Supporting Information

Tandem Catalytic Depolymerization of Lignin by Water-Tolerant Lewis Acids and Rhodium Complexes

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cssc_201600683_sm_miscellaneous_information.pdf

Contents

S1 Experimental Procedures

Materials

1,4-dioxane (99+%, a.c.s. grade, Alfa Aesar), chloro(1,5-cyclooctadiene)rhodium(I) dimer (98%, ABCR), 1,3-bis(diphenylphosphino)propane (98%, ABCR), scandium(III) triflate (95%, Acros), indium(III) triflate (99%, ABCR), gallium(III) triflate (98%, ABCR) and ytterbium(III) triflate (98%, ABCR) were all used as received. Lignin model compounds 2-phenoxy-1-phenylethan-1-ol (**1a**),[1] 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-ol[1] (**1b**) and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (**1d,** obtained as a 5:1 mixture of *erythro*:*threo*) were synthesized according to previously published procedure. Dioxasolv lignin was isolated from poplar sawdust (sieved through a 1mm grid), brewers' spent grains, and commercial pine wood shavings according to a previously published procedure, affording 9, 4 and 3.5 wt% of lignin respectively.[2] The brewers' spent grains were sourced from Daftmill Distillery, Cupar, UK and were air dried to a constant weight before use. Poplar sawdust used in reactions was Soxhlet extracted overnight, dried under vacuum, and ball-milled for 25 days at 60 rpm to afford a very fine powder.[3]

Physical Measurements

GC measurements were performed on a Varian GC equipped with a VF-5 ms capillary column and an FID detector. Mesitylene was used an internal standard; response factors were determined for all products for which reference materials were available, for other compounds these were extrapolated by number of carbon atoms from structurally similar compounds. GC-MS measurements were performed on a Shimadzu GC-2010 using a VF5-ms column, coupled to a Shimadzu GC-MS-QP2010

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mass spectrometer. 2D GC×GC-MS (1st column: VF-5ms 30 m, 0.25 mm ID, df 0.25 μm; 2nd column: VF-17ms, 1 m, 0.15 mm ID, df 0.15 μm) was performed in a GC-MS2010 Ultra (Shimadzu) equipped with a ZX1 thermal modulation system (Zoex). The temperature program started with an isothermal step at 40 °C for 5 min. Next, the temperature was increased to 280 °C by 2.5 °C min^{-1}. The program finished with an isothermal step at 280 °C for 5 min. The modulation applied for the comprehensive GC×GC analysis was a hot jet pulse (375 ms) every 7000 ms. The 2D chromatograms were processed with GC Image software (Zoex). NMR spectra were recorded on a Varian spectrometer operating at 400 MHz (^{1}H) or 100 MHz (^{13}C) in DMSO-d6 (unless mentioned otherwise) and referenced against the signal of the residual protio impurity of the solvent (^{1}H 2.50 ppm, ^{13}C 39.52 ppm). HSQC spectra were recorded on a Bruker Avance II 600 MHz spectrometer equipped with a 5 mm CPTCI ^{1}H-^{13}C/^{15}N/^{2}H cryogenic probe with z-gradients at 25 °C using the Q-CAHSQC pulse program.[4] Matrices of 2048 data points for the ^{1}H-dimension and 128 data points for the ^{13}C-dimension were collected with a relaxation delay of 6 s and spectral widths from 13 to -1 ppm and from 160 to 0 ppm for the ^{1}H and ^{13}C dimensions, respectively. The lignins and lignin products were dissolved in DMSO-d6 after overnight stirring (200 mg/750 μL) and chemical shifts were referenced to the solvent signal (2.50/39.5 ppm). The spectra were processed and analysed using MestReNova software. Prior to Fourier transformation, FIDs were apodized with a π/2 sine square bell function in both dimensions and zero-filled up to 512 points in the ^{13}C-dimension and 4096 points in the ^{1}H-dimension. A semi-quantitative analysis of the HSQC spectra was performed by integration of correlations peaks in the different regions of the spectra with MestReNova. The relative quantity of side chains involved in the interunit and terminal substructures was expressed as a number per 100 aromatic units

(S+G). In the aliphatic oxygenated region, interunit linkages were estimated from Cα−Hα correlations. GPC measurements were performed on a Polymer Labs GPC 50 system, equipped with a series of three PLGel Mixed-E columns and guard a guard column and using THF spiked with 0.1 vol% acetic acid as mobile phase. Detection was done with an external Knauer UV detector at 280 nm and molecular weight determinations were based on calibration with polystyrene standards.

Catalytic experiments

In a typical experiment, a 40 mL stainless steel Parr autoclave was charged with model compound (2.40 mmol), lignin (300 mg) or poplar sawdust (2.0 g), chloro(1,5-cyclooctadiene)rhodium(I) dimer (29.0 mg, 0.060 mmol), 1,3-bis(diphenylphosphino)propane (99.0 mg, 0.240 mmol), scandium(III) triflate (59.1 mg, 0.120 mmol) and 22 mL 9:1 1,4-dioxane:water mixture. After sealing, the autoclave was flushed three times with 50 bars argon and after release of pressure heated to the reaction temperature. After reacting for 2 hours, the heating mantle was removed and the reactor rapidly cooled with an ice-water bath. From the resulting solution was taken a 200 µL sample, which was concentrated *in vacuo* and redissolved in the GPC mobile phase for GPC analysis. To the remainder was added mesitylene and a 0.5 mL sample was passed over 0.5 g of silica gel padded with 0.2 g of magnesium sulfate to remove water and the inorganic compounds; organics were subsequently eluted with 3 mL ethyl acetate and analyzed by GC and GC-MS. In so far possible, quantification was performed against authentic standards; if not response factors were determined by interpolating from known compounds (Table S2).

2-bromo-3',4',5'-trimethoxyacetophenone

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To 120 mL of ethyl acetate is added 40.3 g (180 mmol) of finely ground copper(II) bromide and brought to reflux. 3',4',5'-trimethoxyacetophenone (18.9 g, 90 mmol) was dissolved in 120 mL chloroform and added to the refluxing dark green copper(II) bromide suspension. After refluxing for 4 hours the suspension had turned brownish and HBr evolution ceased; the suspension was allowed to cool to room temperature and the solids removed filtration. The filtrate was concentrated in vacuo to afford 22.8 g of brown oil that solidifies upon standing. The crude material was used directly in the subsequent step without further purification. ^{1}H NMR (CDCl$_3$): δ 7.24 (s, 2H), 4.41 (s, 2H), 3.92 (s, 9H).

2-(2-methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one

The crude material from the previous step was dissolved in 250 mL acetone, to which was added 9.31 g (75 mmol) guaiacol and 11.3 g (81.8 mmol) potassium carbonate. The mixture was refluxed for 3 hours and after cooling to room temperature the solids were removed by filtration. Concentration of the filtrate afforded a yellow-brown solid, which was subjected to recrystallization from 5:1 ethanol:toluene, affording the title compound as 12.5 g (37.6 mmol, 42%) of yellow crystals. Analytical data was in agreement with literature. ^{1}H NMR (CDCl$_3$) δ 7.33 (s, 2H), 6.97 (dt, J = 8.6, 4.2 Hz, 1H), 6.91 (dt, J = 8.1, 1.0 Hz, 1H), 6.86 (dd, J = 4.6 Hz, 1.1 Hz, 2H), 5.26 (s, 2H), 3.92 (s, 3H), 3.90 (s, 6H), 3.87 (s, 3H). ^{13}C NMR (CDCl$_3$) δ 193.91, 153.27, 149.82, 147.50, 143.27, 129.89, 122.62, 120.96, 114.82, 112.24, 106.01, 72.54, 61.07, 56.41, 55.95.

2-(2-methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-ol

2-(2-methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-one (11.4 g, 34.3 mmol) was added to a mixture of 250 mL tetrahydrofuran, 75 mL methanol and 75 mL methanol and gently heated to ca. 50 °C until all material had dissolved. Sodium borohydride (2.64 g, 96.8 mmol) was carefully added in small portions with vigorous gas evolution. After addition of all sodium borohydride, the mixture was stirred for another 2 hours and then quenched with 250 mL of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer extracted three times with 100 mL ethyl acetate. The combined organic layers were washed with brine, dried with magnesium sulfate and concentrated in vacuo to afford 13.3 g of pale yellow oil. The compound was purified by silica gel column chromatography with a 1:1 ethyl acetate:hexanes mixture(Rf ~ 0.45) as eluent, to afford 9.00 g (27.0 mmol, 79%) of a colorless viscous oil, which eventually crystallized as white needles. ^{1}H NMR (CDCl$_3$) δ 7.04 – 6.87 (m, 4H), 6.66 (s, 2H), 5.03 (dd, J = 9.2, 3.0 Hz, 1H), 4.18 (dd, J = 10.0, 3.0 Hz, 1H), 3.97 (dd, J = 10.0, 9.2 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 6H), 3.84 (s, 3H). ^{13}C NMR (CDCl$_3$): δ 153.47, 150.27, 148.08, 137.72, 135.38, 122.78, 121.24, 116.28, 112.13, 103.34, 76.55, 72.59, 60.96, 56.26, 55.97; Elemental analysis calculated for C$_{18}$H$_{22}$O$_6$: C 64.66; H 6.63; found C 64.54 H 6.63

S2 Lignin Characterization
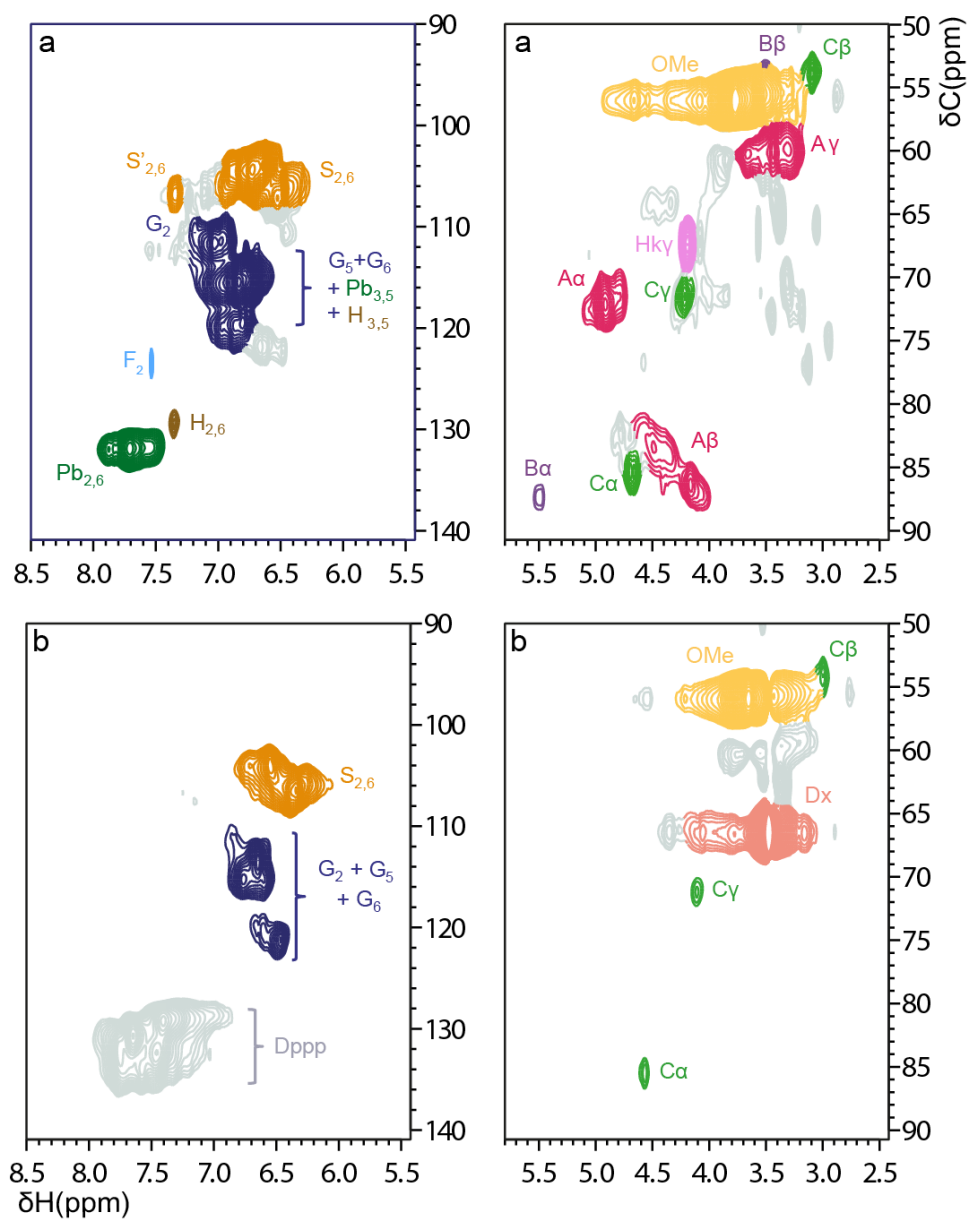
Poplar Lignin

Figure S1: HSQC NMR spectra of poplar dioxasolv lignin before (a) and the freeze-dried reaction mixture after reaction (b, for labelling scheme see Figure S7). After reaction both the signals for the β-O-4 and β-5 linkages have disappeared, demonstrating complete conversion of those ether fragments. Reaction conditions: 300 mg lignin, 0.060 mmol [Rh(cod)Cl]₂, 0.240 mmol dppp, 0.120 mmol (ScOTf)₃; 175 °C, 2 h, 22 mL 1,4-dioxane:water
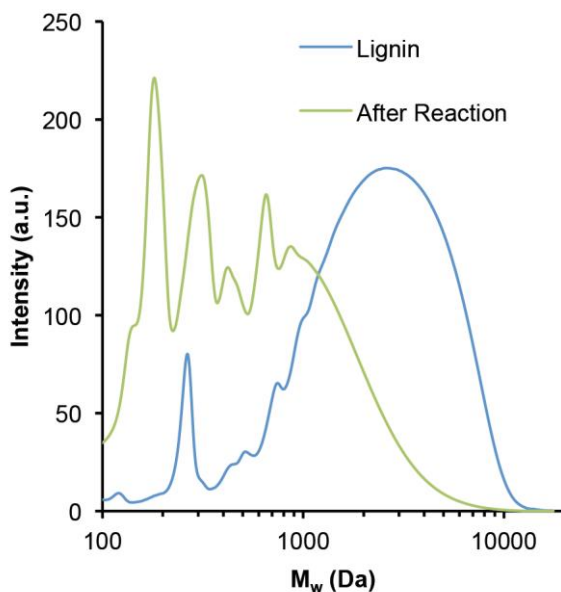
Figure S2: Molecular weight distribution of poplar sawdust dioxasolv lignin before and after reaction, based on GPC data (reaction conditions: 300 mg lignin, 0.060 mmol [Rh(cod)Cl]$_2$, 0.240 mmol dppp, 0.120 mmol (ScOTf)$_3$; 175 °C, 2 h, 22 mL 1,4-dioxane:water; GPC: 0.1% AcOH in THF eluent, polystyrene standards).

Table S1: Quantification of side chains and aromatic units present in poplar lignin the freeze-dried reaction mixture after reaction. Reaction conditions: 300 mg lignin, 0.060 mmol [Rh(cod)Cl]$_2$, 0.240 mmol dppp, 0.120 mmol (ScOTf)^3; 175 °C, 2 h, 22 mL 1,4-dioxane:water

	Poplar lignin	Reaction mixture
β-O-4 (A)[a]	39.4	0.0
β-5 (B)[a]	2.9	0.0
β-β (C)[a]	4.7	1.3
p-hydroxy benzoate (Pb)[a]	16.3	/[c]
S (%)[b]	67.5	84.2
G (%)[b]	32.1	15.8
H (%)[b]	0.4	/[c]

[a] Linkage content per 100 aromatic units
[b] Molar percentage (S+G+H=100)
[c] The presence of signals of *p*-hydroxy benzoate and *p*-hydroxy units cannot be unequivocally established due to overlap with the dppp signals.

Elemental Analysis (wt %): C (60.75%), H (6.23%), N (0.02%), S (0.00%)
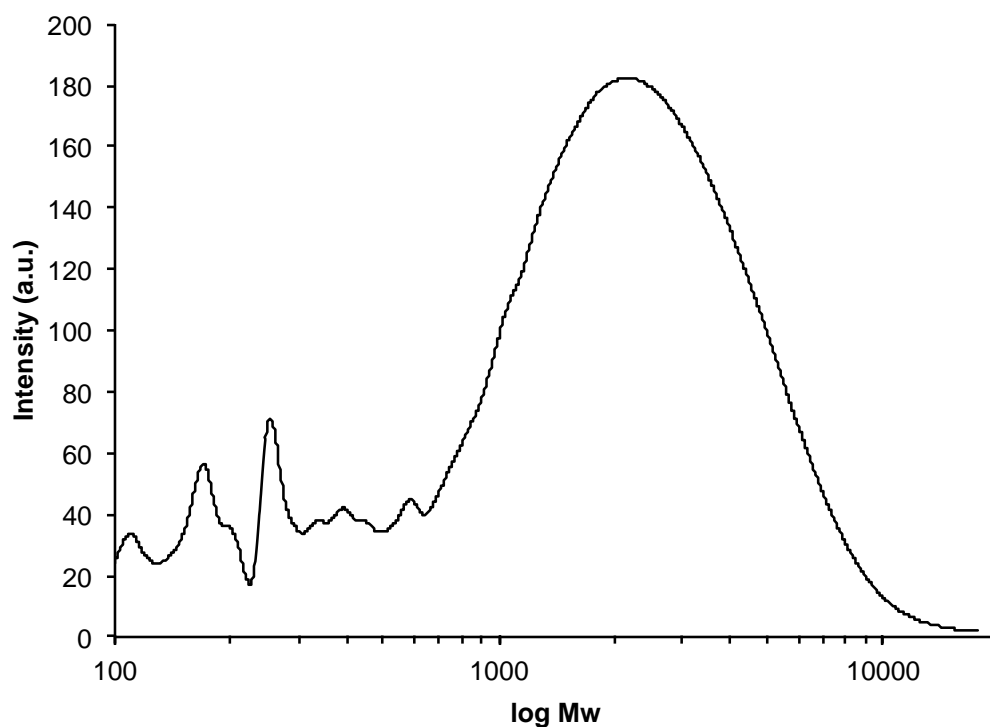
Figure S3: Molecular weight distribution of dioxasolv brewer's grain determined by GPC (THF eluent; polystyrene standards).

Figure S4: HSQC NMR of brewer's grain lignin. For labelling scheme see Figure S7.

Table S2: Quantification of side chains and aromatic units present in brewer's grain

lignin

	Brewer's grain lignin
β-O-4 (A)[a]	42.0
β-5 (B)[a]	9.8
β-β (C)[a]	2.5
p-coumarate (Pca)[a]	3.7
Tricin (T)[a]	0.8
S (%)[b]	30.6
G (%)[b]	65.0
H (%)[b]	4.5

[a] Linkage content per 100 aromatic units
[b] Molar percentage (S+G+H=100)

Elemental Analysis (wt %): C (57.45%), H (5.76%), N (0.66%), S (0.04%)

Pine Lignin
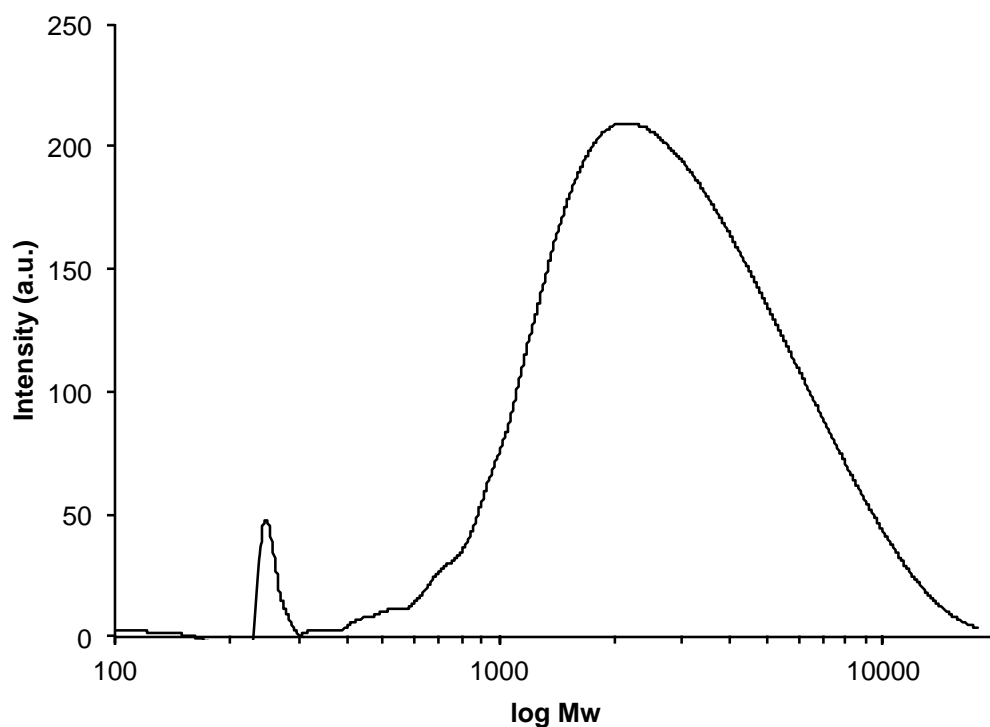
Figure S5: Molecular weight distribution of dioxasolv pine lignin determined by GPC (THF eluent; polystyrene standards).
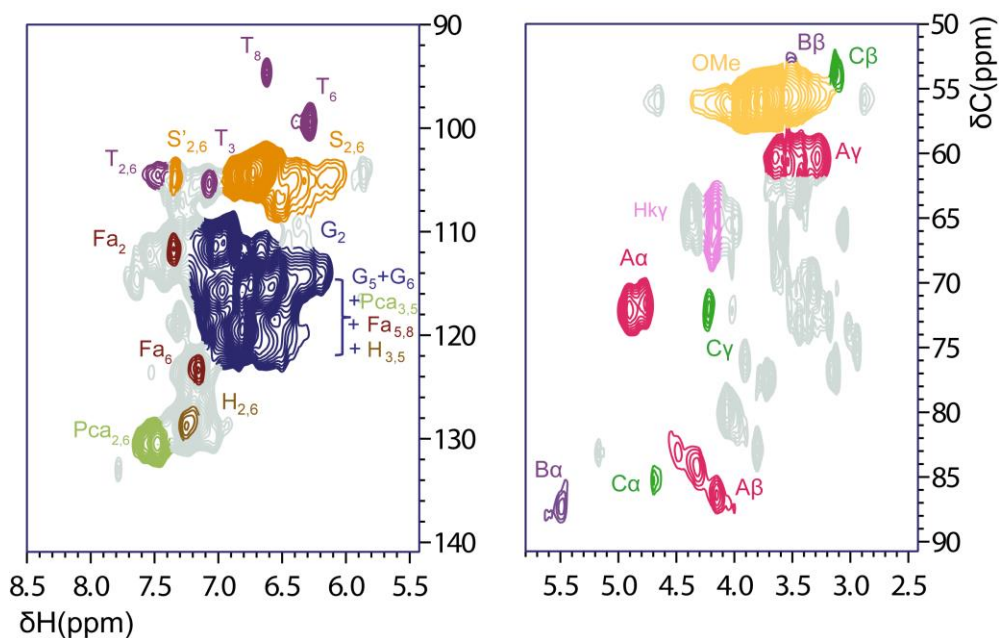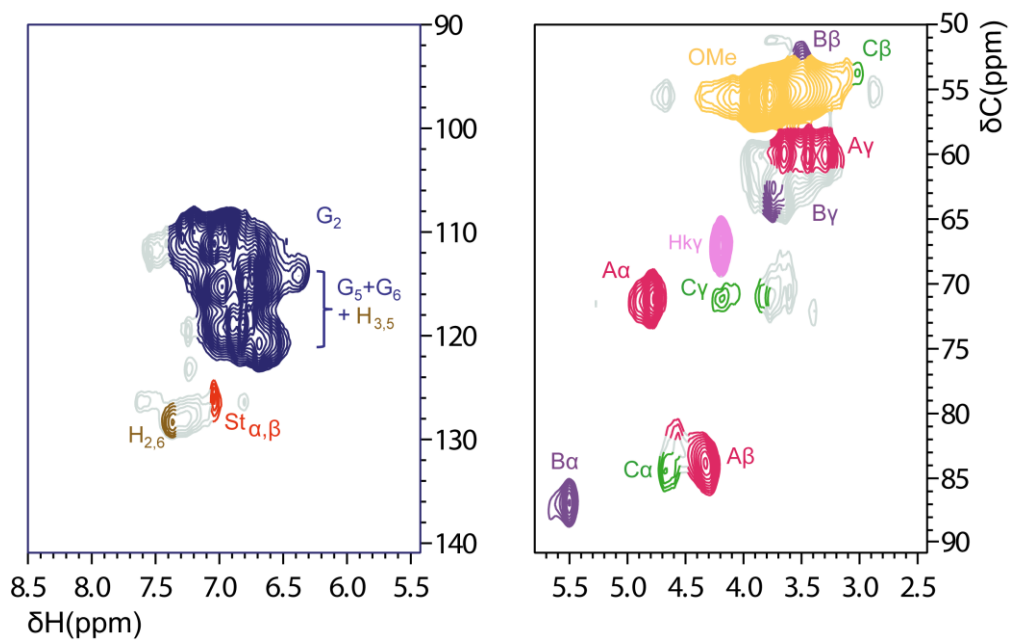

Figure S6: HSQC NMR of pine lignin. For the labelling scheme see Figure S7.

Table S3: Quantification of side chains and aromatic units present in pine lignin

	Pine lignin
β-O-4 (A)[a]	29.0
β-5 (B)[a]	11.9
β-β (C)[a]	4.2
Stilbene (St)[a]	0.6
S (%)[b]	0
G (%)[b]	96
H (%)[b]	4

[a] Linkage content per 100 aromatic units
[b] Molar percentage (S+G+H=100)

Elemental Analysis (wt %): C (64.03%), H (6.86%), N (0.00%), S (0.00%)
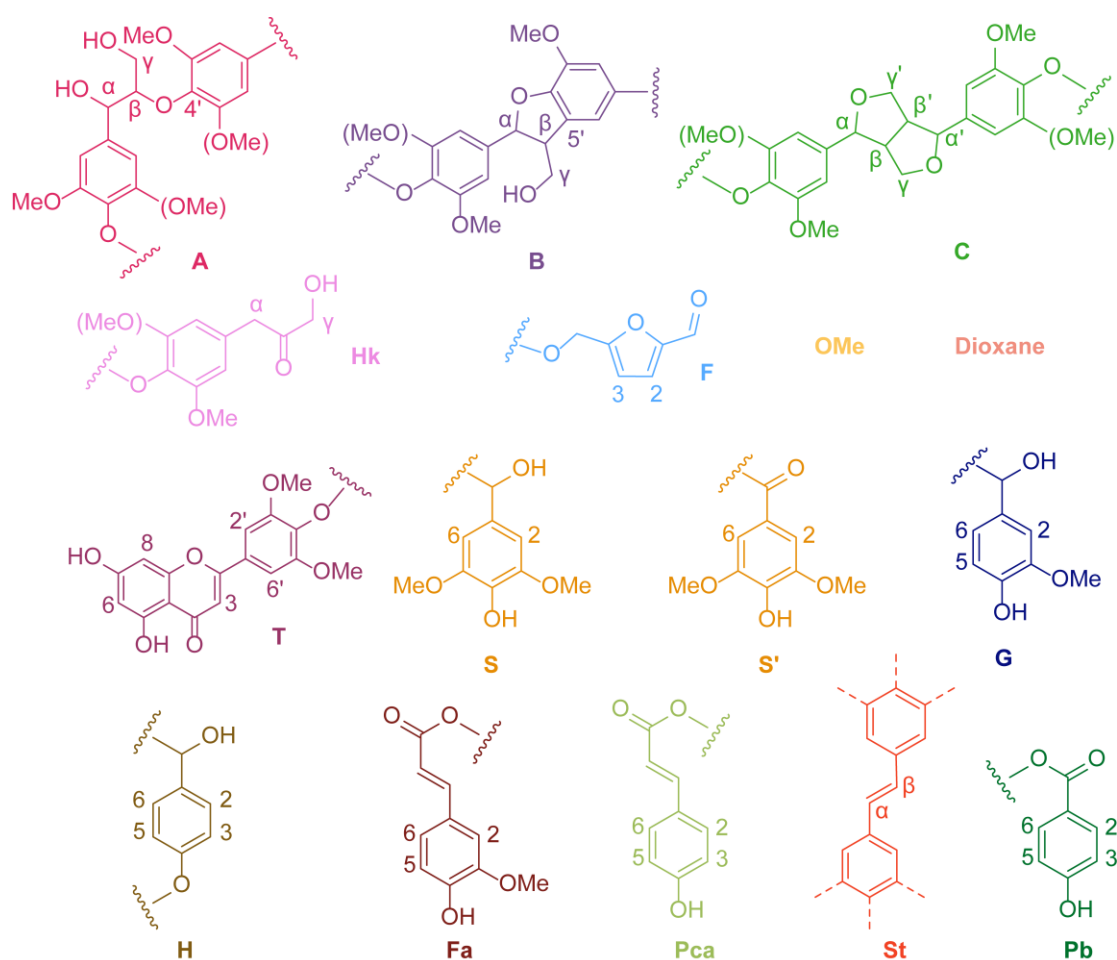
Figure S7: Labelling scheme used in assignments in HSQC NMR spectra.

S3 Additional GPC Data
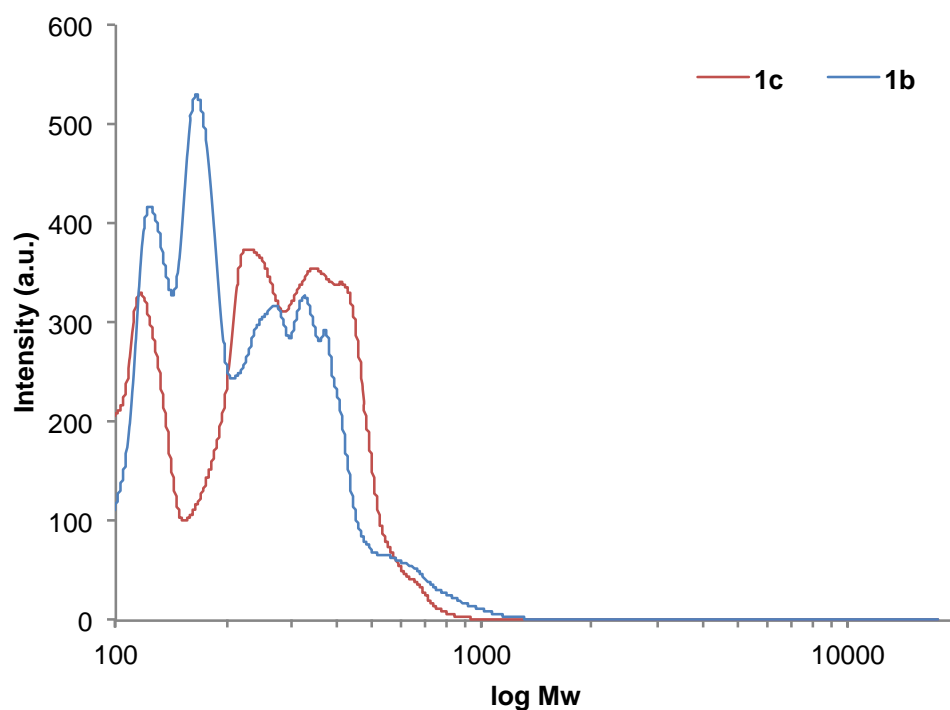
*Figure S8: Molecular weight distribution of reaction mixture after reaction of **1b** and **1c** determined by GPC (THF eluent; polystyrene standards). Conditions: 2.4 mmol substrate, 0.060 mmol [Rh(cod)Cl]₂, 0.240 mmol dppp, 0.120 mmol Sc(OTf)3; 175 °C, 2 h, 22 mL 9:1 1,4-dioxane:water.*
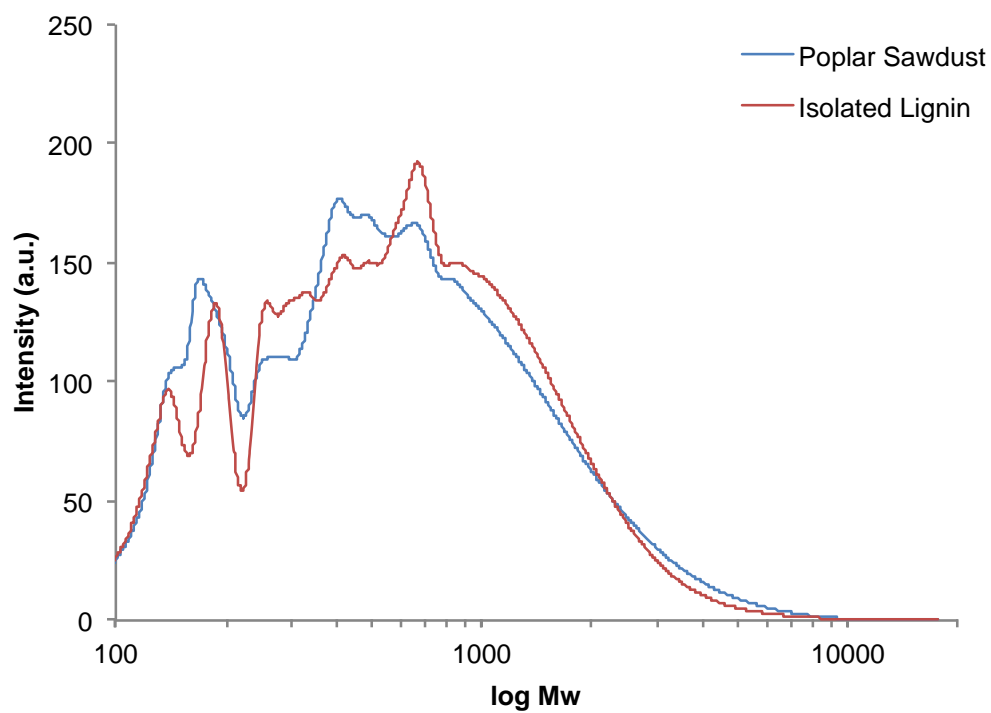
Figure S9: Comparison of molecular weight distribution of reaction mixtures after reaction of poplar lignin and sawdust determined by GPC (THF eluent; polystyrene standards). Conditions: 300 mg lignin or 2.0 g sawdust, 0.060 mmol [Rh(cod)Cl]$_2$, 0.240 mmol dppp, 0.120 mmol Sc(OTf)$_3$; 175 °C, 2 h, 22 mL 9:1 1,4-dioxane:water.
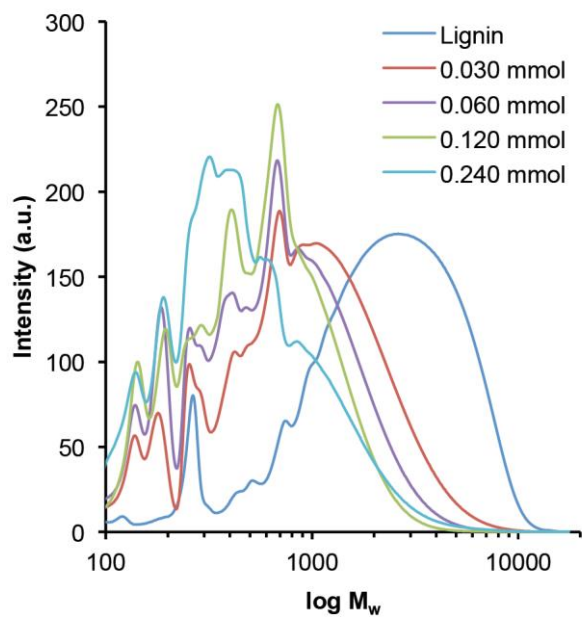
Figure S10: Molecular weight distributions from GPC data of reaction mixtures after depolymerization with different amounts of catalyst. Conditions: 300 mg lignin, 0.5 eq [Rh(cod)Cl]$_2$, 2 eq dppp, Sc(OTf)$_3$ as listed; 175 °C, 2 h, 22 mL 9:1 1,4-dioxane:water.
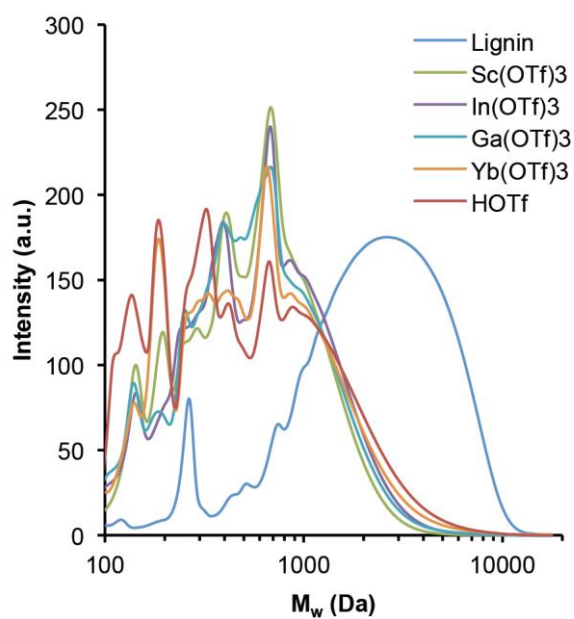
Figure S11: Molecular weight distributions from GPC data of reaction mixtures after depolymerization with different acids. Conditions: 300 mg lignin, 0.060 mmol [Rh(cod)Cl]$_2$, 0.240 mmol dppp, 0.120 mmol acid; 175 °C, 2 h, 22 mL 9:1 1,4-dioxane:water.

S4 GC Calibration

Table S4: Experimentally-determined response factors

Compound	k	C	O	ECN[a] (C-O)
guaiacol	0.6246	7	2	5
syringol	0.6163	8	3	5
4-methylguaiacol	0.7151	8	2	6
3,4-dimethoxytoluene	0.7699	9	2	7
4-ethylguaiacol	0.7822	9	2	7
4-methylsyringol	0.6998	9	3	6
guaiacylacetone	0.7159	10	3	7
Iso-eugenol	0.8276	10	2	8
1b	1.0836	17	5	12

[a] Effective Carbon Number

y = 0.0652x + 0.3027
R² = 0.97965
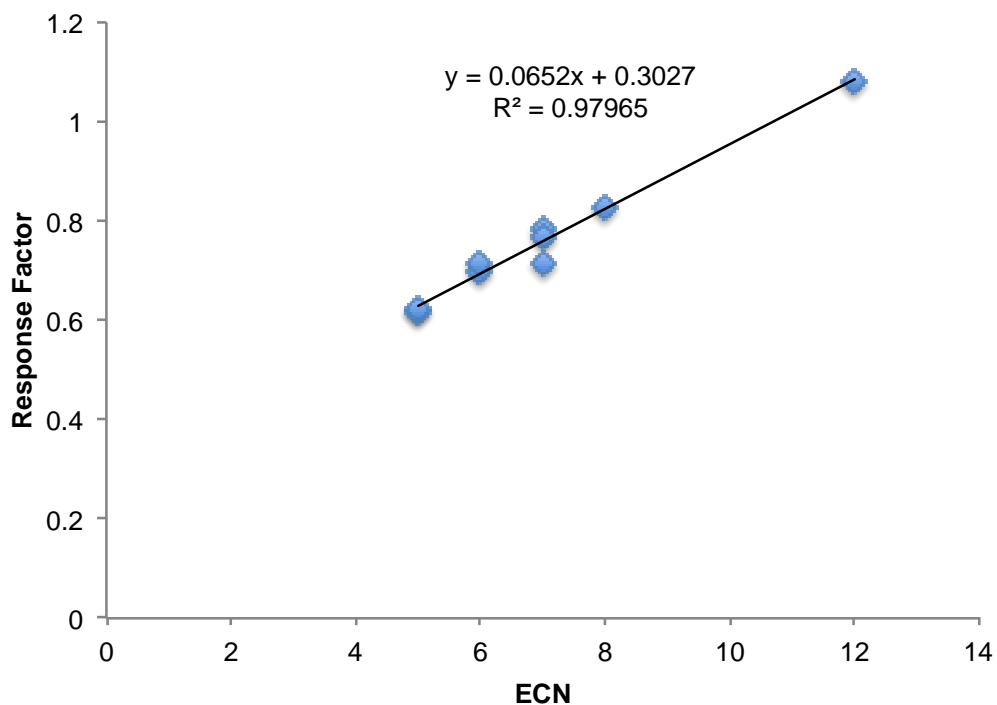
Figure S12: Linear regression between ECN and experimentally determined response factors, which was used to estimate response factors for other compounds.

S5 GC/GC-MS Data for Model Compound Reactions

Chromatogram (All TIC)]

50,532,164

TIC*1.00

1.0   10.0   20.0   30.0   40.0   49.0
                                        min

Chromatogram (Zoom)

3,242,307

TIC*1.00

14.0   15.0   15.6
                                          min

Spectrum
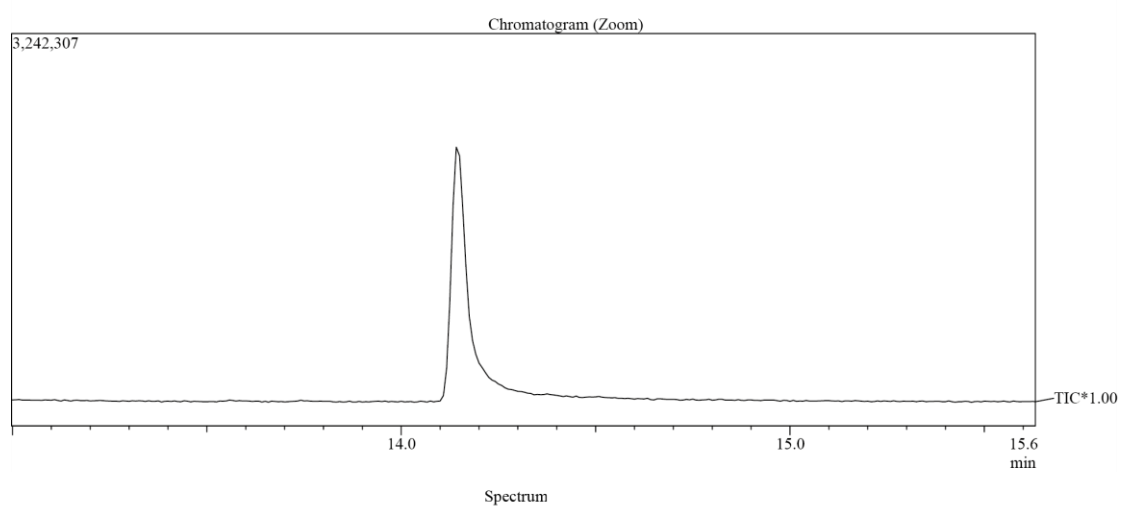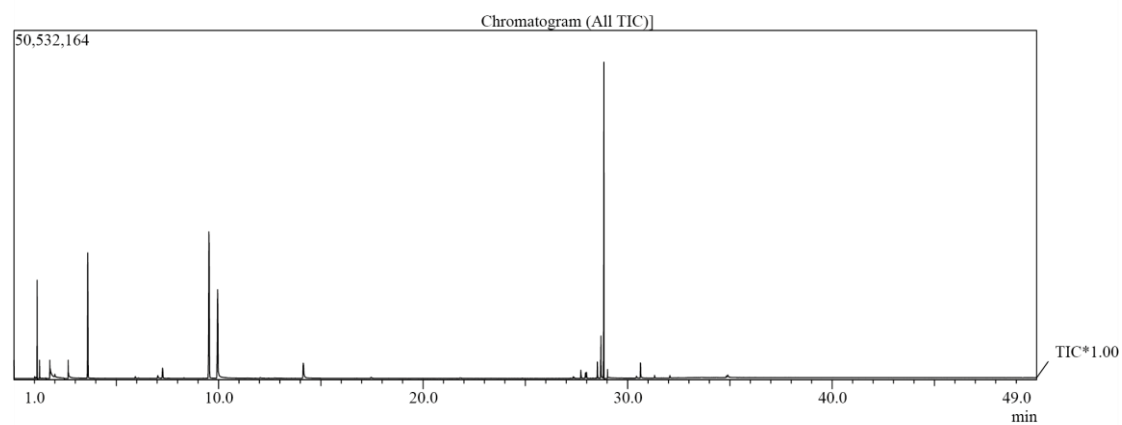
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MassPeaks:631
RawMode:Single 14.142(1698) BasePeak:91.10(800730)
BG Mode:None Group 1 - Event 1
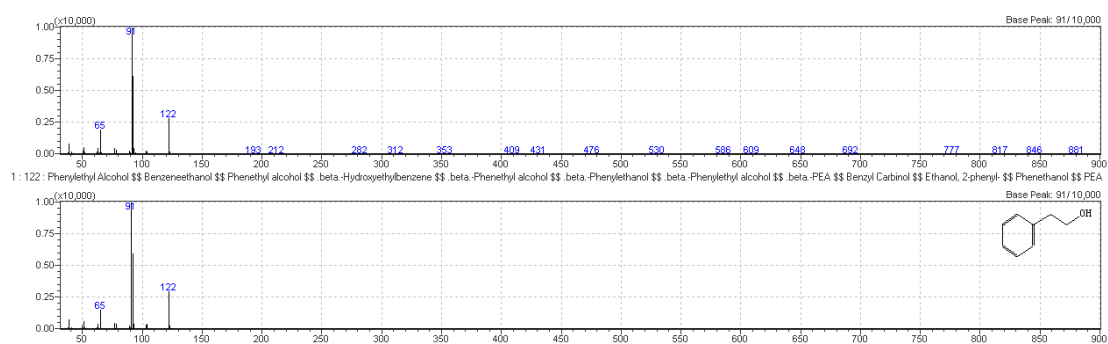
Figure S13: GC-MS Chromatogram corresponding to Table 1, entry 1; showing the formation of 2-phenylethanol.

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Chromatogram (All TIC)]

Chromatogram (Zoom)

Spectrum
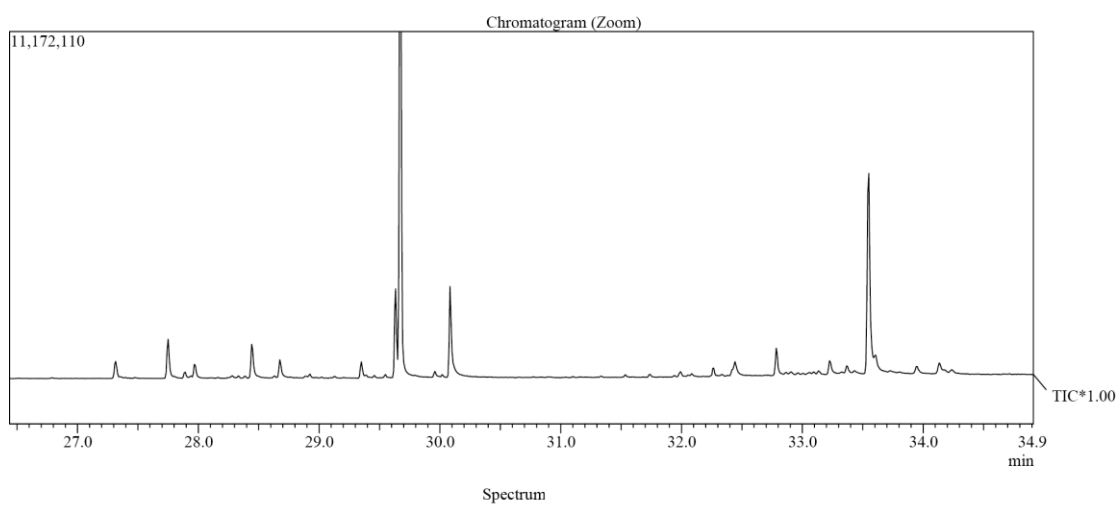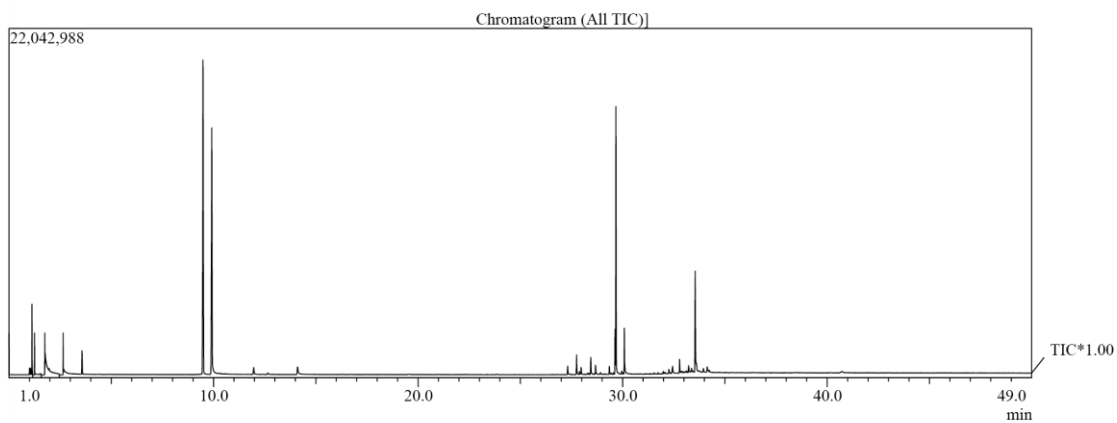
Line#:1   R.Time:29.725(Scan#:3568)
MassPeaks:628
RawMode:Single 29.725(3568) BasePeak:204.10(49790)
BG Mode:None Group 1 - Event 1

1 : 204 : Naphthalene, 2-phenyl- $$ .beta.-Phenylnaphthalene $$ 2-Phenylnaphthalene $$ NSC 407592 $$

Figure S14: GC-MS Chromatogram corresponding to Table 1, entry 2; showing the formation of 2-phenylnaphthalene.

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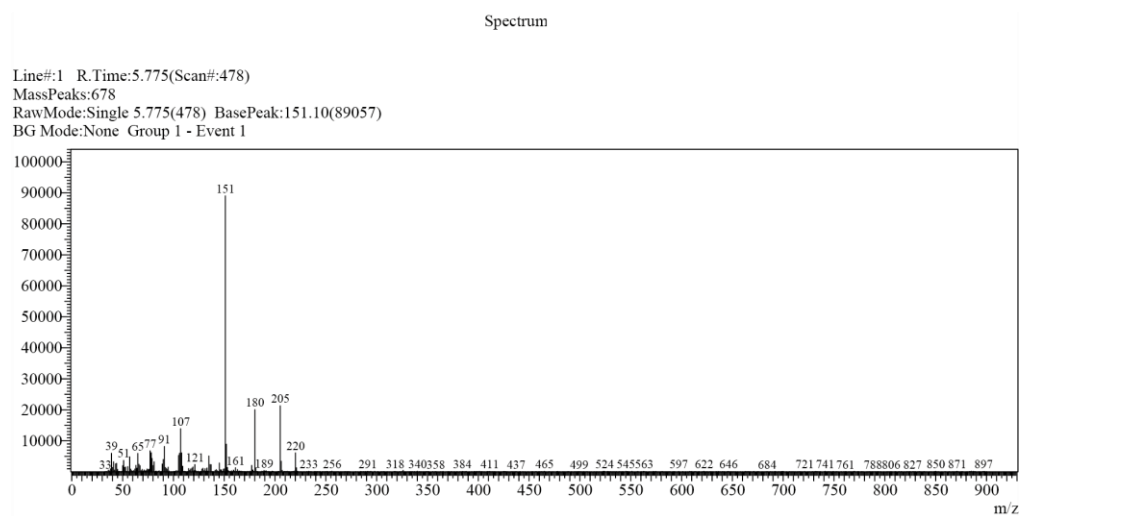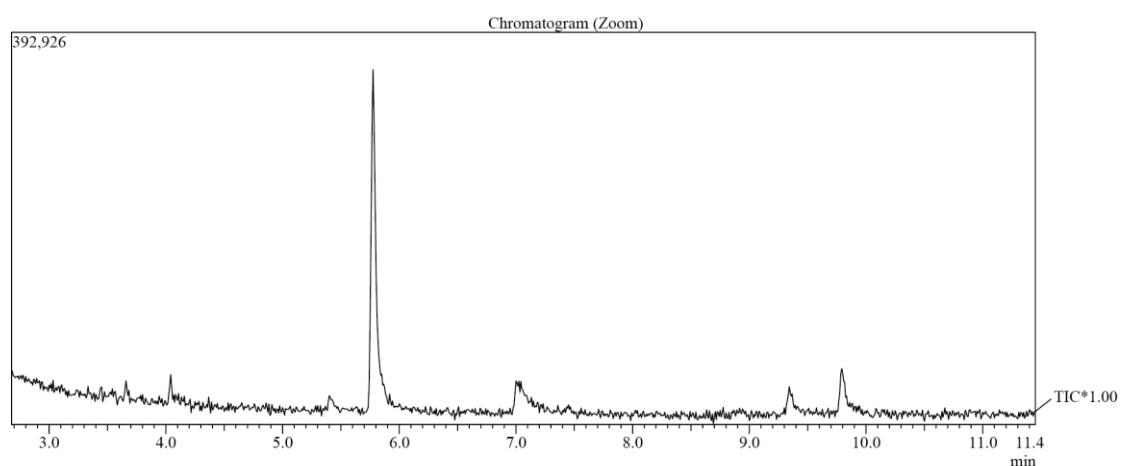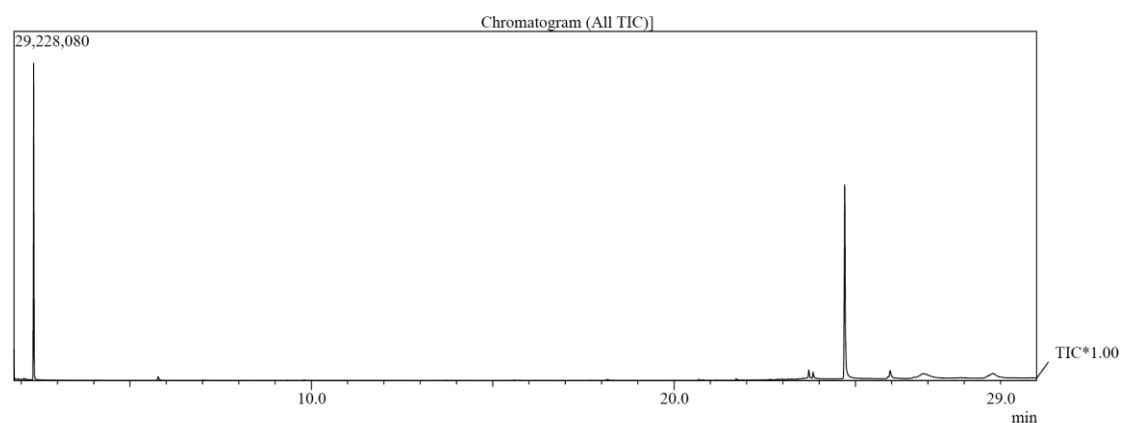
Figure S15: GC-MS Chromatogram corresponding to Table 1, entry 3; showing the formation of homoveratryl aldehyde. The compound is not present in the NIST database; the peak at m/z = 180 corresponds to the molecular ion, whereas the fragment at m/z = 151 is attributed to loss of the carbonyl.
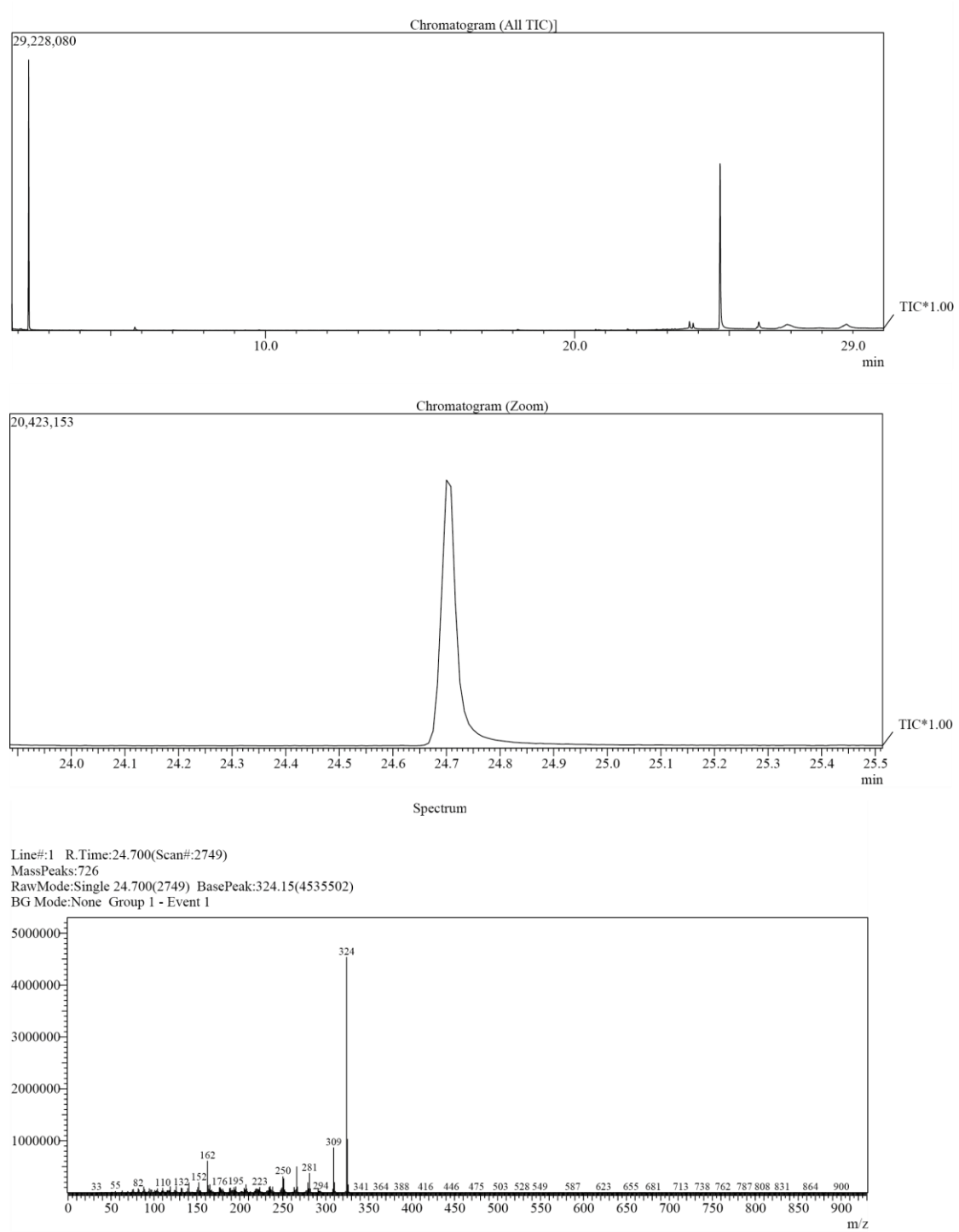
*Figure S16: GC-MS Chromatogram corresponding to Table 1, entry 3; showing the formation of **7b**. The compound is not present in the NIST database; m/z = 324 corresponds the molecular ion.*
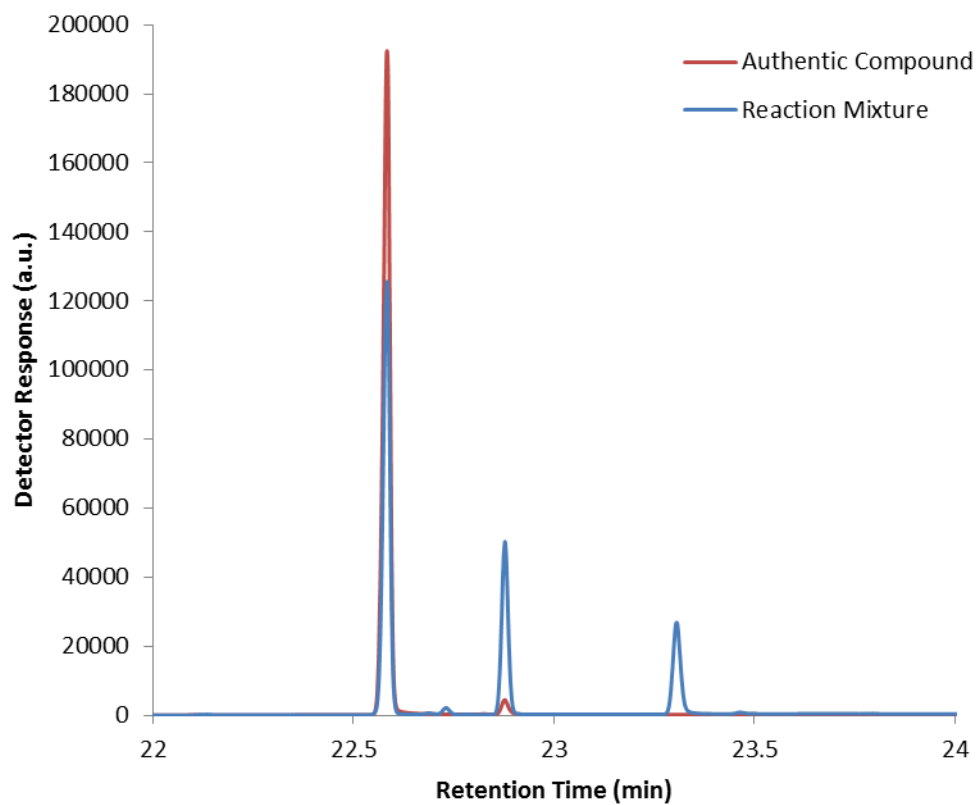
Figure S17: Overlaid GC chromatograms corresponding to Table 1, entry 6 and an authentic sample of cis-**5b**, *demonstrating the predominant formation of the* cis *isomer. The trans isomer is present as a minor impurity in the authentic sample and is also observed in the reaction mixture.*
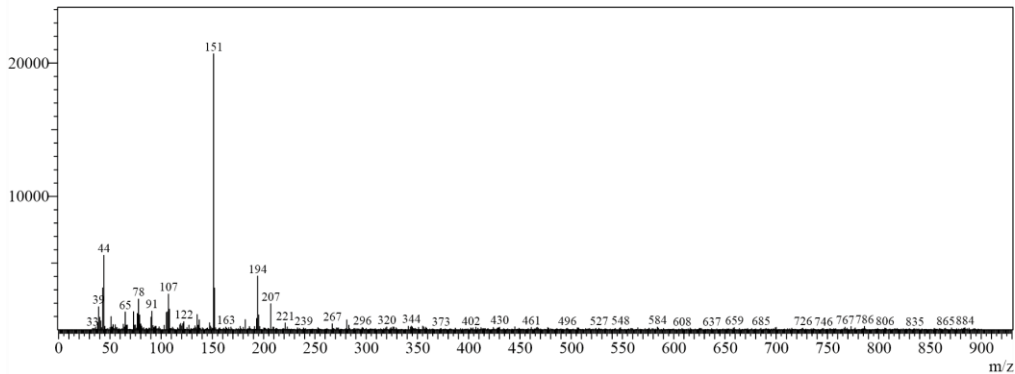
Figure S18: GC-MS Chromatogram corresponding to Table 1, entry 11; showing the formation of 1-veratrylethanone. The compound is not present in the NIST database; the peak at m/z = 194 corresponds to the molecular ion, whereas the fragment at m/z = 151 is attributed to loss of the acetyl functionality.

S6 Complete Product Listing for Reactions with Lignin

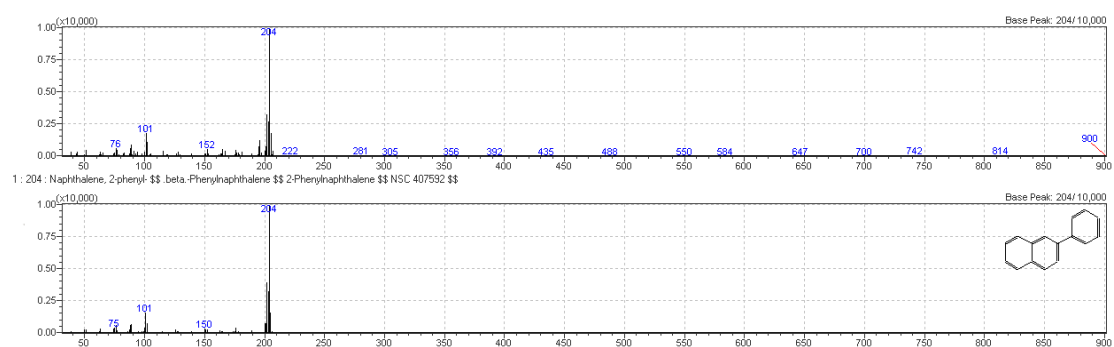*Table S5: Table 2, Entry #1*

Lignin: 302.5 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2301.5		0.706		
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	2.6	0.7151	0.001	138.16	0.2
4-ethylguaiacol	5.04	0	0.7822	0.000	152.19	0.0
4-OH-3-OMe-styrene	5.69	11.2	0.7591	0.005	150.19	0.7
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	2.1	0.6998	0.001	168.19	0.2
trans-isoeugenol	8.27	15.8	0.8276	0.006	164.20	1.0
4-ethylsyringol	9.66	3.4	0.7591	0.001	182.22	0.3
2-oxopropylguaiacol	9.85	0	0.7159	0.000	180.20	0.0
2-propenylsyringol	12.34	30.1	0.8243	0.011	194.23	2.2
1-propenylsyringol	13.46	47.0	0.8243	0.017	194.23	3.4
2-oxopropylsyringol	14.77	0	0.7591	0.000	210.23	0.0
Sum				0.042		8.0

Table S6: Table 2, Entry #2

Lignin: 302.2 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2433		0.716		
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	70.4	0.7151	0.029	138.16	4.0
4-ethylguaiacol	5.04	6.7	0.7822	0.003	152.19	0.4
4-OH-3-OMe-styrene	5.69	3.3	0.7591	0.001	150.19	0.2
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	5.4	0.8276	0.002	164.20	0.3
4-methylsyringol	8.07	51.0	0.6998	0.021	168.19	3.6
trans-isoeugenol	8.27	60.7	0.8276	0.022	164.20	3.5
4-ethylsyringol	9.66	22.2	0.7591	0.009	182.22	1.6
2-oxopropylguaiacol	9.85	13.9	0.7159	0.006	180.20	1.0
2-propenylsyringol	12.34	17.5	0.8243	0.006	194.23	1.2
1-propenylsyringol	13.46	198.9	0.8243	0.071	194.23	13.8
2-oxopropylsyringol	14.77	29.9	0.7591	0.012	210.23	2.4
Sum				0.181		32.0

Table S7: Table 2, Entry #3

Lignin: 309.9 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2430.1		0.711		
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	95.1	0.7151	0.039	138.16	5.4
4-ethylguaiacol	5.04	6.3	0.7822	0.002	152.19	0.4
4-OH-3-OMe-styrene	5.69	0	0.7591	0.000	150.19	0.0
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	67.8	0.6998	0.028	168.19	4.8
trans-isoeugenol	8.27	54.2	0.8276	0.019	164.20	3.1
4-ethylsyringol	9.66	28.4	0.7591	0.011	182.22	2.0
2-oxopropylguaiacol	9.85	18.9	0.7159	0.008	180.20	1.4
2-propenylsyringol	12.34	17.4	0.8243	0.006	194.23	1.2
1-propenylsyringol	13.46	207.0	0.8243	0.073	194.23	14.3
2-oxopropylsyringol	14.77	34.3	0.7591	0.013	210.23	2.8
Sum				0.200		35.4

Table S8: Table 2, Entry #4

Lignin: 301.1 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2430.9		0.725		
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	110.9	0.7151	0.046	138.16	6.4
4-ethylguaiacol	5.04	5.9	0.7822	0.002	152.19	0.3
4-OH-3-OMe-styrene	5.69	0	0.7591	0.000	150.19	0.0
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	89.6	0.6998	0.038	168.19	6.4
trans-isoeugenol	8.27	20.9	0.8276	0.008	164.20	1.2
4-ethylsyringol	9.66	18.1	0.7591	0.007	182.22	1.3
2-oxopropylguaiacol	9.85	22.9	0.7159	0.010	180.20	1.7
2-propenylsyringol	12.34	7.9	0.8243	0.003	194.23	0.6
1-propenylsyringol	13.46	99.2	0.8243	0.036	194.23	7.0
2-oxopropylsyringol	14.77	44.4	0.7591	0.017	210.23	3.7
Sum				0.167		28.6

Table S9: Table 2, Entry #5

Lignin: 311.1 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2215.3		0.729		
guaiacol	2.76	2.6	0.6246	0.001	124.14	0.2
4-methylguaiacol	3.86	125.8	0.7151	0.058	138.16	8.0
4-ethylguaiacol	5.04	7.1	0.7822	0.003	152.19	0.5
4-OH-3-OMe-styrene	5.69	0	0.7591	0.000	150.19	0.0
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	95.1	0.6998	0.045	168.19	7.5
trans-isoeugenol	8.27	10.6	0.8276	0.004	164.20	0.7
4-ethylsyringol	9.66	36.1	0.7591	0.016	182.22	2.9
2-oxopropylguaiacol	9.85	38.2	0.7159	0.018	180.20	3.2
2-propenylsyringol	12.34	11.4	0.8243	0.005	194.23	0.9
1-propenylsyringol	13.46	14.1	0.8243	0.006	194.23	1.1
2-oxopropylsyringol	14.77	58.0	0.7591	0.025	210.23	5.3
Sum				0.180		30.3

Table S10: Table 2, Entry #6

Lignin: 302.9 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2754.2		0.735		
guaiacol	2.76	4	0.6246	0.002	124.14	0.2
4-methylguaiacol	3.86	139.0	0.7151	0.052	138.16	7.2
4-ethylguaiacol	5.04	4.4	0.7822	0.002	152.19	0.2
4-OH-3-OMe-styrene	5.69	0	0.7591	0.000	150.19	0.0
syringol	6.28	6.8	0.6163	0.003	154.16	0.5
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	128.8	0.6998	0.049	168.19	8.3
trans-isoeugenol	8.27	7.5	0.8276	0.002	164.20	0.4
4-ethylsyringol	9.66	7.5	0.7591	0.003	182.22	0.5
2-oxopropylguaiacol	9.85	52.1	0.7159	0.019	180.20	3.5
2-propenylsyringol	12.34	11.4	0.8243	0.004	194.23	0.7
1-propenylsyringol	13.46	10.5	0.8243	0.003	194.23	0.7
2-oxopropylsyringol	14.77	85.8	0.7591	0.030	210.23	6.3
Sum				0.169		28.5

Table S11: Table 2, Entry #7

Lignin: 313.1 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2091.3		0.709		
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	97.7	0.7151	0.046	138.16	6.4
4-ethylguaiacol	5.04	5.7	0.7822	0.002	152.19	0.4
4-OH-3-OMe-styrene	5.69	0	0.7591	0.000	150.19	0.0
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	85.3	0.6998	0.041	168.19	7.0
trans-isoeugenol	8.27	2.9	0.8276	0.001	164.20	0.2
4-ethylsyringol	9.66	12.9	0.7591	0.006	182.22	1.0
2-oxopropylguaiacol	9.85	24.8	0.7159	0.012	180.20	2.1
2-propenylsyringol	12.34	0	0.8243	0.000	194.23	0.0
1-propenylsyringol	13.46	39.4	0.8243	0.016	194.23	3.1
2-oxopropylsyringol	14.77	49.6	0.7591	0.022	210.23	4.7
Sum				0.149		24.9

Table S12: Table 2, Entry #8

Lignin: 303.2 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2610.3		0.732		
guaiacol	2.76	3.1	0.6246	0.001	124.14	0.2
4-methylguaiacol	3.86	64.1	0.7151	0.025	138.16	3.5
4-ethylguaiacol	5.04	6.2	0.7822	0.002	152.19	0.3
4-OH-3-OMe-styrene	5.69	3.7	0.7591	0.001	150.19	0.2
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	6.8	0.8276	0.002	164.20	0.4
4-methylsyringol	8.07	48.2	0.6998	0.019	168.19	3.2
trans-isoeugenol	8.27	76.0	0.8276	0.026	164.20	4.2
4-ethylsyringol	9.66	25.8	0.7591	0.010	182.22	1.7
2-oxopropylguaiacol	9.85	10.4	0.7159	0.004	180.20	0.7
2-propenylsyringol	12.34	24.0	0.8243	0.008	194.23	1.6
1-propenylsyringol	13.46	268.8	0.8243	0.091	194.23	17.8
2-oxopropylsyringol	14.77	24.3	0.7591	0.009	210.23	1.9
Sum				0.200		35.7

Table S13: Table 2, Entry #9

Lignin: 313.1 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2180.9		0.597		
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	33.8	0.7151	0.013	138.16	1.8
4-ethylguaiacol	5.04	6.4	0.7822	0.002	152.19	0.3
4-OH-3-OMe-styrene	5.69	7.6	0.7591	0.003	150.19	0.4
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	9.2	0.8276	0.003	164.20	0.5
4-methylsyringol	8.07	30.7	0.6998	0.012	168.19	2.0
trans-isoeugenol	8.27	109.5	0.8276	0.036	164.20	5.9
4-ethylsyringol	9.66	20.7	0.7591	0.007	182.22	1.4
2-oxopropylguaiacol	9.85	0	0.7159	0.000	180.20	0.0
2-propenylsyringol	12.34	29.8	0.8243	0.010	194.23	1.9
1-propenylsyringol	13.46	345.3	0.8243	0.115	194.23	22.3
2-oxopropylsyringol	14.77	17.1	0.7591	0.006	210.23	1.3
Sum				0.207		37.8

Table S14: Table 2, Entry #10

Lignin: 301.1 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2314.6		0.707		
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	20.4	0.7151	0.009	138.16	1.2
4-ethylguaiacol	5.04	4.9	0.7822	0.002	152.19	0.3
4-OH-3-OMe-styrene	5.69	0	0.7591	0.000	150.19	0.0
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	20.6	0.6998	0.009	168.19	1.5
trans-isoeugenol	8.27	94.4	0.8276	0.035	164.20	5.7
4-ethylsyringol	9.66	21.2	0.7591	0.009	182.22	1.6
2-oxopropylguaiacol	9.85	0	0.7159	0.000	180.20	0.0
2-propenylsyringol	12.34	27.3	0.8243	0.010	194.23	2.0
1-propenylsyringol	13.46	282.0	0.8243	0.104	194.23	20.3
2-oxopropylsyringol	14.77	13.9	0.7591	0.006	210.23	1.2
Sum				0.183		33.8

Table S15: Table 2, Entry #11

Lignin: 302.5 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2745.8		0.706		
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	33.8	0.7151	0.012	138.16	1.7
4-ethylguaiacol	5.04	9.3	0.7822	0.003	152.19	0.5
4-OH-3-OMe-styrene	5.69	12.0	0.7591	0.004	150.19	0.6
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	29.8	0.6998	0.011	168.19	1.8
trans-isoeugenol	8.27	118.8	0.8276	0.037	164.20	6.1
4-ethylsyringol	9.66	34.3	0.7591	0.012	182.22	2.1
2-oxopropylguaiacol	9.85	0	0.7159	0.000	180.20	0.0
2-propenylsyringol	12.34	30.1	0.8243	0.009	194.23	1.8
1-propenylsyringol	13.46	358.7	0.8243	0.112	194.23	21.7
2-oxopropylsyringol	14.77	18.1	0.7591	0.006	210.23	1.3
Sum				0.206		37.6

Table S16: Table 3, Entry #1

Lignin: 301.6 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2307.8		0.718		
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	85.7	0.7151	0.037	138.16	5.2
4-ethylguaiacol	5.04	9.9	0.7822	0.004	152.19	0.6
4-OH-3-OMe-styrene	5.69	38.4	0.7591	0.016	150.19	2.4
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	28.9	0.6998	0.013	168.19	2.2
trans-isoeugenol	8.27	20.7	0.8276	0.008	164.20	1.3
4-ethylsyringol	9.66	6.0	0.7591	0.002	182.22	0.4
2-oxopropylguaiacol	9.85	6.5	0.7159	0.003	180.20	0.5
2-propenylsyringol	12.34	0	0.8243	0.000	194.23	0.0
1-propenylsyringol	13.46	34.2	0.8243	0.013	194.23	2.5
2-oxopropylsyringol	14.77	6.9	0.7591	0.003	210.23	0.6
Sum				0.099		15.7

Table S17: Table 3, Entry #2

Lignin: 301.1 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2525.3		0.722		
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	277.3	0.7151	0.111	138.16	15.3
4-ethylguaiacol	5.04	12.7	0.7822	0.005	152.19	0.7
4-OH-3-OMe-styrene	5.69	10.8	0.7591	0.004	150.19	0.6
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	0	0.6998	0.000	168.19	0.0
trans-isoeugenol	8.27	33.4	0.8276	0.012	164.20	1.9
4-ethylsyringol	9.66	0	0.7591	0.000	182.22	0.0
2-oxopropylguaiacol	9.85	30.0	0.7159	0.012	180.20	2.2
2-propenylsyringol	12.34	0	0.8243	0.000	194.23	0.0
1-propenylsyringol	13.46	0	0.8243	0.000	194.23	0.0
2-oxopropylsyringol	14.77	0	0.7591	0.000	210.23	0.0
Sum				0.143		20.7

Table S18: Table 3, Entry #3

Sawdust: 2013.0 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2436.1		0.722		
furfural		549.1				
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	166.2	0.7151	0.069	138.16	9.5
HMF		431.1				
4-ethylguaiacol	5.04	31.5	0.7822	0.012	152.19	1.8
4-OH-3-OMe-styrene	5.69		0.7591	0.000	150.19	0.0
syringol	6.28	6.28	0.6163	0.003	154.16	0.5
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	88.8	0.6998	0.038	168.19	6.3
trans-isoeugenol	8.27	55.3	0.8276	0.020	164.20	3.3
4-ethylsyringol	9.66	65.2	0.7591	0.025	182.22	4.6
2-oxopropylguaiacol	9.85	18.1	0.7159	0.007	180.20	1.4
2-propenylsyringol	12.34	18.4	0.8243	0.007	194.23	1.3
1-propenylsyringol	13.46	187.7	0.8243	0.067	194.23	13.1
2-oxopropylsyringol	14.77	31.3	0.7591	0.012	210.23	2.6
Sum				0.261		44.4

Table S19: Table 3, Entry #4

Sawdust: 2004.4 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	2466.4		0.701		
furfural		570.9				
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	195.0	0.7151	0.078	138.16	10.7
HMF		544.2				
4-ethylguaiacol	5.04	18.1	0.7822	0.007	152.19	1.0
4-OH-3-OMe-styrene	5.69	0	0.7591	0.000	150.19	0.0
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	0	0.8276	0.000	164.20	0.0
4-methylsyringol	8.07	109.0	0.6998	0.044	168.19	7.4
trans-isoeugenol	8.27	23.8	0.8276	0.008	164.20	1.3
4-ethylsyringol	9.66	37.6	0.7591	0.014	182.22	2.6
2-oxopropylguaiacol	9.85	0	0.7159	0.000	180.20	0.0
2-propenylsyringol	12.34	0	0.8243	0.000	194.23	0.0
1-propenylsyringol	13.46	98.0	0.8243	0.034	194.23	6.6
2-oxopropylsyringol	14.77	35.0	0.7591	0.013	210.23	2.8
Sum				0.197		32.4

Table S20: Table 3, Entry #5

Sawdust: 2032.0 mg

Compound	RT (min)	A (a.u.)	k	n (mmol)	M_w	m (mg)
mesitylene (IS)	1.98	3120.8		0.714		
furfural	1.51	0				
guaiacol	2.76	0	0.6246	0.000	124.14	0.0
4-methylguaiacol	3.86	0	0.7151	0.000	138.16	0.0
HMF	4.14	0				
4-ethylguaiacol	5.04	63.8	0.7822	0.019	152.19	2.8
4-OH-3-OMe-styrene	5.69	82.7	0.7591	0.025	150.19	3.7
syringol	6.28	0	0.6163	0.000	154.16	0.0
eugenol	7.39	13.9	0.8276	0.004	164.20	0.6
4-methylsyringol	8.07	8	0.6998	0.003	168.19	0.4
trans-isoeugenol	8.27	163.1	0.8276	0.045	164.20	7.4
4-ethylsyringol	9.66	88	0.7591	0.027	182.22	4.8
2-oxopropylguaiacol	9.85	0	0.7159	0.000	180.20	0.0
2-propenylsyringol	12.34	17.6	0.8243	0.005	194.23	0.9
1-propenylsyringol	13.46	258.2	0.8243	0.072	194.23	13.9
2-oxopropylsyringol	14.77	0	0.7591	0.000	210.23	0.0
Sum				0.198		34.8

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