

**Supporting Information**

**Solvothermal liquefaction of alkali lignin to high-yield  
aromatic monomers with suppressing solvent consumption**

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**Table S1.** Yields of vanillin and syringaldehyde obtained from the nitrobenzene oxidation of Kraft lignin

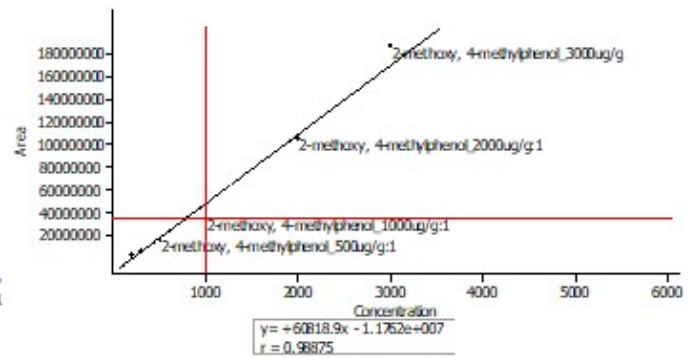
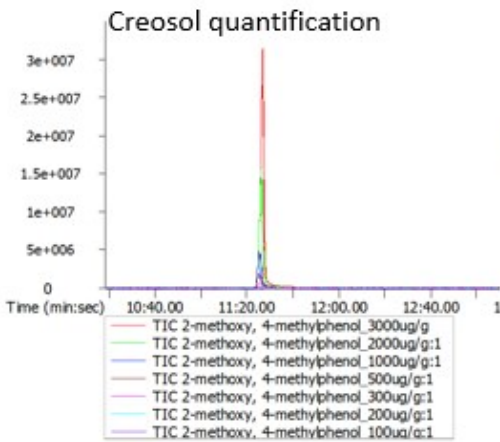
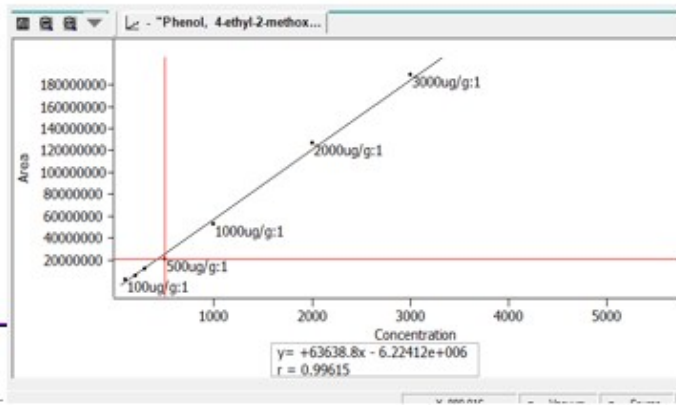
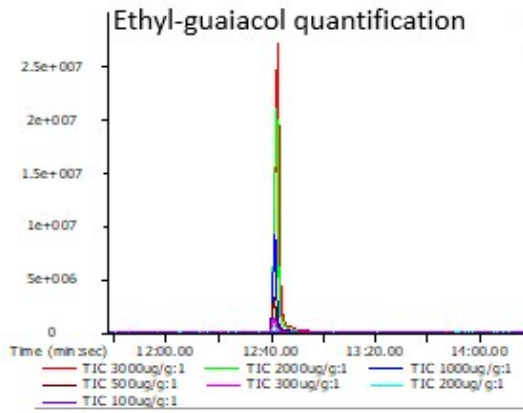
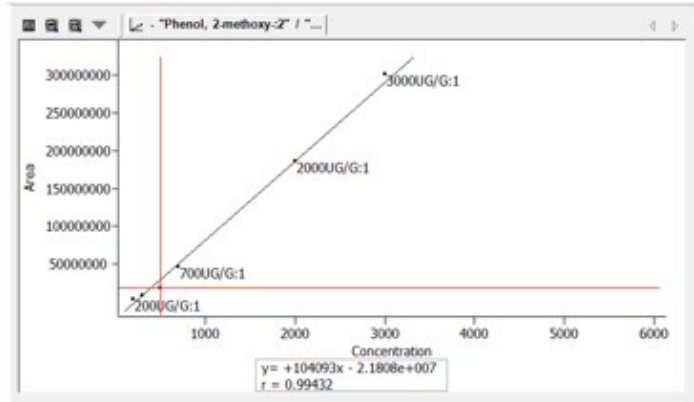
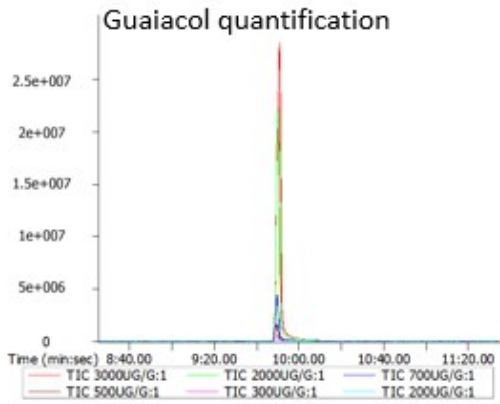
Sample	Vanillin (V)	Syringaldehyde (S)	V + S	S/G	Total yield (wt%)
	(μmol/g of Lignin)				
Alkali lignin	665	36	701	0.053	10.8

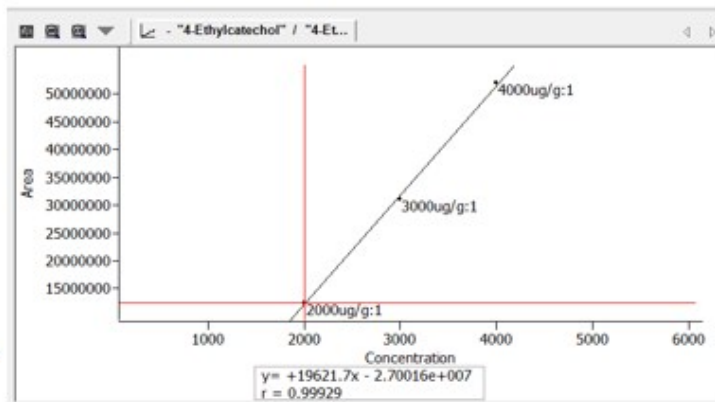
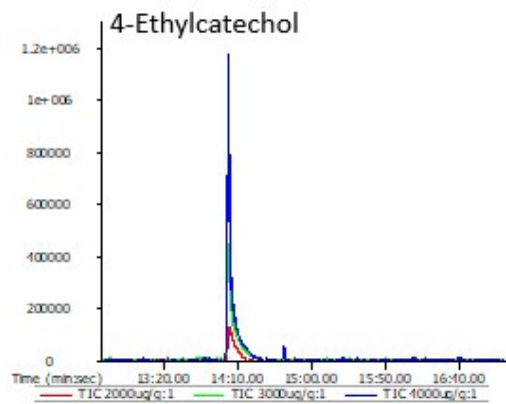
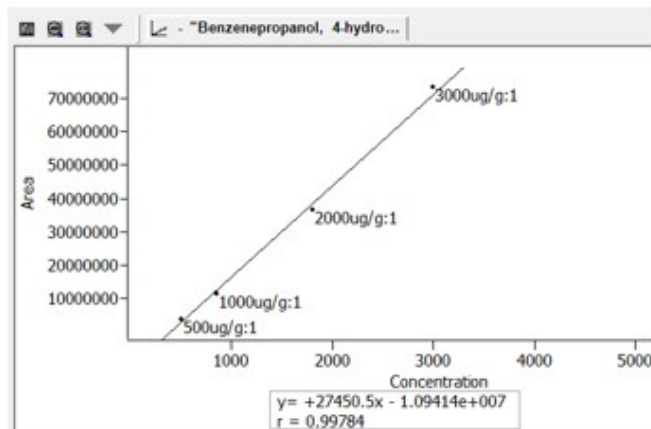
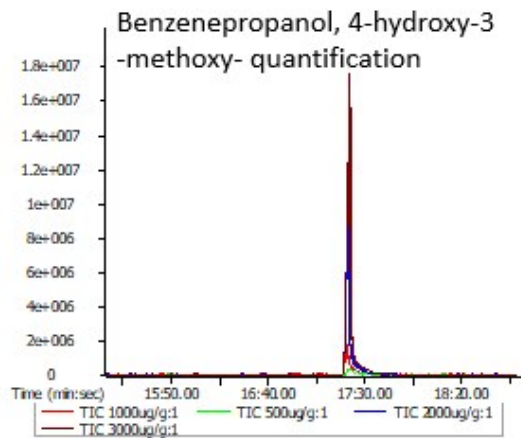
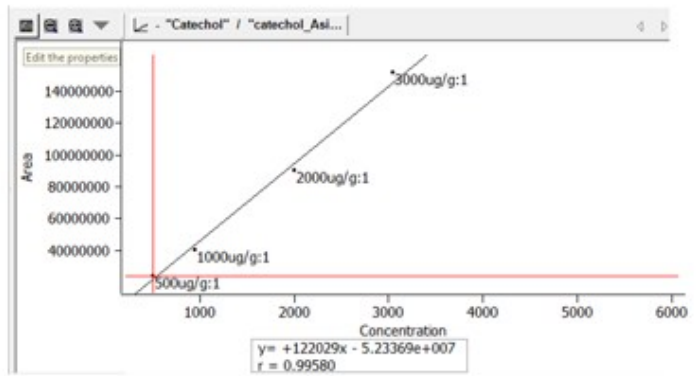
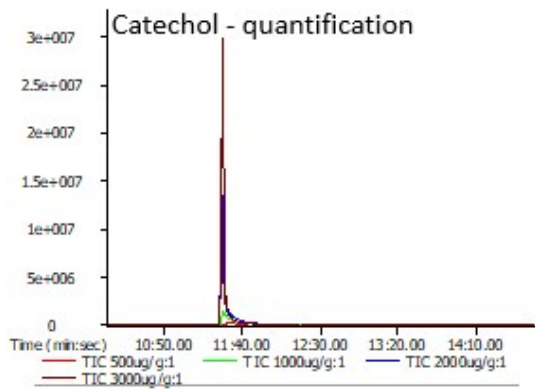
### Monomer's quantification:

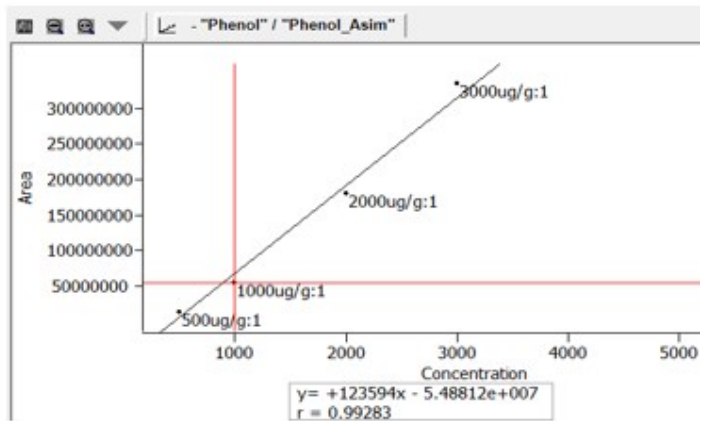
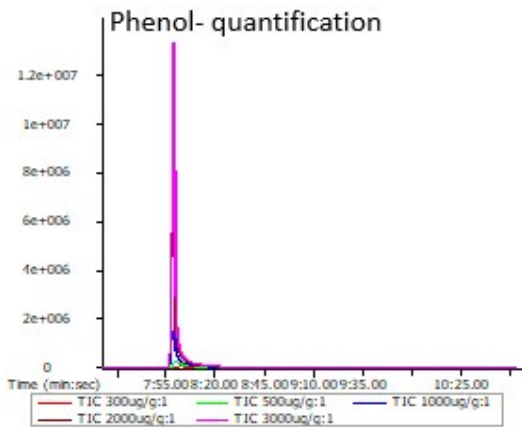
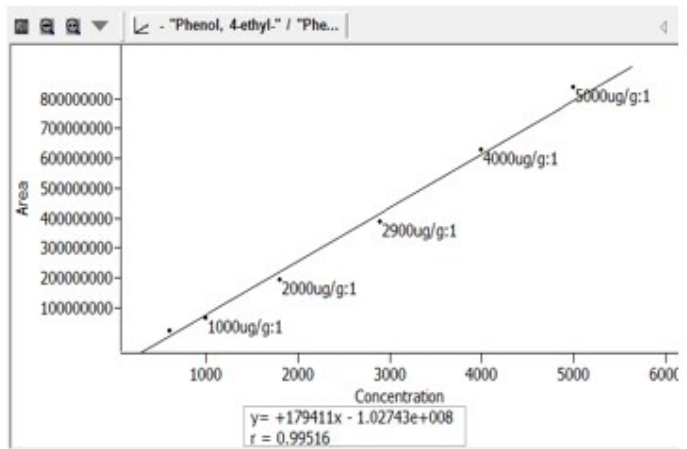
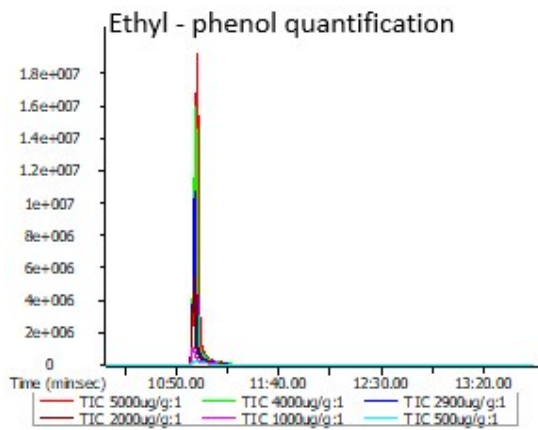
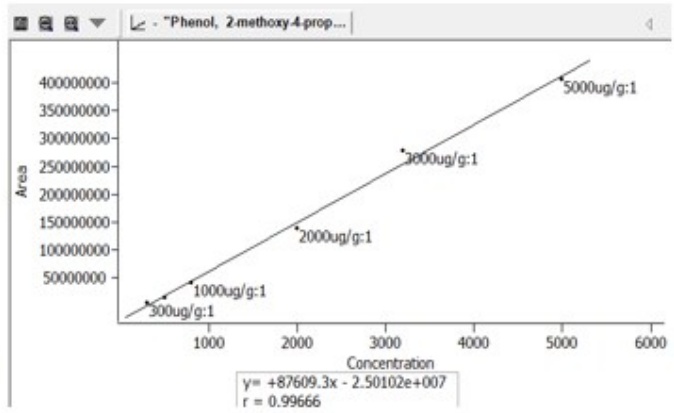
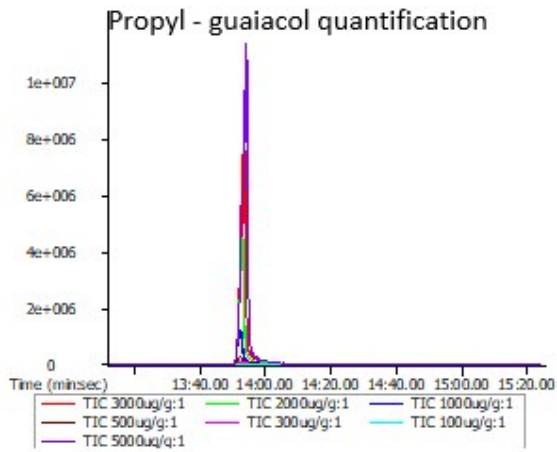
For the monomer quantification, 12 aromatic monomers (phenol, ethyl phenol, toluene, guaiacol, ethyl guaiacol, 4-propyl guaiacol, creosol, catechol, 4-ethyl catechol, 3 methyl catechol, 3-tert-butyl-hydroxyanisole, benzenepropanol,4-hydroxy-3-methoxy) and 9 linear/branched oxygenated hydrocarbons (butanol, propanoic acid ethyl ester, ethane,1,1-diethoxy, acetic acid butyl ester, butanoic acid ethyl ester, diethoxy methane, 2-buten-1-ol, ethyl acetate, 1-ethoxy butane) were purchased. The calibration curves for each model compound are shown below. To quantify commercially unavailable aromatic monomers (3-methoxy-6-methylphenol, 4-propylphenol, and homovanillyl alcohol), an effective carbon number (ECN) method was used. Guaiacol was used as a reference compound to calculate the concentration target compound by the ECN method, as proposed by Schofield.<sup>3, 4</sup> The formula used to quantify the chemical species is:

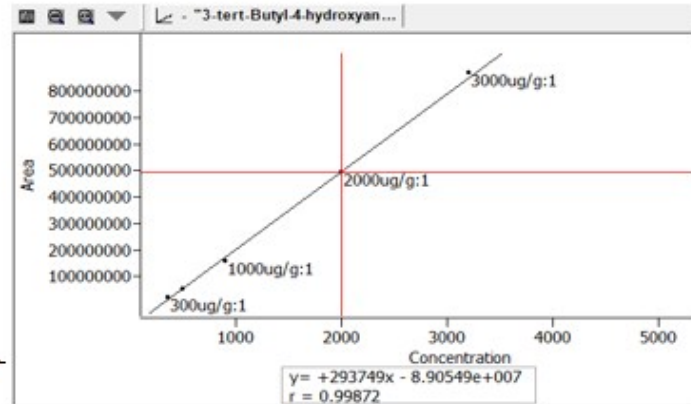
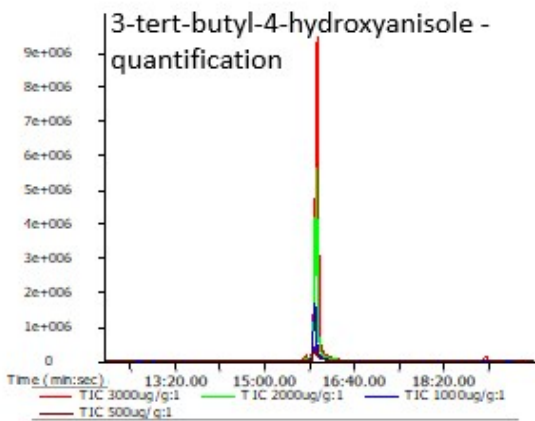
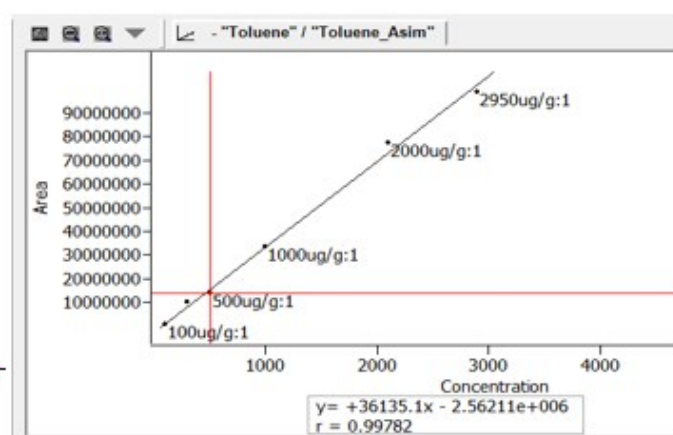
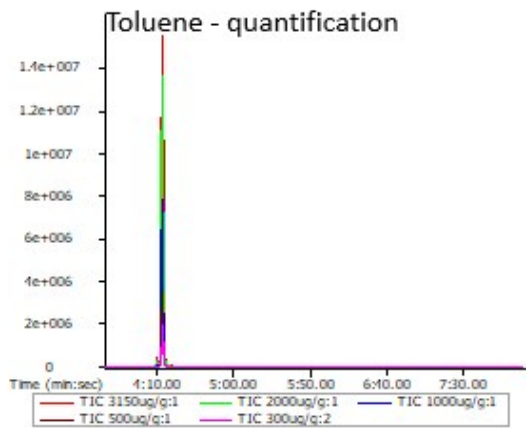
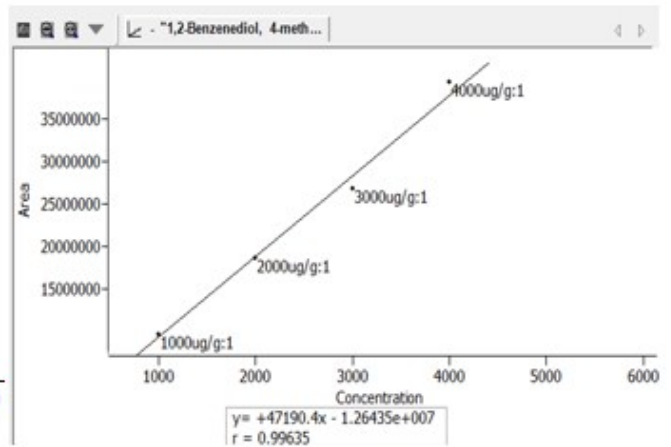
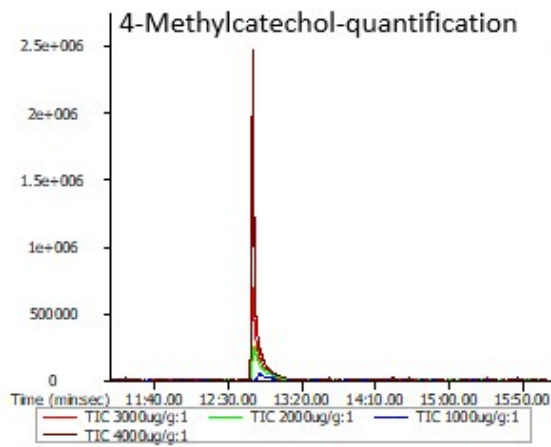
$$C_i = \frac{C_{ref}}{A_{ref}} \times A_i \times \frac{n_{eff,ref}}{n_{eff,i}}$$

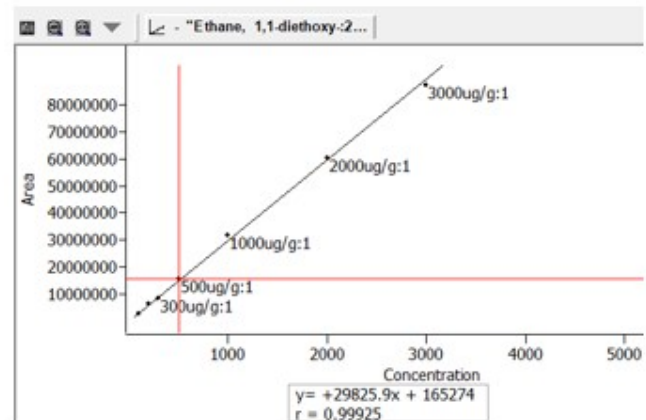
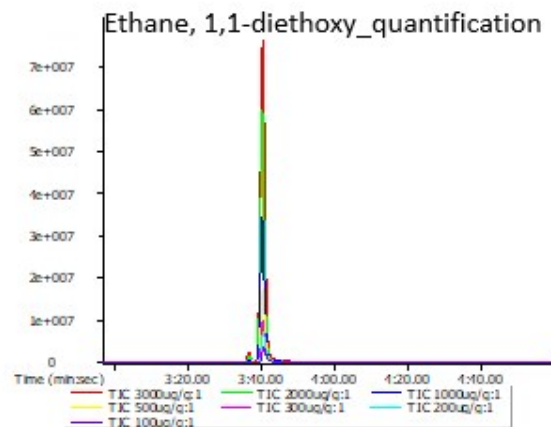
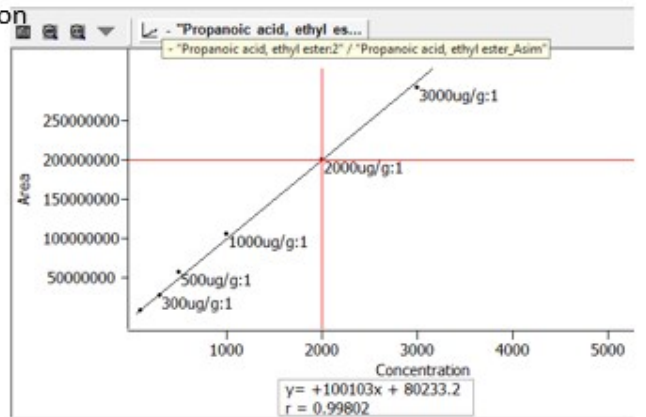
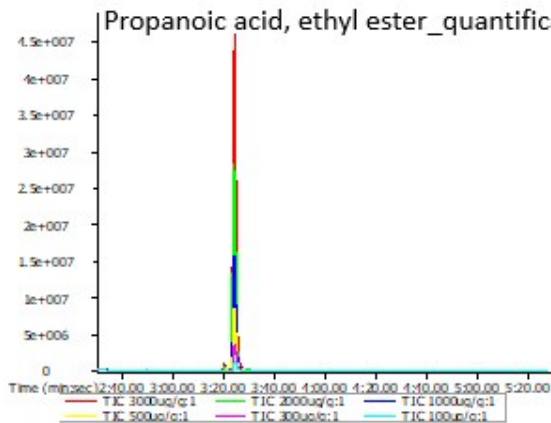
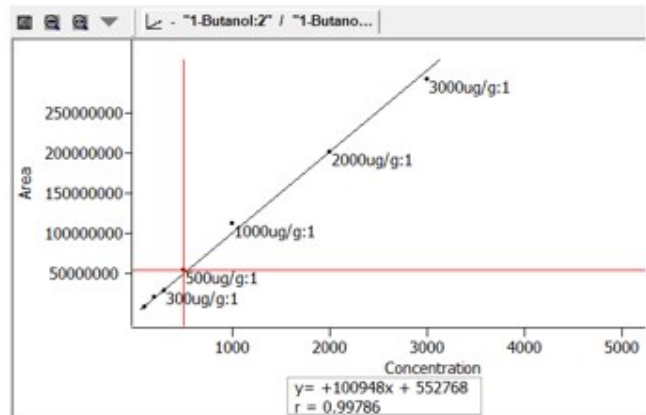
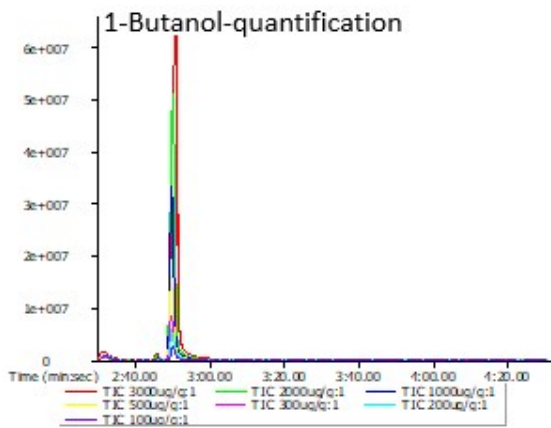
where  $C_i$  and  $C_{ref}$  are the concentrations of target compound and the reference compound, respectively,  $A_i$  and  $A_{ref}$  are the GC peak areas of the target compound and reference compound, respectively, and  $n_{eff}$  is the ECN.





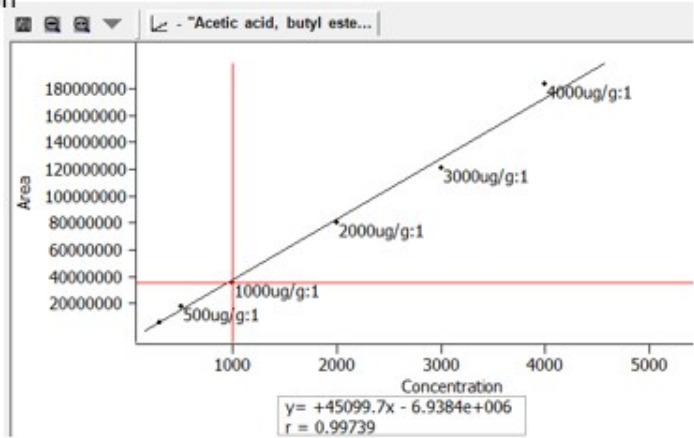
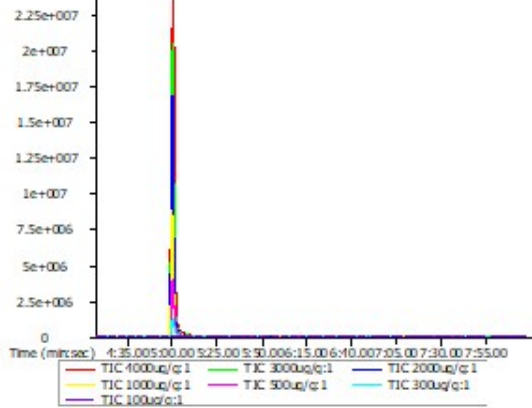




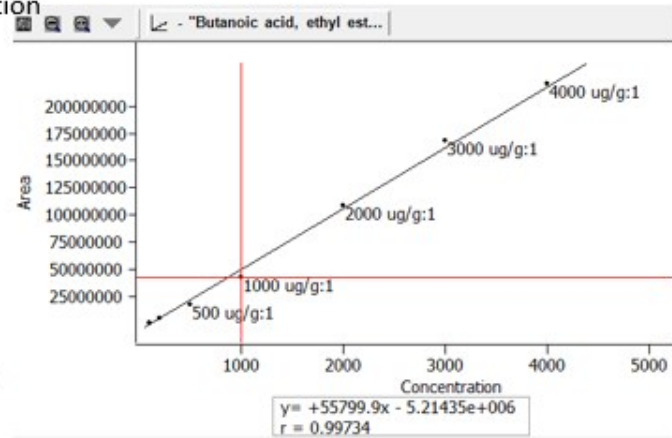
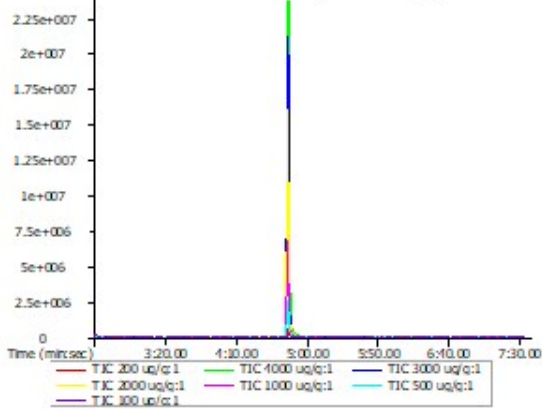




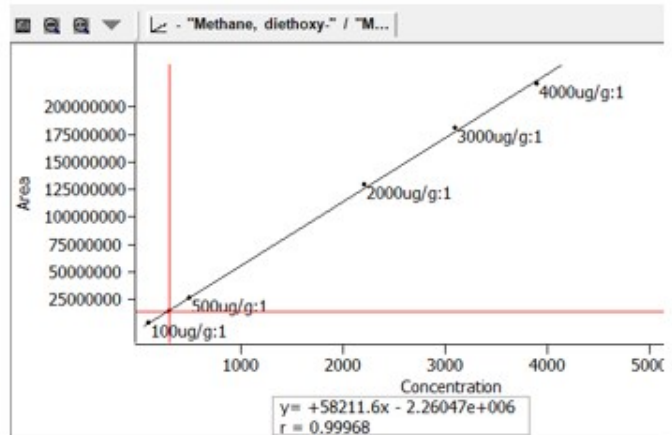
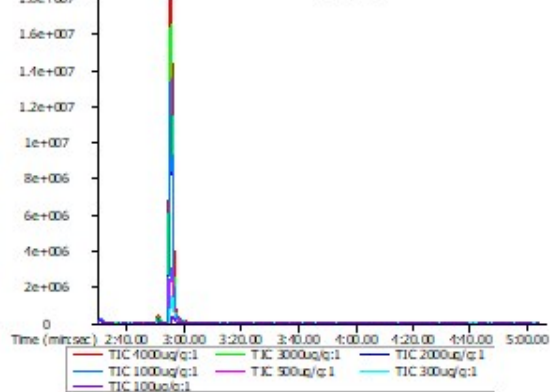
### Acetic acid, butyl ester\_quantification

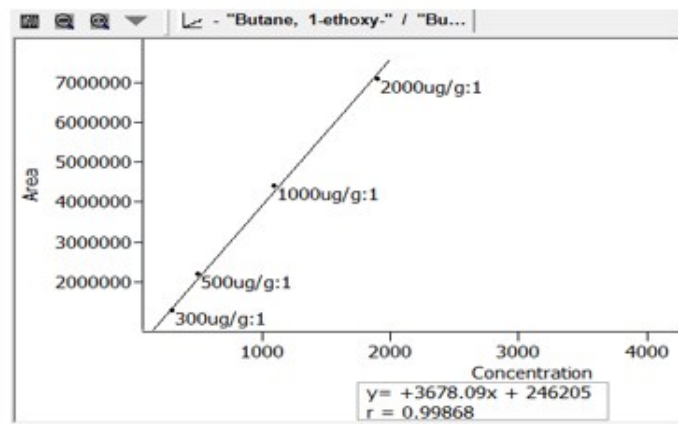
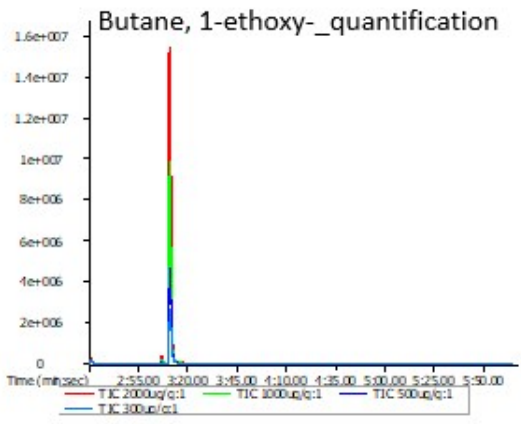
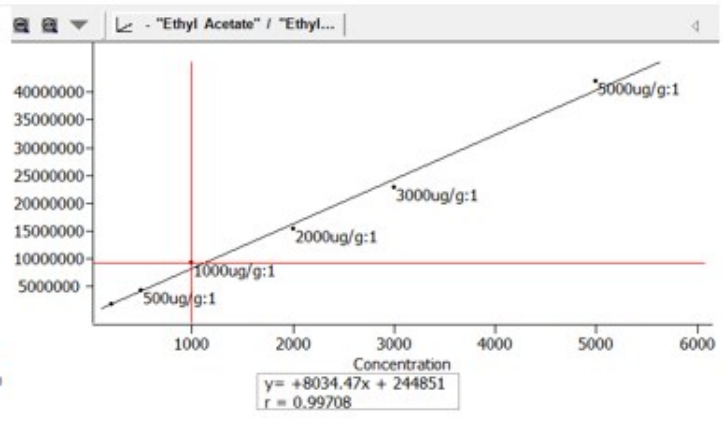
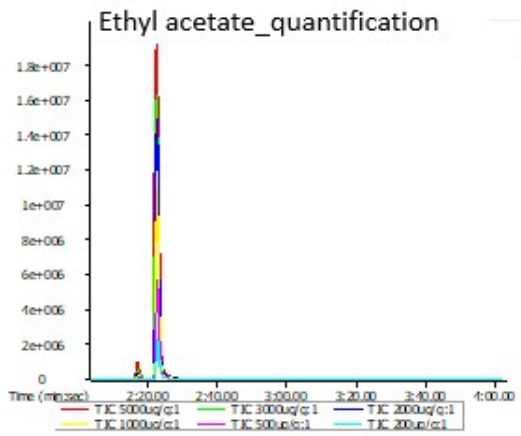
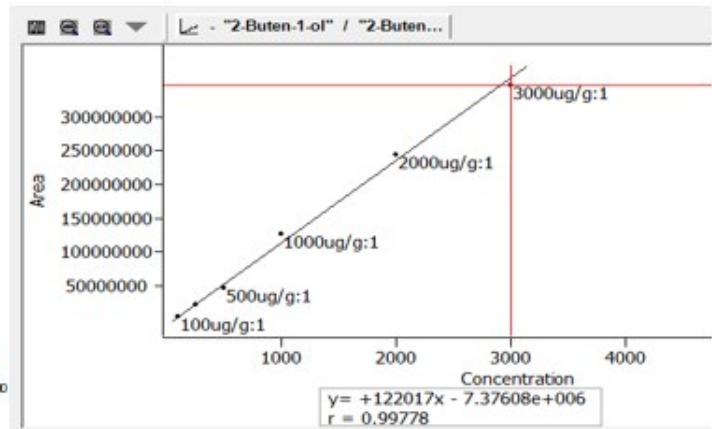
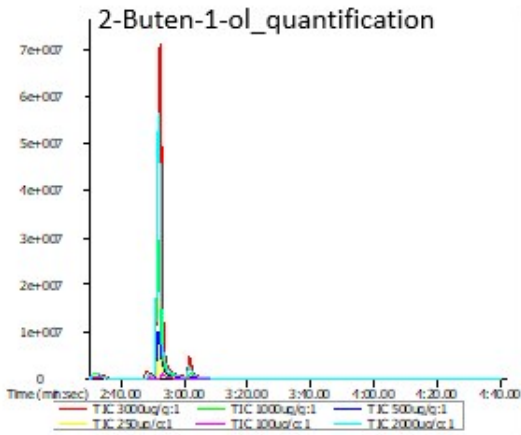


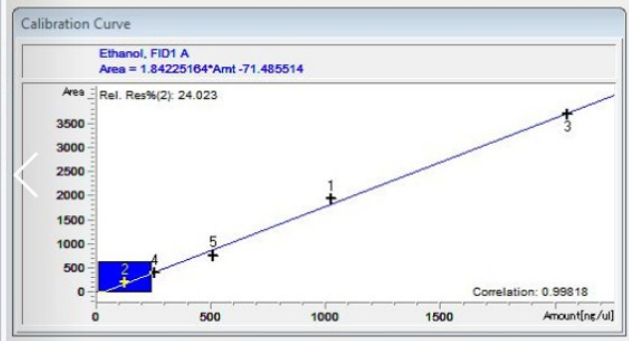
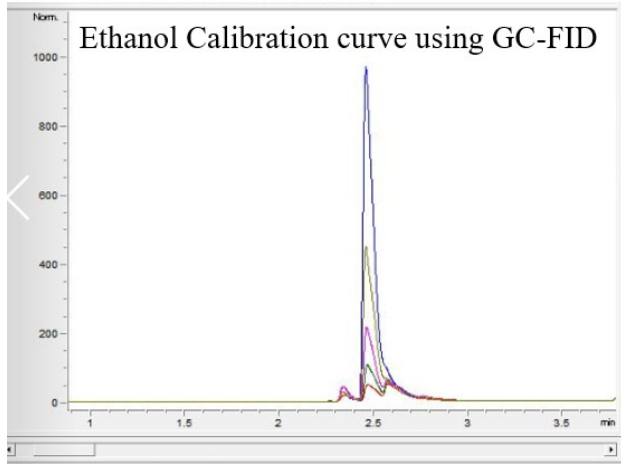
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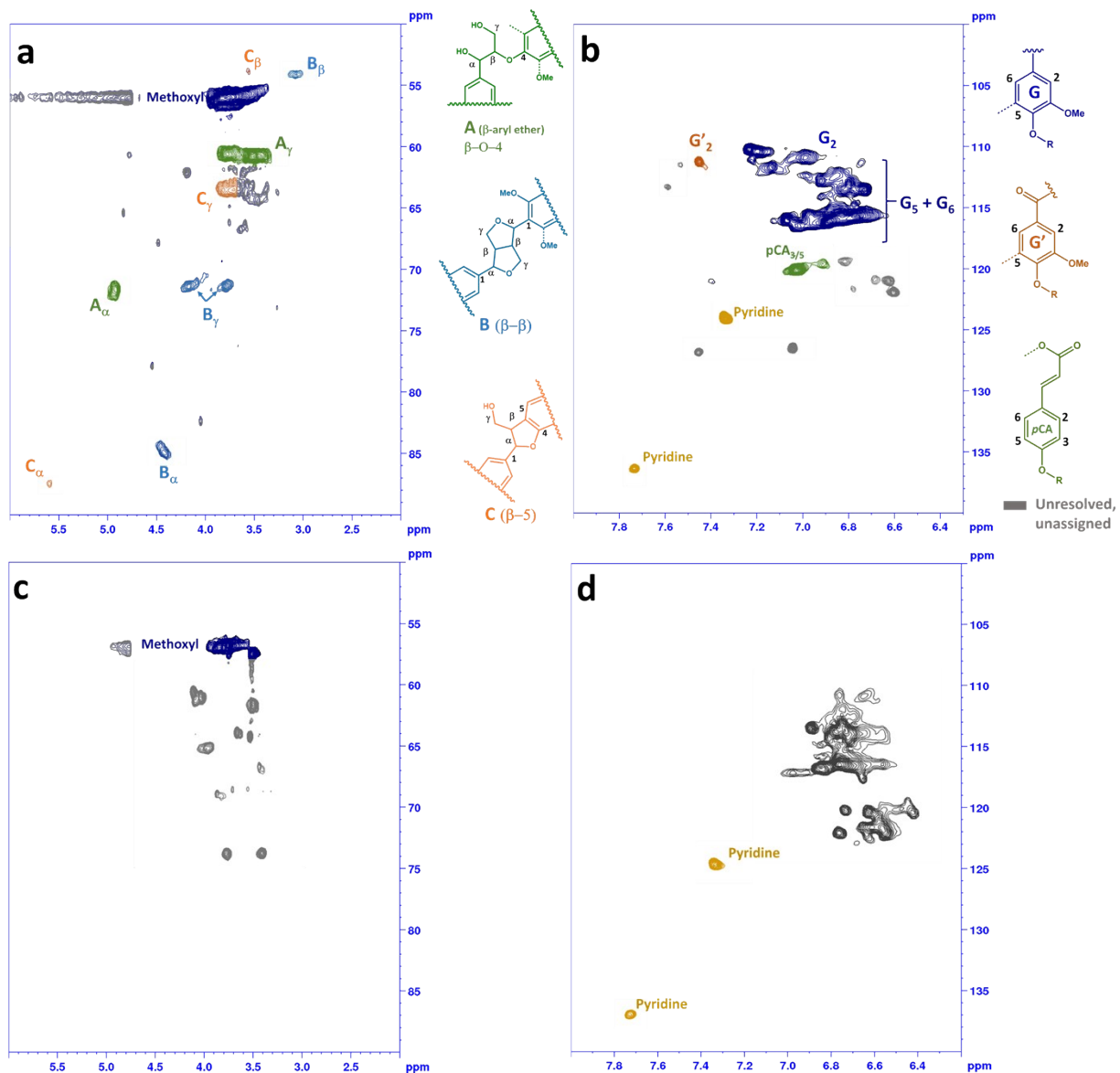


### Methane, diethoxy-\_quantification

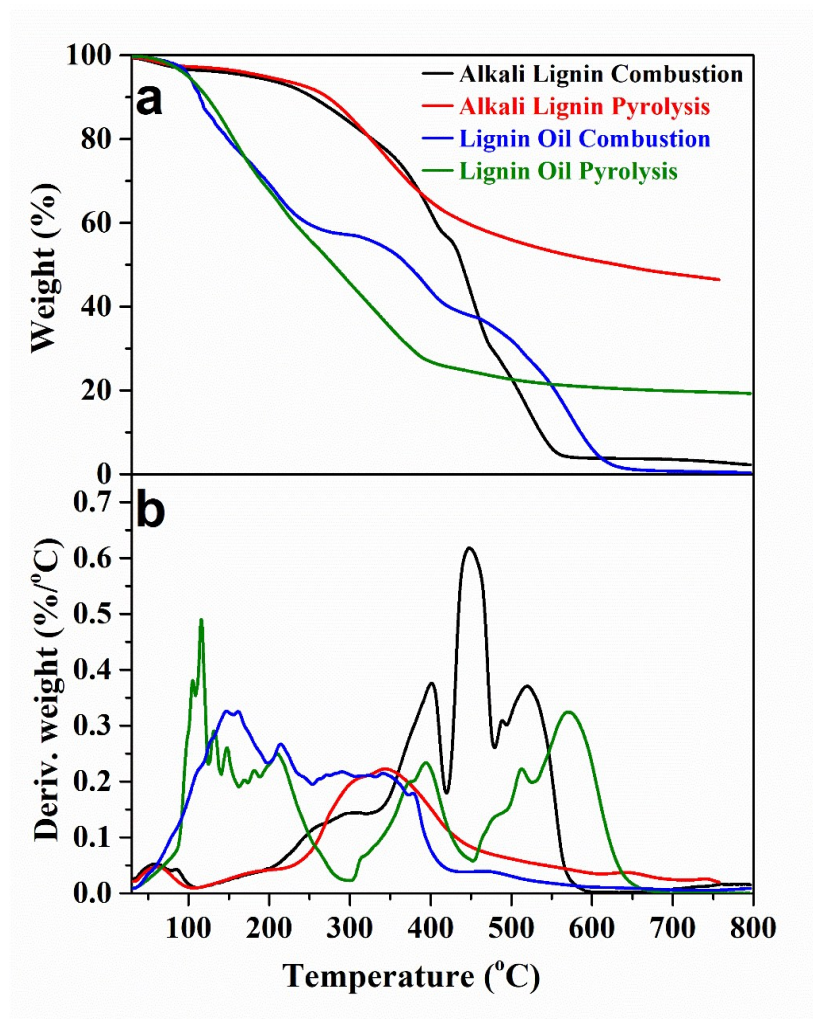








**Fig. S1** Two-dimensional HSQC-NMR spectra of softwood alkali lignin (a) in the aliphatic side chain region ( $\delta_C/\delta_H$  of 50–90/2–6 ppm), (b) in the aromatic ring region ( $\delta_C/\delta_H$  of 100–140/6.2–8.0 ppm) and of the bio-oil (c) aliphatic side chain region ( $\delta_C/\delta_H$  of 50–90/2–6 ppm) and (d) aromatic ring region ( $\delta_C/\delta_H$  of 100–140/6.2–8.0 ppm). The conditions and properties of the bio-oil was listed in Table 1 (entry 4). The peaks are assigned according to the literature.<sup>1, 2</sup>



**Fig. S2** TGA (a) and DTG (b) profiles of the alkali lignin and bio-oil (case 4 in Table 1) collected under airflow condition (combustion) and N<sub>2</sub> flow condition (pyrolysis).

**Table S2** Proximate and ultimate analysis of the alkali lignin and bio-oil.

	Proximate analysis (wt %, d.b.) <sup>a</sup>				Ultimate analysis (wt%, d.a.f.) <sup>b</sup>						
	VM <sup>c</sup>	FC <sup>d</sup>	Ash	Moisture	C	H	O	N	S	O/C	H/C
Lignin	46.5	51.5	2.3	2.7	63.7	5.11	30.0	0.26	1.74 <sup>f</sup>	0.35	0.96
Bio-oil <sup>e</sup>	80.7	18.9	0.3	N.A <sup>g</sup>	69.3	7.31	22.1	0.09	0.36	0.24	1.27

<sup>a</sup> On a dry basis.

<sup>b</sup> On a dry, ash-free basis.

<sup>c</sup> VM: volatile matter.

<sup>d</sup> FC: fixed carbon.

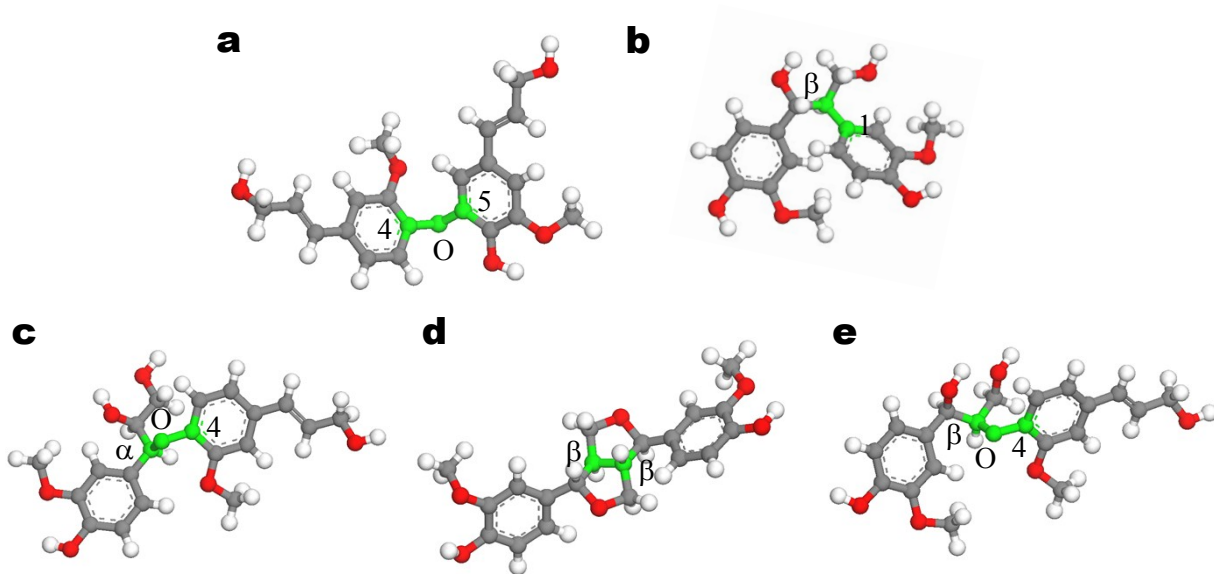
<sup>c,d</sup> VM and FC were determined using thermogravimetric analysis (TGA) in N<sub>2</sub> at 10 °C min<sup>-1</sup> to 800 °C.

<sup>e</sup> The bio-oil was produced at 3 g lignin, 60 g ethanol, and 12 g formic acid for 60 min (case 4 in Table 1)

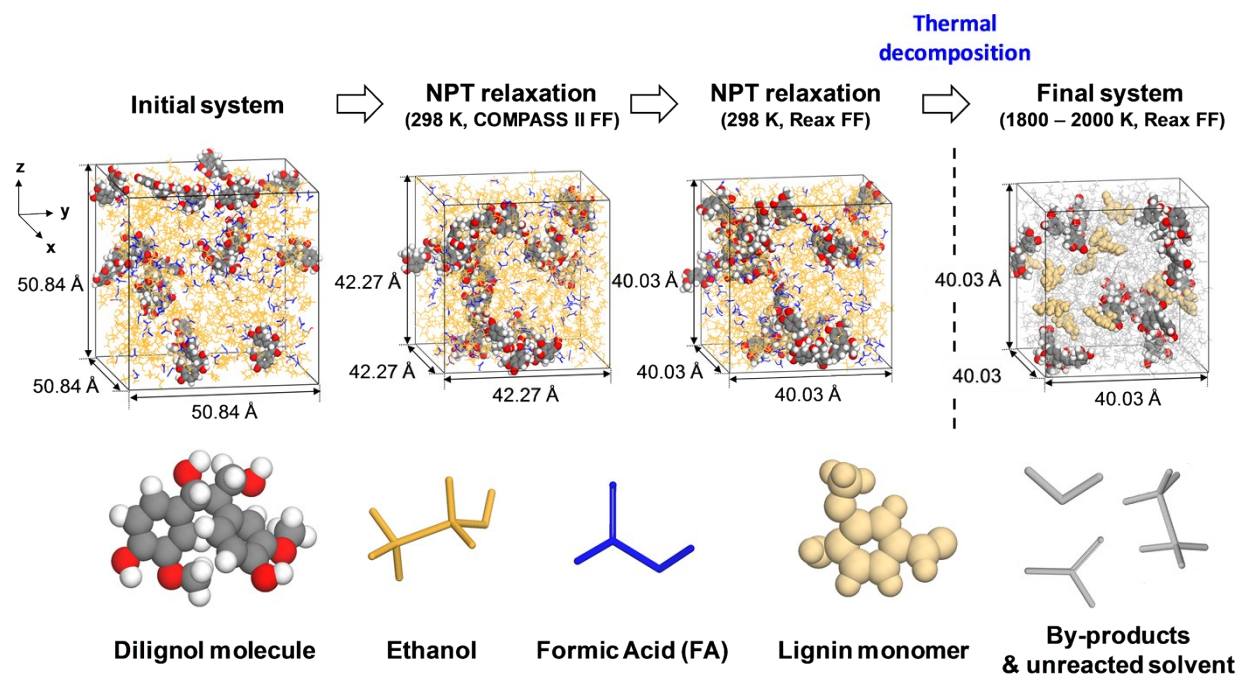
<sup>f</sup> Low-sulfur-containing alkali lignin (1.74 wt% of sulfur) was used instead of high-sulfur-containing conventional Kraft lignin.

<sup>g</sup> The sulfur in bio-oil was only 0.36 wt%. However, no sulfur containing species were detected in bio-oil using GC-TOF/MS. The reason of the contradictory results of GC-TOF/MS and EA could be due to the limitation of GC-MS, which is able to detect only volatile fractions of bio-oil with molecular weights less than 650 m/z. Therefore, we believe that the sulfur detected by EA could be present in the form of non-volatile heavy oil fraction. The rest of sulfur might have been lost in the gaseous form, but due to the limitation of RGA-GC, we are not able to detect any sulfurous gas.

<sup>g</sup> N.A = Not applicable due to the volatile fraction (b.p. < 100 °C) of the bio-oil.



**Fig. S3** Molecular models of **a** 4-O-5, **b**  $\beta$ -1, **c**  $\alpha$ -O-4, **d**  $\beta$ - $\beta$ , and **e**  $\beta$ -O-4 dilignol, respectively. For the clear view, the atoms comprising lignin linkage of the dilignol molecule is colored in green with the notes to indicate the connecting atoms. Carbon, hydrogen, and oxygen atoms are colored in gray, white, and red, respectively, except the linkage atoms.



**Fig. S4** Schematic illustration of simulation models by reax-MD simulation procedure. The lattice parameters were taken from the  $\beta$ -1 dilignol system, and there were less than 1 Å differences between systems. From the initial to NPT relaxation using reax FF, simulation system was composed of three species, i.e. dilignol molecule, ethanol, and formic acid (FA). For the clear view, ethanol and FA were presented by orange and blue stick, respectively. Dilignol molecules were shown by CPK style with each atomic color (i.e. gray, red, and white for carbon, oxygen, and hydrogen, respectively). After the thermal decomposition, final system was composed of unreacted reactants, lignin monomers, and byproducts. Except dilignol molecules, lignin monomers and remaining byproducts including unreacted solvent are shown by ivory CPK molecule, and light gray stick, respectively.



**Table S3** Product yields and solvent consumption by the thermal and catalytic decomposition of methanol, ethanol, and isopropanol in the blank experiments.

No.	Solvent	Reaction conditions <sup>f</sup>	Reaction Pressure	Final Pressure <sup>g</sup>	Gas <sup>h</sup>	Water <sup>i</sup>	SDLPs	Solvent consumption <sup>j</sup>
			MPa		wt%			
1	methanol	200 °C, 30 min	3.9	0	0	0	-	0
2	methanol	250 °C, 30 min	10.2	0	0	0	-	0.37
3	methanol	300 °C, 30 min	20.2	0	0	0	-	1.00
4	methanol	350 °C, 30 min	29.8	0.2	0.32	0.83	-	3.64
5	methanol	400 °C, 30 min	42.0	1.1	1.40	0.93	-	10.08
6	methanol	400 °C, 120 min	46.0	4.1	3.58	1.32	-	23.47
7	methanol <sup>a</sup>	300 °C, 30 min	20.0	0.4	0.4	1.167	-	6.42
8	methanol <sup>a</sup>	350 °C, 30 min	37.5	2.6	2.83	4.36	-	19.81
9	methanol <sup>b</sup>	300 °C, 30 min	20.0	0.6	0.48	0	-	5.25
10	methanol <sup>b</sup>	350 °C, 30 min	42.1	5.0	5.02	2.97	-	20.89
11	ethanol	200 °C, 30 min	2.6	0	0	0	-	0
12	ethanol	250 °C, 30 min	7.8	0	0	0	-	0.14
13	ethanol	300 °C, 30 min	17.8	1.0	0.15	0.4	-	2.01
14	ethanol	350 °C, 30 min	22.0	3.0	0.56	0.67	4.95	11.10
15	ethanol	400 °C, 30 min	34.2	2.2	1.75	1.37	-	16.81
16	ethanol	400 °C, 120 min	40.2	4.3	5.83	7.78	-	45.55
17	ethanol <sup>a</sup>	300 °C, 30 min	16.0	0.7	0.92	1.48	-	11.30
18	ethanol <sup>a</sup>	350 °C, 30 min	30.1	2.5	2.38	6.01	-	29.44
19	ethanol <sup>c</sup>	350 °C, 30 min	34.5	4.4	5.98	7.2	11.46	49.44
20	ethanol <sup>b</sup>	300 °C, 30 min	18.3	0.8	1.02	0	-	12.62
21	ethanol <sup>b</sup>	350 °C, 30 min	27.7	2.1	3.05	4.85	-	25.67
22	ethanol <sup>d</sup>	350 °C, 30 min	31.6	3.8	5.55	6.89	10.35	45.45
23	IPA	200 °C, 30 min	2.5	0	0	0	-	0
24	IPA	250 °C, 30 min	8.3	0	0	0	-	0
25	IPA	300 °C, 30 min	12.3	0.2	0.32	0	-	0.79
26	IPA	350 °C, 30 min	20.3	1.2	1.48	0.21	-	7.42
27	IPA	400 °C, 30 min	35.1	3.6	3.15	0.59	-	14.16
28	IPA	400 °C, 120 min	38.5	6.0	5.47	2.64	-	31.90
29	IPA <sup>a</sup>	300 °C, 30 min	17.2	1.1	1.57	2.82	-	16.60
30	IPA <sup>a</sup>	350 °C, 30 min	27.1	2.0	2.68	5.07	-	20.51
31	IPA <sup>b</sup>	300 °C, 30 min	16.8	0.9	1.22	2.22	-	15.37
32	IPA <sup>b</sup>	350 °C, 30 min	24.1	3.3	2.38	4.42	-	19.78
33	ethanol <sup>c</sup>	350 °C, 30 min	34.4	6.1	4.18	5.61	1.26	4.03

<sup>a</sup> 0.2 g CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (sulfided); <sup>b</sup> Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (activated); <sup>c</sup> 0.5 g CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (sulfided); <sup>d</sup> 0.5 g Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (activated); <sup>e</sup> 12 g formic acid.

<sup>f</sup> Reactions were performed in inert environment (N<sub>2</sub>) at atmospheric pressure. 60 g of solvent was used in all cases.

<sup>g</sup> Final pressure; an indication of solvent decomposition to gas, was recorded after cooling the reactor to room temperature.

<sup>h</sup> Gas was collected in a Tedler bag through wet gas meter. The weight of gas was calculated in two different ways: (1) using Tedler bag's weight difference basis and (2) using an ideal gas law to calculate the total number of moles of individual gas species as detected in RGA-GC (volume of the gas was calculated using wet gas meter). Both values are in good agreement with less than 10% variance. The final weight of gas also included the weight of nitrogen which was used initially to pressurize the reactor.

<sup>i</sup> Moisture content was determined using Karl fisher titration, and average values of three readings were presented.

<sup>j</sup> Solvent consumption was calculated using external standard method by drawing a calibration curve of respective analyte in GC-FID.

**Table S4** Composition of the gases formed by the thermal and catalytic decomposition of methanol, ethanol, and isopropanol in the blank experiments.

	Solvent	Reaction Conditions <sup>f</sup>	Gas composition (mmol)							Total
			H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> +	
1	methanol	200 °C, 30 min	-	-	-	-	-	-	-	0
2	methanol	250 °C, 30 min	-	-	-	-	-	-	-	0
3	methanol	300 °C, 30 min	-	-	-	-	-	-	-	0
4	methanol	350 °C, 30 min	0.71	-	0.21	2.80	-	-	-	3.72
5	methanol	400 °C, 30 min	8.68	7.99	0.48	2.79	-	-	-	19.94
6	methanol	400 °C, 120 min	58.46	49.97	5.92	19.8	-	-	-	134.1
7	methanol <sup>a</sup>	300 °C, 30 min	4.50	-	0.45	3.60	-	-	-	8.55
8	methanol <sup>a</sup>	350 °C, 30 min	54.72	0.13	6.28	29.32	-	-	-	90.45
9	methanol <sup>b</sup>	300 °C, 30 min	12.44	4.98	0.05	0.77	-	-	-	18.24
10	methanol <sup>b</sup>	350 °C, 30 min	57.86	21.36	14.56	57.61	-	-	-	151.3
11	ethanol	200 °C, 30 min	-	-	-	-	-	-	-	0
12	ethanol	250 °C, 30 min	-	-	-	-	-	-	-	0
13	ethanol	300 °C, 30 min	0.24	-	0.002	0.02	0.022	-	-	0.29
14	ethanol	350 °C, 30 min	4.75	0.009	0.20	0.25	0.71	0.02	0.015	5.95
15	ethanol	400 °C, 30 min	19.32	0.52	10.08	9.7	9.15	0.66	0.30	49.73
16	ethanol	400 °C, 120 min	86.5	4.01	17.40	22.01	28.60	1.57	0.60	160.7
17	ethanol <sup>a</sup>	300 °C, 30 min	15.80	0.06	0.016	0.25	3.94	0.007	0.07	20.14
18	ethanol <sup>a</sup>	350 °C, 30 min	30.87	1.62	0.36	2.61	22.37	0.06	0.33	58.21
19	ethanol <sup>c</sup>	350 °C, 30 min	15.26	0.57	2.93	6.09	68.23	0.46	2.4	95.99
20	ethanol <sup>b</sup>	300 °C, 30 min	7.79	2.41	0.07	3.28	0.24	0.05	0.02	13.87
21	ethanol <sup>b</sup>	350 °C, 30 min	24.35	8.93	0.93	19.54	24.57	0.06	0.33	78.71
22	ethanol <sup>d</sup>	350 °C, 30 min	8.56	5.17	2.96	49.59	41.75	0.78	1.06	109.9
23	IPA	200 °C, 30 min	-	-	-	-	-	-	-	0
24	IPA	250 °C, 30 min	-	-	-	-	-	-	-	0
25	IPA	300 °C, 30 min	0.53	-	0.004	0.07	0.002	0.093	0.004	0.706
26	IPA	350 °C, 30 min	20.70	0.05	0.02	1.27	0.0	0.480	0	22.52
27	IPA	400 °C, 30 min	87.48	0.01	0.09	7.56	0.16	4.86	0.07	100.2
28	IPA	400 °C, 120 min	187.0	0.88	0.20	7.54	0.20	5.21	0.10	201.1
29	IPA <sup>a</sup>	300 °C, 30 min	18.04	-	0.03	0.12	-	16.56	0.008	34.76
30	IPA <sup>a</sup>	350 °C, 30 min	42.27	-	2.25	17.87	-	23.01	0.09	85.48
31	IPA <sup>b</sup>	300 °C, 30 min	16.02	-	6.06	0.09	-	10.1	0.03	32.28
32	IPA <sup>b</sup>	350 °C, 30 min	47.01	-	1.9	9.01	-	19.0	0.088	76.99
33	ethanol <sup>c</sup>	350 °C, 30 min	127.1	34.13	52.57	0.67	2.10	-	-	216.57

<sup>a</sup> 0.2 g CoM<sub>O</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (sulfided); <sup>b</sup> 0.2 g Ru/γ-Al<sub>2</sub>O<sub>3</sub> (activated); <sup>c</sup> 0.5 g CoM<sub>O</sub>/γ-Al<sub>2</sub>O<sub>3</sub> (sulfided); <sup>d</sup> 0.5 g Ru/γ-Al<sub>2</sub>O<sub>3</sub> (activated);

<sup>e</sup> 12 g formic acid.

<sup>f</sup> Reactions were performed in inert environment (N<sub>2</sub>) at atmospheric pressure. 60 g of solvent was used in all cases.

**Table S5** Major chemical species formed by the thermal decomposition of methanol determined by GC-TOF/MS.

No.	Compound Name	R.T. (min:sec)	GC Area					
			200 °C, 30 min	250 °C, 30 min	300 °C, 30 min	350 °C, 30 min	400 °C, 30 min	400 °C, 120 min
1	Dimethyl ether	01:28.1	610907	2033418	3837419	22910488	117849735	1289507
2	Cyclopropene	01:29.5		154932	156050	1395229	1481819	
3	Methyl formate	01:31.6	377492	758759	942140	3202644	13479653	53164074
4	2-Butene, 2-methyl-	01:41.3						2219716
5	Methylal	01:42.9			299042		9301080	82793316
6	Acetic acid, methyl ester	01:45.7					6008449	4346434
7	1,3,5,7-Tetroxane	01:59.4				6629045	35215055	22428438
8	1-Propanol	01:59.7						1608783
9	Ethane, 1,1-dimethoxy-	02:02.9					105178	7083878
10	2-Propenoic acid, methyl ester	02:11.2					1777537	8671430
11	Carbonic acid, dimethyl ester	02:12.5				344767	1228444	
12	Methyl propionate	02:17.6					1539152	9355864
13	1-Propanol, 2-methyl-	02:22.8					602744	9649555
14	Propane, 2,2-dimethoxy-	02:28.6	18461659	5573325	2912089	1667020	2267167	4092919
15	Methyl isobutyrate	02:48.4						6233244
16	Methyl methacrylate	03:08.3						3736726
17	Butanoic acid, 2-methyl-, methyl ester	04:14.4						2483270
18	1-Butanol, 3-methoxy-, acetate	04:34.2						1000829
19	2(3H)-Furanone, dihydro-3-methyl-	08:28.3						3227410
20	Butanoic acid, 2,3-dimethyl-, methyl ester	09:19.3						2267568

**Table S6** Major chemical species formed by the thermal decomposition of ethanol determined by GC-TOF/MS.

No.	Compound Name	R.T. (min:sec)	GC Area					350 °C, 30 min (EtOH-F.A)
			250 °C, 30 min	300 °C, 30 min	350 °C, 30 min	400 °C, 30 min	400 °C, 120 min	
1	Butane	01:32.0					50963504	
2	2-Butene	01:33.7					2393551	
3	Isobutane	01:40.9				3220677	6497234	
4	Ethyl ether	01:42.2			526602	12832227	76186193	
5	Isopropyl Alcohol	01:42.6					184583847	
6	Acetic acid, methyl ester	01:46.8				5269144	8047334	
7	Ethyl formate	01:46.9						107882
8	2-Propen-1-ol	01:52.4					1529033	
9	1-Pentene, 3-methyl-	01:52.8				756109	5393700	
10	1-Propanol	01:54.2				2791065	9317437	
11	Pentane, 2-methyl-	01:55.0					1712742	
12	Pentane, 3-methyl-	01:59.3				1127668	36073211	
13	1-Hexene	02:01.7					1557826	
14	2-Propanone	02:03.6					26710008	
15	2-Butanone	02:04.0				154581079	202989835	
16	Butane	02:04.5					3185407	
17	2-Hexanol	02:06.7					7010112	
18	2-Butanol	02:07.4			353934	93486337	360653683	586506
19	Ethyl Acetate	02:10.6	1140829	20918933	173611464	87275678	43218220	1079278
20	2-Pentene, 3-methyl-, (Z)-	02:12.7					12059146	
21	Cyclopentane, methyl-	02:17.3				1401607	19894903	
22	Methyl propionate	02:17.6					1827726	
23	Butane, 2-ethoxy-	02:27.6					4153236	
24	2-Butenal, (E)-	02:29.0			9188003	2913551	11575330	
25	2,3-Butanediol	02:31.3			42357081	239343531	3460250	
26	1-Butanol	02:37.0			8594794	104281113	248722862	4982688
27	2-Propen-1-ol, 2-methyl-	02:38.6				50046387	15183769	
28	Hexane, 3-methyl-	02:40.8					8010327	
29	Cyclohexene	02:45.4				1480050	27138711	
30	2-Buten-1-ol, (Z)-	02:46.4			13494118	14703795	25234603	
31	(R)-(-)-2-Pentanol	02:47.9				19718935	65835623	
32	2-Pentanone	02:48.8				2586068	190191230	
33	Methane, diethoxy-	02:51.9						3743911
34	Butane, 1-ethoxy-	02:54.6					3779989	
35	3-Pentanone	02:56.1					1164628	
36	Formic acid, 1-methylpropyl ester	02:56.1						364699
37	Heptane	02:57.2					7528613	
38	(S)-(+)-2-Pentanol	02:59.6				68637089	238667534	
39	3-Pentanol	03:00.4					14066466	
40	Propanoic acid, ethyl ester	03:06.5					31230040	3539377
41	Cyclopentene, 3-ethyl-	03:16.1					1532872	
42	Ethane, 1,1-diethoxy-	03:20.8		370506	2766017	21083427	77339555	62764644
43	Cyclopentane, ethyl-	03:27.9					2195163	

44	Furan, tetrahydro-2,5-dimethyl-	03:28.2		6276954	
45	Cyclohexene, 3-methyl-	03:32.7		2314564	
46	1-Butanol, 2-methyl-, (S)-	03:33.2		3135529	
47	2-Pentanone, 3-methyl-	03:43.7		124841630	
48	3-Heptene, 5-methyl-	03:44.8		2277246	
49	3-Pentanol, 3-methyl-	03:47.9	1138042	98634260	96561
50	Furan, tetrahydro-2,5-dimethyl-	03:57.1		3439514	
51	1-Pentanol	04:01.4		6496715	
52	3-Hexene, 3-ethyl-	04:04.8		1548658	
53	Heptane, 3-methyl-	04:05.1		12588109	
54	Hexane, 3-ethyl-	04:05.9		1213583	
55	3-Hexanone	04:18.6		44561266	
56	Heptane, 3-methylene-	04:23.1		5083542	
57	2-Hexanone	04:23.5	3580648	103245321	
58	4-Ethyl-2-hexene	04:24.8		3776784	
59	2-Pentanol, 3-methyl-	04:25.5	8368568	77220301	
60	2-Pentanol, 3-methyl-	04:29.8	8694539	75254749	
61	3-Ethyl-2-hexene	04:33.7		4323771	
62	2,3-Dimethyl-1-hexene	04:34.9		4026087	
63	3-Hexanol	04:35.2		47184043	
64	Heptane, 2,4-dimethyl-	04:37.2		3282887	
65	Butanoic acid, ethyl ester	04:38.6	10426761	17985352	
66	2-Hexanol	04:41.4	37597208	62990552	741320
67	Heptane, 3-methylene-	04:48.1		3797301	
68	Acetic acid, butyl ester	04:56.3	3459388	38142029	
69	Propane, 1,1-diethoxy-	05:01.1			320391
70	Cyclohexene, 1,4-dimethyl-	05:16.9		1446637	
71	1-Penten-3-one, 2-methyl-	05:24.1		14442820	
72	Cyclohexane, ethyl-	05:25.5		1959880	
73	2-Pentanone, 3-ethyl-	05:27.4		14483621	
74	3-Hexanone, 4-methyl-	05:30.9		2451281	
75	Cyclohexanone	05:35.4		2548604	
76	1-Butanol, 2-ethyl-	05:35.6		3364391	
77	2,2,4-Trimethyl-3-pentanol	05:37.5		2121630	
78	2-Pentanone, 3-ethyl-	05:38.3		3694517	
79	1-Pentanol, 3-methyl-	05:42.1		47473456	
80	Cyclohexene, 3-ethyl-	05:47.9		11613438	
81	2-Hexanone, 5-methyl-	05:56.9		1987893	
82	4-Methyl-2-hexanol	06:10.1		5563006	
83	2-Heptanol	06:13.1		2479385	
84	2-Pentanol, 3-methyl-	06:14.9		21235483	
85	1-Hexanol	06:16.6		9921316	
86	4-Heptanone	06:19.8		4716900	
87	2-Hexanol, 3-methyl-	06:35.5		3091356	
88	2-Hexanol, 3-methyl-	06:42.3		1748838	
89	2-Pentanol	06:45.5		1456765	
90	2-Heptanone	06:47.5		10127515	
91	4-Heptanol	06:52.1		1602939	
92	3-Heptanol	07:01.2		1977210	
93	2-Heptanol, (S)-	07:07.6		36790657	

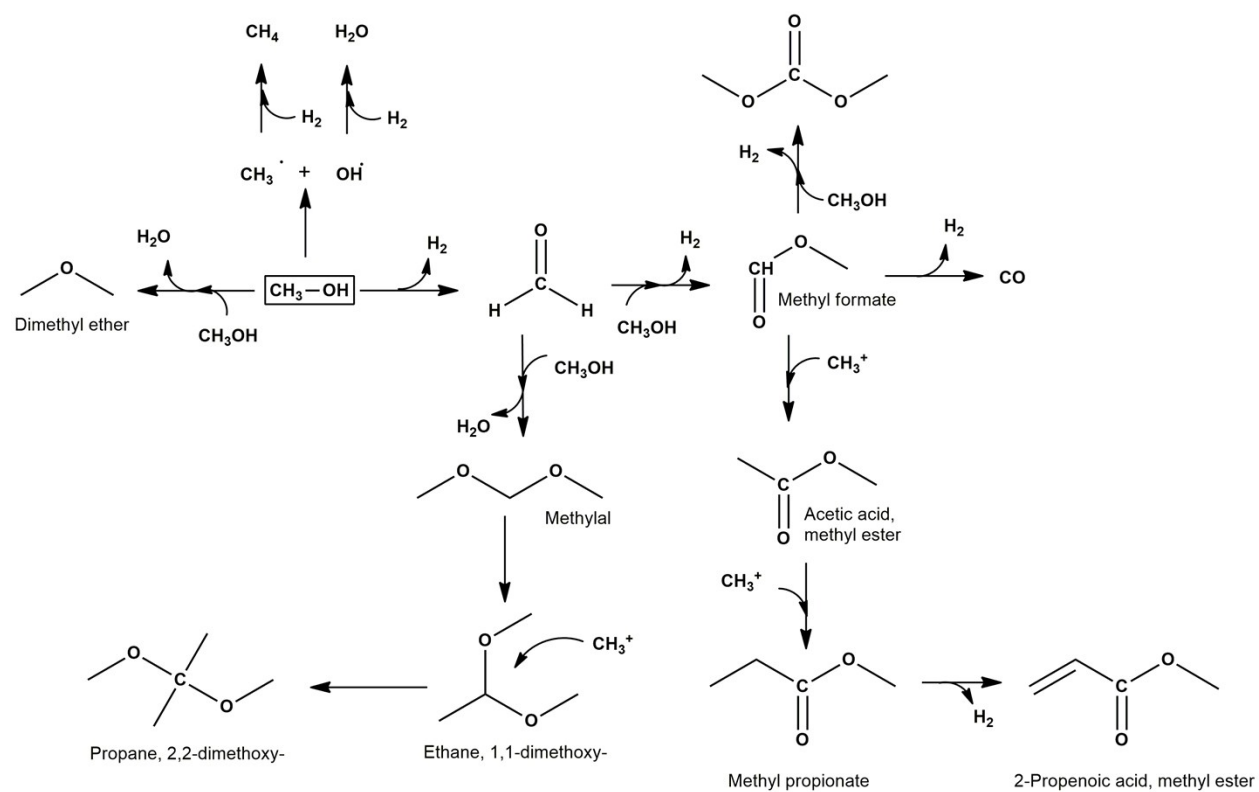
94	Butane, 1-(1-ethoxyethoxy)-	07:26.9		1388668
95	3-Hexanone, 4-ethyl-	07:38.5		5457047
96	4-Heptanone, 3-methyl-	07:47.6		7408169
97	2,4-Dimethylhept-1-ene	08:09.3		1283694
98	3-Octanone	08:12.7		1914744
99	3-Heptanol, 3-methyl-	08:13.8		27623717
100	2-Heptanone, 4-methyl-	08:15.2		4452808
101	Octane, 4-ethyl-	08:36.4		1446449
102	Hexane, 1-nitro-	08:44.9		2675865
103	2-Heptanol, 5-methyl-	08:50.2		2714309
104	2-Heptanone, 5-methyl-	08:52.7		2863184
105	4-Heptanol, 3-methyl-	09:01.8		1550491
106	4-Octanone	09:08.7		2961888
107	2-Heptanol, 3-methyl-	09:19.8		2270618
108	2-Octanone	09:40.2		9729998
109	3-Octanol	09:53.9		1956530
110	Hexanoic acid, ethyl ester	09:55.9	1039844	3019776
111	2-Octanol	10:01.8		34880453
112	1-Butanol, 3-methyl-	11:02.0		1613158
113	3-Octanol, 3-methyl-	11:09.3		1668847
114	2-Nonanol	13:02.6		2989659
115	3-Octanol, 3,6-dimethyl-	13:06.0		1643521
116	3-Nonanol, 3-methyl-	14:09.0		1670366

**Table S7** Major chemical species formed by the thermal decomposition of isopropanol determined by GC-TOF/MS.

No.	Compound Name	R.T. (min:sec)	GC Area			
			300 °C, 30 min	350 °C, 30 min	400 °C, 30 min	400 °C, 120 min
1	1-Pentene, 2-methyl-	01:51.3		2226115	5793786	82155435
2	Butyl isocyanatoacetate	01:54.4				16843985
3	2-Propyn-1-ol, acetate	01:54.5				9611785
4	Diisopropyl ether	01:55.2		506731	2145968	14537624
5	1-Pentene, 3-methyl-	01:56.7				176930329
6	2-Pentene, 4-methyl-, (E)-	01:56.9	1063456	19323246	56617230	346355239
7	Pentane, 1-propoxy-	02:01.2				5223299
8	Pentane, 2,2-dimethyl-	02:03.0				10561325
9	Pentane, 2,4-dimethyl-	02:04.9				39919567
10	1,3-Pentadiene, 2-methyl-	02:09.9		832849	2249027	
11	(Z)-2,4-Hexadiene	02:11.4		902683	2563214	12508985
12	Amylene hydrate	02:12.6				69357212
13	1-Pentene, 2,4-dimethyl-	02:13.2		410996		28795181
14	2-Pentene, 2,4-dimethyl-	02:15.7		27175		49721076
15	Cyclopentene, 3-methyl-	02:16.0				5786493
16	Propane, 2,2-dimethoxy-	02:17.3	631278	907711		
17	2-Butanone, 3-methyl-	02:21.2				7906511
18	Isopropyl acetate	02:21.7		1499313	3165845	7963277
19	Hexane, 2-methyl-	02:22.9				41601342
20	3,5-Dimethylcyclopentene	02:23.1				784512
21	Pentane, 2,3-dimethyl-	02:25.0				5625185
22	Hexane, 3-methyl-	02:28.1				7817070
23	Cyclopentane, 1,1-dimethyl-	02:28.7				9060491
24	(R)-(-)-2-Pentanol	02:34.3				18997243
25	Cyclopentane, 1,3-dimethyl-, cis-	02:34.7				14971119
26	2-Pentanone	02:35.6			28059267	493560137
27	Cyclopentane, 1,3-dimethyl-	02:36.5				14967366
28	Isopropyl Alcohol	02:40.5				17876622
29	(S)-(+)-2-Pentanol	02:45.2			28955038	740412463
30	2-Hexene, 2-methyl-	02:45.5			3452592	23015925
31	2,4-Dimethylfuran	02:54.6				17268656
32	Cyclopentane, 1,1,3-trimethyl-	03:03.2				18095638
33	5,5-Dimethyl-1,3-hexadiene	03:04.5				6798791
34	Hexane, 2,5-dimethyl-	03:06.7				10167430
35	2-Butanol, 2,3-dimethyl-	03:10.1		6035371	43899629	340982453
36	2-Pentanol, 2-methyl-	03:12.9		34949459	308098275	1.345E+09
37	Methyl Isobutyl Ketone	03:16.2		37382120	265849060	1.518E+09
38	4-Penten-2-one, 4-methyl-	03:25.5			27293194	115226007
39	1-Hexene, 4-methyl-	03:26.2				11824157
40	2-Hexanol, (S)-	03:36.5				197449959
41	2-Pentanol, 4-methyl-	03:37.7		10962267	149354496	1.795E+09
42	Toluene	03:42.8				6747739
43	3-Hexanol	03:51.3				7289821
44	Cyclohexane, 1,3-dimethyl-, cis-	03:56.9				16417797
45	2-Pentanone, 4,4-dimethyl-	03:57.5				14980781
46	2-Hexanone	04:05.7				363824511
47	2-Pentanol, 2,4-dimethyl-	04:09.4				120059835
48	3-Penten-2-ol, 4-methyl-,	04:12.8			34440725	158183970
49	3-Penten-2-one, 4-methyl-	04:15.6				450144209
50	2-Hexanol	04:21.2				484427019

51	Cyclohexane, 1,4-dimethyl-	04:27.5	12175316
52	3-Heptene, 2,6-dimethyl-	04:32.8	6929183
53	Heptane, 2,4-dimethyl-	04:44.7	5998677
54	1,3-Dimethyl-1-cyclohexene	04:49.5	12432938
55	Cyclohexene, 3,5-dimethyl-	04:52.1	32263067
56	Heptane, 2,6-dimethyl-	04:54.8	5134475
57	2,3-Dimethyl-2-heptene	04:58.9	6915885
58	3,4,4-Trimethylcyclohexene	05:03.6	8003836
59	2-Hexanol, 2-methyl-	05:04.0	8063057
60	Cyclohexane, 1,1,3-trimethyl-	05:09.6	22426745
61	3-Heptene, 2,6-dimethyl-	05:15.4	5613477
62	2-Penten-1-ol, 2-methyl-	05:19.7	12294980
63	2-Hexanone, 5-methyl-	05:35.0	144948807
64	Cyclohexene, 3,5,5-trimethyl-	05:40.7	30012420
65	2-Hexanol, 5-methyl-	05:51.3	167575205
66	p-Xylene	05:54.5	49659136
67	Cyclohexene, 3,3,5-trimethyl-	06:08.4	14406197
68	Cyclohexene, 3,3,5-trimethyl-	06:25.8	11119333
69	2-Hexanol, 2,5-dimethyl-, (S)-	06:35.3	8659191
70	4-Heptanone, 2-methyl-	07:18.6	15594546
71	2-Heptanone, 4-methyl-	07:46.0	8509582
72	4-Heptanol, 2-methyl-	08:01.5	7927181
73	Cyclohexanol, 4-methyl-, cis-	08:03.6	5882631
74	Benzene, 1,2,3-trimethyl-	08:37.2	219193619
75	4-Heptanone, 2,6-dimethyl-	08:39.7	22411627
76	1-Octene, 4-methyl-	08:56.7	7277456
77	2-Heptanone, 4,6-dimethyl-	09:11.8	10382975
78	2-Heptanol, 2,6-dimethyl-	09:20.8	12091715
79	Cyclohexanol, 3,5-dimethyl-	09:25.9	10508056
80	4-Heptanol, 2,6-dimethyl-	09:28.5	7809168
81	Cyclohexanol, 3,5-dimethyl-	09:37.2	20566582
82	2-Hexanol, 3,4-dimethyl-	09:44.2	10963144
83	trans-3,5-Dimethylcyclohexanone	10:02.7	8101939
84	4-Octanone, 2-methyl-	10:10.9	5356721
85	Cyclohexanol, 3,5-dimethyl-	10:18.4	13315541
86	Cyclopentane, 2-ethylidene-1,1-dimethyl-	10:21.8	5814219
87	Cyclohexanone, 3,3,5-trimethyl-	10:45.9	16938370
88	Cyclohexanol, 3,3,5-trimethyl-	10:53.1	10426148
89	Cyclohexanol, 3,3,5-trimethyl-	11:13.5	20640953
90	Isophorone	13:10.7	36151327





**Fig. S5** Plausible reaction mechanism for methanol-derived products.

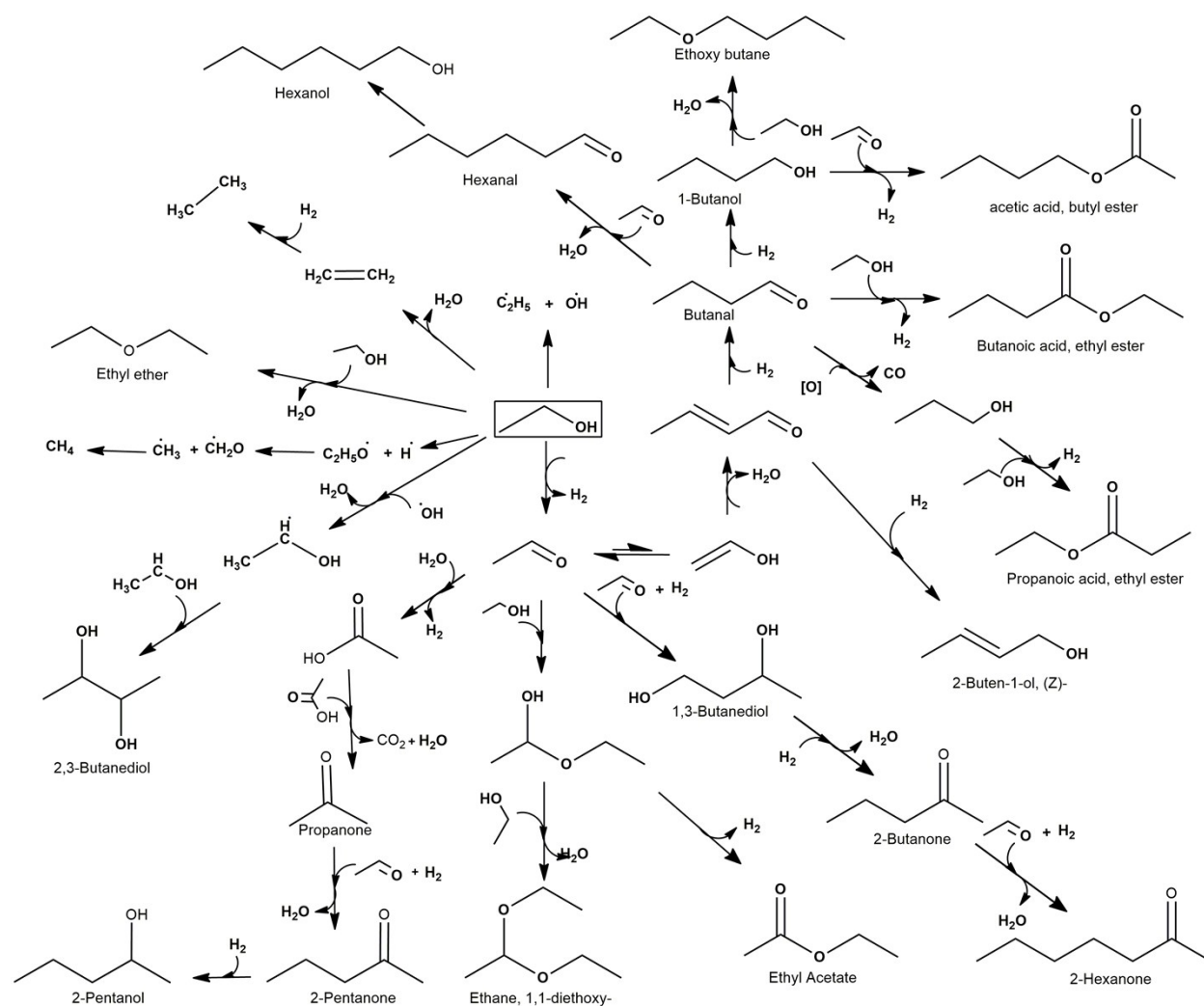
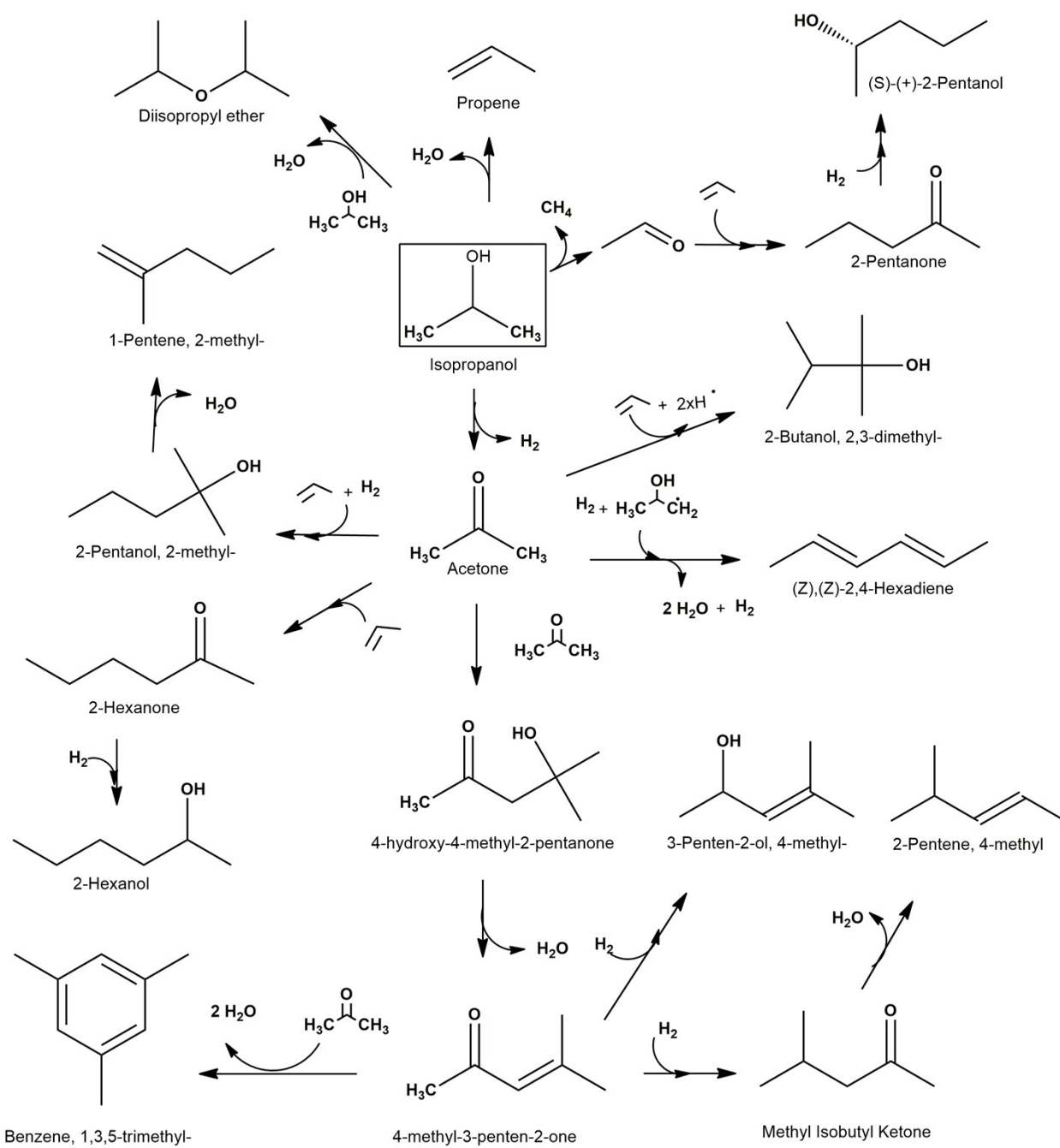
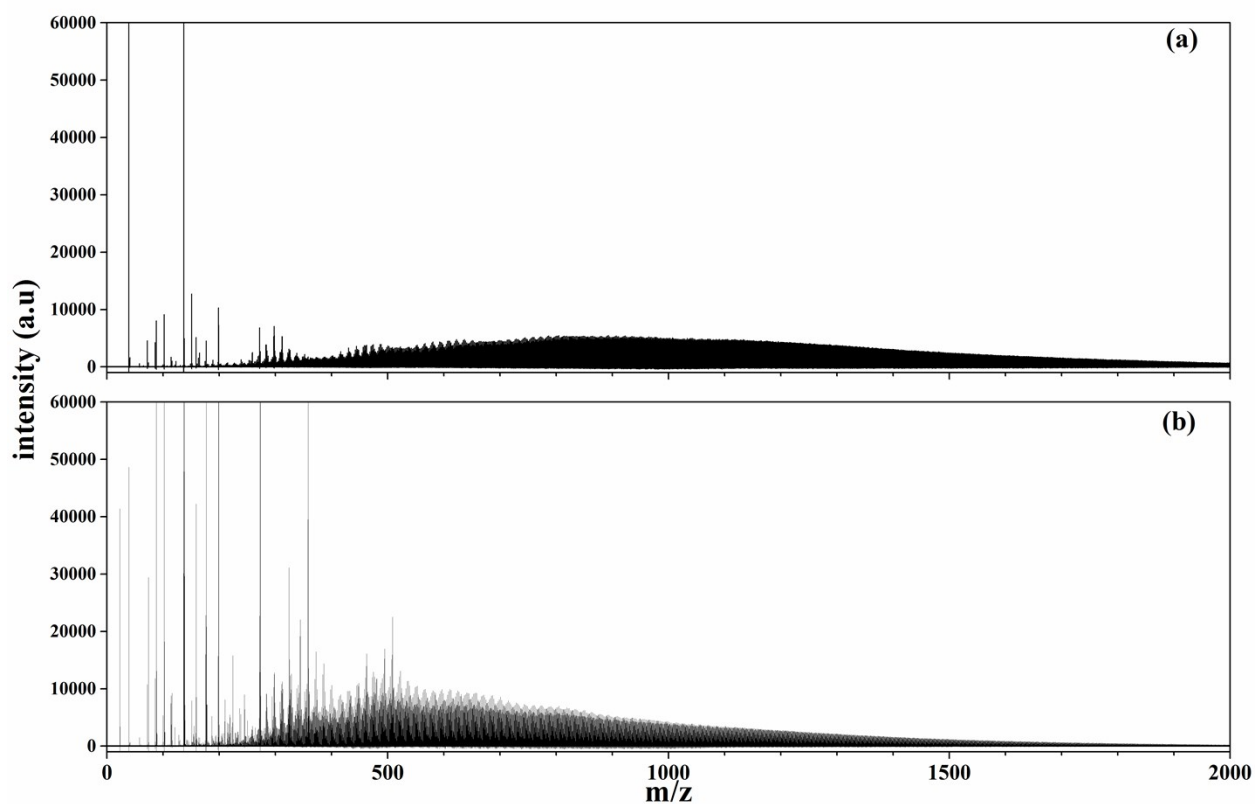


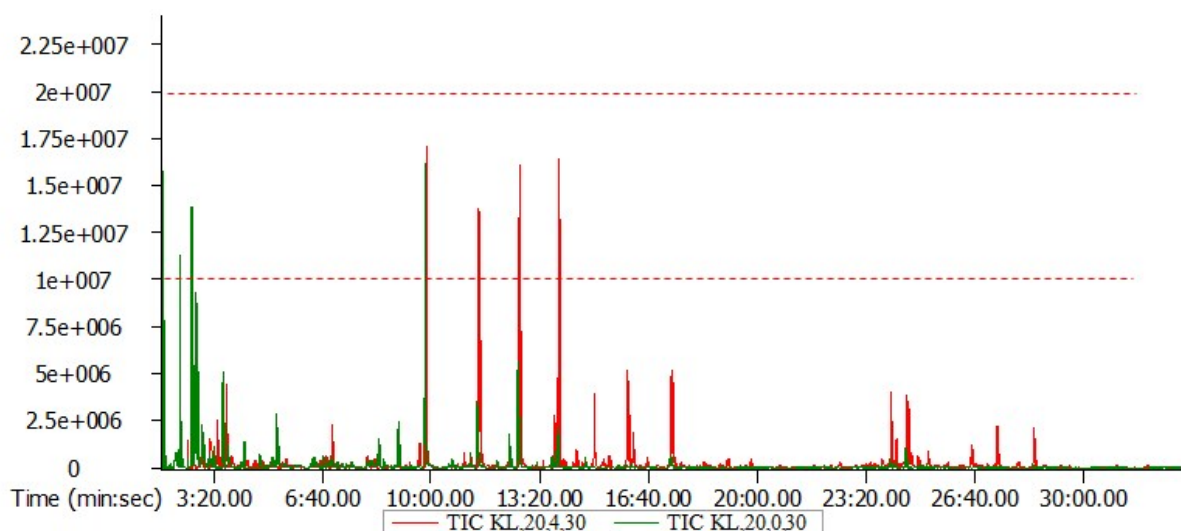
Fig. S6 Plausible reaction mechanism for ethanol-derived products.



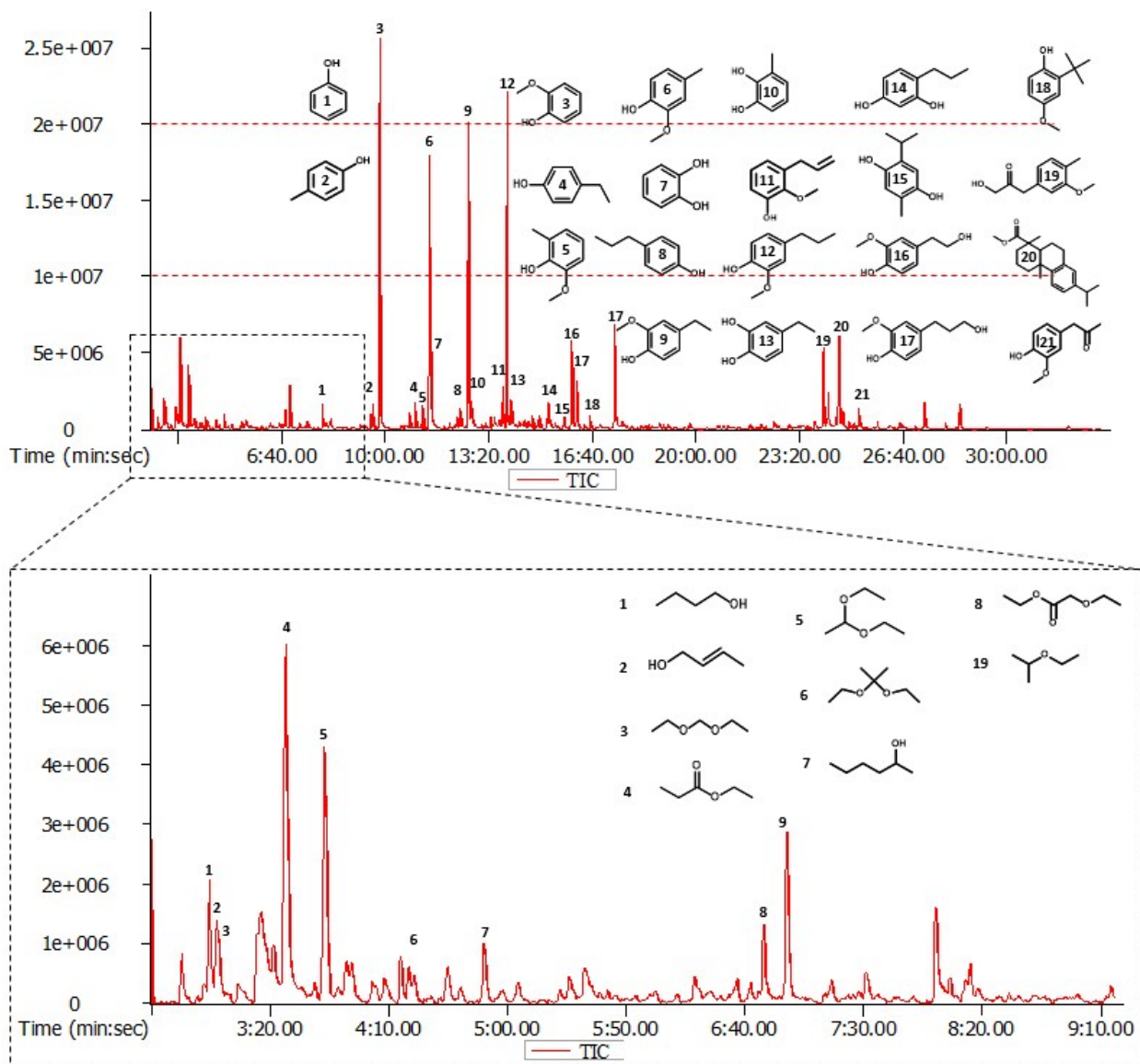
**Fig. S7** Plausible reaction mechanism for isopropanol derived products.



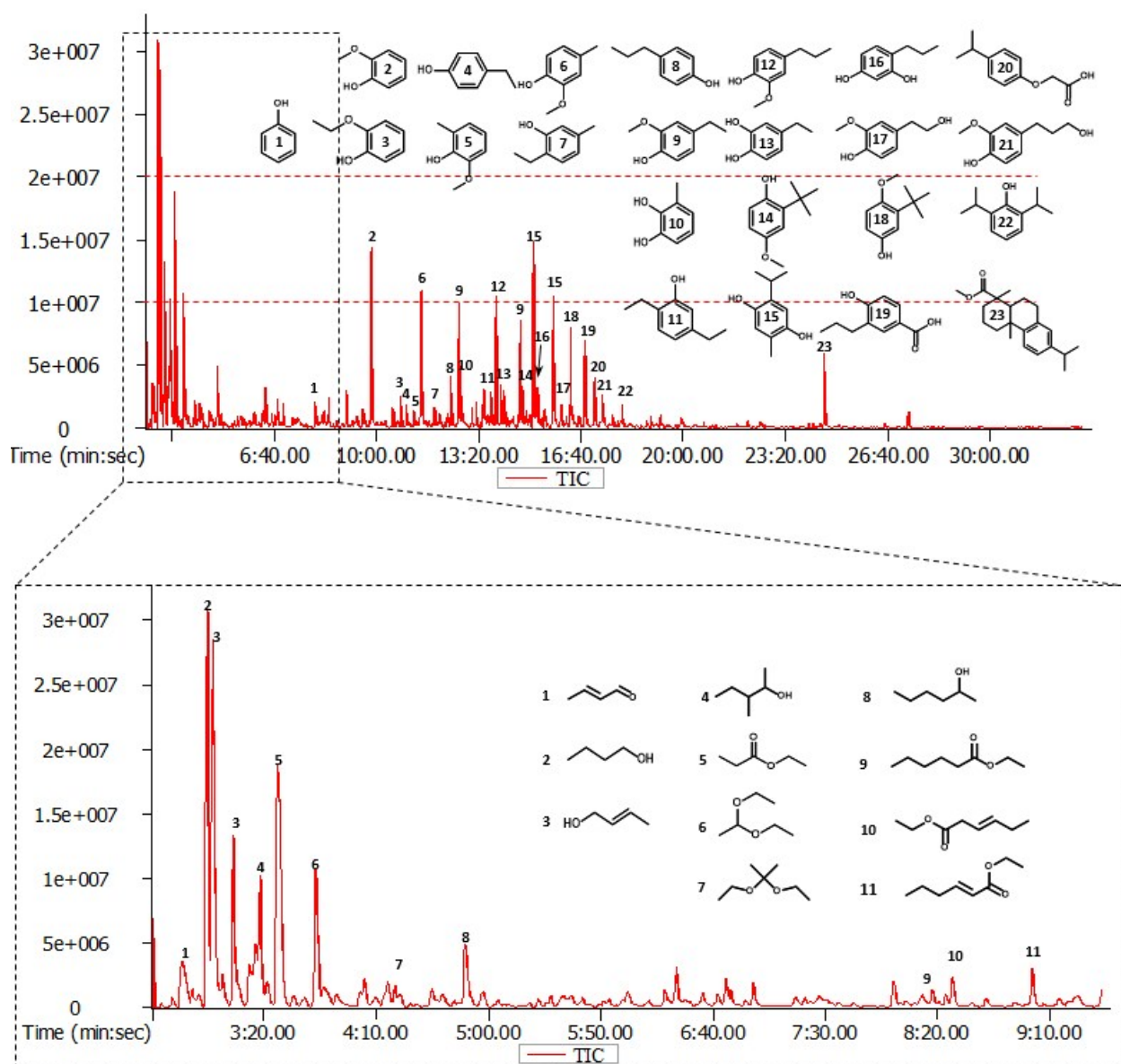
**Fig. S8** MALDI-TOF/MS spectra of the dried bio-oils produced from the experiment of (a) entry 1 and (b) entry 4 in Table 1. Entry 1 reaction condition: 3 g alkali lignin, 60 g ethanol, 0 g formic acid, 30 min, 350 °C, 23.2–24.0 MPa. Entry 4 reaction condition: 3 g alkali lignin, 60 g ethanol, 12 g formic acid, 30 min, 350 °C, 30.0–39.4 MPa.



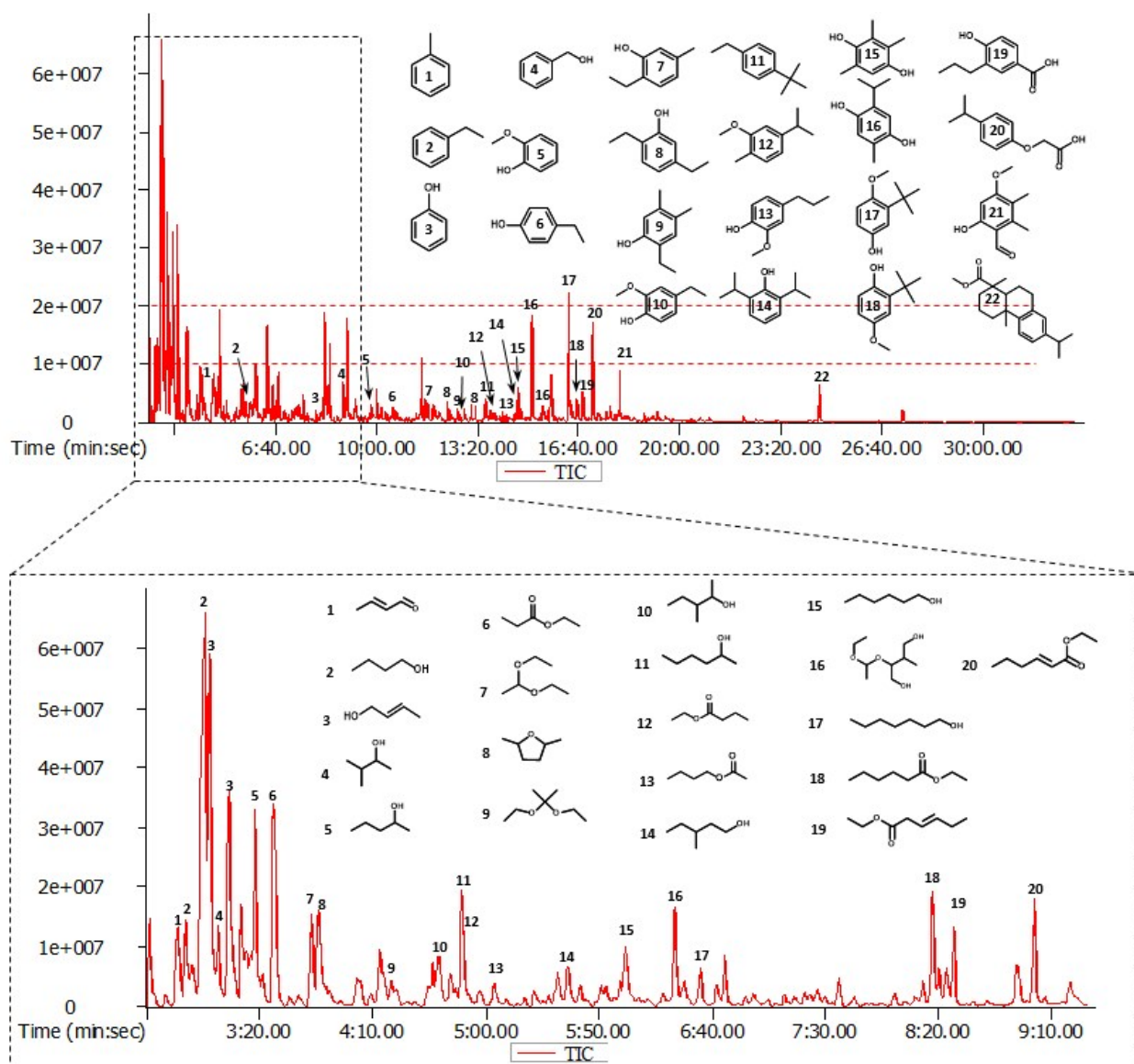
**Fig. S9** Superposition of the gas chromatograms for entry 1 (green) and entry 4 (red) in Table 1 to compare the product distribution. Entry 1 reaction condition: 3 g alkali lignin, 60 g ethanol, 0 g formic acid, 30 min, 350 °C, 23.2–24.0 MPa. Entry 4 reaction condition: 3 g alkali lignin, 60 g ethanol, 12 g formic acid, 30 min, 350 °C, 30.0–39.4 MPa.



**Fig. S10** Gas chromatogram of the bio-oil collected immediately after the reaction in entry 5 in Table 1. Reaction condition: 3 g alkali lignin, 60 g ethanol, 12 g formic acid, 60 min, 350 °C, 29.5–42.1 MPa.

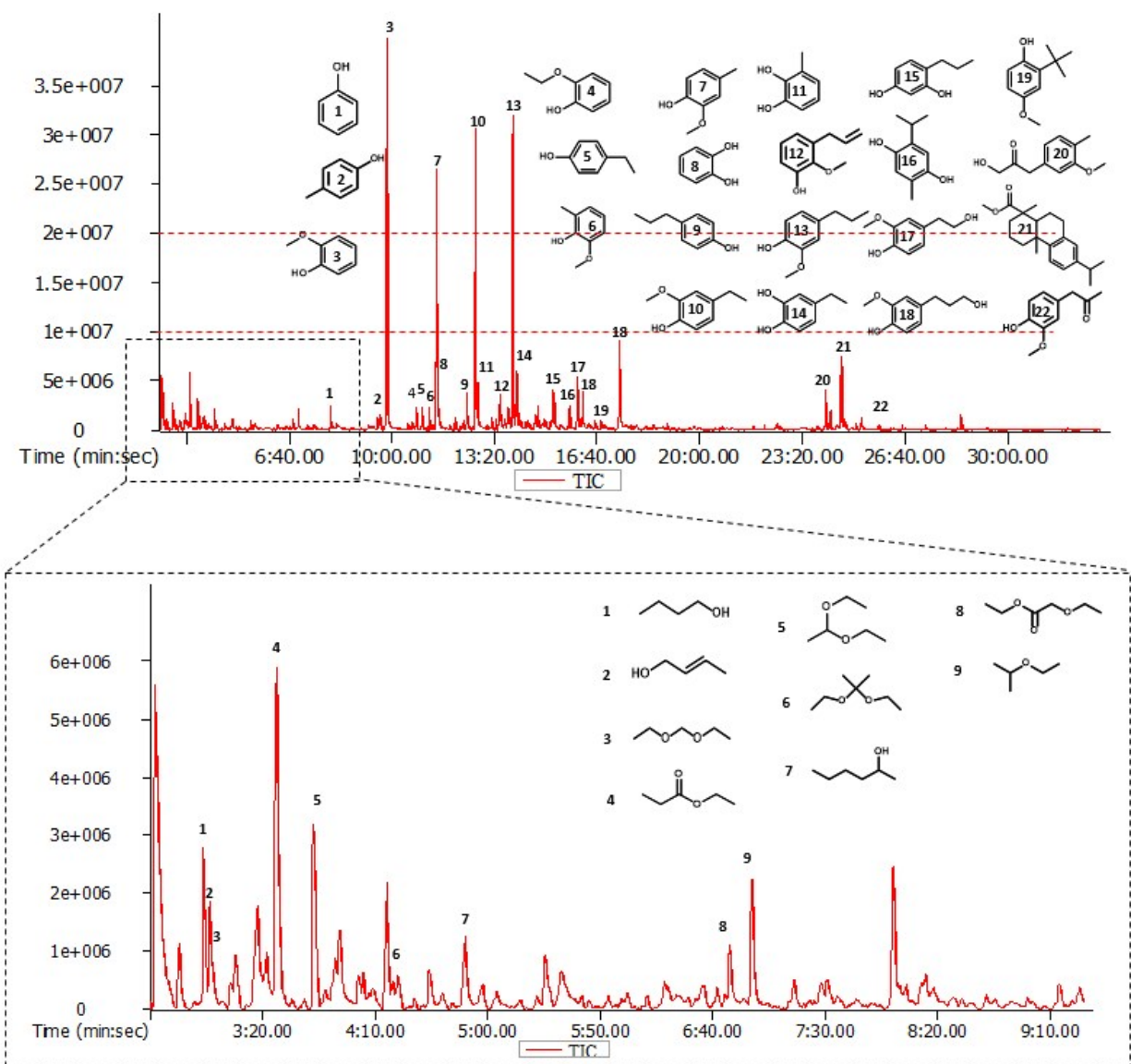


**Fig. S11** Gas chromatogram of the bio-oil collected immediately after the reaction in entry 6 in Table 1. Reaction condition: 3 g alkali lignin, 60 g ethanol, 12 g formic acid, 300 min, 350 °C, 29.8–43.6 MPa.

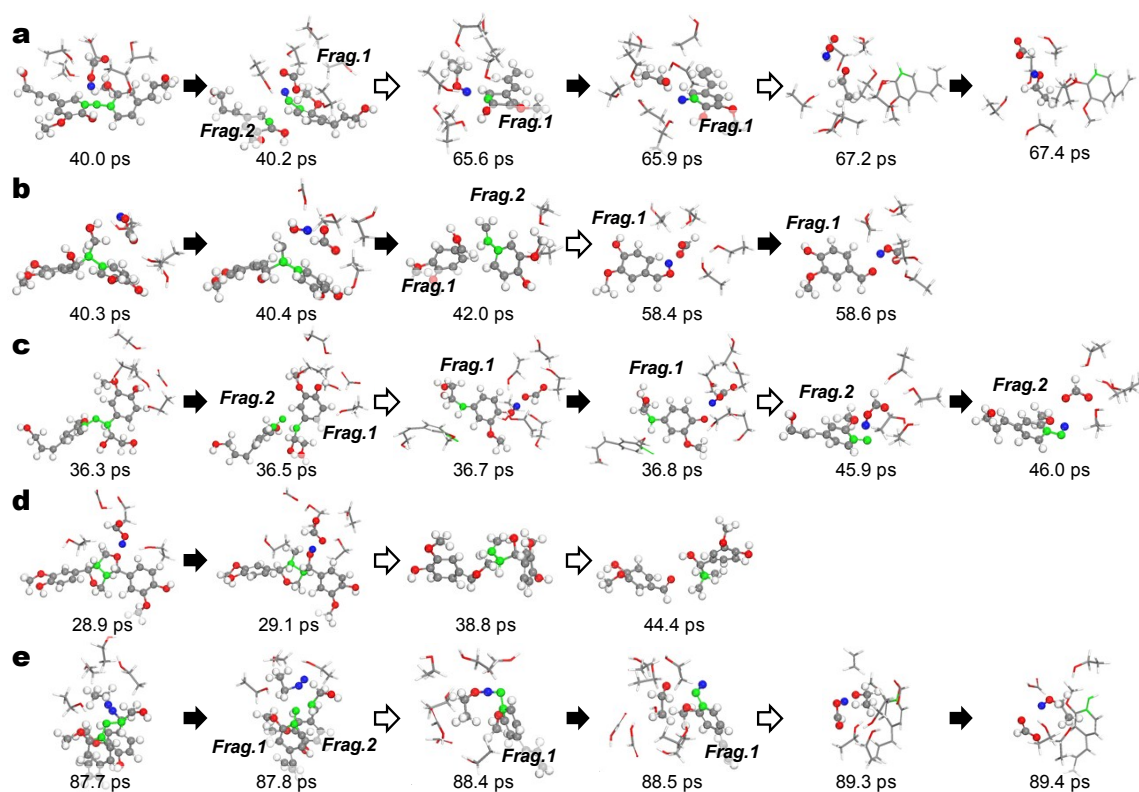


**Fig. S12** Gas chromatogram of the bio-oil collected immediately after the reaction in entry 7 in Table 1. Reaction condition: 3 g alkali lignin, 60 g ethanol, 12 g formic acid, 900 min, 350 °C, 29.3–44.9 MPa.





**Fig. S13** Gas chromatogram of the bio-oil collected immediately after the reaction in entry 8 in Table 1. Reaction condition: 6 g alkali lignin, 60 g ethanol, 12 g formic acid, 60 min, 350 °C, 30.8–41.7 MPa.



**Step-by-step decomposition mechanisms:** The lignin linkage was found to be spontaneously cleaved by hydrogen supplied by the solvent or by heat, and it was observed that the formed radical fragment was stabilized by receiving hydrogen from the solvent. A detailed description is given; **a** the 4-O-5 dilignol molecule initiated the dilignol depolymerization by the hydrogen decomposed at FA. This hydrogen bound to the central oxygen of the 4-O-5 dilignol molecule between 40.0 and 40.2 ps and broke the 4-O-5 bond to form two lignin molecules, Frag.1 and Frag.2. Among them, one radical lignin molecule (Frag.1) received hydrogen from adjacent other ethanol and became stable product at 65.9 ps. At this time, the decomposed ethanol brought hydrogen from neighboring FA and it was observed that ethanol was regenerated at 67.4 ps, **b** The depolymerization mechanism of  $\beta$ -1 dilignol molecule was initiated by the fact that the hydrogen decomposed in FA formed water by binding with OH around the  $\beta$ -1 linkage of the dilignol molecule at 40.4 ps. The alkyl chain in which  $H_2O$  was removed was transformed into a C=C bond in the form of a vinyl group, and the neighboring C-C ( $\alpha$ - $\beta$ ) bond was broken to form two lignin molecules of Frag.1 and Frag.2 at 42.0 ps. The radical lignin molecule (Frag.1) produced by the depolymerization reaction formed FA with an aldehyde group, providing hydrogen with adjacent HCOO (hydrogen free FA radical) at 58.6 ps, **c** the initiation of

depolymerization of  $\alpha$ -O-4 dilignol molecule was resulted from the dissociation of C-O bond by heat, forming two radical lignin molecules Frag.1 and Frag.2 at 36.5 ps. Frag.1 with carbon radicals was observed to transfer hydrogen of the phenol group to neighboring HCOO (FA-free radicals away from hydrogen) to form FA at 36.8 ps and Frag.2 with oxygen radicals received hydrogen transferred from FA around the oxygen to form stable lignin molecule at 46.0 ps, **d** it was confirmed that the depolymerization reaction of  $\beta$ - $\beta$  dilignol molecule was initiated by hydrogen separated from FA similarly to 4-O-5 and  $\beta$ -1 cases. At 29.1 ps, the hydrogen released from FA was bound to the oxygen of the tetrahydrofuran containing the  $\beta$ - $\beta$  bond, resulting in the ring opening due to the dissociation of the C-O bond. Similar to the dissociation of  $\beta$ -1, the radical carbon was transformed into vinyl, while the remaining C-C ( $\alpha$ - $\beta$ ) bond of the tetrahydrofuran was broken, resulting in a further ring opening at 38.8 ps. Finally, the C-O bond was broken and separated into two molecules at 44.4 ps, and **e** the depolymerization of  $\beta$ -O-4 dilignol molecule began with the break of the C-O bond by heat at 87.8 ps, similar to the depolymerization reaction of  $\alpha$ -O-4 linkage dilignol molecule. At this stage, however, radicals disappeared from the Frag.2 molecule as OH was transferred to the neighboring C<sub>2</sub>H<sub>5</sub> (i.e., decomposed ethanol). The remaining radical lignin molecule, Frag.1, was hydrolyzed to yield a stable product at 88.4 ps. It has been observed that the ethanol was regenerated by taking hydrogen from the neighboring FA at 89.4 ps.

## References

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