Supplementary Information (SI) for

Analysis of gas chromatography/mass spectrometry data for catalytic lignin depolymerization using positive matrix factorization

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Experimental Procedures.

Lignin extraction. Pulp grade chips (about 4 cm^2 and thicknesses of 0.5–1 cm) of hybrid poplar (*Populus spp.*) were used for organosolv fractionation. The biomass sample was treated in a flow-through reactor with a 16:34:50 wt% mixture of methyl isobutyl ketone (MIBK), ethanol, and water. Sulfuric acid (0.05 M) was used as catalyst and fractionation performed at a temperature of 150 °C for 120 min. The black liquor fraction containing dissolved lignin and hemicellulose was separated into a hemicellulose rich aqueous phase and a lignin rich organic phase by adding solid NaCl (10 g per 100 mL of deionized water in the initial solvent mixture) in a separation funnel. After observation of phase separation between the aqueous and organic phases, the aqueous phase that rests at the bottom of the separatory funnel was drained. The organic phase was washed twice by adding 30% v/v deionized water to remove residual sugars and ethanol from the organic phase. Lignin from organic phase phases was isolated by rotary evaporation, followed by trituration of the solid residue with diethyl ether (5 times ~200 mL) and final washing with deionized water (3 L deionized water, room temperature, 12 h). The final lignin was filtered through a paper filter and dried in a vacuum oven at temperature of 80°C for 12 h. Organosolv lignin samples were extracted with methanol at room temperature and solid to liquid ratio of 1:10. Extraction was for about 15 h and then the solution was filtered under vacuum. Methanol insoluble fraction recovered as solid on the filter paper and methanol soluble fraction isolated by rotary evaporation of the filtrates. All lignin samples were dried in a vacuum oven at temperature of 80 °C for 12 h.

Catalyst synthesis. A solution of 250 mL deionized water containing $Mg(NO_3)_2 \cdot 6H_2O$ (30.8 g, 0.12 mol), $Cu(NO_3)_2 \cdot 3H_2O$ (7.25 g, 0.03 mol), and $Al(NO_3)_3 \cdot 9H_2O$ (18.76 g, 0.05 mol), was slowly added to a Na_2CO_3 buffer (5.3 g, 0.05 mol in 375 mL) at 65 °C with vigorous stirring. The pH of the mixture was maintained at approximately 10 by alternating aliquots of 1 M NaOH to the reaction mixture. After the addition of the metal solution was complete, the reaction slurry was stirred overnight. The light blue precipitate was isolated by filtration and washed with a sodium carbonate solution (0.05 mol in 1 L distilled water) for a minimum of four hours, then filtered and washed with deionized water. The precipitate was dried overnight at 110 °C resulting in Cu_{20}HTC.[4]

GC-TCD analysis. To quantify the gas contents, 100 µL of raw gas products was manually injected into the gas chromatography system (GC, 7890B, Agilent Technologies) with thermal conductivity detector (TCD). Inlet temperature was set to 250 °C. Supelco Carboxen-1010 PLOT column (ID: 0.32 mm, average thickness: 15 µm, and length: 30 m) was used with an isotherm method at 75 °C for 10 mins. Helium was used as a carrier gas. Gas products were identified and quantified by the standard gas mixture comprising CO, CO_2, H_2, N_2, and O_2 in helium (custom-mixed by scott specialty gases, Plumsteadville, PA).

GPC analysis. GPC analysis was performed to determine the molecular weight distribution of the liquid products. In a Waters e2695 system with a 2489 UV detector (260 nm), a three-column sequence of WatersTM Styragel columns (HR0.5, HR1, and HR3) was used for the analysis. Tetrahydrofuran (THF) was used as eluent, and the flow rate was 1.0 ml/min. 1 mL of raw liquid product was first filtered to a 2 mL HPLC vial through a 0.45-µm nylon membrane filter, and 50 µL of this sample was injected into the instrument. Molecular weights (M_n and M_w) were calibrated against a polystyrene calibration curve. A calibration curve was constructed by fitting a third-order polynomial equation to the retention volumes obtained from six narrow polystyrene standards and two small molecules (diphenylmethane and toluene) ranging in molecular weight from 92 to 3.4 × 104 g/mol. The curve fit had an R^2 value of 0.99.

Thermal gravimetric analysis. Gravimetric analysis was conducted on the solids residues after dioxane washes. The thermogravimetric analyses were carried out in a Q5000 TGA instrument

(TA instrument). ~5-10 mg dry solid samples were placed onto a platinum TGA pan. Furnace was programed to heat to 900 °C in 2 mins with air (ultrazero grade) flowrate of 10 L/h and nitrogen flowrate of 25 L/h. Furnace was held at 900 °C for additional 10 mins until no further changes in sample weight observed. Weight loss percentages were recorded to calculate the catalyst content in the solid residues.

Quantitative ^{31}P NMR. ^{31}P NMR was performed after derivatization of the untreated MS and MIS lignin with 2–chloro– 4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP). N-Hydroxy-5-norbornene-2,3-dicarboxylic acid imide and chromium (III) acetylacetonate were used as an internal standard and a relaxation agent, respectively. The quantitative ^{31}P NMR spectra were recorded using a Varian 400-NMR spectrometer at frequency of 162 MHz using a 90° pulse angle, 25 s pulse delay, and 256 transients at room temperature.

Quantitative ^{13}C NMR. For quantitative ^{13}C NMR spectroscopy, 150 mg of lignin was dissolved in 0.75 mL of DMSO-d_6. Chromium (III) acetylacetonate were used as relaxation agent (0.01 M). An inverse-gated decoupling pulse sequence was used with a 90° pulse angle, 1.7 s relaxation delay and an acquisition time of 1.40 s. A total of 20,000 scans were recorded.

^{13}C ^{1}H (HSQC) NMR. HSQC NMR was carried out using a Varian 400-MR spectrometer operating at frequency of 399.78 MHz for proton and 100.54 MHz for carbon. For 2D (HSQC) spectroscopy, 100 mg of lignin were dissolved in 0.75 mL of DMSO-d6. NMR spectra were recorded at 25°C using the (HC)bsgHSQCAD pulse program. The experiment used 32 transients and 512 time increments in the ^{13}C dimension. A 90° pulse with a pulse delay of 1.5 s, an acquisition time of 0.15 s and a $^{1}J_{CH}$ of 147 Hz were employed. DMSO was used as an internal reference.

Nitric acid digestion. Solid residues from depolymerization were treated with 5 ml of 70% HNO_3 at room temperature for 16 h. Mixture was heated to 50 °C for another hour, then, cooled to room temperature. Leftover solids (Char) were recovered by filtration through glass fiber filters. Leftover solids were washed with excessive amount of water DI water for three time and then dried for gravimetric analysis.

Figures:

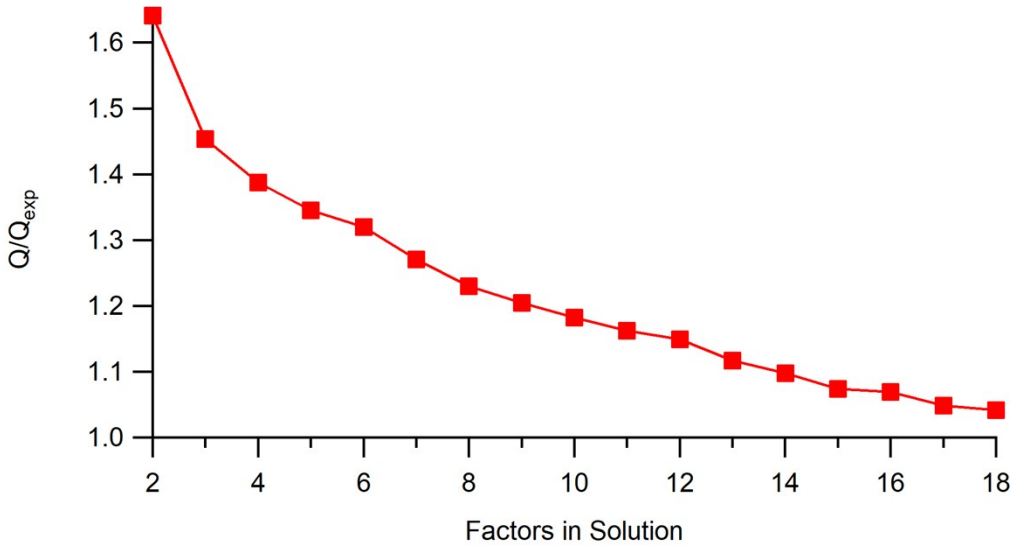

Figure S1. Q/Q_{exp} values for the 2-18 factor solutions obtained using PMF.

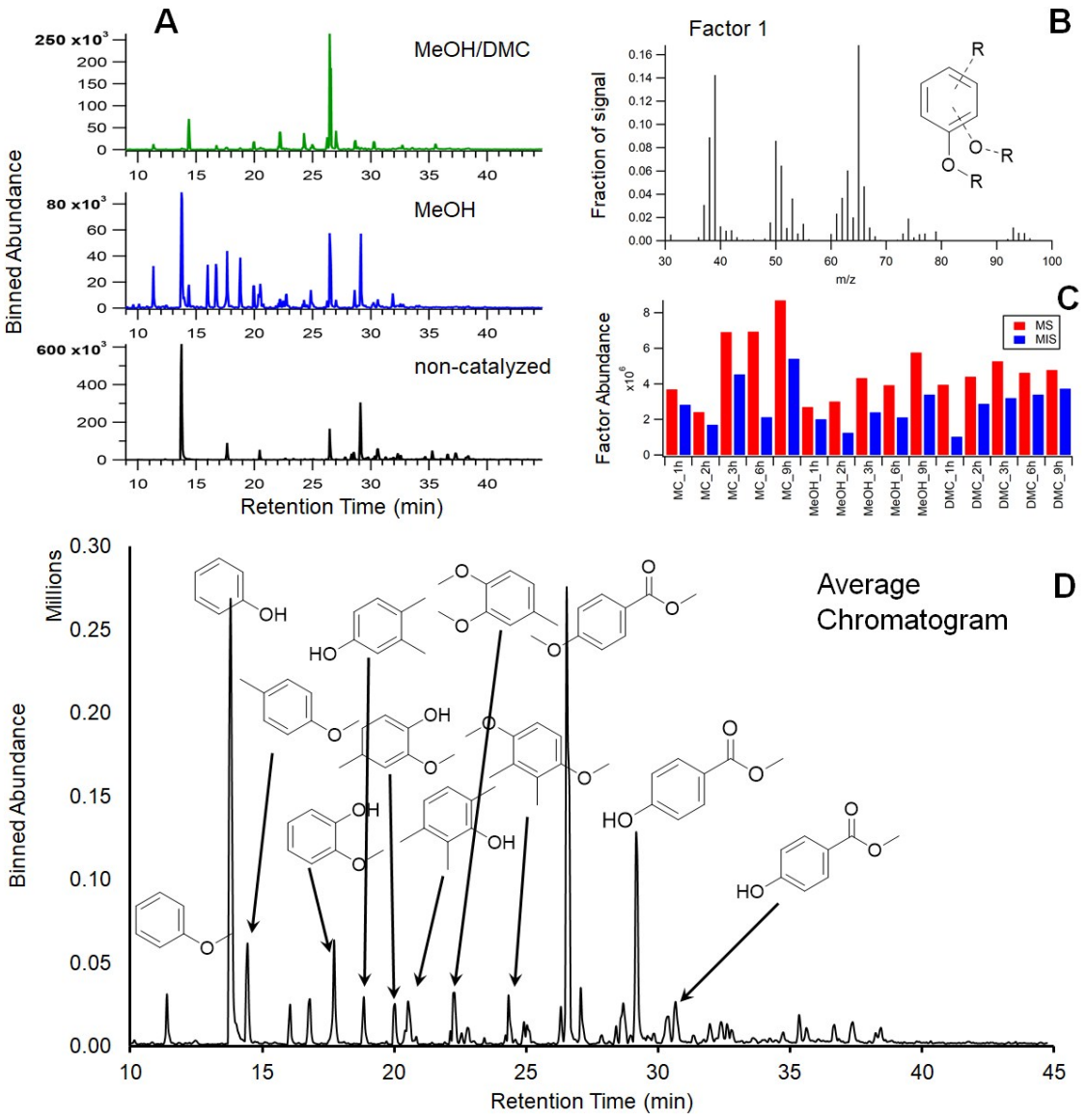

Figure S2. Factor 1 is defined by compounds that generate mass spectral fragments that are less polar and/or more volatile aromatics (13-factor solution). A) PMF-reconstructed Factor 1 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 1 mass spectrum. C) Factor 1 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 1 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 1 average chromatograms for product samples from the combination of all reaction conditions. Individual compound structures identified in (D) were verified by Palisade Complete Mass Spectral Database mostly with more than 90 % matching.

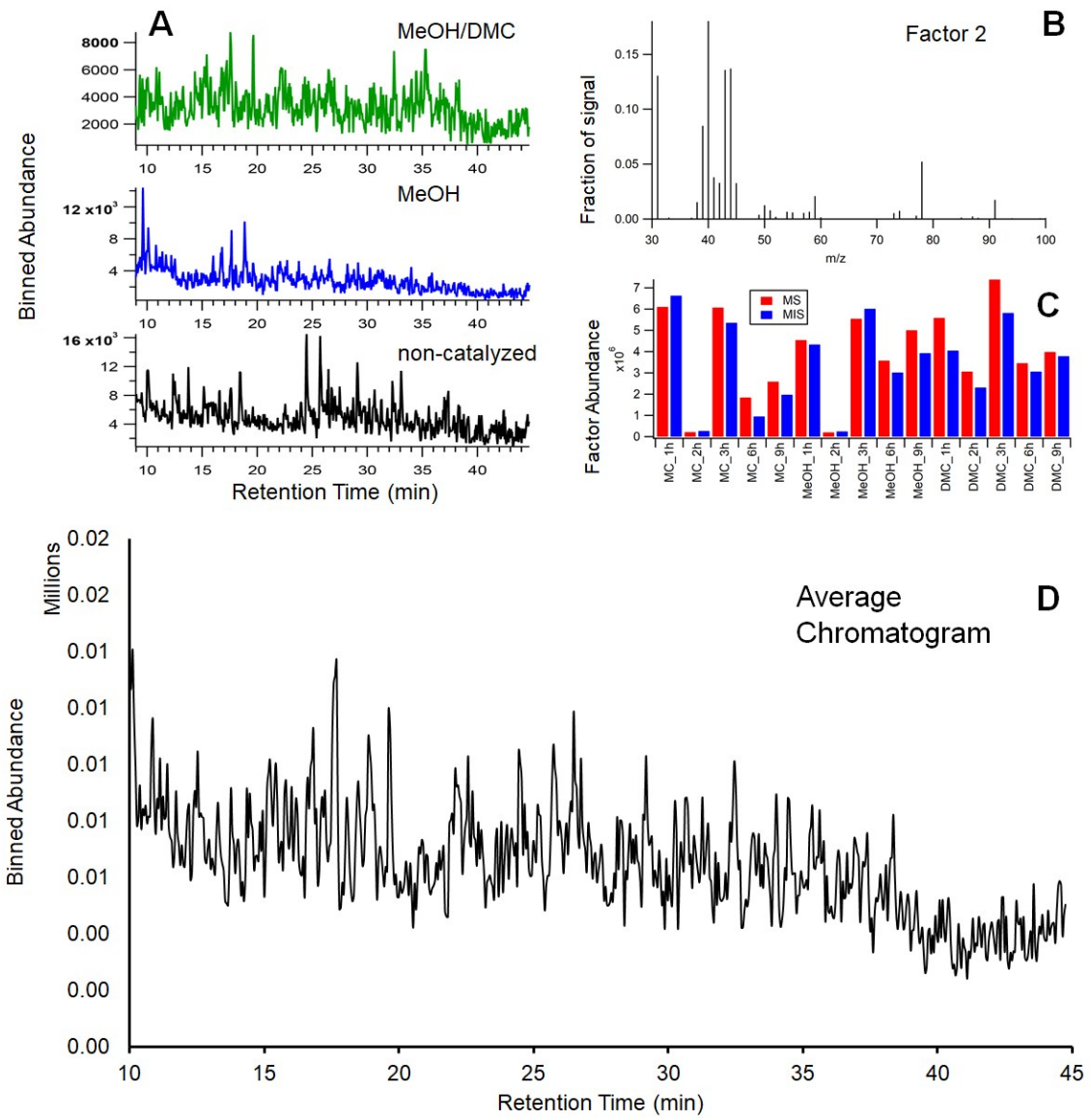

Figure S3. Factor 2 is defined by compounds that generate mass spectral fragments that are air and light molecular weight contaminates (13-factor solution). A) PMF-reconstructed Factor 2 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 2 mass spectrum. C) Factor 2 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 2 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 2 average chromatograms for product samples from the combination of all reaction conditions.

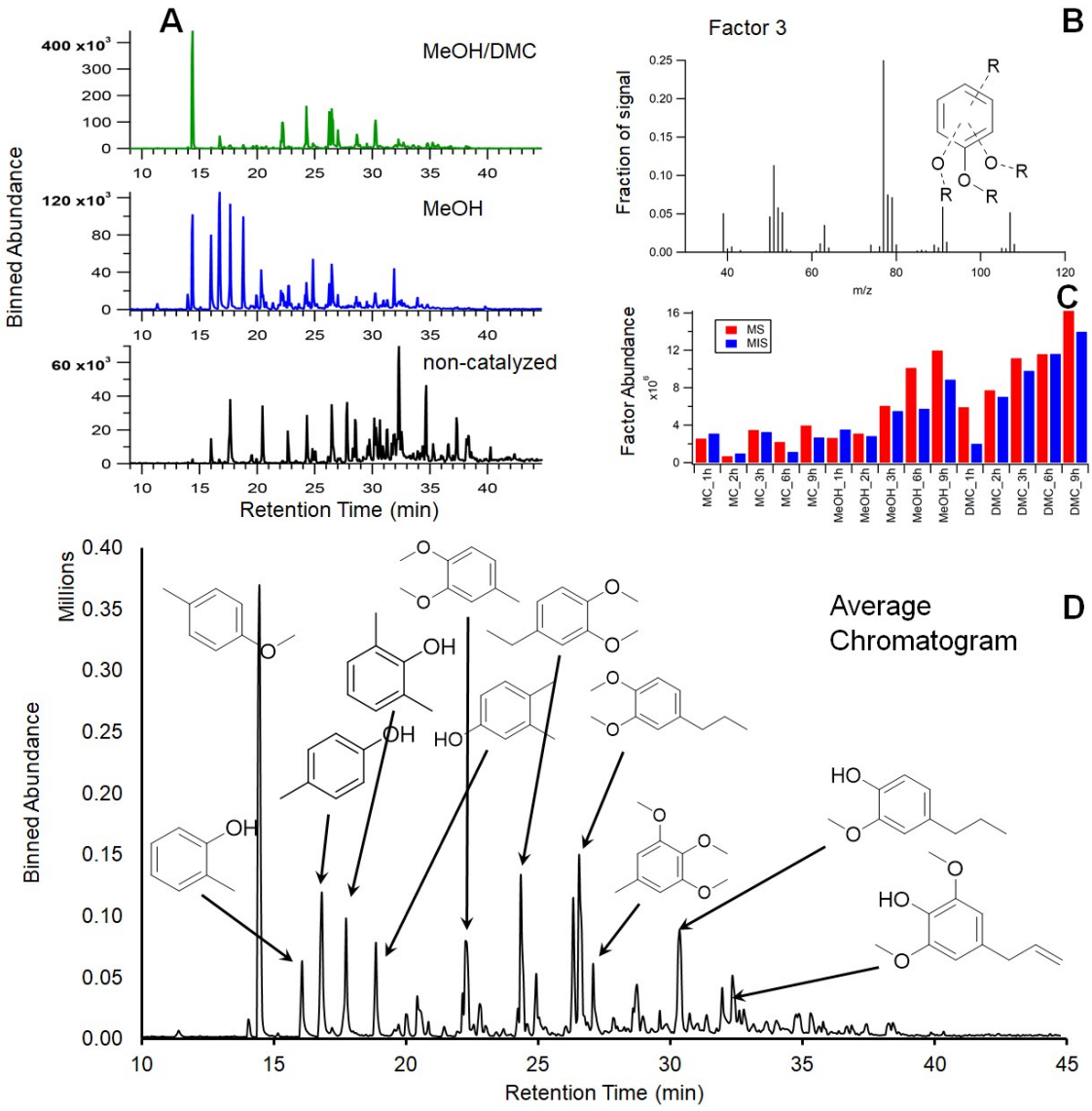

Figure S4. Factor 3 is defined by compounds that generate mass spectral fragments that are less polar and/or more volatile aromatics (13-factor solution). A) PMF-reconstructed Factor 3 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 3 mass spectrum. C) Factor 3 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 3 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 3 average chromatograms for product samples from the combination of all reaction conditions. Individual compound structures identified in (D) were verified by Palisade Complete Mass Spectral Database mostly with more than 90 % matching.

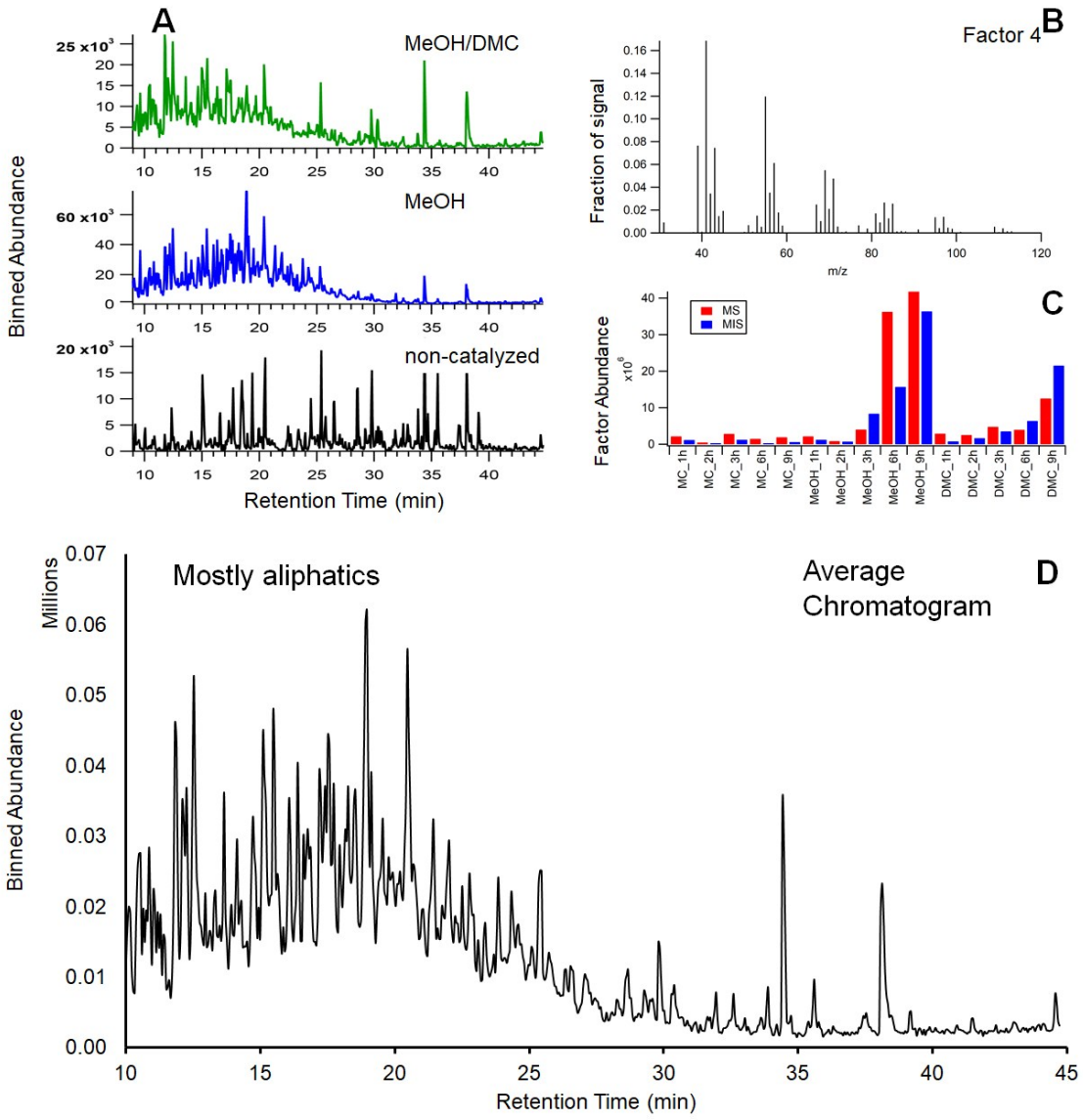

Figure S5. Factor 4 is defined by compounds that generate mass spectral fragments that are aliphatics (13-factor solution). A) PMF-reconstructed Factor 4 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 4 mass spectrum. C) Factor 4 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 4 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 4 average chromatograms for product samples from the combination of all reaction conditions. Individual compound structures identified in (D) were verified by Palisade Complete Mass Spectral Database with average 56 % matching.

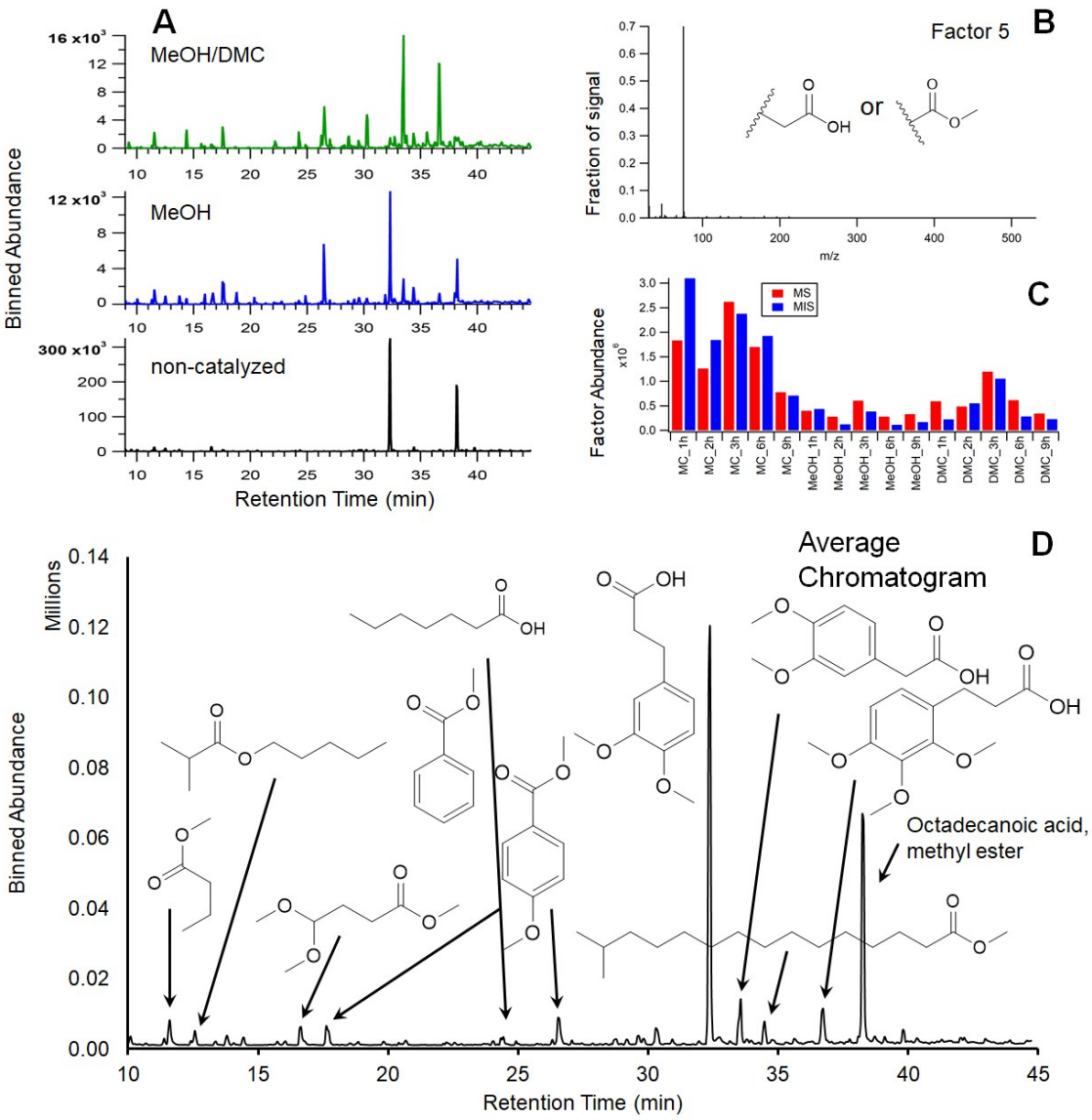

Figure S6. Factor 5 is defined by compounds that generate mass spectral fragments that are carboxylates (13-factor solution). A) PMF-reconstructed Factor 5 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 5 mass spectrum. C) Factor 5 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 5 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 5 average chromatograms for product samples from the combination of all reaction conditions. Individual compound structures identified in (D) were verified by Palisade Complete Mass Spectral Database mostly with more than 90 % matching.

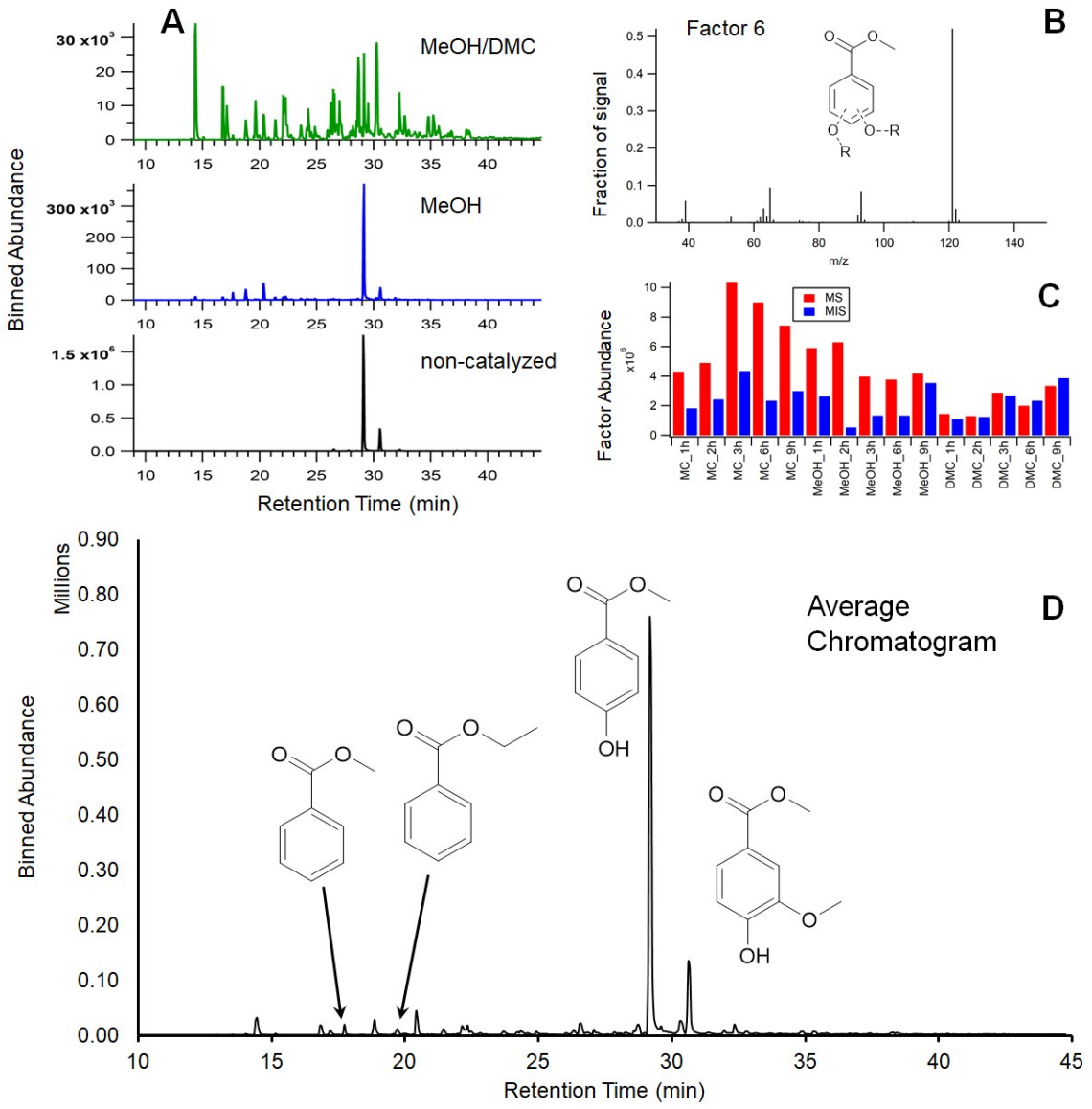

Figure S7. Factor 6 is defined by compounds that generate mass spectral fragments that are benzoates (13-factor solution). A) PMF-reconstructed Factor 6 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 6 mass spectrum. C) Factor 6 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 6 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 6 average chromatograms for product samples from the combination of all reaction conditions. Individual compound structures identified in (D) were verified by Palisade Complete Mass Spectral Database mostly with more than 90 % matching.

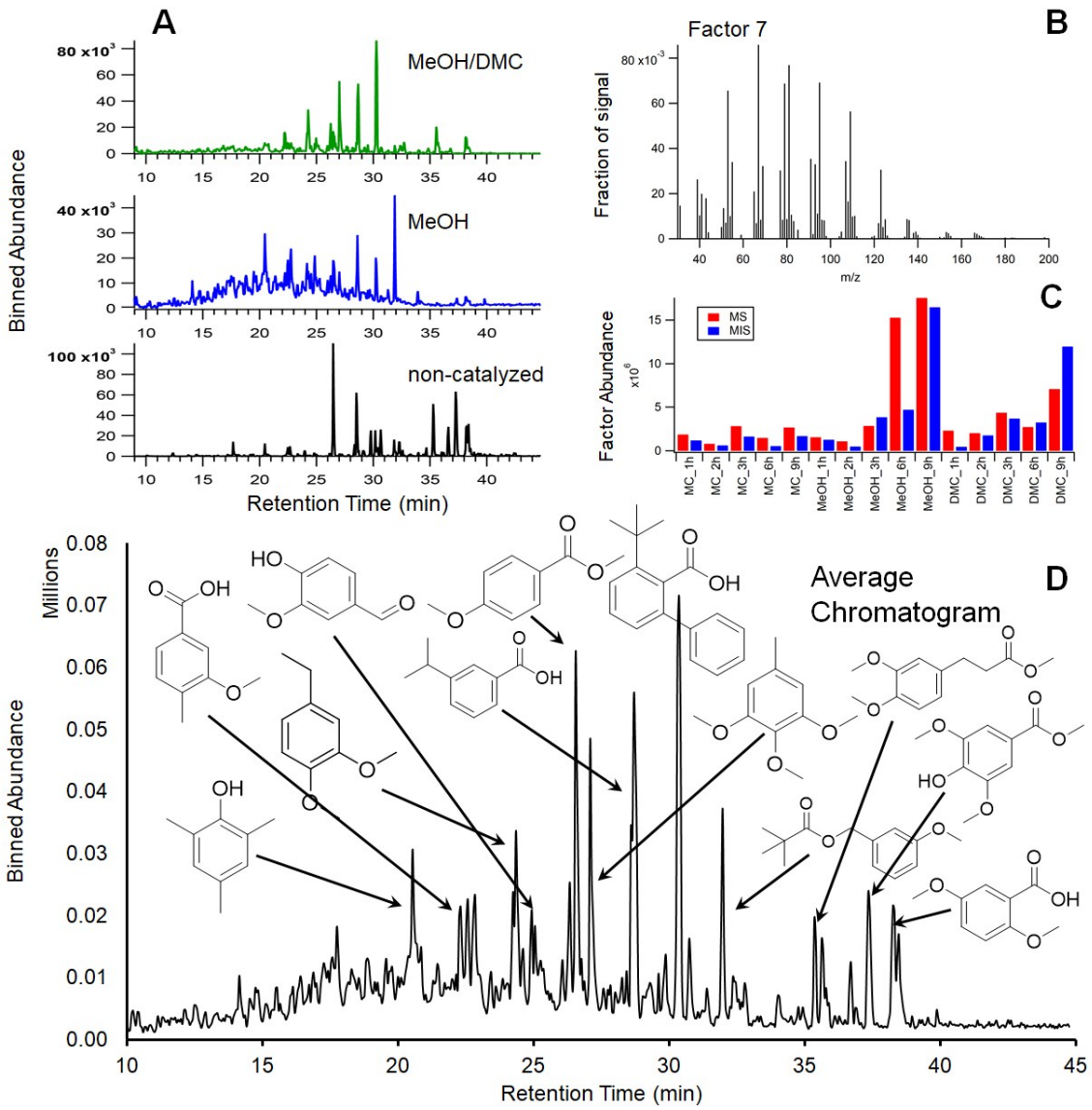

Figure S8. Factor 7 is defined by compounds that generate mass spectral fragments that are more polar and/or less volatile aromatics (13-factor solution). A) PMF-reconstructed Factor 7 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 7 mass spectrum. C) Factor 7 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 7 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 7 average chromatograms for product samples from the combination of all reaction conditions. Individual compound structures identified in (D) were verified by Palisade Complete Mass Spectral Database mostly with more than 70 % matching.

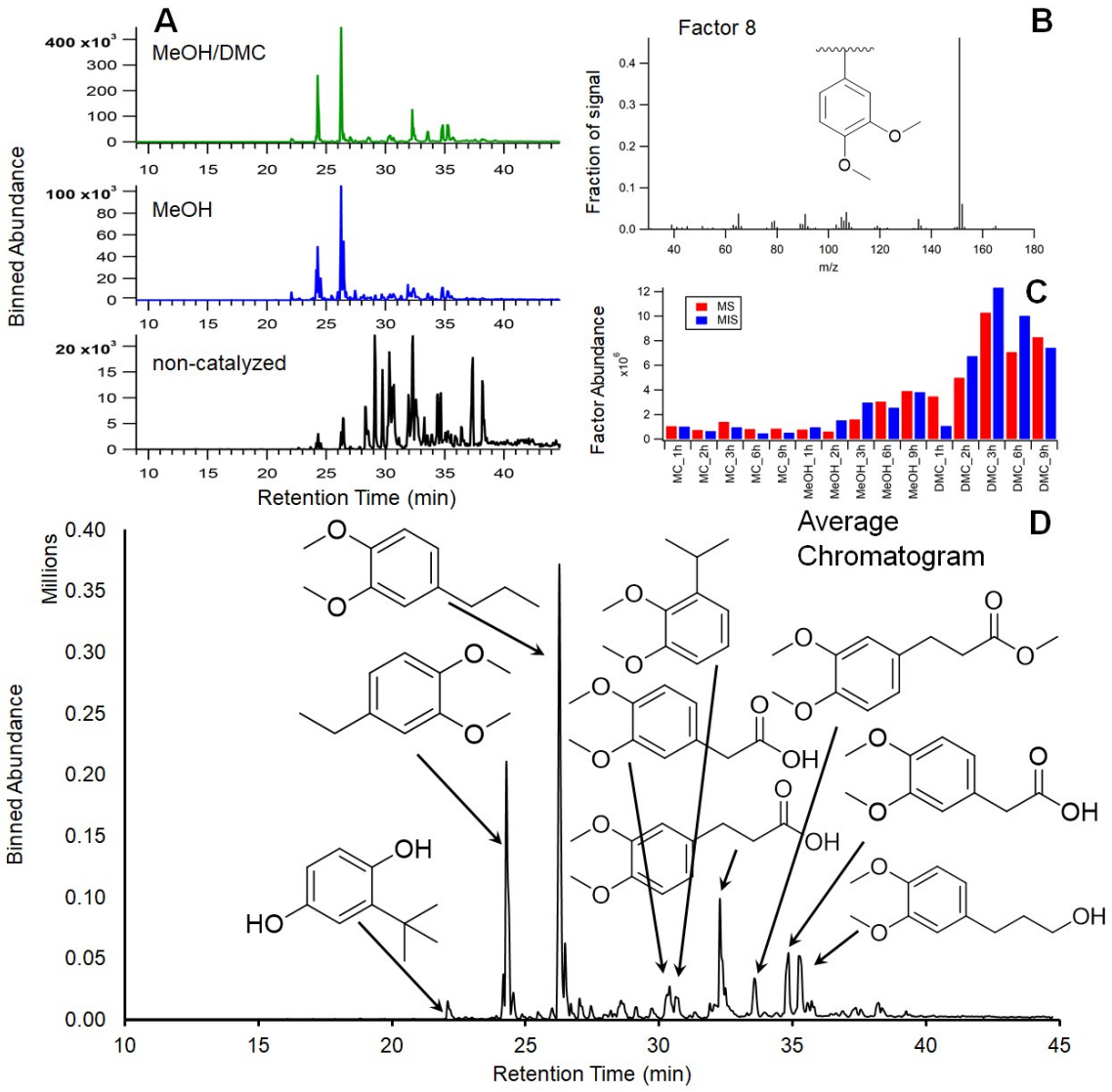

Figure S9. Factor 8 is defined by compounds that generate mass spectral fragments that are dimethoxy benzyls (13-factor solution). A) PMF-reconstructed Factor 8 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 8 mass spectrum. C) Factor 8 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 8 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 8 average chromatograms for product samples from the combination of all reaction conditions. Individual compound structures identified in (D) were verified by Palisade Complete Mass Spectral Database mostly with more than 90 % matching.

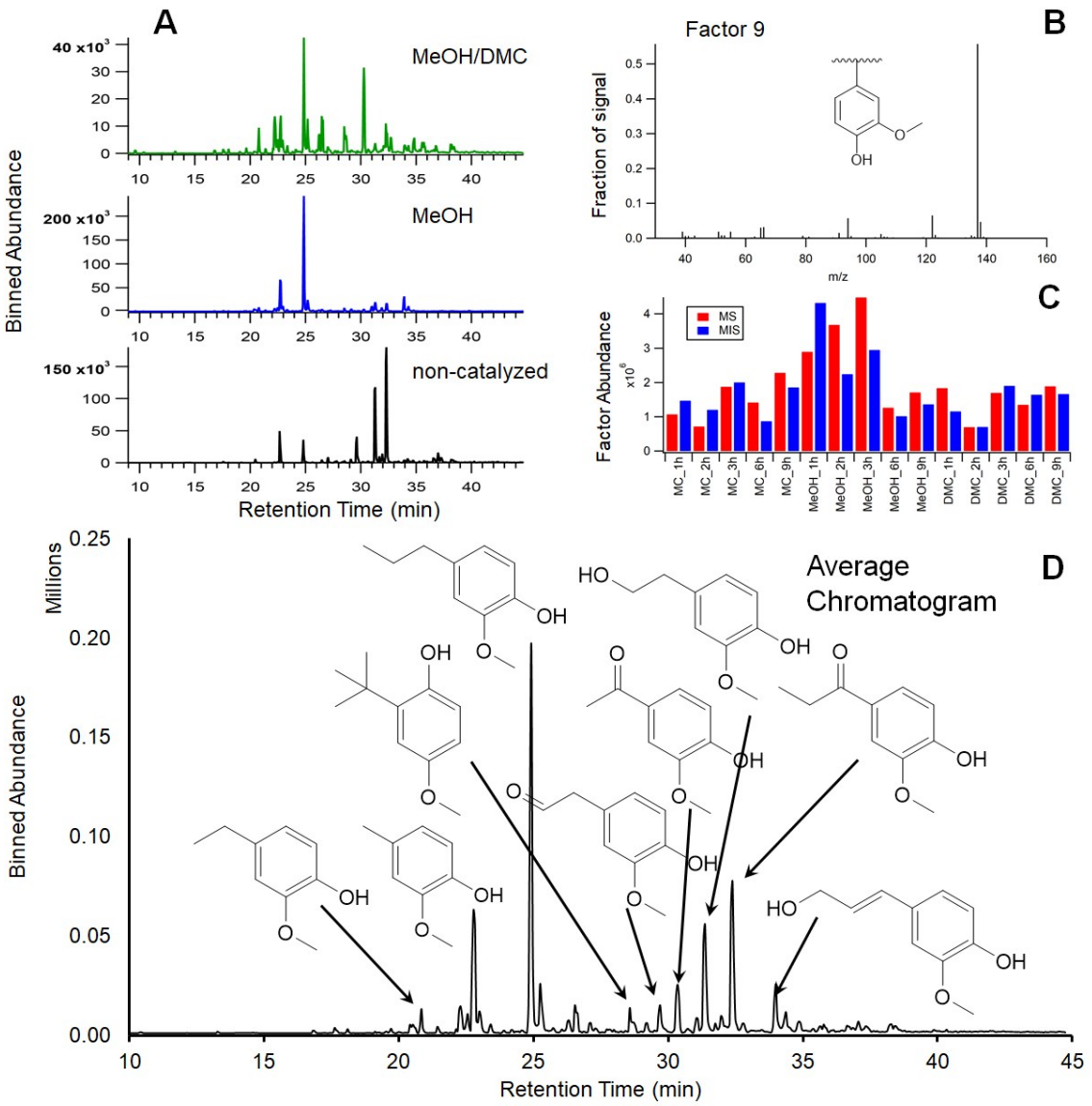

Figure S10. Factor 9 is defined by compounds that generate mass spectral fragments that are methoxy phenyls (13-factor solution). A) PMF-reconstructed Factor 9 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 9 mass spectrum. C) Factor 9 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 9 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 9 average chromatograms for product samples from the combination of all reaction conditions. Individual compound structures identified in (D) were verified by Palisade Complete Mass Spectral Database mostly with more than 90 % matching.

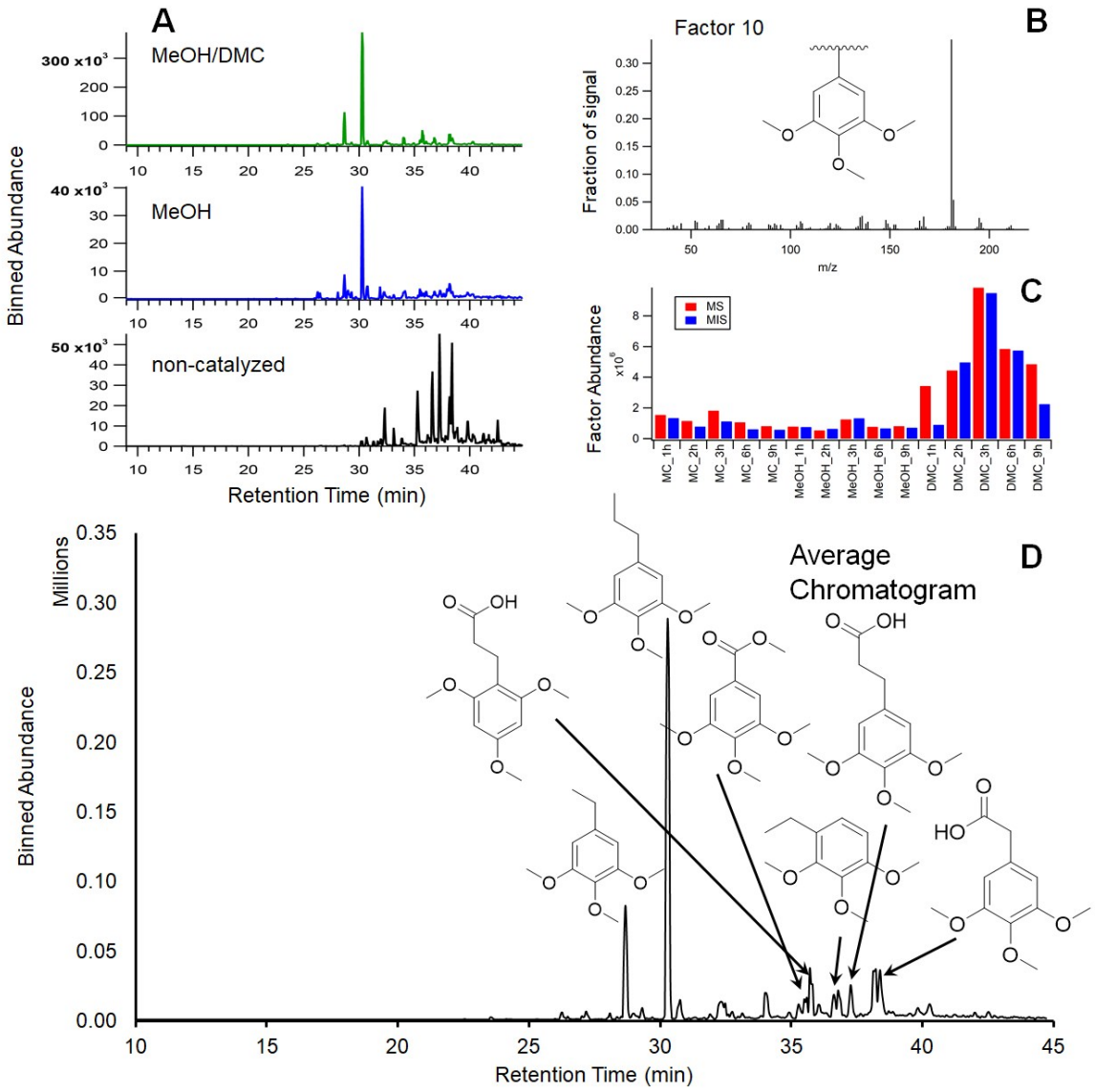

Figure S11. Factor 10 is defined by compounds that generate mass spectral fragments that are trimethoxy benzyls (13-factor solution). A) PMF-reconstructed Factor 10 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 10 mass spectrum. C) Factor 10 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 10 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 10 average chromatograms for product samples from the combination of all reaction conditions. Individual compound structures identified in (D) were verified by Palisade Complete Mass Spectral Database mostly with more than 90 % matching.

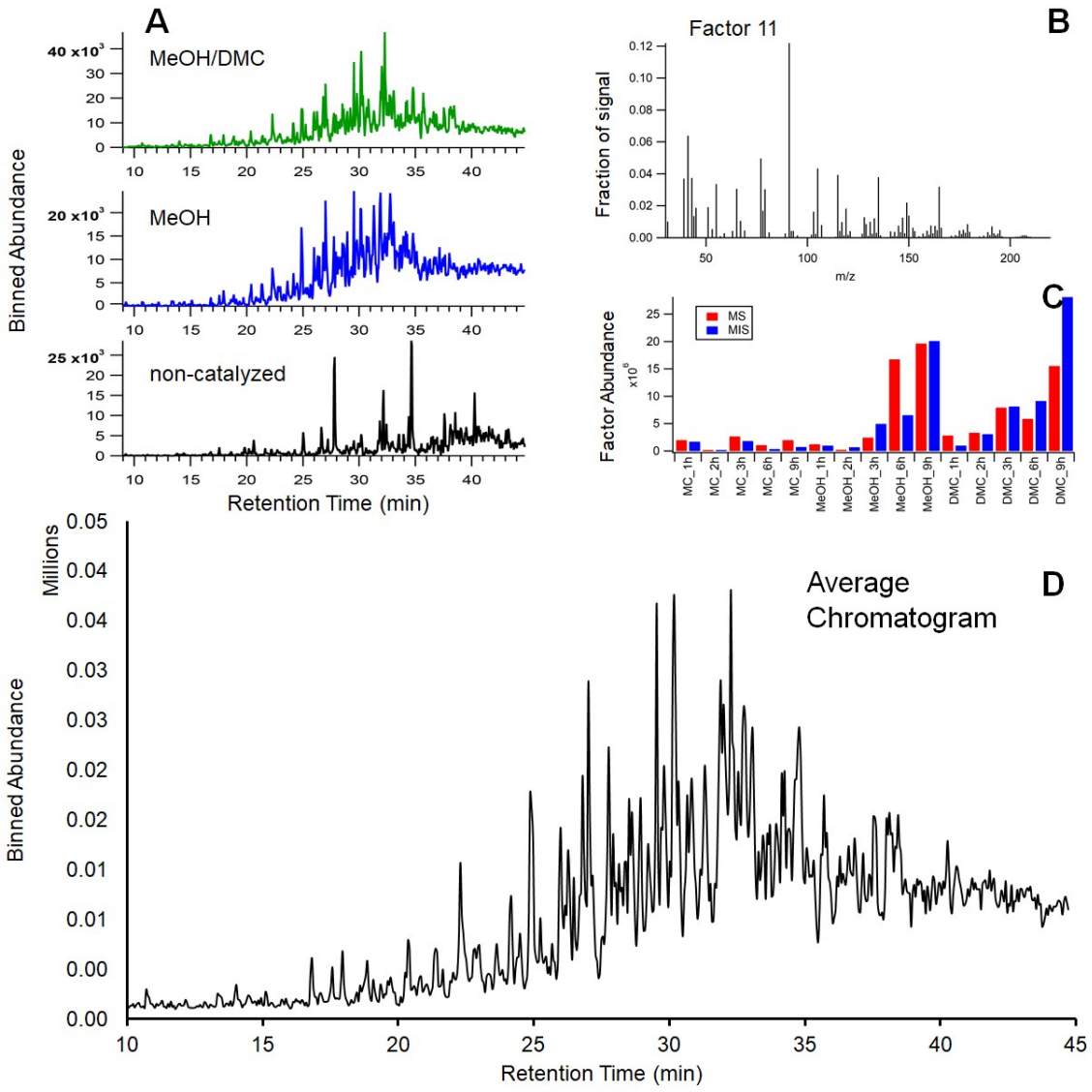

Figure S12. Factor 11 is defined by compounds that generate mass spectral fragments that are unresolved complex mixtures (13-factor solution). A) PMF-reconstructed Factor 11 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 11 mass spectrum. C) Factor 11 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 11 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 11 average chromatograms for product samples from the combination of all reaction conditions.

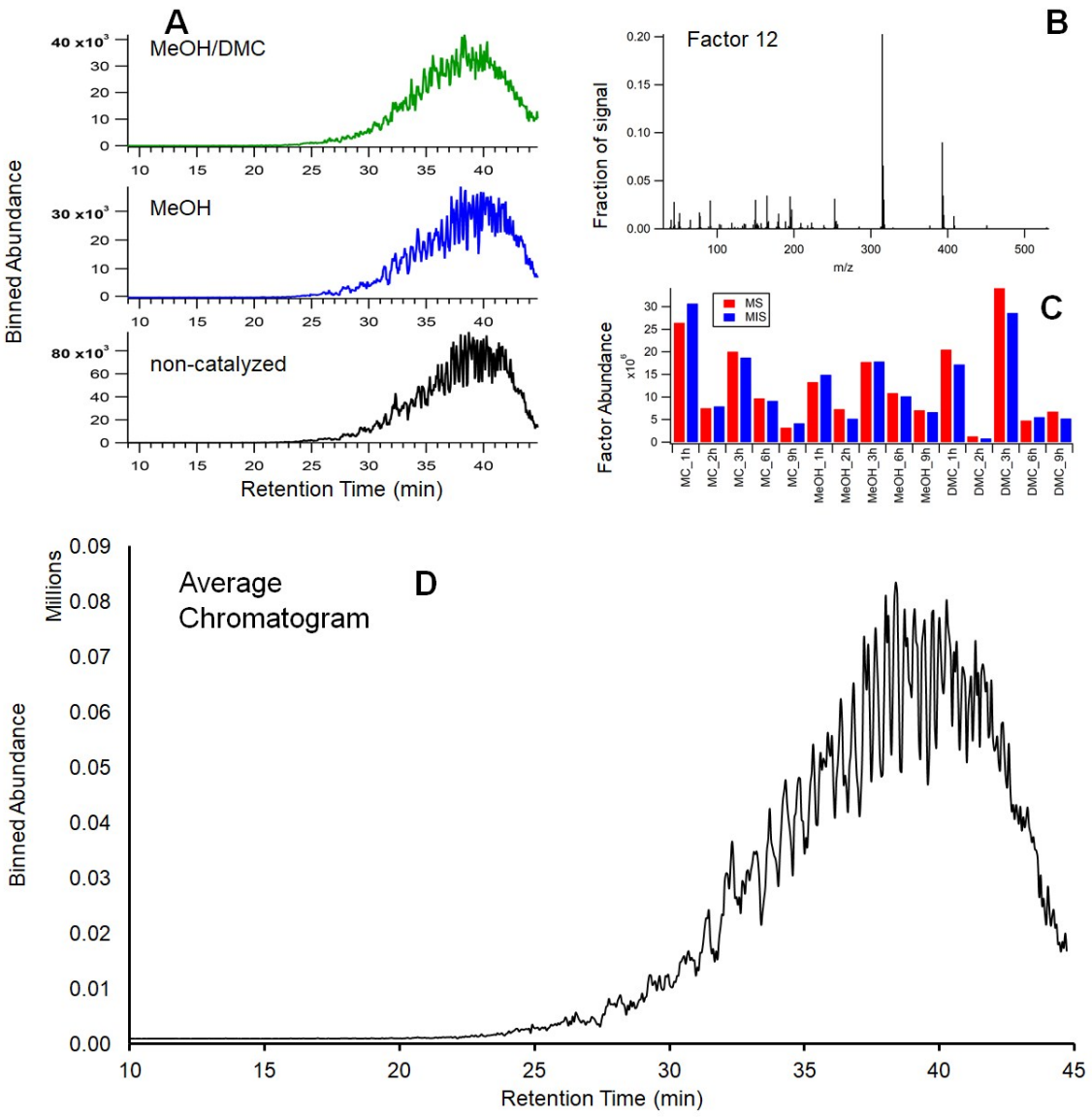

Figure S13. Factor 12 is defined by compounds that generate mass spectral fragments that are column bleed residues (13-factor solution). A) PMF-reconstructed Factor 12 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 12 mass spectrum. C) Factor 12 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 12 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 12 average chromatograms for product samples from the combination of all reaction conditions.

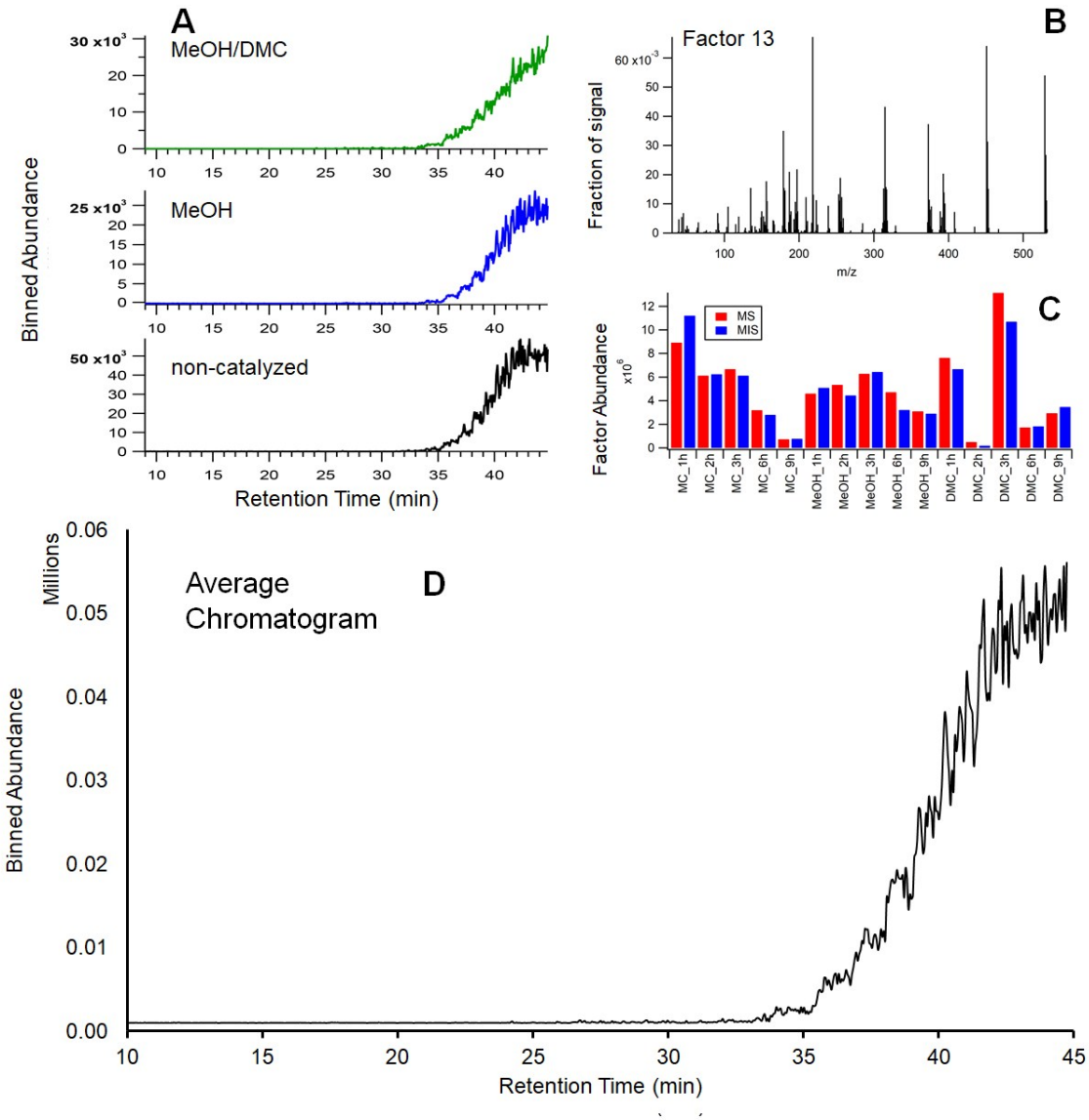

Figure S14. Factor 13 is defined by compounds that generate mass spectral fragments that are column bleed residues (13-factor solution). A) PMF-reconstructed Factor 13 average chromatograms for product samples from catalyzed reactions in MeOH/DMC (green), catalyzed reactions in MeOH (blue), and non-catalyzed reactions in MeOH (black). B) The Factor 13 mass spectrum. C) Factor 13 abundance in the product samples generated from non-catalyzed reactions in MeOH (MC), catalyzed reactions in MeOH (MeOH), and catalyzed reactions in MeOH/DMC (DMC) each undergoing reaction for 1, 2, 3, 6, and 9 h. The Factor 13 abundance is shown for the product generated from methanol-soluble (MS; red) and methanol-insoluble (MIS; blue) fraction of lignin extracted from a hybrid poplar biomass source. D) PMF-reconstructed Factor 13 average chromatograms for product samples from the combination of all reaction conditions.

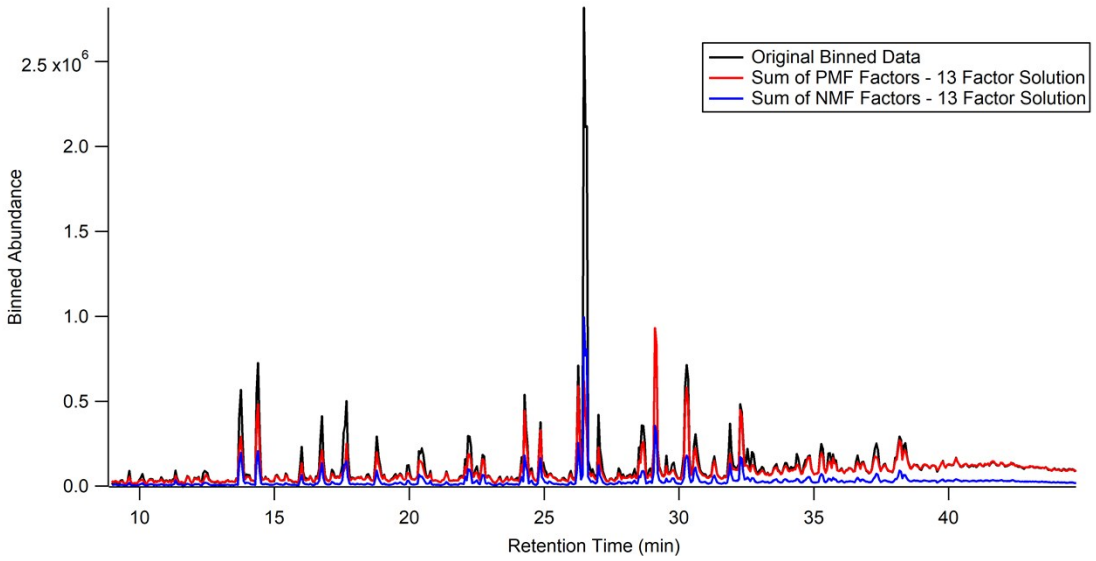

Figure S15. Average TIC for all 30 binned chromatograms (black, i.e. input data for factor analysis), the summed chromatograms resulting from the 13 factor PMF solution (red), and the summed chromatograms resulting from the 13 factor NMF solution (blue).

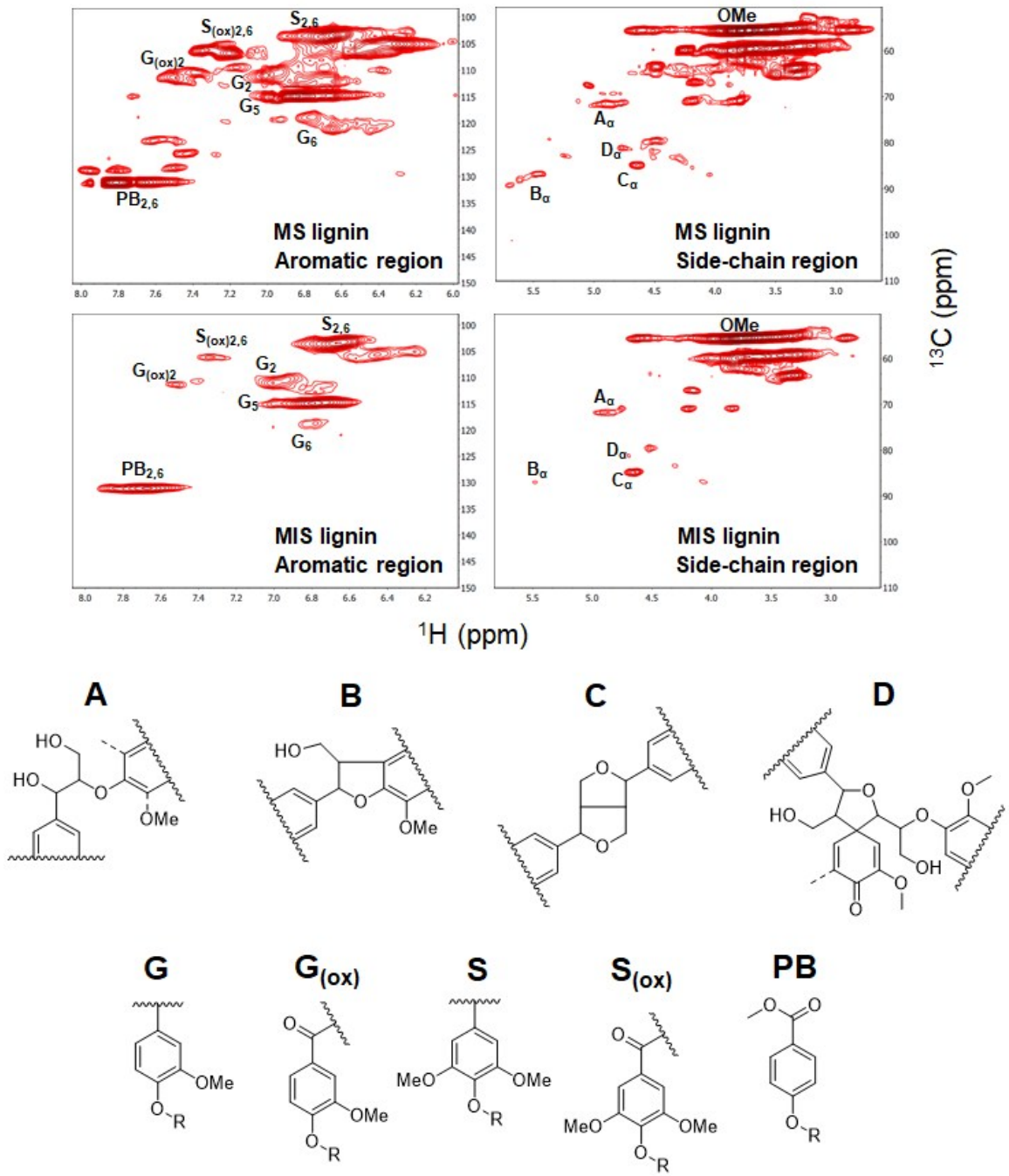

Figure S16. ^{13}C ^{1}H HSQC NMR spectra of untreated MS and MIS lignin: (A) β–O–4′ aryl ether, (B) phenylcoumaran, (C) resinol, and (D) spirodienone linkages; (OMe) methoxyl groups; and (S) syringyl, (G) guaiacyl, (S_{ox}) α-oxidized syringyl, (G_{ox}) α-oxidized guaiacyl, (H) *p*-hydroxyphenyl, and (PB) *p*-hydroxybenzoate monomers.

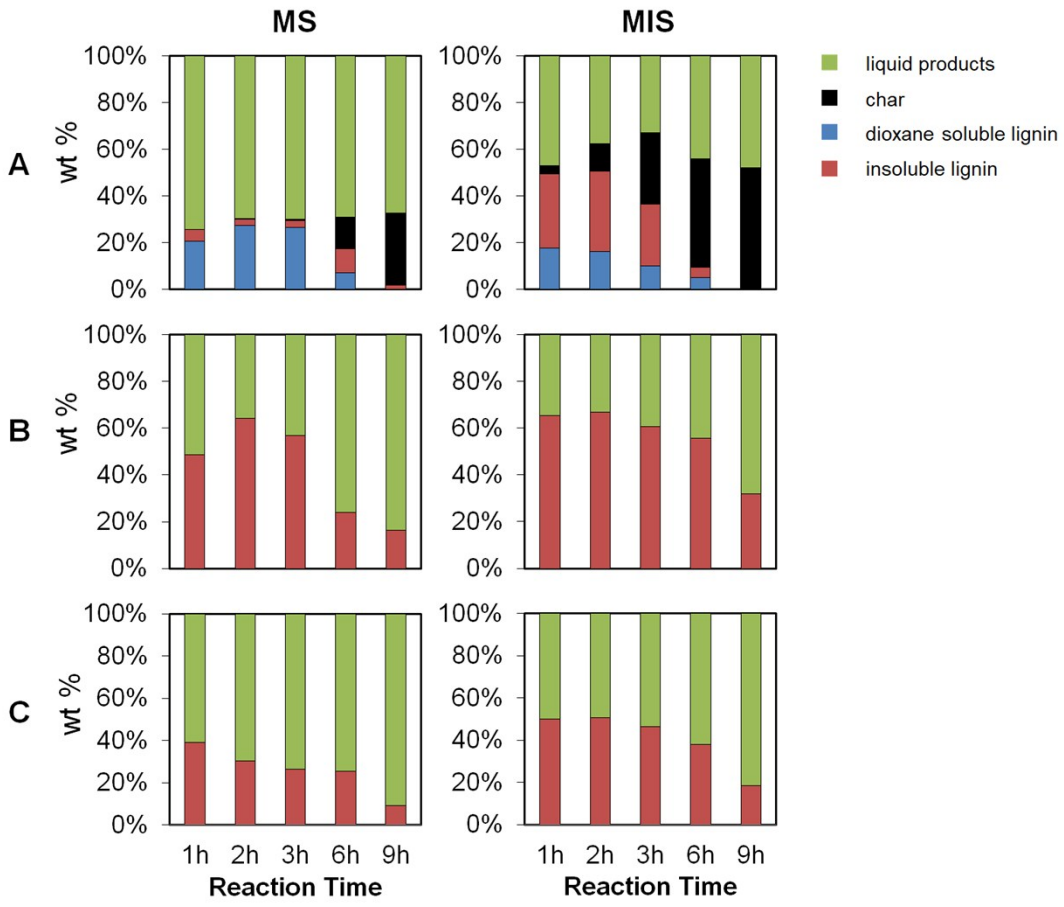

Figure S17. Carbon balance of all liquid and solid products from MS/MIS lignin depolymerization for non-catalyzed (A), MeOH (B), and MeOH/DMC (C) conditions for 1-9 h.

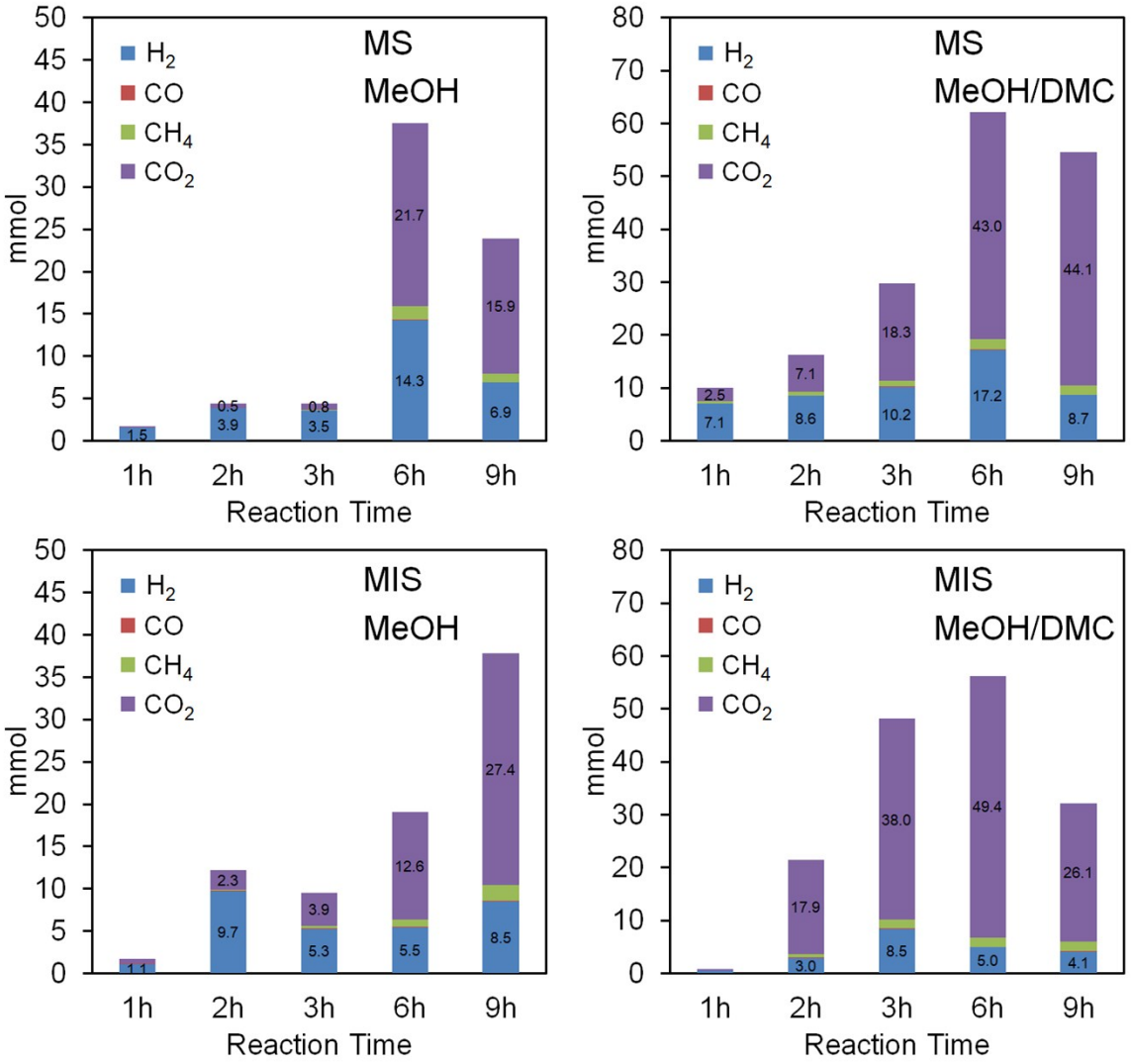

Figure S18. Yields of gas in mmol from MS/MIS lignin depolymerization in non-catalyzed, MeOH, and MeOH/DMC conditions for 1-9 h.

Tables.

Table S1. GC-MS detected peak assignments for compounds in samples from MS/MIS lignin depolymerization in non-catalyzed, MeOH, and MeOH/DMC conditions for 1-9 h. Assignments are based on mass spectral database searches using the Palisade Complete Mass Spectral Database (600 K edition, Palisade Mass Spectrometry, Ithaca, NY)

Number	Compound List	Retention Time (min)	Matching %
1	hydroxy acetic acid methyl ester	2.21	63
2	1-propanol	2.267	90
3	1-butanol	2.385	18
4	formic acid ethyl ester	2.396	28
5	2-butanol	2.561	83
6	2,2-dimethoxy propane	2.7	86
7	tetrahydro-6,6-dimethyl-2H-Pyran-2-one	2.836	78
8	1-butanol	2.857	83
9	3-buten-1-ol	2.965	68
10	1-ethoxy-2-propanol	3.18	78
11	2-methoxy ethanol	3.351	81
12	benzoic acid, 3-pyridyl ester	3.652	23
13	1,2-butylene glycol	3.845	72
14	trimethoxy methane	4.296	78
15	3-methoxy-1-butanol	4.393	72
16	3-pentanol	4.415	74
17	3-heptanol	4.457	45
18	2,2-dimethyoxybutane	4.51	76
19	2-methylbutan-1-ol	4.682	59
20	2-(2-methoxyethoxy) ethanol	4.822	40
21	1,2,3-trimethyl cyclopentene	4.854	93
22	4-methyl-2-pentanone	5.026	64
23	1,4-dioxane	5.06	96
24	toluene	5.423-5.477	94
25	2-(2-ethoxyethaoxy) ethanol	5.61	64
26	alpha-methyl-1,4-benzenedimethanol	5.981	50
27	trans-2,5,5-trimethyl-1,3-hexadiene	6.175	83
28	isopropyl butanoate	6.42	38
29	3,5,5-trimethyl cyclohexene	6.475	43
30	trans-2,5,5-trimethyl-1,3-hexadiene	6.507	49
31	1,3-dimethyl-2-methylene cyclohexane	6.69	43
32	methoxy acetic acid, methyl ester	6.883	86
33	propyl hydrazine	6.905	83
34	3-hexanol	7.141	64

35	1,1-dimethoxy ethane	7.13	78
36	1,2-butanediol	7.152	76
37	5-methyl-3-hexanone	7.227	49
38	1,1-dimethoxy-2-propanone	7.31	93
39	methyl dimethoxyacetate	7.699	9
40	cis-2-methyl-cyclopentanol	7.946	90
41	2-hexen-1-ol	7.989	35
42	xylene	8.249-8.281	88
43	5-methyl-2-(1-methylethyl) cyclohexanol	8.944	53
44	carbamic acid, methyl ester	9.009	43
45	4-methyl -1-heptene	9.127	59
46	1-heptyne	9.138	56
47	1- butanol	9.148	9
48	vinyl-2-(ethoxy)ethyl ether	9.32	45
49	2octyl cyclopropanetetradecanoic acid, methyl ester	9.331	40
50	heptadecane	9.395	50
51	1,1,3-trimethoxypropane	9.535	50
52	cyclohexanol	9.631	76
53	4,5-diethyl-1,2-dimethyl cyclohexene	9.642	83
54	2,5-dimethyl-2-(1-methylethenyl) cyclohexanone	9.653	64
55	cyclohexanol	9.685	50
56	Furfural	10.05	87
57	1,3-pentadiene	10.157	72
58	2,3-dimethyl-3-undecanol	10.372	42
59	1,6-hexanediol	10.383	42
60	pantolactone	10.48	53
61	3-hydroxy-3-methylpent-4-enal	10.49	53
62	3,5-dimethyl cyclohexanol	10.608	38
63	d-siomenthol	10.63	40
64	propane	10.705	4
65	4-pentenal	10.747	59
66	2-methyl cyclohexanol	10.834	95
67	2,6-dimethyl-2-heptanol	10.89	68
68	trans-2-methyl cyclohexanol	11.016	91
69	4-methyl cyclohexanol	11.145	50
70	4-methylcyclohexene	11.242	50
71	methoxy benzene	11.361-11.414	97
72	1-cyclopropyl-2-propen-1-one	11.321	53
73	isopropenyl allyl acetylene	11.381	9
74	1.4-cyclohexanedimethanol	11.457	47
75	1-heptyne	11.542	59
76	trimethoxymethane	11.56	50

77	butanoic acid, 4-methoxy, methyl ester	11.735	64
78	2,2-dimethylcyclohexanone	11.8	64
79	4-methyl-1-heptanol	11.811	50
80	(S)-2-hexen-4-ol	11.832	50
81	3-acetyl-2,6-heptanedione	12.047	53
82	methoxy cyclheptane	12.122	43
83	3-penten-2-ol	12.133	52
84	3,4-dimethylcyclohexanol	12.143	50
85	2,4-dimethylcyclohexanol	12.24	64
86	4-oxo-5-methoxy-2-penten-5-olide	12.39	94
87	3-methylpent-2-ene-1,5-diol	12.466	36
88	4-pentenal	12.466	25
89	3,3-dimethyl cyclohexanol	12.476	46
90	2-methyl propanoic acid pentyl ester	12.51	63
91	1-hexene	12.906	49
92	1-ethoxy-octane	13.067	47
93	2-methyl-3-pentanol	13.174	47
94	E-1,5,9-decatriene	13.271	64
95	1,2-dimethyl-cyclopent-2-enecarboxylic acid	13.464	42
96	2-methyl-1-octene	13.582	47
97	3,3,4-trimethylcyclohexanone	13.593	53
98	4-pentenal	3.603	49
99	phenol	13.79	99
100	1-methoxy-2-methylbenzene	14.012	93
101	2-heptenal	14.022	50
102	phenol acetate	14.087	43
103	2-methyl-2-oxiranyl-cyclobutanone	14.108	53
104	2-methyl-1-buten-3-yne	14.376	53
105	1-methoxy-4-methylbenzene	14.444	99
106	methyl furoate	14.473	38
107	3-methyl cyclohexene	14.677	50
108	1,5-heptadiene	14.806	38
109	1-tetradecanol	15.01	80
110	15-tetracosenoic acid, methyl ester	15.03	80
111	2-hexenal	15.074	59
112	4-pentyn-1-ol	15.106	49
113	4-oxo-pentanoic acid, methyl ester	15.139	80
114	2-ethyl hydrazinecarboxylic acid, methyl ester	15.18	78
115	2-methyl-1-pentene	15.214	46
116	1H-pyrrole-2,5-dione	15.41	39
117	2,3-bis(methylene)-1,4-butanediol	15.439	45
118	1(2-methylbutyl) cyclopentane	15.461	42

119	dodecanal	15.482	47
120	2-ethoxy-2-(2-furyl)ethanol	15.6	43
121	2-isopropyl-5-methyl-1-heptanol	15.622	38
122	bis(2-butoxyethyl) ether	15.76	40
123	2-methyl phenol	16.03	98
124	4-methyl phenol	16.083	97
125	butanedioic acid, dimethyl ester	16.126-16.169	83
126	butanedioic acid, dimethyl ester	16.158	83
127	(2,4,6-trimethylcyclohexyl) methanol	16.255	38
128	2-heptyne	16.341	58
129	3-heptadecenal	16.352	47
130	3,3,5-trimethyl cyclohexanol	16.577	35
131	4,4-dimethoxy-butanoic acid, methyl ester	16.599	48
132	5,5-dimethoxy-3-methyl-2-penten-3-ol	16.61	50
133	4-methylphenol	16.695-16.747	96
134	2,4-dimethylanisole	16.805	96
135	2,3-dimethylanisole	16.846	86
136	4-oxo-pentanoic, ethyl ester	17.08	38
137	p-cumenol	17.157	56
138	heptyl isobutyl ketone	17.189	93
139	3-(1-methylethyl)-phenol	17.21	86
140	1-methyl-1-(2-methyl-2-propenyl) cyclopentane	17.221	68
141	3-cyclopropylcarbonyloxydodecane	17.297	47
142	2-penten-1-ol	17.38	47
143	2-methyl-2-cyclopenten-1-one	17.49	49
144	Benzoic acid, methyl ester	17.576-17.623	98
145	2,6-dimethyl phenol	17.704	97
146	2-methoxy phenol	17.741	96
147	2-methylene cyclohexanol	17.94	70
148	3,3-dimethyl-2-methylene-4,7-oxo-cyclopentane[a]cyclohept-5-ene	18.07	52
149	5-hexyl-2-furaldehyde	18.112	46
150	(1,3-dimethyl-2-methylene-cyclopentyl) methanol	18.145	48
151	9-octadecen-1-ol	18.25	47
152	1-dodecanol	18.37	38
153	3-butyn-1-ol	18.424	62
154	4-cyclohexyl-3-(methoxycarbonyl)-2-methyl-4-butanolide	18.52	50
155	(trimethyl-butyl)-cyclohexane	18.63	56
156	1,3-dioxolane-2-methanol, 2,4-dimethyl	18.714	40
157	3,4-dimethyl phenol	18.81	98

158	2,4-dimethylphenol	18.853	97
159	(methoxymethyl) benzene	18.864	76
160	8-hydroxyocta-1,2-diene-4-one	18.982	50
161	(E)-1-(benzyloxy)-2,3-epoxyocatane	19.09	46
162	1-(2,2-dimethylcyclobutyl)ethanone	19.132	47
163	1-methyl-3-vinyl-3-cyclohexen-1-ol	19.218	43
164	1,4,4-trimethylcyclohexa-2-en-1-ol	19.422	68
165	2-cyclohexen-1-ol, 3,5,5-trimethyl	19.454	47
166	4-methyl benzenemethanol	19.529	47
167	benzoic acid ethyl ester	19.561	86
168	2-ethenyl-2-butenal	19.647	64
169	1-methoxy-4-propyl benzene	19.658	93
170	2-(4-methoxyphenyl)ethanol	19.701	68
171	1-methyl-6-propyl phenol	19.712	80
172	7-[(tetrahydro-2H-pyran-2-yl)oxy]-2-octen-1-ol	19.723	38
173	5-hexyn-1-ol	19.776	42
174	2-methoxy-4-methyl phenol	19.97	99
175	(2S,6S)-(2,6-dimethylcyclihexylidene) methanone	20.012	74
176	1,2-dimethoxy benzene	20.023	97
177	(2S,4S)-5,5-dimethyl-2,4-hexanediol	20.173	14
178	4-methoxy-2-methyl phenol	20.302	76
179	2-ethyl-2,5-dimethylcyclopent-2-enone	20.313	74
180	2,3,4-trimethyl phenol	20.388	98
181	2,6-dimethyl-2,4-heptadiene	20.485	64
182	2-methyl cyclododecanone	20.506	80
183	4-methyl-2-methoxy phenol	20.496-20.540	98
184	1-furyl-1-ethoxy-ethanol	20.657	50
185	methyl-4-pentynoate	20.753	38
186	3,4-dihydroxyacetophenone	20.786	72
187	4-ethyl-2-methoxy phenol	20.807	94
188	2,6,6-trimethyl-1-cyclohexene-1-carboxaldehyde	20.839	58
189	4-hydroxy-benzoic acid methyl ester	21.419	5
190	5,5-dimethyl-1-propyl-1,3-cyclopentadiene	21.891	9
191	endo, exo-3,7-dioxatetracyclodeca-9-ene	21.945	83
192	trans-2-nonadecene	20.968	47
193	2,3,6-trimethyl phenol	21.419	95
194	Cis-4-(tetrahydropyran-2-yloxy)cyclohex-2-enol	21.44	47
195	4-propyl phenol	21.88	74
196	1-formyl-2,2,6-trimethyl-3-cis-(3-methylbut-2-enyl)5-cyclohexene	21.966	46
197	2-(1,1-dimethylethyl)-1,4-benzenediol	22.106	76
198	2-(4-methoxyphenyl)ethanol	22.154	90

199	3,4-dimethoxy toluene	22.224-22.275	99
200	2,4,6-trimethyl phenol	22.299	93
201	3,4-dimethylanisole	22.31	60
202	5-ethoxymethyl furfural	22.4	64
203	2,3,5-trimethyl phenol	22.439	95
204	4 ethyl-4-methyl-2-cyclohexen-1-one	22.492	60
205	3-ethyl guaiacol	22.503-22.514	66
206	1,4-dimethoxy-2-methyl benzene	22.514	87
207	1-(2-furanyl)-3-pentanone	22.535	70
208	2-butynedioic acid, dimethyl ester	22.621	37
209	2-methoxy benzeneethanol	22.718	87
210	4-ethyl-2-methoxy phenol	22.747	98
211	3,4-dimethoxy toluene	22.75	91
212	4-methoxy acetophenone	22.825	72
213	4-ethyl-2-methoxy phenol	22.943	93
214	(2-phenethylcarbamoyl-ethyl)-carbamic acid, benzyl ester	22.965	64
215	ethenyl benzene	23.008	38
216	3,4-diethyl-2,5-dimethyl-2,4-hexadiene	23.029	49
217	3,5-dihydroxy acetophenone	23.34	63
218	2,3,5-trimethyl-1,4-benzenediol	23.351	72
219	4-hydroxy-2,4,5-trimethyl-2,5-cyclohexadien-1-one	23.383	47
220	4-methoxy-1,2-benzenediol	23.394	83
221	2 methoxy-1,4-benzenediol	23.448	78
222	8,8-dimethyl-1,9-diazabicyclo[5.5.0]decane-5,10-dione	23.566	82
223	4-methyl-2-propylphenol	23.63	81
224	2-methylocta-2,4,6-trienedial	23.652	64
225	methyl-8-oxooctanoate	23.759	35
226	2-(2-methyl-2-propenyl)cyclohexanone	23.834	68
227	1-cyclohexene-1-carboxylic acid	24.006	43
228	1,4-dimethoxy-2,3-diemthylbenzene	24.188	86
229	4-ethyl-1,2-dimethoxy phenol	24.307	99
230	2-methoxy-4-vinylphenol	24.348	97
231	heptanoic acid	24.5	64
232	1,4-dimethoxy-2,3-dimethylbenzene	24.535	92
233	5-Allyl-6-methyl-3,3a,4,6-tetrahydropyrolo[3,4-c]isoxazole	24.543	83
234	2-(3-methyl-2-butenylidene)cyclohexanone	24.586	64
235	2-methoxy-4-ethyl-6-methyl phenol	24.596	86
236	2-methoxy-4-propyl phenol	24.852-24.872	96

237	2-methyl-5-(1-methylethyl) phenol	24.876	93
238	2,3,5,6-tetramethyl phenol	24.994	89
239	1,2,3-trimethoxy benzene	25.015	97
240	Cis-1-hydroxy-2-methoxy-4-propenyl benzene	25.079	64
241	5-methylnicotinic acid	25.187	59
242	2-methoxy-4-propyl phenol	25.23	87
243	2-methoxy-4-propyl phenol	25.262	76
244	1-(3,4-dimethoxyphenyl) ethanone	25.283	72
245	8-oxa-9-azabicyclo[3.2.2]non-6-ene	25.316	43
246	cyclotetradecane	25.348	46
247	cis-1-ethyl-2-methyl cyclopentane	25.4	76
248	2,3-dimethyl-4-methoxy phenol	25.477	64
249	5-methoxy-2,3,4-trimethyl phenol	25.53	64
250	4-(3-hydroxy-1-propenyl)-2-methoxy phenol	25.595	59
251	hexanoic acid	25.67	52
252	4-D-2-methyl-3-pentanol	25.745	53
253	4,4-dimethyl heptanedioic dimethyl ester	25.83	86
254	3,4-dimethoxy propiophenone	25.981	53
255	1-(2,4-dihydroxy-3-propylphenyl)ethanone	25.992	83
256	3,4-dimethoxy propiophenone	26.014	52
257	1-(2-hydroxy-5-methoxy-4-methylphenyl) ethanone	26.067	43
258	1,4-dimethoxy-2,3,5-trimethyl benzene	26.164	74
259	1,2,3-trimethoxy benzene	26.196	86
260	1,2-dimethoxy-4-n-propyl benzene	26.28-26.322	98
261	2,6 dimethoxy phenol	26.538	97
262	4-methoxybenzoic acid, methyl ester	26.497-26.552	99
263	3-methoxychromene	26.679	62
264	5-methoxy-2,3,4-trimethyl phenol	26.7	80
265	5-hepten-3-yn-2-ol, 6-methyl-5-(1-methylethyl)	26.711	76
266	1-(2-hydroxy-6-(methoxymethyl)phenyl) ethanone	26.829	52
267	ethyl-2-methyl-5-cyanopenta-2,4-dienoate	26.862	50
268	4-(2-methyl-cyclohex-1-enyl)-but-3-en-2-one	26.904	46
269	2-methoxy-5-(2'hydroxyethyl) phenol	27.055	57
270	1,2,3-trimethoxy-5-methyl benzene	27.093	99
271	1,2-dimethyl-2-(1-naphthyl) cyclopropane	27.184	72
272	5-ethyl-1,2,3-trimethoxy benzene	27.194	50
273	di-t-butyl phenol	27.216	60
274	8,8-dimethyl-1,9-diazabicyclo[5.3.0]decane-5,10-dione	27.248	80
275	1,2-dimethoxy-4-n-propyl benzene	27.463	66
276	anisaldehyde dimethyl acetal	27.509	52
277	1-methyl-2-(phenylmethyl) benzene	27.527	52

278	2-hydroxy-5-methoxy benzaldehyde	27.699	52
279	Isopropylidenecyclobutenone	27.742	50
280	3,4-dimethoxy propiophenone	27.774	68
281	2-(phenylethynyl) phenol	27.785	72
282	2-methoxy-4-(1-propenyl) phenol	27.836	96
283	1-(2,4-dimethoxyphenyl)-1-propanone	27.957	81
284	3,4-diethoxy benzaldehyde	28.021	47
285	4-methoxybenzoic acid, ethyl ester	28.107	94
286	5-methoxy-2,3,4-trimethyl phenol	28.182	94
287	4-methoxy-2,4,6-trimethyl cyclohexa-2,5-dienone	28.204	74
288	4-hydroxy-3-methoxy benzaldehyde, vanillin	28.364	98
289	m-isopropylbenzoic acid	28.418	49
290	(1,1-dimethylethyl)-4-methoxy-phenol	28.547	87
291	1,2,3-trimethoxy benzene	28.59	83
292	2,6-dimethoxy-4-methyl phenol	28.611	95
293	5-ethyl-1,2,3-trimethoxy benzene	28.676	98
294	5-ethyl-1,2,3-trimethoxybenzene	28.729	98
295	3-[3,4-(methylenedioxy)phenyl]propan-1-ol	28.88	78
296	methyl 3-methoxy-4-methyl benzoate	28.901	87
297	(5R0-1-methyl-5-(1-methyl-1-ethenyl)2,3-diazabicyclo[3.3.0.]octane	28.966	53
298	1,2-dimethyl-4-(phenylmethyl) benzene	29.02	50
299	4-hydroxylbenzoic acid, methyl ester	29.152	98
300	3-hydroxy benzoic acid, methyl ester	29.233	87
301	methyl-3-(5-acetyl-2-tienyl)-2-propenoate	29.298	53
302	(2-methoxyethoxy) benzene	29.417	32
303	4-(1,1-dimethylethyl) benzenemethanol	29.545	87
304	homo-vanillin (4-hydroxy-3-methoxy-phenyl) actaldehyde	29.653	72
305	3-isopropyl-1,2-dimethoxybenzene	29.717	82
306	3,4-dimethoxy benzaldehyde	29.797	96
307	trans-methyl iso-eugenol	29.814	95
308	1-(2-ethenyl-1-cyclohexenyl)-2-methyl-2-propen-1-ol	30.05	35
309	1,2,3,4-tetrahydro-9-propyl anthracene	30.173	52
310	2-ethoxy-3,4,6,7,8,9-hexahydro-8,8-dimethyl-6-oxo-2H-chromene	30.19	59
311	4-ethyl syringol	30.2	91
312	tert-butyl biphenyl carboxylic acid	30.254	89
313	1,2,3-trimethoxy-5-propylbenzene	30.28-30.332	96
314	1-(4-hydroxy-3-methoxyphenyl) ethanone, acetovanillone	30.393	96
315	methyl 3-(5-formyl-2-furyl_)-2-propenoate	30.404	43
316	3,4-dimethoxy benzeneacetic acid	30.415	87

317	3-(3,4-dimethoxyphenyl) propionic acid	30.479	58
318	4-hydroxybenzoic acid, methyl ester	30.594	98
319	1,3-dimethoxy-2-(prop-2-enyl) benzene	30.683	60
320	4-hydroxy-3-methoxybenzoic acid, methyl ester	30.701	97
321	propio-syringone	30.768	62
322	3,5-bis(1-methylethyl) phenol	30.823	64
323	2-methoxy benzoic acid ethyl ester	30.941	87
324	4-(ethoxymethyl)-2-methoxy phenol	30.995	38
325	2-hydroxy-5-methoxy benzaldehyde	31.199	51
326	Homovanillyl alcohol	31.287	96
327	2-methoxy-4-propyl-phenol	31.338	90
328	3,4-diethoxy benzaldehyde	31.349	53
329	2-(2,5-dimethoxy-phenyl) propionaldehyde	31.36	49
330	3,4-diethoxy benzaldehyde	31.392	46
331	4-vinyl syringol	31.692	64
332	2-acetyl-3,6-dimethyl benzoic acid	31.821	49
333	4-propyl syringol	31.864	86
334	syringyl aldehyde	31.908	89
335	3-methoxybenzyl-2,2-dimethyl propanoate	31.918	64
336	ethyl vanillate	31.982	47
337	1-(2,5-dimethoxy-4-methylphenyl)-2-propanone	32.047	46
338	trans-isoelemicin	32.058	76
339	1,2,3-trimethoxy-5-(2-propenyl) benzene	32.111	95
340	2,6-dimethoxy-4-(2-propenyl) phenol	32.197	68
341	3-(3,4-dimethoxyphenyl) propionic acid	32.294	53
342	2,2-dimethoxyethoxy benzene	32.336	78
343	3-(3,4-dimetoxyphenyl)propionic acid	32.347	49
344	(7,7-dimethyl-1-oxo-2,3,4,5,6,7-hexahydro-1H-inden02-yl)acetic acid, ethyl ester	32.42	50
345	benzofuran-4(5H)-one, 6,7-dihydro-, oxime	32.433	48
346	4-hydroxy-3-methoxy benzoic acid, methyl ester	32.476	48
347	2-(2,4,5-trimethylphenyl)propylene oxide	32.573	93
348	4-hydroxy-3-methoxy propiophenone	32.585	96
349	3,4-dimethoxy benzoic acid, methyl ester	32.734	92
350	2-(1,1-dimethyl-2-propenyl)-3,6-dimethyl pehnol	32.734	76
351	3,4-dimethoxybenzoic acid, methyl ester	32.767	98
352	2-phenoxyethyl-beta-pehnylpropionate	32.809	48
353	2,6-dimethoxy benzoic acid, methyl ester	33.077	93
354	1,2,4-triethyl-5-methyl benzene	33.142	56
355	methyl syringate	33.163	49
356	3,4-dimethoxy benzaldehyde	33.303	47
357	6-methoxy-2,2-dimethyl-1-indanone	33.313	38
358	(2,2-dimethoxyethyl) benzene	33.464	52

359	trans-4-propenyl syringol	33.496	53
360	alpha, 4-dihydroxy-3-methoxy benzeneacetic acid methyl ester	33.555	87
361	3,4-dimethoxy benzeneacetic acid	33.603	98
362	4-hydroxy-3-methoxy-benzeneacetic acid	33.883	76
363	coniferyl alcohol	33.916	91
364	o-Methylmaleimycin	33.979	68
365	2-(2-formylvinyl)azulene-1-carbaldehyde	34.022	46
366	2,2-diphenylpropionic acid	34.086	52
367	dimethyl 4-(2'-furyl)-1-methyl-2,3-dihydro-1H-indole-6,7-dicarboxylate	34.183	55
368	4-[(4-hydroxy-3-methoxyphenoxy)methyl)]-3-methoxybenzaldehyde	34.263	46
369	4-hydroxy-3-methoxy-phenylacetylformic	34.301	60
370	8-(biphenyl-2-ylmethyl)-5-ethyl-2,3,5,6-tetrahydroimidazo[1,2-a] pyridine	34.333	47
371	tridecanoic acid, methyl ester	34.398	97
372	14-methyl-pentadecanoic acid, methyl ester	34.441	89
373	2,6-dimethoxy-4-(2-propenyl) phenol	34.678	91
374	3-(3,4-dimethoxyphenyl)-1-propanol	34.795	93
375	3,4-dimethoxy benzenepropanol	34.842	86
376	3,4-dimethoxy benzenepropanoic acid, methyl ester	35.246	92
377	3,4-dimethoxy benzenepropanoic acid, methyl ester	35.299	94
378	syringaldehyde	35.309	97
379	hexadecanoic acid, ethyl ester	35.568	99
380	3,4,5-benzoic acid, methyl ester	35.611	94
381	2,5-dimethoxybenzoic acid	35.74	52
382	4-hydroxy-3,5-dimethoxy benzaldehyde	35.793	50
383	2-ethyldiphenyl methane	36.029	34
384	methyl-2-oxo-1-propyl cycloheptanecarboxylate	36.094	38
385	1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone	36.652	96
386	(2,2-dimethoxyethyoxy) benzene	36.695	54
387	(3-methoxyphenyl) carbamic acid, methyl ester	36.802	42
388	3-(2,3,4-trimethoxypehnyl)propionic acid	36.845	50
389	alpha, hydroxy-3-methoxy benzeneacetic acid, methyl ester	37.017	35
390	(Z)-7-phenyl-1,4-heptadien-6-yne	37.168	46
391	4-hydroxy-3,5-dimethoxybenzoic acid, methyl ester	37.305	97
392	syringyl acetone	37.386	92
393	Octadecanoic acid, methyl ester	38.048	95
394	2,5-dimethoxy benzoic acid	38.155	72
395	2,2-dimethoxyethoxy benzene	38.23	76
396	ethyl 4-hydroxyphenylcarbamate	38.4	68
397	o-2-benzimidazolyl phenol	38.584	30

Table S2. List of major characteristic *m/z* values.[1-3]

Characteristic m/z	Factors	Likely Molecular Formula	Fragment Identity
39	1, 3, 6-10	C_3H_3	aromatic
41	4, 11	C_3H_5	aliphatic
45	10	C_2H_5O	aliphatic alcohol
50	1	C_4H_2	aromatic
51	3	C_4H_3	aromatic
52	10	C_4H_4	aromatic
53	7	C_3HO or C_4H_5	aliphatic alcohol or aliphatic
55	4, 9, 11	C_4H_7	aliphatic
63	3	C_5H_3	aromatic
65	1, 6, 8, 9, 11	C_5H_5	aromatic
69	4	C_5H_9	aliphatic
74	1	CH_2=C(OH)OCH	methyl ester
75	5	C_2H5O-C=O+2H[a] or C_2H_5COO+2H[a]	carboxylate or carboxylic
77	3, 11	C_6H_5	aromatic
79	8-10	C_6H_5+2H[a]	aromatic
83	4	C_6H_{11}	aliphatic
91	3, 8	$C_6H_5CH_2$	benzylic
92	10	$C_6H_5CH_2$+H[a]	benzylic
93	1, 6	C_6H_5O	phenolic
94	9	C_6H_5O+H[a]	phenolic
95	7	C_6H_5O+2H[a]	phenolic
97	4	C_7H_{13}	aliphatic
105	9-11	C_6H_5C=O or C_6H_5-CH_2CH_2	benzocarbonyl or ethylbenzyl
107	3, 8	$CH_2C_6H_4OH$ or $C_6H_5CH_2O$	benzylic alcohol or benzylic ether
109	7	C_6H_5-CH_2O+2H[a]	benzylic ether
111	4	C_8H_{15}	aliphatic
119	8	C_6H_5-$C(CH_3)_2$	isopropylbenzyl
121	6	C_6H_5COO	benzoate
122	9	$CH_3OC6H4CH2$	methoxy benzyl
137	9	$CH_3OC_6H_3OHCH_2$	methoxy phenyl
151	8	$(CH_3O)_2C_6H_3CH_2$	dimethoxy benzyl
167	10	$(CH_3O)_2C_6H2OHCH_2$	dimethoxy phenyl
181	10	$(CH_3O)_3C_6H_2CH_2$	trimethoxy benzyl
195	10, 12	$(CH_3O)_3C_6H_2CH_2CH_2$	trimethoxy benzyl

[a]The "+H" notation means that the ion was formed by a rearrangement that involved the transfer of a hydrogen atom from some other part of the molecule.

Table S3. Distribution of hydroxyl group contents (mmol/g) based on quantitative ^{31}P NMR data for untreated MS and MIS lignin.

Sample	Carboxylic acid	Phenolic OH				Total Phenolic OH	Aliphatic OH
		H	C_5 substituted*	G	S		
MS	0.18	0.56	0.16	0.84	2.19	3.75	1.37
MIS	0.01	0.29	0.42	0.53	1.21	2.45	2.15

* C_5 substituted: β-5, 4-O-5, and 5-5 substructures

Table S4. Distribution of carbons functional group contents (percent) based on quantitative ^{13}C NMR data for untreated MS and MIS lignin.

% Carbon	MS	MIS
Aliphatic C	6.51	1.96
Methoxyl-aromatic C	27.0	15.6
Aliphatic C-O	3.17	11.6
Aromatic C-H	15.4	17.3
Aromatic C-C	8.74	26.6
Aromatic C-O	37.8	26.0
Carbonyl C	1.42	0.84

Table S5. GPC detected number-average molecular weight (M_n), weighted-average molecular weight (M_w), and polydispersity index (PDI) of untreated and depolymerized MS lignin in non-catalyzed, MeOH, and MeOH/DMC conditions for 1-9 h. Molecular weights were determined based on a polystyrene standard calibration curve.

MS	M_n	M_w	PDI
untreated	883	1734	1.96
non-catalyzed 1h	625	1038	1.66
non-catalyzed 2h	461	987	2.14
non-catalyzed 3h	476	793	1.67
non-catalyzed 6h	346	671	1.94
non-catalyzed 9h	280	415	1.48
MeOH 1h	445	745	1.67
MeOH 2h	238	398	1.67
MeOH 3h	236	372	1.58
MeOH 6h	250	443	1.78
MeOH 9h	245	370	1.51
MeOH/DMC 1h	223	495	2.22
MeOH/DMC 2h	238	454	1.91
MeOH/DMC 3h	228	491	2.15
MeOH/DMC 6h	231	421	1.82
MeOH/DMC 9h	234	363	1.55

Table S6. GPC detected M_n, M_w, and PDI of untreated and depolymerized MIS lignin in non-catalyzed, MeOH, and MeOH/DMC conditions for 1-9 h. Molecular weights were determined based on a polystyrene standard calibration curve.

MIS	Mn	Mw	PDI
untreated	2923	7867	2.69
non-catalyzed 1h	480	779	1.62
non-catalyzed 2h	361	732	2.03
non-catalyzed 3h	430	637	1.48
non-catalyzed 6h	408	892	2.18
non-catalyzed 9h	296	463	1.56
MeOH 1h	298	496	1.67
MeOH 2h	217	377	1.74
MeOH 3h	208	318	1.52
MeOH 6h	228	452	1.98
MeOH 9h	270	417	1.55
MeOH/DMC 1h	317	771	2.43
MeOH/DMC 2h	241	445	1.85
MeOH/DMC 3h	247	513	2.08
MeOH/DMC 6h	231	441	1.9
MeOH/DMC 9h	266	410	1.54

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