Supporting Information

Compositional Analysis of Organosolv Poplar Lignin by Using High-Performance Liquid Chromatography/High-resolution Multi-stage Tandem Mass Spectrometry

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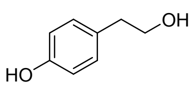
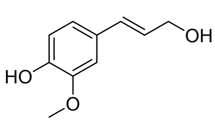
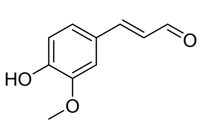
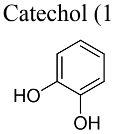
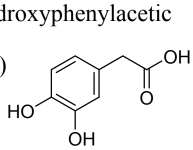
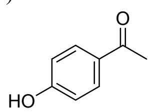
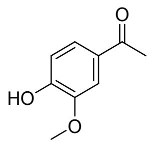
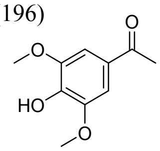
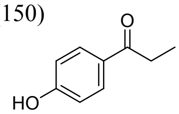
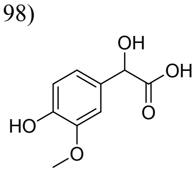
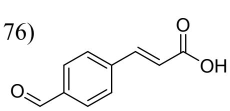
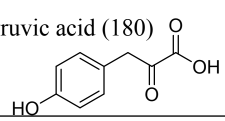
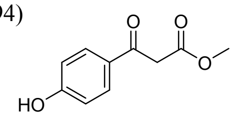
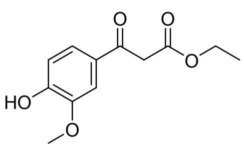
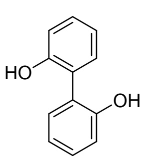
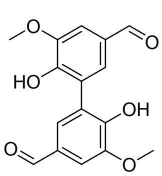
Table S1. Lignin-related model compounds, their molecular weight (in parenthesis), and proposed structures as well as the m/z-values of the CAD fragment ions of the deprotonated compounds with their relative abundances measured in MS^2 to MS^4 experiments. In each column, the product ions are given in the descending order of their relative abundances. In each column, the data are shown in the order of m/z value of precursor ion, formula of neutral fragment lost upon CAD, *m/z* value of the product ion (in parenthesis), and the relative abundance of the product ion. The reproducibility of the relative abundances of the fragment ions was within ±15%. In each stage of fragmentation, the most abundant fragment ions were isolated and subjected to CAD in the ion trap at a normalized collision energy of 35. This process was repeated until no more fragmentation could be observed (up to MS^5 experiments). All blank cells mean that no further fragmentations were observed.

Model compound (molecular weight in Da) **Structure**	**MS^2**	**MS^3**	**MS^4**	**MS^5**
Alcohols				
2-(4-Hydroxyphenyl)-ethanol (138) 	137-H_2O (119) 100% 137-CH_2O (107) 25% 137-$CH_3O^\bullet$ (106) 25%			
Coniferyl alcohol (180) 	179-H_2O (161) 100% 179-$^\bullet CH_3$ (164) 80% 179-H_2O-$^\bullet CH_3$ (146) 50% 179-CH_4 (163) 45%	161-$^\bullet CH_3$ (146) 100%		
Aldehydes				
Coniferyl aldehyde (178) 	177-$^\bullet CH_3$ (162) 100%	162-CO (134) 100% 162-$^\bullet CHO$ (133) 30% 162-C_2H_2O (120) 20% 162-2CO (106) 20%		
Catechols				
Catechol (110) 	109-H_2O (91) 100% 109-CO (81) 80%			
3,4-Dihydroxyphenylacetic acid (168) 	167-CO_2 (123) 100%	123-CO (95) 100% 123-H_2O (105) 40% 123-$^\bullet CH_3$ (108) 30%		

		123-CH_2O (93) 30%		
Ketones				
4'-Hydroxyacetophenone				
(136)	135-C_2H_2O (93) 100%			
	135-•CH_3 (120) 35%	120-CO (92) 100%		
Acetovanillone (166)	165-•CH_3 (150) 100%	150-CO (122) 100%		
				
Acetosyringone	195-•CH_3 (180) 100%	180-•CH_3 (165) 100%	165-CO (137) 100%	137-CO (109) 100%
(196)			165-2CO (109) 5%	137-CO_2 (93) 5%
				
4'- Hydroxy-	149-•C_2H_5 (120) 20%	120-CO (92) 100%		
propiophenone	149-C_3H_4O• (93) 20%			
(150)				
				
Two functionalities in the side chain				
DL-4-Hydroxy-3-	197-•CH_3-CO_2 (138) 100%			
methoxymandelic acid	197-•CH_3-•CO_2H (137) 50%			
(198)				
				
4-Formylcinnamic acid	175-CO_2 (131) 100%	131-C_2H_2 (105) 100%		
(176) 		131-CO (103) 65%		
4-Hydroxyphenyl-	179-CO-CO_2 (107) 100%			
pyruvic acid (180)	179-CO (151) 20%	151-CO_2 (107) 100%		
	179-CO_2 (135) 5%	135-CO (107) 100%		

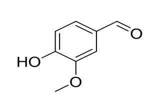
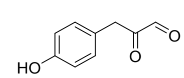
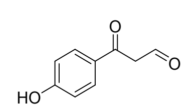
Methyl 3-(4-hydroxy-	193-CH_3OH-CO_2 (117) 100%			
phenyl)-3-oxo-propanoate	193-CH_3OH (161) 15%	161-CO_2 (117) 100%		
(194) 				
Ethyl 3-(4-hydroxy-3-	237-$^{\bullet}CH_3$ (222) 100%	222-C_2H_5OH-CO (148) 100%	148-CO_2 (104) 100%	
methoxyphenyl)-3-oxo-	237-C_2H_5OH-CO_2 (147) 25%	222-C_2H_5OH (176) 70%		
propanoate (238)		222-C_2H_5OH-CO_2 (132) 65%		
		222-C_2H_4OCO (150) 55%		
		222-$C_2H_5OCO^{\bullet}$ (149) 55%		
		222-CO (194) 40%		
		222-$C_2H_5OCO^{\bullet}$-CO (121) 30%		
		222-C_2H_5OH-CO-CO_2 (104) 15%		
	237-C_2H_5OH (191) 10%	191-CO_2 (147) 100%		
	237-C_2H_5OH-$^{\bullet}CH_3$-CO_2 (132) 5%	191-$^{\bullet}CH_3$ (176) 20%		
5,5-Lignin dimers				
2,2'-Biphenol (186)	185-H_2O (167) 90%			
				
5,5’-Bisvanillin (302)	301-$^{\bullet}CH_3$ (286) 100%	286-H_2O (268) 100%	268-CO (240) 100%	240-CO (212) 100%
		286-$^{\bullet}CHO$ (257) 95%	268-$^{\bullet}CHO$ (239) 20%	240-$^{\bullet}CHO$ (211) 15%
		286-H_2O-CO (240) 55%	268-2CO (212) 10%	
		286-$^{\bullet}OH$ (269) 50%		
		286-$^{\bullet}OH$-H_2 (267) 45%		

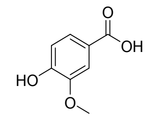
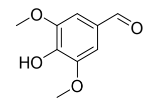
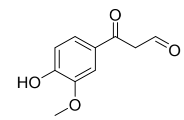
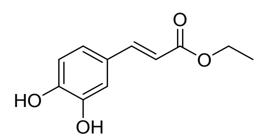
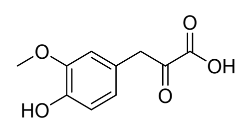
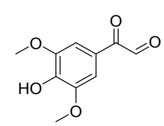
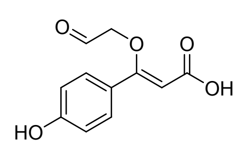
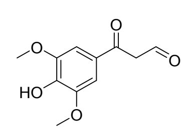
		$286-H_2O-{\bullet}CHO$ (239) 35% $286-CO-{\bullet}CHO$ (229) 15% $286-{\bullet}CH_3$ (271) 10%

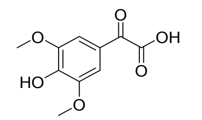
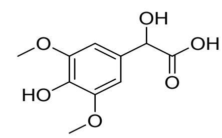
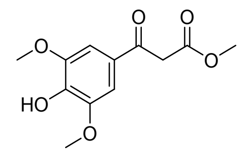
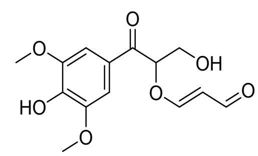
HPLC/MS^n method development

The previously reported HPLC methods[1,2] were found not to be very reproducible. Several changes were made to improve the previous methods. First, 0.1% formic acid (v/v) was added into the mobile phase as an additive to maintain a stable pH during the HPLC process. Second, the concentration of the acetonitrile content of the mobile phase at time 0 min of the HPLC gradient was increased to 30% to prevent the potential precipitation of analytes when they are diluted with a large amount of the water phase at the start of the HPLC run. Third, because the mobile phases contain formic acid (or ammonium formate) that was used as an additive, the volume of ammonium hydroxide necessary to induce a post-column pH change is too great to be experimentally feasible. Thus, ammonium hydroxide was not introduced via post-column infusion to deprotonate the analytes. Lignin-related compounds can get ionized adequately under (-)ESI without adding ammonium hydroxide as a dopant, as is indicated by the successful ionization of all the model compounds used in this study. The improved separation of this modified method enabled a large number of analytes to be detected. Lignin related monomers, dimers, trimers, and even tetramers were successfully isolated and analyzed in this study. Previous studies, however, suggested that only small analytes, such as lignin monomers and dimers, were present in the organosolv switchgrass lignin mixtures studied.[1]

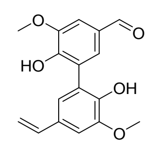
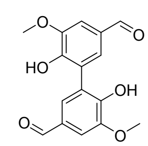
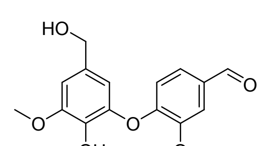
Table S2. Retention times (R.T.) of the eluted compounds from HPLC, *m/z* values of the deprotonated compounds formed upon (-) ESI from unknown analytes in organosolv poplar mixture, fragment ions of the deprotonated molecules with their relative abundances obtained upon CAD performed in MS^2 to MS^4 experiments, and structures proposed for each analyte. In each stage of fragmentation, the product ions are shown in the order of descending relative abundances. The reproducibility of the relative abundances of the fragment ions was within ±15%. The data in the columns are shown in the order of m/z values of precursor ions, formula of neutral fragments lost upon CAD, *m/z* values of fragment ions (in parenthesis), and their relative abundances.

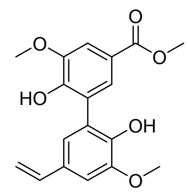
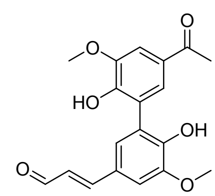
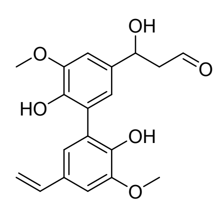
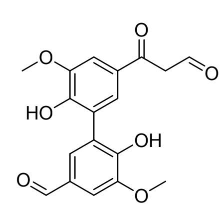
R.T. (min)	m/z	Elemental composition	RDBE	MS^2	MS^3	MS^4	Proposed structures
				Monomers			
11.3	**151**[a]	$C_8H_7O_3$	5.5	$151-{\bullet}CH_3$ (136) 100%	136-CO (108) 30% $136-CO_2$ (92) 100%		
8.1	**163**	$C_9H_7O_3$	6.5	163-CO (135) 100% $163-CO_2$ (119) 22% 163-2CO (107) 20% $163-CO-CO_2$ (91) 10%	135-CO (107) 100%		
12.8	**163**	$C_9H_7O_3$	6.5	$163-CO-CH_2CO$ (93) 100%			

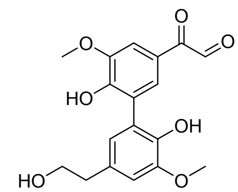
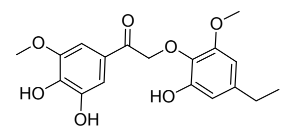
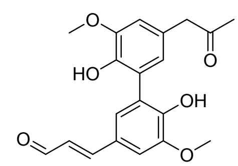
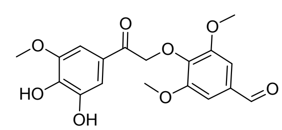
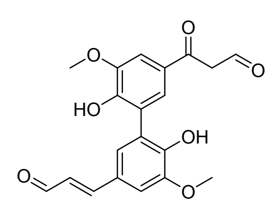
				163-CO_2 (119) 4%			
6.6	**167** [a]	$C_8H_7O_4$	5.5	167-•CH_3 (152) 100% 167-CO_2 (123) 10%	152-CO (124) 100% 152-CO_2 (108) 20%		
9.8	**181** [a]	$C_9H_9O_4$	5.5	181-•CH_3 (166) 100%	166-•CH_3 (151) 100%	151-CO (123) 100%	
13.5	**193**	$C_{10}H_9O_4$	6.5	193-•CH_3 (178) 100%	178-C_2H_2O (136) 100% 178-CO (150) 10% 178-C_2H_2O-CO (108) 5% 178-2CO (122) 3%	136-CO (108) 100%	
15.0	**207**	$C_{11}H_{11}O_4$	6.5	207-C_2H_4 (179) 100% 207-C_2H_4-CO_2 (135) 30% 207-C_2H_4-H_2O (161) 20%	207-CO_2 (135) 100%		
6.4	**209**	$C_{10}H_9O_5$	6.5	209-CO_2 (165) 100% 209-•CH_3 (194) 15% 209-CO-CO_2 (137) 10%	165-CO (137) 100% 165-•CH_3 (150) 10%		
9.4	**209**	$C_{10}H_9O_5$	6.5	209-•CH_3 (194) 100%	194-•CH_3 (179) 50% 194-CO (166) 30% 194-2CO (138) 30% 194-C_2H_2O-CO (124) 100%		
5.8	**221**	$C_{11}H_9O_5$	7.5	221-CO_2 (177) 100% 221-H_2O (203) 30% 221-CO-CO_2 (149) 20% 221-CO (193) 10%	177-•CH_3-CO (134) 100% 177-CO (149) 60% 177-CH_2CO-CO (107) 40% 177-H_2O (159) 20%		
13.8	**223**	$C_{11}H_{11}O_5$	6.5	223-•CH_3 (208) 100%	208-•CH_3 (193) 100% 208-•CH_3-2CO (137) 70%	193-CO (165) 100% 193-2CO (137) 70% 193-CO-C_2H_2O (123) 20% 193-3CO (109) 20% 193-CO-CO_2 (121) 15% 193-CO_2 (149) 10%	

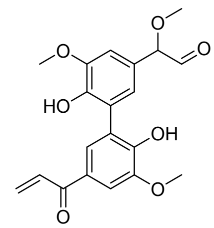
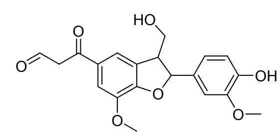
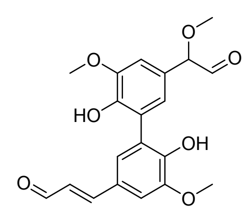
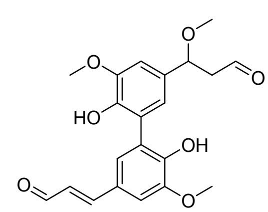
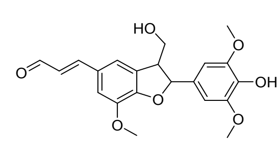
						$193-2CO-C_2H_2O$ (95) 10%	
4.9	**225**	$C_{10}H_9O_6$	6.5	$225-CO-CO_2$ (153) 100% $225-H_2O$ (207) 20% $225-CO-CO_2-{}^\bullet CH_3$ (138) 15% $225-C_3H_4O_4$ (121) 10%	$153-{}^\bullet CH_3$ (138) 100% $153-2\ {}^\bullet CH_3$ (123) 10% $153-CH_3OH$ (121) 10%	$138-{}^\bullet CH_3$ (123) 100%	
5.4	**227**	$C_{10}H_{11}O_6$	5.5	$227-H_2O$ (209) 100%	$209-{}^\bullet CH_3$ (194) 100%	$194-{}^\bullet CH_3$ (179) 100% 194-CO (166) 10%	
17.9	**253**	$C_{12}H_{13}O_6$	6.5	$253-{}^\bullet CH_3$ (238) 100%	$238-{}^\bullet CH_3$ (223) 100% $238-C_3H_5O_2{}^\bullet$ (165) 10% $238-C_4H_5O_3{}^\bullet$ (137) 5%		
7.3	**295**	$C_{14}H_{15}O_7$	7.5	$295-{}^\bullet CH_3$ (280) 100% $295-CH_2O$ (265) 20% $295-2CH_2O$ (235) 20% $295-CH_2O-CO_2$ (221) 5%	$280-{}^\bullet CH_3$ (265) 100% $280-C_4H_5O_2{}^\bullet$ (195) 23% $280-C_5H_6O_3$ (166) 7% $280-C_6H_6O_4$ (138) 7% $280-C_2H_5O_2{}^\bullet$ (219) 5%		

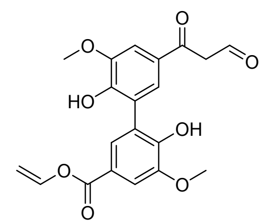
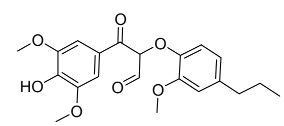
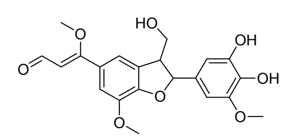
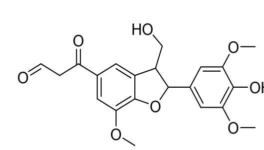
Dimers

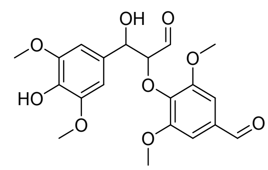
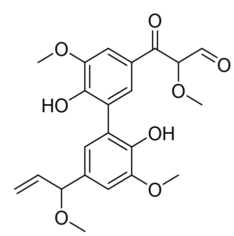
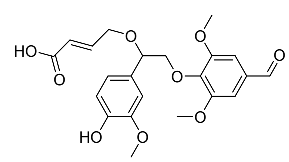
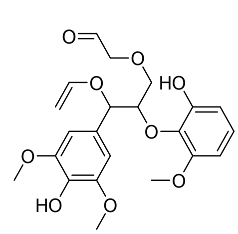
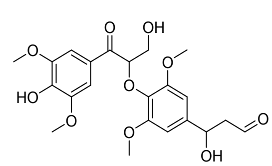
25.5	**299**	$C_{17}H_{15}O_5$	10.5	$299-{}^\bullet CH_3$ (284) 100%	$284-{}^\bullet CH_3$ (269) 100% $284-{}^\bullet CH_3-CO_2$ (225) 10%	269-CO (241) 100% $269-H_2O$ (251) 15% $269-CO_2$ (225) 10% $269-CO-CO_2$ (197) 10%	
16.8	**301**[a]	$C_{16}H_{13}O_6$	10.5	$301-{}^\bullet CH_3$ (286) 100% $301-{}^\bullet CH_3-CO$ (258) 50%	$286-H_2O$ (268) 100% $286-{}^\bullet CHO$ (257) 90% $286-H_2O-CO$ (240) 60% $286-{}^\bullet OH$ (269) 50% $286-H_2-{}^\bullet OH$ (267) 45% $286-H_2O-{}^\bullet CHO$ (239) 35% $286-CO-{}^\bullet CHO$ (229) 20% $286-{}^\bullet CH_3$ (271) 15%	268-CO (240) 100% $268-{}^\bullet CHO$ (239) 20% 268-2CO (212) 10%	
16.3	**303**	$C_{16}H_{15}O_6$	9.5	$303-{}^\bullet CH_3$ (288) 100% $303-CH_2O$ (272) 25% $303-CH_3OH$ (271) 25%	$288-{}^\bullet CH_3$ (273) 100% $288-C_8H_8O_3$ (136) 35% $288-C_8H_8O_3-CO$ (108) 20%	$273-H_2O$ (255) 100% 273-CO (245) 85% $273-CO-H_2O$ (227) 25%	

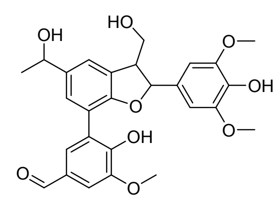
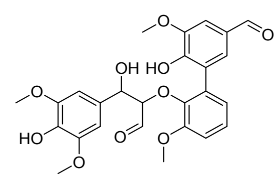
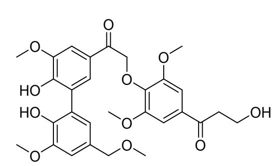
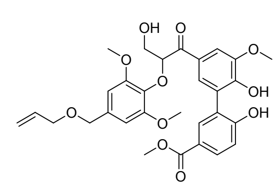
				303-CH_3OH-CO (243) 10%	288-$C_7H_4O_3$ (152) 5%	273-CO_2 (229) 20%	
						273-$C_7H_4O_3$ (137) 15%	
						273-CO_2-CO (201) 5%	
21.4	**329**	$C_{18}H_{17}O_6$	10.5	329-•CH_3 (314) 100%	314-•CH_3 (299) 100%	299-•CH_3 (284) 100%	
				329-2•CH_3 (299) 10%		299-CO (271) 35%	
						299-•CH_3-CO (256) 30%	
						299-CO_2 (255) 30%	
						299-CH_2O (269) 15%	
						299-•CH_3-CO_2 (240) 15%	
						299-H_2O (281) 10%	
						299-CH_3OH (267) 10%	
						299-CO-H_2O (253) 5%	
23.8	**341**	$C_{19}H_{17}O_6$	11.5	341-•CH_3 (326) 100%	326-•CH_3 (311) 100%	311-CO (283) 100%	
				341-2•CH_3 (311) 10%	326-C_2H_2O (284) 20%	311-H_2O (293) 90%	
					326-C_2H_2O-CO (256) 20%	311-CO-C_2H_2O (241) 45%	
						311-C_2H_2O-H_2O (251) 40%	
						311-•CHO-C_2H_2O (240) 40%	
						311-H_2O-CO (265) 36%	
18.5	**343**	$C_{19}H_{19}O_6$	10.5	343-•CH_3 (328) 100%	328-•CH_3 (313) 100%	313-CO (285) 100%	
				343-2•CH_3 (313) 10%	328-CO-C_2H_4O (256) 35%	313-$C_2H_6O_2$ (251) 90%	
					328-C_2H_4O (284) 20%	313-$C_3H_4O_2$ (241) 45%	
					328-$C_4H_7O_2$• (241) 10%	313-H_2O (295) 30%	
						313-$C_3H_2O_2$ (243) 30%	
						313-C_2H_4O (269) 20%	
						313-$C_3H_4O_3$ (225) 10%	
						313-$C_4H_4O_3$ (213) 10%	
						313-$C_7H_6O_2$ (191) 10%	
19.8	**343**	$C_{18}H_{15}O_7$	11.5	343-•CH_3 (328) 100%	328-CH_2CO-CO (258) 100%	258-•CH_3 (243) 100%	
				343-•CH_3-CH_2CO-CO (258) 20%	328-•CH_3-2CO (257) 30%	258-CH_2CHO• (215) 40%	
				343-•CH_3-CH_2CO (286) 7%	328-CH_2CO (286) 20%	258-CH_4 (242) 30%	
					328-H_2O (310) 10%	258-•CHO (229) 30%	
					328-•CHO (299) 8%		

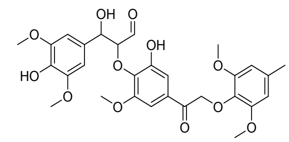
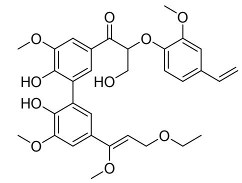
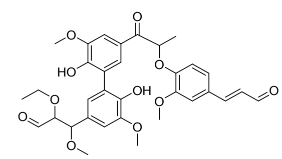
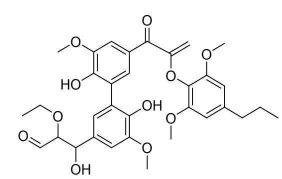
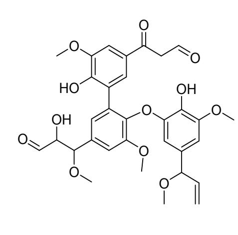
10.7	**345**	$C_{18}H_{17}O_7$	10.5	345-CO (317) 100%	317-•CH_3 (302) 100%	302-•CH_3 (287) 100%	
				345-•CH_3 (330) 40%	317-2•CH_3 (287) 20%		
				345-H_2O (327) 35%			
				345-•CH_3-CO-CH_2O (272) 25%			
				345-CH_2O (315) 20%			
				345-•CH_3-CO (302) 15%			
				345-•CH_3-CO_2 (286) 15%			
				345-$C_4H_6O_2$ (259) 10%			
14.5	**347**	$C_{18}H_{19}O_7$	9.5	347-•CH_3 (332) 100%	332-$C_9H_{10}O_3$ (166) 100%	166-CO (138) 100%	
				347-$C_{10}H_{13}O_3$ (166) 25%	332-$C_9H_{10}O_3$-CO (138) 70%		
				347-$C_{10}H_{13}O_3$•-CO (138) 10%	332-C_2H_4 (304) 15%		
					332-•CH_3 (317) 10%		
					332-$C_8H_8O_3$ (180) 10%		
					332-$C_9H_{10}O_3$-CO-•CH_3 (123) 10%		
23.1	**355**	$C_{20}H_{19}O_6$	11.5	355-•CH_3 (340) 100%	340-•CH_3 (325) 100%	325-•CH_3 (310) 100%	
				355-2•CH_3 (325) 20%		325-CO_2 (281) 20%	
						325-CO (297) 20%	
						325-CH_2O (295) 10%	
						325-H_2O (307) 10%	
						325-•CH_3-CO_2 (266) 10%	
17.2	**361**	$C_{18}H_{17}O_8$	10.5	361-•CH_3 (346) 100%	346-CO (318) 100%	318-•CH_3 (303) 100%	
				361-•CH_3-CO (318) 50%	346-$C_9H_8O_4$ (166) 10%	318-•CH_3-H_2O (285) 20%	
				361-•CH_3-$C_9H_8O_4$ (166) 5%	346-$C_8H_6O_4$ (180) 5%	318-2•CH_3 (288) 10%	
					346-$C_9H_8O_4$-CO (138) 5%		
					346-CO-•CH_3 (303) 5%		
21.7	**369**	$C_{20}H_{17}O_7$	12.5	369-•CH_3 (354) 100%	354-C_2H_2O-CO (284) 100%	284-CH_4 (268) 100%	
				369-C_2H_2O-CO-•CH_3 (284) 15%	354-•CH_3 (339) 60%	284-•CH_3 (269) 55%	
					354-$C_3H_3O_2$• (283) 40%	284-H_3O• (265) 45%	
					354-CO (326) 40%	284-•CH_3-CO (241) 20%	
					354-•CHO (325) 35%	284-CO (256) 15%	

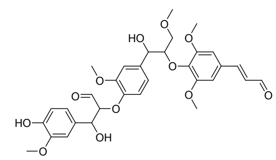
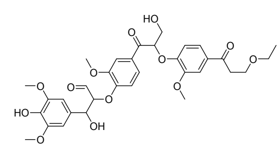
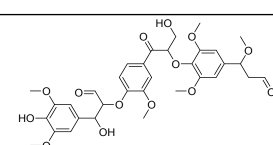
					354-H_2O (336) 20%	284-•CHO (255) 10%	
					354-C_2H_2O (312) 15%	284-•CH_3-CO_2-CO (197) 10%	
					354-$C_4H_2O_3$ (256) 10%	284-•CH_3-CO_2 (225) 5%	
15.6	**371**	$C_{20}H_{19}O_7$	11.5	371-•CH_3 (356) 100%	356-•CHO (327) 100%	327-•CH_3 (312) 100%	
				371-CO (343) 30%	356-•CH_3 (341) 10%	327-2•CH_3 (297) 50%	
				371-•CH_3-CO (328) 30%	356-CO (328) 10%	327-C_2H_6O (281) 20%	
				371-•CH_3-•CHO (327) 30%	356-•CH_3-CO (313) 10%		
				371-CH_3OH (339) 20%			
18.7	**371**	$C_{20}H_{19}O_7$	11.5	371-•CH_3 (356) 100%	356-•CH_3 (341) 100%	341-CO (313) 100%	
				371-H_2O (353) 80%	356-CO (328) 10%	341-•CH_3 (326) 50%	
				371-$C_8H_8O_2$ (235) 40%		341-2•CH_3 (311) 30%	
				371-CH_2O (341) 20%		341-•CH_3-CO (298) 15%	
				371-$C_8H_8O_2$-•CH_3 (220) 10%			
				371-$C_8H_8O_2$-•CH_3-CO (192) 10%			
23.4	**371**	$C_{20}H_{19}O_7$	11.5	371-•CH_3 (356) 100%	356-•CH_3 (341) 100%	341-•CH_3 (326) 100%	
				371-CH_2O (341) 20%	356-C_2H_2O-CO (286) 7%	341-CO (313) 50%	
					356-C_2H_2O (314) 5%	341-CO_2 (297) 40%	
						341-CH_3OH-•CH_3-CO (266) 35%	
						341-•CH_3-CO_2 (282) 10%	
10	**385**	$C_{21}H_{21}O_7$	11.5	385-•CH_3 (370) 100%	370-•CH_3 (355) 100%	355-CO (327) 100%	
					370-CH_2O (340) 20%	355-•CH_3 (340) 20%	
					370-•CH_3-CH_2O (325) 10%	355-CO_2 (311) 20%	
						355-2CO (299) 20%	
						355-CO-CO_2 (283) 10%	
16.9	**385**	$C_{21}H_{21}O_7$	11.5	385-$C_9H_{10}O_3$ (219) 100%	219-•CH_3 (204) 100%	204-CO (176) 100%	
				385-$C_9H_{10}O_3$-CO-•CH_3 (176) 30%	219-•CH_3-CO (176) 60%		
				385- $C_9H_{10}O_3$-•CH_3 (204) 20%	219-CO (191) 30%		
				385-C_2H_4O (341) 15%			
				385-C_2H_4O-CO (313) 15%			

				385-•CH_3 (370) 10%			
				385-H_2O (367) 10%			
				385-CO (357) 10%			
				385-•CH_3-H_2O (352) 7%			
				385-$C_9H_{10}O_3$-CO (191) 7%			
				385-$C_9H_{10}O_3$-•CHO (190) 5%			
22.3	**385**	$C_{20}H_{17}O_8$	12.5	385-•CH_3 (370) 100%	370-C_2H_2O-CO (300) 100%	300-•CH_3-CO (257) 100%	
				385-C_2H_2O-CO-•CH_3 (300) 50%	370-C_2H_2O-•CHO (299) 30%	300-•CH_3 (285) 40%	
				385-C_2H_2O-CO (315) 25%	370-C_2H_2O (328) 20%	300-$C_3H_4O_2$ (228) 30%	
				385-•CH_3-C_2H_2O (328) 15%	370-H_2O (352) 10%	300-•CHO (271) 10%	
				385-•CH_3-H_2O (352) 5%		300-2•CH_3-CO (242) 7%	
24.4	**387**	$C_{21}H_{23}O_7$	10.5	387-•CH_3 (372) 100%	372-•CH_3-CO (329) 100%	329-•CH_3 (314) 100%	
				387-$C_{10}H_{13}O_2$ (222) 55%	372-•CH_3-2CO (301) 95%		
				387-2•CH_3-CO (329) 45%	372-•CH_3 (357) 50%		
				387-CH_2CO-CO (317) 40%	372-$C_9H_{10}O_2$ (222) 50%		
				387-$C_{11}H_{16}O_2$ (207) 15%	372-$C_{10}H_{11}O_2$• (209) 20%		
				387-$C_{12}H_{16}O_4$ (163) 10%	372-$C_{11}H_{12}O_3$ (180) 15%		
				387-2•CH_3-2CO (301) 10%	372-•$C_{11}H_{13}O_4$ (163) 10%		
7.7	**401**	$C_{21}H_{21}O_8$	11.5	401-•CH_3 (386) 100%	386-•CH_3 (371) 100%	371-$C_8H_8O_3$ (219) 100%	
					386-CH_2O (356) 20%	371-CO (343) 55%	
					386-•CH_3-CH_2O (341) 10%	371-•CH_3 (356) 30%	
					386-•$C_9H_{11}O_3$ (219) 10%	371-H_2O (353) 30%	
						371-CH_2O (341) 30%	
						371-CO-•CH_3 (328) 20%	
						371-•$C_7H_7O_3$ (232) 10%	
						371-$C_8H_8O_3$-CO (191) 10%	
						371-•CH_3-H_2O (338) 7%	
18.3	**401**	$C_{21}H_{21}O_8$	11.5	401-H_2O (383) 100%	383-•CH_3O (352) 100%	352-•CH_3 (337) 100%	
				401-$C_9H_{10}O_3$ (235) 50%	383-•CH_3 (368) 85%		
				401-•CH_3 (386) 20%	383-CH_2O (353) 60%		
				401-CH_2O (371) 20%	383-CH_2O-CO_2 (309) 20%		

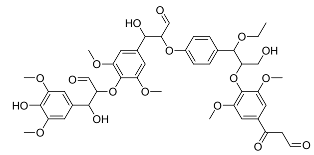
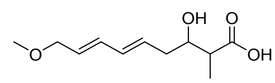
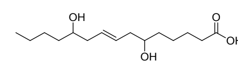
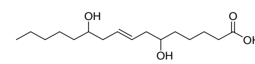
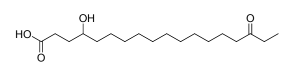
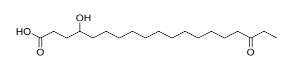
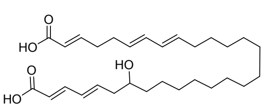
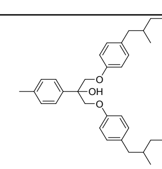
				401-$C_2H_4O_3$ (325) 20% 401-$C_9H_{10}O_3$-•CH_3-CO (192) 15% 401-$C_9H_{10}O_3$-•CH_3 (220) 10% 401-$C_9H_{10}O_3$-•CHO (206) 10%	383-•CH_3-H_2O (338) 10%		
14.7	**405**	$C_{20}H_{21}O_9$	10.5	405-$C_{11}H_{12}O_5$ (181) 100% 405-$C_9H_{10}O_4$ (223) 60% 405-$C_{11}H_{12}O_5$-•CH_3 (166) 30% 405-$C_{11}H_{12}O_5$-2•CH_3 (151) 20% 405- $C_9H_{10}O_4$-•CH_3 (208) 10% 405-CO (377) 10%	181-•CH_3 (166) 100%	166-•CH_3 (151) 100%	
10.5	**415**	$C_{22}H_{23}O_8$	11.5	415-•CH_3 (400) 100%	400-•CH_3 (385) 100% 400-CH_2O (370) 20% 400-•CH_3-CH_2O (355) 10%	385-CO (357) 100% 385-•CH_3 (370) 60% 385-CO-•CH_3 (342) 20% 385-2CO (329) 20% 385-CO-H_2O (339) 15%	
12.1	**431**	$C_{22}H_{23}O_9$	11.5	431-$C_{13}H_{14}O_5$ (181) 100% 431-CO_2 (387) 30% 431-•CH_3-CO_2 (372) 25% 431-$C_{13}H_{14}O_5$-•CH_3 (166) 25% 431-$C_{13}H_{14}O_5$-2•CH_3 (151) 20% 431-H_2O (413) 15% 431-•CH_3 (416) 10% 431-CH_2O (401) 10%	181-•CH_3 (166) 100%	166-•CH_3 (151) 100%	
11	**433**	$C_{22}H_{25}O_9$	10.5	433-$C_2H_4O_2$ (373) 100% 433-CH_2O (403) 40% 433-•CH_3 (418) 20% 433-CH_4O_2 (385) 5%	373-•CH_3 (358) 100% 373-$C_8H_{11}O_3$• (218) 15%	358-$C_7H_8O_3$ (218) 100% 358-•CH_3 (343) 70% 358-$C_7H_8O_3$-•CH_3 (203) 20% 358-$C_{11}H_{12}O_3$ (166) 20% 358-$C_{11}H_{12}O_3$-CO (138) 20%	
8.9	**449**	$C_{22}H_{25}O_{10}$	10.5	449-CH_2O (419) 100%	419-$C_{10}H_{12}O_4$ (223) 100%	223-•CH_3 (208) 100%	

				449-$C_{11}H_{12}O_5$ (225) 60%	419-2CH_2O (359) 70%	223-2•CH_3 (193) 15%	
				449-$C_{11}H_{14}O_5$ (223) 20%	419-$C_{10}H_{12}O_4$-CO (195) 60%		
				449-$C_{11}H_{12}O_5$-CH_2O (195) 20%	419-CH_2O (389) 55%		
				449-$C_8H_{10}O_3$ (295) 15%	419-$C_8H_{10}O_3$ (265) 30%		
				449-H_2O (431) 15%	419-$C_{10}H_{12}O_4$-•CH_3 (208) 20%		
				449-H_2O-CH_2O (401) 10%	419-$C_{10}H_{12}O_4$-•CH_3-CO (180) 20%		
				449-$C_8H_{10}O_3$-CH_2O (265) 10%	419-H_2O (401) 10%		
				449-$C_{11}H_{12}O_5$-H_2O (207) 10%	419-$C_{10}H_{12}O_4$-2•CH_3-CO (165) 10%		
				Trimers			
22.7	**495**	$C_{27}H_{27}O_9$	14.5	495-•CH_3 (480) 100%	480-•CH_3 (465) 15%	465-•CH_3 (450) 100%	
				495-2•CH_3 (465) 15%	480-$C_9H_{10}O_3$ (314) 15%		
				495-$C_{10}H_{13}O_3$• (314) 15%	480-$C_{10}H_{10}O_4$ (286) 15%		
				495-$C_{10}H_{13}O_3$•-CO (286) 15%	480-$C_9H_8O_4$ (300) 7%		
21	**497**	$C_{26}H_{25}O_{10}$	14.5	497-$C_{11}H_{12}O_5$ (273) 100%	273-•CH_3 (258) 100%	258-•CH_3 (243) 100%	
				497-$C_{15}H_{14}O_5$ (223) 65%			
				497-CH_2O (467) 20%			
				497-$C_{11}H_{12}O_5$-•CH_3 (258) 20%			
				497-$C_{15}H_{14}O_5$-•CH_3 (208) 10%			
21.9	**555**	$C_{29}H_{31}O_{11}$	14.5	555-$C_{11}H_{13}O_5$• (330) 100%	330-•CH_3 (315) 100%	315-•CH_3 (300) 100%	
				555-CH_2O-CH_3OH (493) 65%		315-2•CH_3 (285) 10%	
				555-CH_2O (525) 30%			
				555-•CH_3-$C_{11}H_{13}O_5$• (315) 25%			
				555-$C_{18}H_{20}O_7$ (207) 15%			
23.2	**567**	$C_{30}H_{31}O_{11}$	15.5	567-CH_3OH (535) 100%	535-CH_2O (505) 100%	505-•CH_3 (490) 100%	
				567-•CH_3 (552) 70%	535-•CH_3 (520) 80%	505-C_2H_4 (477) 30%	
				567-CH_2O-CH_3OH (505) 40%	535-•CH_3-CH_2O (490) 80%		
				567-•CH_3-CH_3OH (520) 20%			
				567-$C_{12}H_{16}O_4$ (343) 20%			
				567-•CH_3-CH_2O-CH_3OH (490) 15%			
				567-$C_{15}H_{20}O_6$ (271) 10%			
				567-$C_{21}H_{22}O_7$ (181) 8%			
				567-2CH_2O-CH_3OH (475) 8%			

18.2	**571**	$C_{29}H_{31}O_{12}$	14.5	571-$C_{11}H_{12}O_5$ (347) 100% 571-CH_2O (541) 16% 571-$C_{18}H_{20}O_7$ (223) 10% 571-$C_{10}H_{10}O_5$ (361) 6% 571-$C_{11}H_{12}O_5$-•CH_3 (332) 6%	347-•CH_3 (332) 100% 347-$C_{10}H_{13}O_3$• (166) 20% 347-$C_{10}H_{13}O_3$•-CO (138) 10%	332-$C_9H_{10}O_3$ (166) 100% 332-$C_9H_{10}O_3$-CO (138) 50% 332-•CH_3 (317) 10% 332-$C_8H_8O_3$ (180) 10%	
19.9	**579**	$C_{32}H_{35}O_{10}$	15.5	579-•CH_3 (564) 100% 579-$C_{10}H_{13}O_2$• (414) 32% 579-2•CH_3 (549) 30% 579-•CH_3-$C_{10}H_{13}O_2$• (399) 7%	564-•CH_3 (549) 100% 564-•CH_3-H_2O (531) 10% 564-$C_9H_{10}O_2$ (414) 10% 564-•CH_3-$C_9H_{10}O_2$ (399) 7%	549-•CH_3 (534) 100% 549-$C_9H_{12}O_2$ (397) 75% 549-H_2O (531) 50% 549-•CH_3-CO (506) 41% 549-CH_2O (519) 35% 549-CO (521) 30% 549-$C_{10}H_{13}O_2$• (384) 30% 549-C_2H_6O (503) 20% 549-H_2O-CH_2O (501) 20%	
25.4	**607**	$C_{33}H_{35}O_{11}$	16.5	607-$C_4H_6O_2$ (521) 100% 607-C_2H_6O (561) 85% 607-•CH_3 (592) 70% 607-C_3H_6O (549) 30% 607-$C_3H_2O_2$ (537) 30% 607-2•CH_3 (577) 25% 607-CH_3OH (575) 20% 607-$C_4H_8O_2$ (519) 15%	521-•CH_3 (506) 100%	506-•CH_3 (491) 100% 506-$C_{12}H_{13}O_3$• (301) 25% 301-•CH_3 (286) 15%	
19.5	**609**	$C_{33}H_{37}O_{11}$	15.5	609-•CH_3 (594) 100% 609-$C_{11}H_{15}O_3$• (414) 30% 609-2•CH_3 (579) 27% 609-$C_{11}H_{15}O_3$• - •CH_3 (399) 10%	594-•CH_3 (579) 100% 594-$C_{10}H_{12}O_3$ (414) 15% 594-•CH_3-H_2O (561) 10% 594-$C_{10}H_{12}O_3$-•CH_3 (399) 10%	579-•CH_3 (564) 100% 579-$C_{10}H_{14}O_3$ (397) 75% 579-H_2O (561) 65% 579-CH_2O (549) 45% 579-CO (551) 40% 579-•CH_3-CO (536) 40% 579-$C_{11}H_{15}O_3$• (384) 30% 579-CH_2O-H_2O (531) 15% 579-$C_9H_{10}O_3$ (413) 15% 579-C_2H_5OH (533) 12% 579-•CH_3-CH_2O (534) 10%	
25.9	**609**	$C_{32}H_{33}O_{12}$	16.5	609-•CH_3 (594) 100% 609-CH_3OH (577) 55% 609-CH_3OH-CH_2O (547) 25% 609-CH_3OH-•CH_3 (562) 18% 609-CH_3OH-CO (549) 18%	594-•CH_3O (563) 100% 594-•CH_3 (579) 80% 594-H_2O (576) 75% 594-CH_2CO (552) 20% 594-CH_2CO-•CHO-H_2O (505) 12%	563-•CH_3 (548) 100% 563-2•CH_3 (533) 50% 563-H_2O (545) 25% 563-•CH_3-CH_2O (518) 10% 563-$C_4H_6O_2$ (477) 10%	

				609-•CH_3-CH_2CO (552) 5% 609-•CH_3-CH_2CO-CO (524) 5%	594-•CHO (565) 10% 594-•CH_3-H_2O (561) 10% 594-CH_2CO-•CHO (523) 10% 594-CH_2CO-CO-H_2O (506) 10% 594-CH_2CO-CO-H_2O-•CH_3 (491) 10% 594-CH_2CO-CO (524) 8% 594-$C_{11}H_{11}O_4$ (387) 8%	563-$C_{11}H_{14}O_4$ (353) 7%	
19.4	**611**	$C_{32}H_{35}O_{12}$	15.5	611-CH_2O (581) 100% 611-H_2O (593) 80% 611-$C_{10}H_{10}O_4$ (417) 30% 611-$C_{22}H_{26}O_8$ (193) 30% 611-CH_3OH (579) 20% 611-H_2O-CH_2O (563) 20% 611-CH_3OH-CH_2O(549) 15% 611-$C_{10}H_{10}O_4$-CH_2O (387) 15% 611-2CH_2O (551) 12% 611-$C_{14}H_{16}O_5$ (347) 12% 611-$C_{10}H_{10}O_4$-CH_2O-•CH_3 (372) 10% 611-$C_{15}H_{18}O_6$ (317) 8%	581-CH_2O (551) 100% 581-H_2O (563) 85% 581-CH_3OH (549) 30% 581-$C_{10}H_{12}O_3$ (401) 25% 581-$C_{11}H_{14}O_4$ (371) 25% 581-$C_{14}H_{16}O_5$ (317) 25% 581-CH_3OH-CH_2O (519) 17% 581-CH_3OH-CO (521) 16% 581-$C_8H_{10}O_3$ (427) 10%		
19.1	**641**	$C_{33}H_{37}O_{13}$	15.5	641-CH_2O (611) 100% 641-$C_{22}H_{26}O_8$ (223) 80% 641-H_2O (623) 60% 641-$C_{11}H_{12}O_5$ (417) 50% 641-CH_2O-CH_3OH (579) 30% 641-H_2O-CH_2O (593) 30% 641-$C_{11}H_{12}O_5$-CH_2O (387) 15% 641-$C_{14}H_{16}O_5$ (377) 15% 647-$C_{14}H_{16}O_5$-CH_2O (347) 15% 641-2CH_2O (581) 10%	611-CH_2O (581) 100% 611-H_2O (593) 60% 611-CH_3OH (579) 30% 611-CH_2O-CH_3OH (549) 20% 611-$C_{12}H_{16}O_5$ (371) 20% 611-$C_{14}H_{16}O_5$ (347) 15% 611-$C_{11}H_{14}O_4$ (401) 12% 611-$C_9H_{12}O_4$ (427) 10% 611-$C_{21}H_{24}O_7$ (223) 5%	581-$C_{11}H_{14}O_4$ (371) 100% 581-CH_3OH (549) 70% 581-$C_8H_{10}O_3$ (427) 40%	
16.2	**657**	$C_{33}H_{37}O_{14}$	15.5	657-$C_{12}H_{15}O_5$• (418) 100% 657-H_2O (639) 95% 657-$C_{11}H_{13}O_5$• (432) 75% 657-CH_2O (627) 60% 657-$C_{11}H_{12}O_5$ (433) 60% 657-2CH_2O (597) 10% 657-$C_{13}H_{16}O_7$ (373) 10% 657-$C_{22}H_{26}O_9$ (223) 10%	418-•CH_3 (403) 100% 418-H_2O (400) 80% 418-2CH_2O (358) 50% 418-CH_3O• (387) 30% 418-$C_{11}H_{13}O_5$• (193) 30% 418-$C_{10}H_{11}O_4$ (223) 10%	403-CH_2O (373) 100%	

Tetramers

22.2	**865**	$C_{44}H_{49}O_{18}$	20.5	865-$C_{11}H_{12}O_5$ (641) 100% 865-CH_2O (835) 50% 865-H_2O (847) 45% 865-2H_2O (829) 10% 865-H_2O-CH_2O (817) 10% 865-$C_2H_6O_2$ (803) 10% 865-$C_{11}H_{12}O_5$-CH_2O (611) 10% 865-$C_{11}H_{12}O_5$-$C_{11}H_{14}O_5$ (415) 10% 865-$C_{11}H_{12}O_5$-$C_{11}H_{12}O_5$ (417) 5%	641-CH_2O (611) 100% 641-$C_{11}H_{12}O_5$ (417) 85% 641-$C_{22}H_{26}O_8$ (223) 80% 641-H_2O (623) 65%		
				Not-lignin related compounds			
12.9	**213**	$C_{11}H_{17}O_4$	3.5	213-CO_2-H_2O (151) 100% 213-H_2O (195) 35%	151-CH_4 (135) 100% 151-C_3H_6 (109) 5%	135-•CH_3 (120) 100%	
26	**271**	$C_{15}H_{27}O_4$	2.5	271-H_2O-CO_2 (209) 100% 271-H_2O (253) 45%	209-C_2H_4 (181) 100%		
27.8	**285**	$C_{16}H_{29}O_4$	2.5	285-CO_2-H_2O (223) 100% 285-H_2O (267) 30%	223-CO (195) 100%		
31.4	**313**	$C_{18}H_{33}O_4$	2.5	313-H_2O-CO_2 (251) 100% 313-H_2O (295) 20%	251-C_2H_4 (223) 100%		
32.9	**327**	$C_{19}H_{35}O_4$	2.5	327-H_2O-CO_2 (265) 100%	265-C_2H_4 (237) 100%		
35.6	**473**	$C_{29}H_{45}O_5$	7.5	473-CO_2 (429) 100% 473-CO_2-H_2O (411) 5%	429-CO_2-C_2H_4 (357) 100% 429-CO_2 (385) 50% 429-H_2O (411) 35% 429-$C_6H_8O_2$ (317) 20%	357-H_2O (339) 100% 357-C_2H_4 (329) 10%	
40.1	**473**	$C_{32}H_{41}O_3$	12.5	473-$C_{11}H_{14}O$ (311) 100% 473-$C_{10}H_{14}O$ (323) 65% 473-$C_{22}H_{28}O_2$ (149) 10%	311-$C_{11}H_{14}O$ (149) 100%		

[a]Verified by comparing with authentic model compounds or previously published data for authentic model compounds.[3]

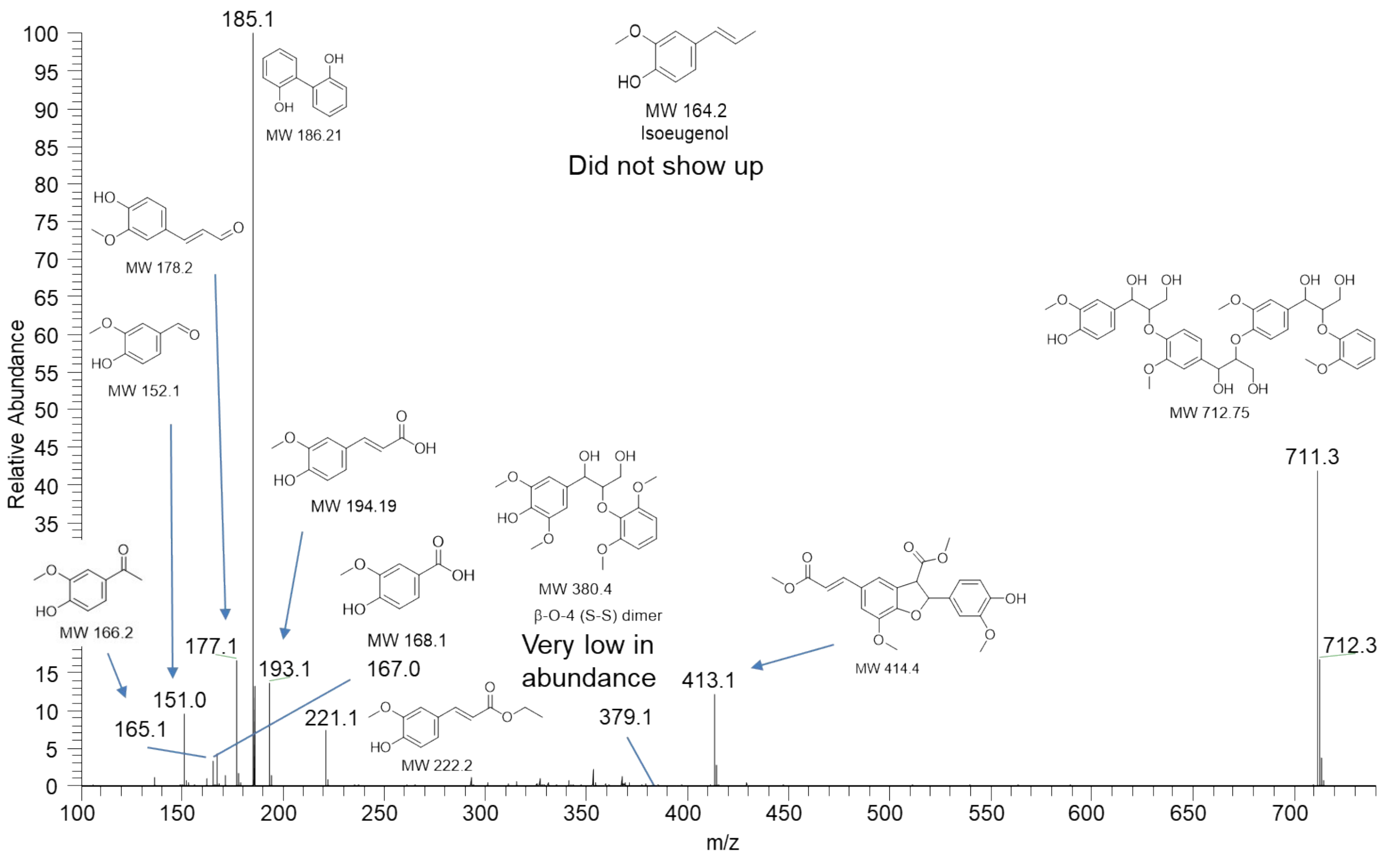


Figure S1. High-resolution mass spectrum measured for an equimolar mixture of 11 lignin model compounds by using (-)ESI HRMS. While most other compounds display similar ionization efficiencies (relative abundances between 5 and 15%), a few exceptions are seen. Deprotonated isoeugenol was not detected and deprotonated β-O-4 (S-S) dimer had a very low abundance (both possibly due to the lack of electron-withdrawing substituents and lack of ability to stabilize the negative charge via hydrogen bond formation) . However, another lignin dimer and a tetramer had very high relative abundances.

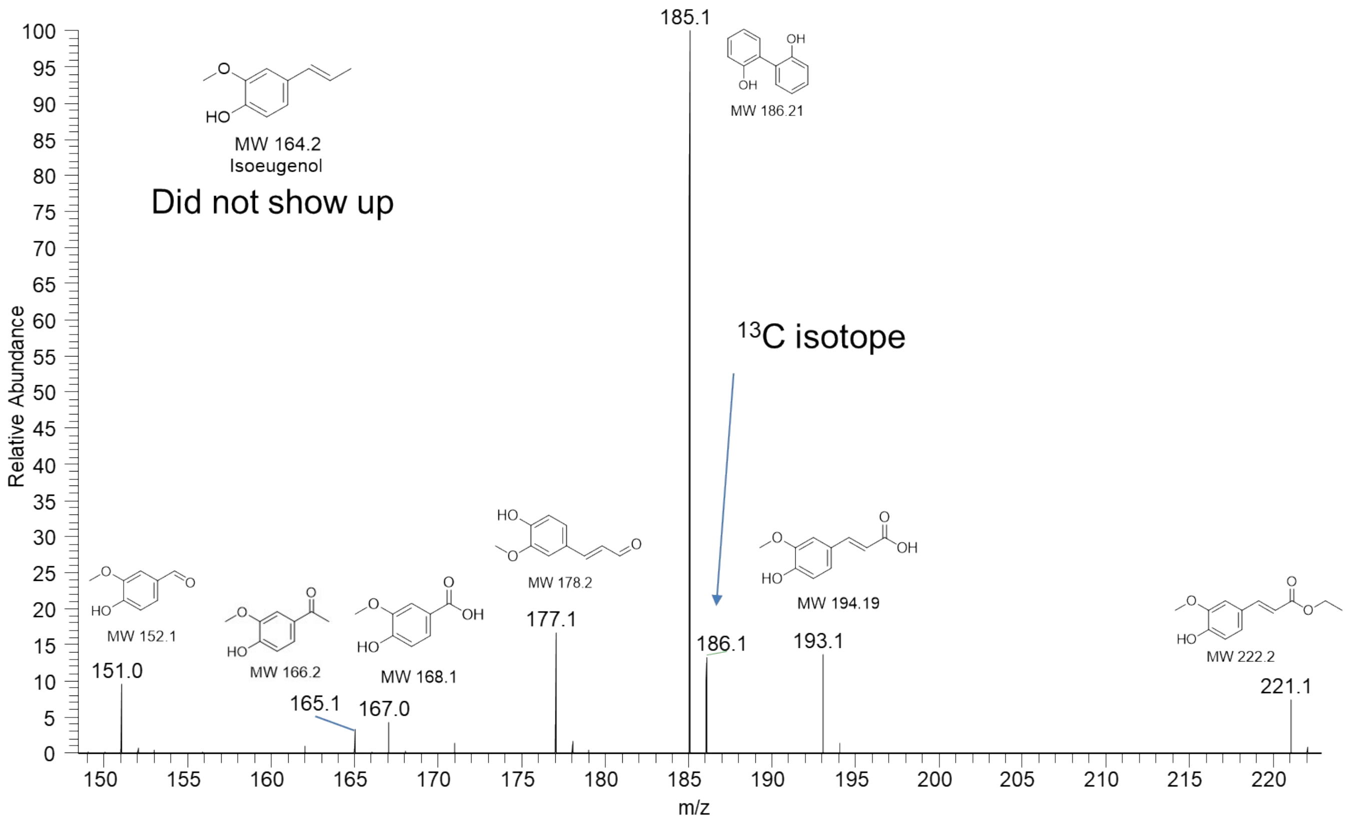
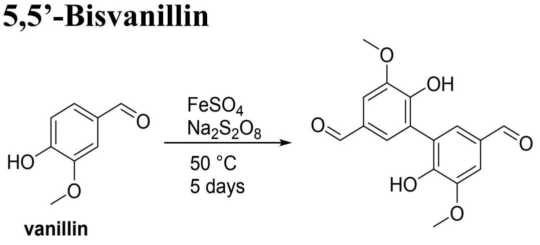


Figure S2. Zoomed in high-resolution mass spectrum measured for the equimolar mixture of 11 lignin model compounds by using (-)ESI HRMS at the range of *m/z* of 150 to 222.

Synthesis of lignin model compounds

5,5’-Bisvanillin

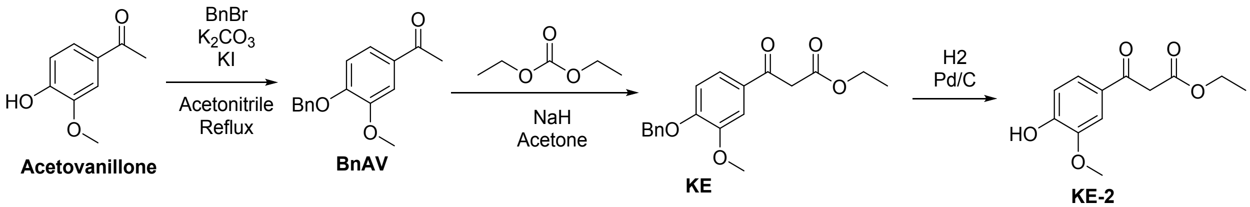


Scheme S1. Synthetic route for 5,5'-bisvanillin

The synthesis of 5,5’-bisvanillin followed previously reported procedures.[4] To vanillin (10.0 g, 65.7 mmol) in 700 mL of water, $FeSO_4$ (365 mg, 1.3 mmol) was added under stirring. After the mixture was heated at 50 ºC for 10 min, $Na_2S_2O_8$ (7.8 g, 32.9 mmol) was added and the reaction mixture was stirred at 50 ºC for 5 days. After 5 days of reaction, the brown precipitate formed was removed by vacuum filtration. The brown filter cake was dissolved in aqueous NaOH solution (2M) and aqueous HCl solution (2M) was then added to the mixture to form a brown precipitate, which was isolated by vacuum filtration to obtain the product 5,5'-bisvanillin as brown solid (9.5 g, 95%).

^{1}H NMR (800 MHz, DMSO-d_6) δ 9.73 (s, 2H), 7.47 (s, 2H), 7.28 (s, 2H), 3.82 (s, 6H).
HRMS: Calculated. for $C_{16}H_{13}O_6$: 301.0718 $[M-H^+]^-$, found: 301.0715.

Ethyl 3-(4-hydroxy-3-methoxyphenyl)-3-oxopropanoate (KE-2)



Scheme S2. Synthetic route for ethyl 3-(4-hydroxy-3-methoxyphenyl)-3-oxopropanoate (KE-2).

The synthesis of intermediate KE followed a previously reported procedure with slight modifications.[5] Compound KE-2 was synthesized following this procedure: into a solution of KE (100 mg, 0.30 mmol) in 2 mL of methanol, 10 mg of 10% Pd-C was added. The system was degassed and was filled with hydrogen gas from a balloon. After two hours of reactions at room temperature, TLC monitoring indicated that the reaction had completed. The reaction mixture was filtered through a celite pad, and the filtrate was concentrated via reduced pressure evaporation to yield KE-2 as light-yellow oil (41.8 mg, 41.8%).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.50 (d, J = 8.2 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.15 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 3.94 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H).
^{13}C NMR (200 MHz, $CDCl_3$) δ 189.76, 167.13, 152.37, 146.80, 128.60, 124.20, 113.98, 110.55, 64.23, 57.06, 45.72, 12.78.
HRMS: Calculated. for $C_{16}H_{13}O_6$: 237.0768 $[M-H^+]^-$, found: 237.0773.

References

1. Jarrell, T. M.; Marcum, C. L.; Sheng, H.; Owen, B. C.; O'Lenick, C. J.; Maraun, H.; Bozell, J. J.; Kenttämaa, H. I., Characterization of organosolv switchgrass lignin by using high performance liquid chromatography/high resolution tandem mass spectrometry using hydroxide-doped negative-ion mode electrospray ionization. *Green Chem.* **2014,** *16* (5), 2713-2727.
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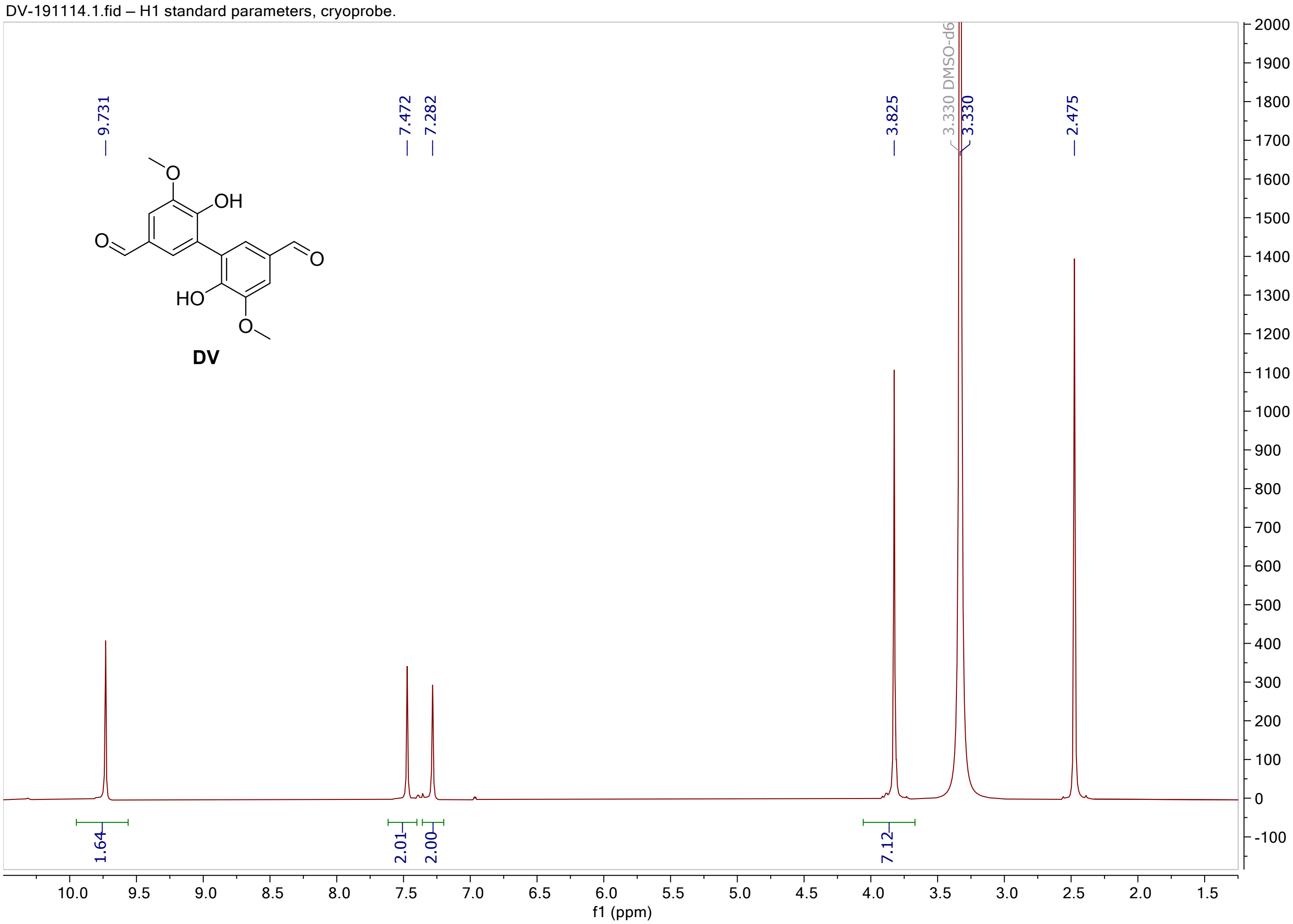
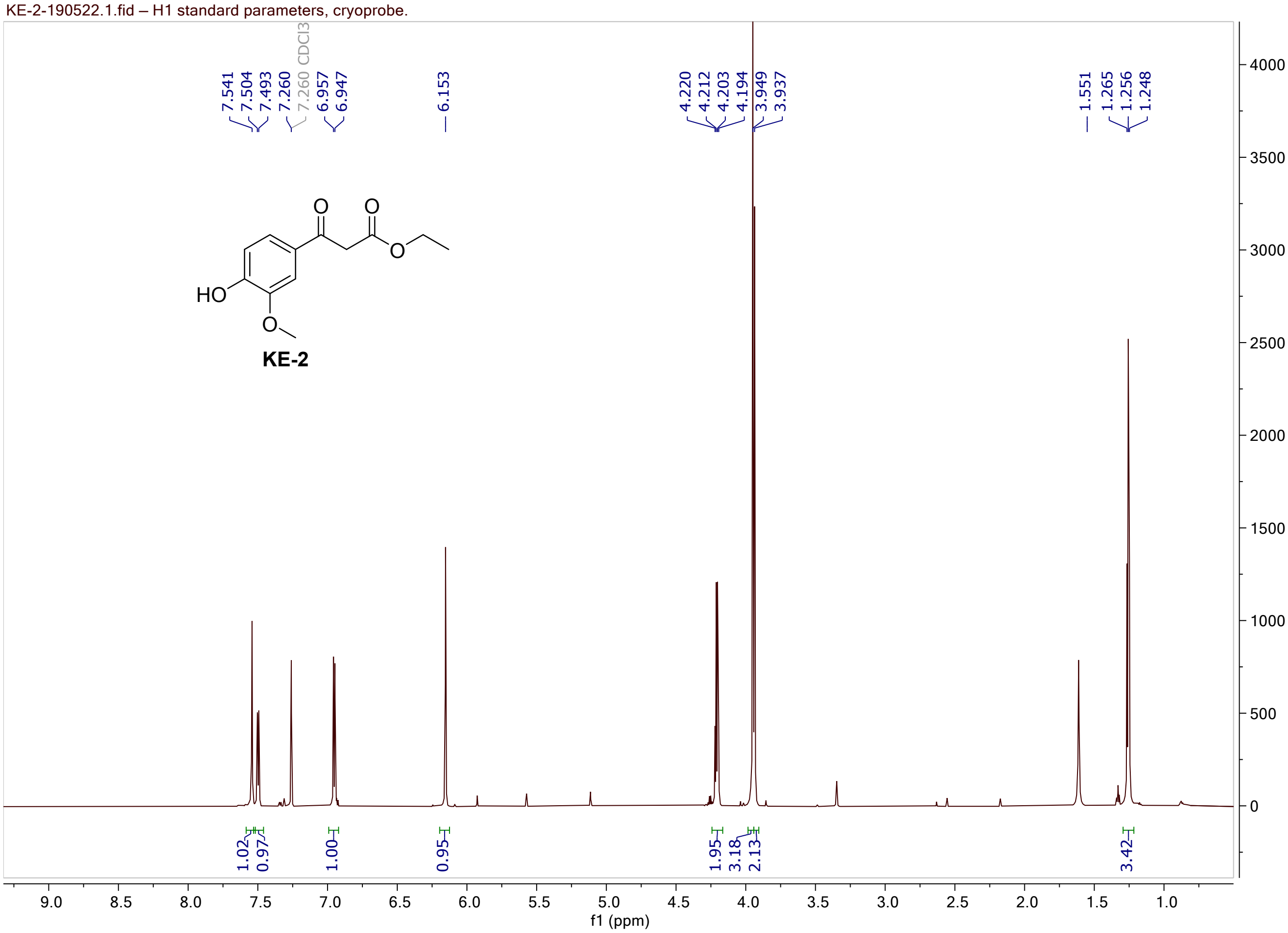
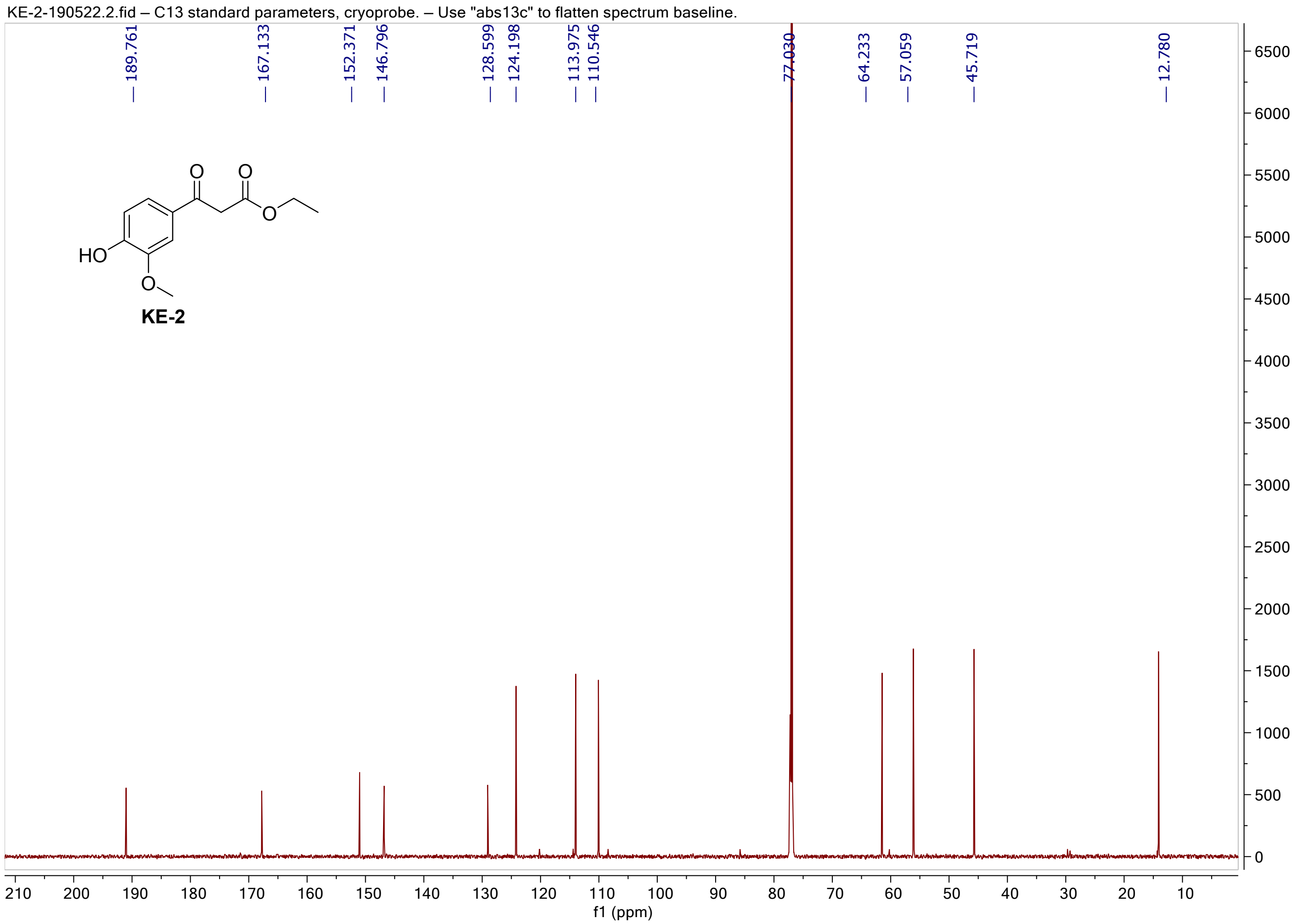
3. Marcum, C. L.; Jarrell, T. M.; Zhu, H.; Owen, B. C.; Haupert, L. J.; Easton, M.; Hosseinaei, O.; Bozell, J.; Nash, J. J.; Kenttämaa, H. I., A fundamental tandem mass spectrometry study of the collision-activated dissociation of small deprotonated molecules related to lignin. *ChemSusChem* **2016,** *9* (24), 3513-3526.
4. Delomenede, M.; Bedos-Belval, F.; Duran, H.; Vindis, C.; Baltas, M.; Negre-Salvayre, A., Development of novel antiatherogenic biaryls: design, synthesis, and reactivity. *J. Med. Chem.* **2008,** *51* (11), 3171-3181.
5. Forsythe, W. G.; Garrett, M. D.; Hardacre, C.; Nieuwenhuyzen, M.; Sheldrake, G. N., An efficient and flexible synthesis of model lignin oligomers. *Green Chem.* **2013,** *15* (11), 3031-3038.

NMR Spectra



DV-191114.1.fid – H1 standard parameters, cryoprobe.
9.731
7.472
7.282
3.825
3.330 DMSO-d6
3.330
2.475
DV
1.64
2.01
2.00
7.12
f1 (ppm)


KE-2-190522.1.fid – H1 standard parameters, cryoprobe.
7.541
7.504
7.493
7.260
7.260 CDCl3
6.957
6.947
6.153
4.220
4.212
4.203
4.194
3.949
3.937
1.551
1.265
1.256
1.248
HO
O
O
O
O
KE-2
1.02
0.97
1.00
0.95
1.95
3.18
2.13
3.42
f1 (ppm)



Cartesian coordinates

Table S_3-1. Deprotonated acetovanillone

C	-0.35865	-2.06095	0.000052
C	-1.56378	-1.26775	-6.9E-05
C	-1.32284	0.18006	-1.6E-05
C	-0.06287	0.710955	0.000137
C	1.097426	-0.11453	0.000277
C	0.901031	-1.50818	0.000201
O	-2.4749	0.926226	-0.00014
C	-2.31967	2.316125	0.000097
O	-2.70868	-1.75177	-0.0002

E(elec)	-574.021052	au
Enthalpy (273.15 K)	-573.846338	au
Gibbs Energy (273.15 K)	-573.895842	au

C	2.404868	0.504753	0.000446
C	3.636486	-0.40247	-0.00021
O	2.586372	1.722494	-0.00033
H	-0.4976	-3.13686	0.00002
H	0.106359	1.780847	0.000179
H	1.760662	-2.17251	0.000274
H	-3.32446	2.739577	0.000085
H	-1.77866	2.66393	0.88958
H	-1.77851	2.664232	-0.88918
H	4.522324	0.230922	-0.00067
H	3.648195	-1.04687	0.882061
H	3.64731	-1.04691	-0.88248

Table S_3-2. Product of methyl radical loss from the methoxy group

C	-1.01822	-1.60472	0.000006	E(elec)	-534.113202	au
C	-2.0216	-0.55233	-0.00001	Enthalpy (273.15 K)	-533.981188	au
C	-1.50519	0.872651	0.000016	Gibbs Energy (273.15 K)	-534.027879	au
C	-0.07939	1.050468	0.000017			
C	0.820576	-0.00332	0.000023			
C	0.320298	-1.34498	0.00002			
O	-2.29555	1.832579	0			
O	-3.22931	-0.79995	-2.8E-05			
C	2.264428	0.278119	0.000032			
C	3.23229	-0.90201	-1.6E-05			
O	2.724482	1.409159	-3.3E-05			
H	-1.39457	-2.62272	-1E-06			
H	0.293067	2.069018	0.000019			
H	1.017204	-2.17677	0.000025			
H	4.247526	-0.50914	-0.00004			
H	3.080339	-1.52895	0.881807			
H	3.080289	-1.52892	-0.88185			

Table S_3-3. Product of methyl radical loss from the ketone group

C	-0.22227	-2.09012	0.000033	E(elec)	-534.064597	au
C	-1.31049	-1.13931	-1.4E-05	Enthalpy (273.15 K)	-533.931628	au
C	-0.88365	0.269661	-4.1E-05	Gibbs Energy (273.15 K)	-533.977892	au
C	0.433144	0.632302	-2.6E-05			
C	1.468414	-0.35303	0.000023			

C	1.096278	-1.70992	0.000045
O	-1.93022	1.154789	-8.6E-05
C	-1.60067	2.513954	0.000095
O	-2.50817	-1.4626	-2.9E-05
C	2.84223	0.02917	0.000035
O	3.379211	1.102966	-6.3E-05
H	-0.507	-3.13662	0.00006
H	0.738989	1.672218	-4.8E-05
H	1.88767	-2.45463	0.00008
H	-2.54338	3.061338	0.000161
H	-1.02041	2.789997	0.890043
H	-1.02041	2.790247	-0.88978

Table S_3-4. Methyl radical

C	0	0	-0.00022	E(elec)	-39.820903	au
H	0	1.078829	0.000447	Enthalpy (273.15 K)	-39.78708	au
H	-0.93429	-0.53941	0.000447	Gibbs Energy (273.15 K)	-39.809925	au
H	0.934293	-0.53941	0.000447			