Supporting Information

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**Selective Route to 2-Propenyl Aryls Directly from Wood by a Tandem Organosolv and Palladium-Catalysed Transfer Hydrogenolysis**

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General Considerations

Commercial reagents were obtained from Aldrich as well as deuterated solvents and were used without further purification. Pine (Pinus sylvestris) sawdust and Birch (Betula pendula) as firewood logs were provided by Däcksta Såg, Gimo, Sweden. $^1$H NMR spectra and $^{13}$C NMR spectra were recorded on an Agilent 400-MR (400 MHz and 101 MHz) spectrometer. Coupling constants ($J$) are reported in hertz, and chemical shifts are reported in parts per million ($\delta$) relative to CHCl$_3$ (7.26 ppm for $^1$H and 77.00 ppm for $^{13}$C), (CD$_3$)$_2$SO (2.50 ppm for $^1$H and 39.52 ppm for $^{13}$C) and (CD$_3$)$_2$CO (2.05 ppm for $^1$H and 29.84 ppm for $^{13}$C) as an internal standard. The description of the signals include: $s$ = singlet, $d$ = doublet, $t$ = triplet, $m$ = multiplet, $dd$ = doublet of doublets. 2D-NMR spectra were acquired on an Agilent 400-MR spectrometer. The standard Agilent implementations of gHSQCAD experiments were used. IR spectra were recorded by a Perkin Elmer FT-IR Spectrometer. Flash chromatography was performed using silica gel (Merck kieselgel 60 H 37-70 $\mu$m). The routine monitoring of reactions were performed using TLC (Merck kieselgel 60 0.20 mm layer, UV254), and the plates were visualized with UV light at 254 nm or stained with ethanolic solution of phosphomolybdic acid and then heated if necessary. For size exclusion chromatography (SEC) YL 9110 HPLC-GPC system (YL Instrument Co.,Ltd., Dongan-gu, Anyang-si, Kyoung-gi-do, 431-836, The Republic of Korea) with three Styragel columns (HR 0.5, HR 1, HR 3 7.8×300 mm each) connected in series (flow rate: 1ml/min; injection volume: 50 $\mu$l; solvent: THF), with a UV detector (280 nm) and autosampler were used. The system was calibrated using ReadyCal-Kit Poly(styrene). (MP 266, 682, 1250, 2280, 3470, 4920, 9130, 15700, 21500, 28000, 44200, 66000 Da). For GC–MS analysis a Varian CP-3800 gas chromatograph (A fused silica capillary column SLB-5ms (30 m × 0.25 mm × 0.25 $\mu$m, Supelco GC Columns)) coupled to a Varian Saturn 2200 GC–MS/MS spectrometer with the following settings was used (for routine analysys): injector temperature, 280 °C; carrier gas, helium at 1mL/min; temperature program, 50 °C 20 °C/min to 300 °C, 3 min isocratic; ions were detected in full scan mode m/z 40–650; (for lignin samples) 75 °C 3 min isocratic, 5 °C/min to 150 °C, 0.5 to 160 °C, 2 to 190 °C, 5 °C/min to 240 °C, 70 °C/min to 325 °C, 3 min isocratic; ions were detected in full scan mode m/z 35–500. For high temperature, small scale reactions Microwave reactor Biotage Initiator 2.0 was used. For high temperature reactions Parr Series 4576-B HP/HT reactor was used with magnetic stirring drive.
Synthesis of model compounds

Synthesis 1-(3,4-dimethoxyphenyl)propan-1-ol (8)\textsuperscript{[1]}

\[
\begin{array}{c}
\text{MeO} \quad \text{MeO} \\
\text{O} \\
\text{MeO} \quad \text{MeO} \\
\text{O} \\
\end{array}
\xrightarrow{\text{PAA}}
\begin{array}{c}
\text{MeO} \quad \text{MeO} \\
\text{O} \\
\text{MeO} \quad \text{MeO} \\
\text{O} \\
\end{array}
\]

A mixture of 1,2-dimethoxybenzene (5.00 g, 36.2 mmol), polyphosphoric acid (11.00 g, 42.6 mmol) and propionic acid (9.0 ml, 120 mmol) was stirred and heated at 100 °C for 90 min. The reaction mixture was cooled to RT, diluted with cold water and extracted with ether (2 × 150 ml). The combined organic extract was washed with 5% (w/w) NaOH solution, washed with water and then with brine, dried over anhydrous MgSO\textsubscript{4}, filtered and evaporated to give a crude residue. The crude mixture obtained was recrystallized from ethanol to give 1-(3,4-dimethoxyphenyl)propan-1-non as a white solid in 69% yield (4.85 g 25.0 mmol). m.p. (EtOH) 58.5-59.0 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 7.58 (dd, \(J = 8.6\) Hz, 1.9 Hz, 1H), 7.53 (d, \(J = 1.9\) Hz, 1H), 6.88 (d, \(J = 8.6\) Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 2.96 (q, \(J = 7.3\) Hz, 2H), 1.21 (t, \(J = 7.3\) Hz, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\): 199.1, 152.8, 148.7, 129.9, 122.2, 109.8, 109.7, 55.7, 55.6, 30.9, 8.3. Spectral data were in accordance with those previously reported.\textsuperscript{[2]}

\[
\begin{array}{c}
\text{MeO} \quad \text{MeO} \\
\text{O} \\
\text{MeO} \quad \text{MeO} \\
\text{O} \\
\end{array}
\xrightarrow{\text{NaBH}_4 \text{ EtOH}}
\begin{array}{c}
\text{MeO} \quad \text{MeO} \\
\text{OH} \\
\text{MeO} \quad \text{MeO} \\
\end{array}
\]

1-(3,4-dimethoxyphenyl)propan-1-non (3.00 g, 15.5 mmol) and NaBH\textsubscript{4} (1.17 g, 30.9 mmol) was stirred in 50 ml of ethanol at RT. The reaction was monitored by TLC. After full consumption of starting material the reaction was quenched by slow addition of NH\textsubscript{4}Cl saturated water solution (50 mL) and extracted with diethyl ether (2 × 100 mL). The combined organic extracts were washed with brine and dried over anhydrous MgSO\textsubscript{4}, filtered and evaporated to give a crude oil. The oil was purified by column chromatography (pentane/ethyl acetate, 1:1 (v/v)) to give 1-(3,4-dimethoxyphenyl)propan-1-ol as a transparent oil in 92% yield (2.79g 14.2 mmol). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 6.97–6.82 (m, 3H), 4.49 (m, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.25 (br.s, 1H), 1.80–1.67 (m, 2H), 0.89 (m, 3H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\): 149.1, 148.5, 137.3,118.8, 113.1, 108.7, 76.1, 56.4, 56.1, 31.8, 10.6. Spectral data were in accordance with those previously reported.\textsuperscript{[3]}

S-3
Synthesis of erythro- and threo-1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol diastereomers (4)

Synthesis of 2-bromo-1-(3,4-dimethoxyphenyl)ethanone[4]

To a solution of 1-(3,4-dimethoxyphenyl)ethanone (4.00 g, 22.2 mmol) in 100 mL of chloroform a solution of Br₂ (3.72 g, 23.3 mmol) in 100 mL of chloroform was added dropwise over 5 h at RT. The reaction mixture was washed with saturated Na₂S₂O₃ water solution (cooled to 5 °C), saturated Na₂SO₄ water solution, and brine. The organic layer was collected and dried over anhydrous MgSO₄. The solvent was evaporated in vacuo and the crude product was purified by recrystallization from ethanol to give 2-bromo-1-(3,4-dimethoxyphenyl)ethanone as a white solid in 97% yield (5.62 g, 21.70 mmol).

¹H NMR (400 MHz, CDCl₃) δ: 7.61 (dd, J = 8.4 Hz, 2.1 Hz, 1H), 7.54 (d, J = 2.1 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 4.40 (s, 2H), 3.96 (s, 3H), 3.94 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ: 190.1, 154.0, 149.3, 127.1, 123.9, 110.9, 110.1, 56.2, 56.1, 30.4. Spectral data were in accordance with those previously reported.[5]

Synthesis of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone[4]

A 250 mL round bottom flask equipped with a reflux condenser and dropping funnel was charged with 2-methoxyphenol (2.60 g, 21.2 mmol) and K₂CO₃ (6.67 g, 48.2 mmol) in acetone (100 mL) and stirred at RT. To this solution, 2-bromo-1-(3,4-dimethoxyphenyl)ethanone (5.00 g, 19.3 mmol) in acetone (50 mL) was added dropwise over 30 min at RT. The resulting suspension was stirred at reflux for 4 h. The suspension was filtered and concentrated in vacuo. The crude product was purified by recrystallization from ethanol to give 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone as a white solid in 98% yield (5.72 g, 18.9 mmol). mp 93.8-94.3 °C.

¹H NMR (400 MHz, CDCl₃) δ: 7.69 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 7.62 (d, J = 1.8 Hz, 1H), 6.99 – 6.82 (m, 5H), 5.28 (s, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ: 193.2, 153.8, 149.7, 149.2, 147.6, 127.8, 122.7, 122.3, 120.8, 114.7, 110.4, 110.1, 72.0, 56.1, 55.9, 55.8. Spectral data were in accordance with those previously reported.[6]
Synthesis of erythro- and threo-1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol diastereomers

To a stirred suspension of K$_2$CO$_3$ (1.30 g, 9.0 mmol) and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone (2.50 g, 8.3 mmol) in ethanol (99.5%) (100 mL), a water solution of formaldehyde (36.5-38%) (0.74 mL, 10.0 mmol) was added at RT. The reaction was monitored by TLC, after full consumption of starting material NaBH$_4$ (1.00 g, 25.0 mmol) was added and the reaction mixture was stirred for 1 h at RT. The reaction mixture was concentrated in vacuo, quenched by slow addition of NH$_4$Cl saturated water solution (50 mL) and extracted with diethyl ether (2 × 100 mL). The combined organic extract was washed with brine and dried over anhydrous MgSO$_4$, filtered and evaporated to give a crude oil. The oil was purified by column chromatography (gradient pentane/ethyl acetate 1:1 (v/v) to ethyl acetate) to give mixture of erythro- and three-diastereomers of the title compound as a transparent glassy solid in 72% yield (1.98 g, 5.9 mmol). Erythro: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.13-6.82 (m, 7H), 4.97 (dd, $J = 4.8, 3.4$ Hz, 1H), 4.16 (dd, $J = 5.7, 4.8, 3.5$ Hz, 1H), 3.91 (ddd, $J = 12.2, 5.7, 5.6$ Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.66 (ddd, $J = 12.2, 7.6, 5.6$ Hz, 1H), 3.48 (d, $J = 3.4$ Hz, 1H), 2.81 (dd, $J = 7.6, 5.6$ Hz, 1H); Threo: $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.13-6.82 (m, 7H), 4.98 (dd, $J = 7.8, 2.2$ Hz, 1H), 4.03 (ddd, $J = 7.8, 3.9, 3.3$ Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.70 (d, $J = 2.2$ Hz, 1H), 3.62 (ddd, $J = 12.5, 5.0, 3.3$ Hz, 1H), 3.48 (dd, $J = 12.5, 8.5, 3.9$ Hz, 1H), 2.77 (dd, $J = 8.5, 5.0$ Hz, 1H); Erythro + threo $^{13}$C NMR (101 MHz, CDCl$_3$) δ: 151.6, 151.4, 148.6, 147.7, 147.0, 132.6, 132.2, 124.3, 124.2, 121.8, 121.7, 121.0, 120.8, 119.7, 118.5, 112.3, 111.1, 110.0, 109.3, 89.4, 87.3, 73.9, 72.7, 61.0, 60.7, 56.0. Spectral data were in accordance with those previously reported.[7]

Modelling tandem organosolv transfer hydrogenolysis

Pd/C (5 wt%) (0.032 g, 0.015 mmol, 5 mol%) and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (0.100 g, 0.300 mmol) were added to a 5 mL vial. 2.0 mL of water and 2.0 mL of ethanol were added via syringe. The vial was purge with slow flow of argon...
and sealed. The vial was placed in a microwave for 60 min at 195 °C. The vial was cooled to RT and reaction mixture was filtrated through a celite pad, using diethyl ether (10 mL) as eluent. Solvent was removed in vacuo. Crude mixture was analysed by NMR and GC–MS see attached spectra. In the case when glucose (0.108 g, 0.600 mmol) was used it was added before the vial was sealed. Otherwise, the same procedure was followed.

In the case when formic acid (via a syringe 0.023 mL, 0.600 mmol) was used it was added before the vial was sealed. Otherwise, the same procedure was followed.

Pd/C (5 wt%) (0.027 g, 0.013 mmol, 5 mol%) and 1-(3,4-dimethoxyphenyl)propan-1-ol (0.050 g, 0.255 mmol) were added to a 5 mL vial. 2.0 mL of water and 2.0 mL of ethanol were added via syringe. The vial was purge with slow flow of argon and sealed. The vial was placed in a microwave for 60 min and 195 °C. The vial was cooled to RT and reaction mixture was filtrated through a celite pad, using diethyl ether (10 mL) as eluent. Solvent was removed in vacuo. Crude mixture was analysed by NMR and GC–MS see attached spectra.

Pd/C (5 wt%) (0.040 g, 0.018 mmol, 5 mol%) and 3-phenylpropan-1-ol (0.050 g, 0.367 mmol) were added to a 5 mL vial. 2.0 mL of water and 2.0 mL of ethanol were added via syringe. The vial was purge with slow flow of argon and sealed. The vial was placed in a microwave for 60 min and 195 °C. The vial was cooled to RT and reaction mixture was filtrated through a celite pad, using diethyl ether (10 mL) as eluent. Solvent was removed in vacuo. Crude mixture was analysed by NMR and GC–MS see attached spectra.
Determination of moisture content in wood

Moisture content was measured by EN 14774-1:2009 method. Briefly, 10.00 g of grounded wood sample (2mm screen sieve) was dried at 105 °C for 24h. Moisture content was determined gravimetrically, by weight loss. Pine 12% and birch 8%.

Determination of the lignin content in wood

The lignin content in wood (without bark) was measured by the TAPPI standard method (T 222 om-02). Briefly, 5.00 g of grounded wood sample (2mm screen sieve) was treated with an ethanol/benzene mixture 1:2 (v/v) in a Soxhlet extractor for 4 h to remove resin, wax and fat of wood sample. Then it was washed with ethanol four times and dried at 70 °C for 4 h (loss in mass were approximately 1%). The dry powder (1.00 g) was placed in a flask and mixed with 72 wt% H₂SO₄ (15 mL) gradually in an ice-bath under stirring. The flask was placed in a 25 °C bath for 2.5 h and was periodically stirred. After that, the mixture was diluted with 200 ml of deionized water and refluxed for 4 h, and then cooled down to RT. The solution was left undisturbed overnight at 4 °C, and then filtered. The filtered residue was washed with deionized water until it was neutral. The solid was collected and dried under vacuum overnight. The residual was weighted. To calculate lignin content in wood samples equation 1 was used. The content of lignin in birch is 20% (0.20 g) and in pine is 28% (0.28 g).

\[ m(\text{lignin}) = (m(\text{wood sample}) \times (1 - \text{moisture} - \text{extractables})) \times \text{lignin content} \]

Equation 1. Calculation of reaction yield.

Catalytic reactions

Pine wood

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\[ \text{MeO} \quad \text{Pd/C (5 mol%)} \quad \text{EtOH/H₂O} \quad 195^\circ\text{C}, 1\text{h} \quad \text{HO} \quad \text{OMe} \quad 3a \quad 23\% \text{yield} \]
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Untreated pine sawdust (Pinus sylvestris) 10.00 g (2mm sieve screen) (approximate content of lignin is 2.40 g, MW of lignin monomer was chosen as 196, 12.2 mmol), 100 mL of ethanol/water mixture 1:1 (v/v) and Pd/C (5 wt%) (1.3 g, 5 mol%) were placed in a 200 mL cylindrical liner made of borosilicate glass in 250 mL autoclave reactor. The reactor was sealed and purged with argon (4 bars) 3 times to expel air. Pressurized with hydrogen (4 bars) to activate palladium and remove traces of oxygen. Then purged with argon (4 bars) 3 times to expel hydrogen. The reaction was conducted at 195 °C at a stirring speed of 300 rpm with
temperature program, 6 °C/min to 195 °C, 60 min isocratic, then cool down to 35 °C (cooling approximately take 30 min). Reaction mixture was filtered through glass filter, washed with 3 × 20 ml of ethanol, then 3 × 20 ml acetone and 20 ml of water. Filtrate was concentrated in vacuo to give 3.2 g of oily residue. The solid residue was dried over night at 70 °C, resulted in 6.7 g of which 1.3 g was catalyst and 5.4 g was pulp residue. That is equal to a 61% pulp yield (see additional experiment section). The oil obtained was analyzed by 2D NMR (HSQC). Characteristic resol crosspeaks were absent (Cα-Hα correlations at δC/δH 82.9/4.82 ppm, Cβ-Hβ correlations at δC/δH 53.9/3.03 ppm and Cγ-Hγ correlations at δC/δH 70.9/4.15 and 3.78 ppm). Phenylcoumaran bonds cross peaks: Cα-Hα correlations observed at δC/δH 87.1/5.45 ppm, Cβ-Hβ correlations observed at δC/δH 53.0/3.44 ppm and Cγ-Hγ correlations observed at δC/δH 62.2/3.76 ppm, were observed. The β-O-4’ bond cross peaks: Cα-Hα correlations observed at δC/δH 70.8/4.73 ppm, Cβ-Hβ correlations observed at δC/δH 83.7/4.26 ppm and Cγ-Hγ correlations observed at δC/δH 59.9/3.35-3.80 ppm, were observed. Phenylcoumaran and β-O-4’ bonding motif amount has been decreased by 46% and 94% respectively in comparison with blank (uncatalyzed) experiment, quantification was done according to Bolm et al.[8] New crosspeaks have been observed in products mixture, that corresponds to 4-propenyl phenols δC/δH 110.8/5.65, 110.8/5.60, 110.8/5.06, 110.8/5.03, 115.2/5.00. The SEC analysis showed significant decrease in molecular weight in comparison with control experiment: 41.6% Mn = 894, Mw = 1282, with polydispersity index (PDI) equals 1.43 (was 70.8% Mn = 1288, Mw = 2898, PDI = 2.25), oligomer region 17.8% Mn = 362, Mw = 370, PDI = 1.02 (was 20.0% Mn = 362, Mw = 375, PDI = 1.04) and monomer region 40.6% Mp = 264 (was 9.2% Mp = 261). GC–MS analysis was performed according to Toste et al., with minor modifications.[9] The oil obtained was analyzed by GC–MS: to 5.0 mg of oil in 1.0 mL of THF 0.1 mL of N,Obis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMSCl) was added. Mixture was kept at 70 °C for 30 min. Identification of compounds was achieved by comparing mass spectra with the National Institute of Standards and Technology (NIST) database entries as well as comparison to literature data.[10,11] Following compounds has been identified: trimethylsilyl 2-((trimethylsilyloxy)propanoate (12) MS (70eV) m/z (%) 219 (23), 191 (59), 190 (32), 149 (26), 148 (12), 147 (100), 117 (73), 73 (70); trimethylsilyl 2-((trimethylsilyloxy)acetate (13) MS (70eV) m/z (%) 205 (34), 177 (38), 161 (9), 149 (34), 148 (19), 147 (100), 73 (42); 2,2,8,8-tetramethyl-5-((trimethylsilyloxy)-3,7-dioxaocta-2,8-disilanone (14) MS (70eV) m/z (%) 293 (6), 218 (36), 205 (68), 203 (16), 149 (44), 147 (100), 133 (20), 117 (37), 103 (30), 73 (84); (4-ethyl-2-methoxyphenoxy)trimethylsilane (11a(tms))MS (70eV) m/z (%) 225 (11) [M+H]+, 224 (45) [M]+, 210 (13), 209 (55), 195 (100), 180 (32), 73 (14); (2-methoxy-4-vinylphenoxy)trimethylsilane (15) MS (70eV) m/z (%) 223 (10) [M+H]+, 222 (59)
Then an oily substance was washed with ethyl acetate 3 × 150 mL to separate lignin from hemicellulose and partially from wax and resins residue. Hemicellulose and hydrolysed sugar residues were washed with acetone (2 × 50 mL) to remove the rest of wax and resins, and resulted in 1.6 g of light grey solid (18% w/w). Ethyl acetate fraction was combined and concentrated in vacuo to give 1.3 g of light-brown oil. A part of oil (0.350 mg) was purified by column chromatography (gradient pentane/ethyl acetate from 3:1 to 1:1 (v/v)) to give 0.111 g of pale yellow oil of 2-methoxy-4-propenylphenol E and Z isomers 10:1. 

**1H NMR** (400 MHz, (CD$_3$)$_2$CO) $\delta$: 7.50 (br.s 1H), 6.99 (m, 1H), 6.79 (m, 1H), 6.74 (m, 1H), 6.31 (dq, $J$ = 15.8 Hz, 1.8 Hz, 1H), 6.09 (dq, $J$ = 15.8 Hz, 6.7 Hz, 1H), 3.85 (s, 3H), 1.81 (dd, $J$ = 6.7 Hz, 1.8 Hz, 3H);

**13C NMR** (101 MHz, CDCl$_3$) $\delta$: 146.7, 144.8, 130.8, 130.7, 123.4, 119.3, 114.5, 108.1, 55.9, 18.4. Spectral data were in accordance with those previously reported.[12]

\[
yield = \frac{\frac{m(\text{isolated product})}{m(\text{loaded on column})} \times m(\text{oil obtained})}{Mw(\text{product})} \left(\frac{m(\text{total Klason lignin})}{Mw(\text{lignin monomer})}\right) \times 100\%
\]

**Equation 2.** Calculation of reaction yield.

theoretical yield = \left(\frac{\text{yield}}{\text{expected yield}}\right) \times 100\%

**Equation 3.** Calculation of theoretical yields.

So applying this two equations the yield of 2-methoxy-4-propenylphenol is 23% and theoretical yield is 92%.
Birch wood

Untreated birch (*Betula pendula*) 10.00 g (2mm sieve screen or wood chips 2 cm×0.2 cm×1.5 cm) (approximate content of lignin is 1.84 g, MW of lignin monomer was chosen as 226, 8.14 mmol), 100 ml of ethanol/water mixture 1:1 (v/v) and Pd/C (5 wt%) (0.9 g, 5 mol%) were placed in a 200 mL cylindrical liner made of borosilicate glass in 250 mL autoclave reactor. The reactor was sealed and purged with argon (4 bars) 3 times to expel air. Pressurized with hydrogen (4 bars) to activate palladium and remove traces of oxygen. Purged with argon (4 bars) 3 times to expel hydrogen. The reaction was conducted at 195 °C at a stirring speed of 300 rpm with temperature program, 6 °C/min to 195 °C, 60 min isocratic, then cool down to 35 °C (cooling approximately take 30 min). Reaction mixture was filtered through glass filter, washed with 3 × 20 ml of ethanol, then 3 × 20 ml acetone and 20 ml of water. Filtrate was concentrated in vacuo to give 3.95 g of oily residue. The solid residue was dried over night at 70 °C, resulted in 6.0 g of which 0.9 g was catalyst and 5.1 g was pulp residue. That is equal to a 55% pulp yield (see additional experiment section).

The oil obtained was analyzed by 2D NMR (HSQC). Characteristic resinol crosspeaks: Ca-Ha correlations at δC/δH 85.5/4.66 ppm, Cβ-Hβ correlations at δC/δH 53.9/3.09 ppm and Cy-Hγ correlations at δC/δH 71.0/4.20 and 3.82 ppm, were observed. Phenylcoumaran bonds cross peaks: Ca-Ha correlations observed at δC/δH 87.4/5.48 ppm, Cβ-Hβ correlations observed at δC/δH 53.0/3.53 ppm and Cy-Hγ correlations observed at δC/δH 62.0/3.75 ppm, were observed. The β-O-4’ bond cross peaks: Ca-Ha correlations observed at 6C/δH 72.3/4.93 ppm, Cβ-Hβ correlations observed at δC/δH 86.1/4.17 ppm and Cy-Hγ correlations observed at δC/δH 59.5/3.71-3.38 ppm, were observed. Resinol, phenylcoumaran and β-O-4’ bonding motif amount has been decreased by 47%, 54% and 91% respectively in comparison with blank (uncatalyzed) experiment, quantification was done according to Bolm *et al.*[8] New crosspeaks have been observed in products mixture, that corresponds to 4-propenyl phenols δC/δH 111.2/5.69, 111.1/5.64, 111.1/5.09, 111.1/5.06, 115.3/5.08, 115.3/5.08. The SEC analysis showed significant decrease in molecular weight in comparison with control experiment: 39.1% Mn = 915, Mw = 1097, PDI = 1.19 (was 72.2% Mn = 1225, Mw = 2380, Mw/Mn = 1.94), 32.5% Mn = 421, Mw = 431, PDI = 1.02 (was 21.0% Mn = 399, Mw = 410, PDI = 1.02), 28.4% Mp = 265 (was 6.8% Mp = 298). GC–MS analysis was performed according to Toste *et al.*, with minor modifications.[9] The oil obtained was analyzed by GC–MS: to 5.0 mg of oil in 1.0 mL of THF 0.1 mL of BSTFA containing 1% TMSCl was
added. Mixture was kept at 70 °C for 30 min. Identification of compounds was achieved by comparing mass spectra with the NIST database entries as well as comparison to literature data.\textsuperscript{[10,11]} Not full sililation has been reached, identification between $E$ and $Z$ 4-propenyl phenols isomers due to MS spectra hasn’t been done, assumption has been made due to retention time, following compounds has been identified: trimethylsilyl 2-((trimethylsilyloxy)propanoate (12) MS (70eV) $m/z$ (%) 219 (23), 191 (59), 190 (32), 149 (26), 148 (12), 147 (100), 117 (73), 73 (70); trimethylsilyl 2-((trimethylsilyloxy)acetate (13) MS (70eV) $m/z$ (%) 205 (34), 177 (38), 161 (9), 149 (34), 148 (19), 147 (100), 73 (42); 2-methoxy-4-((prop-1-enyl)phenol (3a-E) MS (70eV) $m/z$ (%) 164 (100) [M]$^+$, 149 (41), 131 (23), 121 (22), 103 (24), 91 (20), 77 (22), 55 (15); 3,5-dimethoxy-4-((trimethylsilyloxy)benzaldehyde (16) MS (70eV) $m/z$ (%) 254 (34) [M]$^+$, 239 (37), 225 (17), 224 (100), 209 (35), 73 (21), 57 (11); (2-methoxy-4-((prop-1-enyl)phenox)trimethylsilanilane (3a-E(tms)) MS (70eV) $m/z$ (%) 237 (22) [M+H]$^+$, 236 (98) [M]$^+$, 221 (31), 207 (20), 206 (100), 73 (9); 4-(3-hydroxyprop-1-enyl)-2-methoxyphenol/TMS (17) MS (70eV) $m/z$ (%) 252 (42) [M]$^+$, 237 (26), 223 (20), 222 (100), 179 (9), 73 (7); 2,6-dimethoxy-4-(prop-1-enyl)phenol (3b-Z) MS (70eV) $m/z$ (%) 194 (100) [M]$^+$, 179 (23), 151 (20), 131 (15), 119 (21), 91 (21); (2,6-dimethoxy-4-((prop-1-enyl)phenox)trimethylsilanilane (3b-Z(tms)) MS (70eV) $m/z$ (%) 266 (53) [M]$^+$, 251 (18), 237 (18), 236 (100), 205 (8), 221 (8), 73 (8); 2,6-dimethoxy-4-((prop-1-enyl)phenol (3b-E) MS (70eV) $m/z$ (%) 195 (16) [M+H]$^+$, 194 (100) [M]$^+$, 179 (21), 151 (17), 119 (19), 91 (18); (2,6-dimethoxy-4-((prop-1-enyl)phenox)trimethylsilanilane (3b-E(tms)) MS (70eV) $m/z$ (%) 267 (20) [M+H]$^+$, 266 (94) [M]$^+$, 251 (31), 237 (22), 236 (100), 205 (10), 73 (10). Then an oily substance was washed with ethyl acetate 3 $\times$ 150 mL, to separate lignin from hemicellulose and partially from wax and resins residue. Hemicellulose and hydrolysed sugar residues were washed with acetone (2 $\times$ 50 mL) to remove the rest of wax and resins, resulted in 1.0 g of light grey solid (11% w/w). Ethyl acetate fraction was combined and concentrated in vacuo to give 2.81 g of light-brown oil. A part of oil (0.350 mg) was purified by column chromatography (gradient pentane/ethyl acetate from 3:1 to 1:1 (v/v)) to give 0.096 g of pale yellow oil of 2,6-dimethoxy-4-propenylphenol $E$ and $Z$ isomers 10:1. That corresponds to 49% yield of 2,6-dimethoxy-4-propenylphenol and 92% theoretical yield. (E)-2,6-dimethoxy-4-(prop-1-enyl)phenol (3b): \(\textsuperscript{1}H\) NMR (400 MHz, (CD\(_3\))\(_2\)CO) $\delta$: 7.13 (br.s, 1H), 6.65 (s, 2H), 6.30 (dq, $J = 15.8$ Hz, 1.7 Hz, 1H), 6.12 (dq, $J = 15.8$ Hz, 6.6 Hz, 1H), 3.82 (s, 6H), 1.81 (dd, $J = 6.6$ Hz, 1.7 Hz, 3H); \(\textsuperscript{13}C\) NMR (101 MHz, CDCl\(_3\)) $\delta$: 148.8, 135.3, 132.3, 129.8, 123.4, 104.4, 56.6, 18.4. Spectral data were in accordance with those previously reported.\textsuperscript{[13]} And 0.006 g of pale yellow oil of 2-methoxy-4-propenylphenol $E$ and $Z$ isomers 10:1. That corresponds to 3% yield of and 6% theoretical yield.
Also purification by distillation was performed 2.8 g of oil was distilled by bulb-to-bulb distillation at 5 mbar at 250 °C – the lowest boiling fraction was collected separately to give 1.15 g of light-yellow oil. The SEC analysis showed monomers fraction of Mp = 265. Monomers fraction obtained is 62% (w/w) on total Klason lignin.

**Additional experiment**

Additional experiment was performed where Pd/C was placed in catalytic beds (two doubled tea bags made of cellulose and protected with stainless steel lath). Experiment was conducted the same way as previously described where no significant difference was detected.
**Empirical calculation of expected yields**

Lignin is a polymer with randomly cross-linked C9 phenol units. Most C9 units are linked to two other C9 units either by C-C or C-O bonds. Our strategy of producing monomers and dimers is through the cleavage of β-O-4’ ether linkages with retention of other bonds. Thus, units which have both sides linked to other units by β-O-4’ ether bonds will be converted to monomers. Similarly, if two units are connected by other inter-unit bond type and linked to other parts by β-O-4’ ether bonds, they will be converted into dimers. If assume that lignin is one linear molecule the probability of a C9 unit to be linked to other units by β-O-4’ ether bond on both sides is $x^2$ where $x$ is total content of β-O-4’ ether bond, which means the ideal yield of monomer formed from β-O-4’ ether bond cleavage is $x^2$. Since the percentage of β-O-4’ ether linkage for pine is approximately 50%, the theoretical yield of monomers should be approximately 25%. In a case of birch we should take into account also α-O-4’ bonds as far as they present there in sufficient amounts and our method could cleave them as well. Birch approximately contains 60-70% of β-O-4’ ether linkage and also 1-3% of α-O-4’ linkage so theoretical yield of monomers should be 40-53%.\textsuperscript{14-17}

**Hydrogen origin**

The reactions were performed in a similar manner as for the catalytic reaction directly on wood material. Styrene (0.10 g, 0.96 mmol) was added to a suspension of 4 mL of ethanol/water mixture 1:1 (v/v) and Pd/C (5 wt%) (0.1 g, 5 mol%). The reactor was sealed and purged with argon (4 bars) 3 times to expel air. Pressurized with hydrogen (4 bars) to activate palladium and remove traces of oxygen. Then purged with argon (4 bars) 3 times to expel hydrogen. The reaction was conducted at 190°C at a stirring speed of 600 rpm for 1 h. Cooled to the RT. Analytical sample of 0.01 mL was taken and mixed with 0.05 mL of CDCl\textsubscript{3} filtered through syringe filter (regenerated cellulose, 0.45 µm, 13 mm, Agilent Technologies) directly to NMR tube. Yields were determined by $^1$H NMR spectroscopy: signals at 5.20 ppm (dd, $J = 10.7, 0.9$ Hz, 1H) for styrene and at 2.65 ppm (q, $J = 8.0$ Hz, 2H) for ethylbenzene were compared, to determine transfer hydrogenation pathway from ethanol to for acetaldehyde 9.75 ppm (q, $J = 2.9$ Hz, 1H). 12±3% of styrene has been transformed into ethylbenzene 4±2% of acetaldehyde has been detected. When purging with hydrogen gas has been omitted 9±2% of ethylbenzene and same amount of acetaldehyde has been detected. The results obtained show that the transfer hydrogenolysis pathway from ethanol is a minor pathway (>10%). The main product of the reaction of wood is isoeugenol where saturation of double bond has not been observed. Hydrogen used for activation of catalyst and oxygen removing should also not affect the reaction pathway (less than 5% observed).
References


A reaction scheme showing the conversion of a starting material (4) to products (5, 6, and 7) through the action of formic acid (HCOOH) and Pd/C catalyst. The products are represented as follows:

- **5**: 65% yield
- **6**: 8% yield
- **7**: 22% yield

The reaction conditions are 195°C, 1 h in EtOH/H2O.

**Ar** = p.m.-di-OMe-C6H4

**Ar’** = o-MeO-C6H4

**H NMR (400 MHz, CDCl3)**

The NMR spectrum shows peaks at various chemical shifts, with assignments indicated for each compound.
S-19
$3a$

$^1$H NMR (400 MHz, (CD$_3$)$_2$CO)

$E$

$Z$

(CD$_3$)$_2$CO

S-23
HSQC spectra of crude lignin form pine wood (uncatalysed reaction)
1D trace (¹H) from HSQC, unresolved spectra (crude lignin from pine wood, uncatalysed reaction)
Enlargement of HSQC, ether bond type fingerprints region (crude lignin from pine wood, uncatalysed reaction).
HSQC spectra of crude oil form pine wood (catalysed reaction), intensive signals in aliphatic region probably belongs to waxes, resins and fats.
1D trace (\(^1\)H) from gHSQCAD, new signals easily observable in product mixture, better resolved spectra (crude oil from pine wood, catalysed reaction)
Enlargement of HSQC, ether bond type fingerprints region (crude oil from pine wood, catalysed reaction).
$^1$H NMR (400 MHz, (CD$_3$)$_2$CO)

3b
HSQC spectra of crude lignin form birch wood (uncatalysed reaction)
1D trace (\(^1\text{H}\)) from HSQC, unresolved spectra (crude lignin from birch wood, uncatalysed reaction)
Enlargement of HSQC, ether bond type fingerprints region (crude lignin from birch wood, uncatalysed reaction).
HSQC spectra of crude oil from birch wood (catalysed reaction).
HSQC spectra of EtOAc soluble oil fraction from birch wood (catalysed reaction).
1D trace ($^1H$) from HSQC, resolved spectra (crude oil from birch wood, catalysed reaction),
Enlargement of HSQC, ether bond type fingerprints region (crude oil from birch wood, catalysed reaction).
SEC diagram of lignin from pine wood (uncatalysed reaction)
SEC diagram of crude oil from pine wood (catalysed reaction)
SEC diagram of lignin from birch wood (uncatalysed reaction)
SEC diagram of crude oil from birch wood (catalysed reaction)
SEC diagram of distilled oil from birch wood (catalysed reaction)