Supporting Information

Catalytic disassembly of an organosolv lignin via hydrogen transfer from supercritical methanol

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CONTENTS

Expanded descriptions of experimental procedures

Preparation of HTC: To a stirred solution of sodium-carbonate (5.3 g, 0.15 mol) in 300 mL deionized water, a solution of $MgCl_2.6H_2O$ (24.40 g, 0.12 mol), $AlCl_3.6H_2O$ (12.07 g, 0.05 mol) and $Cu(NO_3)_2{\cdot}2H_2O$ (6.97 g, 0.03 mol) was added drop-wise at 60 ^oC over a one hour period. The pH of the solution was constantly monitored and kept between 10 and 11 with small aliquots of 1M NaOH solution. The suspension was vigorously stirred at 60 ^oC for 3 days. Then, the green solid was filtered, dried and redissolved again in 200 mL of 2 M sodium carbonate solution. It was stirred for 5 hours, filtrated and washed with distilled water until the rinse gave a negative chloride ion test with silver-nitrate. The material was characterized by powder XRD.

Extraction and molecular weight characterization of organosolv lignin: The extraction of methanol soluble lignin ("organosolv lignin") was carried out following procedure and slightly modified from that of the literature (E. E. Harris, J. D'Ianni, H. Adkins, *J. Am. Chem. Soc.* **1938**, 60, 1467-1470). Finely sanded poplar sawdust (100 g) was pretreated with 1 L ethanol/toluene 1:1 mixture. After filtration and drying for overnight in vacuo the dry sawdust was placed in a round bottom flask equipped with a reflux condenser and 800 mL methanol and 2 mL concentrated HCl was added. The mixture was heated to reflux and the suspension was *vigorously* stirred for 8 days. The methanol solution turned deep brown after this time. After filtration, the solution volume was reduced about 50% on a rotary evaporator and then added to on 2 L of ice. A beige solid precipitated immediately, and this was collected by filtration and then washed with copious amounts of cold water until the pH of the filtrate was neutral. The isolated organosolv lignin was dried in vacuo for overnight. Yield: 2.24 g. This material is soluble in ethanol, methanol, chloroform, tetrahydrofuran, dioxane, dimethylformamide, ethyl acetate and diethylether. Elemental analysis of the organosolv lignin showed it to contain 60.7 % C; 6.1 % H and 0.3 % N (O not determined).

The molecular weight of this material was determined by gel permeation chromatography (GPC). A 2 mg sample of the material was dissolved in 1 mL THF and filtrated over a Teflon filter pad. The average molecular weight is 2.5 x 10^3 g/ mol with polydispersity of 1.3 (Figure S-2 and Table S-1).

Figure S-1. GPC of organosolv lignin.[1]

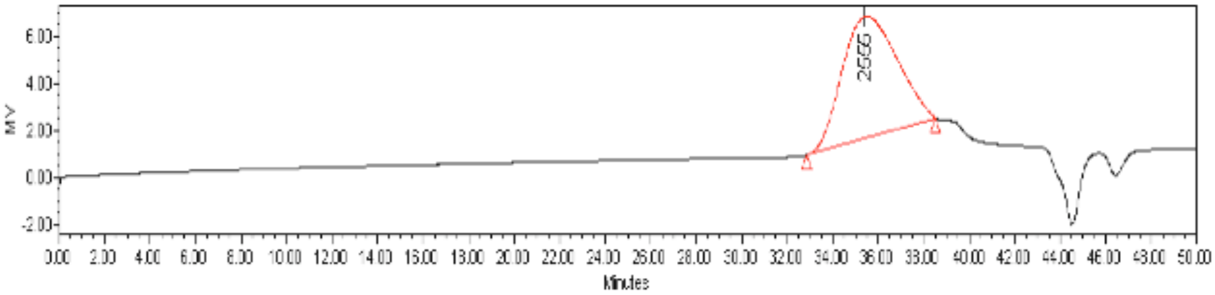

Table S-1. Data of GPC analysis of organosolv lignin

Peak	Ret. Time (min)	M_W (g/mol)	Polydispersity	M_w Range (g/mol)	Percentage
1	35.40	2464	1.27	1941-3000	100

NMR evaluation of organosolv lignin. A 100 mg sample of this material was completely dissolved in 0.7 mL $CDCl_3$ and analyzed by ^{1}H NMR and ^{13}C NMR APT measurements (Figures S-3 and S-4, respectively).In the ^{13}C APT NMR spectrum, the characteristic aromatic O-CH_3's of a syringyl unit occur at 56.4 ppm. There is another group of signals at 57.6 ppm, which would correspond to an O-CH_3 at the α-carbon. Two signals at 60.0 and 60.4 ppm belong to the -CH_2- at γ -carbon. Here again, two main groups of signals can be distinguished. The CH- carbons signals of the propyl chain are represented as 82-84 ppm for both the α and β carbons of the propyl chain and 4 main groups of signals can be found: 82.7, 83.9, 85.3 and 85.94 ppm. There is

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[1] We have also carried out the GPC experiments using DMF as the solvent but found significantly different results. In this case, a molecular weight of ~8000 was obtained for lignin; however when a more dilute sample was examined a lighter fraction similar to that of the THF was observed, so we suspect lignin aggregation occurs at higher concentration. For the product mixture, the GPC of THF solutions showed a single peak in the GPC corresponding to monomers with a mass of about 191 g mol^{-1}. In contrast, in DMF solution in addition to the peak in the 148-208 g/mol range, a smaller fraction 440-860 g/mol range was seen, however, the contribution of the latter dropped from 24% to 10% when the sample concentration was decreased twofold, again suggesting some type of aggregation under these conditions.

a weak positive signal at 72.1 ppm that probably belongs to the -CH_2- bridge in structure. The aromatic region also proves uniformity and mostly syringyl type units. There are three groups of signals at 103.2 ppm and 104.5 ppm and 104.8 ppm with the latest the most intensive negative signals belonging to the non-substituted carbons on the aromatic rings of syringyl and guaiacyl units. The group of signals with 134.7, 134.9 and 135.8 ppm correspond to the substituted quaternary aromatic carbons in the methoxy (2) and (4) position. There is a relatively weak signal group in the region 145-147 ppm belonging to quaternary carbons (6) at propyl chains. The quaternary carbons (3) at the phenolic carbons are indicated at 153.0 and 153.1 ppm as positive signals.

Figure S-2. ^{1}H NMR spectrum of 100 mg organosolv lignin in 1.0 mL $CDCl_3$

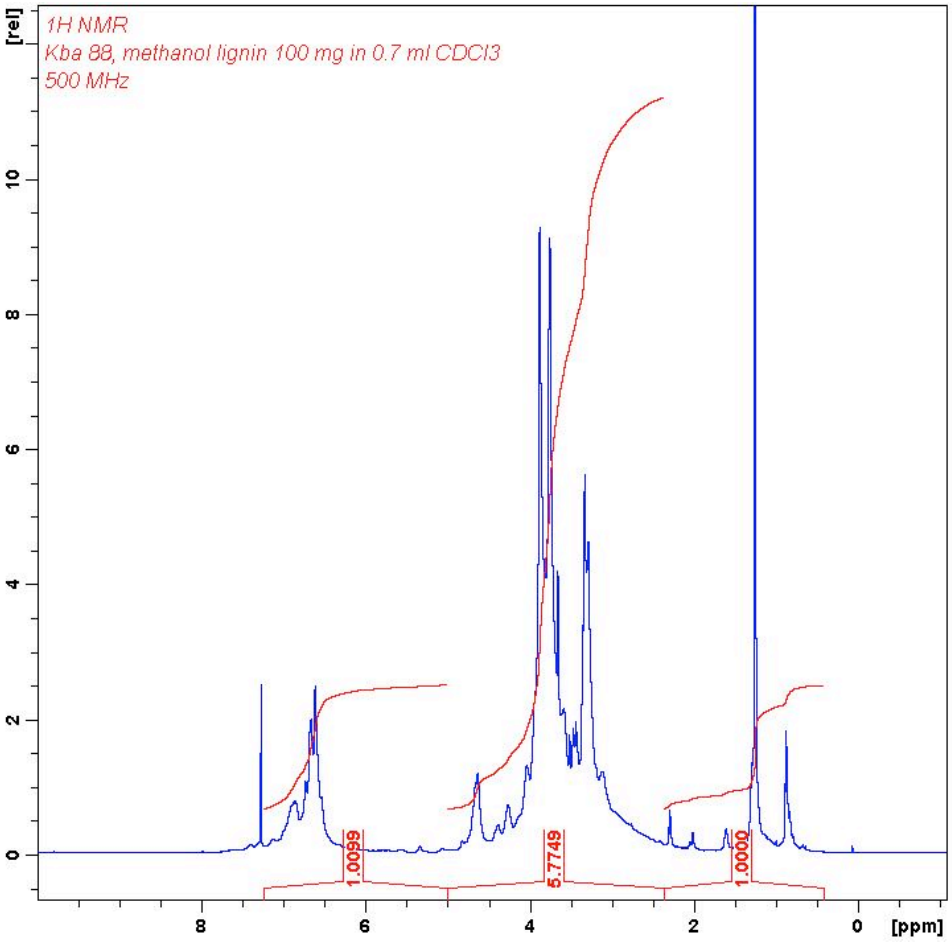


Figure S-3. ^{13}C APT NMR of 100 mg organosolv lignin in 0.7 mL $CDCl_3$

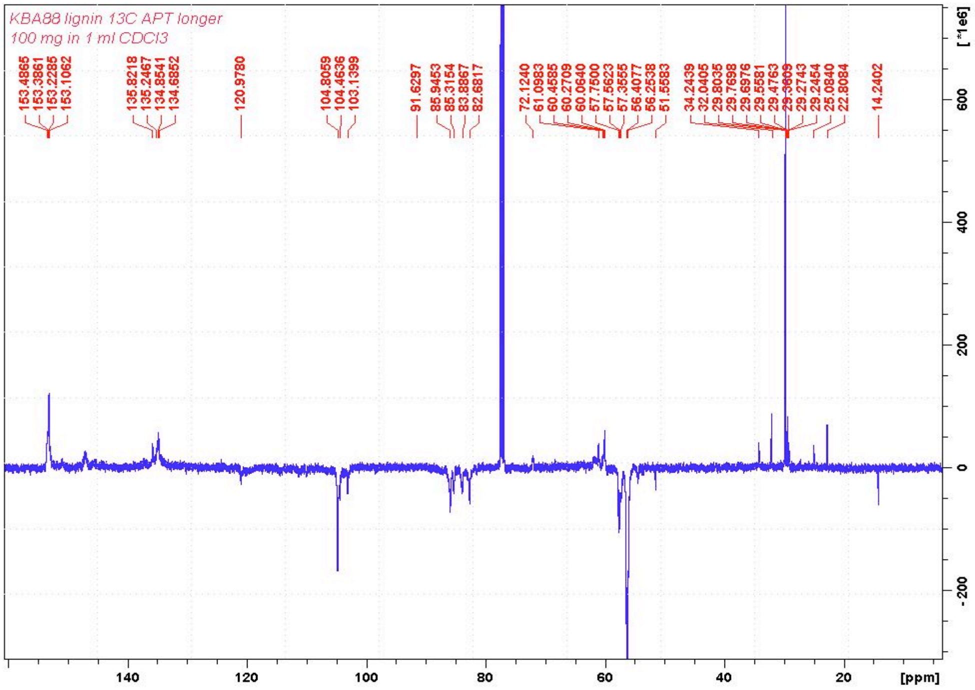
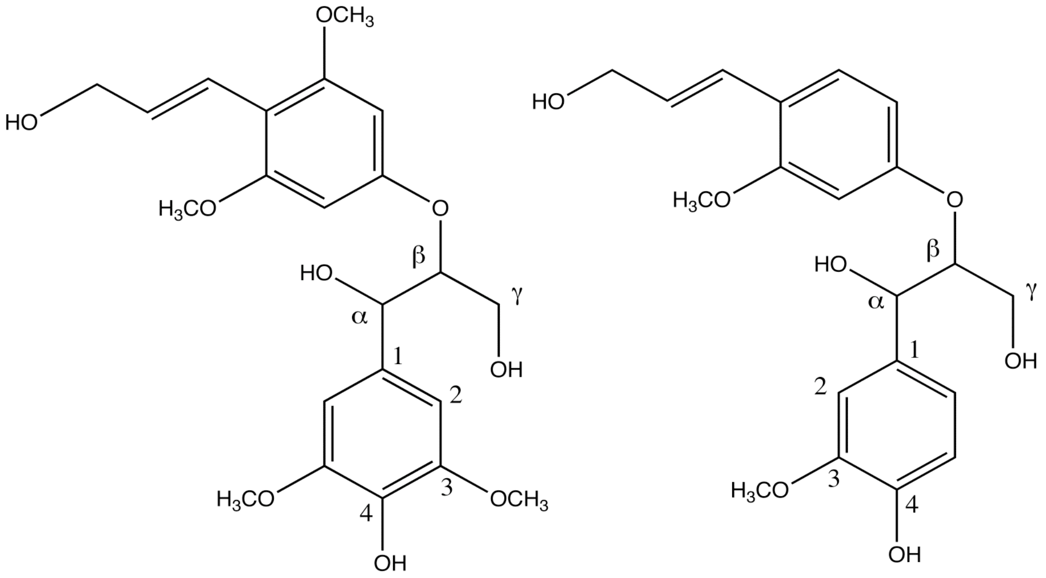


Figure S-4. Structures β-O-4 dimers of syringyl (left) and guaiacyl (right) units.



Product analysis:

The products of the reaction were analyzed as follows. After the reaction, (in some cases) the reactors were vented under a water filled vessel so that the gases could be collected and the volumes measured using Archimedes principle. A typical run of 24 h gave ~550 mL total gas volume, the composition of which was measured using a programmable Agilent model 6890 GC equipped with a 10 m Carbosieve packed column and thermal conductivity detector. The isothermal program at 60 ^{o}C using helium carrier gas allowed for the separation of H_2, CH_4, CO and CO_2, the quantified values (from calibration curves) being 18.2, 1.8, 2.0 and 0.89 mmole, respectively.

After opening the reactors, a small liquid sample was taken and directly injected to the GC-MS. Afterwards, the whole content of the vessel was transferred in a centrifuge tube with ca. 6 mL methanol and centrifuged at 7000 rpm for 5 min.. The liquid phase containing the reaction products was decanted. The solid was washed 3 times with methanol, centrifuged and the methanol washings were collected. The solid was dried overnight in vacuo and weighed.

Methanol was removed from the organic phase by rotary evaporation and the remaining oily material was weighed. This gives the amount of methanol soluble non-volatiles. The whole material was dissolved again in $CDCl_3$ and analyzed by NMR spectroscopy. A small aliquot of this solution was analyzed again with GC-MS.

GPC analysis of the methanol soluble products: A separate run of 100 mg substrate and 100 mg of Cu_{20}PMO was conducted, and after usual workup, the solvent was removed and the remaining solid was dissolved in 1 mL THF and analyzed by gel permeation chromatography (Figure S-5 and Table S-2)).[2]

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[2] See footnote 1.

Figure S-5. GPC analysis of the products.

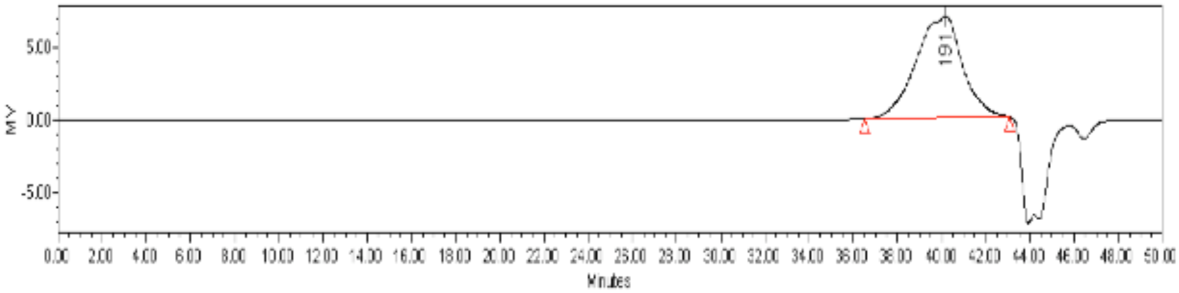


Table S-2. Data of GPC analysis of the products

Peak	Ret. Time (min)	M_W (g/mol)	Polydispersity	M_w Range (g/mol)	Percentage
1	40.2	191	1.48	186-387	100.0

Gravimetric analysis of reaction products: Several separate runs were conducted for 24 hours with 100 mg of organosolv lignin and 100 mg of Cu_{20}PMO catalyst. After the described workup, the solids were kept in the centrifuge tubes and dried in a desiccator until no weight loss was evident. Table S-3 summarizes the results, which clearly indicate that very little, if any, insoluble char was formed in the presence of the catalyst, although substantial char (~40 mg) was formed in an analogous run in the absence of catalyst.

Table S-3. Gravimetric analysis of the solids recovered after catalysis runs (24 h at 300 °C) using 100 mg of organosolv lignin and 100 mg of Cu_{20}PMO catalyst in 3.0 mL of CH_3OH.

Run	**Solids (mg)**	**Deviation**
1	98.2	-3.5
2	102.0	+0.3
3	105.0	+3.3
4	95.4	-6.3
5	108.0	+6.3
Ave.	**101.7**	**±4.9**

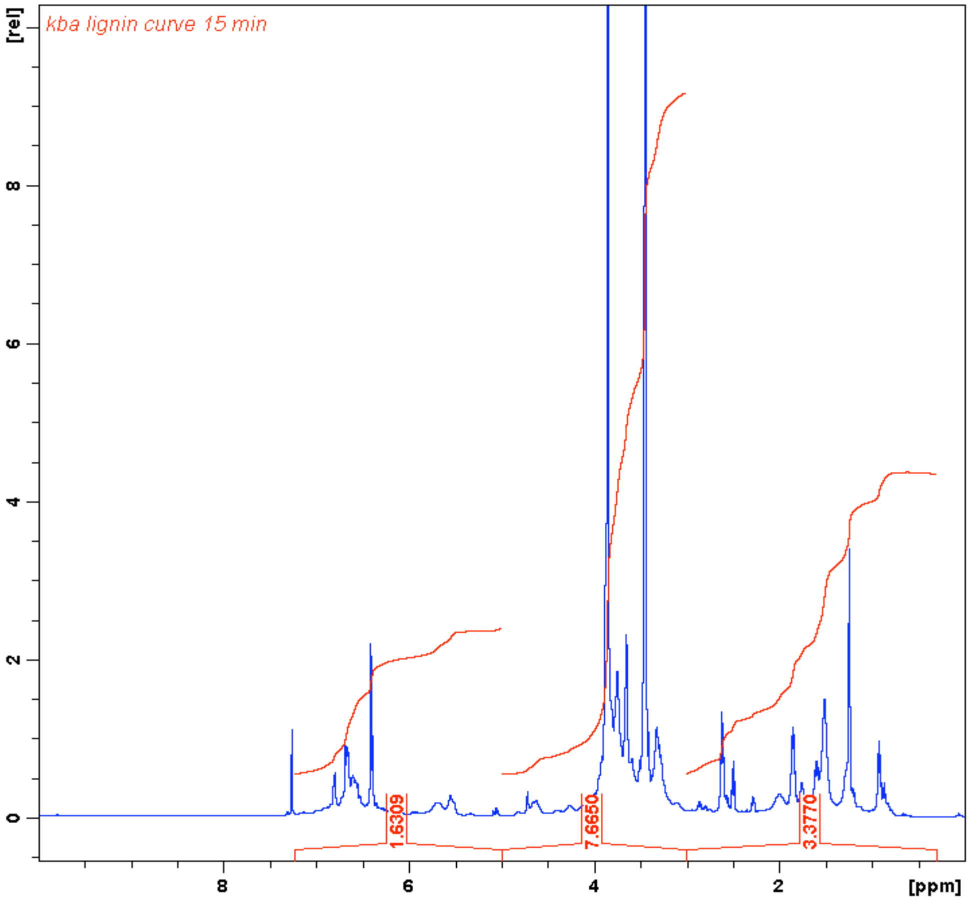
Table S-4 summarizes the gravimetric analysis of the relatively non-volatile products obtained from separate runs were conducted with 100 mg of substrate and 100 mg of Cu_{20}PMO catalyst or with 50 mg substrate and 50 mg catalyst. After the described workup, the liquid phase was transferred from the centrifuge tube to a round bottom flask, and the solvent was completely removed by rotary evaporation. The flask was weighed to determine the amount of the remaining organic material and to evaluate the yields of relatively non-volatile products.

Table S-4. Yields of relatively non-volatile liquid phase products from organosolv lignin..

Run	**Organosolv lignin (mg)**	**Liquid phase products (mg)**	**Yield (%)**	**Deviation**
1	100	56.3	56.3	0
2	100	58.2	58.2	+1.9
3	100	60.1	60.1	+3.8
4	50	26.5	53	-3.3
5	50	26.2	52.4	-3.9
6	50	28.8	57.6	+1.3
Average	**yield**		**56.3 %**	**± 2.8**

*NMR spectroscopic analysis of the liquid phase***.** A number of runs were conducted with 100 mg of lignin and 100 mg of Cu_{20}PMO catalyst or with 50 mg lignin and 50 mg catalyst. After described workup, the liquid phase was transferred to a round bottom flask and the solvent was removed by rotary evaporation. The remaining material was dissolved in 1 mL $CDCl_3$ and NMR measurement was carried out. As reference, the residual proton signal from $CDCl_3$ was used. The spectra were manually phase corrected and base line corrected using automatic base line correction with a polynomial function. Regions 7.2-5 ppm, 5-3 ppm and 3-0.3 ppm were separately integrated.

Figure S-6. ^{1}H NMR spectrum of products after a 15 min. run under standard conditions.



Sample calculation of experimental indices from data of Figure S-6:

Total number of H = sum of integrals = 1.63 + 7.67 + 3.38 = 12.67

$\mathbf{A_E}$ = (1.63 / 12.68) *100 = **12.9**

$\mathbf{O_E}$ = (7.67 / 12.68) *100 = **60.5**

$\mathbf{H_E}$ = (3.38 / 12.68) *100 = **26.7**

Figure S-7. ^{1}H NMR spectrum of products after 30 min.

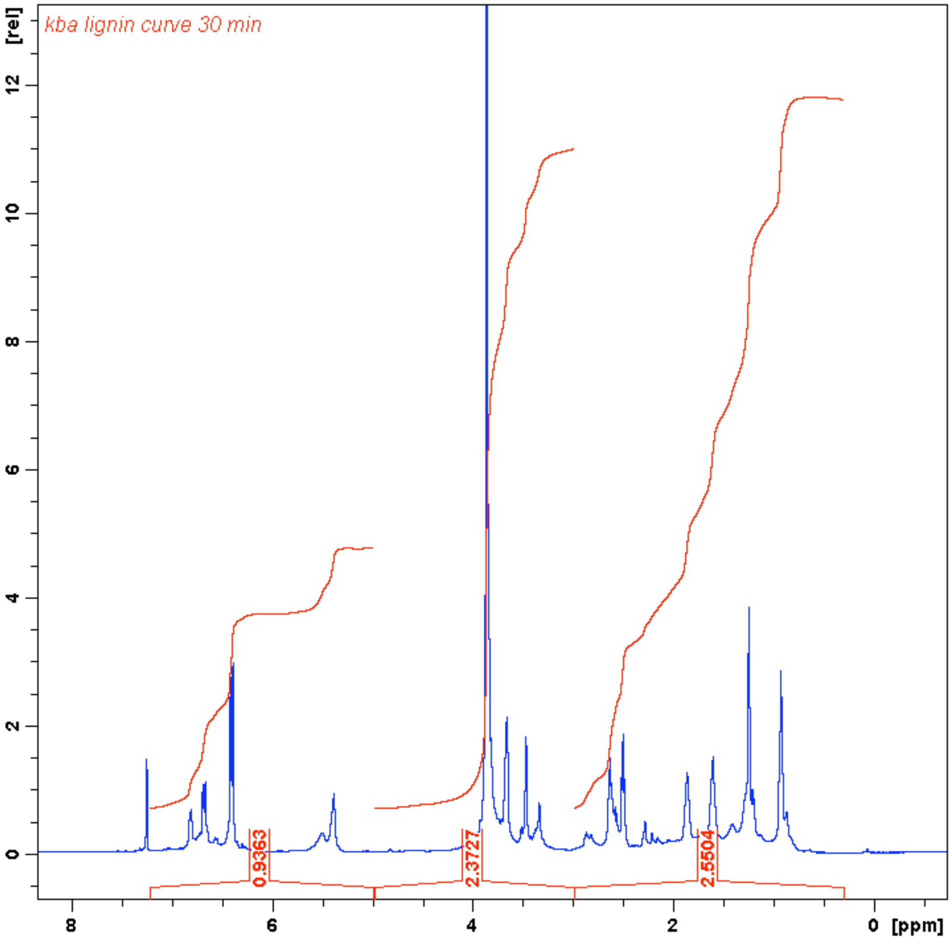


Figure S-8. ^{1}H NMR spectrum of products after 1 h.

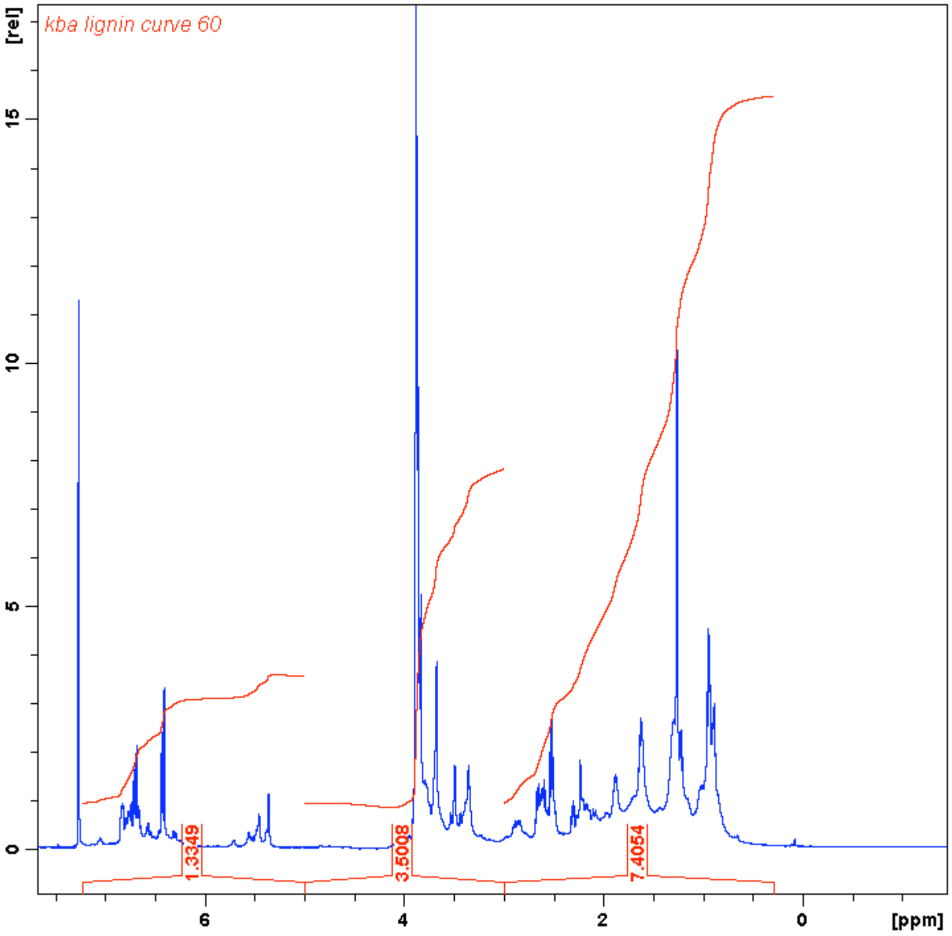


Figure S-9. ^{1}H NMR spectrum of products after 2 h.

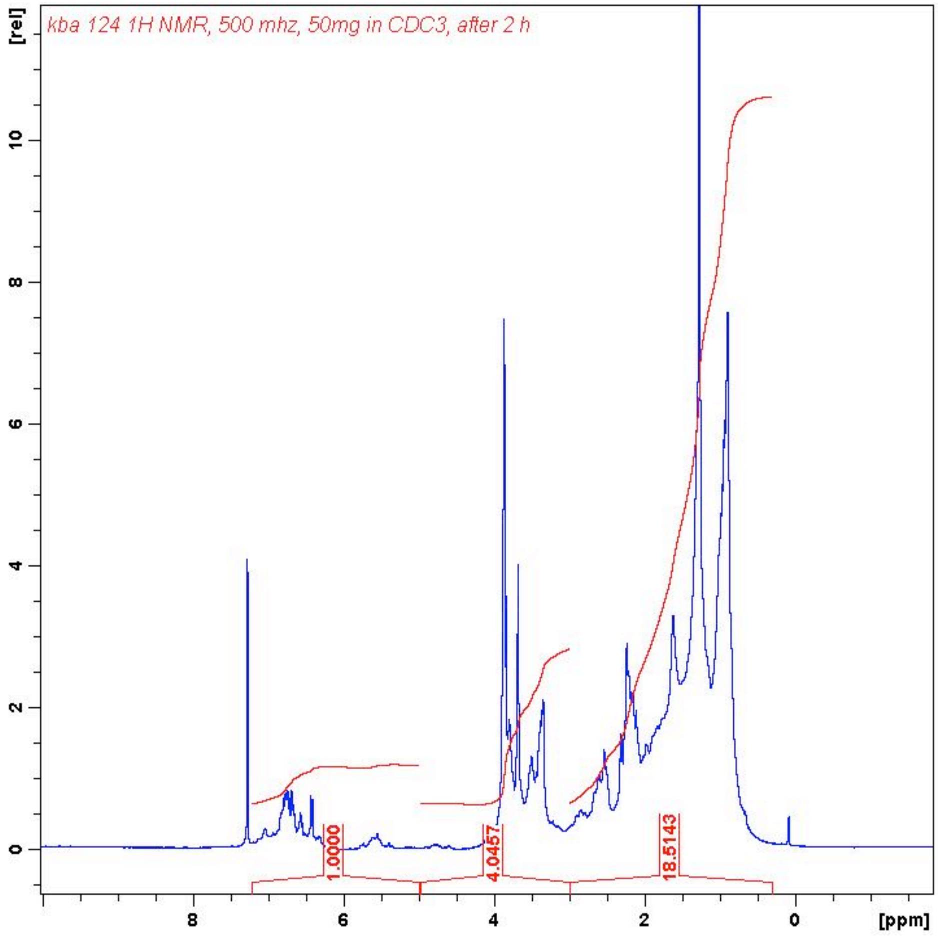


Figure S-10. ^{1}H NMR spectrum of products after 4 h.

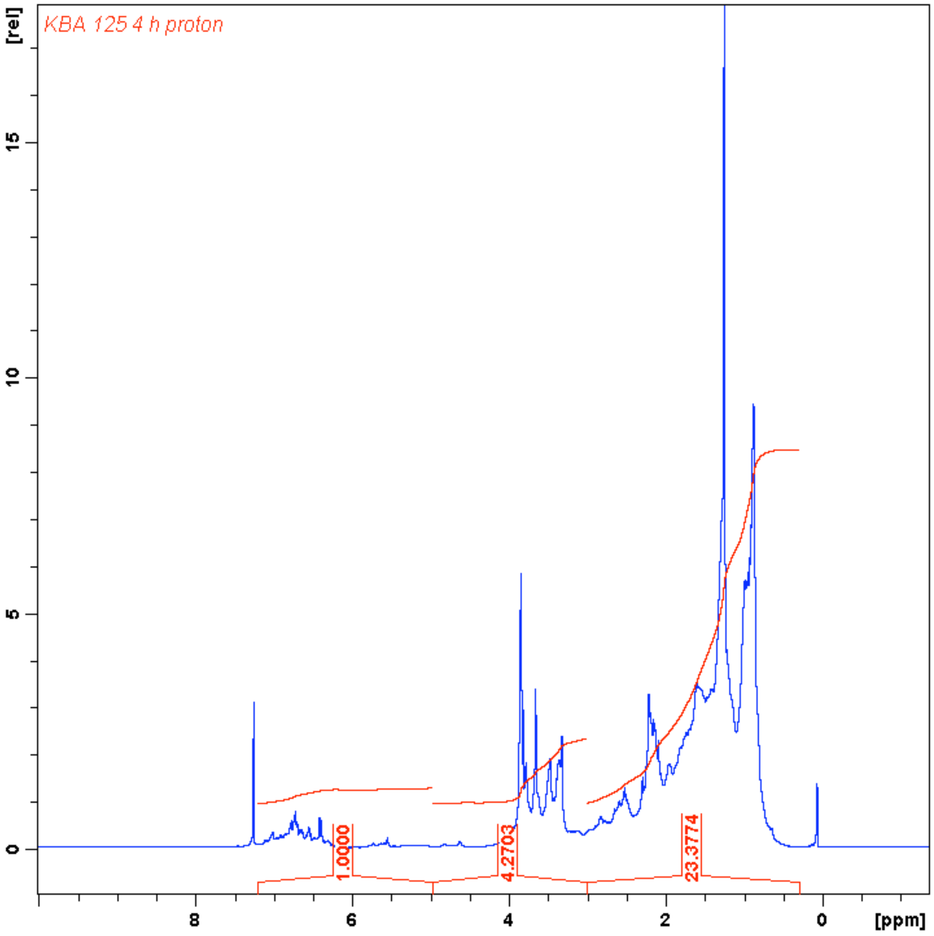


Figure S-11. ^{1}H NMR spectrum of products after 12 hours

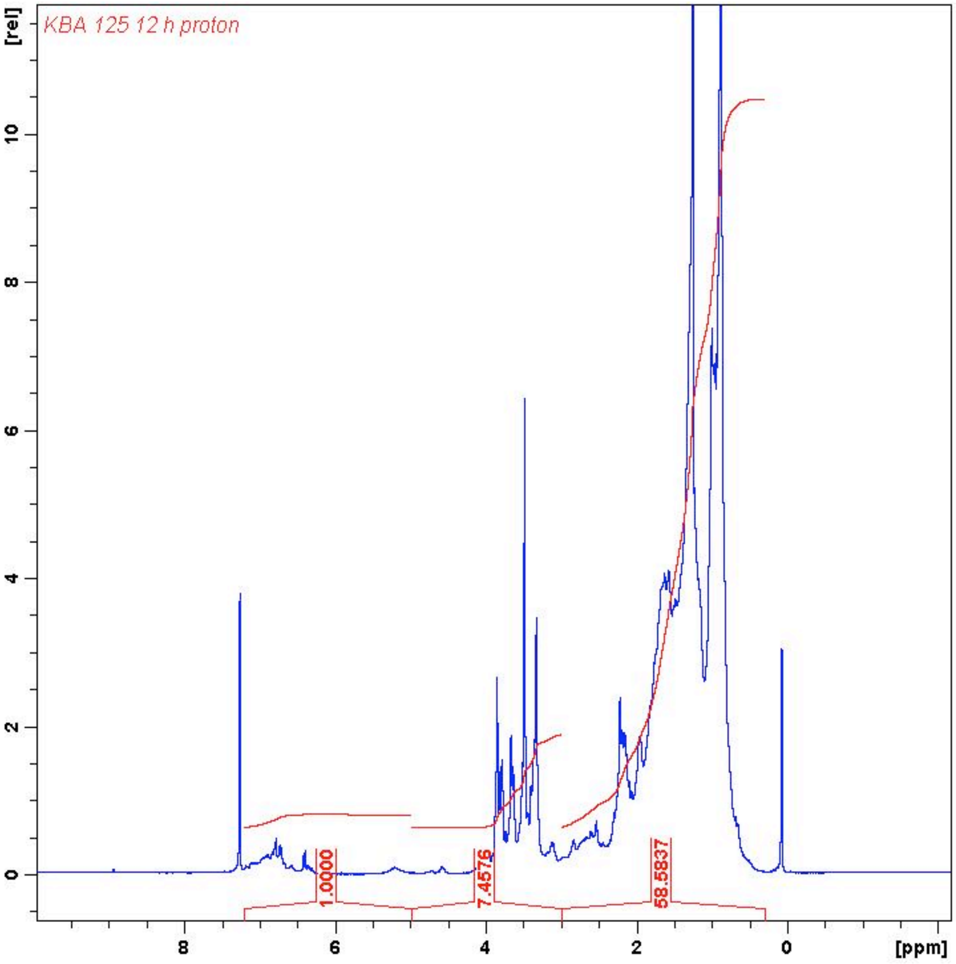


Figure S-12. ^{1}H NMR spectrum of products after 24 h.

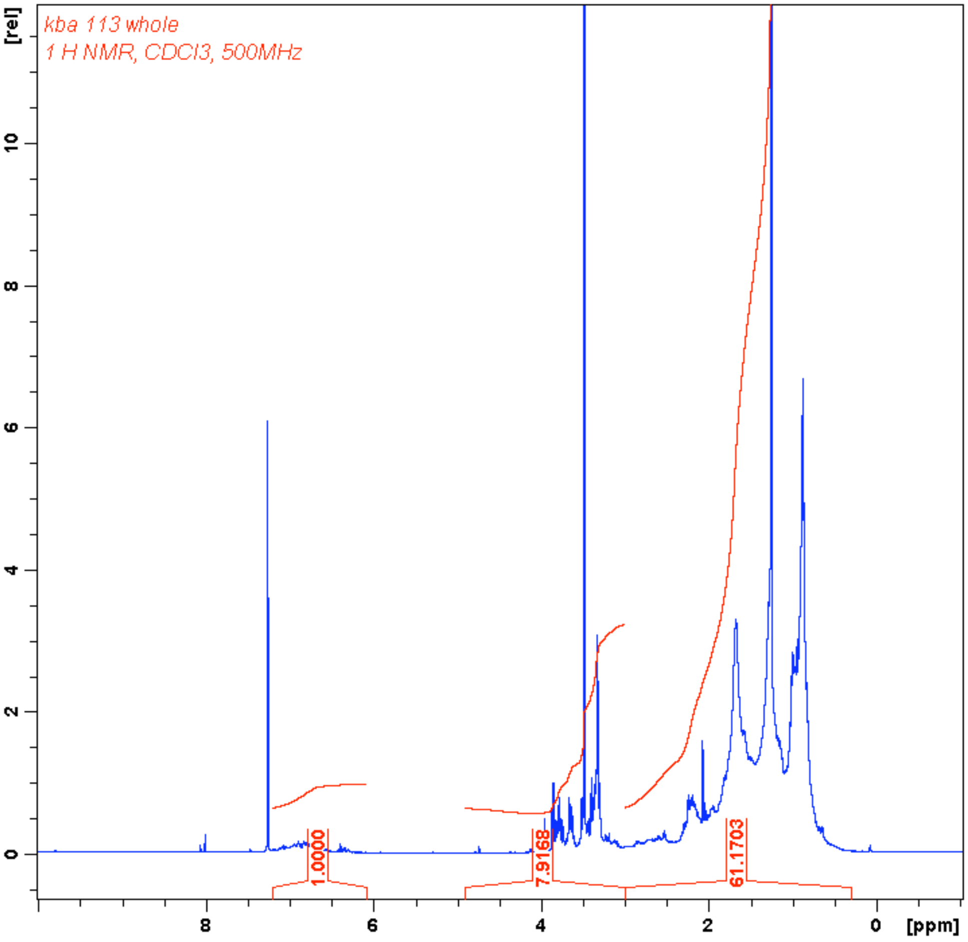


Figure S-13. ^{1}H NMR spectrum of products after 24 h (second run)

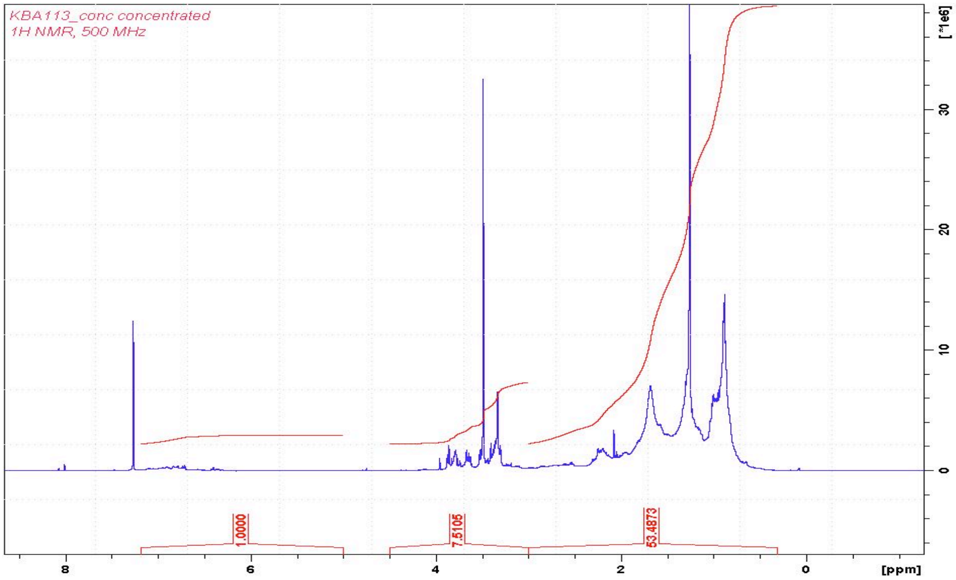


Figure S-14. ^{1}H NMR spectrum of second run products (Fig. 13) after shaking with added D_2O.

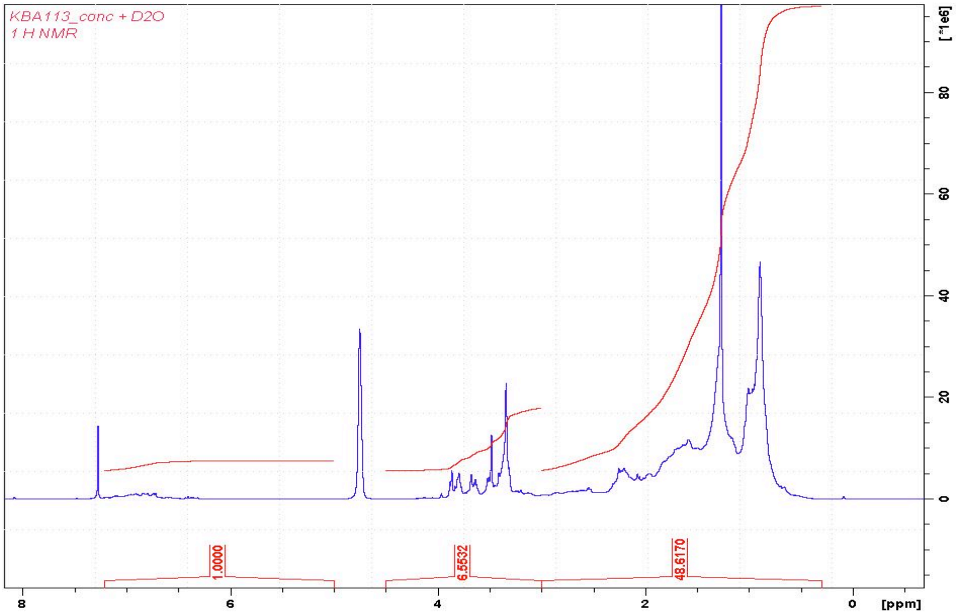


Table S-5. A_E, O_E and H_E indices for reaction products from independent set of experiments involving reaction of 50 mg organosolv lignin and 50 mg $Cu_{20}PMO$ catalyst in 3 mL CH_3OH in a 10 mL minireactor heated to 300 °C for different time intervals. The last three columns of the table show values after the sample was shaken with D_2O to probe possible exchangeable hydrogens. The lignin sample was obtained in the same manner as that used in the experiments described by Figures S-6 to S-12 but was done so independently.

Experiment	time (h)	A_E	O_E	H_E	A_E (D_2O)	O_E (D_2O)	H_E (D_2O)
substrate	0	13.5	75. 3	11.2			
1	1	8.1	33.4	58.5	8.5	33.2	58.3
2	2	2.9	19.3	77.7	4.3	18.9	76.8
3	4	1.8	13.9	84.3	1.8	12.9	85.3
4	6	0.9	11.7	87.4	1.3	11.0	87.7
5	8	0.8	13.3	85.9	1.3	10.9	87.9
6	14	0.7	10.0	89.2	1.1	10.3	88.6

Figure S-15: Temporal changes in the A_E, O_E and H_E values for a second set of orgaonosolv lignin disassembly experiments. (Data from Table S-5).

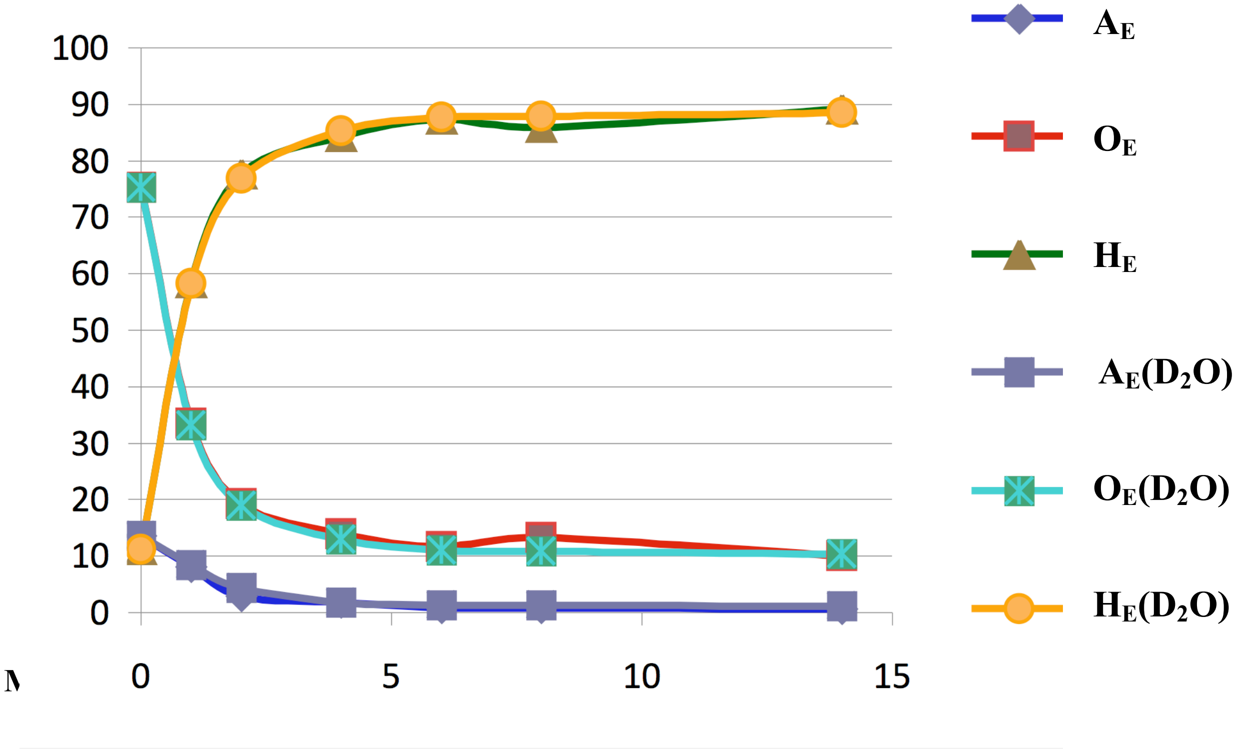


Figure S-16 displays the GC-MS analysis of the components in the product mixture obtained after 24 h reaction with 100 mg Cu_{20}PMO and 100 mg organosolv lignin in 300 ^{o}, sc-MeOH. Clearly the result is a complex mixture of compounds, many of them similar in nature. The peaks are summarized in Table S-6. The patterns seen for many of these are consistent with the formation of various cyclohexanols as suggested in the text.. This is evidenced by fragments 55, 69, 81, 95, 109 that belong to a cyclohexyl backbone [Z. M. Akhtar, C. E. Brion, L. D. Hall, *Organic Mass Spectrometry*, **1973**, *7*, 647-666]. Representative mass spectra are shown in Figures S-17 (a-n).

Figure S-16. GC-MS analysis of the components in the product mixture obtained after 24 h reaction with 100 mg Cu_{20}PMO and 100 mg organosolv lignin in 300 ^{o}, sc-MeOH.

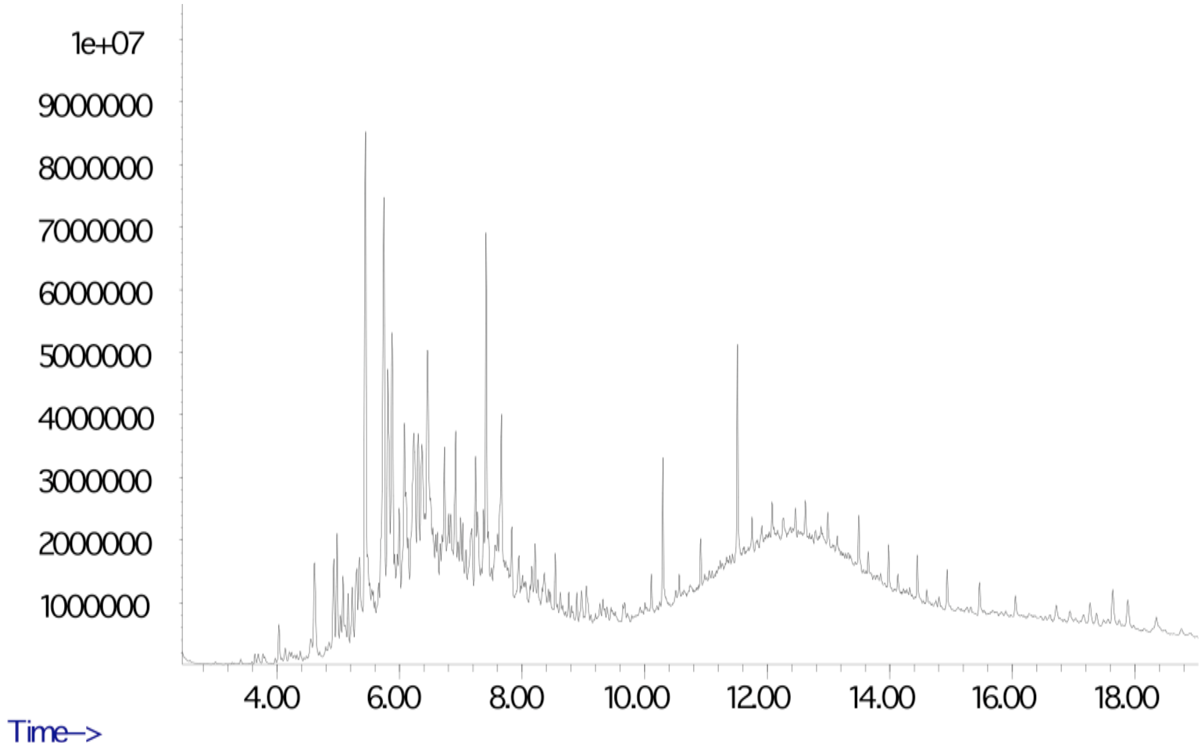
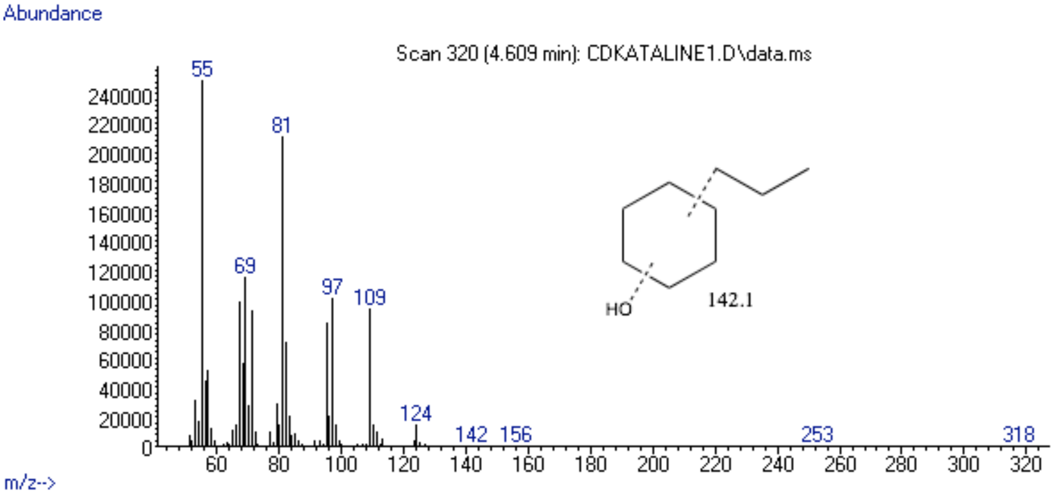


Table S-6. Summary of larger components seen in the GC-MS trace shown in Figure S-14.

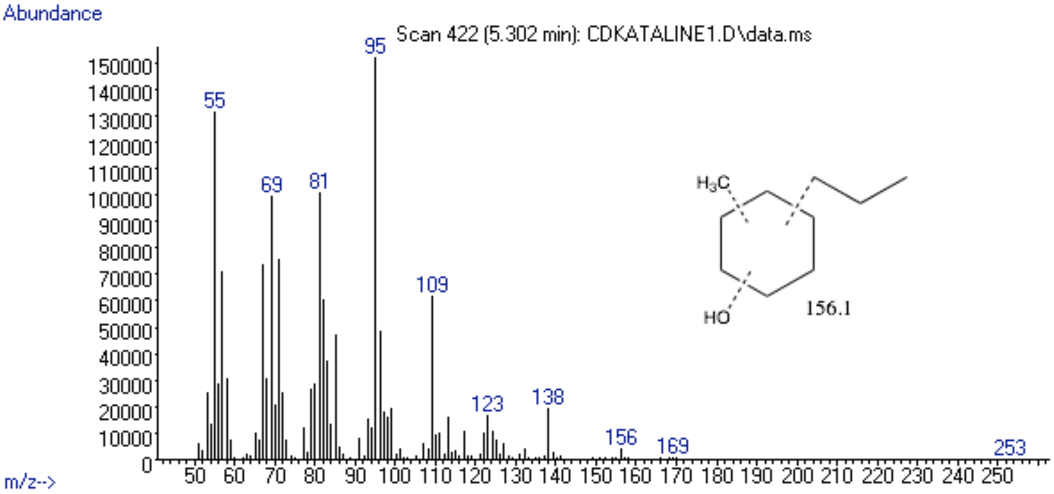
Peak	ret. time (min)	area	area %*	peak	ret. time (min)	area	area %*
1[88]	**4.62**	**35556434**	**1.12**	24	7.42	109291028	3.45
2	4.93	29065061	0.92	**25**	**7.56**	**40199424**	**1.27**
3	4.98	33152785	1.05	26	7.60	29341361	0.93
4	5.08	28977879	0.91	27	7.66	110600249	3.49
5	**5.31**	**33847259**	**1.07**	**28**	**7.83**	**47131400**	**1.49**
6	5.35	44680197	1.41	29	7.95	39534777	1.25
7	**5.45**	**212346346**	**6.70**	**30**	**8.21**	**26224722**	**0.83**
8	**5.74**	**200774614**	**6.33**	31	8.37	30958846	0.98
9	**5.81**	**120876465**	**3.81**	32	8.55	16106621	0.51
10	5.83	140802284	4.44	33	10.11	16689111	0.53
11	6.00	44940448	1.42	**34**	**10.30**	**48767284**	**1.54**
12	**6.08**	**90181168**	**2.84**	35	11.34	40745493	1.29
13	**6.24**	**152411851**	**4.81**	**36**	**11.52**	**103225634**	**3.26**
14	6.31	84203506	2.66	37	11.76	59329780	1.87
15	6.37	105299063	3.32	38	11.84	51891988	1.64
16	**6.47**	**182721739**	**5.76**	39	12.08	74802476	2.36
17	6.74	70637796	2.23	40	12.27	81849949	2.58
18	6.80	52249672	1.65	**41**	**12.63**	**77238867**	**2.44**
19	6.84	56379244	1.78	42	12.88	77418870	2.44
20	**6.91**	**75810273**	**2.39**	43	12.99	52530432	1.66
21	6.96	28594481	0.90	44	13.15	51159512	1.61
22	7.01	38526019	1.22	45	13.50	46739342	1.47
23	7.24	76759366	2.42				

*Note that the different peaks have different response sensitivities with regard to the MS detection, so the relative peak intensities are not quantitative evaluations of the material represented by that elution time. The values shown in this column are offered simply to provide a qualitative view of the relative quantities of the various compounds formed. ** MS for components marked in bold appear in Figure S-15.

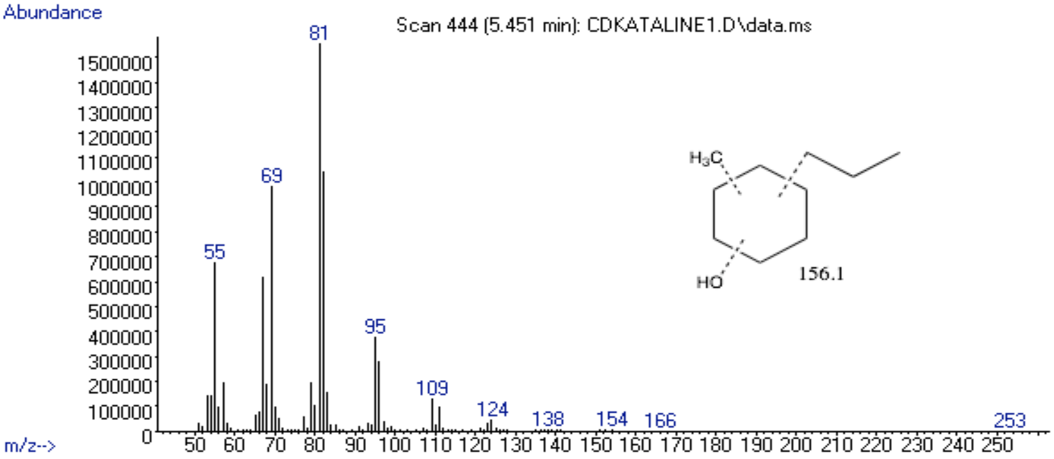
Figure S-17. Mass spectra of representative peaks chosen from Table S-6



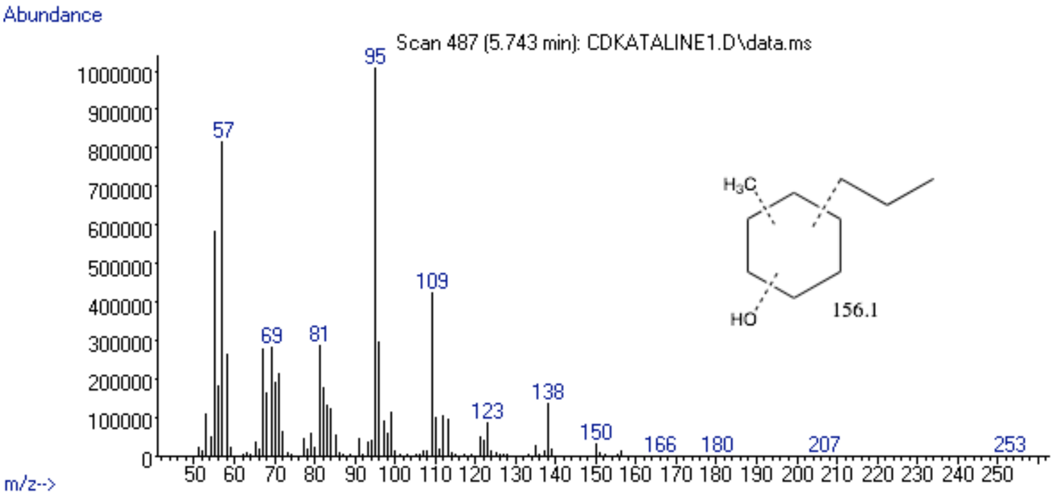
(a) peak 1



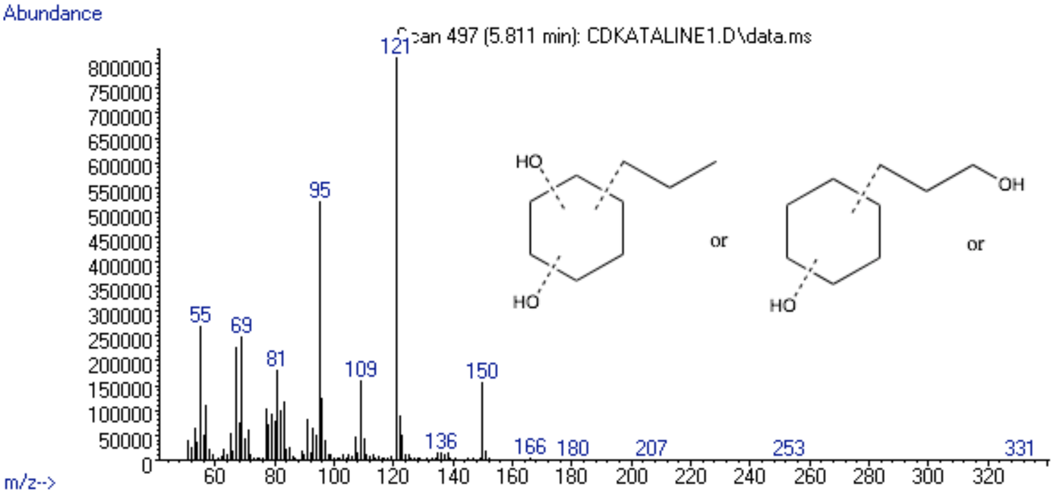
(b) peak 5



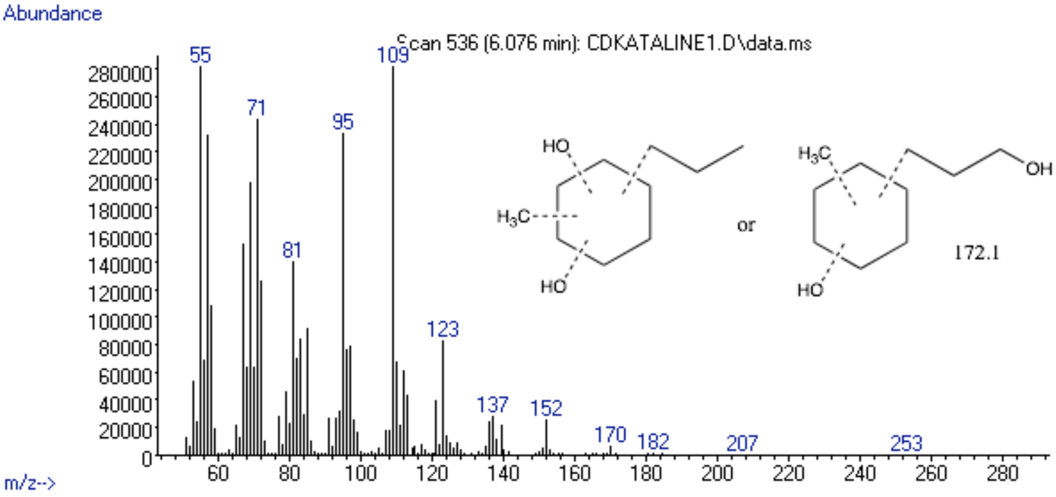
(c) peak 7



(d) peak 8



(e) peak 9



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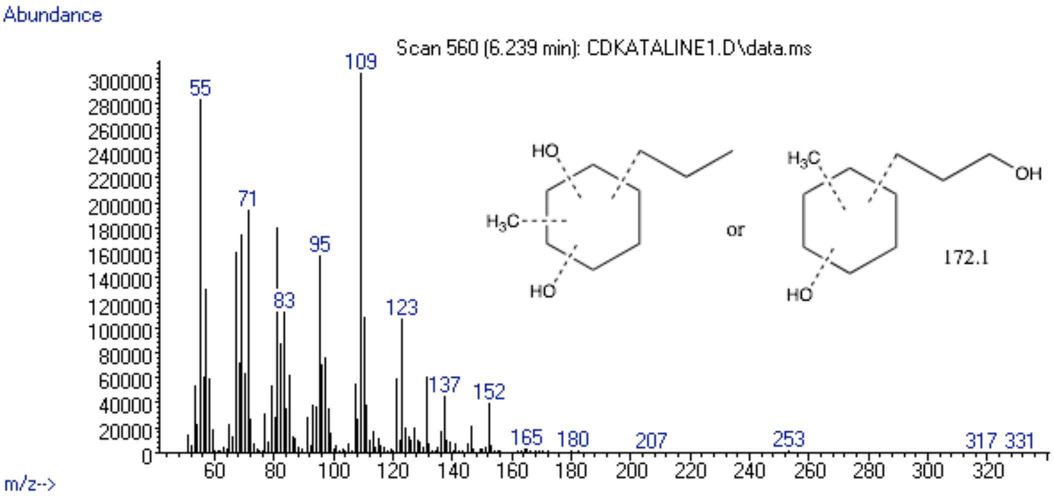

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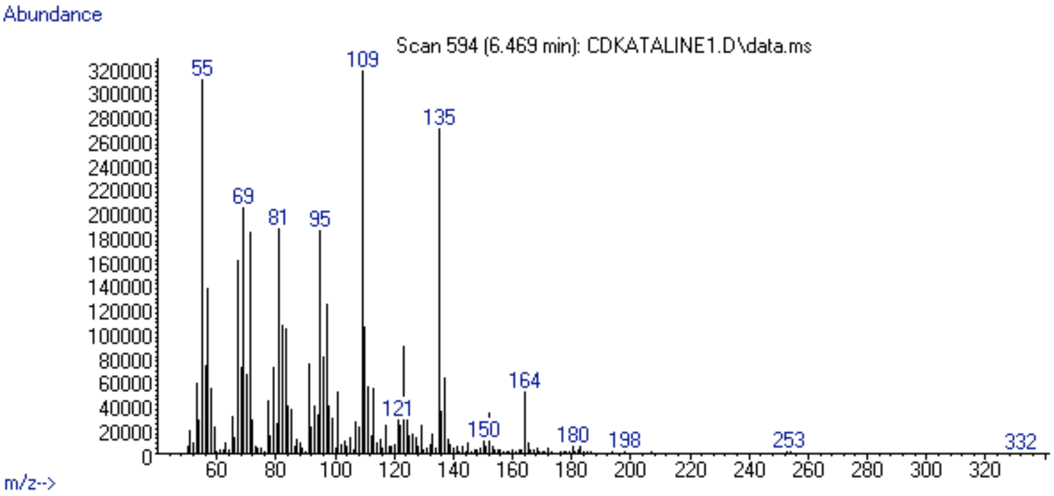

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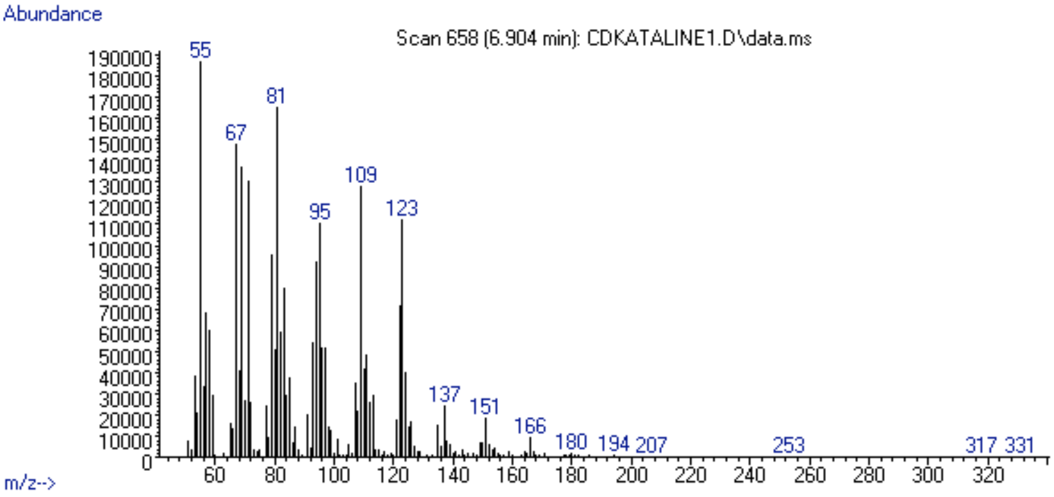

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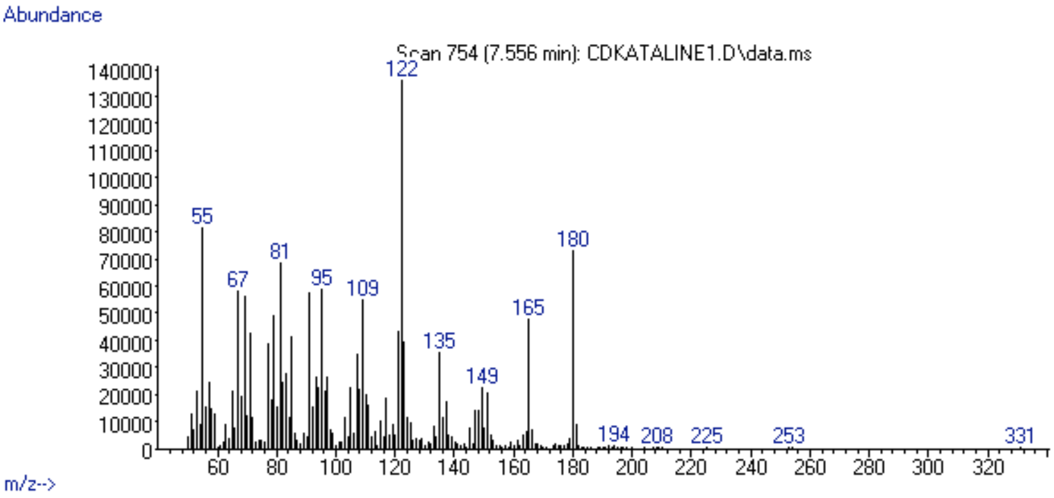

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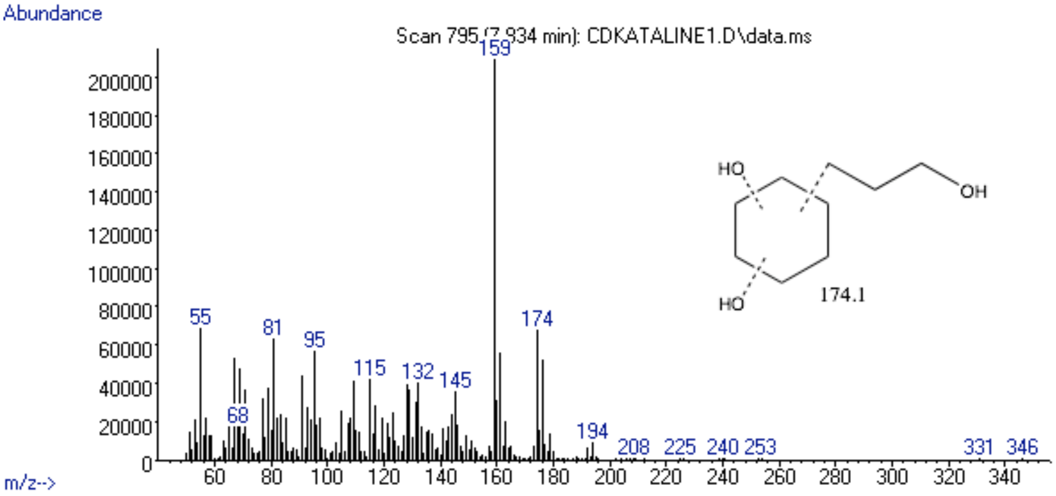

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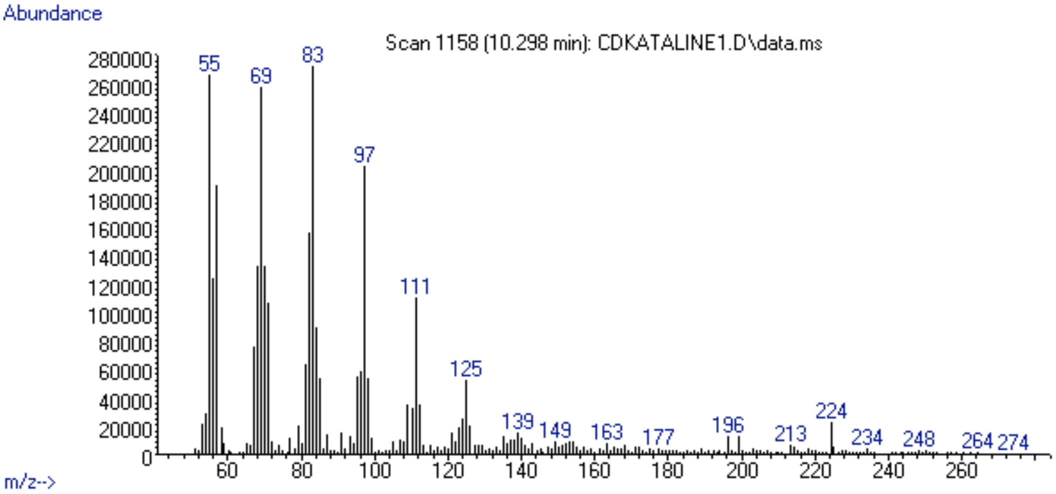

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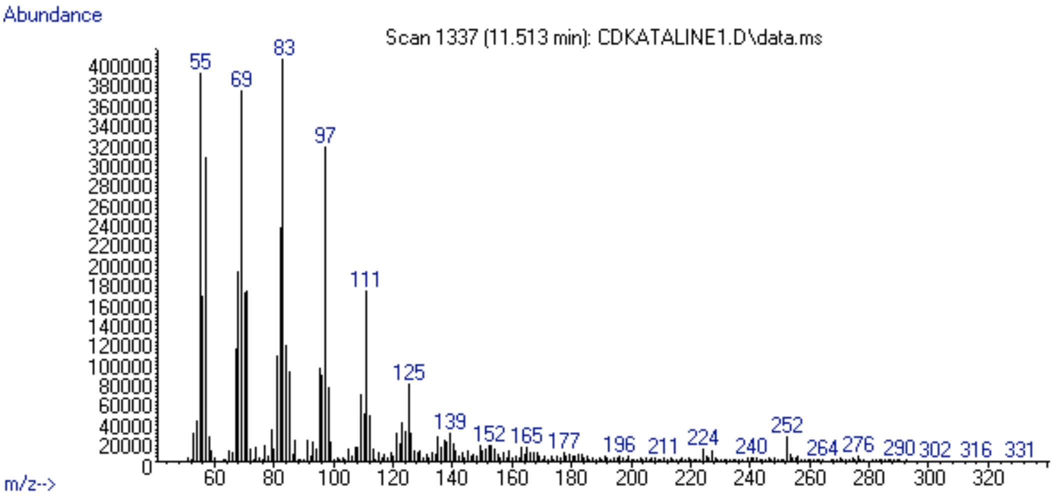
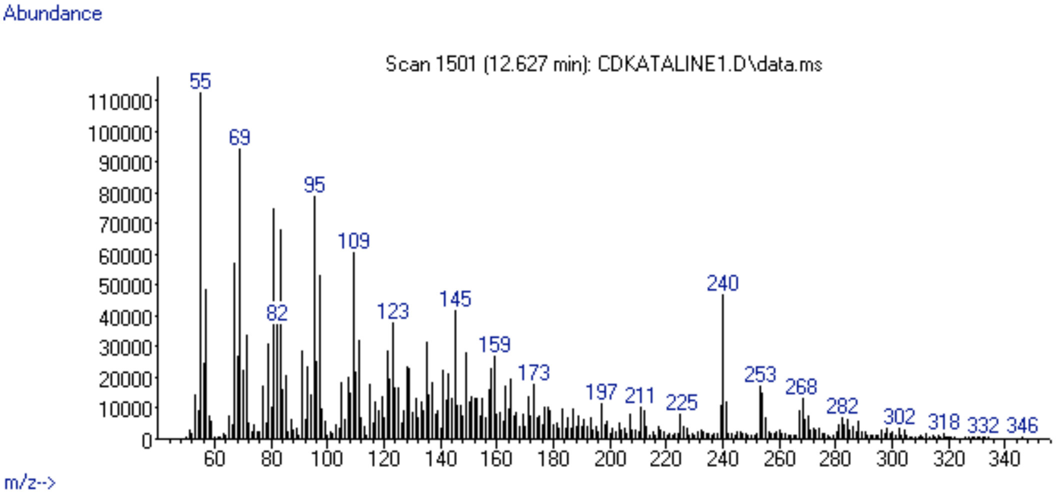


(m) peak 36



(n) peak 41