"Lignophines": Lignin-based tertiary phosphines with metal-

scavenging ability

Supporting Information

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S-1. Materials and Methods

All reactions and manipulations were carried out under N2 atmosphere using standard glovebox or Schlenk techniques unless otherwise stated. Solvents were obtained from Caledon Laboratories, dried using an MBraun solvent purification system, collected in vacuo, and stored under N2 atmosphere over 4 Å molecular sieves. Dimethylsulfoxide- d_6 (DMSO- d_6) was purchased from Cambridge Isotope Laboratories and was used without any further purification. Kraft lignin (1; $M_w \approx 10,000$ g/mol; PDI ≈ 2.0 ; measured by GPC-UV analysis) was provided by FPInnovations-Thunder Bay Bio-Economy Technology Centre, crushed into powder using a mortar and pestle and heated at 45 °C for 48 h under vacuum (-762 mmHg; C9 = 180g). Phosphine gas (PH₃) was supplied by Cytec Solvay Group. All other reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Solution phase Nuclear Magnetic Resonance (NMR) spectroscopy was conducted on a Varian INOVA 400 MHz spectrometer (¹H: 399.8 MHz, ¹³C: 100.5 MHz, ¹⁹F: 376.4 MHz, ³¹P: 161.8 MHz) or a 600 MHz (¹H: 599.5 MHz, ¹³C: 150.8 MHz, ³¹P: 242.6 MHz) Varian INOVA instrument. ¹H NMR spectra were referenced to CHD₂SOCD₃ (2.50 ppm) and ${}^{31}P{}^{1}H{}$ NMR spectra were referenced using an external standard (85% H₃PO₄; $\delta_P = 0$). FT-IR spectroscopy was performed on samples in KBr pellets using a Bruker Tensor 27 FT-IR spectrometer, with a resolution of 4 cm⁻¹. Thermogravimetric analyses were carried out on samples weighing ca. 5-6 mg, using Ramp mode at temperatures increased from 25 °C to 1000 °C at the rate of 10 °C /min on a Q600 SDT TA Instrument and analyzed using TA Universal Analysis. ICP-OES analyses were performed on 10 mL samples using a Varian Vista-MPX-RL ICP-OES instrument.

S-2. Synthesis of 1ML

Kraft lignin (1, 1000 mg, 5.5 mmol) was added to 10 mL tetrahydrofuran (THF) in a 100 mL roundbottom flask under vigorous stirring. The mixture was stirred for ca. 5 min to obtain a homogeneous darkbrown solution. 1-methylimidazole (0.1 mL, 0.10 mg, 1.25 mmol) and methacrylic anhydride (0.82 mL, 0.84 g, 5.5 mmol) were then added to the previous solution and stirred at 54 °C for 54 minutes under an N_2 atmosphere (Scheme S-1). After 54 minutes, the reaction mixture was of a medium brown color. The brown mixture was then added dropwise to 100 mL hexanes under stirring to precipitate a light brown powder. The obtained powder was dissolved in 10 mL DCM and washed with water to remove the catalyst and any unreacted reagent. The aqueous phase was disposed of after each wash. The organic phase was then precipitated in 100 mL hexanes and dried at room temperature under vacuum to give 1.465 g (146.5 wt% product yield) **1ML**. ¹H NMR (DMSO-*d*₆, 600 MHz): δ_H 1.89 (br, 3H, CH₃), 5.82 (br, 1H, vinyl), 6.14 (br, 1H, vinyl).



Scheme S-1 Methacrylation of 1 with methacrylic anhydride to synthesize 1ML

S-2A. Determination of the extent of methacrylation (EOM)

The EOM was determined via a modified approach to a report by Argyropoulos.¹ Specifically, **1** (0.05 g, 0.28 mmol) was added to 2 mL THF in a round-bottom flask under vigorous stirring in the dry-box. The mixture was stirred for ca. 5 min. to obtain a brown solution. NEt₃ (0.19 g, 261 µl, 1.88 mmol) was added to the mixture under stirring. Chlorodiisopropylphosphine ([CH(CH₃)₂]₂PCl; 0.085 g, 90 µl, 0.56 mmol) was added to the mixture while stirring vigorously. The reaction mixture was stirred for ca. 10 min. at ambient temperature, before it was precipitated by adding 10 mL n-pentane and dried in vacuo to obtain a light brown powder. The dried powder was swelled in 1.7 mL THF and ³¹P{¹H} NMR spectroscopy was performed on the resulting solution using 50 µl of a 0.05 molar solution of PPh₃ in THF as external standard. The same procedure was carried out separately for the **1ML** sample and finally, the EOM was

determined though comparing the integrations of the observed peaks, relative to the external standard (Figure S-1).



The peak region of $\delta_P = 136.0 - 170.0$ ppm was attributed to the product of the reactions as illustrated in Figure S-1, the corresponding integrations of which (y_A and y_B) were used in comparison with the integration of the external standard peak (x) as described below in order to determine the EOM.

$$EOM(\%) = \left[1 - \left(\frac{y_B/x_B}{y_A/x_A}\right)\right] \times 100$$

given: $x_A = x_B$ EOM(%) = $\left[1 - \left(\frac{y_B}{y_A}\right)\right] \times 100$ As a result, it was determined that approximately 70% of the -OH groups on 1 were successfully capped by methacrylate groups in **1ML** through the methacrylation reaction as described in Scheme S-1.

S-3 Synthesis of 1PH₂

1ML (200 mg, swelled in 100 mL CH₃CN) and AIBN (6 mg, 3 wt.%) were transferred to a 300 mL autoclave. The autoclave was then degassed by purging N_2 for ca. 10 min and pressurized with phosphine gas (PH₃, 80 psi). The vessel was then stirred for 1 h, at which point it was re-pressurized with PH₃ and heated to 50 °C with stirring for 24 h. Afterward, the pressurized PH₃ was released in a controlled environment, where it was ignited and burned. Subsequently, the vessel was brought into the glovebox, opened, and the mixture (swelled light-brown substance in solvent) was centrifuged and dried in vacuo to obtain **1PH₂** in the form of a light-brown powder (112.5 % recovered mass yield)

S-3A Determination of the extent of hydrophosphination (EOHP)

20 mg of the obtained **1PH₂** sample was swelled in 2 mL CH₃CN and transferred into an NMR tube. Separately, 40 μ L of a 0.025 mol/L solution of PPh₃ in CH₃CN was transferred to a capillary tube, which was then flame sealed and inserted into the NMR tube containing the **1PH₂** sample and the ³¹P{¹H}NMR spectrum of the mentioned tube was recorded (Figure S-2).



Figure S-2 ${}^{31}P{}^{1}H$ NMR spectrum of $1PH_2$

The signal at $\delta_P = -148$ is consistent with molecular primary phosphines and was attributed to $1PH_2$. Another peak was observed at $\delta_P = -82$, consistent with molecular secondary phosphines, which was attributed to the result of two methacrylate groups linking to one phosphorus atom and forming a secondary lignophine (1PH1). The amount of the 1PH1 formed was determined to be ca. 3%, which was considered negligible in determining the obtained material as primary lignophine (1PH2). The EOHP was determined as described below:

Considering ca. 70% of the -OH functionalities were methacrylated in 1ML:

$$1 \mod 1 \times 1.5 \frac{\mod 0H}{\mod 1} \times 70\% = 1.05 \mod \text{methacrylate on one } C9$$

$$mod. C9 = 180g + (1.05 mol meth. \times 85.03 \frac{g}{mol}) - (1.05 mol H \times 1.008 \frac{g}{mol}) = 268.24 g$$

Considering the integration of the peak at $\delta_P = -148$:

$$10^{-3} mmol PPh_3 \times \frac{3.01}{0.06} \times \frac{268.24}{20} = 0.6727 mol$$

Thus, approximately 0.6727 mol of the methacrylate groups on 1ML were capped.

Considering the integration of the peak at $\delta_P = -82$:

$$10^{-3} mmol PPh_3 \times \frac{0.05}{0.06} \times \frac{268.24}{20} \times \frac{2 mol meth.}{1 mol 1PH1} = 0.0222$$

Thus, approximately 0.0222 mol of the methacrylate groups on the 1ML were capped.

Finally, to determine the EOHP:

$$EOHP(\%) = \frac{0.6727 + 0.222}{1.05} \times 100 = 66\%$$

S-4 Synthesis of 1P^{Hex} and 1P^{RFn}

The obtained $1PH_2$ (100 mg) was swelled in 50 mL CH₃CN in a 250 mL pressure tube. AIBN (63 mg, 3 wt.%) was added to the pressure tube, followed by addition of excess 1-hexene (2000 mg, 23.76 mmol) or 1H,1H,2H-perfluoro-1-hexene (2000 mg, 8.12 mmol) for the synthesis of $1P^{Hex}$ or $1P^{RFn}$, respectively. The mixtures were then heated at 40 °C with vigorous stirring for 24 h. Afterward, each mixture was centrifuged and decanted. The resulting swelled powders (both light-brown) were then tritiated in excess CH₃CN and centrifuged thrice to remove any unreacted reagents. Finally, each sample was dried in vacuo to obtain the corresponding tertiary lignophines (both light-brown powders). The recovered mass yields were 114 wt.% and 121 wt.% for $1P^{Hex}$ and $1P^{RFn}$, respectively.

S-5 Metal-sequestration procedures

S-5A RCM of diethyl diallylmalonate by GI

A stock solution of diethyl diallylmalonate (**2**; 30 μ L, 0.12 mmol, 210 mM) in DCM-*d*₂ was prepared in a 4 mL screw-top vial with a septum cap in the glovebox (**2-stock**). Separately, a stock solution of **GI** (5 mg, 0.006 mmol, 0.02 M) in DCM-*d*₂ (287 μ L) was prepared (dark purple), followed by a serial dilution using 53 μ L of the mentioned **GI** stock solution with 298 μ L DCM-*d*₂ to obtain a 3.2 mM **GI** stock solution (**GI-stock**; dark purple). An NMR tube was then charged with 200 μ L **GI-stock** and 100 μ L DCM-*d*₂, and capped with a septum. The **2-stock** and the NMR tube were then taken out of the glovebox and sealed with parafilm. The NMR spectrometer probe was preheated to 30 °C and stabilized. Subsequently, 300 μ L **2-stock** was injected into the mentioned NMR tube was then placed inside the spectrometer, the temperature was equilibrated for 2 min at 30 °C, and ¹H NMR spectra were acquired in 1 min intervals for 30 minutes. The RCM conversion was quantified by relative integration of **2** to **3**.

S-5B Treatment of 2 with GI in the presence of 1P^{Hex}

Stock solutions were prepared as previously described in S-5A. For each run, A 4 mL screw-top vial was charged with corresponding amounts of $1P^{Hex}$ (5 mg or 10 mg), GI-stock (200 µL) and DCM- $d_2(100 \mu L)$ and transferred to an NMR tube. The mixture was then allowed to incubate for a predetermined amount of time (1 h and 24 h), which resulted in considerable lightening of the dark purple color of the solution. Afterward, the substrate was added following the same method as described in section S-5A and the reaction mixture was monitored as previously described in S-5A. For each reaction, a ¹H NMR spectrum was obtained after 24 h of reaction time to determine the conversion percentages over longer periods. The obtained results showed that by incubating with 10 mg $1P^{Hex}$ for 24 h, no product was formed after 24 h, which suggested complete sequestration, within the detection limits, of GI under these conditions. Meanwhile, the other 3 reaction mixtures showed increased conversions after 24 h, which was attributed

to the continuance of product formation due to the presence of non-sequestered GI in the reaction mixtures.

S-5C Attempted RCM of 2 with 1P^{Hex} pre-loaded with GI

Stock solutions were prepared as previously described in S-5A. A 4 mL screw-top vial was charged with $1P^{Hex}$ (5 mg), GI-stock (200 µL) and DCM- d_2 (100 µL) and transferred to an NMR tube. The mixture was then allowed to incubate for 20 min, which resulted in considerable lightening of the dark purple color of the solution. Afterward, the incubated mixture was dried in vacuo, resulting a light brown powder, which was then suspended in CH₃CN, centrifuged, and decanted to remove any remaining GI that is not bound to the $1P^{Hex}$. This washing process was repeated four times. Afterward, the residual solvent was removed *in vacuo* to give $1P^{Hex}$ pre-functionalized with ruthenium as a light brown powder. The solid was transferred to an NMR tube using DCM- d_2 (300 µL), which was then capped with a septum. Subsequently, the substrate was added, and the reaction was monitored as previously described in S-5A. The corresponding ¹H NMR spectra had no peaks corresponding to **3**. A ¹H NMR spectrum of the mixture was obtained after 24 h and again no peaks corresponding to **3** were observed. The obtained results suggested that the $1P^{Hex}$ pre-functionalized with ruthenium does not participate in the RCM reaction or leach into solution under the catalytic conditions, which further demonstrated that the observed RCM product **3**, under some conditions used in S-5B (B-D in Figure 2), was a result of non-sequestered GI that remained in solution.

S-5D ICP-OES Analysis of Ruthenium after Exposure to 1P^{Hex}

Stock solutions were prepared as previously described in S-5A. Three sets of two 4 mL screw-top vials, **A**, **B**, and **C** were charged with **GI-stock** (300 μ L). Sets **A** and **B** were also charged with solid 1P^{Hex} (10 mg) and were incubated for 1 h and 24 h, respectively, which resulted in considerable lightening of the dark purple color of the solution. After this initial incubation period all sets of vials, **A**, **B**, and **C**, were charged with **2-stock** (300 μ L) and heated at 30 °C for 30 minutes. The samples were then filtered through a 13 mm 0.22 μ m PTFE syringe filter into a pre-weighed 20 mL vial and the solvent was

removed under reduced pressure. The masses of the recovered residues were recorded. The samples were digested in 5 mL of aqua regia and boiled for 20 minutes, left to cool to room temperature, and diluted to 10 mL with aqua regia. The samples were then analyzed using a Varian Vista-MPX-RL ICP-OES instrument to determine the ppm (mg/L) of ruthenium in each sample. The values were converted to µg Ru/g residue (ppm) and these values are provided in Table S-1.

Entry	Removal	Incubation	ppm (µg/g)	Ru Removed	Ru Removed
	Method	time (h)		(%) ^c	(%) ^d
1	None (control) ^b	0	4480	0	
2	1P ^{Hex}	1	1280	71	69
3	1P ^{Hex}	24	362	92	91

Table S-1 Residual Ru and % metal removed from RCM reactions treated with $1P^{Hex a}$

^a 106 mM **2**, 1 mol% **GI** (1.06 mM), and 10 mg/0.5 mg **GI/1P^{Hex}**: ^b **1P^{Hex}** was not added as a scavenger. ^c %Ru Removed = [(Avg Controls)–(Avg 1h or 24 h Inc)]/ (Avg Controls) *100; ^d %Ru Removed = [(ideal loading)–(Avg 1h or 24 h Inc)]/ (ideal loading) *100. Ideal loading = 4196 ppm

S-6 Elemental Analysis of 1P^{Hex} and 1ML

Solid samples (ca. 8 mg each) in 4 mL screw-cap vials were submitted to the Biotron facility (at Western University) for elemental analysis (EA) and the data is presented in Table S-2. The samples were run on an Elementar vario ISOTOPE cube with a $R^2 > 0.99$.

Table S-2 CHNS Analytical Results obtained from an Elementar vario ISOTOPE cube with an $R^2 > 0.99$. (Table directly from the Biotron report)

		Sample Weight	Nitrogen	Nitrogen	Carbon	Carbon	Hydrogen	Hydrogen
Sample	Parameter Code	(mg)	Final Conc (mg)	Final Conc (%)	Final Conc (mg)	Final Conc(%)	Final Conc (mg)	Final Conc (%)
1P^Hex	CHNS (CHN)	6.578	0.097	1.47	4.161	63.26	0.46	6.987
1ML	CHNS (CHN)	1.554	0.006	<mrl< td=""><td>1.012</td><td>65.11</td><td>0.099</td><td>< MRL</td></mrl<>	1.012	65.11	0.099	< MRL
< MRL (Metho	d Reporting Limit)							

Experimental EA for **1ML** were found to be: C, 65.11%; H, \leq MRL; N, \leq MRL (Table S-3, Entry 1). Both the nitrogen and hydrogen concentrations were lower than the method reporting limit (MRL). The predicted EA for **1ML**, based on the monomer unit of lignin (Figure S-3), was determined to be: C, 67.31%; H, 6.31% (Table S-3, Entry 2). To account for the actual yield of the methacrylation step (70%) in the synthesis of **1ML**, a weighted predicted composition was calculated (Equation S-1). The predicted values for **1ML** (corrected) are: C, 66.97%; H, 6.02% (Table S-3, Entry 3). A comparison to the experimental EA shows a 1.86% lower concentration for C.

Experimental EA for $1P^{Hex}$ were found to be: C, 63.26%; H, 6.987%; N, 1.47% (Table S-2, Entry 4). The predicted EA for the ideal $1P^{Hex}$ structure (Figure S-3) with 100% conversion at all steps was determined to be: C, 69.66%; H, 10.27% (Table S-3, Entry 5). To account for the actual yields of the methacrylation (70%) and hydrophosphination (66%) steps in the synthesis of $1P^{Hex}$, a weighted predicted composition was calculated (Equation S-1). The predicted values for $1P^{Hex}$ (corrected) are: C, 68.69%; H, 8.83% (Table S-3, Entry 6). A comparison to the experimental EA shows a 5.43% lower concentration for C and 1.84% lower concentration for H.

Entry	Sample	%C	%Н	%N
1	Experimental 1ML	65.110	< MRL ^b	< MRL ^b
2	Predicted 1ML	67.31	6.31	0
	(Quantitative)			
3	Predicted 1ML	66.97	6.02	0
	(corrected) ^c			
4	Experimental 1P ^{Hex}	63.26	6.987	1.470
5	Predicted 1P^{Hex}	69.66	10.27	0
	(Quantitative)			
6	Predicted 1P ^{Hex}	68.69	8.83	0
	$(corrected)^d$			

Table S-3 Predicted and experimental EA for %C, %H, and %N.^a

^{*a*}Experimental EA was determined using a Elementar vario ISOTOPE cube and predicted EA values were determined from Chemdraw. ^{*b*}MRL = method reporting limit. ^{*c*}Prediction for sample with 70% yield of the methacrylation step in the synthesis. ^{*d*}Prediction for sample with 70% yield of methacrylation and 66% yield of hydrophosphination steps in the synthesis.

A difference in the EA between the experimental and predicted for these polymers is not surprising due to incomplete conversion of the methacrylation and hydrophosphination reactions. However, even when considering the 70% methacrylation and 66% hydrophosphination using a weighted average calculation (Equation S-1), we do not see agreement with the predicted and experimental values. When comparing

the experimental %C values for **1ML** and **1P**^{Hex} (Table S-3, Entries 1 and 4, respectively), a decrease in the %C was observed for the latter. This is opposite of the predicted values that predicts an increase in the %C from ca. 67% to 69% (Table S-3, Entries 3 and 6, respectively). One possible explanation for the decrease in the experimentally observed %C could be due to PH₃ crosslinking some of the methacrylate groups, which would result in fewer alkyl chains being incorporated than expected.



Elemental Analysis: C, 65.05; H, 6.07; O, 28.88 Elemental Analysis: C, 67.54; H, 6.00; O, 26.46 Elemental Analysis: C, 69.66; H, 10.27; O, 11.32; P, 8.76 Figure S-3 Structures used to determine predicted EA for comparison to experimental findings. A) Pre-functionalized lignin, B) 1ML structure, C) 1P^{Hex} structure.

% Carbon $(1P^{Hex} corrected) = (((65.05 \times 0.3) + (67.54 \times 0.7)) \times 0.34) + (69.66 \times 0.66)$

Carbon % $(1P^{Hex} \text{ corrected}) = 68.69\%$

Equation S-1 Example calculation for determining the predicted EA for 70% methacrylation, 66% conversion from 1ML to $1PH_2$, and quantitative conversion from $1PH_2$ to $1P^{Hex}$.

S-7 FTIR spectra



Figure S-4 FTIR spectra of 1ML (A), $1PH_2$ (B), $1P^{Hex}$ (C), and $1P^{RFn}$ (D)

S-8³¹F{¹H} NMR



Figure S-5 ${}^{31}F{}^{1}H$ NMR spectra of AgOTf (A) and $1P^{Ag}(B)$

S-9 Thermal gravimetric analysis



Figure S-6 TGA results of 1ML (A), $1PH_2$ (B), $1P^{Hex}$ (C), and $1P^{RFn}$ (D)