

# Supplementary information: One-pot route to convert technical lignin into versatile lignin esters for tailored bioplastics and sustainable materials

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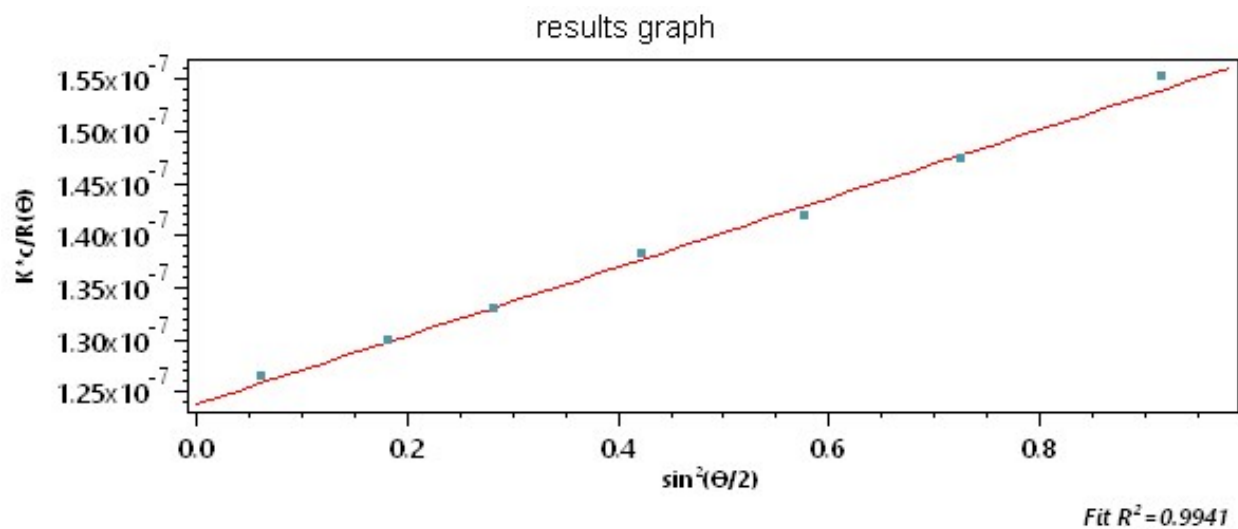
**Table S1** Input materials and chemicals, including lignin, ethylene carbonate (EC), propionic acid (PA), and total added water, and the obtained products, including the volume of CO<sub>2</sub> per gram of lignin, solvent residue, and recovered lignin products (F1, F2, F3, F4, and F5)

	Lignin/g	EC/g	CO <sub>2</sub> /(ml/g)	PA/ml	Solid Residue/g	Solvent Mixture /mL	Total Added Water/mL*	F1/g-	F2 /g	F3/g	F4/g	F5/g
1	10	20.2	110.8	180	1.0	-	-	-	-	-	-	-
2	10	31.2	134.0	180	2.9	-	-	-	-	-	-	-
3	3	9.3	107.7	54	0.017	58	174	0.71	1.3	0.83	0.38	0.4
4	3	9.3	115.3	54	0.019	58	174	0.90	1.3	0.74	0.32	0.3
5	3	9.3	107.7	54	0.015	58	174	0.66	1.4	0.78	0.47	0.3
6	10	31.2	107.6	180	0.35	200	600	3.99	3.8	2.3	0.96	1.3

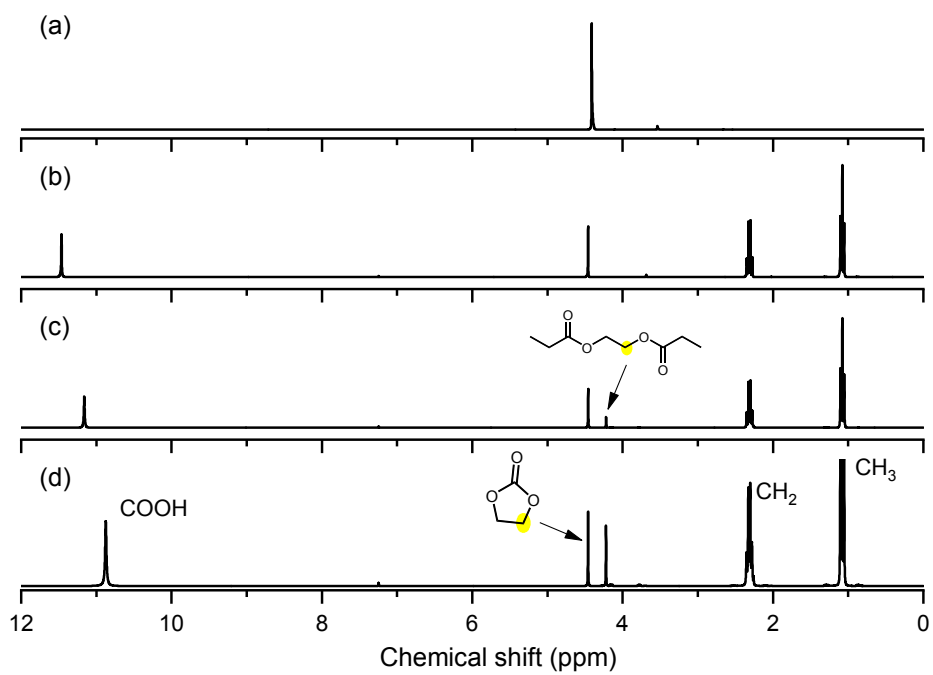
\* the washing water was not involved in this process

**Table S2** The molar mass of standard polystyrene sulfonate (PSS) samples and their hydrodynamic radius ( $R_h$ ) based on the viscometer detector

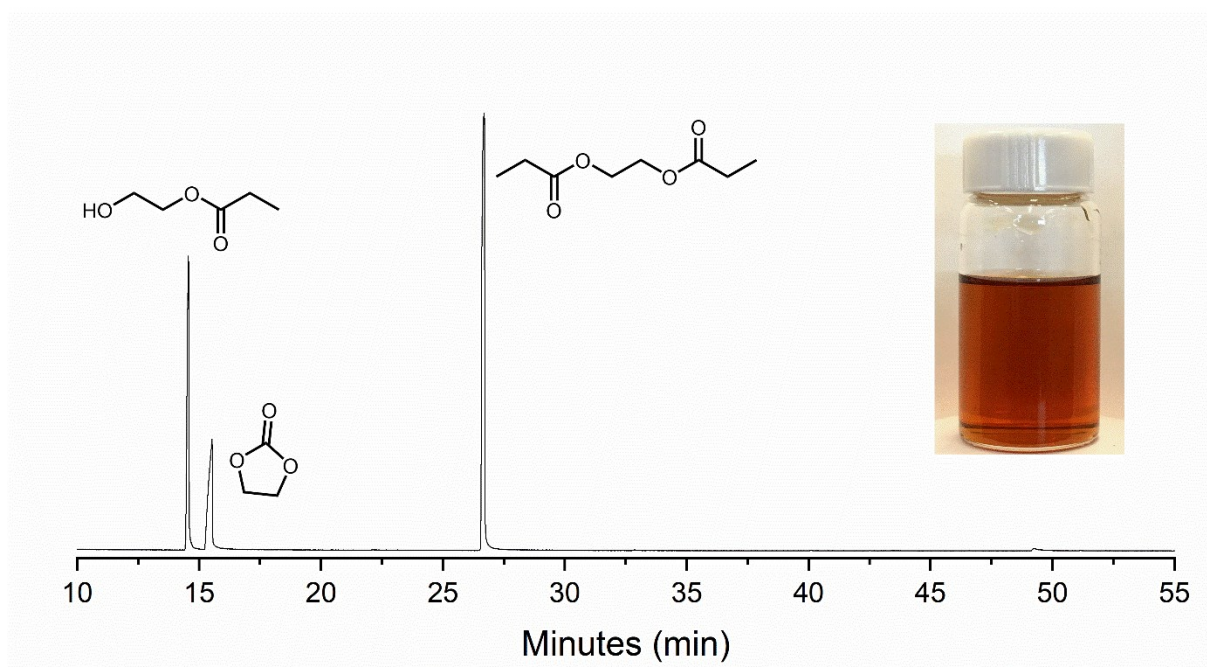
PSS-No.	M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	R <sub>h</sub> (V) <sub>w</sub>
PSS-1	751.5	598.1	34.1
PSS-2	522.7	473.2	21.7
PSS-3	228	222.4	13
PSS-4	42.2	41.9	5.2
PSS-5	32	32	4.5
PSS-6	12.2	12.2	2.6
PSS-7	5.5	5.5	1.8
PSS-8	3.8	3.5	1.5
PSS-9	2.4	2.1	1.1



**Figure S1** Zimm plot of F1 lignin;  $R(\theta)$ : Excess Rayleigh ratio which is measured by the MALS instrument;  $c$ : solute concentration;  $K^*$ : the optical constant which related to the  $dn/dc$ .<sup>1</sup> Note, fluorescence suppressed using 10nm bandpass filters.



**Figure S2**  $^1\text{H}$  NMR spectrum of EC (a), EC/PA mixture (b), EC/PA at  $120^\circ\text{C}$  for 24 h (c), EC/PA at  $120^\circ\text{C}$  for 48 h (d). Sample preparation: 50 mg samples were dissolved into 500  $\mu\text{L}$  deuterium chloroform ( $\text{CDCl}_3$ ) and transferred into 5 mm NMR tubes. Acquisition parameter: scan number 256; delay time 10 s; Pulse length: 14  $\mu\text{s}$ ; Acquisition time: 5.3 s.<sup>2</sup>



**Fig. S3** GC-MS spectrum of collect solvent residue (reddish solution) after the one-pot esterification. For the GC-MS, the solvent residue were analyzed by a 8890 GC system with a 7010B GC/TQ using a DB-5MS UI column (30 m × 0.25 mm × 0.5 μm) of Agilent Technologies (Santa Clara, CA, USA) with helium as a carrier gas at a constant flow rate of 1.1 mL/min. Sample injection was designated at 1 μL with a split ratio of 1:100. The oven temperature was initially set at 50 °C and maintained for 5 min, increased to 300 °C at 3 °C/min rate and kept for 10 min. The electron impact (EI) ionization used for mass detection and the electron energy was set at 70 eV. The scan range was designated from 30 to 500 m/z and the scan time was kept 200 ms with a solvent delay of 8 min for mass data acquisition.

**Table S3** Reagent utilization for traditional esterification methods of solvent fractionated lignin resources (starting with 100 g softwood kraft lignin)\*

Step	Lignin	Solvent	Solvent mass/g	Recovered Lignin mass1/g	Total OH groups / (mmol/g)	Step	Propionyl chloride/g	Solvent Mass/g	Catalyst Mass/g	Precipitated solvent/g <sup>a</sup>	Recovered lignin mass2/ g	PMI /(g/g)
1						2						
	F <sub>EtOAc</sub>	EtOAc	902	24.5	5.90		17.4	165	18.7	2015	19.6	166
	F <sub>Ethanol</sub>	Ethanol	789	32.5	6.55		25.6	219	24.9	2698	26	146
	F <sub>Methanol</sub>	Methanol	792	8.2	6.30		6.2	55	6.3	1017	6.56	287
	F <sub>Acetone</sub>	Acetone	784	14.7	6.15		10.8	99	11.3	1213	11.76	181
	F <sub>Insoluble</sub>	Insoluble	1000	20	5.70		13.7	135	15.3	1640	16	176

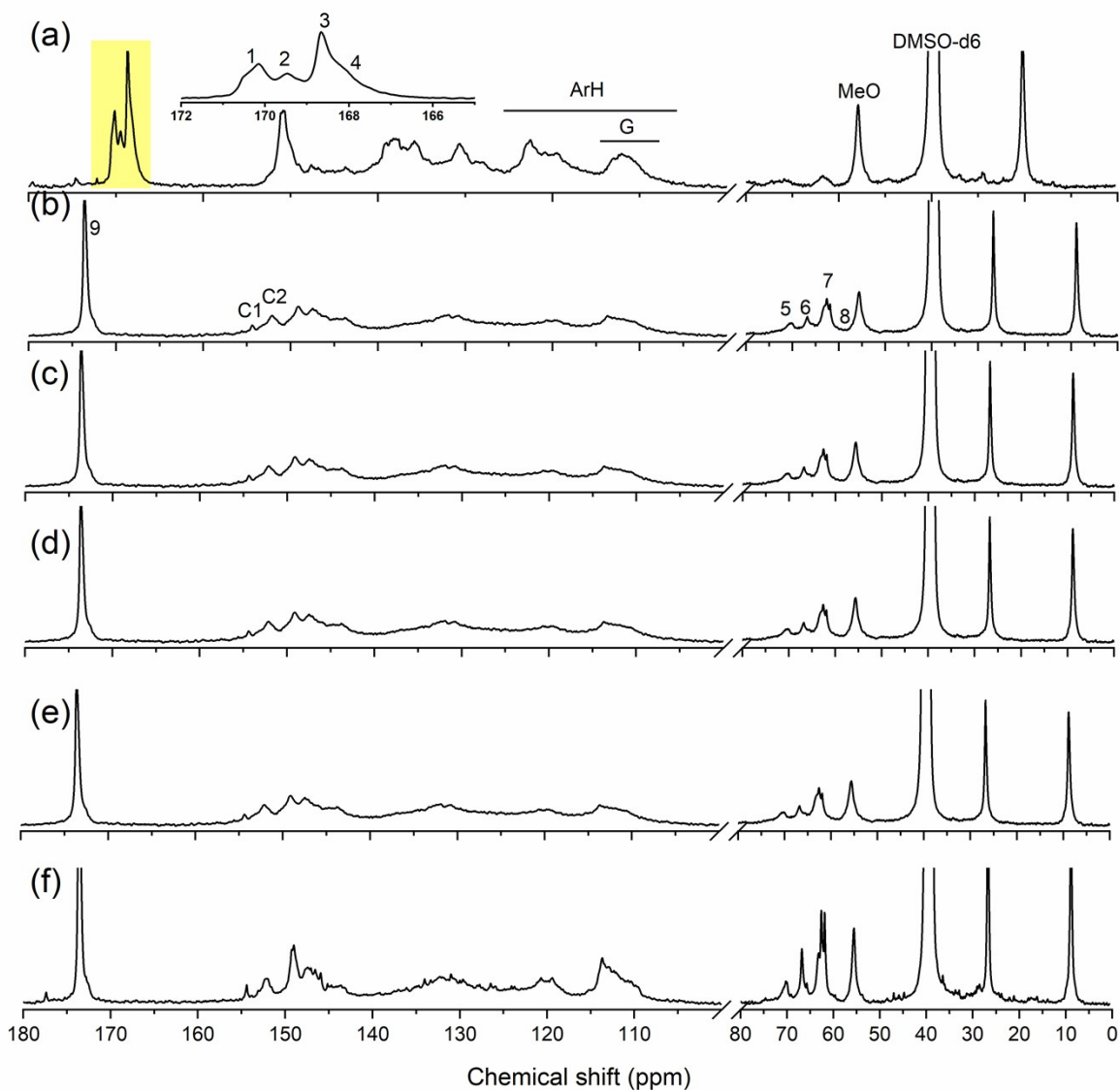
\* the step 1 solvent fractionation process was developed by Duval et al<sup>3-6</sup>. step 2 the esterification process was developed by Koivu et al<sup>7,8</sup>. In this process, the solvent mixture is THF/DMF (4:1) and has a ratio with lignin (7.5 ml/g); the catalyst is pyridine and has a volume ratio with lignin (4 ml/g); the recovered lignin yield after the esterification was assumed as 80%<sup>7,8</sup>. The precipitation solvent is assumed as 10 times of the volume of solvent, reagents, and catalysts in order to recover the lignin particles. The washing reagents were not involved in this process. PMI, process mass intensity

**Table S4** Relative molar mass of different esterified lignin fractions

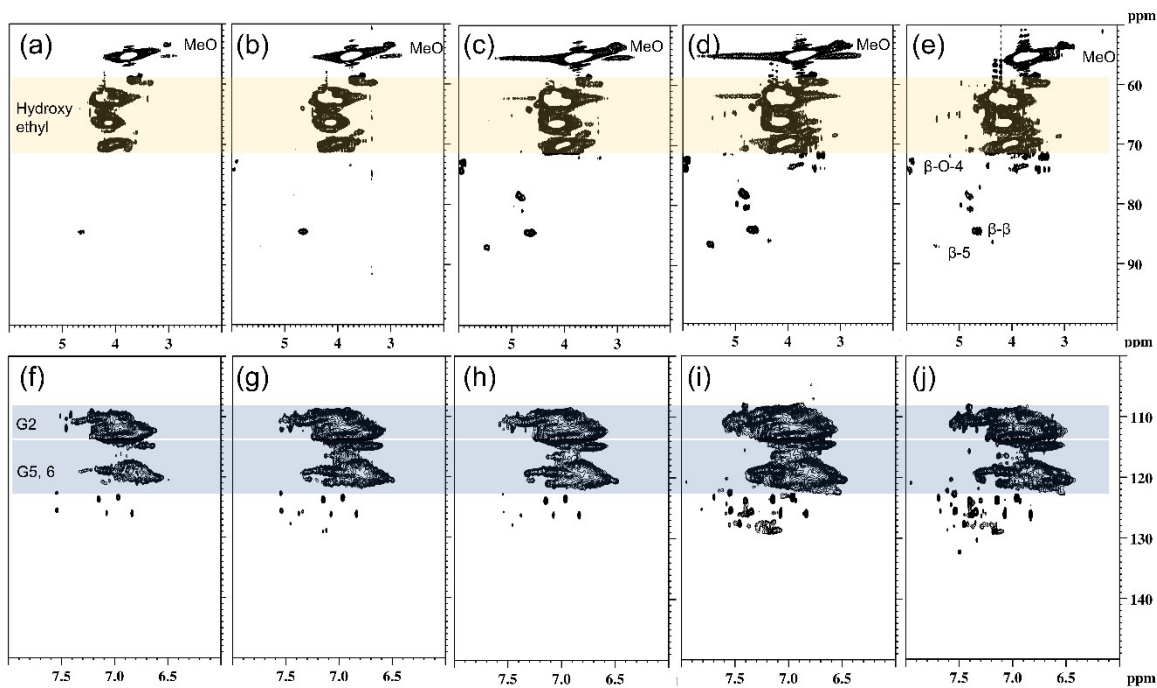
	dRI <sup>a</sup>			IV <sup>b</sup>		
	Mw/kDa	Mn/kDa	Đ	Mw/kDa	Mn/kDa	Đ
Lignin	9.3	1.1	8.4	13.1	0.6	22.0
HELignin	18.2	0.9	19	52.6	0.7	72.7
F1	128.9	14.7	8.7	121.6	16.8	8.7
F2	42.76	4.3	9.9	30	5.7	5.4
F3	4.60	1.4	3.3	4.2	1.4	3.0
F4	1.47	0.6	2.6	1.4	0.5	2.6
F5	0.73	0.3	2.8	0.6	0.2	2.8

<sup>a</sup> dRI, differential refractive index (conventional calibration analysis); <sup>b</sup> IV, intrinsic viscosity detector (universal calibration analysis);





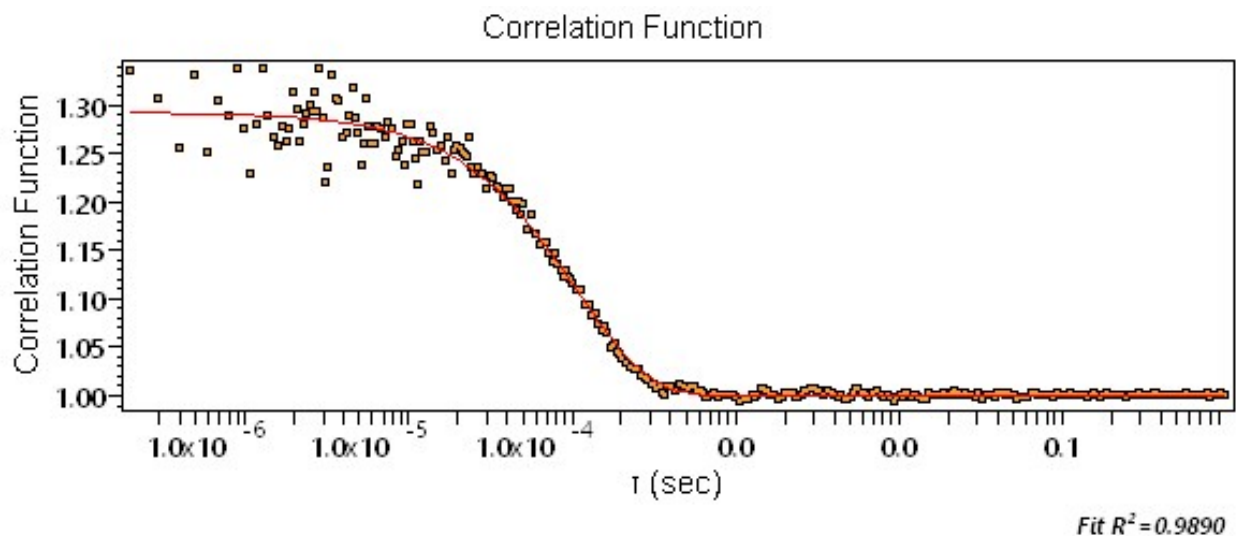
**Figure S4**  $^{13}\text{C}$  NMR spectrum of acetylated lignin and different esterified lignin fractions: (a) F1, (b) F2, (c) F3, (d) F4, and (e) F5; Sample preparation: 150 mg samples were dissolved into 450  $\mu\text{L}$  deuterium dimethyl sulfoxide (DMSO-d<sub>6</sub>), following with the addition of 60  $\mu\text{L}$  relaxation reagent (50 mg/ml chromium(III) acetylacetonate). Sample analysis parameters: acquisition program zgig; scan number 20 000; acquisition time: 1.4 s; delay time: 2 s; pulse length: 8.5  $\mu\text{s}$ . The acetylation procedure is described in our previous work.<sup>9,10</sup>



**Figure S5** 2D HSQC NMR spectra of different lignin fractions including oxygenated aliphatic region (top) and aromatic region (bottom); F1 (a, f), F2 (b, g), F3 (c, h), F4 (d, i), F5 (e, j); Sample preparation: 30 mg samples were dissolved into 500  $\mu$ L deuterium dimethyl sulfoxide (DMSO-d<sub>6</sub>). The sample analyzed parameters: acquisition program hsqcetgpsisp; scan number 16; acquisition time: 1.4 s; delay time: 2 s; pulse length: 8.5  $\mu$ s.<sup>11</sup>

**Table S5** Quantitative and semi-quantitative NMR analysis of lignin structural features including linkages, functional groups, and units

	Chemical shift (ppm)	Lignin	F1	F2	F3	F4	F5
<sup>31</sup> P NMR (mmol/g)							
AlOH	150 – 145.6	2.73	0.49	0.42	0.49	0.47	0.65
ArOH	144.5 – 136	4.77	0.22	0.48	0.25	0.40	0.11
COOH	136 - 133	0.68	0.17	0.16	0.18	0.23	0.46
<sup>13</sup> C NMR (100 Ar)							
Aliphatic hydroxyl groups (AlOH, Peak 1+Peak 2)	175 - 169.03	42.0	-	-	-	-	-
Aromatic hydroxyl groups (ArOH, Peak 3+Peak 4)	169.03 - 166	57.4	-	-	-	-	-
Methoxy groups (MeO)	58 - 54	76.6	81.8	83.4	88.7	85.2	81.9
Aromatic hydrogen (ArH)	125 – 100	218.3	203.3	211.5	223.1	226.0	233.1
Guaiacyl units (G)	115 - 107	81.3	87.3	95.3	105.7	109.7	118.7
Carbonate 1 (C1)	155.9 - 153.3	-	17.3	13.6	10.7	11.0	10.9
propionate (Peak 9)	175 - 170	-	100.6	100.4	103.1	120.5	124.8
Ethyl group $\int_{(75-58)} / 2$		-	82.1	84.8	90.2	104.4	109.4
- Peak 5	75 – 68.5	-	43.6	42.6	44.4	47.8	46.4
- Peak 6	68.5 – 64.5	-	36.1	37.9	41.9	46.3	52.6
Esterified hydroxyethyl - Peak 7	65 – 61.5	-	74.2	79.2	85.9	104.9	109.0
Aliphatic hydroxyethyl - Peak 8	61.5 - 58	-	10.5	9.9	8.2	9.8	10.7
HSQC NMR (100 Ar)							
Stilbene-5 (SB5)	$\delta C (118.9) / \delta H (7.3)$		1.73	1.54	1.74	1.96	1.78
Stilbene-1 (SB1)	$\delta C (126.18) / \delta H (6.7)$		0.67	0.59	0.67	0.87	1.49
Acetovanillion (AV)	$\delta C (110.0) / \delta H (7.5)$		0.97	0.81	0.86	1.1	1.27
Vanilline (V)	$\delta C (111.9) / \delta H (7.4)$		1.43	1.11	1.33	0.85	1.51
Vanillic acid (VA)	$\delta C (124.0) / \delta H (7.4)$		0.38	0.35	0.52	0.64	0.98
$\beta$ - $\beta$	$\delta C (80.0) / \delta H (4.6)$		3.61	3.46	3.51	3.01	2.62
$\beta$ -5	$\delta C (86.7) / \delta H (5.5)$		1.66	1.6	1.57	1.14	0.78
$\beta$ -O-4	$\delta C (73.5) / \delta H (5.9)$		2.29	2.59	2.93	2.4	1.46



**Figure S6** Plot of correlation function (equation S1) for the calculation of diffusion coefficient ( $D_t$ ) based on quasi-elastic light scattering analysis (QELS) signal from the MALS detector (Angle 12);

$$g^{(2)}(\tau) = 1 + \beta e^{-2D_t q^2 \tau} \dots\dots (S1)$$

The hydrodynamic radius was calculated based on the Stokes-Einstein equation (S2)

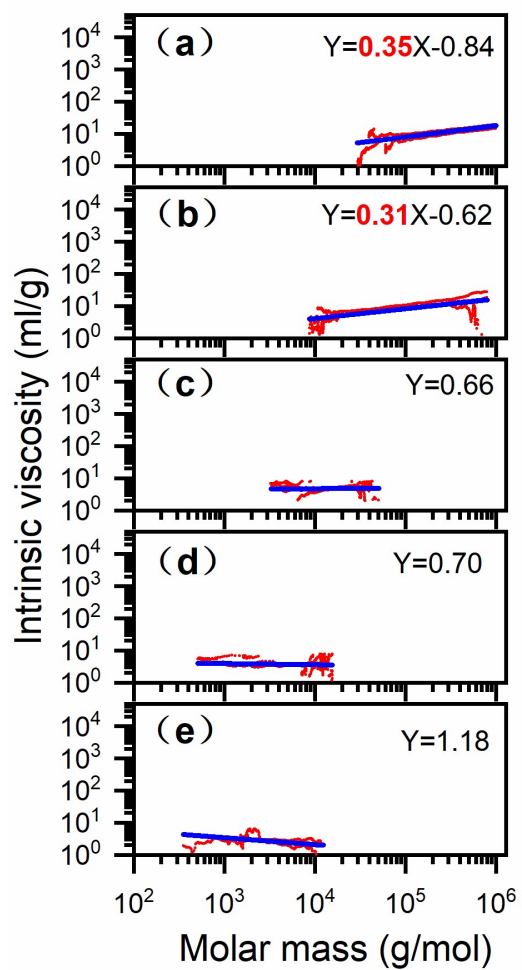
$$D_t = \frac{kT}{6\pi\eta R_h} \quad (S2)$$

K: Boltzmann's constant; T: temperature (Kelvin);  $\eta$ : viscosity of solvent;  $R_h$ : hydrodynamic radius

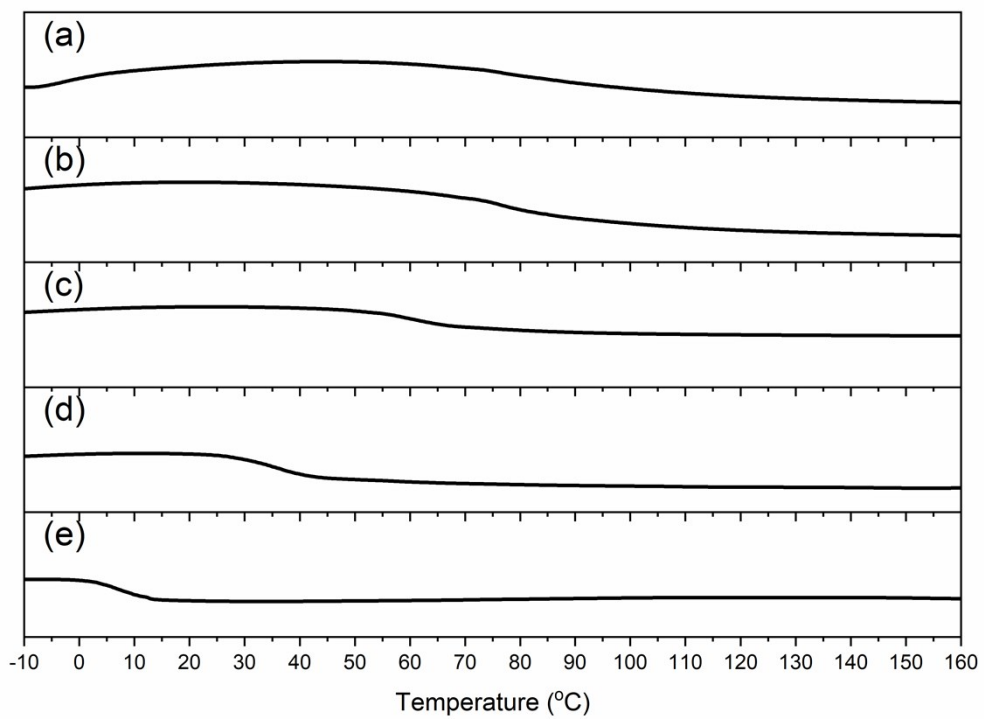
**Table S6** Conformation and hydrodynamic radius information of different lignin fractions

	$D_t^a$ / (cm <sup>2</sup> /sec)	$R_g^b$ /nm	$R_h$ (Q) <sup>c</sup> / nm	$R_g/R_h$	$R_h(V)^d$ / nm
F1	1.53E-07	19.73	8.43	2.34	10.2
F2	-	-	-	-	4.1
F3	-	-	-	-	2.8
F4	-	-	-	-	2.0
F5	-	-	-	-	1.0

<sup>a</sup> diffusion coefficient (Dt); <sup>b</sup> gyration radius ( $R_g$ ) and <sup>c</sup> hydrodynamic radius  $R_h$  (Q) are based on the QELS signal from the MALS detector; <sup>d</sup>  $R_h(V)$ , hydrodynamic radius based on the viscometer detector.

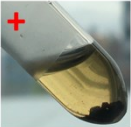

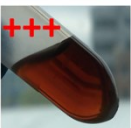
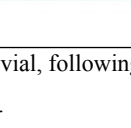



**Figure S7** Mark-Houwink–Sakurada plot of different esterified lignin fraction: (a) F1, (b) F2, (c) F3, (d) F4, and (e) F5; the intrinsic viscosity was calculated in related with the dRI signal



**Figure S8** DSC traces of different esterified lignin fractions: (a) F1, (b) F2, (c) F3, (d) F4, and (e) F5

**Table S7** Solubility test of different esterified lignin fractions

	$\delta_d\text{MPa}^{0.5}$	$\delta_p\text{MPa}^{0.5}$	$\delta_h\text{MPa}^{0.5}$	SKL*	F1	F2	F3	F4	F5	Solubility level
Acetone	16	10	7	++	+++	+++	+++	+++	+++	 +
Tetrahydrofuran (THF)	17	5.7	8	++	+++	+++	+++	+++	+++	 ++
N-Methyl-2-pyrrolidone (NMP)	18	12	7.2	++	+++	+++	+++	+++	+++	 +++
Toluene	18	1.4	2	+	+	+	++	++	+++	 +++
Ethyl acetate	16	5.3	7.2	+	+++	+++	+++	+++	+++	 +++

\* the solubility test was performed by mixing 5 mg lignin fraction with 0.5 ml different organic solvent in a 2 ml vial, following with vortex mixing thoroughly. After overnight stabilization, the solubility was evaluated based on above images.



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