Mild and controlled lignin methylation with

trimethylphosphate: towards a precise control of lignins

functionality

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ELECTRONIC SUPPLEMENTARY INFORMATION

Determination of optimum reaction conditions



Figure S 1. Evolution of the molar mass of methylated SW-KL with the reaction time at 120 °C (10 eq. TMP, 1 eq. K₂CO₃)



Figure S 2. ¹H NMR spectra (DMSO-*d*₆, 400 MHz) of intial and methylated lignins (10 eq. TMP, 1 eq. K₂CO₃, 120 °C, 1 h): SW-KL (a), WS-SL (b), HW-OL1 (c) and HW-OL2 (d). Peaks at 10.1 ppm are related to 2,3,4,5,6-pentafluorobenzaldehyde used as internal standard, peaks at 3.33 ppm are due to water and peaks at 2.5 ppm are the solvent peaks (DMSO).



Figure S 3. SEC traces of HW-OL1 (a) and HW-OL2 (b) after acetylation and after methylation (10 eq. TMP, 1 eq. K₂CO₃, 120 °C, 1 h)

Table S 1. Number-average molar mass and dispersity of the different lignins after acetylation or methylation (10 eq. TMP, 1 eq. K_2CO_3 , 120 °C, 1 h)

Lignin	Treatment	M _n (g mol⁻¹)	Ð
SW-KL	Acetylation	1220	2.15
	Methylation ^a	1130	1.96
	Methylation ^a	1220	1.93
	Methylation ^a	1300	2.00
WS-SL	Acetylation	870	2.11
	Methylation	nd ^b	nd ^b
HW-OL1	Acetylation	1810	1.99
	Methylation	1710	2.17
HW-OL2	Acetylation	1760	1.95
	Methylation	1820	2.25

^a Three distinct experiments with similar reaction conditions ^b *nd* = not determined (partially insoluble in THF)



Figure S 4. ¹H NMR spectra (400 MHz, DMSO-*d*₆) of 3 distinct samples of SW-KL after methylation in similar conditions (10 eq. TMP, 1 eq. K₂CO₃, 120 °C, 1 h). Peaks at 10.1 ppm are related to 2,3,4,5,6-pentafluorobenzaldehyde used as internal standard, peaks at 3.33 ppm are due to water and peaks at 2.5 ppm are the solvent peaks (DMSO).



Figure S 5. FTIR spectra of 3 distinct samples of SW-KL after methylation in similar conditions (10 eq. TMP, 1 eq. K₂CO₃, 120 °C, 1 h)



Figure S 6. SEC of 3 distinct samples of SW-KL after methylation in similar conditions (10 eq. TMP, 1 eq. K₂CO₃, 120 °C, 1 h)



Figure S 7. ¹H (a) and ³¹P NMR spectra (b) of TMP, the crude reaction mixture of SW-KL methylation after 3 and 60 min of reaction (10 eq. TMP, 1 eq. K₂CO₃, 120 °C) and the isolated methylated SW-KL. The rectangles correspond to the zoom shown in the manuscript (Figure 5).



Figure S 8. Details of ¹H (a) and ³¹P NMR spectra (b) of the crude reaction mixture of SW-KL methylation after different reaction times (10 eq. TMP, 1 eq. K₂CO₃, 120 °C)



Figure S 9. Mole percent of DMP in the reaction mixture depending on the reaction time (SW-KL, 10 eq. TMP, 1 eq. K₂CO₃, 120 °C), as measured by ³¹P NMR. Error bars represent the standard deviations of 3 replicates of the experiment.



Figure S 10. ¹H NMR spectra of TMP and the blank reaction medium (no lignin, TMP, K₂CO₃, 120 °C, 1 h)





Figure S 11. Evolution of the conversion of G, H and 5-substituted phenolic OH groups with varying catalyst content: SW-KL (a), HW-OL1 (b), WS-SL (c)