

Supporting Information

Lignin oxidation by MnO₂ under the irradiation of blue light

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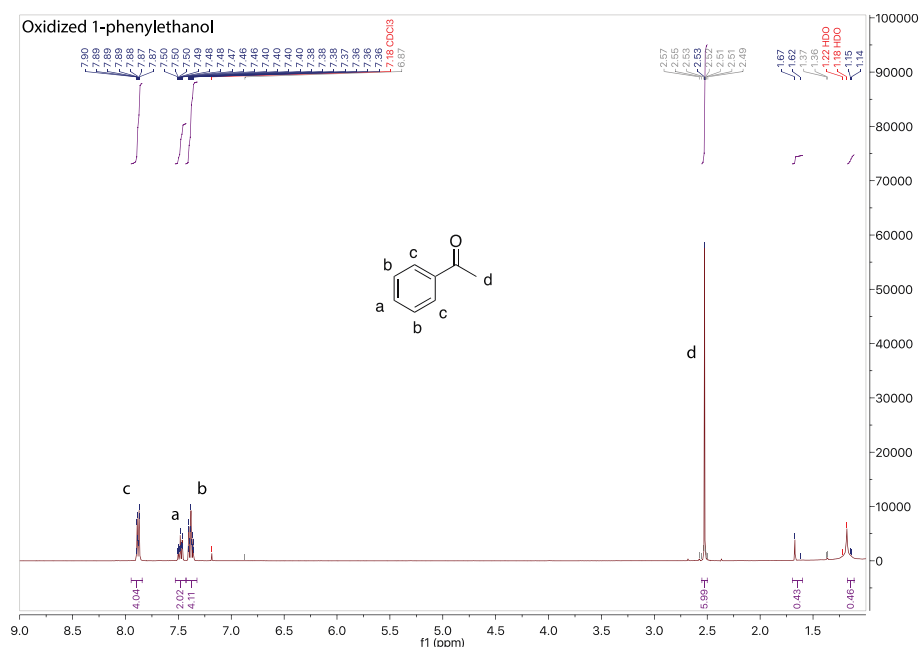


Fig. S1. ¹H-NMR of 1-phenylethanol under the irradiation of blue light with standard condition (Table 2 Entry 4, 98% conversion)

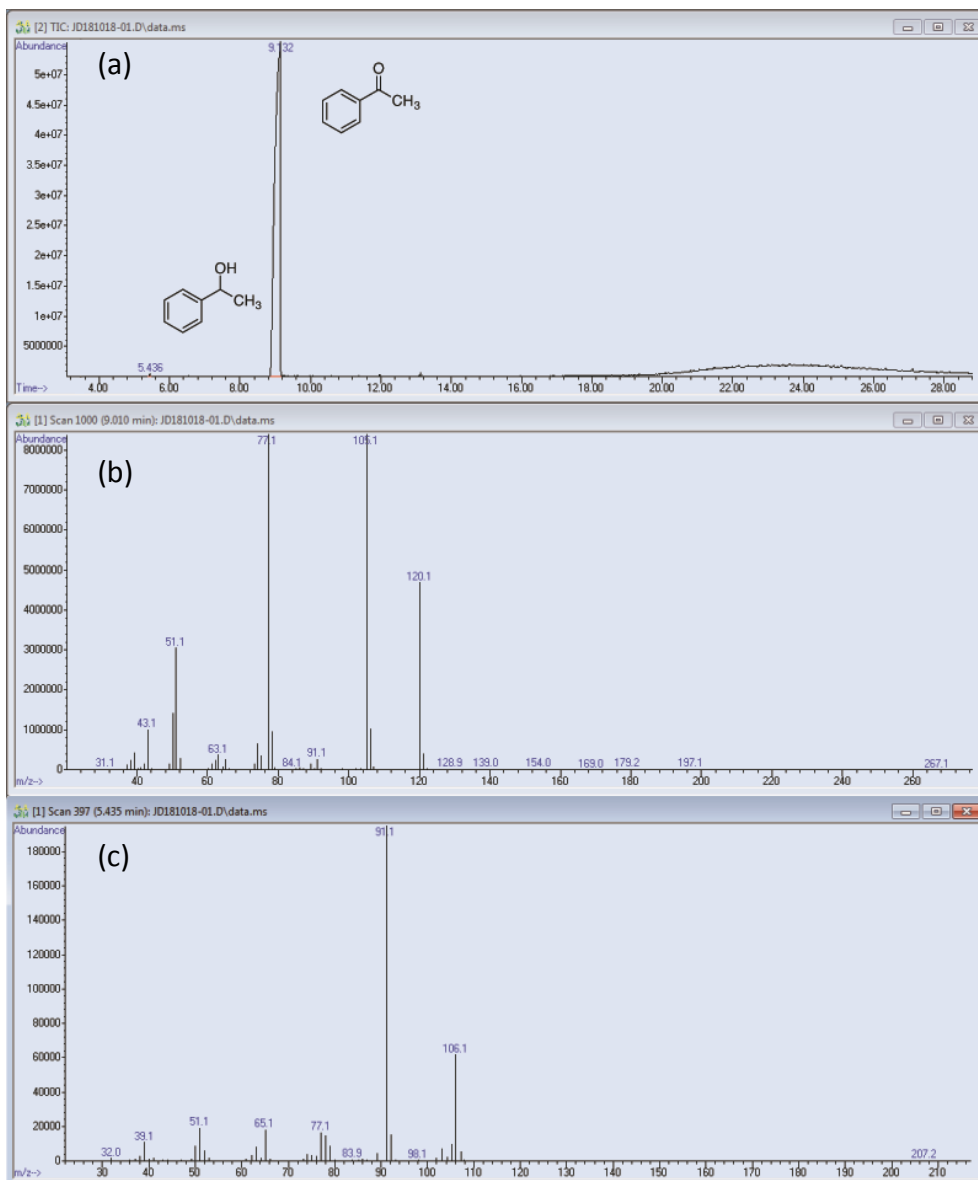


Fig. S2. (a): GC chromatogram of oxidation of 1-phenylethanol under the standard condition; (b) Mass spectra of acetophenone with the retention time of 9.131 min (98% conversion); (c) Mass spectra of unreacted 1-phenylethanol with the retention time of 5.439 min

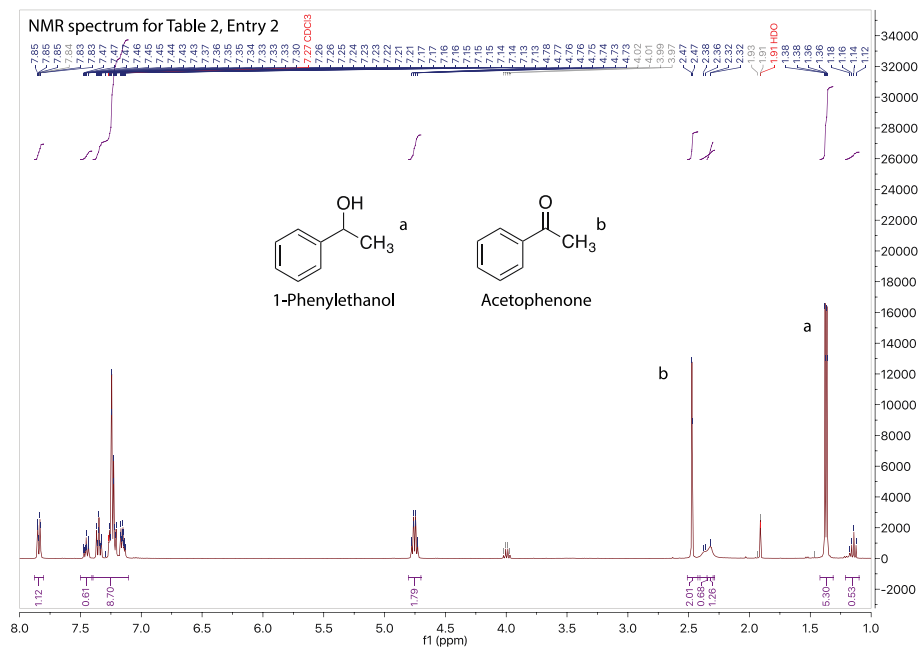


Fig. S3. ^1H -NMR of 1-phenylethanol under the irradiation of UV light (365 nm), with 5 mmol MnO_2 (Table 2, Entry 2, 26%)

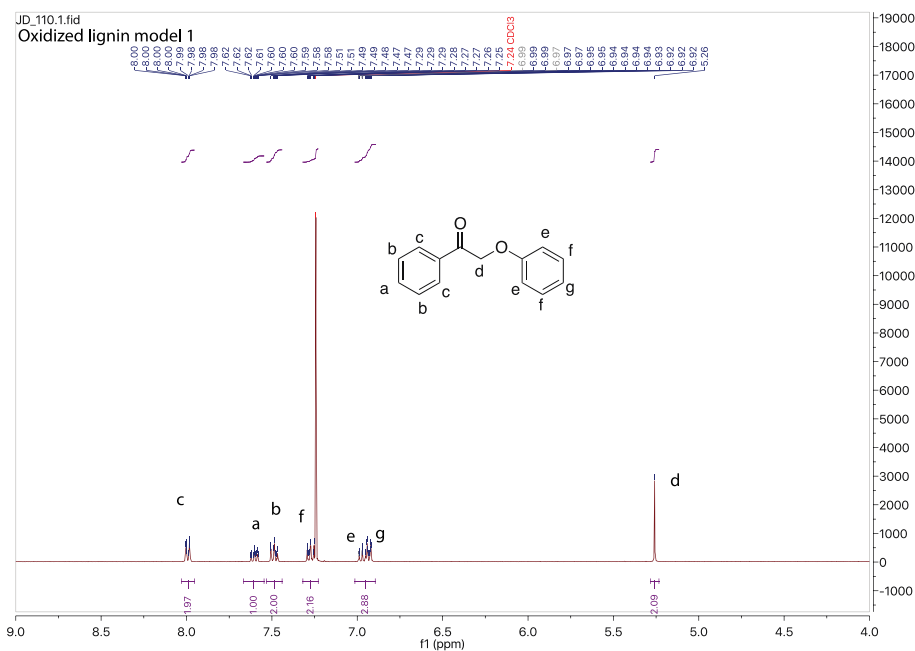


Fig. S4. ^1H -NMR of lignin model 1 under the irradiation of blue light with standard condition (94% conversion)

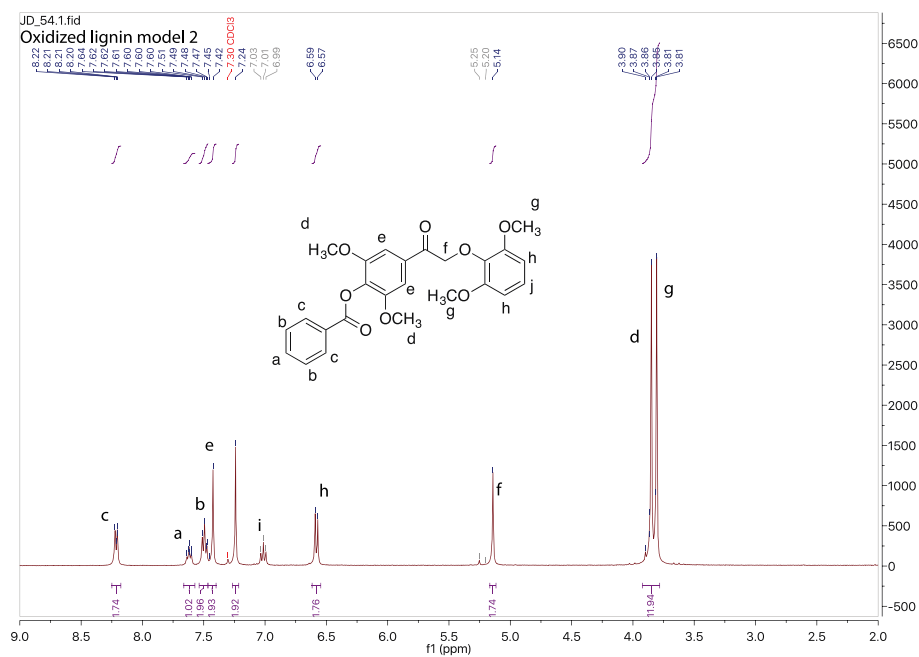


Fig. S5. $^1\text{H-NMR}$ of lignin model 2 under the irradiation of blue light with standard condition (95%)

The conversion of lignin model 2 was based on the ratio of the signal form proton at the position “e” before to after oxidaiton. The signal of this proton shifted after oxidaiton.

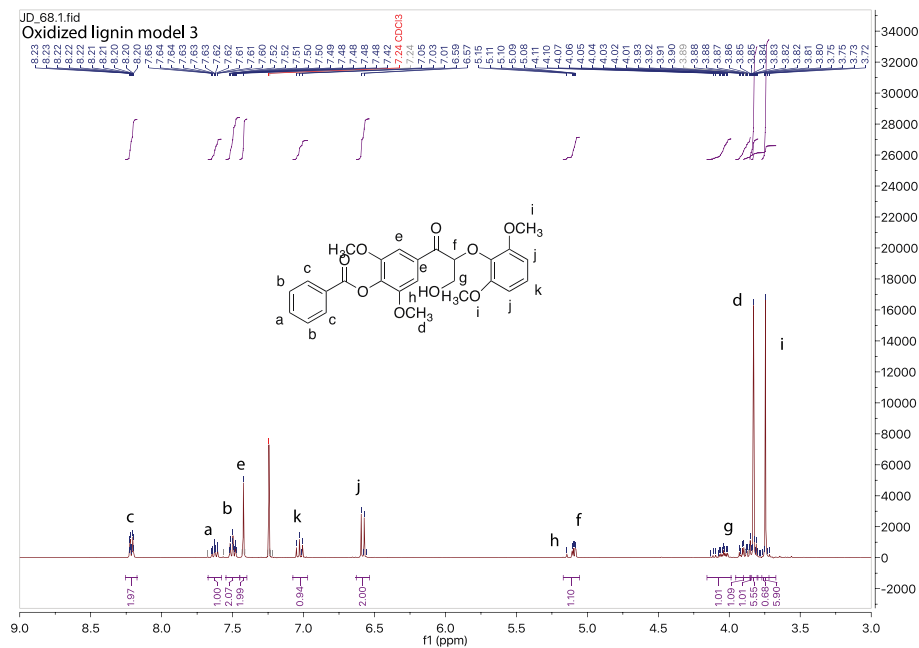


Fig. S6. $^1\text{H-NMR}$ of lignin model 3 under the irradiation of blue light with standard condition (94% conversion)

The conversion of lignin model 3 was based on the ratio of the signal form proton at the position “e” before to after oxidaiton. The signal of this proton shifted after oxidaiton.

Table S1: Conversions of all the screening reaction on model compounds.

Entry	Table 1	Table 2	Table 3	Table 4	Table 5
1	58%	97%	75%	27%	76%
2	60%	26%	29%	0%	19%
3	75%	75%	37%	73%	67%
4	13%	98%	26%	67%	10%
5	97%	51%	-	97%	-
6	97%	25%	-	0%	-
7	-	97%	-	94%	-
8	-	-	-	95%	-
9	-	-	-	94%	-

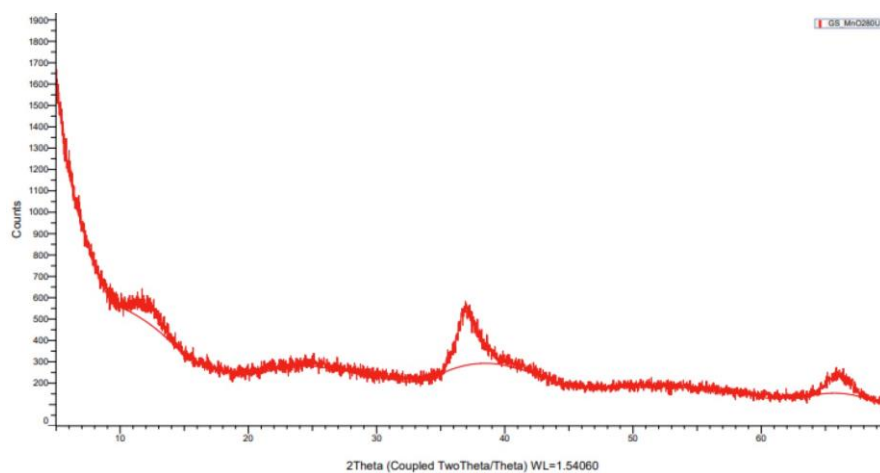


Fig. S7. XRD of recycled δ -MnO₂ after reactive in the furnace at the temperature of 475°C for 4 hours. The XRD of recycled δ -MnO₂ showed it's still δ -MnO₂.

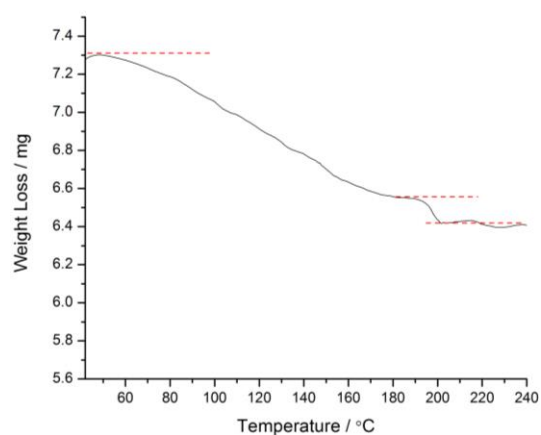


Fig. S8. TGA spectrum of recovered δ -MnO₂.

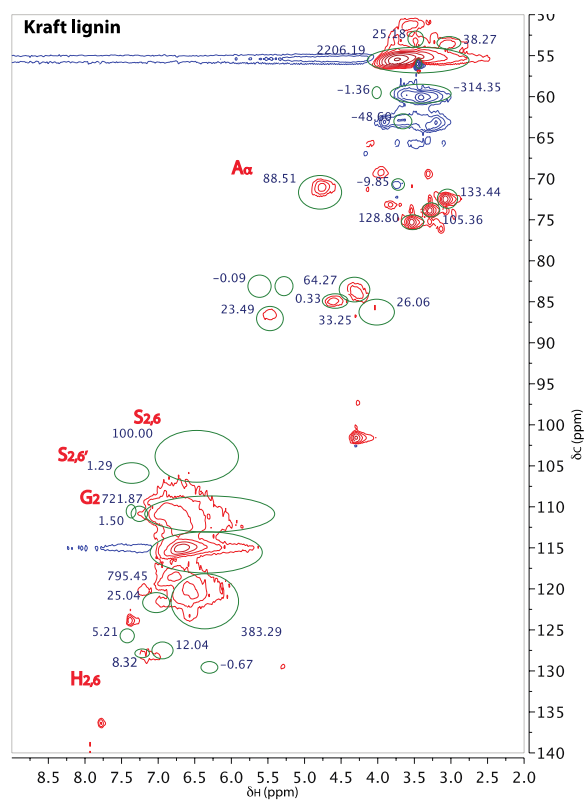


Fig. S9. HSQC-NMR of native kraft lignin

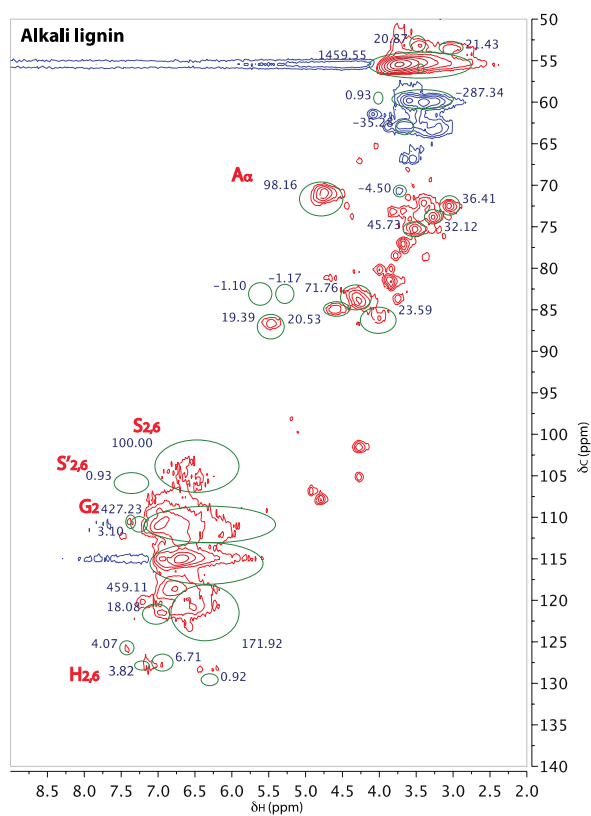


Fig. S10. HSQC-NMR of native alkali lignin

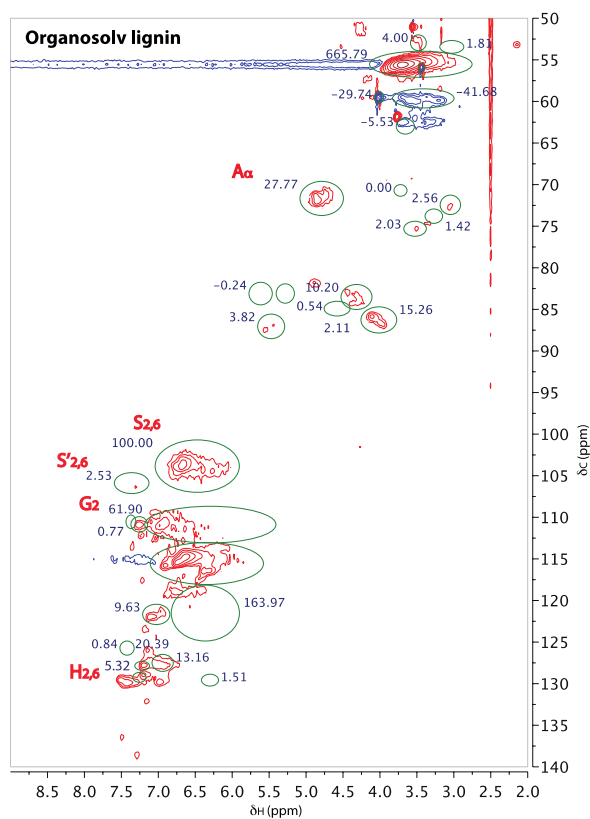


Fig. S11. HSQC-NMR of native organosolv lignin

Table S2 Integrations of three native lignin structure

	Kraft lignin	Alkali lignin	Organosolv lignin
G2	721.87	427.73	61.90
G'2	0	0	0
G'6	0	0	0
S2,6	0	17.43	100
S'2,6	1.29	0.93	2.53
H2,6	8.32	3.82	5.32
$G_{total}=G2+G'2+G'6-H2,6$	713.55	423.91	56.58
$S_{total}=(S2,6+S'2,6)/2$	0.645	9.18	51.265
$H_{total}=H2,6$	8.32	3.82	5.32
Total= $G_{total}+ S_{total}+ H_{total}$	722.515	436.91	113.165
Aα	88.51	98.16	27.77
Percentage of β-O-4 linkage= Aα/Total x 100	12.25%	23.16%	24.54%

Table S3 Analysis of three native lignin structure

	Kraft lignin	Alkali lignin	Organosolv lignin
S/G/H units ratio	0.1% / 99.3% / 0.6%	2% / 97% / 1%	44%/53%/3%
β-O-4*	12.25%	23.16%	24.54%
	Oxidized Kraft lignin	Oxidized Alkali lignin	Oxidized Organosolv lignin
β-O-4*	1%	3%	2%

* per aromatic circle

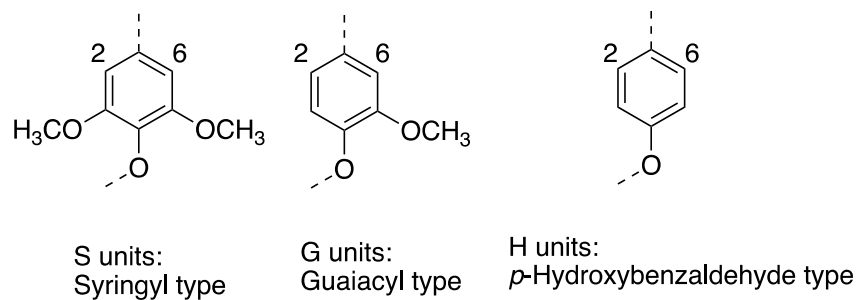


Fig. S12. Structure of three basic units in lignin

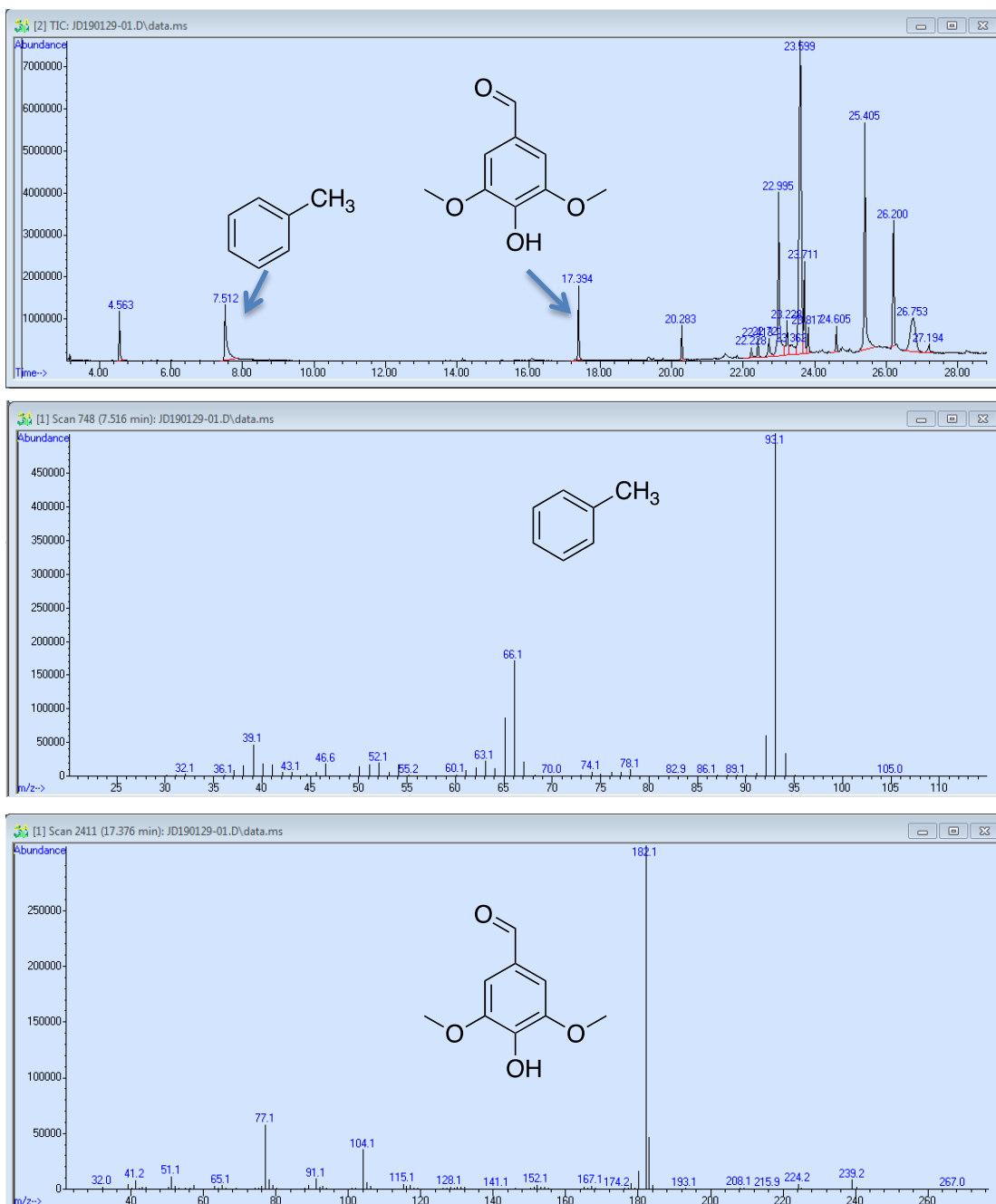


Fig. S13. GC-MS spectrum of ethyl acetate soluble fraction from depolymerised organosolv lignin

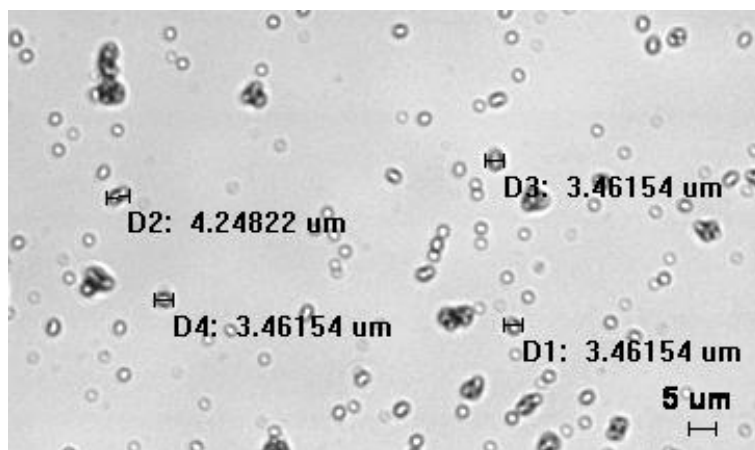


Fig. S14. Optical microscope image of MnO₂