Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

[N-Methyl-2-pyrrolidone][C1-C4 Carboxylic Acid]: A Novel Solvent System with Exceptional Lignin Solubility

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S1. Materials and Characterization

S1.1 Materials

N-Methyl-2-pyrrolidone (NMP, >99%), propionic acid (Pro, ≥99.5%), oxalic acid (Oxa, ≥99%), malonic acid (Mal, 99%), succinic acid (Suc, ≥99%), 4-nitroaniline (4-NA, ≥99%), 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate (Dye 30, 90%), and alkali lignin were purchased from Sigma Aldrich. N, N-diethyl-4-nitroaniline (DENA, 97%) was purchased from Oakwood chemical. Formic acid (For, 97%) and acetic acid (OAc, 100%) were purchased from Acros organics and Fisher Scientific, respectively. All chemicals were used as received without further treatment.

S1.2 Preparation of [NMP][C1-C4 Carboxylic Acid]

NMP/monocarboxylic acid (mono-CA) solvent was prepared with 1:1 molar ratio. NMP/dicarboxylic acid (di-CA) was prepared with three different molar ratios, 1:1, 1.5:1 and 2:1. Specifically, carboxylic acid (CA) was kept in ice water and NMP was added dropwise into the system with magnetic stirring. After adding NMP, the mixture was further stirred for 48 hours at room temperature with purged N_2 gas.

S1.3 Characterization

The density of the solvents was determined by gravimetric analysis. After calibrating a 1.0 mL pipet with 1.0 g/mL of water, the pipette was used to transfer 1.0 mL of each solvent to measure the solvent mass. The density is calculated based on the measured mass and volume. Each measurement was repeated 10 times and the average value is reported. All measurements were taken at 40 °C (40±1 °C). The structures of solvents were analyzed by proton nuclear magnetic resonance (1H NMR, Varian Mercury-300) in D_2O at 300 MHz. Fourier transform infrared (FT-IR) spectra were recorded with a Digilab Excalibur FTS 3000 series FT-IR Spectrometer using KBr pellets, and the thickness of the pellet is about 1 mm

Solvent polarity was characterized by Kamlet–Taft empirical parameters, including hydrogen bond donor acidity (α), hydrogen bond acceptor basicity (β) and dipolarity/polarizability (Π*). These parameters are calculated from the peak wave length of UV-Vis absorption spectrum. The spectrum is recorded by UV-1601 Shimadzu spectrophotometer in the presence of solvatochromic dyes of Dye 30, DENA and 4-NA. The concentration of probe molecule in solvents is 1×10^{-5} M for Dye 30, 5×10^{-5} M for both DENA and 4-NA. Then, the polarity parameters α, β, Π^*, and $E_T(30)$ can be calculated by using equations (1)~(4).[1]

$$\alpha = \left[E_T(30) - 14.6 \times \left(\Pi^* - 0.23\right) - 30.31\right]/16.5 \tag{1}$$

$$\beta = \left[1.035 \times \frac{10000}{\lambda_{(max,DEMA)}} - \frac{10000}{\lambda_{(max,4-NA)}} + 2.64\right]/2.8 \tag{2}$$

$$\Pi^* = (27.52 - 10000/\lambda_{(max,DEMA)})/3.182 \tag{3}$$

$$E_T(30) = 28591/\lambda_{(max,Dye\ 30)} \tag{4}$$

The thermal decomposition temperature (T_d) of the solvents was determined by thermogravimetric analysis (TGA, TA instrument Q500) in N_2 atmosphere from 20 to 500 °C with a heating rate of 10 °C/min. The glass transition temperature (T_g), devitrification temperature (T_c) and melting temperature (T_m) were determined with a differential thermal analyzer (DSC, TA Instruments Q2000) from -150 to 60 °C for the mono-CA based solvents and from -150 °C to 100 °C for the di-CA based solvents with a heating rate of 10 °C/min, after cooling samples to -150 °C in aluminium pan.

The viscosity of the solvents at 30 s^{-1} shear rate was reported using a Bohlin CVO 100 rheometer. A cone-on-plate geometry was used with a 1^{o} cone angle and 20 mm cone diameter. The lower plate has a diameter of 60 mm. During the experiments, the temperature of the solvents was maintained at 40 and 90 °C throughout the measurement.

S1.4 Solubility of lignin

To determine lignin solubility, 25 mg lignin was added to a glass vial containing 1.0 g [NMP][CA] solvent and stirred at 90 °C under N_2 gas, and visually checked whether it was soluble. If the solution was clear with no undissolved solids, the amount of the lignin was incrementally adjusted to increase the mass fraction and stirred for another 24 hours at 90 °C. The solubility was determined when the solution remained heterogeneous within 24 hours.

S2. NMR Results

S2.1 [NMP][mono-CA]

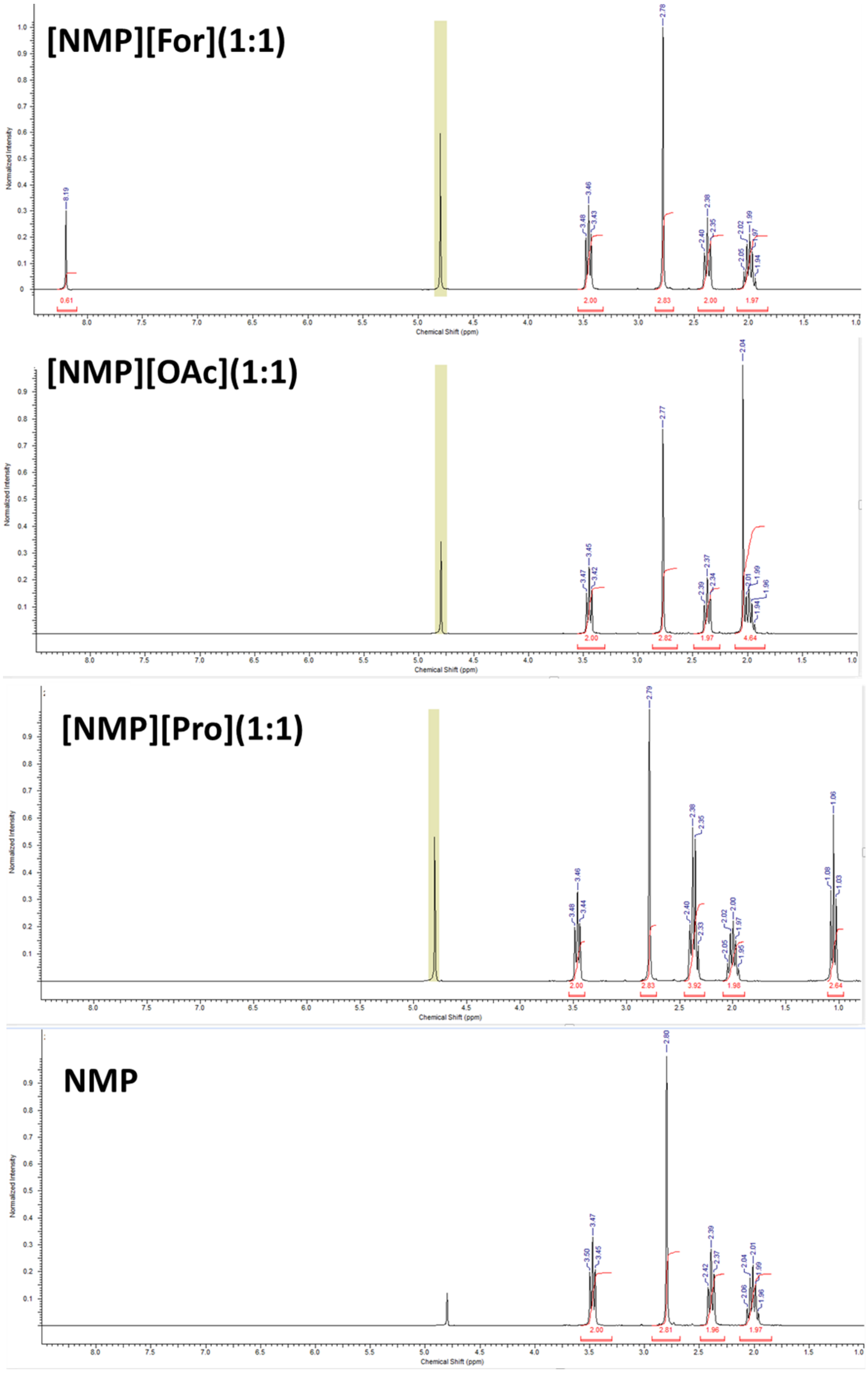

Figure S1. NMR curves of [NMP][mono-CA] solvents.

S2.2 [NMP][Oxa]

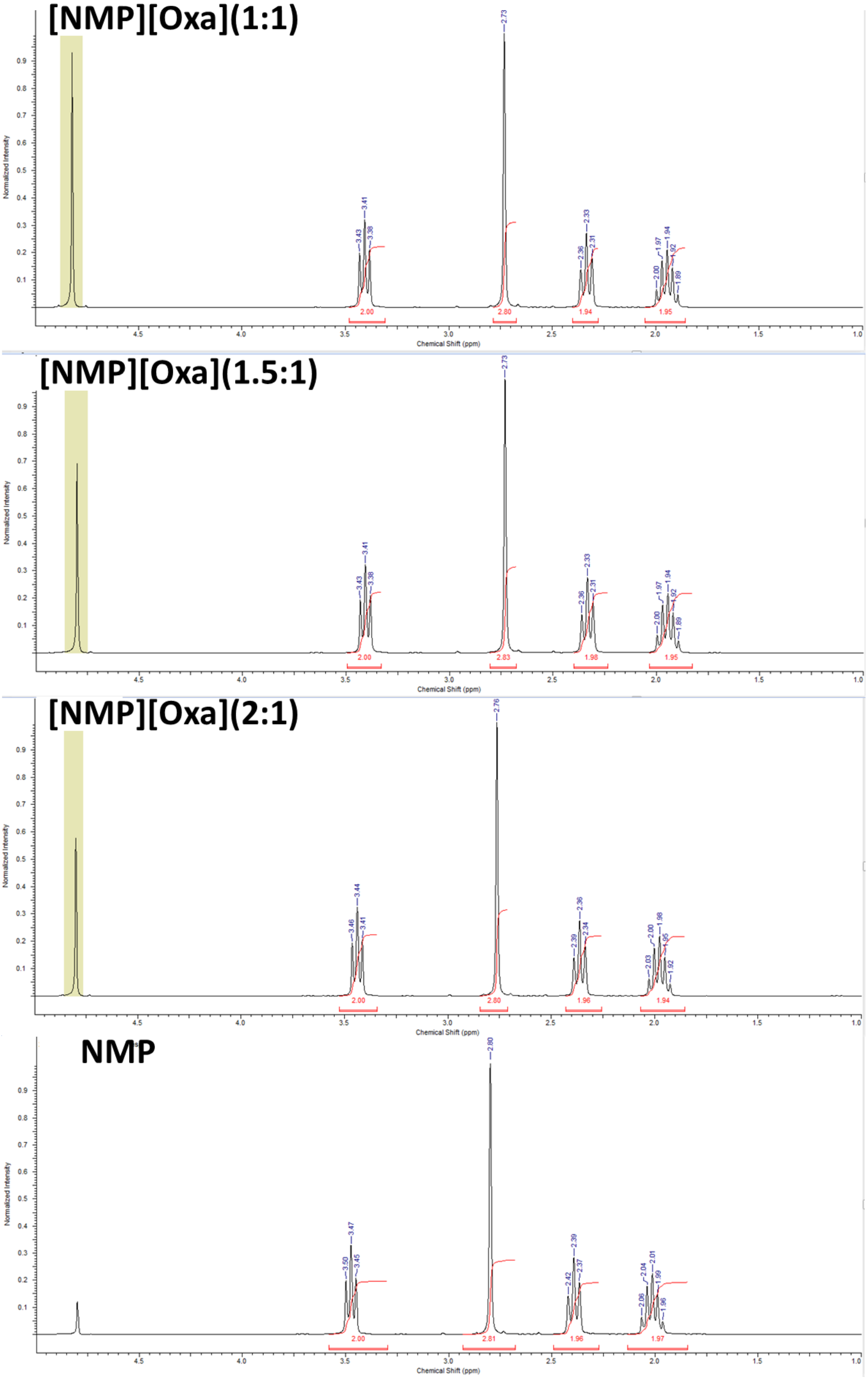

Figure S2. NMR curves of [NMP][OXA] solvents.

S2.3 [NMP][Mal] solvents

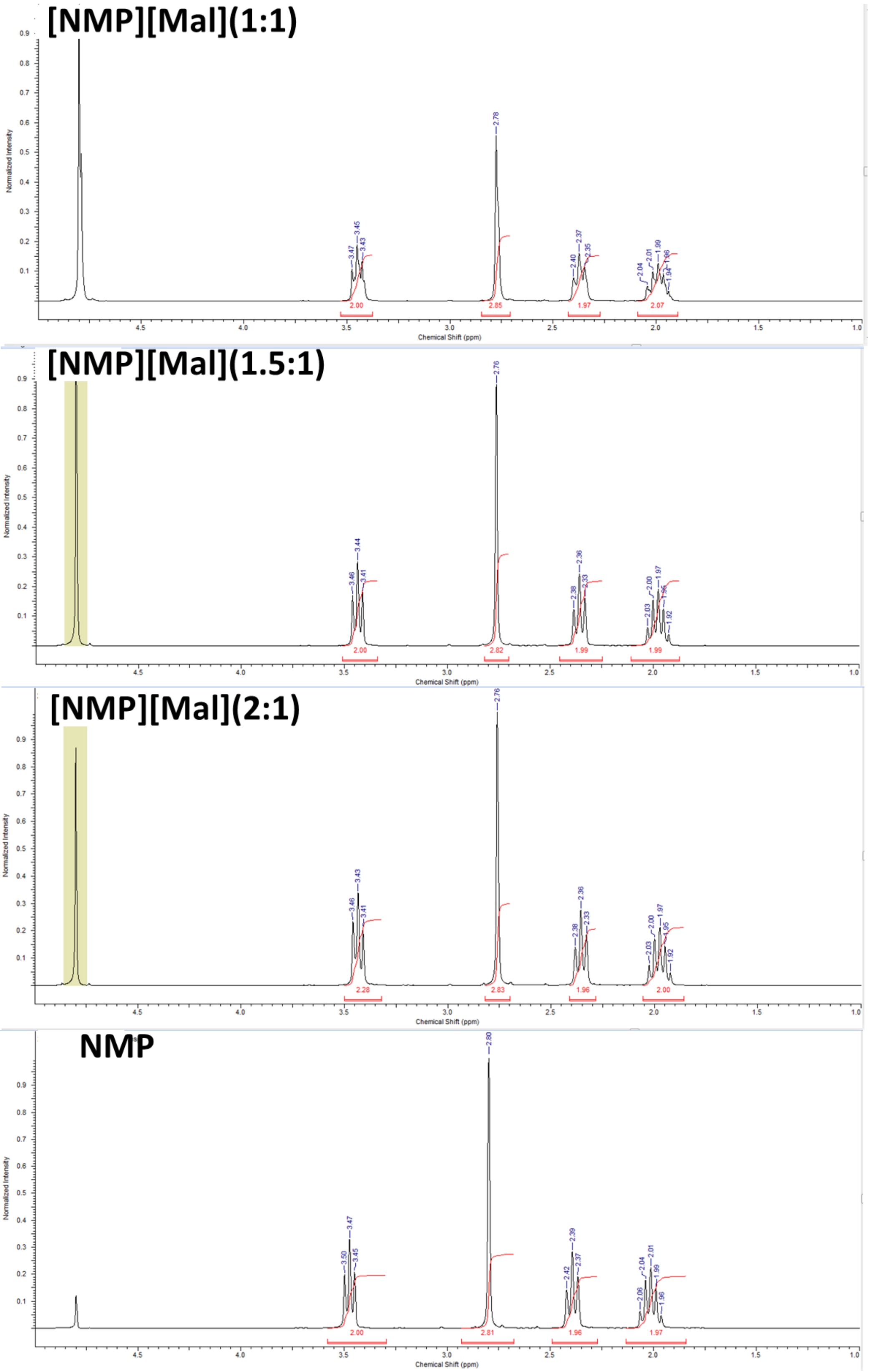

Figure S3. NMR curves of [NMP][Mal] solvents.

S2.4 [NMP][Mal] solvents

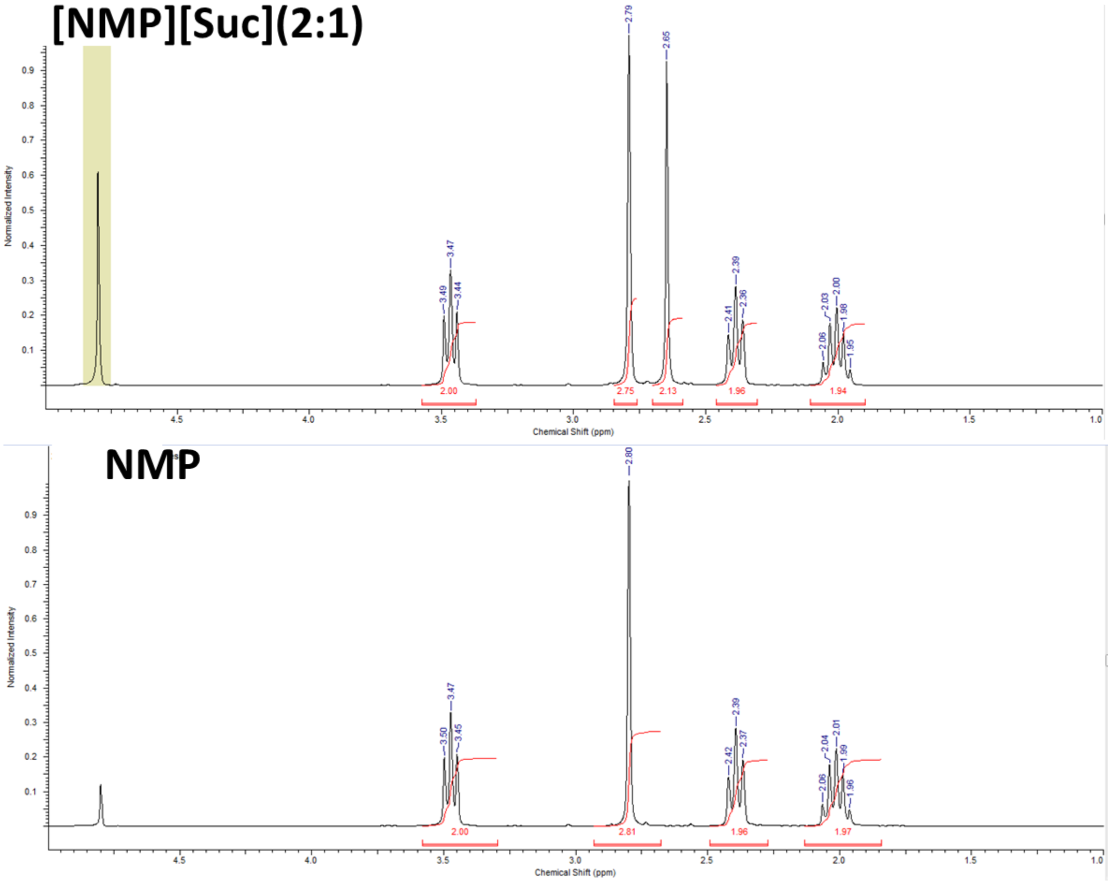

Figure S4. NMR curves of [NMP][Mal] solvents.

S3. FT-IR results

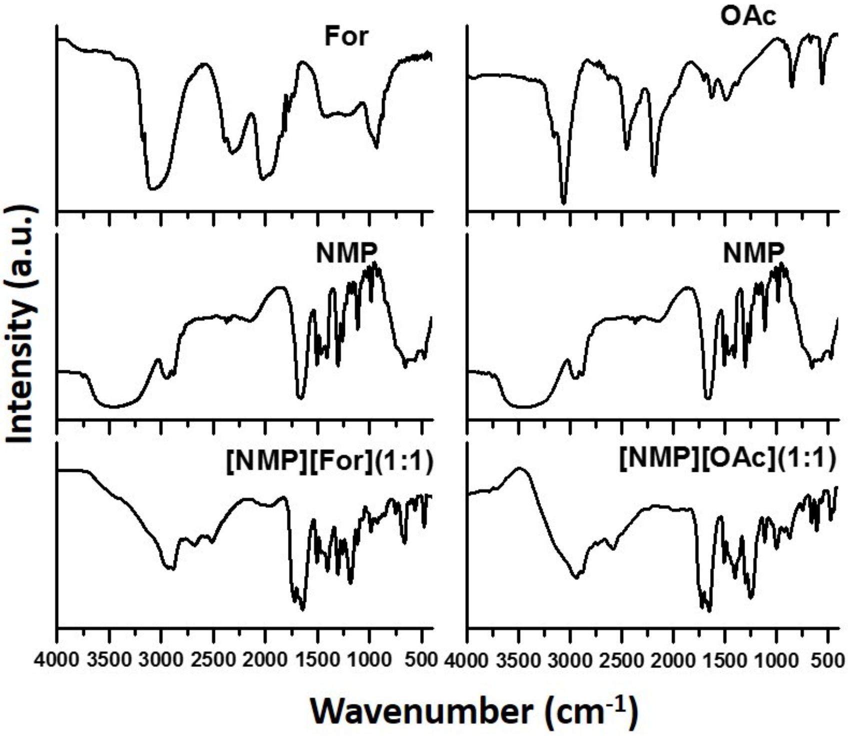

Figure S5. The FT-IR spectrum of [NMP][mono-CA] solvents.

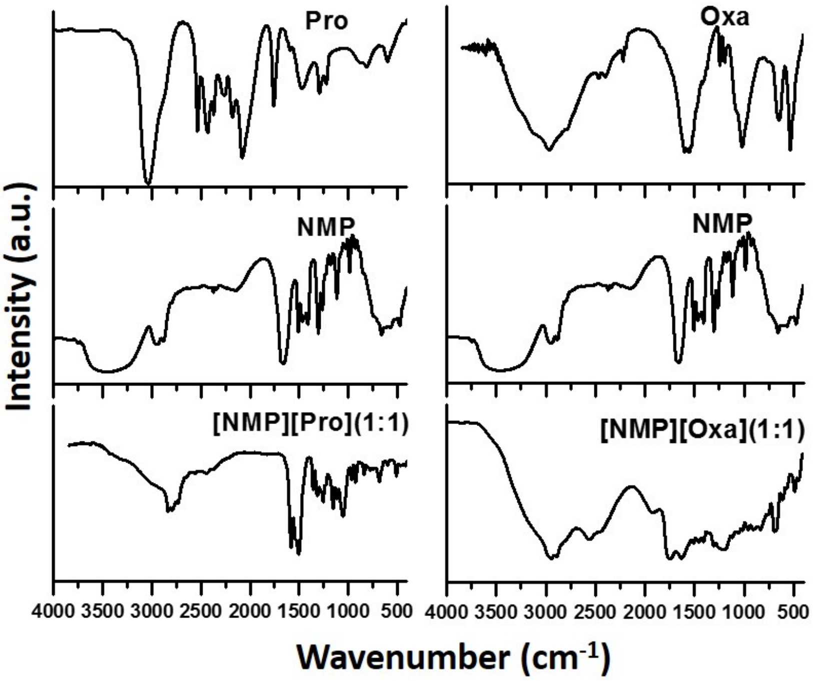

Figure S6. The FT-IR spectrum of [NMP][Pro or Oxa] solvents.

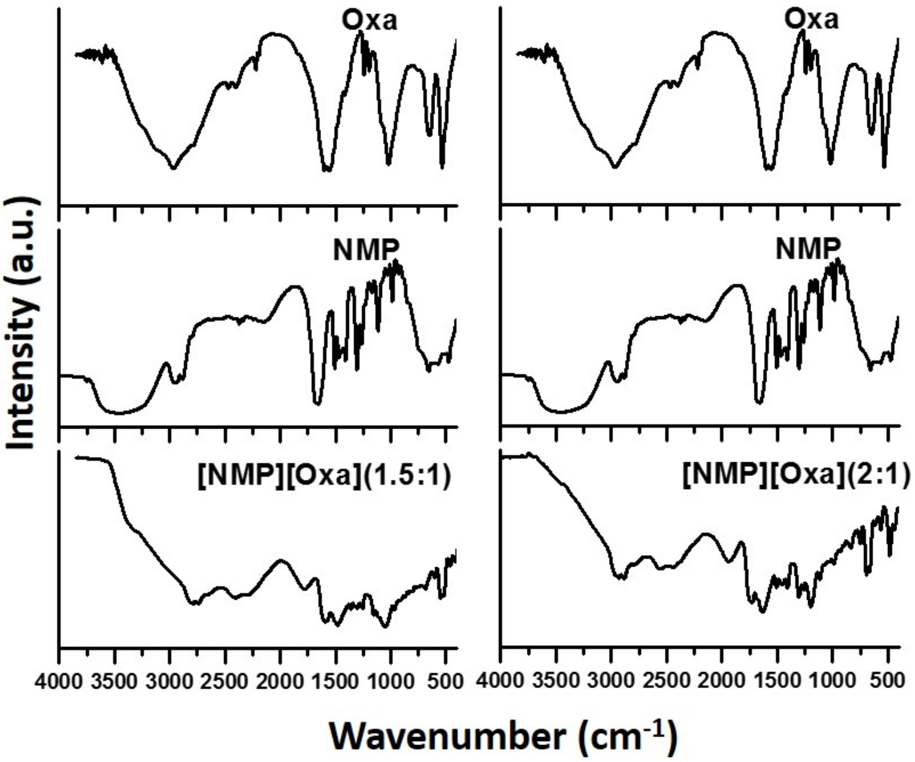

Figure S7. The FT-IR spectrum of [NMP][Oxa] solvents.

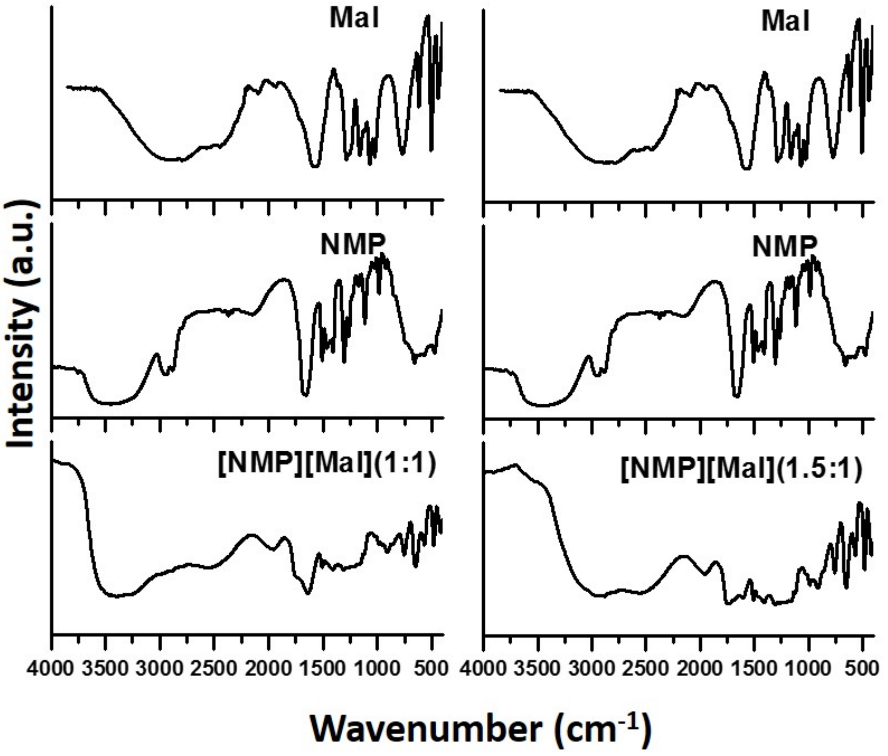

Figure S8. The FT-IR spectrum of [NMP][Mal] solvents.

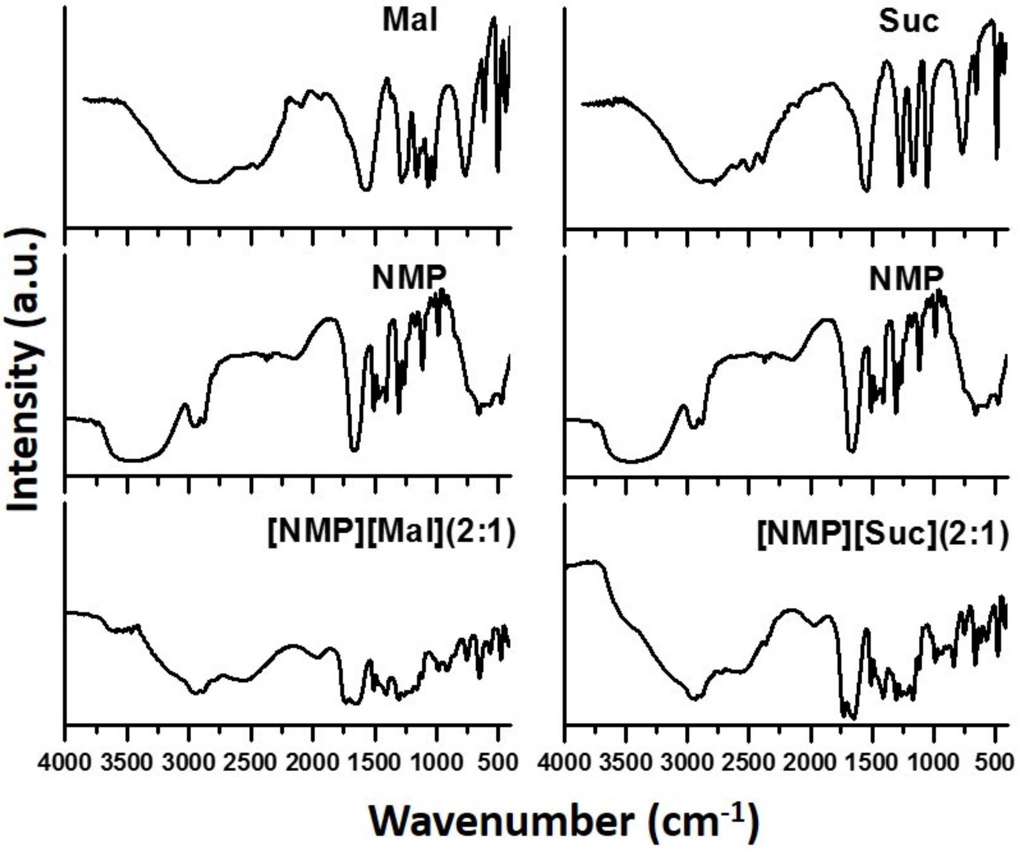

Figure S9. The FT-IR spectrum of [NMP][Mal or Suc] solvents.

S4. TGA and DSC results

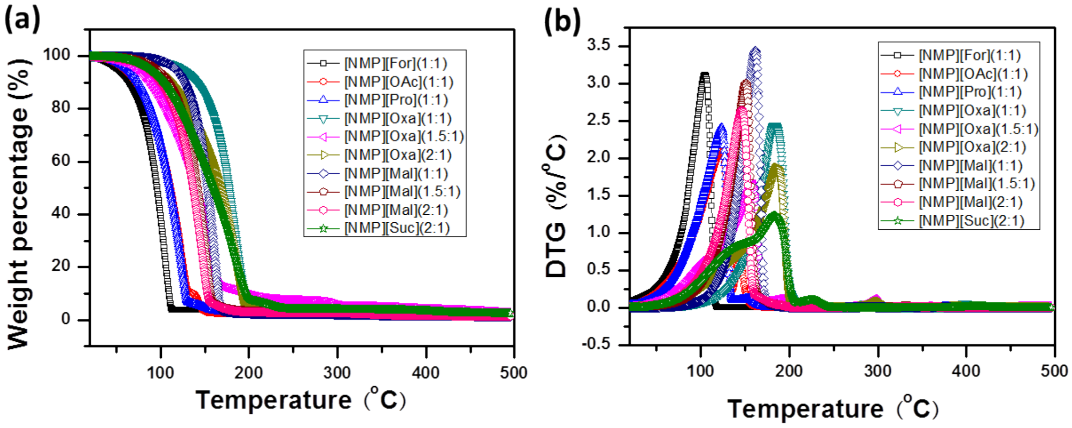

Figure S10. (a) TGA, (b) DTG curves of [NMP][CA] solvents under N_2 atmosphere.

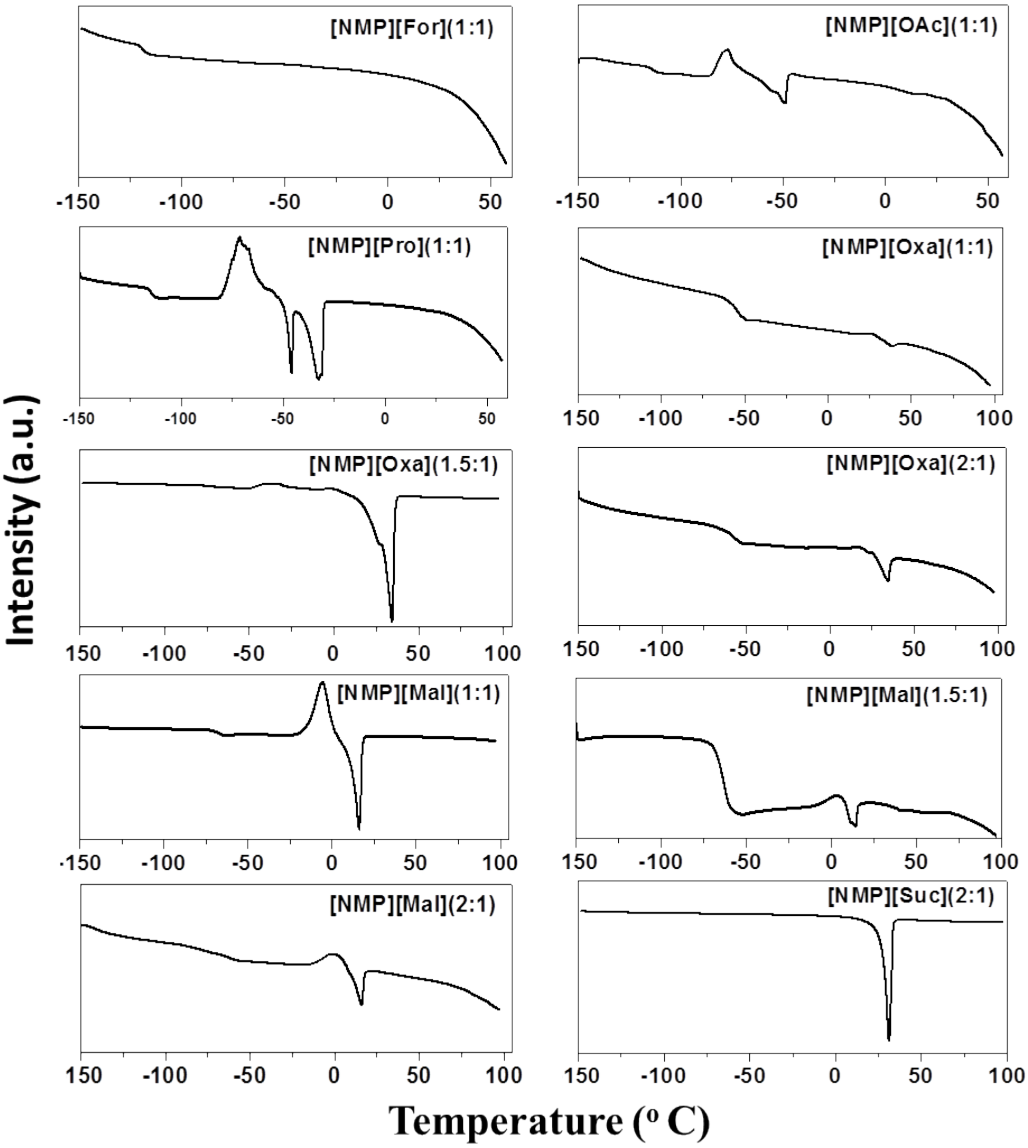

Figure S11. DSC curves of [NMP][CA] solvents.

Table S1. Summation of lignin solubility in different solvents.

	ILs	Maximum lignin solubility (%)	Test conditions	Raw materials	Ref.
1	[Mmim][CH_3SO_4]	>50	90 °C,24h	Kraft lignin	[2]
2	[Emim][BF_4]	5± 5.00	25 °C	Organosolv lignin	[3]
3	[Emim][$(SO_2CF_3)_2N$]	5± 5.00	25 °C	Organosolv lignin	[3]
4	[Emim][$O_2P(OCH_2CH_3)_2$]	52	25 °C	Organosolv lignin	[3]
5	[Emim][CH_3SO_3]	45	25 °C	Organosolv lignin	[3]
6	[Emim][OAc]	54	25 °C	Organosolv lignin	[3]
7	[Emim][NCS]	44~48	25 °C	Organosolv lignin	[3]
8	[Emim][CF_3SO_3]	55	25 °C	Organosolv lignin	[3]
9	[Emim][CF_3CO_2]	54	25 °C	Organosolv lignin	[3]
10	[Bmim][OAc]	>18	110 °C	Alkali lignin	[4]
11	[Bmim][CF_3SO_3]	>50	90 °C,24h	Kraft lignin	[2]
12	[Bmim][BF_4]	4	90 °C,24h	Kraft lignin	[2]
13	[Bmim][PF_6]	Insoluble	70–120 °C	Kraft lignin	[5]
14	[Bmim]Cl	>10	90 °C,24h	Kraft lignin	[6]
15	[Bmim]Br	17.5(g/L)-1.8%	75 °C	Kraft lignin; Assuming density=1.4 Kg/L	[5]
16	[Hmim][CF_3SO_3]	275(g/L)-28%	70 °C	Kraft lignin	[5]
17	[Bm_2im][BF_4]	14.5(g/L)-1%	70–100 °C	Kraft lignin	[5]
18	[$CH_3(OCH_2CH_2)_2$-eim][OAc]	>21	110 °C	Alkali lignin	[4]
19	[$CH_3(OCH_2CH_2)_3$-eim][OAc]	>21	110 °C	Alkali lignin	[4]
20	[Mim][OAc]	>50	90 °C,24h	Kraft lignin	[7]
21	[Amim]Cl	>30	90 °C,24h	Kraft lignin	[2]
22	[Bzmim]Cl	>10	90 °C,24h	Kraft lignin	[2]
23	[Cyanomim]Br	9.53	90 °C,20min	Alkali lignin	[8]
24	[Prmim]Br	6.2	90 °C,20min	Alkali lignin	[8]
25	70%[Emim][OAc]+30%H_2O	30.50	60 °C	Organosolv lignin	[9]
26	70% [Bmim][OAc]+30%H_2O	43.90	60 °C	Organosolv lignin	[9]
27	70% [Hmim][OAc]+30%H_2O	39.80	60 °C	Organosolv lignin	[9]
28	70% [Omim][OAc]+30%H_2O	28.30	60 °C	Organosolv lignin	[9]
29	70% [Bmim][CH_3SO_3]+30%H_2O	48.30	60 °C	Organosolv lignin	[9]
30	[Ch][Gly]	22	90 °C,24h	Kraft lignin	[10]
31	[Ch][Ala]	18	90 °C,24h	Kraft lignin	[10]
32	[Ch][Ser]	17	90 °C,24h	Kraft lignin	[10]
33	[Ch][Thr]	16	90 °C,24h	Kraft lignin	[10]
34	[Ch][Val]	7	90 °C,24h	Kraft lignin	[10]
35	[Ch][Leu]	15	90 °C,24h	Kraft lignin	[10]

36	[Ch][Ile]	17	90 °C,24h	Kraft lignin	[10]
37	[Ch][Met]	15	90 °C,24h	Kraft lignin	[10]
38	[Ch][Phe]	14	90 °C,24h	Kraft lignin	[10]
39	[Ch][Trp]	9	90 °C,24h	Kraft lignin	[10]
40	[Ch][Pro]	17	90 °C,24h	Kraft lignin	[10]
41	[Ch][Asp]	<1	90 °C,24h	Kraft lignin	[10]
42	[Ch][Glu]	2.60	90 °C,24h	Kraft lignin	[10]
43	[Ch][Asn]	1.60	90 °C,24h	Kraft lignin	[10]
44	[Ch][Gln]	5	90 °C,24h	Kraft lignin	[10]
45	[Ch][Lys]	14	90 °C,24h	Kraft lignin	[10]
46	[Ch][His]	14	90 °C,24h	Kraft lignin	[10]
47	[Ch][Arg]	11	90 °C,24h	Kraft lignin	[10]
48	[Ch][For]	19	90 °C,24h	Kraft lignin	[11]
49	[Ch][OAc]	19	90 °C,24h	Kraft lignin	[11]
50	[Ch][But]	17	90 °C,24h	Kraft lignin	[11]
51	[Ch][Piv]	19	90 °C,24h	Kraft lignin	[11]
52	[Ch][Hex]	17	90 °C,24h	Kraft lignin	[11]
53	[Ch][Oct]	16	90 °C,24h	Kraft lignin	[11]
54	[Ch][i-Oct]	17	90 °C,24h	Kraft lignin	[11]
55	[Ch][TFA]	21	90 °C 24h	Kraft lignin	[11]
56	[Ch][Nic]	25	90 °C,24h	Kraft lignin	[11]
57	[Ch][Bz]	17	90 °C,24h	Kraft lignin	[11]
58	[Ch][Glc]	18	90 °C 24h	Kraft lignin	[11]
59	[Ch][Lac]	24	90 °C,24h	Kraft lignin	[11]
60	[Ch][Oxa]	16	90 °C,24h	Kraft lignin	[11]
61	$[Ch]_2[Oxa]$	7	90 °C,24h	Kraft lignin	[11]
62	[Ch][Suc]	6	90 °C,24h	Kraft lignin	[11]
63	$[Ch]_2[Suc]$	2	90 °C,24h	Kraft lignin	[11]
64	[Ch][Mal]	15	90 °C,24h	Kraft lignin	[11]
65	$[Ch]_2[Mal]$	15	90 °C,24h	Kraft lignin	[11]
66	[Ch][Gly]	21	90 °C,24h	Kraft lignin	[11]
67	[Ch][Ala]	19	90 °C,24h	Kraft lignin	[11]
68	[Ch][Boc-Gly]	15	90 °C,24h	Kraft lignin	[11]
69	[Ch][Cbz-Gly]	15	90 °C,24h	Kraft lignin	[11]
70	[Ch][Asp]	2	90 °C,24h	Kraft lignin	[11]
71	$[Ch]_2[Asp]$	5	90 °C,24h	Kraft lignin	[11]
72	[DMEA][For]	28	90 °C,24h	Kraft lignin	[6]
73	[DMEA][OAc]	19	90 °C,24h	Kraft lignin	[6]
74	$[Me(OCH_2CH_2)_2$-$(CH_2CH_3)_3N][OAc]$	>13	110 °C	Alkali lignin	[4]
75	[Py][Ac]	>50	90 °C,24h	Kraft lignin	[7]
76	$[Bmpy][PF_6]$	Insoluble	70–120 °C	Kraft lignin	[5]
77	[Pyrr][OAc]	>50	90 °C,24h	Kraft lignin	[7]
78	$[P_1Me][Met]$	35	60 °C	Alkali lignin	[12]

79	[P$_1$Me][Ser]	30	60 °C	Alkali lignin	[12]
80	[P$_1$Me][Trp]	0	60 °C	Alkali lignin	[12]
81	[P$_1$Me][Asp]	15	60 °C	Alkali lignin	[12]
82	[P$_1$Me][Glu]	25	60 °C	Alkali lignin	[12]
83	[P$_1$Me][Cys]	5	60 °C	Alkali lignin	[12]
84	[P$_1$Me][Gly]	20	60 °C	Alkali lignin	[12]
85	[P$_1$Me][Ala]	20	60 °C	Alkali lignin	[12]
86	[P$_1$Me][Val]	5	60 °C	Alkali lignin	[12]
87	[P$_1$Me][Leu]	25	60 °C	Alkali lignin	[12]
88	[P$_1$Me][Iso]	15	60 °C	Alkali lignin	[12]
89	[P$_1$Me][Pro]	30	60 °C	Alkali lignin	[12]
90	[P$_1$Me][Phe]	15	60 °C	Alkali lignin	[12]
91	[P$_1$Me][Thr]	20	60 °C	Alkali lignin	[12]
92	[P$_1$Me][Tyr]	35	60 °C	Alkali lignin	[12]
93	[P$_1$Me][His]	35	60 °C	Alkali lignin	[12]
94	[P$_1$Me][Lys]	40	60 °C	Alkali lignin	[12]
95	[P$_1$Me][Arg]	35	60 °C	Alkali lignin	[12]
96	Water	<0.1	23 °C	Kraft lignin	[13]
97	Acetone/water(3:7-v/v)	<1	23 °C	Kraft lignin	[13]
98	Acetone/water(1:1-v/v)	~13	23 °C	Kraft lignin	[13]
99	Acetone/water(7:3-v/v)	~9	23 °C	Kraft lignin	[13]
100	Acetone	<0.5	23 °C	Kraft lignin	[13]
101	Ethanol/water(1:1-v/v)	<0.5	23 °C	Kraft lignin	[13]
102	Ethanol/water(7:3-v/v)	~2	23 °C	Kraft lignin	[13]
103	Ethanol	<0.5	23 °C	Kraft lignin	[13]
104	Acetonitrile	<0.5	23 °C	Kraft lignin	[13]
105	Cyclohexane	<0.5	23 °C	Kraft lignin	[13]
106	1,2-dichloroethane	<0.5	23 °C	Kraft lignin	[13]
107	Dichloromethane	<0.1	23 °C	Kraft lignin	[13]
108	Diethylether	<0.1	23 °C	Kraft lignin	[13]
109	Hexane	<0.1	23 °C	Kraft lignin	[13]
110	Isobutylmethylketone	<0.5	23 °C	Kraft lignin	[13]
111	1 wt% KOH aqueous solution	>10	23 °C	Kraft lignin	[13]
112	Dimethyl sulfoxide	>20	90 °C	Kraft lignin	[13]
113	Pyridine	>50	90 °C,24h	Kraft lignin	[7]
114	Methylimidazole	>50	90 °C,24h	Kraft lignin	[7]
115	Pyrrolidone	7.98±0.10	90 °C,24h	Kraft lignin	[7]
116	HAc	0.72±0.04	90 °C,24h	Kraft lignin	[7]
117	[NMP][For]	50	90 °C,24h	Alkali lignin	This work
118	[NMP][oAc]	60	90 °C,24h	Alkali lignin	This work
119	[NMP][Pro]	55	90 °C,24h	Alkali lignin	This work
120	[NMP][Oxa](1-1)	35	90 °C,24h	Alkali lignin	This work
121	[NMP][Oxa](1.5-1)	40	90 °C,24h	Alkali lignin	This work

122	[NMP][Oxa](2-1)	35	90 °C,24h	Alkali lignin	This work
123	[NMP][Mal](1-1)	37.5	90 °C,24h	Alkali lignin	This work
124	[NMP][Mal](1.5-1)	50	90 °C,24h	Alkali lignin	This work
125	[NMP][Mal](2-1)	55	90 °C,24h	Alkali lignin	This work
126	[NMP][Suc](2-1)	45	90 °C,24h	Alkali lignin	This work
127	N-Methyl-2-pyrrolidone	5	90 °C,24h	Alkali lignin	This work
128	Formic acid	1	90 °C,24h	Alkali lignin	This work
129	Propanoic acid	1	90 °C,24h	Alkali lignin	This work
130	Acetic acid	1	90 °C,24h	Alkali lignin	This work
131	[Pyrr][For]	45	90 °C, 24h	Alkali lignin	This work
132	[Pyrr][OAc]	45	90 °C, 24h	Alkali lignin	This work
133	[Pyrr][Pro]	40	90 °C, 24h	Alkali lignin	This work

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