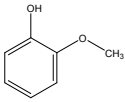
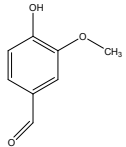
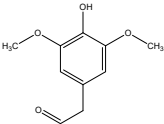
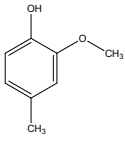
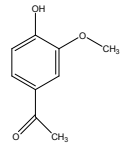
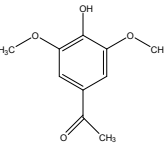
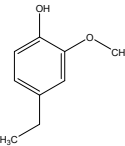
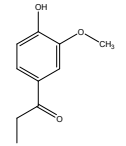
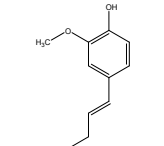
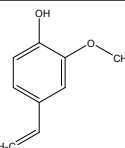
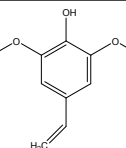
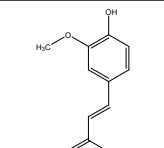
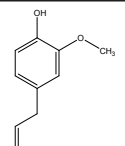
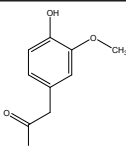
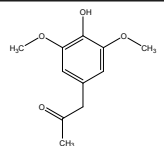
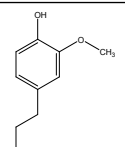
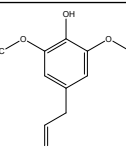
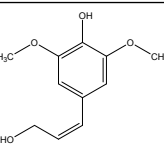
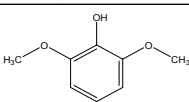
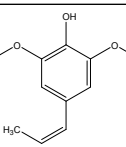
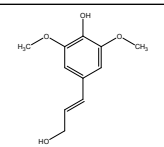
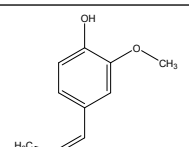
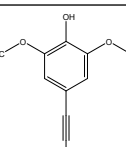
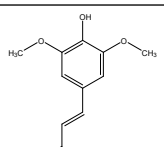
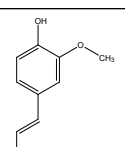
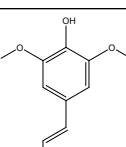
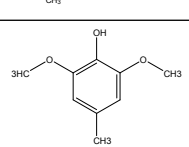
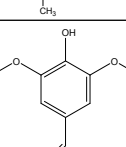


- Supplementary data: Laccase catalyzed grafting of -N-OH type mediators to lignin via radical-radical
- coupling
- Line Munk, Arjen M. Punt, Mirjam A. Kabel, Anne S. Meyer

4 **Table S1.** Identified lignin residues from pyrograms of WSL and BOL samples.

Peak No. Compound CAS number	Chemical structure	Peak No. Compound CAS number	Chemical structure	Peak No. Compound CAS number	Chemical structure
1G Guaiacol 90051		11G Vanillin 121335		21S Homosyringaldehyde -	
2G 4-methylguaiacol 93516		12G Acetovanillone 498022		22S Acetosyringone 2478388	
3G 4-ethylguaiacol 2785899		13G Propiovanillone 1835149		23G <i>Trans</i> -coniferyl-alcohol 458355	
4G 4-vinylguaiacol 7786610		14S 4-vinylsyringol 28343228		24G <i>Trans</i> -coniferaldehyde 458366	
5G Eugenol 97530		15G Guaiacylacetone 2503460		25S Syringylacetone 19037582	
6G 4-propylguaiacol 2785877		16S 4-allyl-syringol 6627889		26S <i>Cis</i> -sinapyl-alcohol 537337	
7S Syringol 91101		17S <i>Cis</i> -4-propenyl syringol 26624135		27S <i>Trans</i> -sinapyl-alcohol 537337	
8G <i>Cis</i> -isoeugenol 97541		18S 1-(3,5-dimethoxy-4-hydroxyphenyl)propyne -		28S <i>Trans</i> -sinapaldehyde 4206580	
9G <i>Trans</i> -isoeugenol 97541		19S <i>Trans</i> -4-propenylsyringol 26624135			
10S 4-methylsyringol 6638057		20S Syringaldehyde 134963			

5 Identities of lignin-derived phenolic S and G compounds above 1% in relative occurrence. Identified with Py-GC/MS.

6 **Table S2:** Molar area distribution of identified G residues (>1%) over total G residues in WSL pyrograms. The summed molar areas of identified G residues were normalized
 7 to 100%. Values are given in percent.

Sample	Guaiacol	4-methylguaiacol	4-ethylguaiacol	4-vinylguaiacol	Eugenol	4-propylguaiacol	Vanillin	Cis-isoeugenol	Trans-isoeugenol	Acetovanillone	Guaiacylacetone	Coniferaldehyde	Trans-coniferyl-alcohol
Blank	15±0	14±0	4±1	40±2	2±0	0±0	6±0	1±0	6±0	3±1	3±0	2±0	5±0
TvL	15±0	15±0	5±1	36±4	1±0	0±0	6±1	1±0	6±0	4±1	3±0	2±0	5±0
Pol	14±0	15±1	4±1	38±2	1±0	1±0	6±1	1±0	6±0	4±0	3±0	2±0	6±1
HBT	13±1	13±1	3±0	42±1	1±0	1±0	5±1	1±0	6±1	3±0	3±0	1±0	8±0
TvL+HBT	14±1	13±1	5±0	38±1	1±0	0±0	6±0	1±0	5±0	4±0	3±0	2±0	8±1
Pol+HBT	14±0	13±1	5±0	38±2	1±0	0±0	6±0	1±0	5±0	4±0	3±0	2±0	7±1
HPI	14±1	13±0	4±1	42±3	1±0	0±0	4±0	1±0	6±0	3±0	3±0	1±0	8±1
TvL+HPI	14±1	13±1	4±1	38±1	1±0	0±0	6±0	1±0	6±0	5±0	3±0	2±0	6±0
Pol+HPI	14±1	13±1	5±1	38±2	1±0	1±0	7±1	1±0	6±0	5±0	3±0	2±0	5±1
TEMPO	14±1	12±1	4±0	41±2	1±0	0±0	6±0	1±0	5±0	3±1	3±0	2±0	8±1
TvL+TEMPO	14±0	14±0	5±1	36±1	1±0	0±0	10±0	1±0	5±0	4±0	3±0	2±0	6±1
Pol+TEMPO	14±0	13±1	5±1	37±2	1±0	1±0	9±0	1±0	5±0	4±0	3±0	2±0	5±0
ABTS	14±0	14±1	4±1	42±1	1±0	0±0	5±0	1±0	6±0	2±0	3±0	2±0	6±0
TvL+ABTS	14±1	16±2	3±0	39±3	1±0	1±0	5±0	1±0	5±0	3±0	3±0	8±2	2±0
Pol+ABTS	13±1	15±1	3±0	39±1	1±0	0±0	6±1	1±0	4±0	3±0	3±0	11±1	1±0

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14 **Table S3:** Molar area distribution of identified S residues (>1%) over total S residues in WSL pyrograms. The summed molar areas of identified G residues were normalized
15 to 100%. Values are given in percent.

Sample	Syringol	4-methylsyringol	4-vinylsyringol	4-allylsyringol	Syringaldehyde	Cis-4-propenylsyringol	Homosyringaldehyde	Cis-1-(3,5-dimethoxy-4-hydroxyphenyl)propyne	Trans-1-(3,5-dimethoxy-4-hydroxyphenyl)propyne	Trans-4-propenylsyringol	Acetosyringone	Syringylactone	Cis-Sinapyl alcohol	Sinapaldehyde	Trans-Sinapyl alcohol
Blank	17±2	15±2	20±2	2±0	6±1	1±0	4±1	2±0	7±9	9±1	8±0	4±1	0±0	2±0	4±0
TvL	17±1	15±1	19±1	2±0	8±0	1±0	5±1	1±0	2±1	9±0	10±0	4±0	0±0	3±0	3±0
PoL	18±1	15±1	19±1	2±0	8±1	1±0	4±0	2±0	1±1	10±1	10±0	5±0	0±0	3±0	3±0
HBT	18±1	13±1	21±1	2±0	6±1	1±0	5±1	1±0	1±1	11±1	8±0	4±0	0±0	2±0	6±1
TvL+HBT	18±1	14±1	19±1	2±0	8±0	1±0	4±1	2±0	1±2	10±0	11±0	5±0	0±0	3±0	6±0
PoL+HBT	18±2	13±1	19±1	2±0	8±0	1±0	4±0	1±0	1±1	10±1	10±1	4±0	0±0	2±0	5±0
HPI	17±2	13±2	19±2	2±0	6±0	1±0	4±0	2±0	6±10	9±2	8±1	4±0	0±0	2±0	6±2
TvL+HPI	18±1	13±1	19±1	2±0	7±0	1±0	4±0	1±0	3±4	9±1	12±1	5±0	0±0	2±0	4±0
PoL+HPI	19±1	14±1	18±1	2±0	7±1	1±0	4±1	1±0	1±1	10±1	12±0	5±0	0±0	2±0	4±1
TEMPO	19±1	13±1	20±1	2±0	7±0	1±0	5±0	1±0	2±1	9±1	8±0	4±0	0±0	3±0	6±0
TvL+TEMPO	17±1	14±0	18±0	2±0	11±1	1±0	4±0	1±0	0±0	9±1	11±1	5±0	0±0	3±0	5±1
PoL+TEMPO	18±1	13±1	18±1	2±0	11±0	1±1	4±1	1±0	1±2	9±1	11±1	4±0	0±0	3±0	4±0
ABTS	17±0	15±0	22±1	2±0	6±0	1±0	5±1	2±0	0±0	12±1	8±0	4±0	0±0	2±0	4±0
TvL+ABTS	17±1	16±1	21±0	2±0	7±0	1±0	8±0	2±0	3±3	9±0	9±1	5±0	0±0	2±0	1±0
PoL+ABTS	16±3	15±2	20±3	2±0	6±1	1±0	7±1	2±0	9±13	8±1	8±1	4±1	0±0	2±1	1±0

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20 **Table S4.** Molar area distribution of identified G residues (>1%) over total G residues in BOL pyrograms. The summed molar areas of identified G residues were normalized
 21 to 100%. Values are given in percent.

Sample	Guaiacol	4-methylguaiacol	4-ethylguaiacol	4-vinylguaiacol	Eugenol	4-propylguaiacol	Vanillin	Cis-isoegenol	Trans-isoegenol	Acetovanillone	Guaiacylacetone	Propiovanillone	Coniferaldehyde	Trans-coniferyl-alcohol
Blank	16±1	20±2	4±0	17±1	1±0	1±0	11±0	1±0	7±1	6±0	4±0	0±0	4±0	8±1
TvL	16±1	21±1	4±0	17±1	2±0	1±0	11±0	1±0	8±0	6±0	4±0	0±0	3±0	7±1
Pol	17±2	18±2	3±1	17±1	1±0	1±0	11±0	1±0	7±0	6±0	4±0	0±0	3±0	10±2
HBT	15±1	20±1	4±0	16±1	2±0	1±0	11±0	1±0	7±1	6±0	3±0	1±0	3±0	8±1
TvL+HBT	15±1	20±1	4±0	16±1	1±0	1±0	11±1	1±0	7±0	6±0	4±0	0±0	3±0	9±1
Pol+HBT	15±1	20±1	4±0	16±0	1±0	1±0	11±0	1±0	7±0	6±0	4±0	0±0	3±0	9±1
HPI	16±1	21±1	4±0	15±1	2±0	1±0	10±0	1±0	7±0	6±0	3±0	0±0	3±0	9±0
TvL+HPI	17±1	19±1	4±0	16±1	1±0	1±0	10±1	1±0	7±0	6±0	4±0	0±0	3±0	8±1
Pol+HPI	17±1	20±1	4±0	16±0	1±0	1±0	10±0	1±0	7±0	6±0	4±0	0±0	3±0	8±0
TEMPO	15±1	21±2	4±0	16±0	1±0	1±0	12±0	1±0	7±0	5±0	4±0	0±0	3±0	7±1
TvL+TEMPO	15±1	20±2	4±0	16±0	1±0	1±0	13±0	1±0	7±0	6±0	4±0	1±0	3±0	7±1
Pol+TEMPO	15±0	21±1	4±0	15±0	1±0	1±0	13±1	1±0	7±0	6±0	4±0	0±0	3±0	7±1
ABTS	16±1	27±0	5±0	20±1	1±0	1±0	9±0	1±0	6±0	4±0	5±0	0±0	2±0	2±0
TvL+ABTS	18±1	28±0	5±0	20±1	1±0	1±0	9±0	1±0	6±0	3±0	5±0	0±0	2±0	1±0
Pol+ABTS	18±1	28±1	5±0	20±1	1±0	1±1	9±0	1±0	6±0	3±0	5±0	0±0	1±0	1±0

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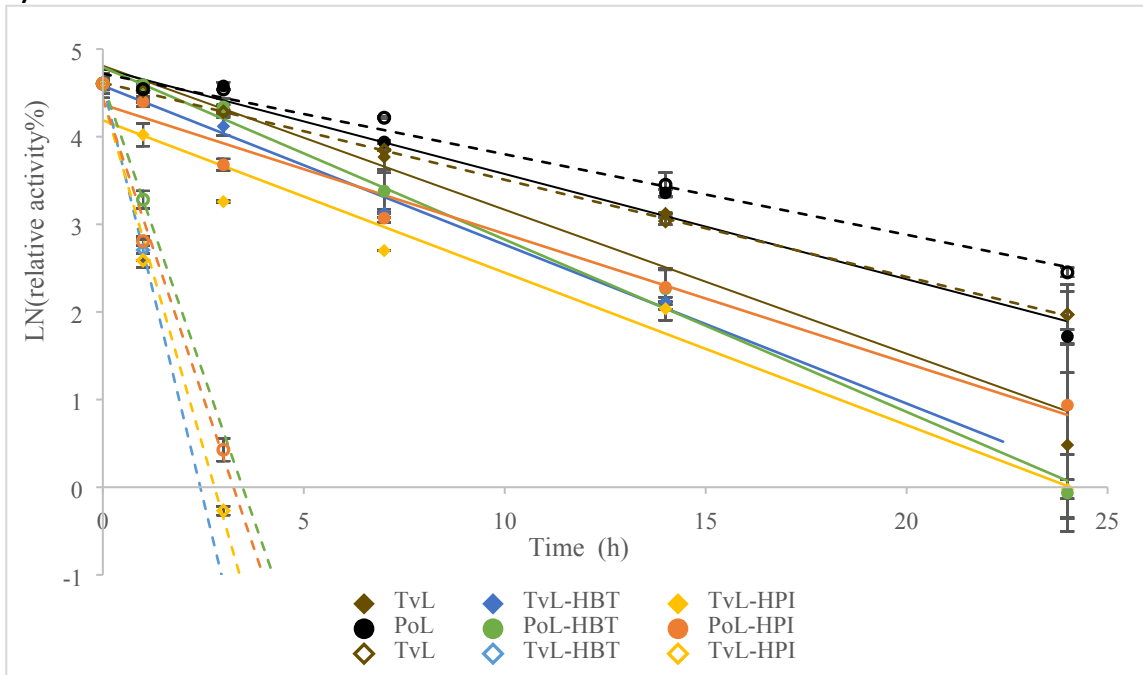
26 **Table S5.** Molar area distribution of identified S residues (>1%) over total S residues in BOL pyrograms. The summed molar areas of identified G residues were normalized
 27 to 100%. Values are given in percent.

Sample	Syringol	4-methylsyringol	4-vinylsyringol	4-allylsyringol	Syringaldehyde	Cis-4-propenylsyringol	Homosyringaldehyde	Cis-1-(3,5-dimethoxy-4-hydroxyphenyl)propyne	Trans-1-(3,5-dimethoxy-4-hydroxyphenyl)propyne	Trans-4-propenylsyringol	Acetosyringone	Syringylactone	Cis-Sinapyl alcohol	Sinapaldehyde	Trans-Sinapyl alcohol
Blank	14±1	15±2	13±1	2±0	15±1	1±0	9±0	1±0	1±0	8±1	8±0	4±0	0±0	3±0	7±1
TvL	14±2	15±1	13±1	2±0	14±0	1±0	8±0	1±0	1±0	9±0	8±0	4±0	1±0	3±0	6±0
PoL	14±2	13±2	14±0	2±0	15±1	1±0	8±1	1±0	1±0	8±1	8±0	4±0	1±0	3±0	8±1
HBT	13±1	15±1	13±0	2±0	14±0	1±0	8±0	1±0	1±0	9±1	8±0	4±0	1±0	3±0	7±0
TvL+HBT	14±2	15±1	13±0	2±0	14±0	1±0	8±1	1±0	1±0	9±0	8±0	4±0	1±0	3±0	7±1
PoL+HBT	13±1	15±1	13±0	2±0	14±0	1±0	8±0	1±1	1±0	9±0	8±0	4±0	1±0	3±0	7±1
HPI	14±1	15±0	12±0	2±0	14±1	1±0	7±0	1±0	1±0	9±0	8±0	3±0	1±0	3±0	7±0
TvL+HPI	15±1	14±0	14±1	2±0	14±1	1±0	8±1	1±0	1±0	9±1	8±0	4±0	0±0	3±0	7±0
PoL+HPI	16±1	15±1	13±1	2±0	13±0	1±0	7±0	1±0	1±0	10±0	8±0	4±0	0±0	3±0	6±0
TEMPO	13±1	15±1	14±1	2±0	15±0	1±0	8±0	1±0	1±0	9±1	7±0	4±0	1±0	3±0	6±0
TvL+TEMPO	14±1	14±1	13±1	2±0	15±0	1±0	8±0	1±0	1±0	9±1	8±0	4±0	1±0	3±0	6±0
PoL+TEMPO	13±0	16±1	13±0	2±0	15±0	1±0	8±0	1±0	1±0	10±0	8±0	4±0	0±0	3±0	6±0
ABTS	15±2	22±0	16±1	2±0	10±0	1±0	8±0	2±0	1±0	9±0	4±0	5±0	0±0	3±0	1±0
TvL+ABTS	16±1	22±1	17±1	2±0	10±1	1±0	9±0	2±0	1±0	8±0	4±0	6±0	0±0	3±0	1±0
PoL+ABTS	17±0	23±1	16±0	2±0	10±1	1±0	9±0	2±0	1±0	8±0	4±0	5±0	0±0	3±0	1±0

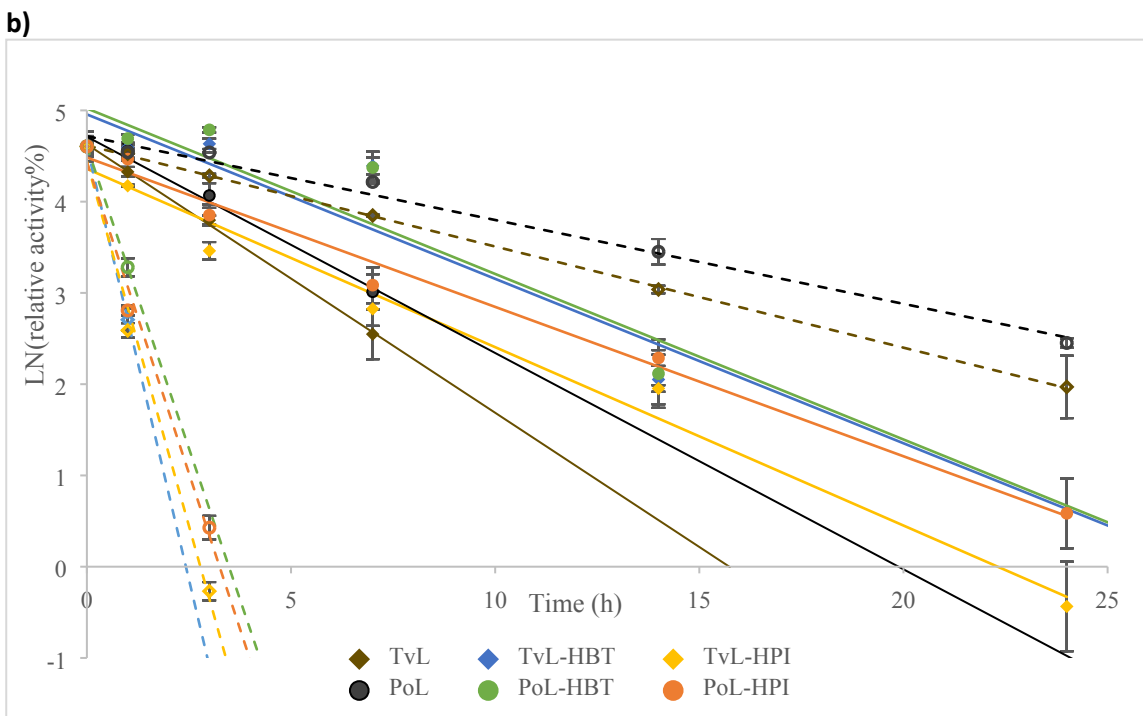
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38 **Figure S1:** Decay of activity measured on syringaldehyde of a) TvL and PoL and in combination with HBT and
39 HPI during treatment on WSL (—) and no substrate (- - -). b) TvL and PoL and in combination with HBT
40 and HPI during treatment on BOL (—) and no substrate (- - -). Data points are averages of two
41 independent samplings shown with \pm s.d. as a vertical bar for each point.
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