Supporting Information

Light-Driven Depolymerization of Native Lignin Enabled by Proton-Coupled Electron Transfer

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General Information

Sawdust samples (ground finings) were ordered from a seller (WildThingsForestry) in Heron, MT via Etsy (www.etsy.com). Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.¹ All solvents were purified according to the method of Grubbs.² Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished by flash chromatography on Silicycle F60 silica gel according to the method of Still.³ All reactions were carried out in well ventilated fume hoods. Thin-layer chromatography (TLC) was performed on Silicycle 250 µm silica gel plates. Visualization of the developed chromatogram was performed by irradiation with UV light. Yields refer to purified compounds unless otherwise noted.

¹H and ¹³C NMR spectra were recorded on a Bruker 500 (500 and 126 MHz for ¹H and ¹³C respectively), and are internally referenced to residual solvent signals, CDCl₃ referenced at δ 7.26 and 77.16 ppm, and DMSO -*d*₆ referenced at δ 2.50 and 39.52 ppm. Data for ¹H is reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, h = sextet, m = multiplet), broad peaks (br), coupling constant (Hz) and assignment. Data for ¹³C NMR is reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. Heteronuclear single quantum coherence spectroscopy (HSQC) was recorded on a Bruker 500 spectrometer. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm⁻¹). High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS (Electrospray Ionization).

Gel permeation chromatography (GPC) was conducted at 35 °C using two 30 cm Polymer Laboratories PLgel Mixed-C columns, a Wyatt Optilab T-rEX refractive index detector ($\lambda = 658$ nm, 25 °C), and a UV diode array detector. THF was used as the mobile phase, and the systems were calibrated with narrow-distribution polystyrene standards.

Synthesis of Lignin Model Dimers

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (1)



The titled compound was synthesized according to a literature report. Spectra are consistent with reported literature.⁴

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (2)



The titled compound was synthesized according to a literature report. Spectra are consistent with reported literature.⁵

(1S,2S)-1,2-Bis(3,4-dimethoxyphenyl)propane-1,3-diol (3)



The titled compound was synthesized according to a literature report. Spectra are consistent with reported literature.⁶





A flame-dried 250-mL round bottomed flask was equipped with a stir bar and placed under an argon atmosphere, and charged with anhydrous THF (40 mL), and a solution of NaHMDS (1.2 equiv., 12.0 mmol, 12.0 mL of a 1.0 M solution in THF), and cooled to -78 °C. Then, a solution of ester S1 (1.0 equiv., 10.0 mmol, 2.25 g) in anhydrous THF (10 mL) was added dropwise over 10 min. The homogeneous solution was allowed to stir at this temperature for an additional 1 h. Then, a solution of aldehyde S2 (1.4 equiv., 14.0 mmol, 3.39 g) in anhydrous THF (14 mL) was added dropwise over 10 min. The reaction mixture was stirred at -78 °C for 5 h, then guenched with sat. ag. ammonium chloride solution (40 mL) at this temperature, before the cooling bath was removed and the mixture allowed to warm to room temperature. The reaction mixture was partitioned between ethyl acetate (50 mL) and water (50 mL), the phases were separated, and the aqueous phase was extracted with further ethyl acetate (3 x 50 mL). The combined organic phases were washed with brine (50 mL) and dried over sodium sulfate. Filtration and concentration *in vacuo* afforded an oil crude, which was purified *via* flash column chromatography on silica (10–70%) ethyl acetate/hexanes) to afford pure hydroxyesters S3 (3.82 g, 82%) as a colourless oil, as a 4:1 mixture of diastereoisomers.



(major diast., 2H, d, ${}^{3}J_{HH} = 7.2$ Hz), 7.34 (major diast., 2H, t, ${}^{3}J_{HH} = 7.0$ Hz), 7.26 – 7.29 (2H, m), 6.88 – 6.91 (2H, m), 6.84 (minor diast., 2H, d, ${}^{3}J_{HH} = 8.7$ Hz), 6.82 (1H, s), 6.65 – 6.69 (3H, m), 6.61 (major diast., 1H, dd, ${}^{3}J_{\text{HH}} = 8.8$ Hz, ${}^{4}J_{\rm HH}$ = 1.8 Hz), 6.56 (major diast., 1H, d, ${}^{4}J_{\rm HH}$ = 1.6 Hz), 6.51 (major diast., 1H, dd, ${}^{3}J_{\rm HH} = 8.2$ Hz, ${}^{4}J_{\rm HH} = 1.6$ Hz), 5.14 - 5.17 (2H, m), 5.05 - 5.10 (3H, m), 4.22 - 4.28 (major diast., 1H, m), 4.14 – 4.19 (major diast., 1H, m), 3.99 – 4.05 (minor diast., 1H, m), 3.93 – 3.98 (minor diast., 1H, m), 3.87 (minor diast., 3H, s), 3.85 (minor diast., 3H, s), 3.83 (minor diast., 3H, s), 3.80 (major diast., 3H, s), 3.76 (major diast., 3H, s), 3.74 (minor diast., 3H, s), 3.72 (major diast., 3H, s), 3.02 (major diast., 1H, d, ${}^{3}J_{\rm HH}$ = 3.6 Hz), 2.57 (minor diast., 1H, s), 2.04 (minor diast., 2H, s), 1.24 (major diast., 2H, t, ${}^{3}J_{\rm HH}$ = 7.4 Hz), 1.04 (minor diast., 2H, t, ${}^{3}J_{\rm HH}$ = 7.4 Hz); 13 C NMR (126 MHz, CDCl₃): δ 173.7 (major diast.), 172.6 (minor diast.), 149.6 (minor diast.), 149.4 (major diast.), 149.0 (minor diast.), 148.9 (minor diast.), 148.8 (major diast.), 148.4 (major diast.), 147.9 (minor diast.), 147.7 (major diast.), 137.2 (minor diast.), 137.2 (major diast.), 134.2 (major diast.), 134.1 (minor diast.), 128.6, 127.9, 127.3, 121.6 (minor diast.), 121.0 (major diast.), 119.2 (minor diast.), 119.1 (major diast.), 113.7 (minor diast.), 113.5 (major diast.), 112.0 (minor diast.), 111.7 (major diast.), 111.2 (minor diast.), 111.0 (major diast.), 110.5 (minor diast.), 110.1 (major diast.), 76.6 (major diast.), 75.2 (minor diast.), 71.1 (minor diast.), 71.0 (major diast.), 61.3 (major diast.), 61.0 (minor diast.), 59.7 (major diast.), 59.4 (minor diast.), 56.1, 56.0, 56.0, 55.9, 55.9, 14.2 (major diast.),

¹**H** NMR (500 MHz, CDCl₃): δ 7.42 (minor diast., 2H, d, ³*J*_{HH} = 7.8 Hz), 7.39

14.1 (minor diast.); **IR** (\tilde{v}_{max} /cm⁻¹, thin film): 3503, 2977, 2936, 2836, 1727, 1605, 1592, 1514, 1463, 1454, 1420, 1371, 1259, 1240, 1139, 1025, 913, 859, 808, 734, 698. **HRMS (ESI)** exact mass calculated for [M] (C₂₇H₃₀O₇) from [M+Na]⁺ requires 466.19915 m/z, found 466.19894 m/z with a difference of 0.46 ppm.

A flame-dried 250-mL round bottomed flask was equipped with a stir bar and placed under an argon atmosphere, and charged with anhydrous THF (50 mL) and cooled to 0 °C. By rapid removal of the septum under a blanket of argon, solid lithium aluminium hydride (3.0 equiv., 24.6 mmol, 0.94 g) was added in one portion, followed by replacement of the septum seal. Then, a solution of hydroxyesters **S3** (1.0 equiv., 8.20 mmol, 3.82 g) in anhydrous THF (20 ml) was added dropwise to the stirring suspension over 10 min (warning – vigorous evolution of hydrogen). The flask containing the ester was rinsed with anhydrous THF (2 x 5 mL), and the rinsings added to the reaction flask. The mixture was stirred at 0 °C for 1 h, then the cooling bath was removed and the mixture stirred at room temperature for a further 18 h. The reaction mixture was cooled to 0 °C, and quenched with slow addition of water (0.94 mL), then 10 wt% aq. sodium hydroxide solution (0.94 mL), then water (2.82 mL). The cooling bath was removed, and the suspension stirred at room temperature for 15 min, before addition of sodium sulfate (5.0 g), and stirred for a further 15 min. Filtration and concentration *in vacuo* afforded an oil crude, which was purified *via* flash column chromatography on silica (50–100% ethyl acetate/hexanes) to afford pure diols **S4** (2.97 g, 85%) as a viscous, colourless oil.



¹**H NMR** (500 MHz, CDCl₃): δ 7.42 (minor diast., 2H,d, ${}^{3}J_{HH} = 7.5$ Hz), 7.39 (major diast., 2H, d, ${}^{3}J_{HH} = 7.3$ Hz), 7.34 (major diast., 2H, t, ${}^{3}J_{HH} = 7.2$ Hz), 7.29 (major diast., 1H, d, ${}^{3}J_{HH} = 7.2$ Hz), 6.78 – 6.85 (minor diast., 3H, m), 6.72 – 6.74 (minor diast., 2H, m), 6.68 – 6.70 (3H, m), 6.57 (major diast., 2H, d, ${}^{3}J_{HH} = 8.4$ Hz), 6.45 (major diast., 1H, d, ${}^{4}J_{HH} = 1.5$ Hz), 5.14 (minor diast., 2H, s),

5.07 (major diast., 2H, s), 4.90 (1H, d, ${}^{3}J_{HH} = 8.6$ Hz), 4.17 (major diast., 1H, t, ${}^{3}J_{HH} = 9.2$ Hz), 3.94 – 3.96 (1H, m), 3.86 (minor diast., 3H, s), 3.82 (minor diast., 3H, s), 3.80 (major diast., 3H, s), 3.76 (major diast., 3H, s), 3.71 (major diast., 3H, s), 3.03 – 3.07 (1H, m), 2.87 – 2.91 (2H, m); 13 C NMR (126 MHz, CDCl₃): δ 149.7 (minor diast.), 149.4 (major diast.), 149.1 (minor diast.), 148.7 (major diast.), 148.4 (minor diast.), 147.9 (major diast.), 147.9 (minor diast.), 147.6 (major diast.), 137.2 (major diast.), 136.1 (major diast.), 135.2 (minor diast.), 131.8 (major diast.), 131.0 (minor diast.), 128.7 (minor diast.), 128.6 (major diast.), 127.9 (major diast.), 127.4 (major diast.), 121.1 (minor diast.), 120.4 (major diast.), 112.1 (minor diast.), 111.4 (minor diast.), 113.7 (minor diast.), 110.2 (major diast.), 79.5 (major diast.), 56.0 (minor diast.), 56.0 (minor diast.), 55.9 (major diast.), 55.9 (major diast.), 55.5 (minor diast.), 56.0 (minor diast.), 56.0 (minor diast.), 55.9 (major diast.), 55.9 (major diast.), 55.5 (minor diast.), 56.0 (minor diast.), 56.0 (minor diast.), 55.9 (major diast.), 5

Diols S4 (1.0 equiv., 6.99 mmol, 2.97 g) were dissolved in ethanol (100 mL) and placed under an argon atmosphere. By rapid removal of the septum under a blanket of argon, palladium on carbon (5 mol%, 0.35 mmol, 370 mg of a 10 wt% catalyst) was added in one portion, followed by replacement of the septum seal. The flask was placed under vacuum, and then a hydrogen atmosphere was introduced *via* balloon. This vacuum procedure was repeated three times, and then the suspension left to stir vigorously at room temperature under a hydrogen atmosphere for 4 h. After this time, the reaction flask was purged with argon, and the reaction mixture filtered through a pad of Celite, rinsing with ethanol (3 x 100 mL). *Warning* – to avoid risk of fire, spent catalyst was not allowed to dry between washes, and immediately placed under water after rinsing). Evaporation of all volatiles gave pure phenols 4 (2.34 g, 100%) as a foaming powder.



¹**H NMR** (500 MHz, CDCl₃): δ 6.85 (minor diast., 2H, dd, ${}^{3}J_{HH} = 7.9$, 3.2 Hz), 6.80 (minor diast., 1H, dd, ${}^{3}J_{HH} = 7.9$ Hz, ${}^{4}J_{HH} = 1.9$ Hz), 6.75 – 6.78 (minor diast., 2H, m), 6.72 (major diast., 1H, d, ${}^{3}J_{HH} = 8.0$ Hz), 6.69 (major diast., 1H, d, ${}^{3}J_{HH} = 8.3$ Hz), 6.59 – 6.62 (2H, m), 6.56 (major diast., 1H, dd, ${}^{3}J_{HH} = 8.2$ Hz, ${}^{4}J_{HH} = 1.8$ Hz), 6.44 (major diast., 1H, d, ${}^{4}J_{HH} = 1.8$ Hz), 4.88 (1H, d, ${}^{3}J_{HH} = 1.8$ Hz), 4.88 (1H, d, {}^{3}J_{HH} = 1.8 Hz), 4.88 (1H, d), 4.88 (1H,

8.9 Hz), 4.17 (1H, dd, ${}^{3}J_{HH} = 10.6$, 7.9 Hz), 3.94 (1H, dd, ${}^{3}J_{HH} = 10.8$, 4.5 Hz), 3.86 (minor diast., 3H, s), 3.83 (minor diast., 3H, s), 3.80 (minor diast., 3H, s), 3.80 (major diast., 3H, s), 3.74 (major diast., 3H, s), 3.72 (major diast., 3H, s), 3.02 – 3.08 (1H, m); 13 C NMR (126 MHz, CDCl₃): δ 149.1 (minor diast.), 148.7 (major diast.), 148.4 (minor diast.), 147.9 (major diast.), 146.7 (minor diast.), 146.3 (major diast.), 145.5 (minor diast.), 145.1 (major diast.), 135.0 (major diast.), 134.0 (minor diast.), 131.8 (major diast.), 131.1 (minor diast.), 120.4 (major diast.), 119.8 (minor diast.), 119.6 (major diast.), 111.1 (minor diast.), 112.4 (minor diast.), 112.1 (major diast.), 111.4 (minor diast.), 111.1 (major diast.), 109.1 (major diast.), 79.6 (major diast.), 75.9 (minor diast.), 66.5 (major diast.), 64.3 (minor diast.), 60.6 (minor diast.), 56.0 (minor diast.), 56.0 (major diast.), 55.9 (major dia

Synthesis of Monomeric Degradation Products

4-(2-Hydroxyethoxy)-3-methoxybenzaldehyde (M3)



The titled compound was synthesized according to a literature report. Spectra are consistent with reported literature.⁷

(E)-3-(4-Acetoxyphenyl)allyl acetate (S6)



p-Coumaric acid (**S5**, 1.0 equiv., 10.0 mmol, 1.64 g) was dissolved in anhydrous methanol (50 mL) and conc. sulfuric acid (5 drops) was added with stirring at room temperature. The reaction was heated to reflux for 24 h. The mixture was cooled, and all volatiles were removed *in vacuo*. The residue was dissolved in ethyl acetate (300 mL), and washed with sat. aq. sodium bicarbonate solution (100 mL) and brine (50 mL). The organic extract was dried over magnesium sulfate, filtered, and concentrated *in vacuo* to afford a pale-yellow oil, which was taken into the next step without further purification, assuming quantitative yield.

The crude ester from above was dissolved in anhydrous dichloromethane (50 mL) and cooled to 0 °C under an argon atmosphere. A solution of DIBAL-H (3.5 equiv., 35.0 mmol, 35 mL of a 1.0 M solution in toluene) was added dropwise with stirring over 15 min. The colourless solution was allowed to stir at 0 °C for 1 h, then quenched with dropwise addition of methanol (2.0 mL). The cooling bath was removed and the reaction mixture was diluted with dichloromethane (50 mL), before addition of sat. aq. Rochelle salt solution (100 mL). The mixture was stirred vigorously at room temperature for 24 h. The phases were separated, and the aqueous phase extracted with dichloromethane (2 x 50 mL). The combined organic phases were washed with brine (50 mL) and dried over magnesium sulfate. Filtration and concentration *in vacuo* afforded a colourless oil, which was taken into the next step without further purification, assuming quantitative yield.

The crude alcohol from above was dissolved in anhydrous pyridine (40 mL) under an argon atmosphere, and treated with acetic anhydride (4.0 equiv., 40 mmol, 3.78 mL). The reaction mixture was stirred at room temperature for 24 h. Solvents were removed *in vacuo* and the residue was then co-evaporated with toluene (3 x 40 mL). The residue was dissolved in ethyl acetate (200 mL) and washed with 1 M aq. hydrochloric acid solution (50 mL), sat. aq. sodium bicarbonate solution (50 mL) and brine (50 mL). The organic extract was dried over magnesium sulfate, filtered, and concentrated *in vacuo* to afford a pale-yellow oil, which was purified by flash column chromatography on silica (0–30% ethyl acetate/hexanes) to afford pure diacetate **S6** (1.93 g, 82% over three steps) as a colourless oil, which solidified on standing.

¹**H** NMR (500 MHz, CDCl₃): δ 7.39 (2H, d, ³*J*_{HH} = 8.6 Hz), 7.05 (2H, d, ³*J*_{HH} = 8.6 Hz), 6.63 (1H, d, , ³*J*_{HH} = 15.7 Hz), 6.24 (1H, dt, , ³*J*_{HH} = 15.8, 6.5 Hz), 4.72 (2H, dd, , ³*J*_{HH} = 6.5 Hz, , ⁴*J*_{HH} = 1.1 Hz), 2.29 (3H, s), 2.10 (3H, s); ¹³**C** NMR (126 MHz, CDCl₃): δ 171.0, 169.5, 150.5, 134.1, 133.3, 127.7, 123.6, 121.9, 65.1, 21.3, 21.1; **IR** (\tilde{v}_{max} /cm⁻¹, thin film): 3038, 2942, 1756, 1734, 1602, 1506, 1435, 1367, 1298, 1208, 1166, 1073, 1016, 966, 910, 856, 808, 775, 712, 662. **HRMS (ESI)** exact mass calculated for [M] (C₁₃H₁₄O₄) from [M+Na]⁺ requires 234.08921 m/z, found 234.08960 m/z with a difference of 1.66 ppm.

(E)-3-(4-Acetoxy-3-methoxyphenyl)allyl acetate (S8)



According to the procedures above for the preparation of diacetate S6, ferulic acid (S7, 1.94 g, 10.0 mmol) gave over three steps diacetate S8 (2.31 g, 87%) as a colourless oil.

¹**H** NMR (500 MHz, CDCl₃): δ 6.95 – 6.99 (3H, m), 6.62 (1H, d, ³*J*_{HH} = 16.0 Hz), 6.23 (1H, dt, ³*J*_{HH} = 16.0, 6.5 Hz), 4.72 (2H, dd, ³*J*_{HH} = 6.5 Hz, ⁴*J*_{HH} = 1.1 Hz), 3.84 (3H, s), 2.31 (3H, s), 2.10 (3H, s); ¹³**C** NMR (126 MHz, CDCl₃): δ 171.0, 169.2, 151.2, 139.7, 135.4, 133.7, 123.6, 123.0, 119.5, 110.3, 65.0, 56.0, 21.1, 20.8; **IR** (\tilde{v}_{max} /cm⁻¹, neat): 3007, 2942, 1762, 1735, 1601, 1509, 1465, 1417, 1367, 1299, 1215, 1190, 1154, 1120, 1075, 1027, 964, 901, 860, 833, 787, 734, 702, 661; **HRMS (ESI)** exact mass calculated for [M] (C₁₄H₁₆O₅) from [M+Na]⁺ requires 264.09977 m/z, found 264.09922 m/z with a difference of 2.08 ppm.

(Z)-3-(4-Acetoxy-3-methoxyphenyl)allyl acetate (S9)

To a screw cap 2-dram vial was charged with a magnetic stir bar, (E)-3-(4-acetoxy-3-methoxyphenyl)allyl acetate (**S8**, 1.0 equiv., 0.5 mmol, 132 mg), and $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (5 mol%, 0.025 mmol, 28.0 mg). The vial was sealed with a Teflon septum, and the mixture was degassed and flushed with Ar. Anhydrous dichloromethane (0.1 M, 5 mL) was then added, and the solution was degassed with Ar for 15 min. The reaction was then irradiated for 20 h with two 34 W Kessil KSH150B blue LED lamps with fans positioned such as the vial was kept at ambient temperature. The reaction mixture was concentrated under reduced pressure. ¹H-NMR analysis of the crude reaction mixture revealed that the ratio of (*Z*)-isomer to (*E*)-isomer was 2.7:1. This residue was purified by preparative TLC (25% diethyl ether/petroleum ether) to afford pure (*Z*)-product **S9** (79.8 mg, 60% yield).

¹**H** NMR (500 MHz, CDCl₃): δ 7.01 (1H, d, ³*J*_{HH} = 7.9 Hz), 6.85 (1H, d, ⁴*J*_{HH} = 1.9 Hz), 6.80 (1H, dd, ³*J*_{HH} = 7.9 Hz, ⁴*J*_{HH} = 1.9 Hz), 6.63 (1H, dt, ³*J*_{HH} = 11.6 Hz, ⁴*J*_{HH} = 1.3 Hz), 5.81 (1H, dt, ³*J*_{HH} = 11.6, 6.7 Hz), 4.83 (2H, dd, ³*J*_{HH} = 6.7 Hz, ⁴*J*_{HH} = 1.4 Hz), 3.83 (3H, s), 2.32 (3H, s), 2.08 (3H, s); ¹³C NMR (126 MHz, CDCl₃): δ 171.0, 169.2, 151.0, 139.2, 135.1, 132.7, 126.2, 122.8, 121.3, 112.9, 61.4, 56.0, 21.1, 20.8; **IR** ($\tilde{\upsilon}_{max}$ /cm⁻¹, thin film): 3028, 2937, 1765, 1737, 1602, 1509, 1464, 1409, 1371, 1320, 1264, 1226, 1200, 1149, 1124, 1032, 902, 862, 836, 756. **HRMS (ESI)** exact mass calculated for [M] (C₁₄H₁₆O₅) from [M+Na]⁺ requires 264.09977 m/z, found 264.09933 m/z with a difference of 1.68 ppm.

General Procedure for Catalytic Reactions on Model Lignin Dimers

General Information and Setup

Reactions were run in 2-dram borosilicate vials equipped with screwcaps and teflon septa under inert atmosphere. Reactions were irradiated with commercially available 34 W Kessil KSH150B Blue LED lamps with fans positioned such that the vials were kept at room temperature throughout irradiation and stirring. As a caution, the light from the lamps is very bright and appropriate safety precautions should be taken.

General Procedure for Catalytic C-C Bond Cleavage of Lignin Model Dimers 1-4

To a screw cap 2-dram vial was charged with a magnetic stir bar, substrate (1.0 equiv., 0.2 mmol), and $[Ir(dF(CF_3)ppy)_2(5,5'-d(CF_3)-bpy)][PF_6]^8$ (3 mol%, 6.0 µmol, 6.8 mg). The vial was brought into a glove box where tetrabutylphosphonium dimethylphosphate⁴ (25 mol%, 0.05 mmol, 19.2 mg) was added. The vial was sealed with a Teflon septum and removed from the glove box. The vial was then put under positive pressure of Ar. Dioxane (0.05 M, 4 mL) was added, followed by TRIP thiophenol⁹ (25 mol%, 0.05 mmol, 11.8 mg). The reaction was irradiated with one blue LED Kessil lamp and stirred at ambient temperature for 48 h. The reaction mixture was concentrated under reduced pressure. The yields were determined by ¹H-NMR analysis relative to an internal standard.

General Procedure for Product Stability Tests (M1, M2 and M3)

To a screw cap 2-dram vial was charged with a magnetic stir bar, monomer (1.0 equiv., 0.2 mmol), and $[Ir(dF(CF_3)ppy)_2(5,5'-d(CF_3)-bpy)][PF_6]$ (3 mol%, 6.0 µmol, 6.8 mg). The vial was brought into a glove box where tetrabutylphosphonium di-*tert*-butyl phosphate⁹ (25 mol%, 0.05 mmol, 24.0 mg) was added. The vial was sealed with a Teflon septum and removed from the glove box. The vial was then put under positive pressure of Ar. Dioxane (0.05 M, 4 mL) was added, followed by 3,4-difluorothiophenol (50 mol%, 0.1 mmol, 11.2 µL). The reaction was irradiated with one blue LED Kessil lamp and stirred at ambient temperature for 24 h. The reaction mixture was concentrated under reduced pressure. The yields were determined by ¹H-NMR analysis relative to an internal standard.

Native Lignin Extraction and Purification

All four lignin samples (grand fir, ponderosa, cedar, and larch) were extracted using a modified protocol that was previously reported by Stahl.¹⁰

The dried and ground sawdust (10 g) was suspended in 120 mL of a dioxane/water mixture (9/1 v/v) containing 0.2 M HCl. The mixture was stirred at reflux (setpoint temperature of 100 °C) under an Ar atmosphere for 30 min. After being cooled to room temperature, the mixture was vacuum-filtered through a Buchner funnel. The filter cake was washed with ca. 100 mL of dioxane/water mixture (9/1 v/v). The combined filtrate was then neutralized with saturated aqueous NaHCO₃ solution until the pH approached to 5–7. Next, the solution was concentrated by rotary-evaporation (45 °C) until the point of precipitation (ca. 50 mL volume remaining). Then, a minimal amount of acetone/water mixture (9/1 v/v) was added if necessary to dissolve any lignin precipitated (<5 mL). This solution was then added dropwise into ca. 400 mL of iced water. The mixture was left in the freezer (-20 °C) for 4 hours, and the precipitate was collected by vacuum filtration to give crude dioxosolv-lignin.

This crude dioxosolv-lignin was dissolved in a minimal amount of acetone/methanol mixture (9/1 v/v) (1 volume). This dark red solution was added dropwise to rapidly stirring diethyl ether (10 volumes). The precipitate lignin was collected via suction filtration and dried under reduced pressure. This purification process was then repeated once more. Purified lignin was then dried overnight under high vacuum at room temperature before usage. The extraction yields for lignin samples and the 2D HSQC NMR spectra of the isolated lignin samples are shown below.

Biomass	Mass of biomass	Mass of extracted lignin	wt% Extracted lignin
Grand Fir	50 g	1.34 g	2.7 wt%
Ponderosa	25 g	0.69 g	2.8 wt%
Cedar	25 g	0.78 g	3.1 wt%
Larch	10 g	0.22 g	2.2 wt%

Table S1. Lignin extraction yields for different samples of biomass.

General Procedure for Catalytic Depolymerization Reaction of Dioxosoly Lignin

Note: For the calculation of reaction stoichiometry and catalyst loading, guaiacyl moiety was selected as a monomeric unit (MW = 166.176 g/mol). The loadings of Ir photocatalyst, phosphate base and thiol were reported as molar concentration for convenience.

To a screw cap 2-dram vial was charged a magnetic stir bar, dioxosolv lignin (48 mg) and $[Ir(dF(CF_3)ppy)_2(5,5'-d(CF_3)-bpy)][PF_6]$ (1.5 mM, 3.0 µmol, 3.4 mg). The vial was brought into a glove box where tetrabutylphosphonium di-*tert*-butyl phosphate (12.5 mM, 0.025 mmol, 12.0 mg) was added. The vial was sealed with a Teflon septum and removed from the glove box. The vial was then put under positive pressure of Argon. Dioxane (2 mL, 0.05 M) was added, followed by 3,4-difluorothiophenol (25 mM, 0.05 mmol, 5.6 µL). The reaction was irradiated with two blue LED Kessil lamps, kept at ambient temperature by using 2 fans, and stirred for 48 h. After the reaction, internal standard (3-acetamidoacetophenone) was added to the reaction mixture, which was then concentrated under reduced pressure. Ethyl acetate was then added. The non-soluble fraction containing monomeric, lower-MW polymeric and oligomeric products was passed through a silica plug. This organic solution was concentrated under reduced pressure, dissolved in EtOH/Hexanes mixture (1/4 v/v), and filtered through a syringe filter. This solution was then submitted to HPLC analysis.

Acetylation of native grand fir lignin (25 mg) and non-soluble residue after depolymerization reaction (20– 25 mg) was performed using previously reported procedure by Stahl and co-workers.¹¹ Native lignin or solid residue was treated with 2 mL of acetic anhydride and 2 mL of pyridine at room temperature to acetylate all alcohol groups. After 48 h, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in EtOAc and washed with brine. The combined organic layers were dried using sodium sulfate and concentrated under reduced pressure. The residue was then subjected to HSQC analysis using DMSO- d_6 as the solvent. The comparision of HSQC spectra of acetylated lignin and acetylated solid residue after the depolymerization reaction are shown below (Figure S16,17).

Procedure for Catalytic Depolymerization Reaction of Dioxosolv Lignin on a Preparative Scale

To a screw cap 60-mL vial was charged a magnetic stir bar, dioxosolv ponderosa lignin (480 mg) and $[Ir(dF(CF_3)ppy)_2(5,5'-d(CF_3)-bpy)][PF_6]$ (1.5 mM, 30.0 µmol, 34 mg). The vial was brought into a glove box where tetrabutylphosphonium di-tert-butyl phosphate (12.5 mM, 0.25 mmol, 120 mg) was added. The vial was sealed with a Teflon septum and removed from the glove box. The vial was then put under positive pressure of Argon. Dioxane (20 mL, 0.05 M) was added, followed by 3,4-difluorothiophenol (25 mM, 0.50 mmol, 56 µL). The reaction was irradiated with four blue LED Kessil lamps, kept at ambient temperature by using 5 fans, and stirred for 72 h. After the reaction, internal standard (3acetamidoacetophenone) was added to the reaction mixture, which was then concentrated under reduced pressure. Ethyl acetate was then added, and the soluble fraction was separated from the insoluble solid. An aliquot of the soluble-fraction was passed through a silica plug. This organic solution was concentrated under reduced pressure, redissolved in EtOH/Hexanes mixture (1/4 v/v), and filtered through a syringe filter. This solution was then submitted to HPLC analysis. The crude organic-soluble extract was dissolved in dichloromethane, and passed through a 2×1 inch plug of silica, eluting with ethyl acetate, to remove highly polar material. The plug was rinsed with ca. 200 mL of ethyl acetate. Solvents were removed, and the residue was purified by flash column chromatography on silica (10 g, 10–100% ethyl acetate/hexanes). The fractions containing vanillin (M2) (eluting early in the procedure) were combined to afford 18.2 mg of ca. 70% pure monomer. The fractions containing 4-(2-hydroxyethoxy)-3-methoxybenzaldehyde (M3)

(eluting late in the procedure) were combined to afford 17.7 mg of ca. 40% pure monomer. The **M2** monomer was further purified by preparative TLC (25% ethyl acetate/hexanes) to afford 11.6 mg of >95% pure **M2** monomer. The **M3** monomer was further purified by first trituration with diethyl ether and syringe filtration, before preparative TLC (70% ethyl acetate/hexanes) to afford 10.1 mg of ca. 70% pure **M3** monomer. The remainder appears to consist of oligomeric and polymeric material.

Figure S1. Reaction set-up for photocatalytic depolymerization reaction of dioxosolv lignin.

a)

b)

Figure S2. (a) Reaction mixture before depolymerization reaction of dioxosolv lignin; (b) Reaction mixture after depolymerization reaction of dioxosolv lignin.

Identification and Quantification of Monomeric Products from Lignin Depolymerization

Products were identified and confirmed by exact mass detected via GC/MS analysis and HPLC retention times to authentic standards that were either purchased or synthesized (Table S2).

Quantification of monomeric products from lignin depolymerization was performed on an Agilent 1260 Infinity Series LC using a commercial Agilent column (4.6 mm \times 250 mm \times 5 µm particle size), followed by integration of UV absorption traces at specified wavelength (230 nm). Mobile phase A was hexanes and B was ethanol. The flow rate was 1.0 mg/mL at room temperature, and the gradient program was 5% B for 25 min. The UV detector acquired spectra from 191–950 nm. Filter bandwidth was set at 4 nm, the wavelength step was set to 1 nm. Of each solution 1 µL was injected onto the column for analysis. 3-acetamidoacetophenone was used as an internal standard; and all compounds quantified by UV absorption were normalized to the standard signal.

Table S2	Retention	times	of mor	nomeric	products	and	internal	standard.
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Compound	Retention time (min)
M1	6.12 – 6.29
M2	8.90 – 9.16
M3	20.97 – 22.0
Internal standard (3-acetamidoacetophenone)	18.29 – 18.71

Figure S3. An example of HPLC traces of the reaction mixture after depolymerization reaction of lignin.

Figure S4. HPLC traces of commercially available internal standard.

Figure S5. HPLC traces of commercially available authentic M1.

Figure S6. HPLC traces of commercially available authentic M2.

Figure S7. HPLC traces of independently synthesized M3.

Application of DFRC Method for the Quantification of β-Aryl Ether Bonds in Dioxosolv Lignin

Ralph and co-workers previously reported the derivatization followed by reductive cleavage (DFRC method) for the cleavage of β -ether bonds in various lignin materials.¹² In this work, it was demonstrated that the results obtained from this method are comparable to those measured from the conventional thioacidolysis method. This suggests that DFRC could be a good way to quantify the amount of β -ether linkages in lignin.

Scheme S1. β -ether bond cleavage by the DFRC method.

All of the four lignin materials used in this study were subjected to the DFRC conditions by following the previously reported procedure.¹²⁻¹³

<u>AcBr Derivatization</u>. Dioxosolv lignin (30 mg) was dissolved in a solution of AcBr/acetic acid (8:92 v/v, 8 mL), and the mixture was stirred at 50 °C for 1 h during which complete solubilization of lignin was achieved. The mixture was then concentrated under reduced pressure by rotavap evaporation at 40 °C.

<u>*Reductive Cleavage*</u>. The residue obtained from the previous step was dissolved in a solution of dioxane/acetic acid/water (5:4:1, v/v), followed by the addition of zinc powder (150 mg). The reaction mixture was well stirred at ambient temperature for 30 min. After the addition of internal standard (5 mg of biphenyl in ethyl acetate), the mixture was quantitatively transferred into a separatory funnel with dichloromethane and saturated NH₄Cl. The pH of aqueous phase was adjusted to less than 3 by adding 1.0 M HCl. The mixture was vigorously mixed, and the organic layer was separated. The aqueous phase was then extracted with DCM twice. The combined organic layers were dried over MgSO₄ and the filtrate was concentrated under reduced pressure.

<u>Acetylation</u>. The residue was dissolved in 3 mL of DCM followed by the addition of acetic anhydride (0.6 mL) and pyridine (0.6 mL). The mixture was stirred at ambient temperature. After 40 min, the mixture was transferred into a separatory funnel with ethyl acetate, and washed with saturated NaHCO₃ (x3). The aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over MgSO₄ and the filtrate was concentrated under reduced pressure. The residue was redissolved in a small amount of ethyl acetate, and passed through a silica plug with a mixture of acetone/hexanes (7/3, v/v). The obtained solution was subjected to GC analysis.

Monomeric products were confirmed via the comparison of GC retention times to the authentic standards that were independently synthesized. Quantification of these products was performed on an Agilent Technologies 7890A GC system equipped with a split-mode capillary injection system and flame ionization detectors. GC conditions: initial column temperature, 50 °C, ramp at 30 °C/min to 300 °C; injection volume, 1 μ L.

Retention time (min)
9.02
8.71
8.43
8.17
6.69

Table S3. Retention times of monomeric products and internal standard.

Figure S8. An example of GC traces of the reaction mixture after degradation reaction of lignin by the DFRC method.

Table S4. Quantification of monomeric products from the degradation of dioxosolv lignin by the DFRC method. All reactions were performed with 30 mg of native lignin. Yields were determined by GC analysis of the crude reaction mixtures relative to an internal standard. In all cases, the amount of \mathbf{P}^c observed by GC is negligible compared to the quantity of other three products.

Biomass	G ^{<i>t</i>} (wt%)	G ^c (wt%)	P ^t (wt%)	Total (wt%)
Grand Fir	12.1	1.0	0.3	13.4
Ponderosa	15.8	1.8	0.2	17.8
Cedar	16.7	1.8	0.1	18.6
Larch	31.7	3.3	2.2	37.2

Note: The total weight percent of monomeric products obtained for these softwood lignin samples is comparable to the value previously reported for pine lignin $(17 \text{ wt})^{.12}$

Determination of the Percentage of β-Aryl Ether Bonds Cleaved Under Photocatalytic Conditions

Assuming the efficiency in cleaving β -ether linkages of the DFRC method is close to quantitative, the number of moles of monomeric products obtained from these reactions is approximately the same as the number of moles of the β -aryl ether bonds in lignin material. If this is the case, it is reasonable to estimate the percentage of the β -aryl ether bonds cleaved under our photocatalytic conditions to be the ratio of the number of moles of monomers (per 1 mg of lignin) obtained from the PCET conditions and the number of moles of monomers (per 1 mg of lignin) obtained from the DFRC method.

The number of moles of monomers per 1 mg of lignin $=\frac{\text{Total number of moles of monomers (mmol)}}{\text{mass of lignin (mg)}}$

Table S5. Determination of the number of moles of monomers from the degradation of dioxosolv lignin by the DFRC method. Mass of lignin used in these reactions was 30 mg.

Biomass	∑n _{monomers} (mmol)	∑n _{monomers} /mg lignin (µmol/mg)
Grand Fir	0.015	0.50
Ponderosa	0.020	0.67
Cedar	0.021	0.70
Larch	0.043	1.43

Table S6. Determination of the number of moles of monomers from the depolymerization of dioxosolv lignin by photocatalytic condition. Mass of lignin used in these reactions was 48 mg.

Biomass	∑n _{monomers} (mmol)	∑n _{monomers} /mg lignin (µmol/mg)
Grand Fir	0.010	0.21
Ponderosa	0.011	0.23
Cedar	0.014	0.29
Larch	0.015	0.31

% β -aryl ether bonds cleaved under the photocatalytic conditions = $\frac{\Sigma \text{moles of monomers/mg lignin (PCET)}}{\Sigma \text{moles of monomers/mg lignin (DFRC)}}$

Table S7.	Calculation	of %β-aryl	ether b	bonds clea	wed unde	r the	photocatal	vtic conditions
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Biomass	% -ether bonds cleaved
Grand Fir	42
Ponderosa	34
Cedar	41
Larch	22

Figure S9. Original HSQC for native grand fir lignin (in DMSO-d₆).

Figure S10. Assigned HSQC for native grand fir lignin (in DMSO-d₆).

Figure S11. Original HSQC for depolymerized grand fir lignin (in DMSO-d₆).

Figure S12. Assigned HSQC for depolymerized grand fir lignin (in DMSO-d₆). Signals attributed to C_{α} -H and C_{β} -H and of the β -O-4 linkage in the original lignin were substantially diminished.

Figure S13. Original HSQC for initial grand fir lignin (in DMSO-d₆). Insignificant aldehyde signal was observed, which was assigned to the drawn aldehyde-containing subunit.

Figure S14. Original HSQC for depolymerized grand fir lignin (in DMSO-d₆). Mixture of different aldehyde-containing products was observed following depolymerization.

Figure S15. Original HSQC for acetylated grand fir lignin (in DMSO-d₆).

Figure S16. Assigned HSQC for acetylated grand fir lignin (in DMSO-d₆).

Figure S17. Original HSQC for acetylated solid residue after depolymerization reaction of grand fir lignin (in DMSO-d₆). No characteristic peaks were observed for lignin, suggesting that this solid residue was possibly some unidentified impurities remaining after extraction rather than lignin.

Figure S18. Original HSQC for native ponderosa lignin (in DMSO-d₆).

Figure S19. Original HSQC for native ponderosa lignin (in DMSO-d₆).

Figure S20. Original HSQC for depolymerized ponderosa lignin (in DMSO-d₆).

Figure S21. Assigned HSQC for depolymerized ponderosa lignin (in DMSO-d₆). Signals attributed to C_{α} -H and C_{β} -H and of the β -O-4 linkage in the original lignin were substantially diminished.

Figure S22. Original HSQC for initial ponderosa lignin (in DMSO-d₆). Insignificant aldehyde signal was observed, which was assigned to the drawn aldehyde-containing subunit.

Figure S23. Original HSQC for depolymerized ponderosa lignin (in DMSO-d₆). Mixture of different aldehyde-containing products was observed following depolymerization.

Figure S24. Original HSQC for native cedar lignin (in DMSO-d₆).

Figure S25. Assigned HSQC for native cedar lignin (in DMSO-d₆).

Figure S26. Original HSQC for depolymerized cedar lignin (in DMSO-d₆).

Figure S27. Assigned HSQC for depolymerized cedar lignin (in DMSO-d₆). Signals attributed to C_{α} -H and C_{β} -H and of the β -O-4 linkage in the original lignin were substantially diminished.

Figure S28. Original HSQC for initial cedar lignin (in DMSO-d₆). Insignificant aldehyde signal was observed, which was assigned to the drawn aldehyde-containing subunit.

Figure S29. Original HSQC for depolymerized cedar lignin (in DMSO-d₆). Mixture of different aldehydecontaining products was observed following depolymerization.

Figure S30. Original HSQC for native larch lignin (in DMSO-d₆).

Figure S31. Assigned HSQC for native larch lignin (in DMSO-d₆).

Figure S32. Original HSQC for depolymerized larch lignin (in DMSO-d₆).

Figure S33. Assigned HSQC for depolymerized larch lignin (in DMSO-d₆). Signals attributed to C_{α} -H and C_{β} -H and of the β -O-4 linkage in the original lignin were substantially diminished.

Figure S34. Original HSQC for initial larch lignin (in DMSO-d₆). Insignificant aldehyde signal was observed, which was assigned to the drawn aldehyde-containing subunit.

Figure S35. Original HSQC for depolymerized larch lignin (in DMSO-d₆). Mixture of different aldehydecontaining products was observed following depolymerization.

NMR Spectra for Isolated Vanillin from Preparative Scale Lignin Depolymerization Reaction (M2)

NMR Spectra for Lignin Model Dimers and Monomeric Products

CD CC CD CC 1111.4 1111.1 109.1 109.1 79.6 49.1 47.9 34.0 131.8 66.5 64.3 60.6 550.0 555.9 555.9 555.9 555.6 14.0 12.4 12.1 48. 46. 35. 21. 19. 19. 4 46. 45. 45. 20. 5.

Overlay GPC for Native and Depolymerized Lignin

Figure S36. GPC analysis of dioxosolv grand fir lignin before and after reaction.

Figure S37. GPC analysis of dioxosolv grand fir lignin before (blue, $M_w = 2371$, $M_n = 1568$) and after reaction (yellow, $M_w = 1621$, $M_n = 1374$).

Figure S38. GPC analysis of dioxosolv larch lignin before and after reaction.

Figure S39. GPC analysis of dioxosolv larch lignin before (blue, $M_w = 1951$, $M_n = 1512$) and after reaction (yellow, $M_w = 1361$, $M_n = 1133$).

----- Native Cedar Lignin

---- Depolymerized Cedar Lignin

Figure S40. GPC analysis of dioxosolv cedar lignin before and after reaction.

Figure S41. GPC analysis of dioxosolv cedar lignin before (blue, $M_w = 2250$, $M_n = 1652$) and after reaction (yellow, $M_w = 1267$, $M_n = 1130$).

Figure S42. GPC analysis of dioxosolv ponderosa lignin before and after reaction.

Figure S43. GPC analysis of dioxosolv ponderosa lignin before (blue, $M_w = 2639$, $M_n = 1888$) and after reaction (yellow, $M_w = 1667$, $M_n = 1168$).

Figure S44. HRMS analysis of original grand fir lignin sample.

Figure S45. HRMS analysis of depolymerized grand fir lignin following depolymerization. An increase in low-MW products was observed compared to the original lignin sample.

DFT computational details and results

All calculations used DFT methodology as implemented in the Gaussian 16 series of computer programs.¹⁴ All complexes underwent geometry optimization, and stationary points were subjected to normal mode analysis. All calculations were performed in the gas phase at 1 atm pressure.

For the calculation of Gibbs Free Energies for the C–C bond cleavage reactions of lignin dimers, we employed the same functional and basis sets as previously reported in the computational study of bond dissociation enthalpies for lignin dimers.¹⁵ M06-2X functional with basis set 6-31G(d) was employed for the geometry optimization and vibrational frequency calculation. The M06-2X functional with basis set 6-311++G(d,p) was used for single-point energy calculation.

A) Calculation of Gibbs Free Energies for the C-C bond cleavage reactions of lignin dimers at 25 °C

Figure S46. Fragmentation of non-phenolic lignin dimer 1.

Table S8.	Thermodynamic	parameters for	r calculating ΔG°	of the fragmenta	ation of non-phenolic lign	in
dimer 1 at	25 °C. Energies	are given in ha	rtree and entropy	is provided in e	ntropy units.	

Entry	Job name	E+ZPE	G	Н	S
1	Lignin dimer 1	-1149.922769	-1149.977089	-1149.898222	165.991
2	3,4-Dimethoxybenzaldehyde (1a)	-574.194037	-574.397110	-574.347864	103.646
3	(2-Hydroxyethyl)guaiacol (1b)	-575.540037	-575.578046	-575.527578	106.218

 $\Delta G^{\circ} = (-575.578046 - 574.397110 + 1149.977089) \times 627.509 = +1.21 \text{ (kcal/mol)}$

Figure S47. Fragmentation of phenolic lignin dimer 2.

Entry	Job name	E+ZPE	G	Н	S
1	Lignin dimer 2	-1110.664578	-1110.716735	-1110.641513	158.318
2	Vanillic aldehyde (2a)	-535.100465	-535.135637	-535.089659	96.769
3	(2-Hydroxyethyl)guaiacol (1b)	-575.540037	-575.578046	-575.527578	106.218

Table S9. Thermodynamic parameters for calculating ΔG° of the fragmentation of phenolic lignin dimer 2 at 25 °C. Energies are given in hartree and entropy is provided in entropy units.

 $\Delta G^{\circ} = (-575.578046 - 535.135637 + 1110.716735) \times 627.509 = +1.92 \text{ (kcal/mol)}$

B) Calculation of Gibbs Free Energies for the C–C bond cleavage reactions of lignin dimers at 160 °C

The Gibbs Free Energies of the cleavage reactions of the β -O-4 model systems 1 and 2 at 25 °C suggest that these processes are thermodynamically unfavorable at ambient temperature; yet, this contrathermodynamic fragmentation was still achieved through the use of the excited-state redox events. Interestingly, Klankermayer and co-workers previously reported a strategy to achieve the similar C–C bond cleavage of dimer 1 (Figure S48), whose mechanism is rather different and the reaction requires heating to 160 °C.¹⁶ This suggests that this cleavage reaction should be thermodynamically favored at 160 °C. To test our calculation method, we also performed the calculation of ΔG° for the fragmentation of dimer 1 and 2 at 160 °C; and indeed, they are both thermodynamically downhill at such high temperature (see below).

Figure S48. Fragmentation of phenolic lignin dimer 2 reported by Klankermayer and co-workers.

Table S10. Thermodynamic parameters for calculating ΔG° of the fragmentation of non-phenolic lignin dimer 1 at 160 °C. Energies are given in hartree and entropy is provided in entropy units.

Entry	Job name	E+ZPE	G	Н	S
1	Lignin dimer 1	-1149.922769	-1150.017118	-1149.875116	205.720
2	3,4-Dimethoxybenzaldehyde (1a)	-574.360020	-574.421467	-574.336879	122.544
3	(2-Hydroxyethyl)guaiacol (1b)	-575.540037	-575.603053	-575.516018	126.089

 $\Delta G^{\circ} = (-575.603053 - 574.421467 + 1150.017118) \times 627.509 = -4.64 \text{ (kcal/mol)}$

Entry	Job name	E+ZPE	G	Н	S
1	Lignin dimer 2	-1110.664578	-1110.754902	-1110.619543	196.096
2	Vanillic aldehyde (2a)	-535.100465	-535.158305	-535.079803	113.727
3	(2-Hydroxyethyl)guaiacol (1b)	-575.540037	-575.603053	-575.516018	126.089

Table S11. Thermodynamic parameters for calculating ΔG° of the fragmentation of phenolic lignin dimer **2** at 160 °C. Energies are given in hartree and entropy is provided in entropy units.

 $\Delta G^{\circ} = (-575.603053 - 535.158305 + 1110.754902) \times 627.509 = -4.05 \text{ (kcal/mol)}$

Optimized Geometries

A) Structures optimized at $25 \,^{\circ}C$

Optimized geometries in Cartesian coordinates (Å) and energies (hartree) for stationary points.

1. Lignin dimer 1:

E(M06-2X/6-31G(d)) = -1149.9624970 Zero-point correction= 0.384067 (Hartree/Particle) Thermal correction to Energy= 0.407670 Thermal correction to Enthalpy= 0.408614 Thermal correction to Gibbs Free Energy= 0.329747 Sum of electronic and zero-point Energies= -1149.578430 Sum of electronic and thermal Energies= -1149.554827 Sum of electronic and thermal Enthalpies= -1149.553883 Sum of electronic and thermal Free Energies= -1149.632751

E(M06-2X/6-311++G(d,p)) = -1150.306836 a.u.

Calculation Type = FREQ Calculation Method = RM06-2X Basis Set = 6-31G(d)Charge = 0 Spin = Singlet RMS Gradient Norm = 0.000003 a.u. Imaginary Freq = 0 Dipole Moment = 2.058515 Debye Point Group = C1

Symbol	Х	Y Z	
Ċ	3.49833600	-1.60878700	-0.52778700
С	2.19956800	-1.66258900	-1.03308100
С	1.37388900	-0.53900700	-0.97615800
С	1.86338700	0.63861100	-0.40833700
С	3.15319500	0.69726300	0.10281400
С	3.98485500	-0.43451900	0.03584300
Н	4.16090200	-2.46706300	-0.57211800
Н	1.83220200	-2.58100000	-1.48409800
Н	1.23793200	1.52426500	-0.36462600
С	-0.06399500	-0.60495400	-1.43150400
Н	-0.18564100	-1.46778600	-2.10917000
С	-1.01792900	-0.84083900	-0.25436300
Н	-1.03407800	0.05952400	0.37407000
0	-0.39901100	0.59709100	-2.08106500
Н	-1.36570400	0.68517500	-2.01813500
0	-2.30398100	-1.03695000	-0.87217300
С	-3.38258000	-0.59471000	-0.15007000
С	-4.23643000	-1.48757900	0.47598400
С	-3.65172900	0.78608100	-0.10541500

С	-5.35669300	-1.02175600	1.16773200
Н	-4.01293600	-2.54721000	0.40261400
С	-4.76139500	1.25197100	0.59042100
С	-5.60905600	0.34109800	1.22689400
Н	-6.02147100	-1.72537700	1.65700700
Н	-4.97858300	2.31305400	0.63448400
Н	-6.47451800	0.71322500	1.76544700
С	-0.68942300	-2.04895800	0.62326600
Н	-1.59377800	-2.31379900	1.17950400
Н	-0.42970800	-2.91008300	-0.01292200
0	0.30109700	-1.77483200	1.58564800
Н	1.15006800	-1.69093800	1.12672300
0	5.26002700	-0.41492000	0.53600400
0	3.59965300	1.87197800	0.64864500

2. <u>3,4-Dimethoxybenzaldehyde (1a)</u>

E(M06-2X/6-31G(d)) = -574.372413 Zero-point correction= 0.178376 (Hartree/Particle) Thermal correction to Energy= 0.189588 Thermal correction to Enthalpy= 0.190532 Thermal correction to Gibbs Free Energy= 0.141286 Sum of electronic and zero-point Energies= -574.194037 Sum of electronic and thermal Energies= -574.182825 Sum of electronic and thermal Enthalpies= -574.181881 Sum of electronic and thermal Free Energies= -574.231127

E(M06-2X/6-311++G(d,p)) = -574.538396 a.u.

Calculation Type = FREQ Calculation Method = RM06-2X Basis Set = 6-31G(d)Charge = 0 Spin = Singlet RMS Gradient Norm = 0.000019 a.u. Imaginary Freq = 0 Dipole Moment = 3.294809 Debye Point Group = C1

Symbol	X	Y Z	2
Ċ	0.15338300	-1.63784900	-0.00001200
С	-1.21769800	-1.38930200	0.00013800
С	-0.78141500	0.99216000	-0.00007100
С	0.58284800	0.75807000	-0.00007700
С	1.05741600	-0.57849200	-0.00022700
Н	0.51361600	-2.65956400	0.00007500
Н	-1.93536700	-2.20310000	0.00027800
Н	-1.16862500	2.00650200	-0.00023600
0	2.40048700	-0.70857700	-0.00044100

0	1.54436900	1.71220100	-0.00009100
С	1.11293900	3.05429000	0.00023300
Н	2.01739100	3.66183300	0.00029100
Н	0.51958100	3.28210300	-0.89390700
Н	0.51979700	3.28182300	0.89459200
С	2.92781700	-2.01805000	0.00030400
Н	4.01126600	-1.90426400	0.00023300
Н	2.61734100	-2.57044200	0.89504600
Н	2.61743600	-2.57148000	-0.89384300
С	-3.13652200	0.18760400	0.00003100
0	-3.99306000	-0.66653800	-0.00001700
Н	-3.41124800	1.26478900	-0.00008700
С	-1.68469400	-0.08257900	0.00000500

3. (2-Hydroxyethyl)guaiacol (1b):

E(M06-2X/6-31G(d)) = -575.565822 Zero-point correction= 0.202533 (Hartree/Particle) Thermal correction to Energy= 0.214048 Thermal correction to Enthalpy= 0.214992 Thermal correction to Gibbs Free Energy= 0.164524 Sum of electronic and zero-point Energies= -575.363288 Sum of electronic and thermal Energies= -575.351774 Sum of electronic and thermal Enthalpies= -575.350830 Sum of electronic and thermal Free Energies= -575.401297

E(M06-2X/6-311++G(d,p)) = -575.742570 a.u.

Calculation Type = FREQ Calculation Method = RM06-2X Basis Set = 6-31G(d) Charge = 0 Spin = Singlet RMS Gradient Norm = 0.000019 a.u. Imaginary Freq = 0 Dipole Moment = 3.367003 Debye Point Group = C1

Symbol	X Y	Z	
0	1.18145900	-0.22236700	-1.26098600
С	-0.00473200	-0.50563500	-0.64792300
С	-0.38853500	-1.83973000	-0.57639800
С	-0.87028500	0.49043300	-0.15223700
С	-1.61097200	-2.20698900	-0.01327000
Н	0.29199500	-2.57783100	-0.99139800
С	-2.08223200	0.11998600	0.42492500
С	-2.45059800	-1.22554600	0.49140900
Н	-1.89446600	-3.25306000	0.03040900

Н	-2.75285300	0.87585000	0.81644700
Н	-3.40209400	-1.49261800	0.93924300
С	2.26389800	0.29841800	0.88116700
Н	3.08014300	0.89794800	1.29595500
Н	1.34480400	0.57925300	1.41620800
0	2.59654200	-1.05375400	1.09808100
Н	1.84357200	-1.58385300	0.79631900
0	-0.43450400	1.77371300	-0.27709500
С	-1.27942200	2.79590300	0.20491800
Н	-1.45273100	2.69430700	1.28305500
Н	-0.76165000	3.73407000	0.00685900
Н	-2.24265400	2.79302100	-0.31856600
С	2.13070900	0.61991300	-0.59763700
Н	1.87692900	1.67360900	-0.74211400
Н	3.07404100	0.39805700	-1.10214100

4. Lignin dimer 2:

E(M06-2X/6-31G(d)) = -1110.678377 Zero-point correction= 0.355186 (Hartree/Particle) Thermal correction to Energy= 0.377307 Thermal correction to Enthalpy= 0.378251 Thermal correction to Gibbs Free Energy= 0.303029 Sum of electronic and zero-point Energies= -1110.323191 Sum of electronic and thermal Energies= -1110.301070 Sum of electronic and thermal Enthalpies= -1110.300126 Sum of electronic and thermal Free Energies= -1110.375348

E(M06-2X/6-311++G(d,p)) = -1111.019764 a.u.

Calculation Type = FREQ Calculation Method = RM06-2X Basis Set = 6-31G(d)Charge = 0 Spin = Singlet RMS Gradient Norm = 0.000006 a.u. Imaginary Freq = 0 Dipole Moment = 1.657778 Debye Point Group = C1

Symbol	Х	Y	Ζ
C	3.82901400	-1.50302400	-0.55993500
С	2.52917800	-1.58842000	-1.06320500
С	1.67250800	-0.49272500	-0.99830800
С	2.14055400	0.69861400	-0.43471500
С	3.43128200	0.79852200	0.05948600
С	4.28950100	-0.31539500	-0.00251200

Н	4.49617300	-2.36007100	-0.61982500
Н	2.18784500	-2.51842400	-1.51049800
Н	1.49691800	1.57143700	-0.39497300
С	0.23311900	-0.59623600	-1.43993000
Н	0.12409800	-1.47239200	-2.10276500
С	-0.70640600	-0.83392900	-0.25175300
Н	-0.73553700	0.07407800	0.36512900
0	-0.13271600	0.58795100	-2.10560600
Н	-1.10051000	0.65632600	-2.03663300
0	-1.99405000	-1.06499400	-0.85409400
С	-3.07439100	-0.63326600	-0.12833600
С	-3.90488600	-1.53313900	0.51862400
С	-3.36979100	0.74268700	-0.10086300
С	-5.02761400	-1.07897100	1.21422000
Н	-3.66164100	-2.58926200	0.45839800
С	-4.48187600	1.19716400	0.59864100
С	-5.30585700	0.27946300	1.25610200
Н	-5.67408800	-1.78807400	1.71983700
Н	-4.71916900	2.25440900	0.62940200
Н	-6.17346600	0.64260600	1.79734100
С	-0.34484300	-2.02413400	0.63715300
Н	-1.23688500	-2.30007400	1.20757800
Н	-0.07561900	-2.88743600	0.00749200
0	0.65170400	-1.72063800	1.58465100
Н	1.48526900	-1.59054800	1.10852800
0	3.87247200	1.98735600	0.56714500
С	4.07981000	1.97736900	1.97427700
Н	4.38141900	2.98980500	2.24536500
Н	3.15034400	1.71979100	2.49616000

5. Vanillic aldehyde (2a):

E(M06-2X/6-31G(d)) = -535.087472 Zero-point correction= 0.149214 (Hartree/Particle) Thermal correction to Energy= 0.159076 Thermal correction to Enthalpy= 0.160020 Thermal correction to Gibbs Free Energy= 0.114042 Sum of electronic and zero-point Energies= -534.938258 Sum of electronic and thermal Energies= -534.928396 Sum of electronic and thermal Enthalpies= -534.927452 Sum of electronic and thermal Free Energies= -534.973430

E(M06-2X/6-311++G(d,p)) = -535.249679 a.u.

Calculation Type = FREQ Calculation Method = RM06-2X Basis Set = 6-31G(d) Charge = 0 Spin = Singlet RMS Gradient Norm = 0.000009 a.u. Imaginary Freq = 0 Dipole Moment = 2.764070 Debye Point Group = C1

Symbol	X	7 Z	
Ċ	-0.19227500	1.89281400	0.00003100
С	-1.40234900	1.20818800	-0.00003700
С	-0.19210200	-0.89121000	-0.00014300
С	1.01832300	-0.21519400	-0.00005700
С	1.01282200	1.19772300	0.00002500
Н	-0.17299100	2.98029700	0.00010200
Н	-2.35104800	1.73439400	-0.00002200
Н	-0.21745500	-1.97671500	-0.00023300
0	2.24458300	-0.79015600	-0.00009200
С	2.28956600	-2.19941200	0.00050800
Н	3.34556200	-2.46737900	0.00088200
Н	1.80717000	-2.61265100	0.89491500
Н	1.80763500	-2.61341400	-0.89379900
С	-2.67980400	-0.92247800	-0.00020300
0	-3.77222500	-0.40319700	-0.00021500
Н	-2.57846300	-2.02933300	-0.00029400
С	-1.40216000	-0.18195400	-0.00012400
0	2.22209300	1.80462500	0.00008800
Н	2.09185600	2.76375900	0.00020100

B) Structures optimized at 160 °C

Optimized geometries in Cartesian coordinates (Å) and energies (hartree) for stationary points.

1. <u>Lignin dimer 1:</u>

E(M06-2X/6-31G(d)) = -1149.9624970 Zero-point correction= 0.384067 (Hartree/Particle) Thermal correction to Energy= 0.430348 Thermal correction to Enthalpy= 0.431720 Thermal correction to Gibbs Free Energy= 0.289718 Sum of electronic and zero-point Energies= -1149.578430 Sum of electronic and thermal Energies= -1149.532149 Sum of electronic and thermal Enthalpies= -1149.530777 Sum of electronic and thermal Free Energies= -1149.672779

E(M06-2X/6-311++G(d,p)) = -1150.306836 a.u.

Calculation Type = FREQ Calculation Method = RM06-2X Basis Set = 6-31G(d) Charge = 0 Spin = Singlet RMS Gradient Norm = 0.000003 a.u. Imaginary Freq = 0 Dipole Moment = 2.058515 Debye Point Group = C1

Symbol	Х	Y	Ζ
Č	3.49833600	-1.60878700	-0.52778700
С	2.19956800	-1.66258900	-1.03308100
С	1.37388900	-0.53900700	-0.97615800
С	1.86338700	0.63861100	-0.40833700
С	3.15319500	0.69726300	0.10281400
С	3.98485500	-0.43451900	0.03584300
Н	4.16090200	-2.46706300	-0.57211800
Н	1.83220200	-2.58100000	-1.48409800
Н	1.23793200	1.52426500	-0.36462600
С	-0.06399500	-0.60495400	-1.43150400
Н	-0.18564100	-1.46778600	-2.10917000
С	-1.01792900	-0.84083900	-0.25436300
Н	-1.03407800	0.05952400	0.37407000
0	-0.39901100	0.59709100	-2.08106500
Н	-1.36570400	0.68517500	-2.01813500
0	-2.30398100	-1.03695000	-0.87217300
С	-3.38258000	-0.59471000	-0.15007000
С	-4.23643000	-1.48757900	0.47598400
С	-3.65172900	0.78608100	-0.10541500
С	-5.35669300	-1.02175600	1.16773200
Н	-4.01293600	-2.54721000	0.40261400
С	-4.76139500	1.25197100	0.59042100
С	-5.60905600	0.34109800	1.22689400
Н	-6.02147100	-1.72537700	1.65700700
Н	-4.97858300	2.31305400	0.63448400
Н	-6.47451800	0.71322500	1.76544700
С	-0.68942300	-2.04895800	0.62326600
Н	-1.59377800	-2.31379900	1.17950400
Н	-0.42970800	-2.91008300	-0.01292200
Ο	0.30109700	-1.77483200	1.58564800
Н	1.15006800	-1.69093800	1.12672300
0	5.26002700	-0.41492000	0.53600400
0	3.59965300	1.87197800	0.64864500
С	3.84206200	1.80086600	2.05078800
Н	4.14337500	2.80263800	2.35940900
Н	2.92614400	1.51394900	2.57988600
Н	4.63633400	1.08413600	2.27926900
С	6.14640400	0.45235100	-0.16552000
Н	7.12085500	0.34276400	0.31195900
Н	6.21789700	0.15190200	-1.21705200
Н	5.81335200	1.49232000	-0.10418400
0	-2.76637100	1.56683400	-0.78305600

С	-2.92815400	2.96869600	-0.71263300
Н	-2.89045900	3.31540400	0.32622500
Н	-2.09402100	3.39209000	-1.27168200
Н	-3.87535100	3.27976900	-1.16787800

2. <u>3,4-Dimethoxybenzaldehyde (1a)</u>

E(M06-2X/6-31G(d)) = -574.372413 Zero-point correction= 0.178376 (Hartree/Particle) Thermal correction to Energy= 0.200146 Thermal correction to Enthalpy= 0.201517 Thermal correction to Gibbs Free Energy= 0.116929 Sum of electronic and zero-point Energies= -574.194037 Sum of electronic and thermal Energies= -574.172267 Sum of electronic and thermal Enthalpies= -574.170896 Sum of electronic and thermal Free Energies= -574.255484

E(M06-2X/6-311++G(d,p)) = -574.538396 a.u.

Calculation Type = FREQ Calculation Method = RM06-2X Basis Set = 6-31G(d)Charge = 0 Spin = Singlet RMS Gradient Norm = 0.000019 a.u. Imaginary Freq = 0 Dipole Moment = 3.294809 Debye Point Group = C1

Symbol	X Y	ζ Z	<u>,</u>
Č	0.15338300	-1.63784900	-0.00001200
С	-1.21769800	-1.38930200	0.00013800
С	-0.78141500	0.99216000	-0.00007100
С	0.58284800	0.75807000	-0.00007700
С	1.05741600	-0.57849200	-0.00022700
Н	0.51361600	-2.65956400	0.00007500
Н	-1.93536700	-2.20310000	0.00027800
Н	-1.16862500	2.00650200	-0.00023600
0	2.40048700	-0.70857700	-0.00044100
0	1.54436900	1.71220100	-0.00009100
С	1.11293900	3.05429000	0.00023300
Н	2.01739100	3.66183300	0.00029100
Н	0.51958100	3.28210300	-0.89390700
Н	0.51979700	3.28182300	0.89459200
С	2.92781700	-2.01805000	0.00030400
Н	4.01126600	-1.90426400	0.00023300
Н	2.61734100	-2.57044200	0.89504600
Н	2.61743600	-2.57148000	-0.89384300
С	-3.13652200	0.18760400	0.00003100
0	-3.99306000	-0.66653800	-0.00001700

Н	-3.41124800	1.26478900	-0.00008700
С	-1.68469400	-0.08257900	0.00000500

3. (2-Hydroxyethyl)guaiacol (1b):

E(M06-2X/6-31G(d)) = -575.565822 Zero-point correction= 0.202533 (Hartree/Particle) Thermal correction to Energy= 0.225180 Thermal correction to Enthalpy= 0.226552 Thermal correction to Gibbs Free Energy= 0.139517 Sum of electronic and zero-point Energies= -575.363288 Sum of electronic and thermal Energies= -575.340642 Sum of electronic and thermal Enthalpies= -575.339270 Sum of electronic and thermal Free Energies= -575.426305

E(M06-2X/6-311++G(d,p)) = -575.742570 a.u.

Calculation Type = FREQ Calculation Method = RM06-2X Basis Set = 6-31G(d) Charge = 0 Spin = Singlet RMS Gradient Norm = 0.000019 a.u. Imaginary Freq = 0 Dipole Moment = 3.367003 Debye Point Group = C1

Symbol	Х	Y	Z
0	1.18145900	-0.22236700	-1.26098600
С	-0.00473200	-0.50563500	-0.64792300
С	-0.38853500	-1.83973000	-0.57639800
С	-0.87028500	0.49043300	-0.15223700
С	-1.61097200	-2.20698900	-0.01327000
Н	0.29199500	-2.57783100	-0.99139800
С	-2.08223200	0.11998600	0.42492500
С	-2.45059800	-1.22554600	0.49140900
Н	-1.89446600	-3.25306000	0.03040900
Н	-2.75285300	0.87585000	0.81644700
Н	-3.40209400	-1.49261800	0.93924300
С	2.26389800	0.29841800	0.88116700
Н	3.08014300	0.89794800	1.29595500
Н	1.34480400	0.57925300	1.41620800
0	2.59654200	-1.05375400	1.09808100
Н	1.84357200	-1.58385300	0.79631900
0	-0.43450400	1.77371300	-0.27709500
С	-1.27942200	2.79590300	0.20491800
Н	-1.45273100	2.69430700	1.28305500
Н	-0.76165000	3.73407000	0.00685900
Н	-2.24265400	2.79302100	-0.31856600
С	2.13070900	0.61991300	-0.59763700

Н	1.87692900	1.67360900	-0.74211400
Н	3.07404100	0.39805700	-1.10214100

4. Lignin dimer 2:

E(M06-2X/6-31G(d)) = -1110.678377 Zero-point correction= 0.355186 (Hartree/Particle) Thermal correction to Energy= 0.398849 Thermal correction to Enthalpy= 0.400221 Thermal correction to Gibbs Free Energy= 0.264862 Sum of electronic and zero-point Energies= -1110.323191 Sum of electronic and thermal Energies= -1110.279528 Sum of electronic and thermal Enthalpies= -1110.278156 Sum of electronic and thermal Free Energies= -1110.413516

E(M06-2X/6-311++G(d,p)) = -1111.019764 a.u.

```
Calculation Type = FREQ
Calculation Method = RM06-2X
Basis Set = 6-31G(d)
Charge = 0
Spin = Singlet
RMS Gradient Norm = 0.000006 a.u.
Imaginary Freq = 0
Dipole Moment = 1.657778 Debye
Point Group = C1
```

Symbol	Х	Y	Ζ
С	3.82901400	-1.50302400	-0.55993500
С	2.52917800	-1.58842000	-1.06320500
С	1.67250800	-0.49272500	-0.99830800
С	2.14055400	0.69861400	-0.43471500
С	3.43128200	0.79852200	0.05948600
С	4.28950100	-0.31539500	-0.00251200
Н	4.49617300	-2.36007100	-0.61982500
Н	2.18784500	-2.51842400	-1.51049800
Н	1.49691800	1.57143700	-0.39497300
С	0.23311900	-0.59623600	-1.43993000
Н	0.12409800	-1.47239200	-2.10276500
С	-0.70640600	-0.83392900	-0.25175300
Н	-0.73553700	0.07407800	0.36512900
0	-0.13271600	0.58795100	-2.10560600
Н	-1.10051000	0.65632600	-2.03663300
0	-1.99405000	-1.06499400	-0.85409400
С	-3.07439100	-0.63326600	-0.12833600
С	-3.90488600	-1.53313900	0.51862400
С	-3.36979100	0.74268700	-0.10086300
С	-5.02761400	-1.07897100	1.21422000
Н	-3.66164100	-2.58926200	0.45839800

С	-4.48187600	1.19716400	0.59864100
С	-5.30585700	0.27946300	1.25610200
Н	-5.67408800	-1.78807400	1.71983700
Н	-4.71916900	2.25440900	0.62940200
Н	-6.17346600	0.64260600	1.79734100
С	-0.34484300	-2.02413400	0.63715300
Н	-1.23688500	-2.30007400	1.20757800
Н	-0.07561900	-2.88743600	0.00749200
0	0.65170400	-1.72063800	1.58465100
Н	1.48526900	-1.59054800	1.10852800
0	3.87247200	1.98735600	0.56714500
С	4.07981000	1.97736900	1.97427700
Н	4.38141900	2.98980500	2.24536500
Н	3.15034400	1.71979100	2.49616000
Н	4.86756200	1.27209800	2.25377100
0	-2.50580400	1.53013300	-0.79763500
С	-2.69245800	2.92973800	-0.74491200
Н	-2.65225900	3.29129800	0.28877300
Н	-1.87081800	3.36024300	-1.31685600
Н	-3.64898200	3.21728200	-1.19609300
0	5.55022300	-0.15840800	0.48588500
Н	6.04365400	-0.98019200	0.35290200

5. Vanillic aldehyde (2a):

E(M06-2X/6-31G(d)) = -535.087472 Zero-point correction= 0.149214 (Hartree/Particle) Thermal correction to Energy= 0.168504 Thermal correction to Enthalpy= 0.169876 Thermal correction to Gibbs Free Energy= 0.091374 Sum of electronic and zero-point Energies= -534.938258 Sum of electronic and thermal Energies= -534.918967 Sum of electronic and thermal Enthalpies= -534.917595 Sum of electronic and thermal Free Energies= -534.996098

E(M06-2X/6-311++G(d,p)) = -535.249679 a.u.

Calculation Type = FREQ Calculation Method = RM06-2X Basis Set = 6-31G(d)Charge = 0 Spin = Singlet RMS Gradient Norm = 0.000009 a.u. Imaginary Freq = 0 Dipole Moment = 2.764070 Debye Point Group = C1

Symbol	X Y	Z	
С	-0.19227500	1.89281400	0.00003100
С	-1.40234900	1.20818800	-0.00003700
С	-0.19210200	-0.89121000	-0.00014300
С	1.01832300	-0.21519400	-0.00005700
С	1.01282200	1.19772300	0.00002500
Н	-0.17299100	2.98029700	0.00010200
Н	-2.35104800	1.73439400	-0.00002200
Н	-0.21745500	-1.97671500	-0.00023300
0	2.24458300	-0.79015600	-0.00009200
С	2.28956600	-2.19941200	0.00050800
Н	3.34556200	-2.46737900	0.00088200
Н	1.80717000	-2.61265100	0.89491500
Н	1.80763500	-2.61341400	-0.89379900
С	-2.67980400	-0.92247800	-0.00020300
0	-3.77222500	-0.40319700	-0.00021500
Н	-2.57846300	-2.02933300	-0.00029400
С	-1.40216000	-0.18195400	-0.00012400
0	2.22209300	1.80462500	0.00008800
Н	2.09185600	2.76375900	0.00020100

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