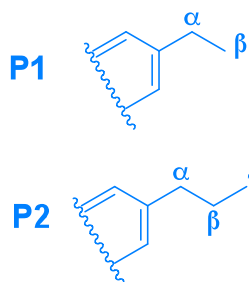
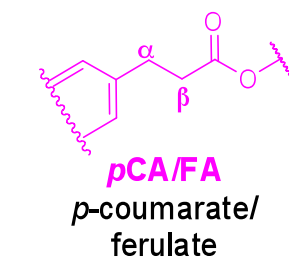


Figure S8. HSQC spectra of the degraded ethanol-soluble lignin after fragmentation and of the material obtained from the control experiment (aliphatic region)

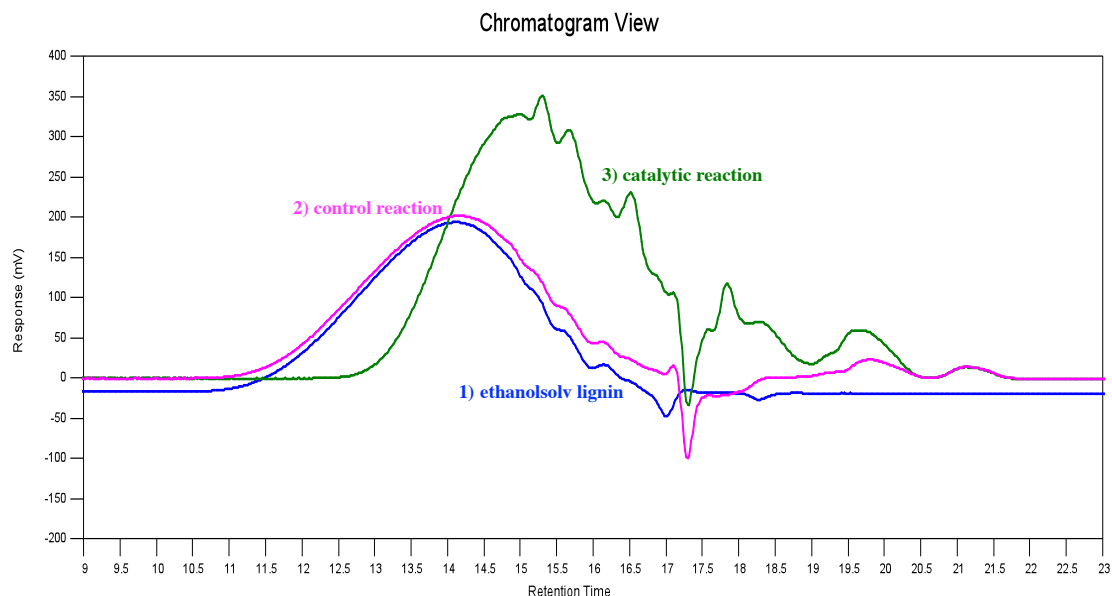


Figure S9. GPC graphs of 1) ethanol-solv lignin, 2) material obtained from the control experiment and 3) degraded ethanol-solv lignin after fragmentation reaction

The procedure for Pd/C catalyzed fragmentation of dioxane-solv lignin under an atmospheric pressure of hydrogen (Figure 2 and Entry 3, Table 2)

The reaction was conducted according to the general procedure with Pd/C (63.9 mg, 6.00×10^{-2} mmol, 20.0 mol%), dioxane-solv lignin (59.4 mg, 0.300 mmol), dioxane (1.2 ml) and H₂ (15 psi) at 200 °C for 24 h. The resulting dark brown oily film (40.9 mg, 69% yield of recovery) was analyzed by HSQC and GPC experiments. GC analysis of the aliquot obtained from the reaction mixture showed the formation of 4-Ethylphenol **19** (0.39 mg), 4-Ethylguaiacol **14** (1.99 mg), 2-Methoxy-4-propylphenol **21** (1.24 mg), 4-ethyl-2,6-dimethoxyphenol **20** (2.32 mg), 2,6-dimethoxy-4-propylphenol **22** (1.30 mg), dihydroconiferyl alcohol **23** (0.37 mg), and 4-(3-Hydroxypropyl)-2,6-dimethoxyphenol **24** (0.40 mg) in combined 13.5 wt% yield.

A control experiment was conducted exactly as described above except for the exclusion of Pd/C catalyst in the reaction. A dark brown solid was obtained (57.1 mg, 96% yield of recovery), analyzed by HSQC and GPC experiments and the data was used for comparison purposes (cf. Figure 2 in the main text).

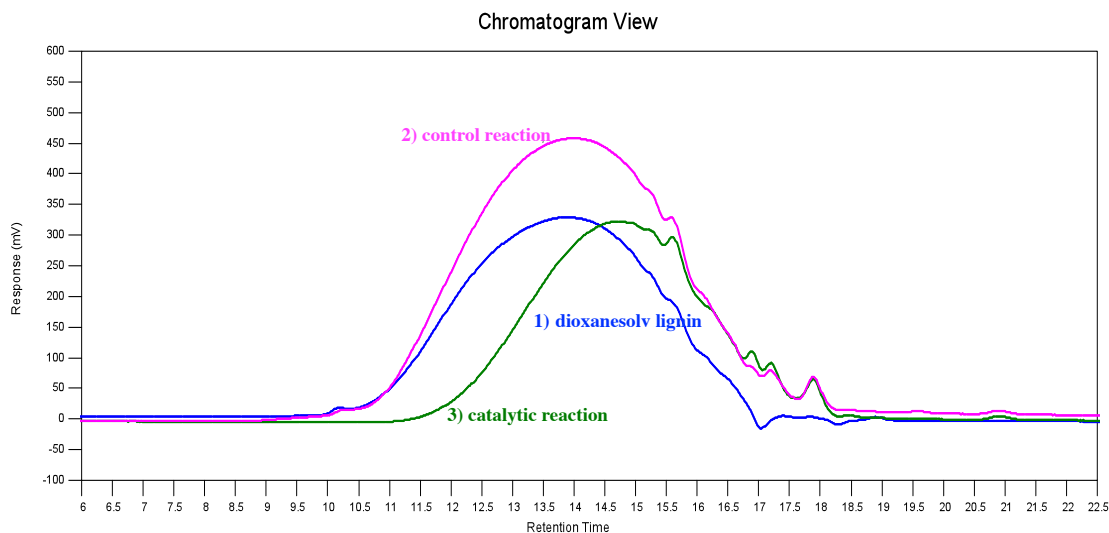
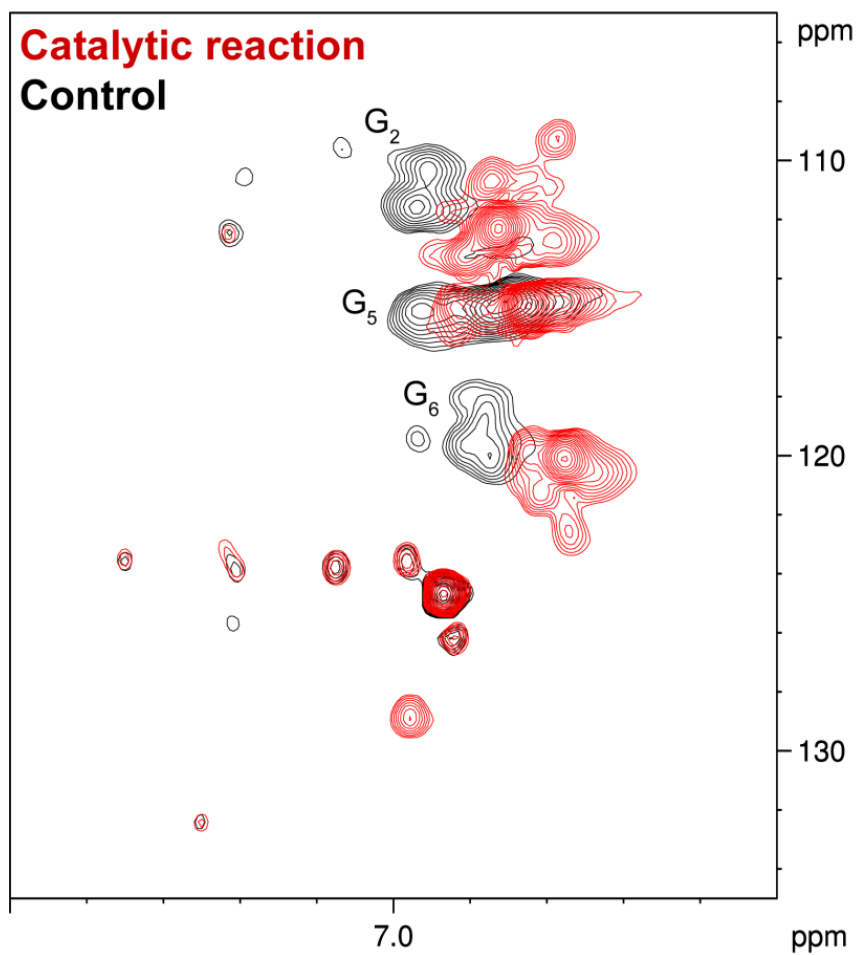


Figure S10. GPC graphs of 1) dioxanesolv lignin, 2) material obtained from the control experiment and 3) degraded dioxanesolv lignin after fragmentation reaction

The procedure for Pd/C catalyzed fragmentation of dioxanesolv pine lignin under an atmospheric pressure of hydrogen (Figure 2 and Entry 4, Table 2)

The reaction was conducted according to the general procedure with Pd/C (63.9 mg, 6.00×10^{-2} mmol, 20.0 mol%), dioxanesolv pine lignin (59.4 mg, 0.300 mmol), dioxane (1.2 ml) and H₂ (15 psi) at 200 °C for 24 h. The resulting dark brown oily film (46.9 mg, 79% yield of recovery) was analyzed by HSQC and GPC. GC analysis of the aliquot obtained from the reaction mixture showed that 4-ethylphenol **19** (0.38 mg), 4-ethylguaiacol **14** (3.27 mg), 2-methoxy-4-propylphenol **21** (0.99 mg), 4-ethyl-2,6-dimethoxyphenol **20** (<0.05 mg), 2,6-dimethoxy-4-propylphenol **22** (<0.05 mg), dihydroconiferyl alcohol **23** (0.83 mg), and 4-(3-hydroxypropyl)-2,6-dimethoxyphenol **24** (<0.05 mg) formed in a combined yield of 9.3 wt%.

A control experiment was conducted exactly as described above except for the exclusion of the Pd/C catalyst in the reaction. A dark brown solid was obtained (59.1 mg, >99% yield of recovery). The solid was analyzed by HSQC and GPC, and the data were used for comparison purposes (cf. Figure 2 in the main text).



Pine lignin has dominant G unit; the catalytic reaction generated alkyl chains

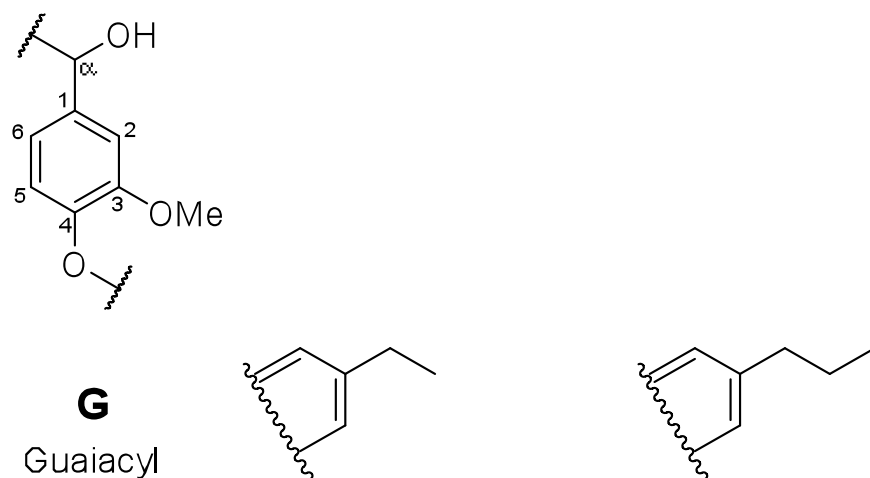


Figure S11. HSQC spectra of the degraded dioxanesolv pine lignin and of the material obtained from the control experiment (aromatic region)

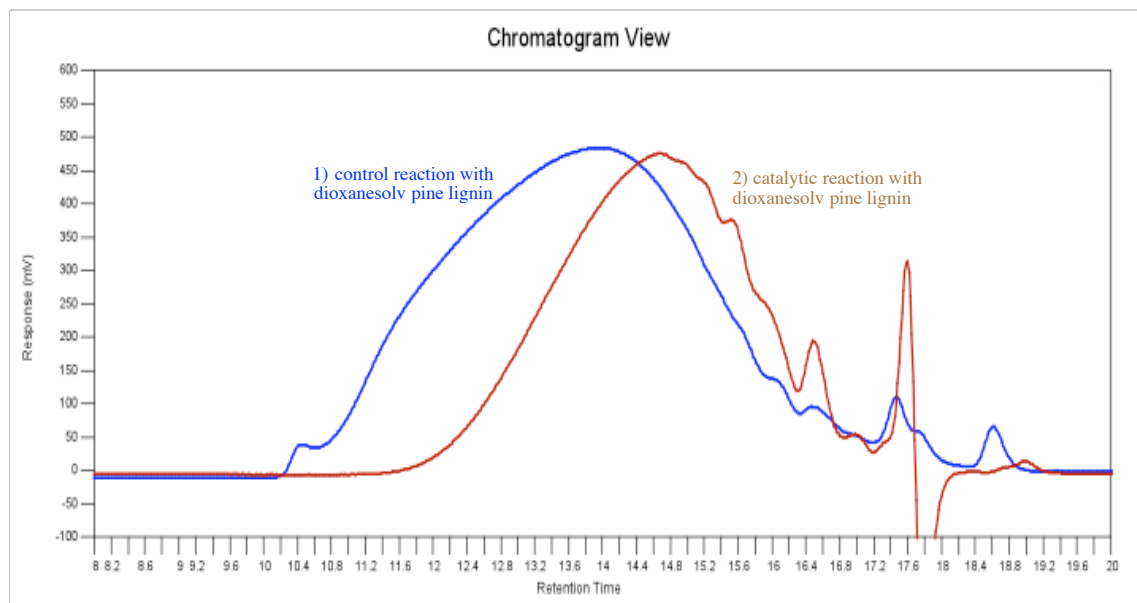
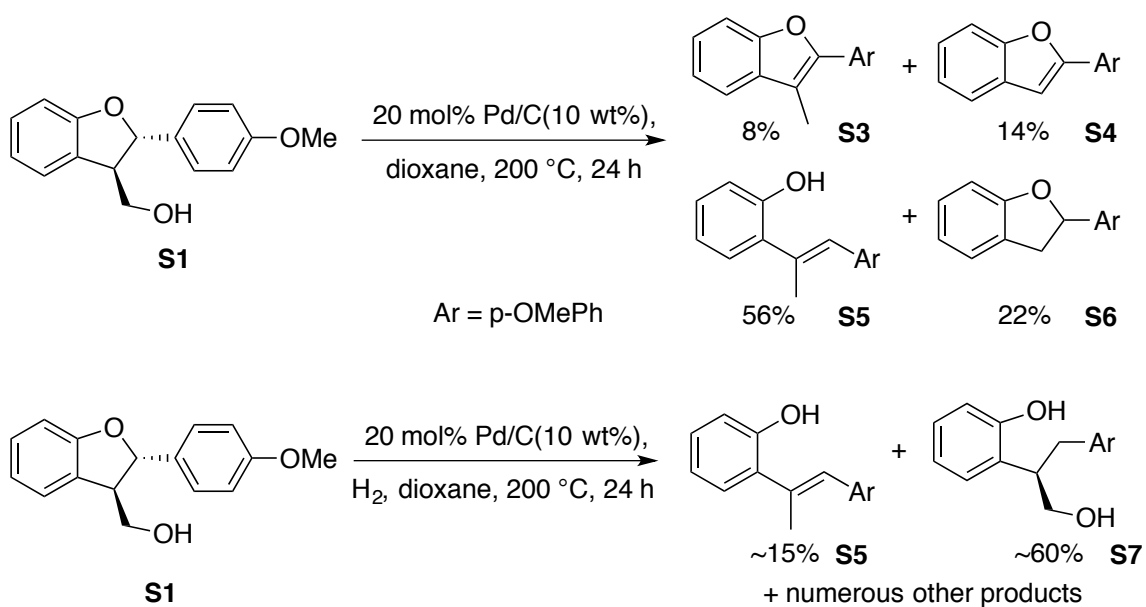


Figure S12. GPC graphs of 1) material obtained from the control experiment and 2) degraded dioxanesolv pine lignin after the fragmentation reaction

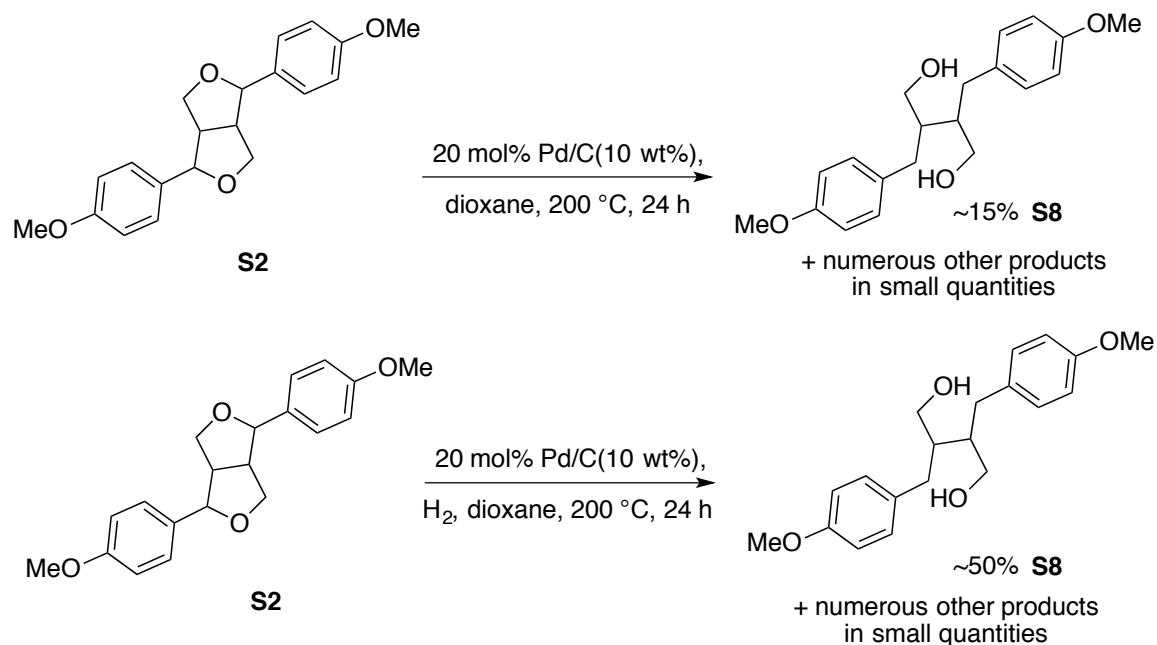


Scheme S1. Fragmentation of the phenylcoumaran model compound with and without 15 psi of hydrogen

The procedure for Pd/C catalyzed fragmentation of the phenylcoumaran model compound under an atmospheric pressure of hydrogen

The reaction was conducted according to the general procedure with Pd/C (63.9 mg, 6.00×10^{-2} mmol, 20.0 mol%), (2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)methanol (**S1**, 76.9 mg, 0.300 mmol), dioxane (1.2 ml) and H₂ (15 psi) at 200 °C for 24 h. The resulting clear light yellow oil (69.2 mg, 90% yield of recovery) was analyzed by ¹H NMR spectroscopy. The crude ¹H NMR analysis showed that **S7** formed in 60% yield as the major identifiable product.¹¹ About 15% of **S5** also formed (nitrobenzene as the internal standard). In addition, many unidentifiable byproducts formed, as observed in the baseline of the crude ¹H NMR spectrum at >98% conversion of the phenylcoumaran model substrate.

An experiment was conducted exactly as described above, except for the exclusion of 15 psi of hydrogen in the reaction. The hydrogen was substituted by an atmospheric pressure of nitrogen. A clear, light yellow oil was obtained (73.8 mg, 96% yield of recovery) and analyzed by ¹H NMR spectroscopy. The crude ¹H NMR analysis showed the formation of **S3** in 8% yield, **S4** in 14% yield, **S5** in 56% yield and **S6** in 22% yield with added nitrobenzene as the internal standard. Greater than 98% conversion of the phenylcoumaran model substrate was observed.



Scheme S2. Fragmentation of resinol model compound with and without 15 psi of hydrogen

The procedure for Pd/C catalyzed fragmentation of the resinol model molecule under an atmospheric pressure of hydrogen

The reaction was conducted according to the general procedure with Pd/C (63.9 mg, 6.00×10^{-2} mmol, 20.0 mol%), 1,4-Bis(4-methoxyphenyl)tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan (**S2**, 97.9 mg, 0.300 mmol), dioxane (1.2 ml) and H₂ (15 psi) at 200 °C for 24 h. The resulting clear light yellow oil (86.2 mg, 88% yield of recovery) was analyzed by ¹H NMR spectroscopy. The crude ¹H NMR analysis showed that **S8** formed in 50% yield as the major identifiable product¹² with added nitrobenzene as the internal standard. In addition, many unidentifiable byproducts formed, as observed in the baseline of the crude ¹H NMR spectrum at >98% conversion of the resinol model substrate.

An experiment was conducted exactly as described above, except for the exclusion of 15 psi of hydrogen in the reaction. The hydrogen was replaced by an atmospheric pressure of nitrogen. A clear light yellow oil was obtained (91.0 mg, 93% yield of recovery) and analyzed by ¹H NMR spectroscopy. The crude ¹H NMR analysis showed that **S8** formed in 15% yield as the major identifiable product with added nitrobenzene as the internal standard. In addition, many unidentifiable byproducts formed, as observed in the baseline of the crude ¹H NMR spectrum at 90% conversion of the resinol model substrate.

General procedure for the gram-scale catalytic fragmentation of lignin samples under an atmospheric pressure of hydrogen with reduced loading of Pd/C

In a glovebox, a 250 ml Schlenk vessel equipped with a Teflon screw valve was charged with 10 wt% Pd/C (0.80 g, 0.75 mmol of pure palladium, 5.0 mol%), a lignin sample (3.0 g, 15 mmol) and a magnetic stir bar. Then, dioxane (30 ml) was added, and the mixture was stirred for 5 min to dissolve the lignin. The Schlenk vessel was sealed with the Teflon screw valve and removed from the glovebox. The reaction mixture was degassed via three cycles of freeze-pump-thaw, and the vessel was pressurized with 1 bar (15 psi) of hydrogen at room temperature. The vessel was sealed with the Teflon valve and heated in an oil bath at 180 °C for 24 h. The resulting dark black mixture was cooled to room temperature, diluted with additional dioxane (30 ml), and filtered through a glass frit covered with a bed of Celite under vacuum to remove black solid materials. Additional

portions of dioxane (3 x 10 mL) were used to wash the Celite, and the filtrates were combined to give a clear dark brown solution. The volatile materials were evaporated under vacuum, and the resulting dark black residue was subjected to high vacuum (<50 torr) for at least 48 h to remove the remaining volatile compounds. A dark brown oily gel (90-97% yield of recovery) resulted. The dark brown material was characterized by GPC and subjected to viscosity measurements.

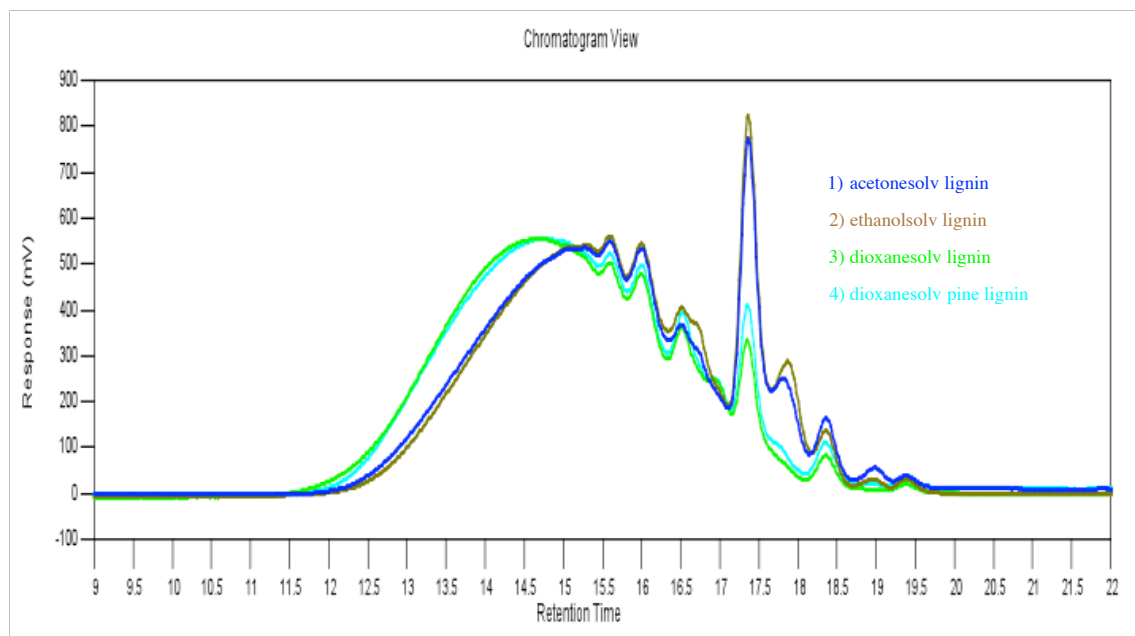


Figure S13. GPC graphs of gram-scale fragmentations of 1) acetonesolv lignin, 2) ethanolsolv lignin, 3) dioxanesolv lignin and 4) dioxanesolv pine lignin

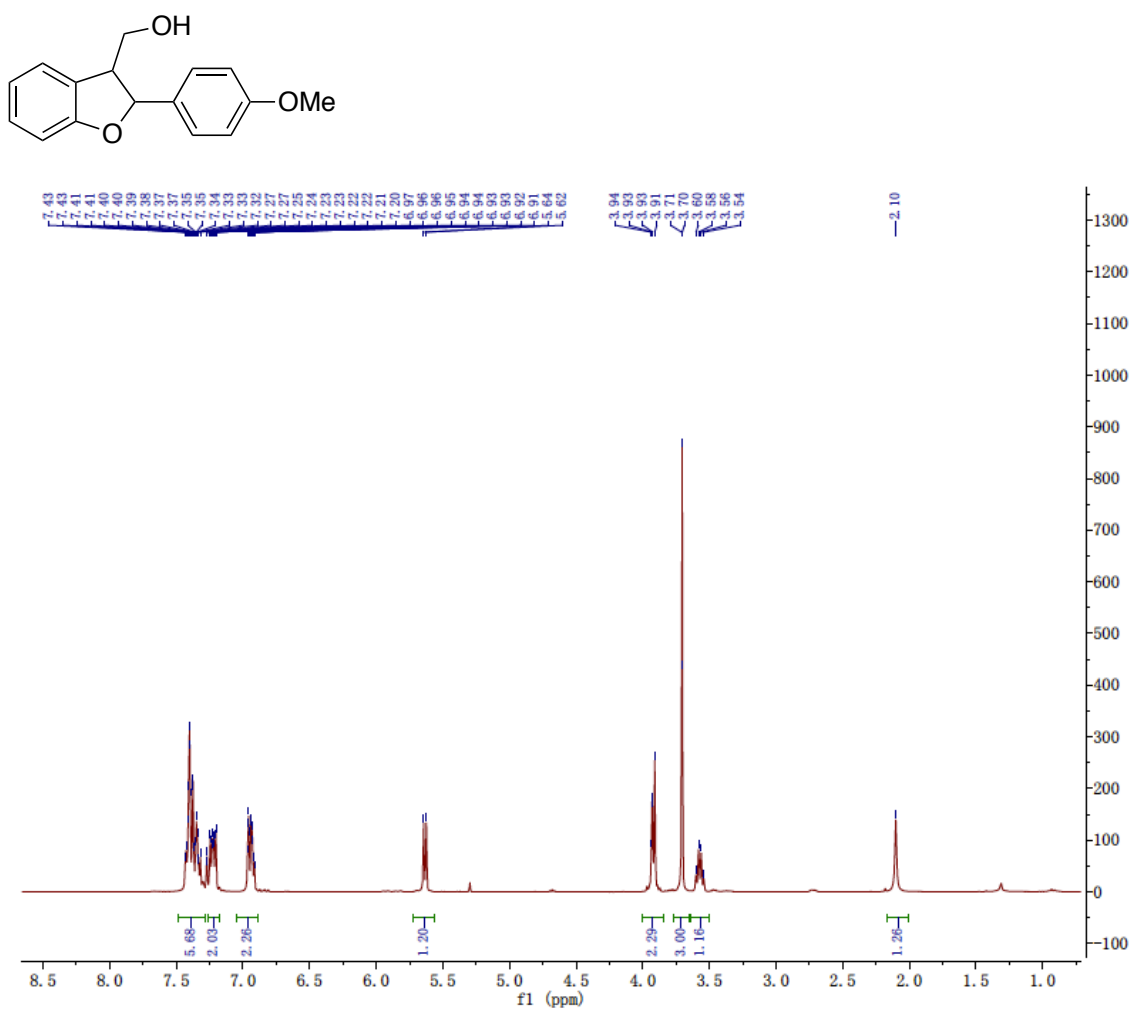
Table S2. Viscosity measurement of dioxansolv lignin blended with various amount of dioxane at 22 and 50 °C

Entry	Dioxane (mg/100 mg of sample)	T (°C)	Viscosity (cP)
1	0	22	>1000
2	0	50	>1000
3	20	22	440.7
4	40	22	128.9
5	60	22	37.5
6	80	22	18.3
7	20	50	305.1
8	40	50	70.7
9	60	50	19.1
10	80	50	9.8

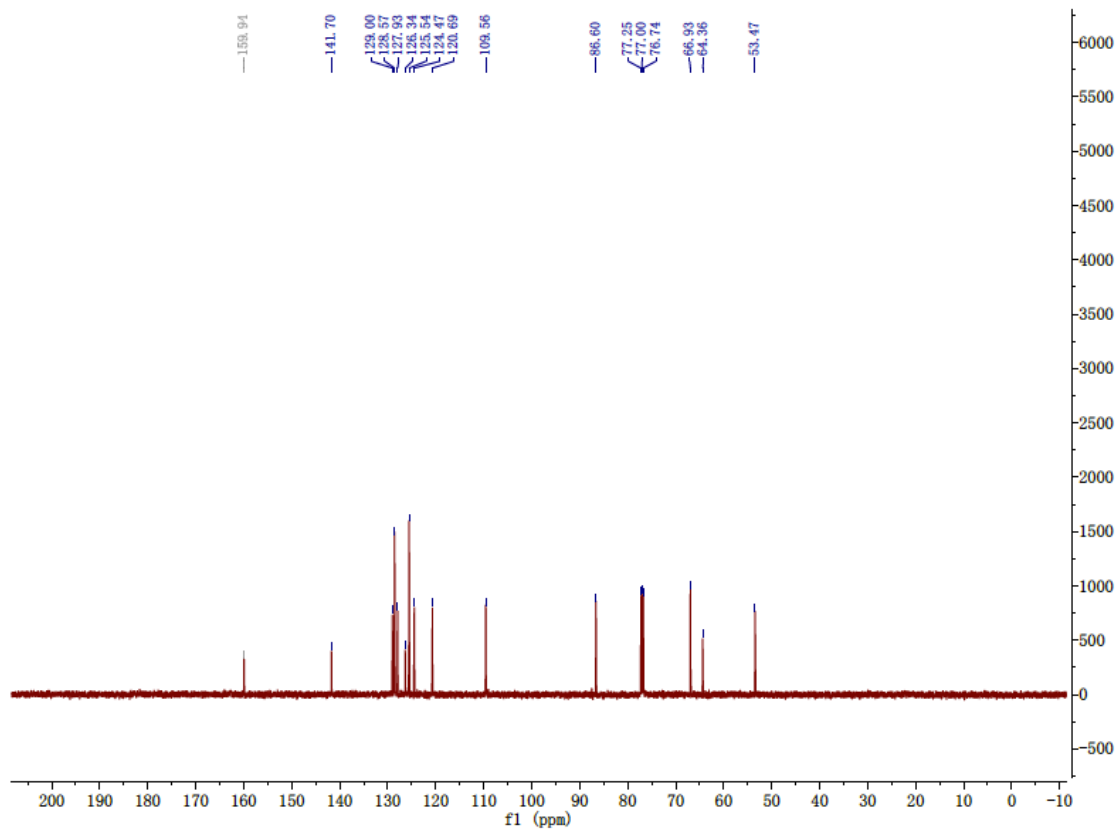
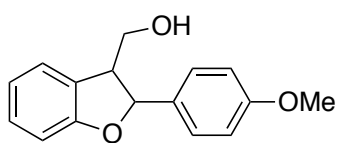
Table S3. Viscosity measurement of dioxansolv lignin blended with various renewable solvents

Dioxanesolv Lignin	$\xrightarrow[15 \text{ psi H}_2, \text{ dioxane, } 180 \text{ }^\circ\text{C, } 24 \text{ h}]{5 \text{ mol\% Pd/C (10 wt\%)}}$	Cleaved Dioxanesolv Lignin
3.6 gram in 50 mL dioxane		3.6 g in 2.9 g 1,4-dioxane, viscosity: 18.3 cP at 22 °C
Cleaved Dioxanesolv Lignin		Cleaved Dioxanesolv Lignin
3.6 g in 4.8 g 2-MeTHF, viscosity: 16.9 cP at 22 °C		3.6 g in 2.9 g 2-hydroxymethylTHF, viscosity: 20.4 cP at 22 °C
Cleaved Dioxanesolv Lignin		Cleaved Dioxanesolv Lignin
3.6 g in 2.9 g 2,5-hydroxymethylTHF, viscosity: 26.7 cP at 22 °C		3.6 g in 2.9 g γ -valerolactone, viscosity: 13.2 cP at 22 °C

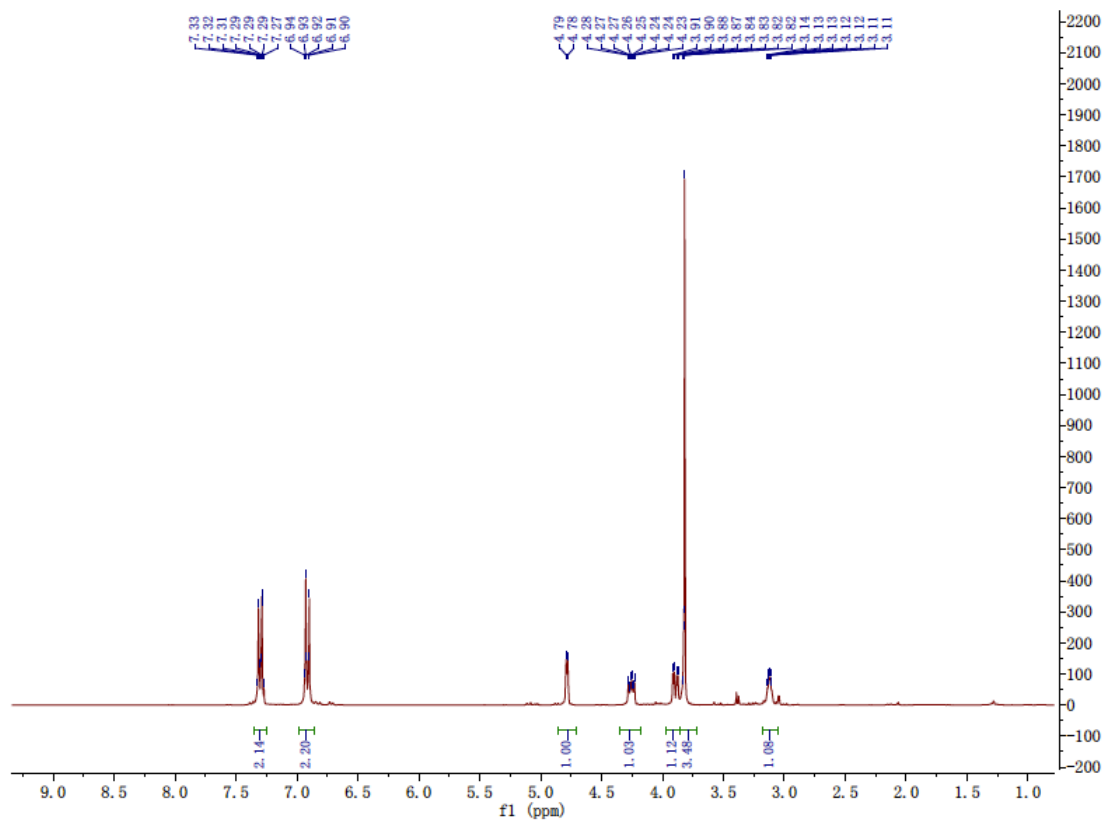
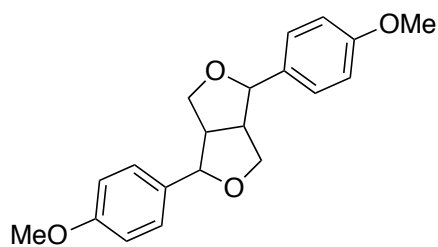
¹H NMR (300 MHz, CDCl₃): (2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)methanol (S1)



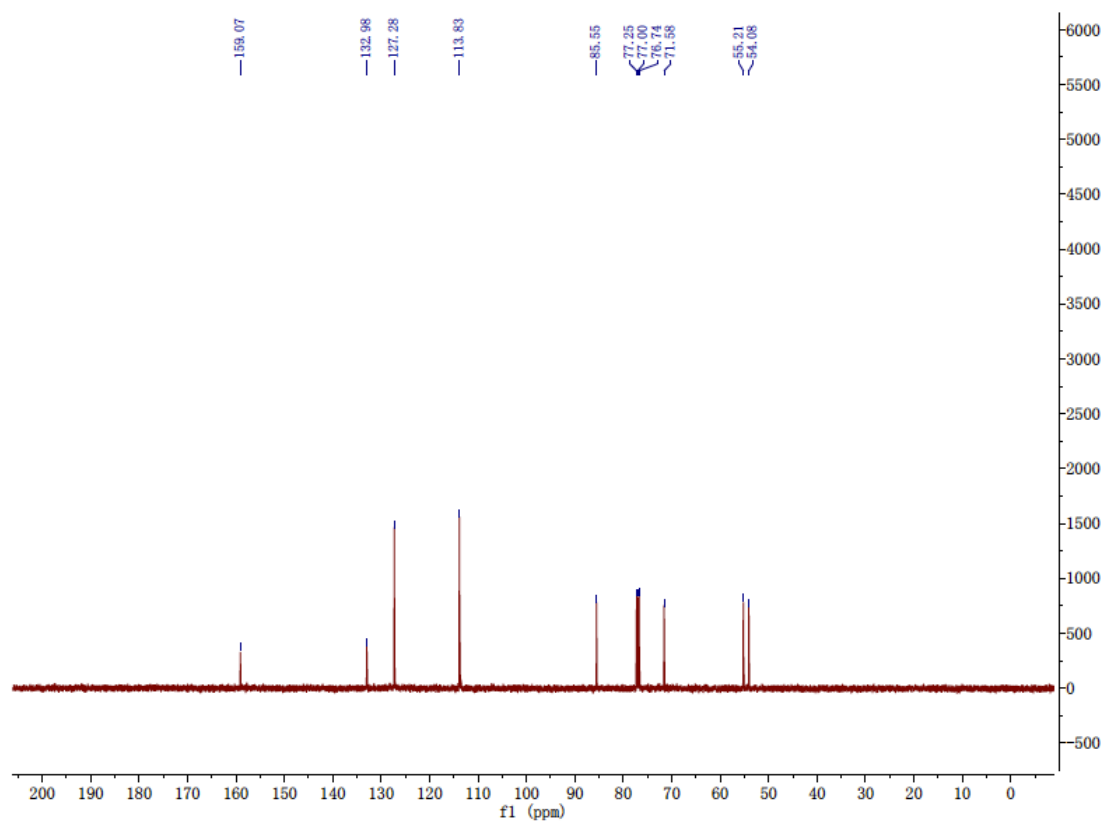
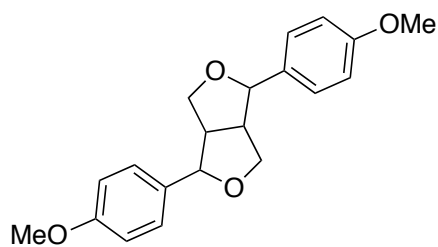
^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): (2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)methanol (S1)



^1H NMR (300 MHz, CDCl_3): 1,4-bis(4-methoxyphenyl)tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan (S2)



^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): 1,4-bis(4-methoxyphenyl)tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan (S2)



References

- [1] (a) Villaverde, J. J.; Li, J.; Ek, M.; Ligeró, P.; Vega, A. *J. Agric. Food Chem.* **2009**, *57*, 6262. (b) Rencoret, J.; Gutiérrez, A.; Nieto, L.; Jiménez-Barbero, J.; Faulds, C. B.; Kim, H.; Ralph, J.; Martínez, A. T.; del Río, J. C. *Plant Physiol.* **2011**, *155*, 667.
- [2] Gao, F.; Webb, J. D.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2016**, *55*, 1474.
- [3] Nichols, J. M.; Bishop, L. M.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2010**, *132*, 12554.
- [4] Wu, A.; Patrick, B. O.; Chung, E.; James, B. R. *Dalton Trans.* **2012**, *41*, 11093.
- [5] Buendia, J.; Mottweiler, J.; Bolm, C. *Chem. Eur. J.* **2011**, *17*, 13877.
- [6] Chan, J. M. W.; Bauer, S.; Sorek, H.; Sreekumar, S.; Wang, K.; Toste, F. D. *ACS Catal.* **2013**, *3*, 1369.
- [7] Jung, J.-C.; Park, O.-S. *Synthetic Communications* **2007**, *37*, 1665.
- [8] Fischer, J.; Savage, G. P.; Coster, M. J. *Org. Lett.* **2011**, *13*, 3376.
- [9] Reale, S.; Attanasio, F.; Spreti, N.; De Angelis, F. *Chem. Eur. J.* **2010**, *16*, 6077.
- [10] Bauer, S.; Sorek, H.; Mitchell, V. D.; Ibáñez, A. B.; Wemmer D. E. *J. Agric. Food Chem.* **2012**, *60*, 8203.
- [11] Shaw, S. A.; Aleman, P.; Christy, J.; Kampf, J. W.; Va, P.; Vedejs, E. *J. Am. Chem. Soc.* **2006**, *128*, 925.
- [12] Belletire, J. L.; Spletzer, E. G.; Pinhas, A. R. *Tetrahedron Lett.* **1984**, *25*, 5969.