Depolymerization of organosolv lignin to aromatic compounds over Cu-doped porous metal oxides

Katalin Barta, Genoa Warner, Evan S. Beach, and Paul T. Anastas

Supporting information

1. GPC traces and details of the extraction and purification of lignin from candlenut nutshells
2. Spectroscopic details of low- and high-molecular weight lignins
3. Representative powder XRD data for synthesized hydrotalcite-like catalyst precursor
4. GPC and ^{1}H NMR spectroscopic data for representative product mixtures after catalytic treatment

1. GPC traces and details of the extraction and purification of lignin from candlenut nutshells.

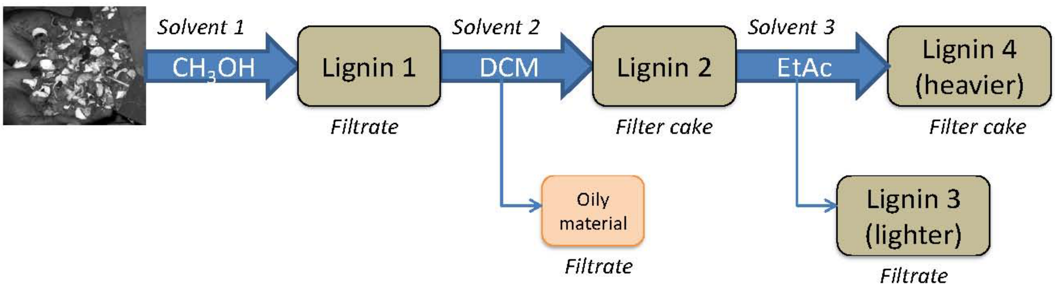


Figure S1. Extraction and fractionation scheme for obtaining purified organosolv lignin fractions from candlenut nutshells.

Table S1. Repeated extraction procedures and corresponding yields ("Oil" is the dichloromethane-soluble portion of Lignin 1):

Entry	Nutshells (g)	Lignin 1 (g)	Yield (%)
1	80	7.95	9.9
2	110	13.62	12.4
3	170	21.58	12.7
4	200	23.00	11.5
5	400	51.47	12.9
6	500	58.3	11.7
7	500	61.4	12.3
8	600	70.6	11.8
Average yield :		**11.9 %**	

Entry	Lignin 1 (g)	Oil (g)	Yield (%)
1	21.5	0.5	2.3
2	17.06	0.483	2.8
3	8.39	0.266	3.1
Average yield :			2.7 %

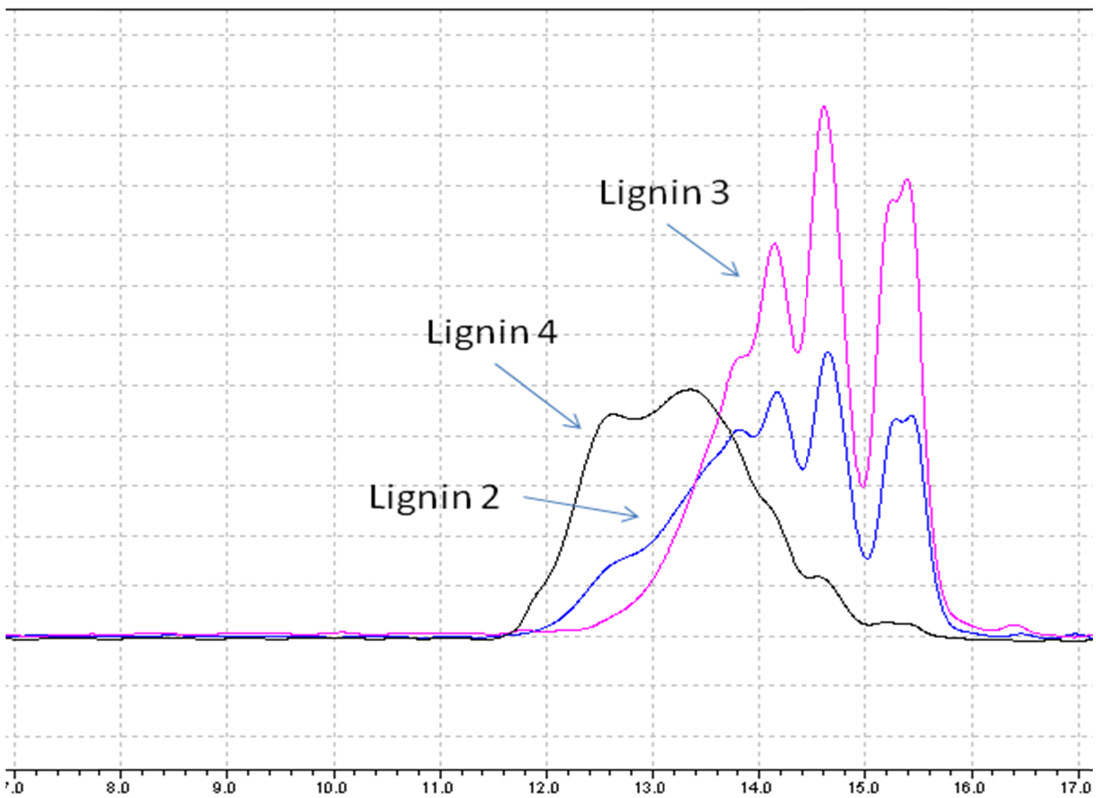


Figure S2. GPC traces of various fractions obtained by solvent extraction of the crude candlenut lignin. Lignin 2 is the dichloromethane-treated fraction. Lignin 3 is the ethyl acetate-soluble portion of Lignin 2 and Lignin 4 is the ethyl acetate-insoluble portion of Lignin 2.

Table S2. Fractionation of Lignin 2 to lighter (Lignin 3) and heavier (Lignin 4) components:

Entry	**Lignin 2 (g)**	**Solids (Lignin 4) (g)**	**Yield (solids) (%)**	**Filtrate (Lignin 3) (g)***
1	7.295	2.851	39.0	4.976
2	16.393	6.634	40.5	11.70
3	20.00	7.192	36.0	14.3
Average yield :			**38.5 %**	

*the filtrate contained a small amount of EtAc, even after prolonged drying.

Table S3. GPC analysis of the obtained lignin fractions (where Lignin 1 is the crude methanol-extracted lignin from nutshells; Lignin 2 is the dichloromethane-treated fraction; Lignin 3 is the ethyl acetate-soluble portion of Lignin 2, Lignin 4 is the ethyl acetate-insoluble portion of Lignin 2, and "Oil" is the residue recovered from the dichloromethane extraction):

Lignin fraction	**M_N**	**Mw**	**$Đ_M$**
Lignin 1	862	1162	1.35
Lignin 2	797	1054	1.32
Lignin 3	736	1133	1.18
Lignin 4	1959	2449	1.18
Oil	242	595	1.18

2. Spectroscopic details of low and high molecular weight lignin

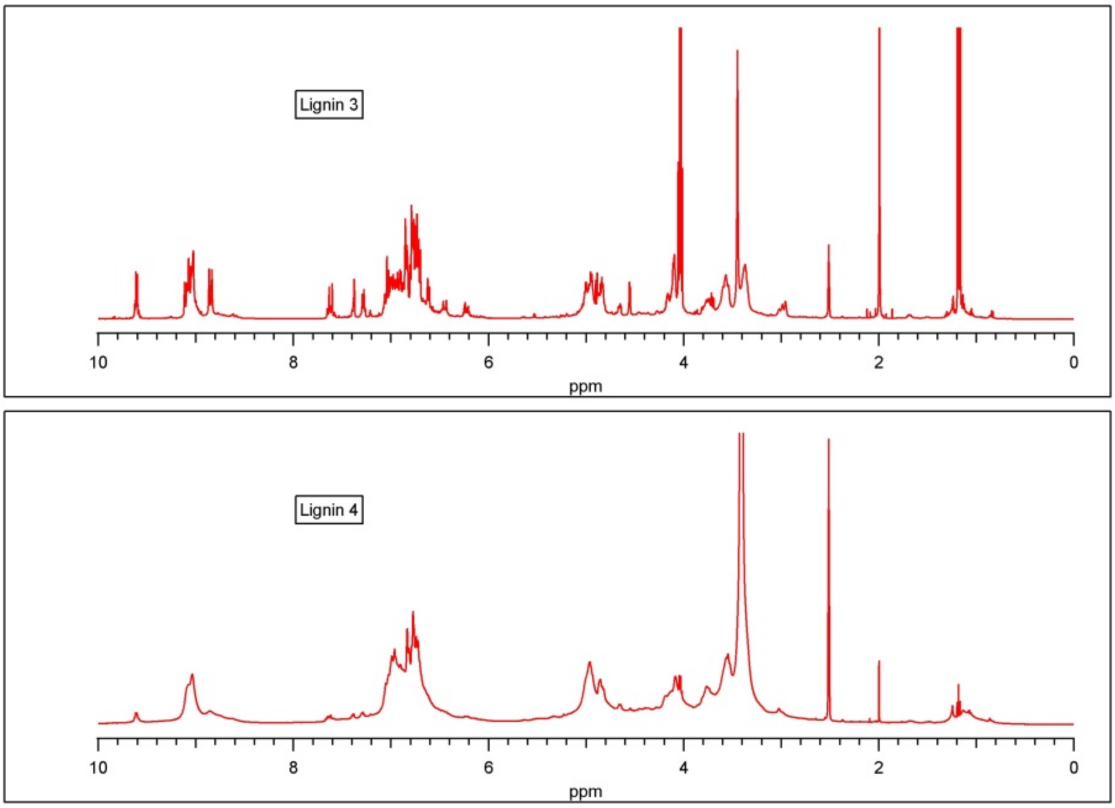


Figure S3. ^{1}H NMR spectra (500.13 MHz, CD_3OD) of Lignin 3 (ethyl acetate-soluble) and Lignin 4 (ethyl acetate-insoluble).

Electronic Supplementary Material (ESI) for Green Chemistry

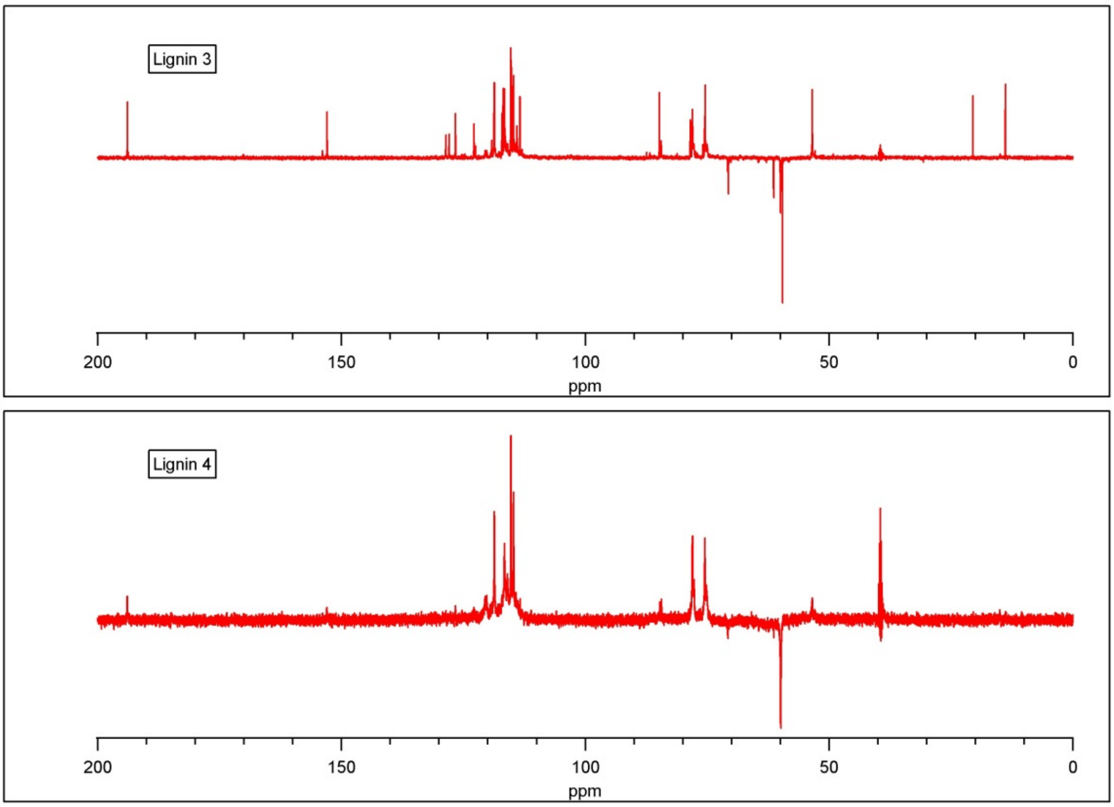


Figure S4. ^{13}C-DEPT-135 NMR spectra (125.76 MHz, DMSO-d_6) of Lignin 3 (ethyl acetate-soluble) and Lignin 4 (ethyl acetate-insoluble).

3. Representative powder XRD data for synthesized hydrotalcite-like catalyst precursor

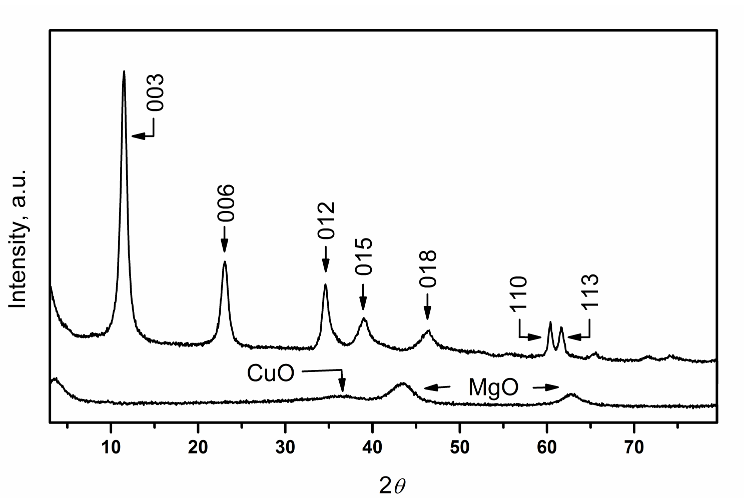


Figure S5. Powder XRD spectrum of a representative HTC precursor (top) and the corresponding PMO post-calcination (bottom).

4. GPC and ^{1}H NMR spectroscopic data for representative product mixtures after catalytic treatment

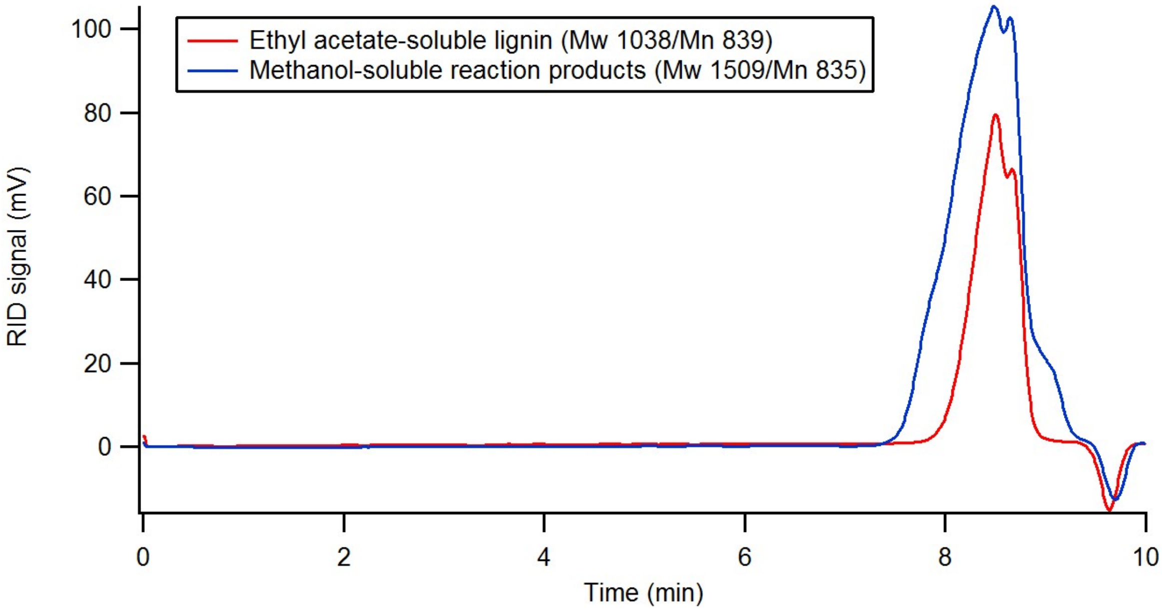


Figure S6: Comparison of GPC traces for Lignin 3 (ethyl-acetate soluble) and product mixture of uncatalyzed lignin treatment (reaction conditions: 1.0 g lignin, 30 mL methanol, 100 mL vessel, 180 °C, 4.0 MPa H_2, 18 h). NOTE: for this figure only, the GPC column used was an Agilent PLgel 5 µm MIXED-C (300 mm x 7.5 mm), also calibrated with polystyrene standards.

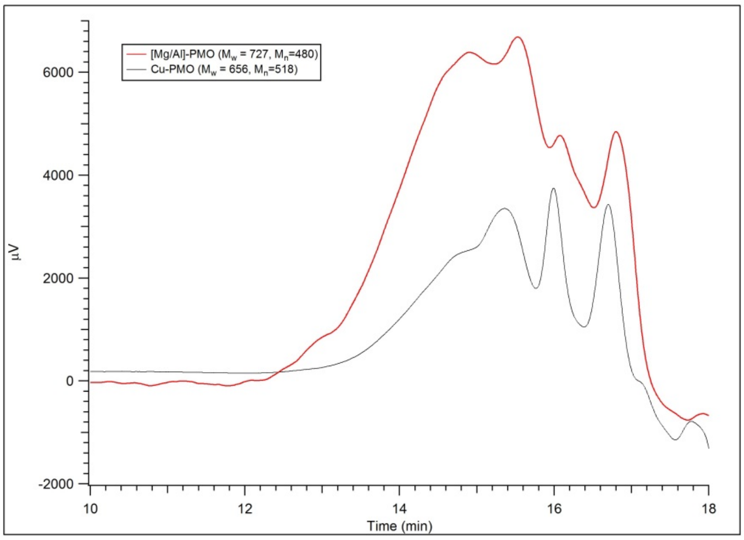


Figure S7: Comparison of GPC traces for product mixtures from copper-free [Mg/Al]-PMO (18 h) or copper-containing Cu-PMO (8 h) treatments. Reaction conditions: 0.5 g catalyst, 1.0 g lignin, 30 mL methanol, 100 mL vessel, 220 °C, 4.0 MPa H_2.

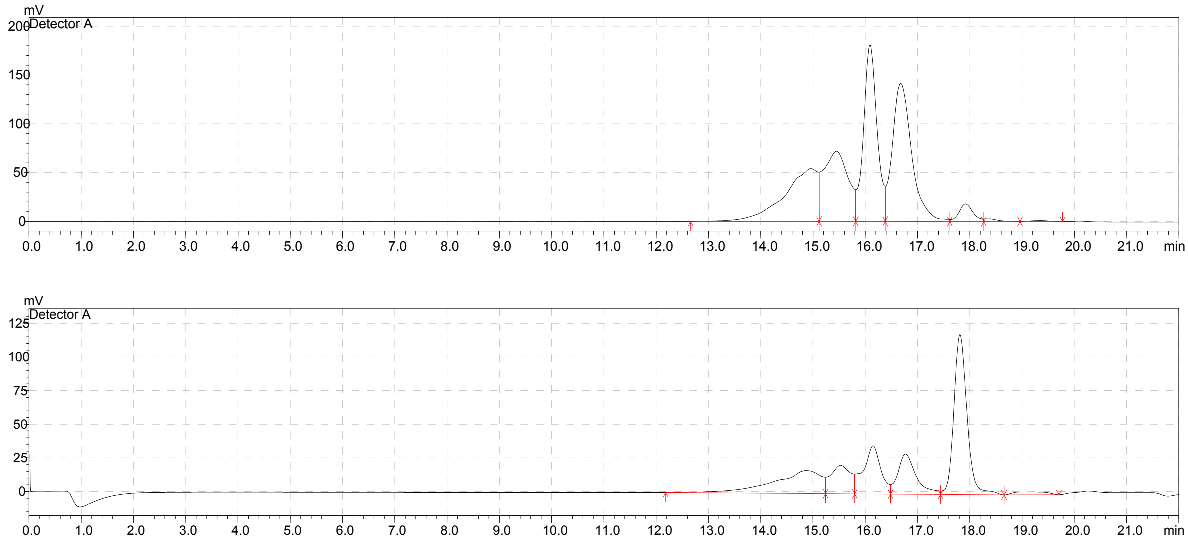


Figure S8: Comparison of GPC traces for product mixtures from Cu-PMO treatments at 220 °C/8 h (top) or 180 °C/18 h (bottom). Reaction conditions: 0.5 g catalyst, 1.0 g lignin, 30 mL methanol, 100 mL vessel, 4.0 MPa H_2.

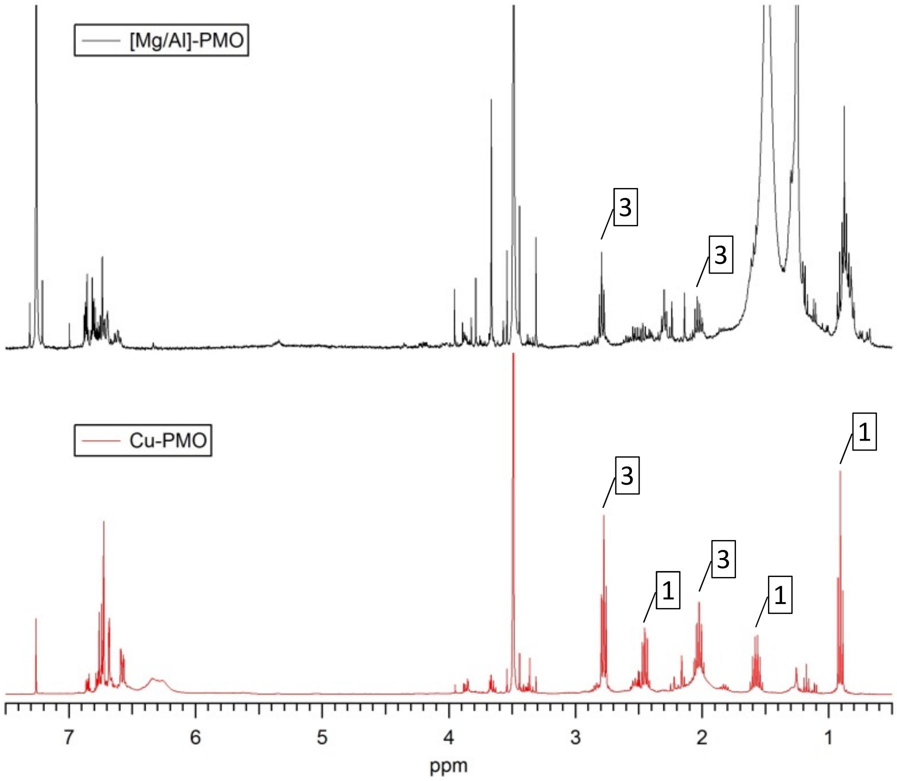


Figure S9: ^{1}H NMR spectra (500.13 MHz, $CDCl_3$) of the product mixtures from [Mg/Al]-PMO (top) and Cu-PMO treatments. Reaction conditions as described in Figure S7 caption. Catechol products are numbered as in the manuscript.

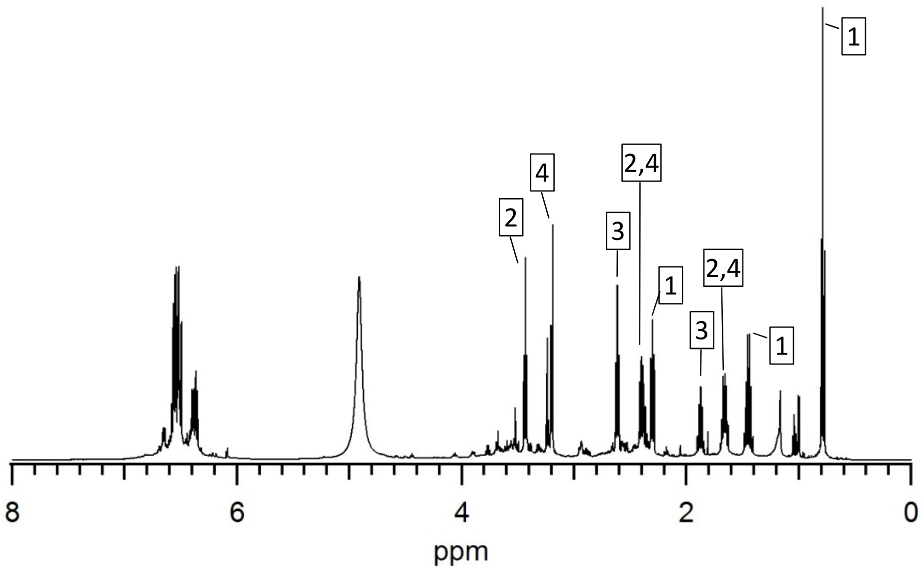


Figure S10. Representative ^{1}H NMR spectrum (500.13 MHz, CD_3OD) of crude products after Cu-PMO treatment. Reaction conditions: 1.0 g catalyst, 4.0 g lignin, 30 mL methanol, 100 mL vessel, 180 °C, 4.0 MPa H_2, 18 h. (Lowest catalyst : lignin ratio tested.)

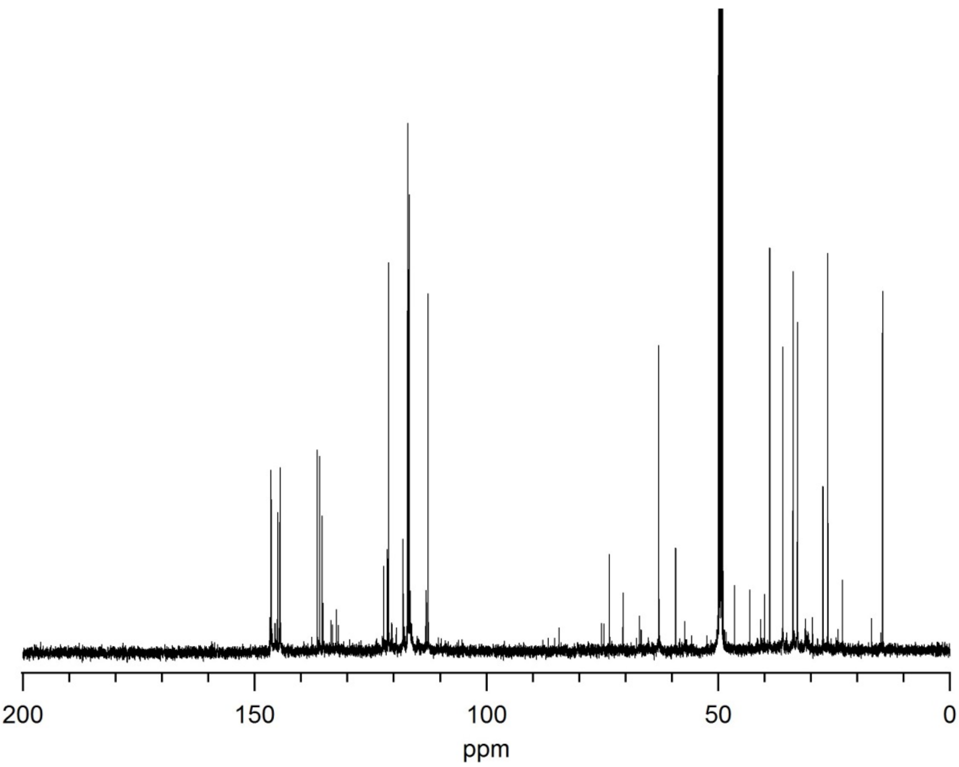


Figure S11. ^{13}C NMR spectrum (125.76 MHz, CD_3OD) for sample depicted in Figure S10.

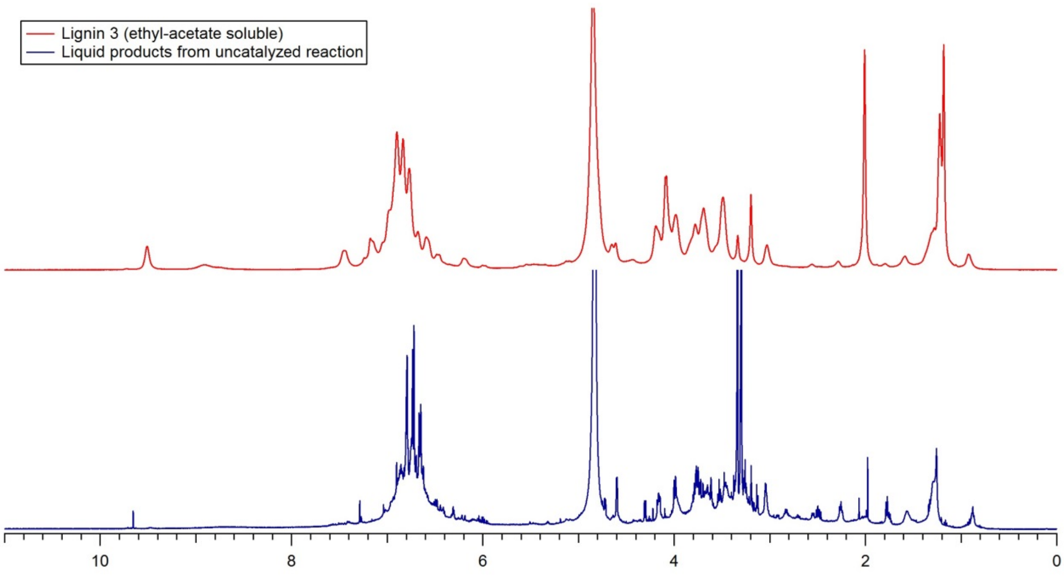


Figure S12. ^{1}H NMR spectra (500.13 MHz, CD_3OD) of starting lignin (top) and methanol-soluble products after uncatalyzed thermal treatment with H_2 (bottom). Reaction conditions: 1.0 g lignin, 30 mL methanol, 100 mL vessel, 180 °C, 4.0 MPa H_2, 18 h.

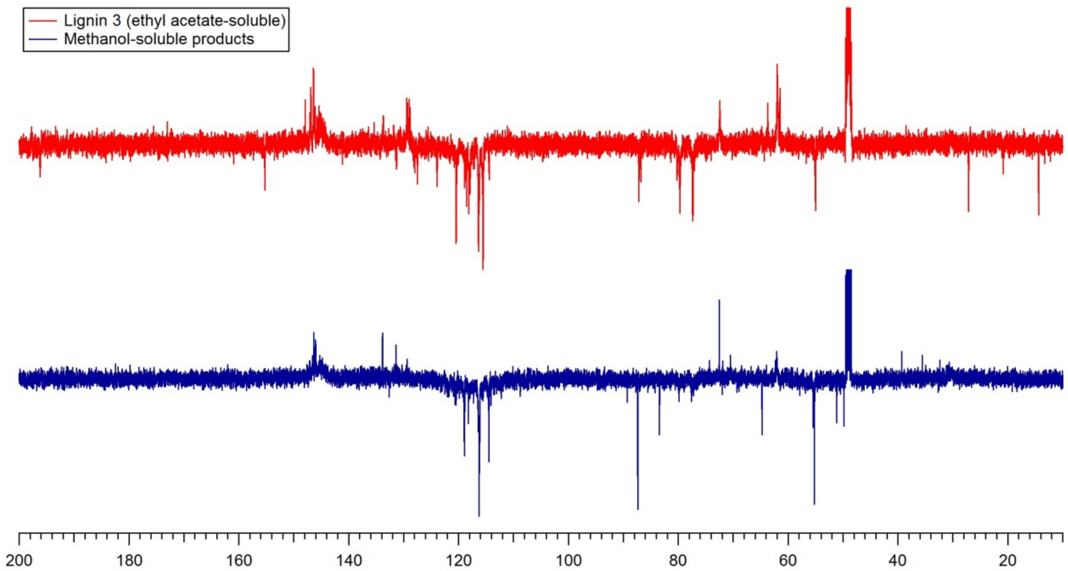


Figure S13. ^{13}C APT spectra (125.76 MHz, CD_3OD) of starting lignin (top) and methanol-soluble products after uncatalyzed thermal treatment with H_2 (bottom). Reaction conditions: 1.0 g lignin, 30 mL methanol, 100 mL vessel, 180 °C, 4.0 MPa H_2, 18 h.

Table S4. Relative distribution of catechols **1-4** in product mixtures derived from Cu-PMO catalytic treatments:

Entry	**PMO**	**PMO (g)**	**Lignin (g)**	**P (H_2, MPa)**	**Temp (^oC)**	**Time (*h*)**	**1**	**2**	**3**	**4**
1 (Table 2, Entry 1)	Cu	0.5	1	4	220	8	1	-	0.95	-
2 (Table 2, Entry 2)	Mg/Al	0.5	1	4	220	18	1	-	1.19	-
3 (Table 2, Entry 3)	Cu	0.5	1	4	180	14	1	1.17	0.34	0.40
350.0 mg of 712.2 mg liquid products applied to column										
- Column fractions 1-2 (6 mg)							-	-	-	-
- Column fractions 3-7 (30.2 mg)							1	-	0.26	0.38
- Column fractions 8-13 (61.5 mg)							1	-	0.30	0.70
- Column fractions 14-20 (177.5 mg)							-	1	-	-
- Column fractions 21+ (8.8 mg)							-	-	-	-
4 (Table 2, Entry 4)	Cu	0.5	1	4	180	20	1	0.78	0.43	0.29
5 (Table 2, Entry 5)	Cu	0.25	1	4	180	18	1	0.94	0.76	-
6 (Table 2, Entry 6)	Cu	0.5	1	none	180	18	-	-	-	-
7 (Table 2, Entry 7)	Cu	1	1	none	180	12	-	-	-	-
8 (Table 2, Entry 8)	none	-	1	4	180	18	-	-	-	-
9 (Table 2, Entry 9)	Cu	0.5	1	4	140	18	1	5.21	0.37	-
10 (Table 2, Entry 10)	Cu	1	2	4	140	20	1	3.23	0.31	-
908.2 mg of 908.2 mg liquid products applied to column										
- Column fractions 1-5 (67.8 mg)							1	-	0.27	0.68
- Column fractions 6-8 (135.7 mg)							1	-	0.30	0.72
- Column fractions 9-18 (433.1 mg)							-	1	-	-
- Column fractions 19-25 (180.5 mg)							-	-	-	-
11 (Table 2, Entry 11)	Cu	3	5	3	180	18	1	0.74	0.33	0.21
12 (Table 2, Entry 12)	Cu	1	4	6	180	14	1	0.94	0.52	0.29
13	Cu	1	1	4	180	12	1	0.83	0.36	0.36
533.8 mg of 533.8 mg liquid products applied to column										
- Column fractions 1-3 (95.3 mg)							1	0.16	0.29	0.36
- Column fractions 4-10 (174.7 mg)							1	0.34	0.31	0.41
- Column fractions 11-13 (91.4 mg)							1	2.13	0.39	0.48
- Column fractions 14-27 (131.2 mg)							-	1.0	0.14	-
- Column fractions 28+ (93.3 mg)							-	-	-	-
14	Cu	2	3	4	180	5	1	1.22	0.33	0.37

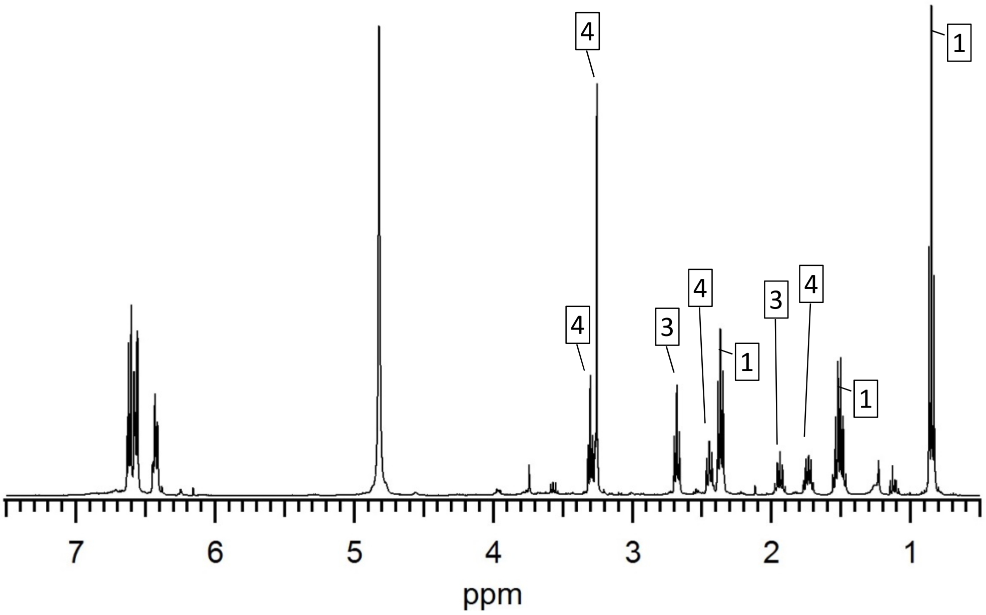


Figure S14: ^{1}H NMR spectrum (400.25 MHz, CD_3OD) of products from Table S4, Entry 5, Column fractions 3-7.

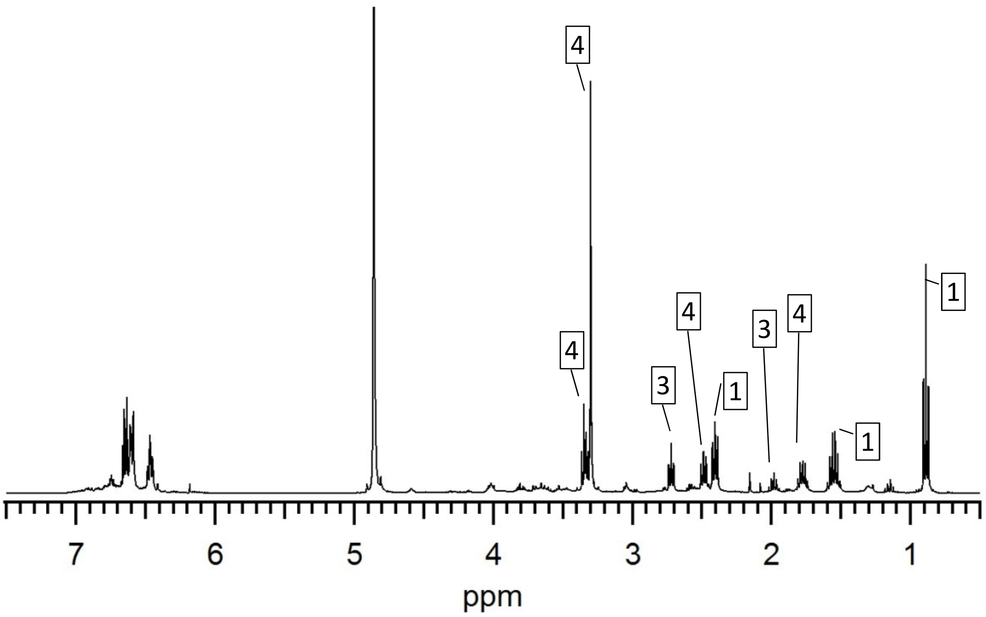


Figure S15: ^{1}H NMR spectrum (400.25 MHz, CD_3OD) of products from Table S4, Entry 5, Column fractions 8-13.

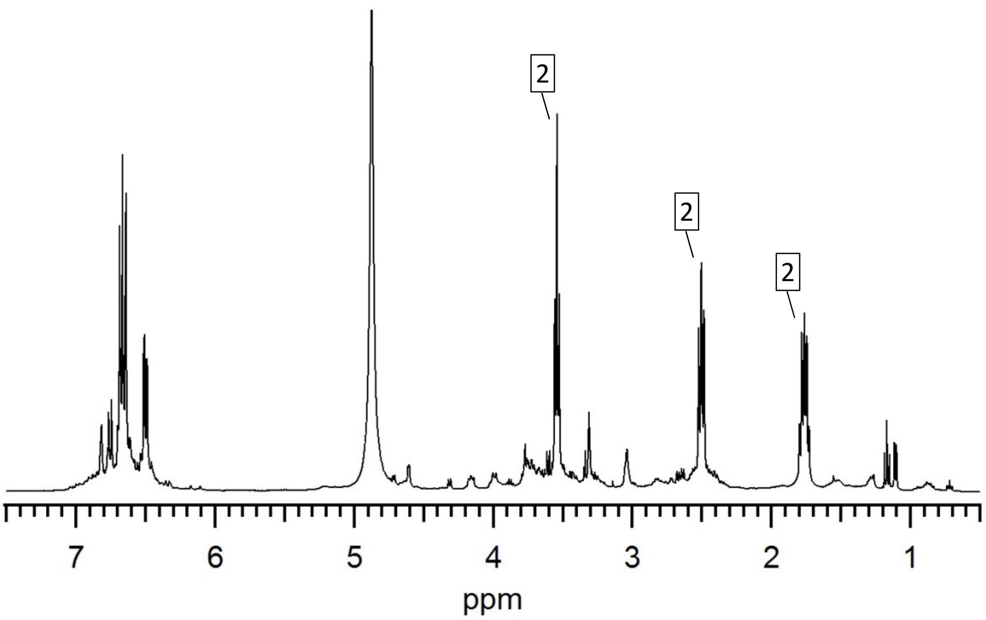


Figure S16: [1]H NMR spectrum (400.25 MHz, CD_3OD) of products from Table S4, Entry 5, Column fractions 14-20.

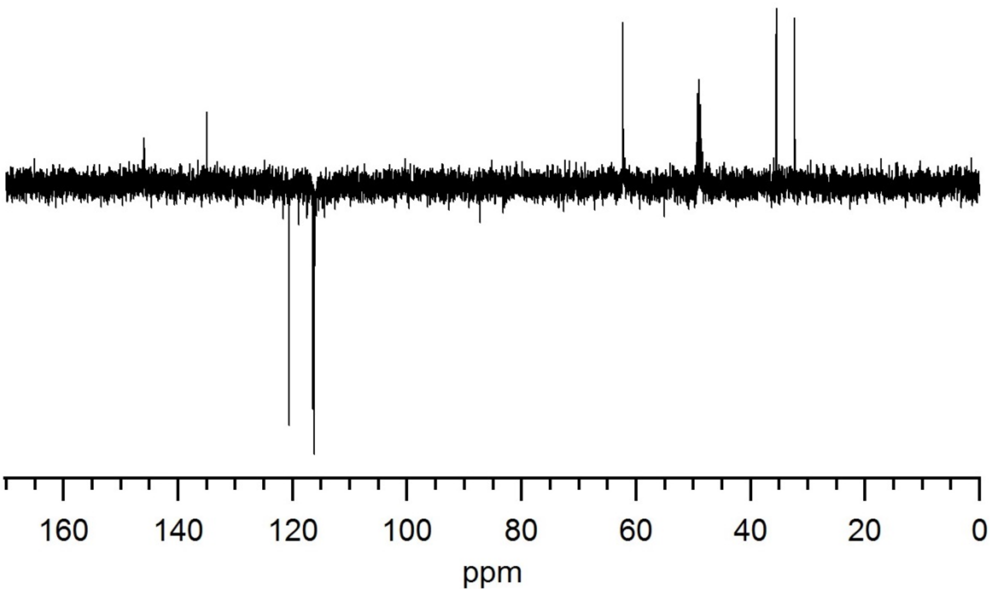
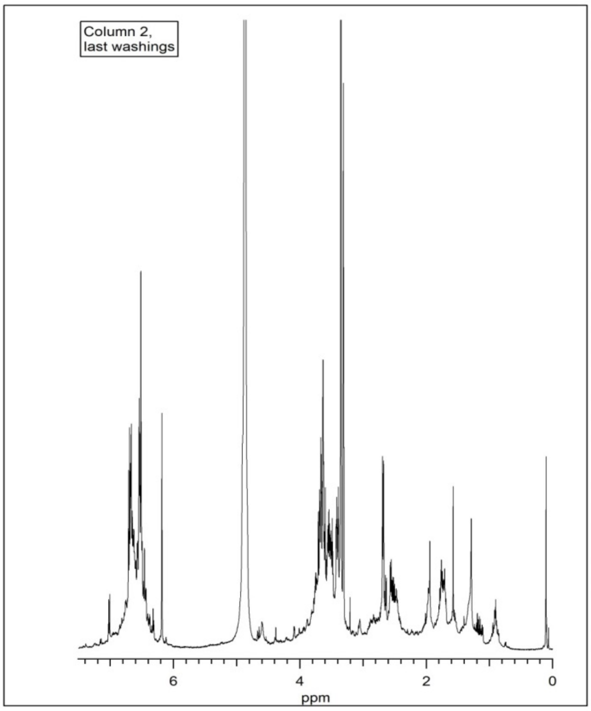


Figure S17: ^{13}C-APT NMR spectrum (100.64 MHz, CD_3OD) of products from Table S4, Entry 5, Column fractions 14-20.



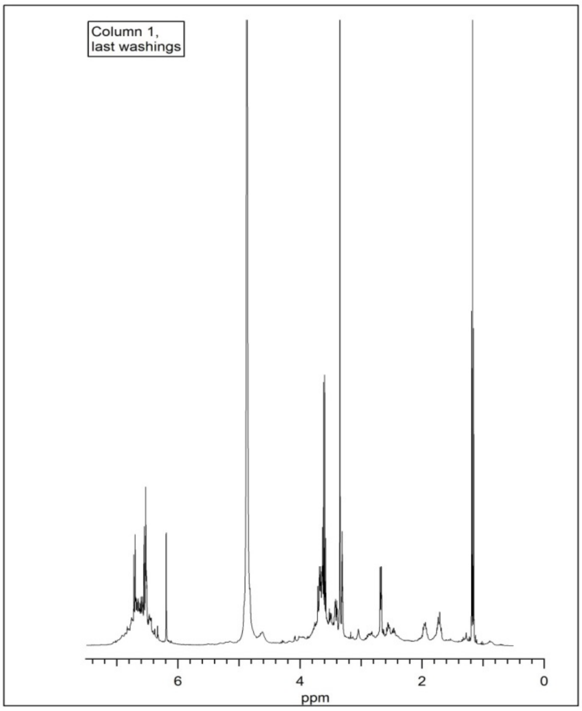


Figure S18 (left): [1]H NMR spectrum (500.13 MHz, CD_3OD) of last column washings from Table 4, Entry 4. **Figure S19 (right)**: [1]H NMR spectrum (400.25 MHz, CD_3OD) of last column washings from Table 4, Entry 5.

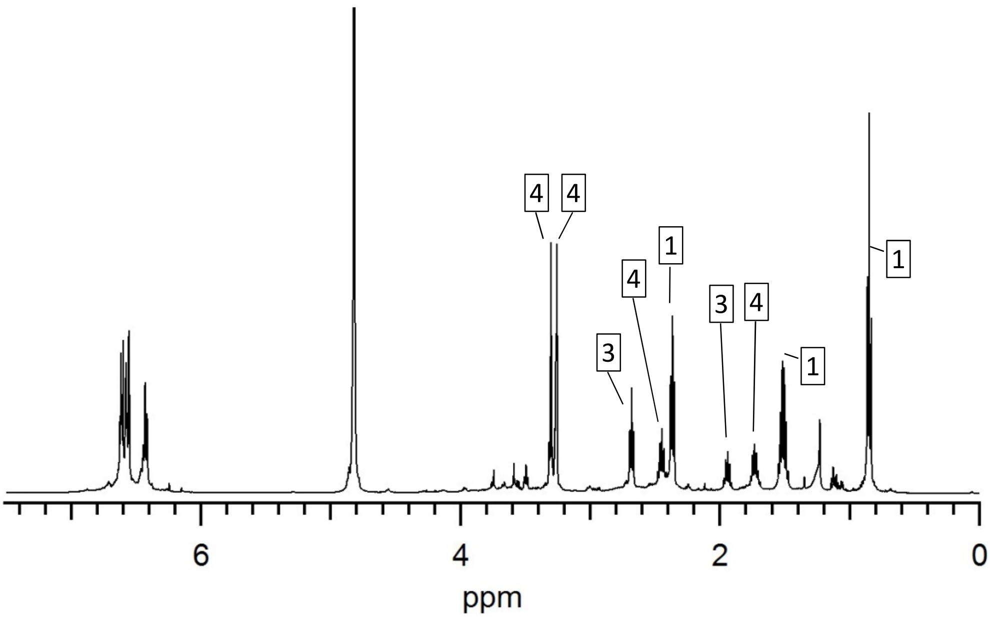


Figure S20: [1]H NMR spectrum of products from Table S4, Entry 4, Column fractions 1-3.

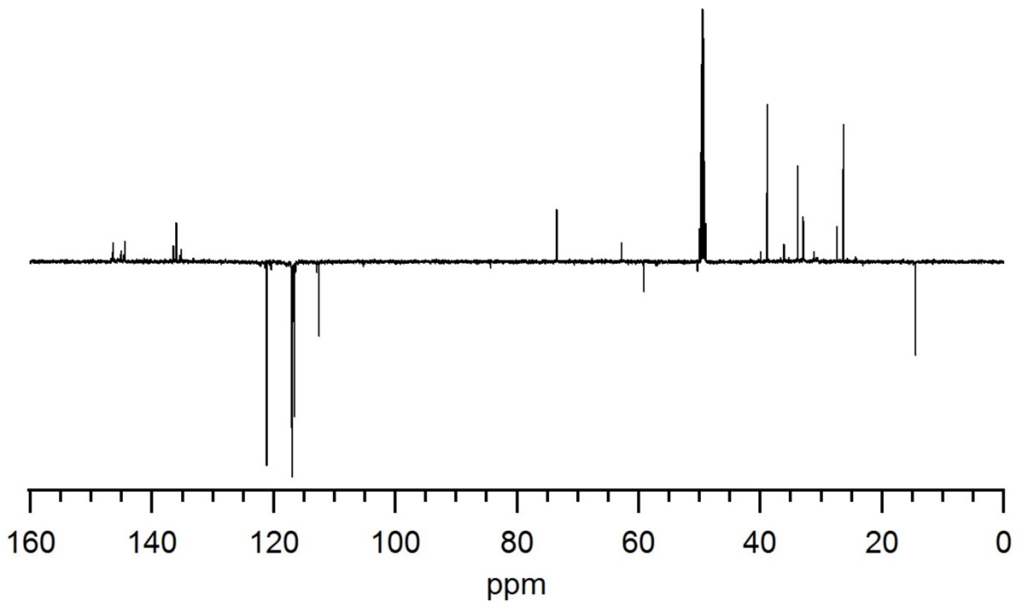


Figure S21: ^{13}C-APT NMR spectrum (125.76 MHz, CD_3OD) of products from Table S4, Entry 4, Column fractions 1-3.

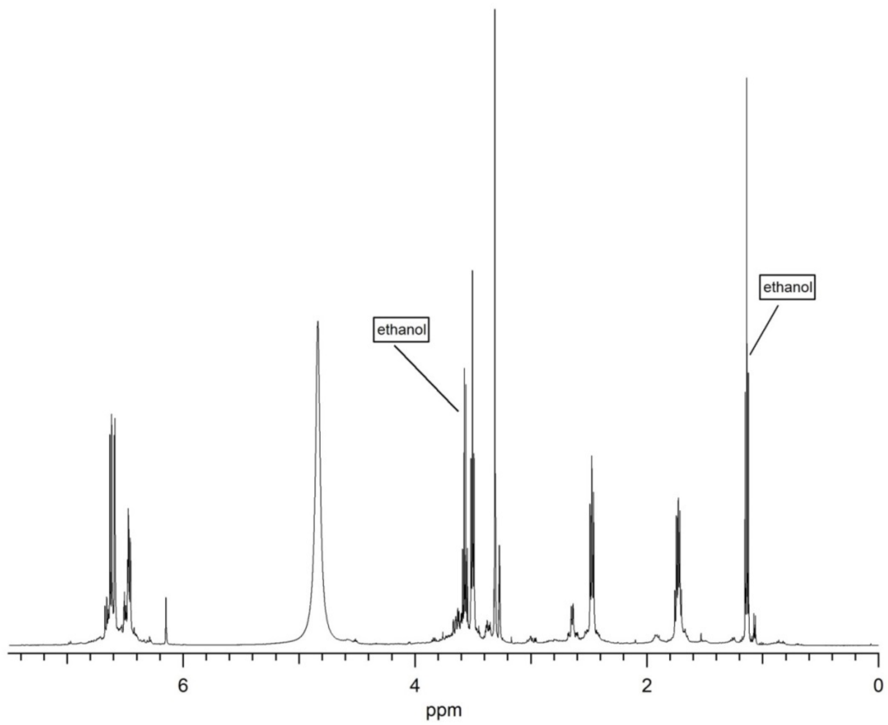


Figure S22: ^{1}H NMR spectrum (500.13 MHz, CD_3OD) of products from Table S4, Entry 4, Column fractions 14-27.

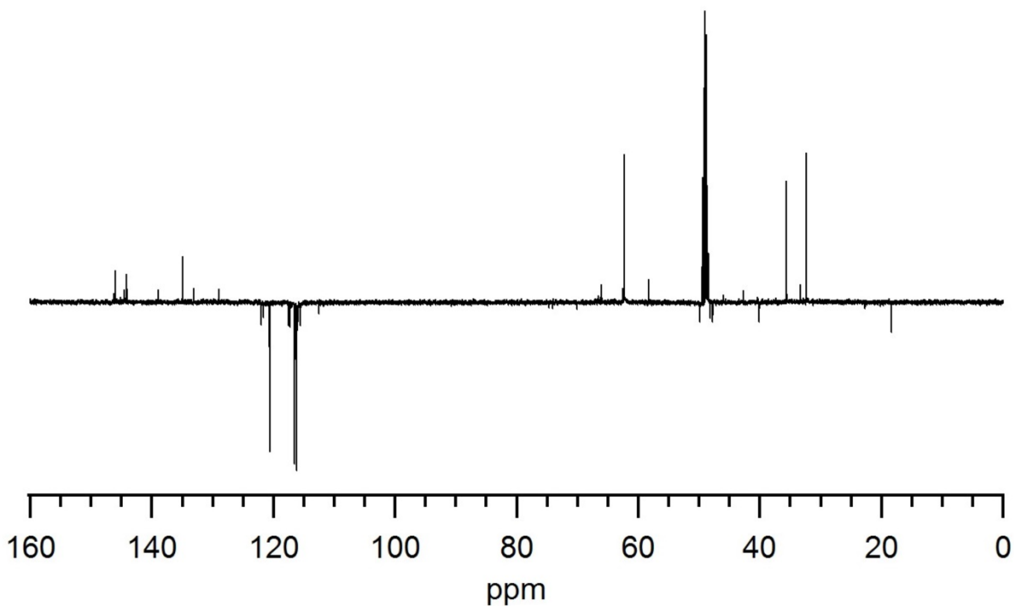


Figure S23: ^{13}C NMR-APTspectrum (125.76 MHz) of products from Table S4, Entry 4, Column fractions 14-27.