

Kinetic Studies of Lignin Solvolysis and Reduction by Reductive Catalytic Fractionation Decoupled in Flow-Through Reactors

Eric M. Anderson^[a], Michael L. Stone^[a], Max Hülsey^[a], Gregg T. Beckham*^[b], Yuriy Román-Leshkov*^[a]

12 Pages

9 Figures

4 Tables

Supporting Information

Additional Figures

Table S1: Monomer yields obtained from batch experiments comparing lignin extraction and lignin reduction limited conditions. Reaction conditions: 1 g poplar (26% lignin), 0.2 g catalyst, 200°C, 50 mL MeOH, 1 h reaction (0.75 h heat up) and 15 or 30 bar H₂.

Catalyst loading (wt%)	H ₂ (bar)	propyl guaiacol (wt%)	propenyl guaiacol (wt%)	propyl syringol (wt%)	propenyl syringol (wt%)	propanol guaiacol (wt%)	propanol syringol (wt%)	hydrogenation selectivity (%)
5	15	0.2	4.6	0.5	4.2	0.0	1.0	15
10	15	2.4	4.2	3.0	5.7	0.4	0.4	36
15	15	4.0	3.1	5.9	5.1	0.7	0.7	58
5	30	4.6	2.7	5.9	3.1	0.4	0.6	66
10	30	5.3	0.6	8.4	1.5	2.0	2.3	89
15	30	4.7	0.5	8.3	1.0	2.5	2.8	92

Table S2: Monomer and oil yields from batch RCF experiments with small particles (0.075<d<0.25 mm). Batch conditions: Milled poplar (1 g, 26% lignin), 15% Ni/C (0.15 g) and methanol (50 mL), 30 bar H₂, 150-215°C and 1 h reaction times (0.5-1h heating ramps).

Temperature (°C)	Propyl guaiacol (wt%)	Propenyl guaiacol (wt%)	Propyl syringol (wt%)	Propenyl syringol (wt%)	Propanol guaiacol (wt%)	Propanol syringol (wt%)	Oil Yield (wt%)
150	1.9	0.4	1.7	0.3	0.3	0.3	13.5
170	2.4	0.8	2.7	0.9	0.3	0.3	25.5
185	3.6	1.2	4.4	2.1	0.3	0.4	35.0
200	4.7	0.5	8.3	1.0	2.5	2.8	47.0
215	5.0	0.8	9.2	1.9	1.7	2.2	60.7

Table S3: Monomer and oil yields from batch RCF experiments with large particles (0.5<d<1.0 mm). Batch conditions: Milled poplar (1 g, 26% lignin), 15% Ni/C (0.15 g) and methanol (50 mL), 30 bar H₂, 150-215°C and 1 h reaction times (0.5-1h heating ramps).

Temperature (°C)	Propyl guaiacol (wt%)	Propenyl guaiacol (wt%)	Propyl syringol (wt%)	Propenyl syringol (wt%)	Propanol guaiacol (wt%)	Propanol syringol (wt%)	Oil yield (wt%)
150	1.2	0.0	1.8	0.0	1.6	1.3	15
170	2.9	0.6	3.4	0.9	0.3	0.4	28
185	2.9	0.3	5.0	0.6	1.6	1.9	37
200	4.5	1.3	6.6	1.7	0.4	0.6	45
215	4.7	0.5	9.0	0.9	1.8	2.3	54

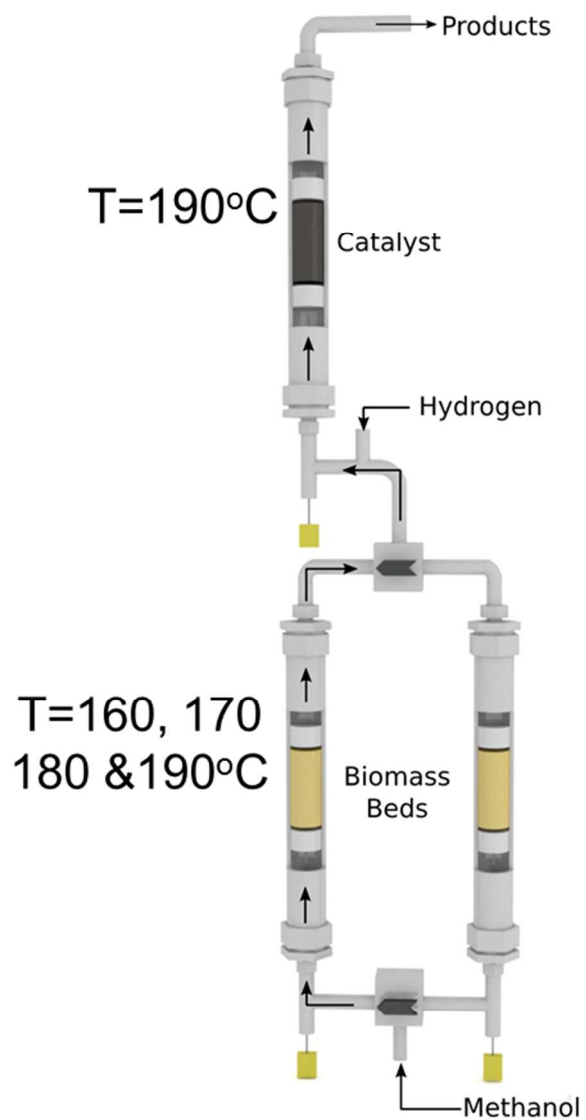


Figure S1: Schematic of the FDBR used to perform solvolysis kinetic studies.

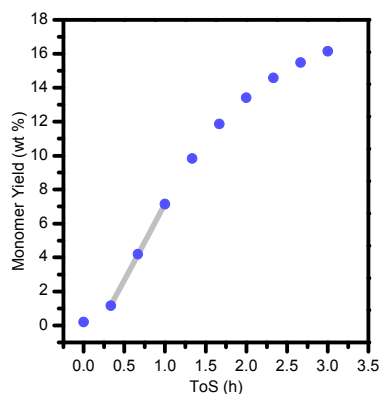


Figure S2: Illustration of extrapolated rate data from a flow through reaction.). Flow conditions: Milled poplar (1 g, 26% lignin), 0.3 g 15% Ni/C (50/50 SiO₂, 100-200 mesh), 50 mL min⁻¹ H₂ (60 bar total pressure), 0.5 mL min⁻¹ MeOH 190 °C.

$$Re = \frac{d_p U_s \rho}{\mu \varepsilon}$$

Eq S1: Reynolds number in a packed bed reactor. Where d_p is the diameter of the particles, U_s is the superficial velocity, ρ is the fluid density, μ is the fluid viscosity and ε is the bed void fraction. The void fraction for the biomass bed was determined by filling a graduated cylinder to a specified volume with biomass and the weight was obtained. Methanol was then added to the same volume and the weight was recorded. The ratio of volume of methanol added to the total volume filled was the void fraction.

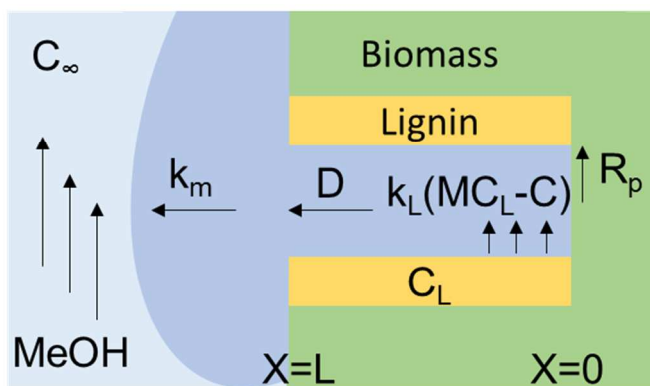


Figure S2: Schematic of a 1D reaction-diffusion occurring in the pores of biomass. Lignin is dissolving and diffusing out of an internal pore into an external boundary layer.

The 1D reaction-diffusion occurring in the pore shows lignin lining the walls of biomass pores dissolving into an internal pore within the biomass particle. There is an external boundary layer outside the pore which is defined by convective flow of the solvent. Lignin dissolution is shown as $k_L(MC_L - C)$ where k_L is the surface rate constant times MC_L (C_L is the solid lignin concentration) which is the solubility limit of lignin fragments in methanol and C is the concentration of lignin in solution. Therefore, when diffusion is very slow and the concentration of lignin fragments hits the solubility limit the dissolution rate goes to zero. The diffusion through the pore is defined by the internal diffusion constant D and occurs from $x=0$ to $x=L$ (the end of the pore, R_p is the radius of the pore). Transport through the external boundary layer is defined by the mass transfer coefficient k_m which depends on the size of the boundary layer.

Table S4: Definition of parameters used in the model with corresponding units.

Parameter	Definition	Unit
R_p	Pore Radius	m
L	Pore Length	m
C_L	Solid Lignin Concentration	Mole m^{-3}
k_L	Surface Rate Constant	$m s^{-1}$
D	Pore Diffusion Constant	$m s^{-2}$
k_m	Boundary Layer Mass Transfer Coefficient	$m s^{-1}$
C_∞	Bulk Lignin Concentration	Mole m^{-3}
N	Flux	Mole $s^{-1} m^{-2}$
r_{obs}	Observed Reaction Rate	Mole $s^{-1} m^{-2}$

Shell balance

$$\pi R_p^2 N|_x - \pi R_p^2 N|_{x+\Delta x} + 2\pi R_p \Delta x k_L (MC_L - C) = 0$$

Dividing by Δx and taking the limit as x becomes very small

$$-\pi R_p^2 \frac{dN}{dx} + 2\pi R_p k_L (MC_L - C) = 0$$

$$N = -D \frac{dC}{dx}$$

Including Fick's Law and canceling terms

$$DR_p \frac{d^2 C}{dx^2} + 2k_L (MC_L - C) = 0$$

Using the following variable substitutions

$$\psi = \frac{C}{C_L}, \chi = \frac{x}{L}$$

$$\frac{DR_p C_L}{L^2} \frac{d^2 \psi}{d\chi^2} + 2k_L C_L (M - \psi) = 0$$

$$\frac{d^2 \psi}{d\chi^2} + L^2 \frac{2k_L}{DR_p} (M - \psi) = 0$$

A dimensionless number ϕ , the Thiele modulus falls out which is a measure of the rate of reaction over the rate of diffusion.

$$\phi = L \sqrt{\frac{2k_L}{DR_p}}$$

Normalized differential equation

$$\frac{d^2 \psi}{d\chi^2} + \phi^2 (M - \psi) = 0$$

Boundary conditions

No flux through the end of the pore

$$\left. \frac{d\psi}{d\chi} \right|_{\chi=0} = 0$$

Flux matching at the exit of the pore

External flux

$$N_{external} = -k_m (C_\infty - C|_{x=L})$$

Internal flux out of the pore

$$N_{Internal} = -D \left. \frac{dC}{dx} \right|_{x=L}$$

Flux matching

$$D \left. \frac{dC}{dx} \right|_{x=L} = k_m (C_\infty - C|_{x=L})$$

Normalized

$$\left. \frac{d\psi}{d\chi} \right|_{\chi=1} = \frac{k_m L}{D} \left(\frac{C_\infty}{C_L} - \psi|_{\chi=1} \right)$$

Two new dimensionless parameters fall out. A dimensionless concentration γ and the Biot number. The Biot number is a measure of the external mass transfer against the internal mass transfer in the pore.

$$Bi = \frac{k_m L}{D}$$

$$\gamma = \frac{C_\infty}{C_L}$$

Normalized boundary condition

$$\left. \frac{d\psi}{d\chi} \right|_{\chi=1} = Bi (\gamma - \psi|_{\chi=1})$$

This leads to the following differential equation with two boundary conditions.

$$\frac{d^2\psi}{d\chi^2} + \phi^2 (M - \psi) = 0$$

$$\left. \frac{d\psi}{d\chi} \right|_{\chi=0} = 0$$

$$\left. \frac{d\psi}{d\chi} \right|_{\chi=1} = Bi(\gamma - \psi|_{\chi=1})$$

The general solution to the differential equation is shown below

$$\psi = M + c_1 e^{\phi\chi} + c_2 e^{-\phi\chi}$$

Applying the no flux boundary condition.

$$c_1 = c_2$$

Applying the other boundary condition the constant was found to be

$$c = \frac{Bi(\gamma - M)}{2\phi Sinh(\phi) - 2BiCosh(\phi)}$$

Solution to the differential equation

$$\psi = M + \frac{Bi(\gamma - M)}{2\phi Sinh(\phi) - 2BiCosh(\phi)} Cosh(\phi\chi)$$

The observed rate of lignin oligomer formation

$$r_{obs} = \eta k_L MC_L$$

The effectiveness factor η is defined as the observed rate normalized to the maximum achievable rate.

$$\eta = \frac{r_{obs}(Area)}{r_{max}(Area)} = \frac{r_{obs}}{2\pi R_p L k_L MC_L}$$

The observed rate has to be equivalent to the flux of lignin fragments out of the pore at steady state

$$\eta = \frac{\pi R_p^2 D \left. \frac{dC}{dx} \right|_{x=L}}{2\pi R_p L k_L MC_L} = \frac{R_p DC_L}{2L^2 k_L MC_L} \left. \frac{d\psi}{d\chi} \right|_{\chi=1}$$

$$\left. \frac{d\psi}{d\chi} \right|_{\chi=1} = \frac{Bi\phi(\gamma - M)}{\phi Sinh(\phi) - BiCosh(\phi)} Sinh(\phi)$$

$$\eta = \frac{R_p D}{2L^2 k_L M} \frac{Bi\phi(\gamma - M)}{\phi Sinh(\phi) - BiCosh(\phi)} Sinh(\phi) = \frac{1}{\phi M} \frac{Bi(\gamma - M)}{\phi Sinh(\phi) - BiCosh(\phi)} Sinh(\phi)$$

In the limiting case where internal transport is the slowest step in comparison to lignin dissolution and external transport the following simplification can be made.

$$BiCosh(\phi) \gg \phi Sinh(\phi)$$

$$\eta = \frac{1}{\phi M} \frac{(M - \gamma)}{\text{Cosh}(\phi)} \text{Sinh}(\phi) = \frac{(M - \gamma)}{\phi M} \text{Tanh}(\phi)$$

Since ϕ is large due to slow internal transport

$$\eta = \frac{(M - \gamma)}{\phi M}$$

$$r_{obs} = \eta 2\pi R_p L r_{max} = \frac{(M - \gamma)}{\phi M} 2\pi R_p L k_L M C_L = (M - \gamma) \pi R_p \sqrt{2Dk_L R_p C_L}$$

The scaling for the apparent rate is shown below for a diffusion limited process. The apparent barrier for diffusion is much lower than a kinetic barrier which leads to the final simplification.

$$E_{app} = \frac{E_D + E_A}{2} \approx \frac{E_A}{2}$$

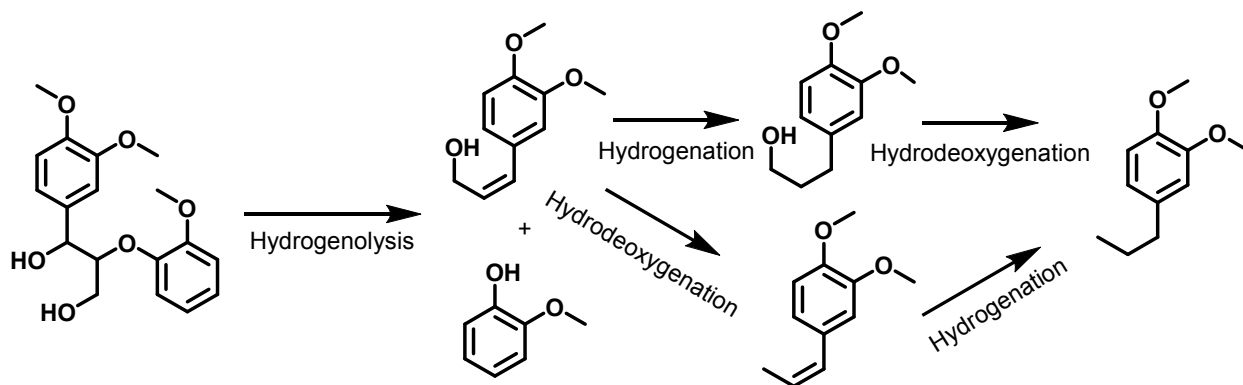


Figure S4: Reaction pathways to produce the observed products from the reductive treatment of POPV.

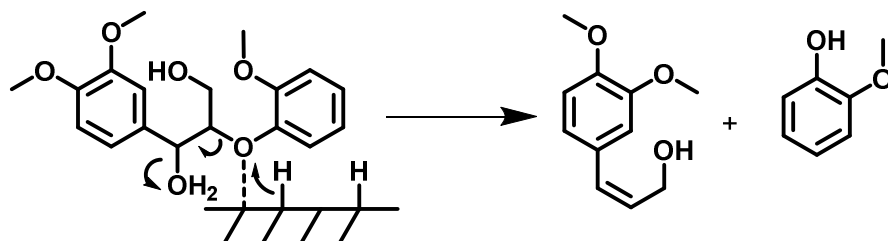


Figure S5: Possible mechanism for β -O-4 hydrogenolysis.

1st step.1.fid

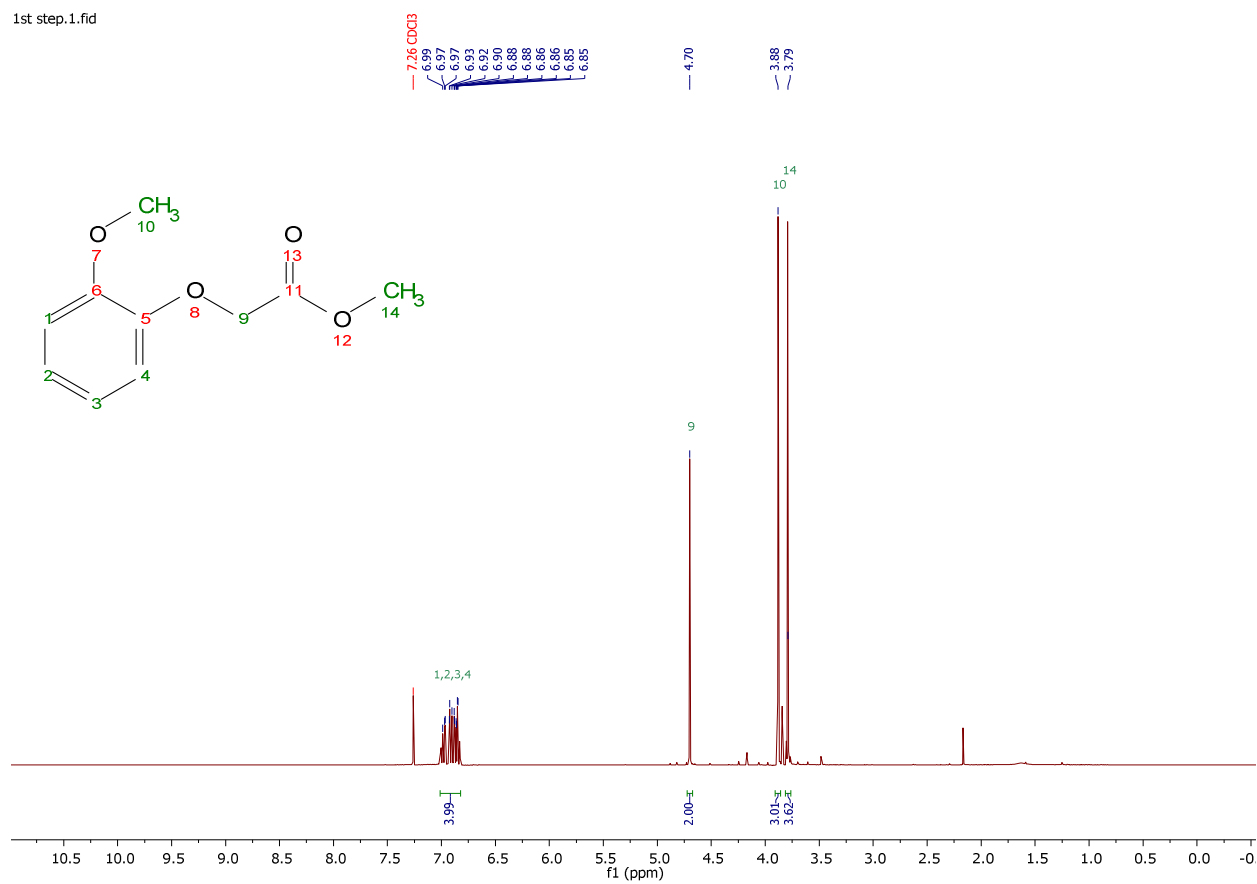


Figure S6: ¹H NMR of Methyl-2-(2-methoxyphenoxy)acetate.

MJS_3.1.fid

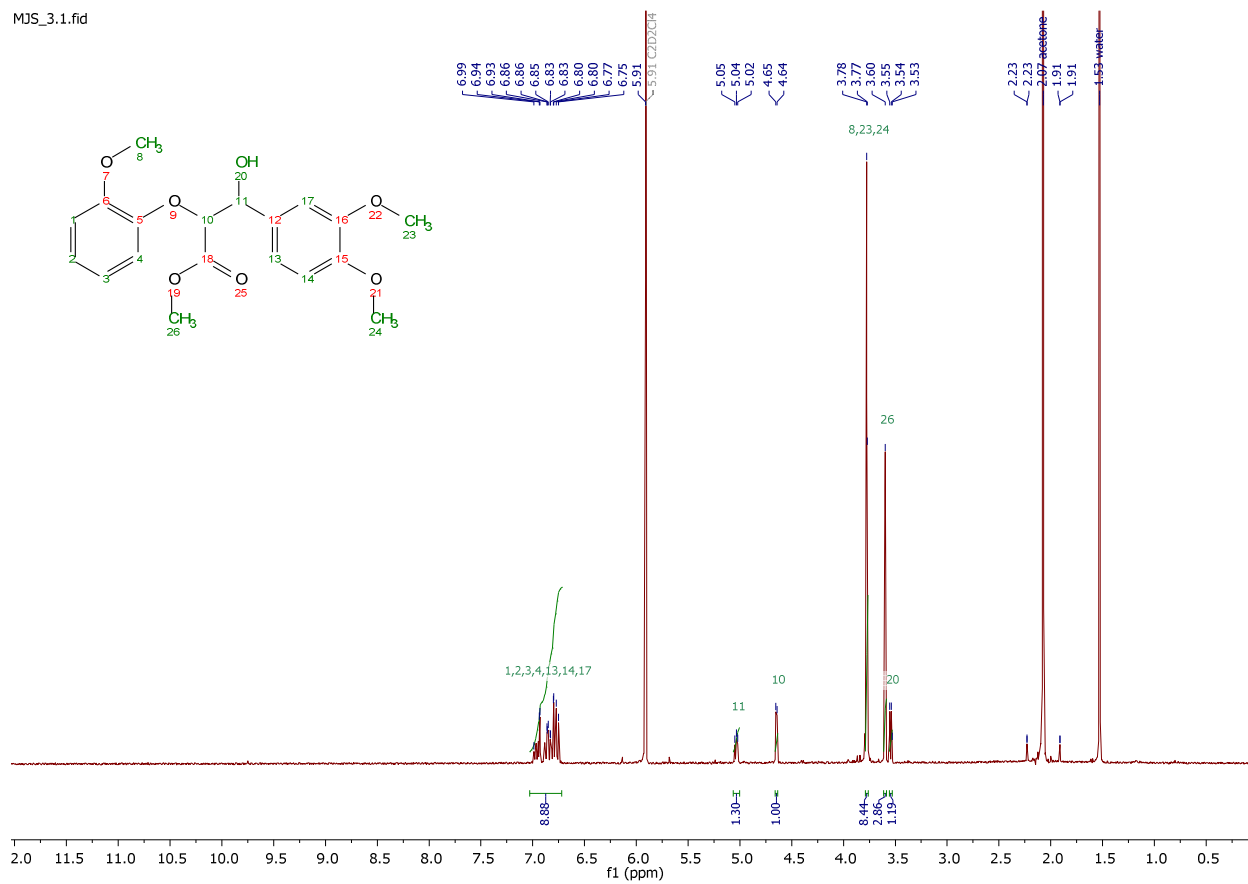


Figure S7: ^1H NMR of 3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate.

2nd try.1.fid

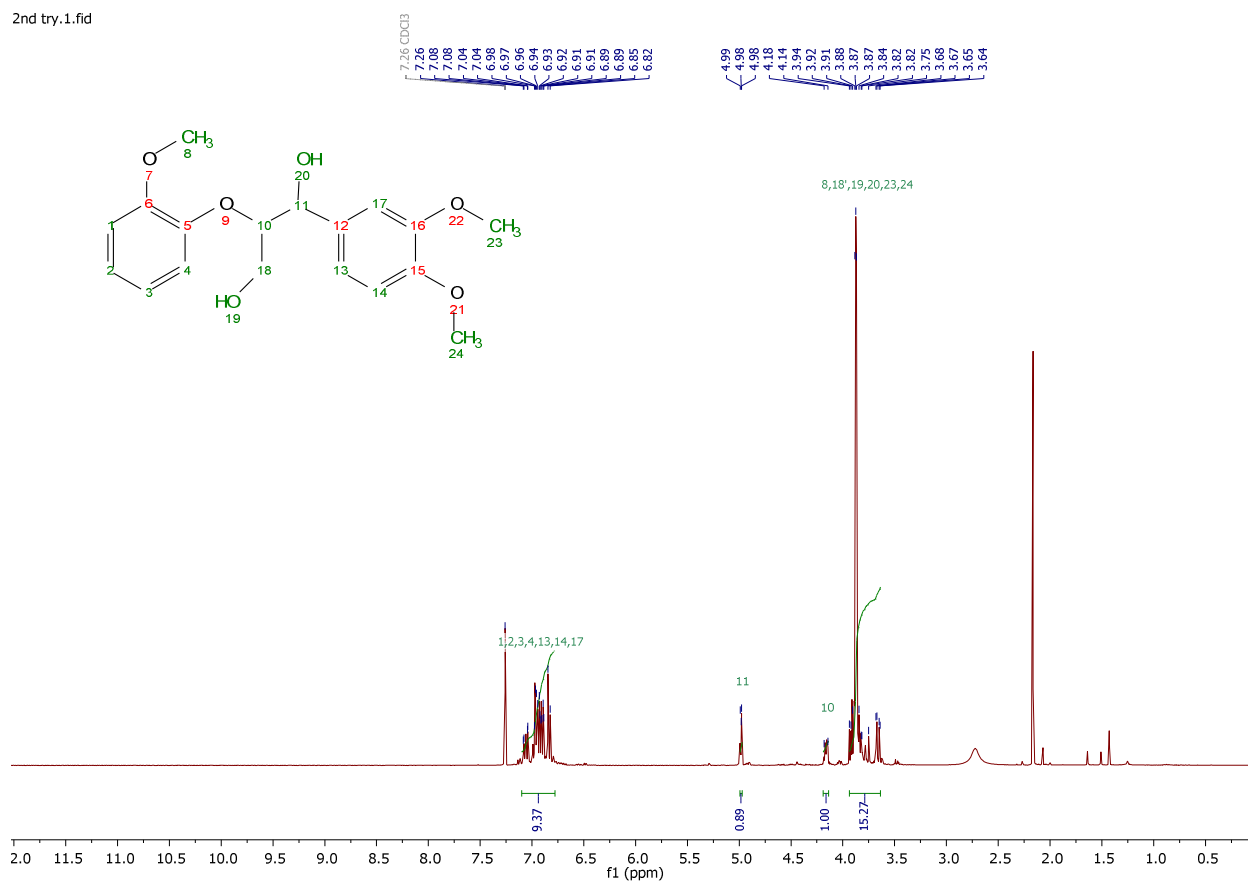


Figure S8: ¹H NMR of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol.

Carbon.1.fid

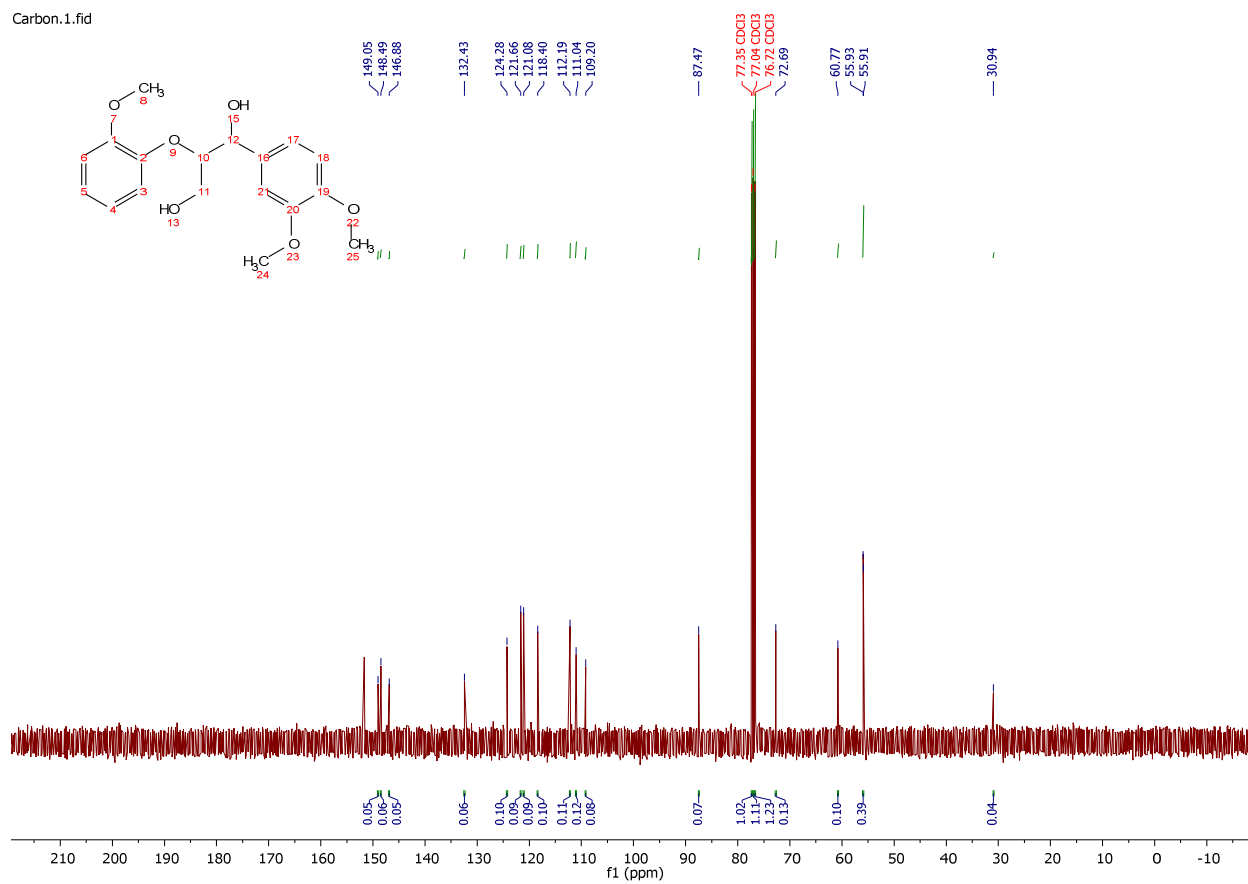


Figure S9: ^{13}C NMR of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol.