

Supplementary Information for

Mechanochemical degradation of lignin and wood by solvent-free grinding in a reactive medium

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Materials and Methods

All experiments were carried out under an argon atmosphere. The starting materials were purchased from commercial suppliers and used without further purification. THF was dried by distillation over Solvona[®] (sodium on molecular sieves) in the presence of benzophenone, and CH₂Cl₂ was dried by distillation over CaH₂. These two solvents were then stored under an argon atmosphere. Flash column chromatography was carried out with silica gel 60 (35–70 mesh). Analytical TLC was performed with silica gel 60 F254 plates, and the products were visualized by UV– and KMnO₄ detection. ¹H NMR and ¹³C NMR spectra were recorded either on a Varian VNMRs 600, a Varian Inova 400 or a Varian Mercury 300 spectrometer, in CDCl₃ using TMS as an internal standard. Chemical shifts (δ) were reported in ppm using TMS as internal standard, and spin–spin coupling constants (*J*) were given in Hz. HRMS were recorded on a FinniganMAT 95 spectrometer (ESI). All compounds gave satisfactory HRMS analyses. The analytical data for the known compounds were found to match with the literature data.

Preparation of substrates 1a-h

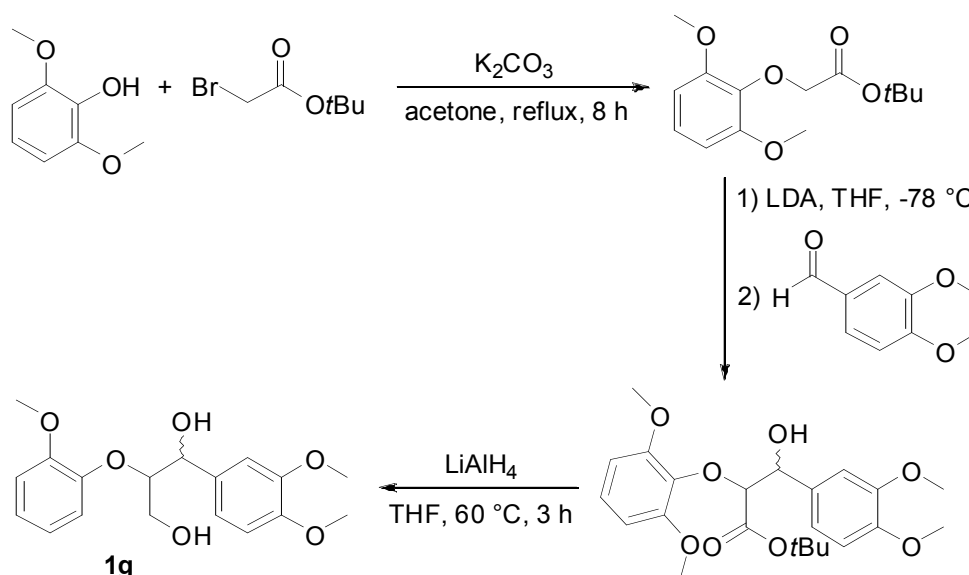
The substrates **1a-e** were prepared according to a reported procedure.^{S1}

Preparation of substrate 1f:

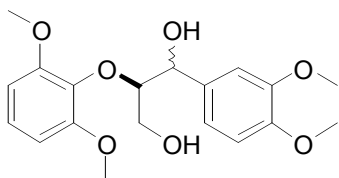
Substrate **1f** was prepared following a reported procedure.^{S2}

Preparation of substrate 1g (*erythro*/*threo*)

Dilignol model compound **1g** (*erythro*/*threo*) was prepared following a similar procedure as describes earlier,^{S1} using *tert*–butyl (2–methoxyphenoxy)acetate as the key intermediate. It was obtained as a mixture of *erythro* and *threo* diastereoisomers, which were not separated by column chromatography.



2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propanediol (**1g**)



The dilignol model compound was prepared from the corresponding *tert.*-butyl ester following the general procedure reported earlier^{S1} using 2.5 equivalents of LiAlH_4 . The purification was performed by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 99:1$ to $95:5$) yielding the title compound (1.7:1 mixture of *erythro* and *threo* diastereoisomers) as a yellow syrup (1.47 g, 66%).

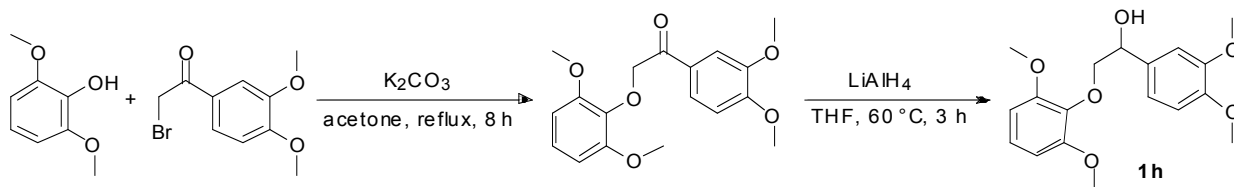
^1H NMR (400 MHz, CDCl_3 , 25°C , TMS): δ 7.11–6.94 (m, 5H), 6.87–6.80 (m, 3H), 6.65 (d, $J = 8.4$ Hz, 2H), 6.64 (d, $J = 8.4$ Hz, 2H), 5.07 (d, $J = 8.7$ Hz, 1H), 5.03 (br.d, $J = 3.2$ Hz, 1H), 4.36 (br.s, 1H), 4.19–4.11 (m, 2H), 3.95–3.92 (m, 1H), 3.91 (s, 6H), 3.89 (s, 3H), 3.89 (s, 9H), 3.87 (s, 3H), 3.86 (s, 3H), 3.58 (dd, $J = 10.8$ Hz and 2.7 Hz, 1H), 3.50 (d, $J = 10.8$ Hz, 1H), 3.40–3.26 (m, 2H), 3.16 (br.s, 1H).

^{13}C NMR (100 MHz, CDCl_3 , 25°C , TMS): δ 153.5 (2C), 153.2 (2C), 149.0, 148.9, 148.7, 148.2, 135.3, 135.0, 132.6, 132.0, 124.5, 124.5, 119.8, 118.1, 111.0, 111.0, 110.3, 109.0, 105.3 (2C), 105.3 (2C), 89.0, 87.0, 74.0, 72.5, 60.6, 60.5, 56.2 (4C), 55.9 (2C), 55.9 (2C).

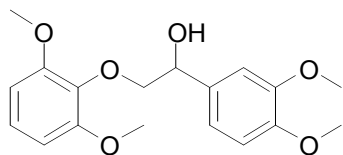
HRMS (ESI, 70 eV): m/z calcd for $\text{C}_{19}\text{H}_{24}\text{O}_7 + \text{Na}^+$: 387.1414 [$M + \text{Na}^+$]; found: 387.1411.

Preparation of substrate 1h:

Monolignol model compound **1h** was prepared following the reported procedure^{S3} using 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanone as the key intermediate.



2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (1h)



The product was prepared following the general reported procedure^{S1} using 2.5 equivalents of LiAlH₄, and the purification was performed by flash chromatography (CH₂Cl₂) yielding the title compound as white solid (72%).

mp. 92–93 °C.

¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ 7.03–6.97 (m, 1H), 6.95 (d, *J* = 1.9 Hz, 1H), 6.87 (ddd, *J* = 8.2, 2.0, 0.6 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.88 (dd, *J* = 10.0, 2.5 Hz, 1H), 4.50 (d, *J* = 1.2 Hz, 1H), 4.37 (dd, *J* = 10.9, 2.7 Hz, 1H), 3.68 (dd, *J* = 10.9, 10.0 Hz, 1H).

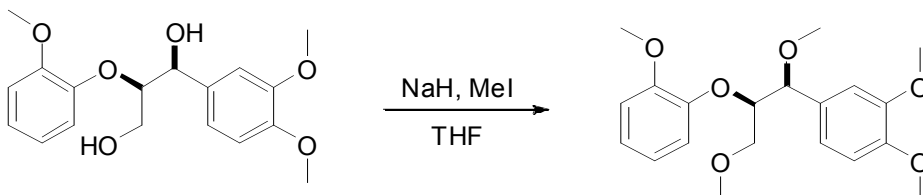
¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ 153.2 (2C), 148.9, 148.5, 136.8, 132.0, 124.0, 118.6, 110.9, 109.4, 105.1 (2C), 80.1, 72.2, 56.0 (2C), 55.9, 55.8.

MS (EI, 70 eV) *m/z* (%): 334.2 (37), 180.1 (36), 167.0 (28), 154.1 (100), 151.1 (31), 139.1 (267), 334.2 (37).

C₁₈H₂₂O₆ (334.36) C 64.66, H 6.63, found C 64.81, H 6.87.

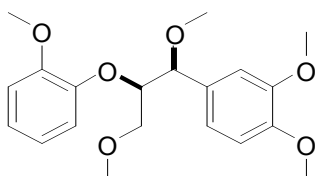
Preparation of the dilignol derivatives 3–8

Preparation of substrate 3:



A dry and argon flushed 25 mL Schlenk flask equipped with a magnetic stirrer and a septum was charged with compound **1a** (334 mg, 1.0 mmol, 1 equiv) and dry THF (5.0 mL). The solution was cooled at 0 °C and NaH (60% w/w in mineral oil, 88 mg, 2.2 mmol, 2.2 equiv) was added, followed by a dropwise addition of MeI (137 μ L, 2.2 mmol, 2.2 equiv). The reaction mixture was stirred overnight at room temperature and quenched by addition of a saturated aqueous solution of NH_4Cl . The mixture was extracted with ethyl acetate (3 x 10 mL), and the combined organic layers were dried over MgSO_4 , filtered, and concentrated. The crude residue was purified by flash chromatography (pentane/ethyl acetate = 6:1) yielding the title compound as a colorless syrup (318 mg, 88%).

1,3-Dimethoxy-1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane (**3**)^{S4}



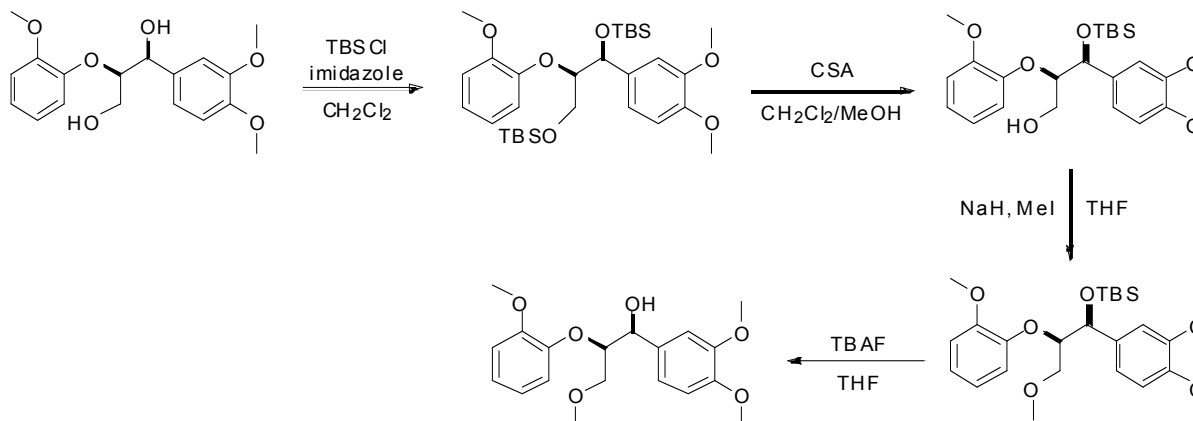
^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ 6.96 (d, J = 1.6 Hz, 1H), 6.94–6.87 (m, 2H), 6.86–6.76 (m, 4H), 4.47–4.42 (m, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 3.76 (s, 3H), 3.75–3.70 (m, 1H) 3.65–3.60 (m, 1H), 3.37 (s, 3H), 3.29 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ 150.8, 148.8, 148.5, 147.9, 130.2, 122.2, 120.8, 120.4, 118.1, 112.3, 110.7, 110.5, 82.6, 82.4, 71.3, 59.2, 57.1, 55.8, 55.8, 55.8.

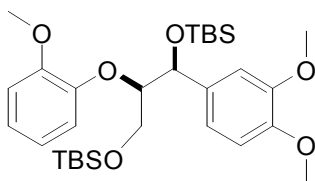
HRMS (ESI, 70 eV): m/z calcd for $\text{C}_{20}\text{H}_{26}\text{O}_6 + \text{Na}^+$: 385.1622 [$M + \text{Na}^+$]; found: 385.1621. No spectral data given in the corresponding reference.^{S4}

Preparation of substrate (4):

Substrate **4** was prepared following a procedure described by Toste,^{S5} starting from compound **1a**.



1,3-Di-[(*tert*-butyldimethylsilyl)oxy]-3-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane



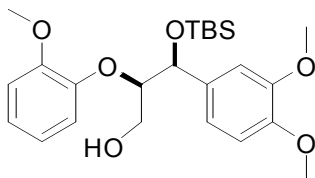
A dry and argon flushed 25 mL Schlenk flask equipped with a magnetic stirrer and a septum was charged with **1a** (1.00 g, 3.0 mmol, 1 equiv) and CH₂Cl₂ (6 mL). To this solution was added imidazole (0.68 g, 10.0 mmol, 3.3 equiv), and TBSCl (1.21 g, 8.0 mmol, 2.7 equiv). The reaction mixture was then stirred at room temperature for 5 hours and concentrated. The residue was purified by flash chromatography (pentane/ethyl acetate = 9:1) yielding the title compound as a colorless syrup (1.60 g, 95%).

¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ 7.01 (d, J = 2.0 Hz, 1H), 6.96–6.90 (m, 2H), 6.87–6.74 (m, 4H), 4.94 (d, J = 5.2 Hz, 1H), 4.38 (q, J = 5.2 Hz, 1H), 3.90 (d, J = 5.2 Hz, 1H), 3.89 (d, J = 5.2 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.74 (s, 3H), 0.87 (s, 9H), 0.84 (s, 9H), 0.05 (s, 3H), 0.00 (s, 3H), –0.04 (s, 3H), –0.15 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ 150.1, 148.9, 148.4, 148.1, 134.2, 121.1, 120.5, 119.5, 116.6, 112.1, 110.5, 110.3, 85.1, 74.1, 62.6, 55.8, 55.7, 55.6, 25.8 (3C), 25.7 (3C), 18.2, 18.1, –4.8, –5.1, –5.5, –5.6.

HRMS (ESI, 70 eV): m/z calcd for C₃₀H₅₀O₆Si₂+Na⁺: 585.3038 [M +Na⁺]; found: 585.3049.

3-[(*tert*-Butyldimethylsilyl)oxy]-3-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol



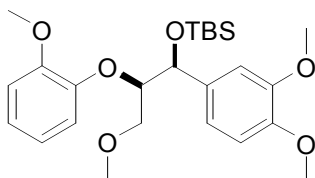
A dry and argon flushed 50 mL Schlenk flask equipped with a magnetic stirrer and a septum was charged with the TBS ether prepared precedently (1.52 g, 2.7 mmol, 1 equiv) and a mixture of CH₂Cl₂/MeOH (1:1, 20 mL). Then the solution was cooled to 0 °C, and CSA (207 mg, 0.89 mmol, 0.33 equiv) was added at this temperature. The reaction mixture was stirred at 0 °C for 2 h and then quenched with saturated aqueous solution of NaHCO₃ (20 mL). The aqueous layer was extracted with CH₂Cl₂ (3 x 10 mL), and the combined organic layers were dried over MgSO₄, concentrated, and purified by flash chromatography (pentane/ethyl acetate = 3:1) yielding the title compound as a colorless syrup (0.92 g, 76%).

¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ 7.02 (d, *J* = 1.6 Hz, 1H), 6.97–6.90 (m, 1H), 6.86–6.83 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.77–6.71 (m, 1H), 6.45 (dd, *J* = 8.0 Hz and 1.6 Hz, 1H), 4.91 (d, *J* = 6.8 Hz, 1H), 4.02 (ddd, *J* = 6.8 Hz, 4.7 Hz and 3.7 Hz, 1H), 3.94–3.88 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 3.83–3.78 (m, 1H), 3.18 (t, *J* = 6.8 Hz, 1H), 0.90 (s, 9H), 0.10 (s, 3H), –0.12 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ 151.0, 148.7, 148.3, 147.8, 134.9, 123.3, 121.3, 119.9, 119.5, 111.9, 110.5, 109.9, 88.1, 74.4, 61.4, 55.8, 55.8, 55.7, 25.7 (3C), 18.1, –4.7, –5.2.

HRMS (ESI, 70 eV): *m/z* calcd for C₂₄H₃₆O₆Si+K⁺: 487.1913 [*M*+K⁺]; found: 487.1916.

3-[(*tert*-Butyldimethylsilyl)oxy]-3-(3,4-dimethoxyphenyl)-1-methoxy-2-(2-methoxyphenoxy)propane



A dry and argon flushed 25 mL Schlenk flask equipped with a magnetic stirrer and a septum was charged with the hydroxy silyl ether prepared before (851 mg, 1.9 mmol, 1 equiv) and dry THF (6.5 mL). The solution was cooled at 0 °C and NaH (60% w/w in mineral oil, 84 mg, 2.1 mmol, 1.1 equiv) was added, followed by a dropwise addition of MeI (131 μL, 2.1 mmol, 1.1 equiv). The reaction mixture was stirred overnight at room temperature, and quenched by addition of a saturated aqueous solution of NH₄Cl. Then, the mixture was extracted with ethyl acetate (3 x 10 mL), and the combined organic

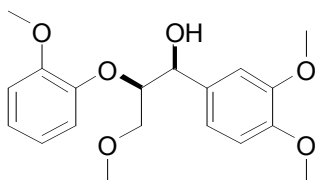
layers were dried over MgSO_4 , filtered, and concentrated. The resulting oil was purified by flash chromatography (pentane/ethyl acetate = 3:1) yielding the title compound as a colorless syrup (843 mg, 96%).

^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ 7.00 (dd, J = 8.0 Hz and 1.6 Hz, 1H), 6.97–6.91 (m, 1H), 6.90–6.82 (m, 1H), 6.82–6.73 (m, 3H), 6.71 (dd, J = 8.0 Hz and 1.6 Hz, 1H), 4.96 (d, J = 6.2 Hz, 1H), 4.30 (ddd, J = 6.2 Hz, 4.7 Hz and 3.2 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.75 (s, 3H), 3.72 (d, J = 4.7 Hz, 1H), 3.64 (dd, J = 10.5 Hz and 3.2 Hz, 1H), 3.34 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), –0.16 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ 150.7, 148.4, 148.2, 148.1, 134.7, 121.9, 120.7, 119.4, 117.8, 112.2, 110.4, 110.3, 84.4, 73.7, 71.2, 59.0, 55.8, 55.7, 55.7, 25.6 (3C), 18.1, –4.8, –5.2.

HRMS (ESI, 70 eV): m/z calcd for $\text{C}_{25}\text{H}_{38}\text{O}_6\text{Si} + \text{Na}^+$: 485.2330 [$M + \text{Na}^+$]; found: 485.2329.

1-(3,4-dimethoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)-1-propanol (4)



A dry and argon flushed 25 mL Schlenk flask equipped with a magnetic stirrer and a septum was charged with the TBS-ether prepared precedently (785 mg, 1.7 mmol, 1 equiv) and THF (7.0 mL). Then a solution of TBAF in THF (2.05 mL, c = 1.0 M, 2.05 mmol, 1.2 equiv) was added dropwise at room temperature. The reaction mixture was stirred for 30 min and concentrated. The crude residue was purified by flash chromatography (pentane/ethyl acetate = 3:1 to 1:1) yielding the title compound as a colorless syrup (544 mg, 92%).

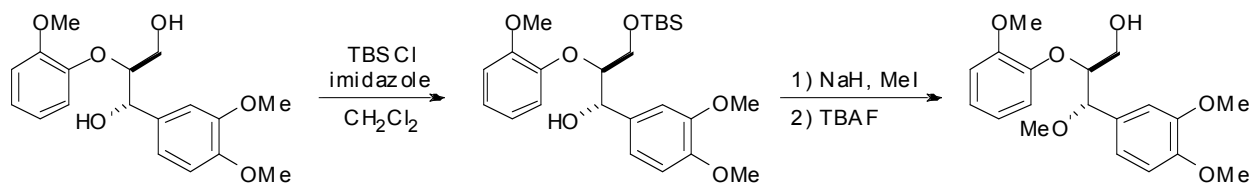
^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ 7.09–7.04 (m, 1H), 7.04–6.98 (m, 2H), 6.93–6.85 (m, 3H), 6.81 (d, J = 8.0 Hz, 1H), 4.87 (t, J = 4.7 Hz, 1H), 4.34 (dt, J = 6.4 Hz and 4.0 Hz, 1H), 3.92 (d, J = 4.7 Hz, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 6.63 (dd, J = 10.5 Hz and 6.4 Hz, 1H), 3.43 (dd, J = 10.5 Hz and 4.0 Hz, 1H), 3.33 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ 151.4, 148.8, 148.3, 147.3, 132.5, 123.7, 121.4, 120.6, 118.6, 112.1, 110.8, 109.6, 85.1, 72.9, 71.4, 59.3, 55.9, 55.8, 55.8.

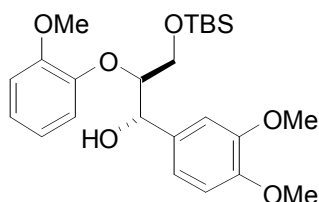
HRMS (ESI, 70 eV): m/z calcd for $\text{C}_{19}\text{H}_{24}\text{O}_6 + \text{Na}^+$: 371.1465 [$M + \text{Na}^+$]; found: 371.1467.

Preparation of substrate 5:

Substrate **5** was prepared following a procedure described by Toste,^{S5} starting from compound **1a**.



3-[(*tert*-Butyldimethylsilyl)oxy]-1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-propan-1-ol



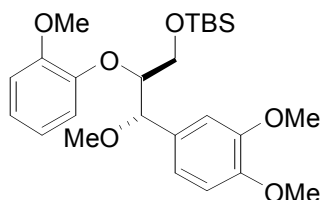
To a solution of **1a** (668 mg, 2.0 mmol, 1 equiv) and imidazole (163 mg, 2.4 mmol, 1.2 equiv) in dry CH₂Cl₂ (3.0 mL) was added TBSCl (317 mg, 2.1 mmol, 1.05 equiv) at room temperature. The reaction mixture was stirred for 6 hours, then concentrated, and purified by flash chromatography (pentane/ethyl acetate = 3:1) yielding the title compound as a colorless syrup (717 mg, 80%).

¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ 7.05 (d, J = 1.6 Hz, 1H), 7.04–6.98 (m, 2H), 6.95–6.89 (m, 3H), 6.89 (td, J = 8.0 Hz and 1.6 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 4.93 (t, J = 3.2 Hz, 1H), 4.28 (dt, J = 4.7 Hz and 4.7 Hz, 1H), 4.10 (d, J = 5.6 Hz, 1H), 3.87 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.85 (d, J = 5.6 Hz, 1H), 3.69 (dd, J = 10.5 Hz and 4.7 Hz, 1H), 0.89 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ 151.24, 148.73, 148.25, 147.61, 132.85, 123.31, 121.22, 120.10, 118.95, 112.15, 110.74, 109.84, 85.72, 73.70, 62.44, 55.86, 55.79, 55.77, 25.81 (3C), 18.18, –5.45, –5.55.

HRMS (ESI, 70 eV): m/z calcd for C₂₄H₃₆O₆Si+Na⁺: 471.2173 [M +Na⁺]; found: 471.2174.

3-[(*tert*-Butyldimethylsilyl)oxy]-1-(3,4-dimethoxyphenyl)-1-methoxy-2-(2-ethoxy-phenoxy) propane



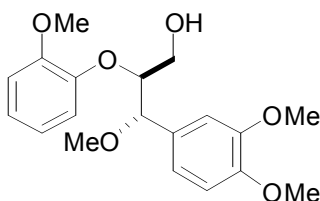
To a solution of the hydroxy silyl ether prepared before (672 mg, 1.50 mmol, 1 equiv) in dry THF (5.0 mL) was added NaH (60% w/w in mineral oil, 66 mg, 1.65 mmol, 1.1 equiv) followed by MeI (103 μ L, 1.65 mmol, 1.1 equiv) in 5 min. The reaction mixture was stirred overnight and quenched by addition of a saturated aqueous solution of NH_4Cl . The mixture was extracted with ethyl acetate (3x10 mL), and the combined organic layers were dried over MgSO_4 , filtered and concentrated. The resulting oil was purified by flash chromatography (pentane/ethyl acetate = 5:1 to 3:1) yielding the title compound as a colorless syrup (471 mg, 68%).

^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 6.99 (d, J = 2.0 Hz, 1H), 6.95–6.84 (m, 3H), 6.83–6.76 (m, 3H), 4.45–4.40 (m, 2H), 3.93–3.87 (m, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.82–3.77 (m, 1H), 3.72 (s, 3H), 3.27 (s, 3H), 0.88 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 150.51, 148.72, 148.52, 148.38, 130.78, 121.77, 120.75, 120.72, 117.61, 112.31, 110.94, 110.39, 83.77, 82.47, 62.11, 57.00, 55.82, 55.78, 55.75, 25.86 (3C), 18.25, –5.42, –5.50.

HRMS (ESI, 70 eV): m/z calcd for $\text{C}_{25}\text{H}_{38}\text{O}_6\text{Si}+\text{K}^+$: 501.2069 [$M+\text{K}^+$]; found: 501.2066.

3-(3,4-Dimethoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)propan-1-ol (5)^{S4, S6}



To a solution of the TBS-ether (416 mg, 0.9 mmol, 1 equiv) in THF (3.0 mL) was added a solution of TBAF in THF (1.1 mL, c = 1.0 M, 1.1 mmol, 1.2 equiv). The reaction mixture was stirred for 30 min and concentrated. The crude residue was purified by flash chromatography (pentane/ethyl acetate = 3:1 to 1:1) yielding the title compound as a colorless syrup (248 mg, 79%).

^1H NMR (400 MHz, CDCl_3 , 25 $^\circ\text{C}$, TMS): δ 6.98–6.92 (m, 3H), 6.88–6.82 (m, 2H), 6.76 (ddd, J = 8.0 Hz, 8.0 Hz and 1.6 Hz, 1H), 6.54 (dd, J = 8.0 Hz and 1.6 Hz, 1H), 4.43 (d, J = 7.2 Hz, 1H), 4.08 (ddd, J = 8.0 Hz, 7.2 Hz and 4.0 Hz, 1H), 3.96–3.90 (m, 1H),

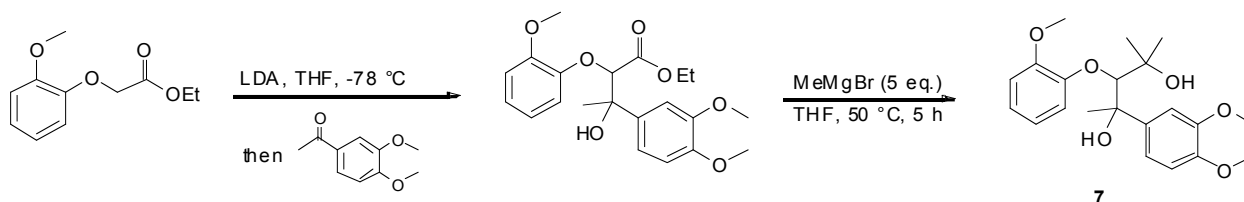
3.88 (s, 3H), 3.87 (s, 3H), 3.86–3.78 (m, 1H), 3.82 (s, 3H), 3.31 (s, 3H), 3.16 (t, $J = 7.2$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3 , 25 °C, TMS): δ 151.17, 149.03, 148.72, 147.56, 131.40, 123.55, 121.31, 120.36, 120.29, 111.98, 110.81, 110.18, 86.64, 82.86, 61.59, 57.09, 55.90, 55.87, 55.75.

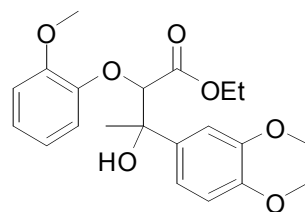
HRMS (ESI, 70 eV): m/z calcd for $\text{C}_{19}\text{H}_{24}\text{O}_6 + \text{Na}^+$: 371.1465 [$M + \text{Na}^+$]; found: 371.1463. No spectral data given in the corresponding reference.

Preparation of substrate 6:

This substrate was prepared in 2 steps, starting from ethyl (2-methoxyphenoxy)acetate:



Ethyl-3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-3-methylpropanoate



A dry and argon flushed 100 mL three-necked flask equipped with a magnetic stirrer, a low temperature thermometer, an argon inlet, and an addition funnel was charged with diisopropylamine (0.84 g, 8.25 mmol, 1.1 equiv) and THF (15 mL). The reaction mixture was cooled to 0 °C and a solution of commercial *n*BuLi in hexanes (5.4 mL, 1.6 M, 8.66 mmol, 1.15 equiv) was added dropwise in 5 min. After stirring for 30 min at 0 °C the reaction mixture was cooled to –78 °C, and a solution of ethyl (2-methoxyphenoxy)-acetate (1.58 g, 7.5 mmol, 1 equiv) in THF (22 mL) was added dropwise over a period of 30 min. After stirring for additional 5 min, a solution of 3,4-dimethoxyacetophenone (1.49 g, 8.25 mmol, 1.1 equiv) in THF (22 mL) was added in 15 min at –78 °C. At the end of the addition, stirring was continued for 90 min at –78 °C, and then distilled water (50 mL) was added. The aqueous phase was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with a 1 N aqueous HCl solution (40 mL), water (40 mL) and brine (40 mL), then dried with MgSO_4 , filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (pentane/ethyl acetate = 8:2 to 1:1) yielding a 1:1 mixture of *erythro*- and *threo* diastereoisomers of the title compound, as a slightly yellow syrup (2.43 g, 83%).

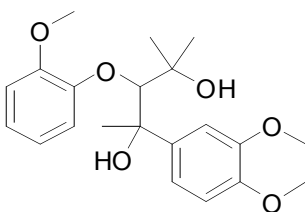
Erythro + *threo* hydroxy-ester:

¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ 7.21 (d, *J* = 2.1 Hz, 1H), 7.13 (d, *J* = 2.1 Hz, 1H), 7.08–6.96 (m, 4H), 6.93–6.75 (m, 8H), 4.64 (s, 1H), 4.62 (s, 1H), 4.12–3.93 (m, 6H), 3.89 (s, 3H), 3.89 (s, 3H), 3.87 (s, 6H), 3.85 (s, 3H), 3.84 (s, 3H), 1.80 (s, 3H), 1.74 (s, 3H), 1.05 (t, *J* = 7.3 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ 170.1, 169.7, 150.4, 150.4, 148.4, 148.4, 148.2, 148.2, 147.5, 147.2, 136.2, 135.9, 123.5 (2C), 120.9, 120.9, 118.0, 117.9, 117.8, 117.7, 112.4, 112.4, 110.5, 110.4, 109.4, 109.2, 86.5, 85.3, 75.6, 75.3, 61.1, 61.0, 55.8 (4C), 55.8 (2C), 26.6, 25.1, 13.9, 13.9.

HRMS (ESI, 70 eV): *m/z* calcd for C₂₁H₂₆O₇+Na⁺: 413.1571 [*M*+Na⁺]; found: 413.1565.

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3,3-trimethyl-1,3-propanediol (6)



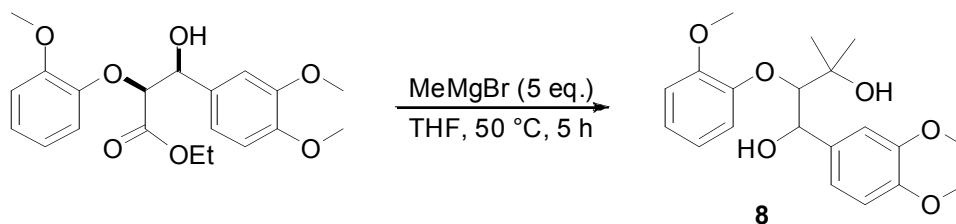
A dry and argon flushed 250 mL Schlenk-flask equipped with a stirring bar, an argon inlet and a septum was charged with the hydroxy ester prepared precedently (520 mg, 1.33 mmol, 1.0 equiv) and THF (5 mL). The reaction mixture was cooled to 0 °C and a solution of commercial MeMgBr in diethyl ether (2.2 mL, 3.0 M, 6.66 mmol, 5 equiv) was added dropwise in 5 min. Then the reaction mixture was warmed to 50 °C and stirred for 5 h. The reaction was allowed to cool at room temperature, and saturated aqueous NH₄Cl solution (10 mL) was added. The aqueous phase was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine (30 mL), then dried with MgSO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (CH₂Cl₂/MeOH = 99:1 to 97:3) yielding the title compound **6** as a colorless syrup (227 mg, 45%).

¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ 7.23 (d, *J* = 2.1 Hz, 1H), 7.02–6.87 (m, 5H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.40 (s, 1H), 3.91 (s, 3H), 3.91 (s, 3H), 3.88 (s, 3H), 3.36 (br.s, 2H), 1.57 (s, 3H), 1.05 (s, 3H), 1.04 (s, 3H).

¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ 149.9, 149.7, 148.7, 147.7, 138.9, 122.0, 121.1, 117.6, 115.1, 112.2, 110.7, 109.0, 90.0, 77.4, 75.4, 56.0, 55.9, 55.8, 30.9, 28.5, 27.2.

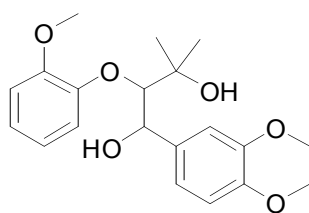
HRMS (ESI, 70 eV): *m/z* calcd for C₁₉H₂₄O₆+Na⁺: 399.1778 [*M*+Na⁺]; found: 399.1772.

Preparation of substrate 7:



The product (substrate **7**) was prepared following the procedure described before (preparation of substrate **6**, step 2) starting from the corresponding hydroxy ester (376 mg, 1.0 mmol, 1 equiv). The preparation of the hydroxy ester is described in ref. *S1*. The purification was performed by flash chromatography (CH₂Cl₂/MeOH = 99:1 to 97:3) yielding the title compound **7** as a slightly yellow syrup (255 mg, 68%).

1-(3,4-Dimethoxyphenyl)-3,3-dimethyl-2-(2-methoxyphenoxy)-1,3-propanediol (**7**)

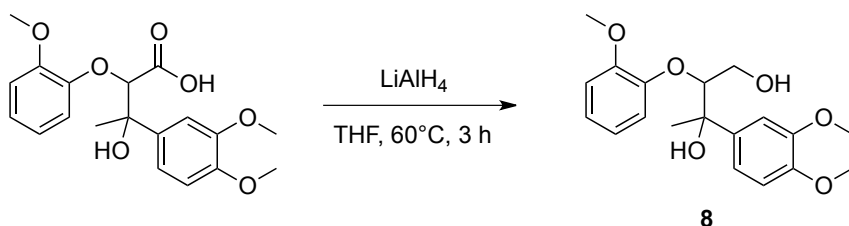


¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ 7.02 (d, J = 2.1 Hz, 1H), 6.98 (dd, J = 8.2 Hz and 2.1 Hz, 1H), 6.87–6.80 (m, 1H), 6.77 (dd, J = 8.2 Hz and 2.1 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 6.68 (ddd, J = 8.2 Hz, 7.0 Hz and 2.1 Hz, 1H), 6.45 (dd, J = 8.2 Hz and 1.4 Hz, 1H), 4.97 (d, J = 7.3 Hz, 1H), 4.16 (d, J = 7.3 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.80 (s, 3H), 3.50 (br.s, 2H), 1.42 (s, 3H), 1.12 (s, 3H).

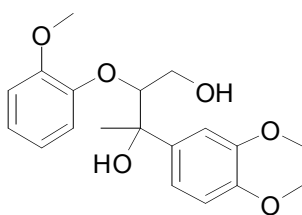
¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ 149.9, 148.8, 148.5, 148.5, 134.1, 122.1, 121.0, 119.4, 116.9, 112.0, 110.7, 110.1, 89.0, 74.6, 74.2, 55.9 (2C), 55.8, 27.1, 25.1.

HRMS (ESI, 70 eV): m/z calcd for C₁₉H₂₄O₆+Na⁺: 385.1622 [M +Na⁺]; found: 385.1623.

Preparation of substrate 8:



The product (substrate **8**) was prepared following the reported procedure,^{S1} starting from the corresponding hydroxy ester (390 mg, 1.0 mmol, 1 equiv). The preparation of the hydroxy ester is described previously for the preparation of substrate **6** (step 1). The purification was performed by flash chromatography (CH₂Cl₂/MeOH = 99:1 to 97:3) yielding a 1:1 mixture of *erythro*- and *threo* diastereoisomers of the title compound **8** as a slightly yellow syrup (285 mg, 82%).



Erythro + *threo* diol:

¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ 7.12 (d, *J* = 2.1 Hz, 1H), 7.11 (d, *J* = 2.1 Hz, 1H), 7.07 (dd, *J* = 8.2 Hz and 1.6 Hz, 1H), 7.05–6.98 (m, 2H), 6.98–6.89 (m, 5H), 6.87–6.82 (m, 3H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.18 (dd, *J* = 5.7 Hz and 3.9 Hz, 1H), 4.15 (t, *J* = 3.9 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.78 (dd, *J* = 12.2 Hz and 5.7 Hz, 1H), 3.66 (dd, *J* = 12.2 Hz and 3.9 Hz, 1H), 3.55 (t, *J* = 4.1 Hz, 2H), 2.82 (br.s, 4H), 1.67 (s, 3H), 1.66 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ 151.1, 150.9, 148.8, 148.6, 148.4, 148.1, 147.9 (2C), 137.6, 137.3, 123.7, 123.6, 121.6, 121.5, 120.2, 119.9, 117.8, 117.2, 112.2, 112.1, 111.0, 110.6, 109.4, 108.6, 90.1, 88.0, 76.6, 75.8, 61.6, 61.1, 55.9 (2C), 55.9 (3C), 55.8, 27.8, 25.1.

HRMS (ESI, 70 eV): *m/z* calcd for C₁₉H₂₄O₆+Na⁺: 371.1465 [*M*+Na⁺]; found: 371.1463.

Fig. S1. HSQC NMR spectrum of untreated organosolv lignin (sample A):

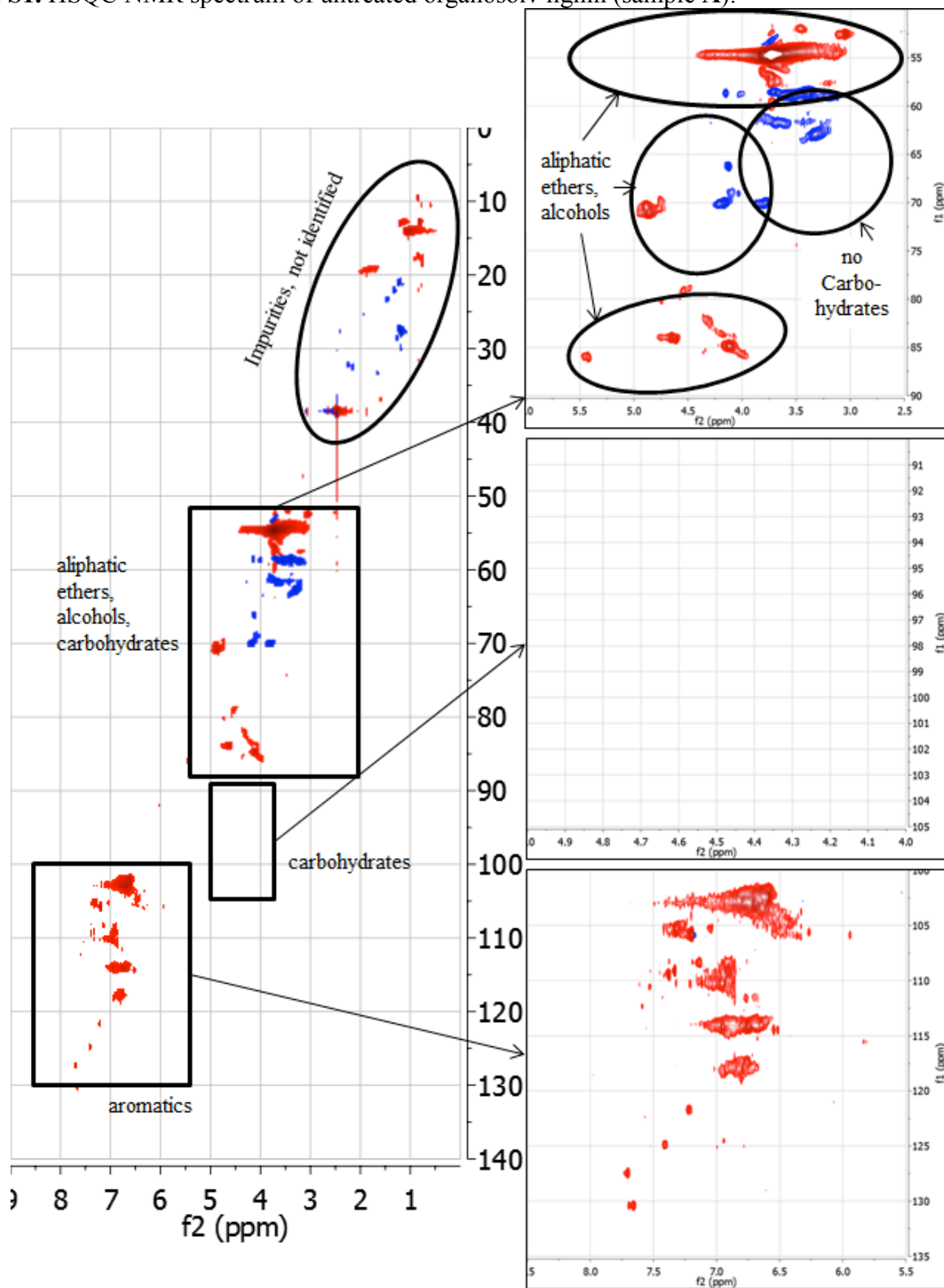


Fig. S2. HSQC NMR spectrum of treated organosolv lignin (sample A):

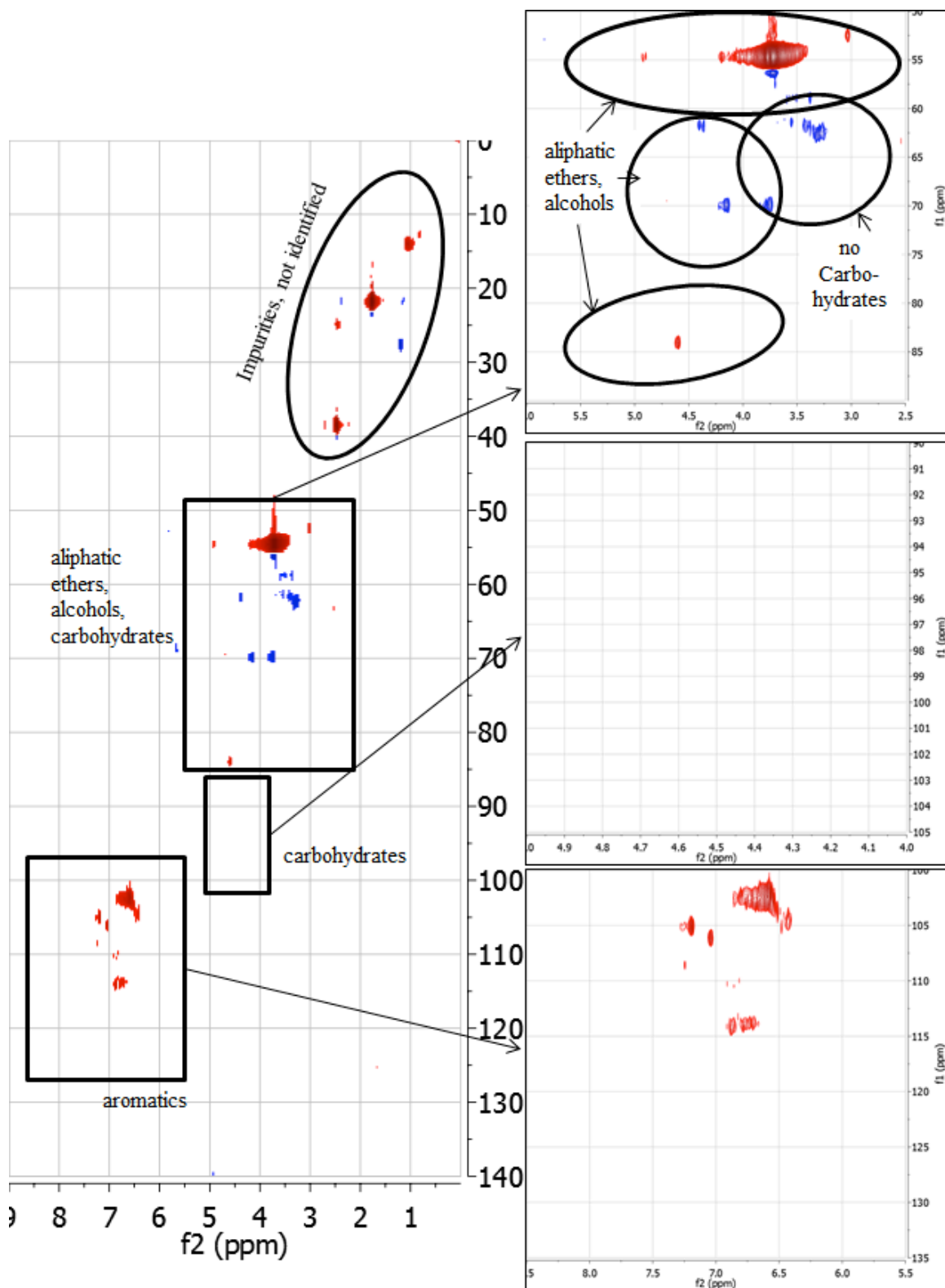


Fig. S3. HSQC NMR spectrum of untreated organosolv lignin (sample **B**):

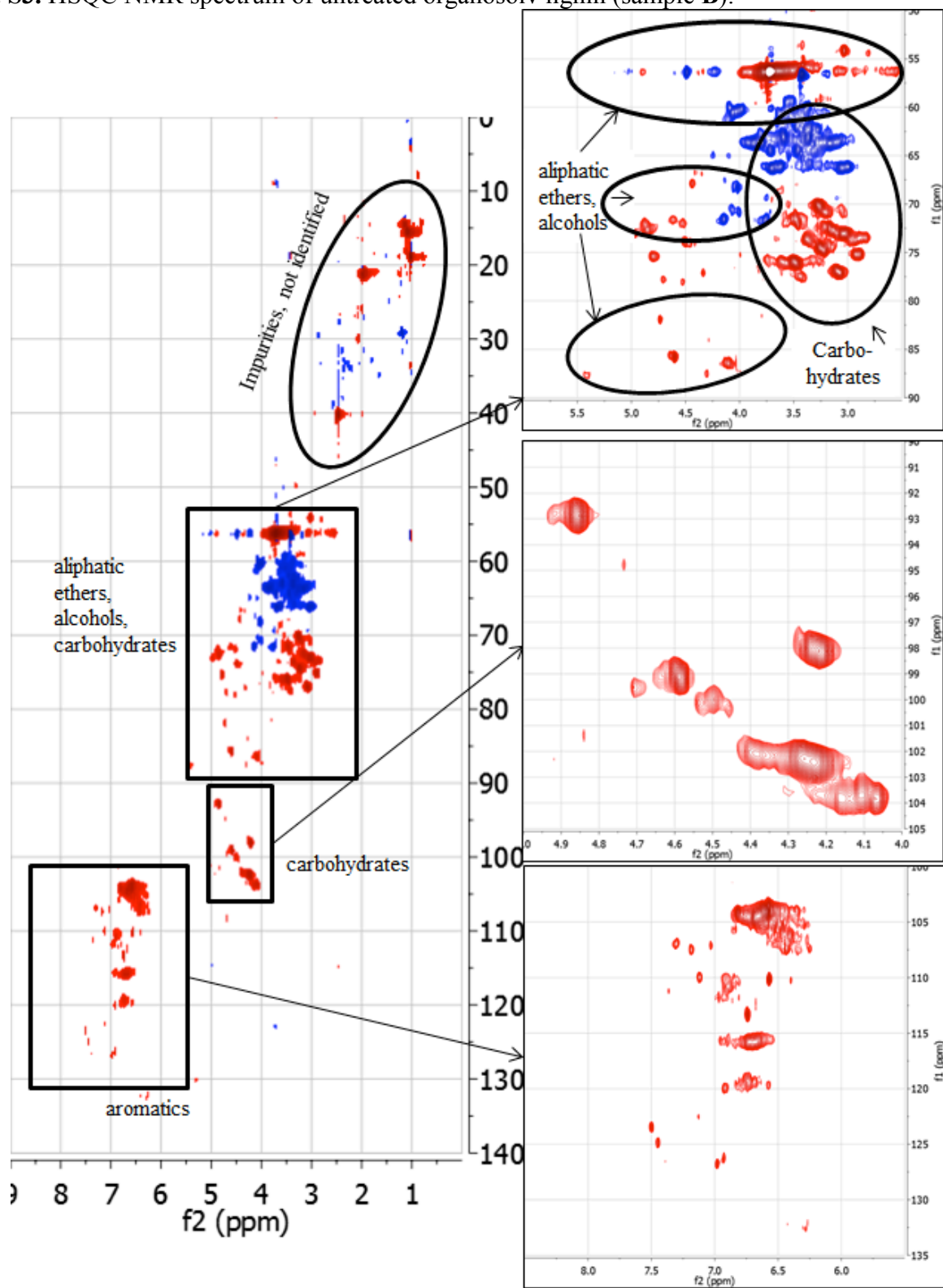


Fig. S4. HSQC NMR spectrum of treated organosolv lignin (sample **B**):

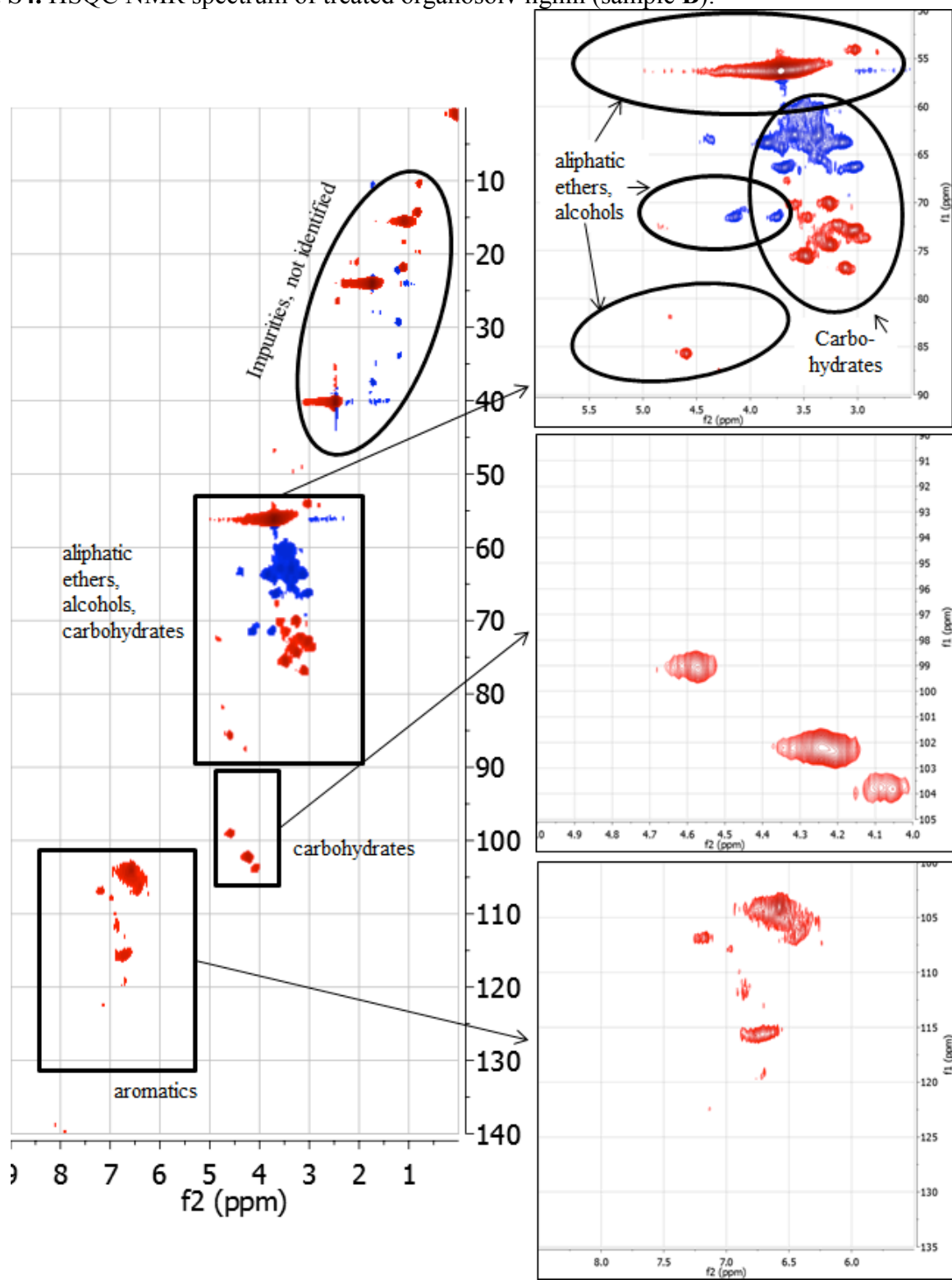
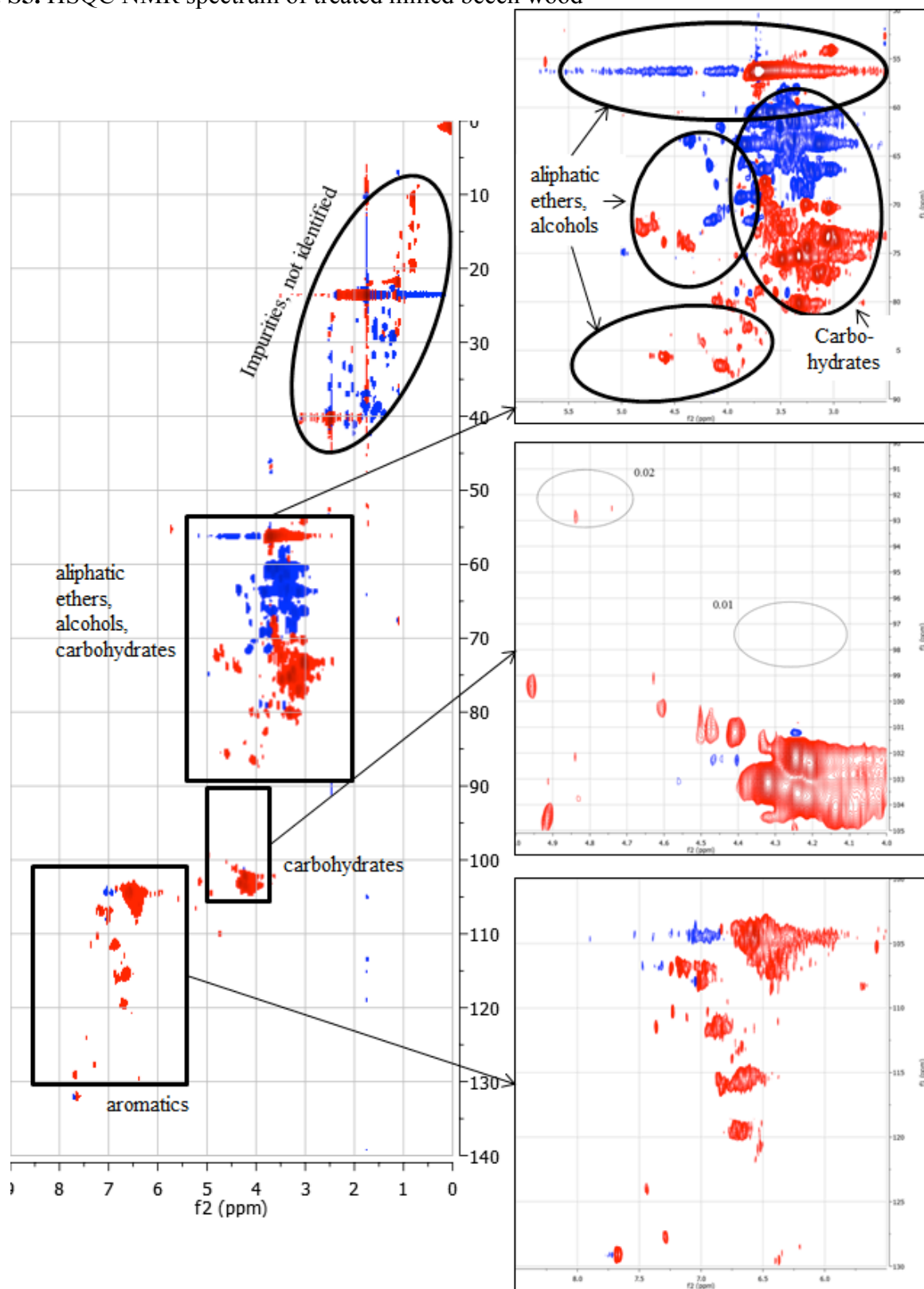


Fig. S5. HSQC NMR spectrum of treated milled beech wood



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