In-situ amino-lignin production from biomass fractionation towards high-efficacy CO_2 capture

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1. Chemicals and materials

All chemicals were purchased from suppliers and used directly without purification. Formic acid (≥98%, Sigma-Aldrich), aniline (≥99.5%, Sigma-Aldrich), and ether (HPLC grade, ≥99.8%, Sigma-Aldrich) were used for the fractionation and purification from lignocellulosic biomass. Veratrylglycerol-β-guaiacyl ether (VG, 97%, Alfa Aesar), a lignin dimer with β–O–4 linkage, was used for mechanism study. 1-hexadecanol (99%, Sigma-Aldrich) was used as the internal standard for quantification analysis of reaction products; Pyridine (HPLC grade, ≥99.9%, Sigma-Aldrich), Chlorotrimethylsilane (TMCS, ≥99.0%, Sigma-Aldrich) and *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA, ≥99.9%, Sigma-Aldrich) were used for sialylation of reaction products; 1,4-dioxane (HPLC grade, ≥99.5%, Sigma-Aldrich), benzene (≥99.0%, Sigma-Aldrich), ethanol (HPLC grade, ≥99.8%, Sigma-Aldrich), acetic acid (HPLC grade, ≥99.7%, Sigma-Aldrich) and dichloromethane (HPLC grade, ≥99.8%, Sigma-Aldrich) were applied to extract and purify the milled wood lignin (MWL); n-Hexane (Sigma-Aldrich), tert-Butyl methyl ether (HPLC grade, ≥99.8%, Sigma-Aldrich) and acetone (HPLC grade, ≥99.8%, Sigma-Aldrich) were applied as the spread solvents for separating the reaction products; Tetrahydrofuran (THF, HPLC grade, ≥99.8%, Sigma-Aldrich) and hydrochloric acid (HCl, 37%, Sigma-Aldrich) were used to the formation of lignin micro/nanoparticles (LMNPs). Dimethyl sulfoxide (DMSO, 99.8% D, Sigma-Aldrich), pyridine (anhydrous, dried by KOH), chloroform-d_6 ($CDCl_3$, 99.8% D, Sigma-Aldrich), Chromium(III) acetylacetonate ($Cr(acac)_3$, 97%, Sigma-Aldrich), endo-N-hydroxy-5-norbornene-2,3-dicarboximide (NHND, 97%, Sigma-Aldrich) and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Cl-TMDP, 95% Sigma-Aldrich) were used for NMR analysis. The enzyme was purchased from Ningxia

Imperial Jade Bio-Technology Co., Ltd. The enzyme activity (151.7 FPU/g) was determined according to the procedure from the National Renewable Energy Laboratory (NREL/TP-510-42628). Three kinds of wood (poplar, pine, and bamboo) were obtained from a pulp mill in China.

2. Experimental methods

2.1 *In-situ* lignin amination during fractionation of lignocellulosic biomass

The fractionation process was performed in a 250 mL hydrothermal reactor equipped with tetrafluoroethylene lining using 85% formic acid/aniline as a reaction reagent. The chips were fully mixed with the reaction reagent at a solid-liquid ratio of 1:10 and then reacted in an oil bath (140 °C) for 2 h. The volume ratio of the formic acid and aniline is 90:10 (v/v) and the volumes of reaction reagent were 150 mL. The oil bath temperature was increased to 140 °C in 30 min and the timing began. After the reaction, the slurry was filtered and fully washed with hot formic acid (70 °C, 4 times) until the filtrate was colorless. The filtrate was collected and then evaporated at 40 °C to recycle the formic acid. The condensed liquid was dropped into ether (10 times ether per 1 volume of liquid). The residue was collected by filtration, dried, and named aminated lignin. The filtrate was evaporated the ether, and the residual formanilide was collected.

2.2 Preparation of milled wood lignin (MWL)

Three different kinds of MWL were prepared according to the following procedure. The ground wood power was removed extractives using benzene /ethanol (2/1, v/v) for 8 h. After that, the extracted powder was ground by a ball mill for 72 h in toluene medium. The ball mill ground

powder was extracted with dioxane/H_2O solution (96/4, v/v) at a solid-liquid ratio (1:25) for 24h and extracted three times. The liquid phase was collected. The extraction was removed the solvent by reducing evaporation and dried by vacuum oven. The solid was named crude lignin. The crude lignin was dissolved into an acetic acid-water solution (9:1, v/v), and precipitated in a dichloromethane-ethanol solution (2:1, v/v), the precipitated solid was dried and named MWL.

2.3 *In-situ* amination of lignin dimer model

500 mg VG was dissolved in 5 mL reaction reagent (85% formic acid: aniline (9:1, v/v)) in a 10 mL hydrothermal reactor, then reacted in an oil bath at 140 °C for 2 h. After the reaction, the reactor was cooled down. The liquid was concentrated and dried by vacuum dryer to remove the reaction reagent (formic acid). The reaction compounds were collected for further analysis.

2.4 Formation of amino-LMNPs

The formation of LMNPs used solvent-antisolvent methods. The THF was used as a solvent to dissolve aminated lignin at different initial concentrations. Then the antisolvent was added by different methods. The different methods were named, and more details were shown in Fig. 4a. The MillQ water was used as antisolvent, and the ratio of THF and water was kept at 1:9. After the addition of antisolvent, the THF was recycled by rotary evaporation, and the suspension was concentrated by centrifugation.

To provide additional CO_2 binding sites, acid hydrolysis was employed to cleave the bonds between amino and aldehyde groups, converting amide into amino groups. Specifically, 10 mg/mL of aminated LMNPs were mixed with hydrochloric acid at a concentration of 1 mol/L.

The mixture was stirred at 500 rpm and kept at room temperature for 24 hours. After the reaction, the hydrochloric acid solution was recovered by centrifugation, and the mixture was washed with MilliQ water until the supernatant reached a neutral pH. The solid was redispersed in water to obtain an amino-LMNPs suspension at a concentration of 5 mg/mL.

2.5 CO_2 adsorption

The CO_2 adsorption of amino-LMNPs was determined by two different methods.

Wet method: the amino-LMNPs colloidal suspension was used to adsorb CO_2 at room temperature, and the schematic diagram of the experimental setup is shown in Fig. S16. The CO_2 gas was purged into LMNPs colloidal suspension at 1 bar and 100 mL/min for 30 min. After the adsorption, the CO_2 adsorption capacity was calculated by gravimetric method. Before testing, the amino-LMNPs colloidal suspension was degassed by an ultrasonic bath. The effect of the resources, formation methods, and the LMNPs concentrations were detected. The adsorbed LMNPs were desorbed by using an HCl solution (1 M) at a concentration of 10 mg/mL. The regenerated LMNPs colloidal suspension was performed by testing the cyclic capacity for 5 cycles.

Dry method: The CO_2 adsorption capacity by the amino-LMNPs was determined using thermogravimetric analyses (TGA, TA Instrument, TGA Q500). The amino-LMNPs were degassed at 105 °C in nitrogen (100 mL/min, 1 bar) for 60 min and then cooled down to 25 °C under nitrogen flow. When the samples reached the adsorption temperature, nitrogen was switched to CO_2 (100 mL/min, 99.99%) at an atmospheric pressure of 1 bar. Once the adsorption reached equilibrium at 25 °C, the amount of adsorbed CO_2 was recorded for 60 min

as a function of time. The weight increase of the CO_2 adsorption capacity at 25 °C was determined by switching the atmosphere from nitrogen to CO_2.

2.6 Enzymatic hydrolysis of the raw materials and cellulose fractions

The enzymatic hydrolysis of the substrates (raw materials and cellulose fractions after delignification) was according to the previous research method.[1] In short: 3 g of substrates was accurately weighed into a pre-sterilized 100 mL conical flask. The acetic acid-sodium acetate buffer solution (pH 4.8, 5.0 wt%) and cellulase (50 FPU/g substrate) were added. The enzymatic hydrolysis was carried out in a constant temperature oscillating reactor (50 °C) for 72 h, and the glucose content in the supernatant was determined by ion chromatography.

3. Analytical methods

3.1 Chemical components analysis of lignin and lignocellulosic biomass

The chemical components of lignocellulosic biomass and lignin mainly include extractives, cellulose, hemicelluloses, and lignin (Kalson lignin and acid-soluble lignin).

The extractives were extracted by benzene-ethanol solution (2:1, v/v). Briefly, 2 $\pm$ 0.0001 g samples were wrapped with pre-extracted filter paper, and then extracted with solution in Soxhlet extractor for 6 h. After the extraction, the residual solid was collected and dried by vacuum dryer. The content of the extractives was calculated by gravimetric method followed the equation (1):

$$Extractives = \frac{m_1 - m_0}{m_0} \times 100 \quad (1)$$

where, m_0 is the weight of the solid after extraction; m_1 is the weight of the samples.

The cellulose content was analyzed by direct nitric acid-ethanol hydrolysis. 1 ± 0.0001 g was mixed with 25 mL nitric acid-ethanol solution (1:4, v/v) in a 250 mL flask equipped with a condenser. The flask was heated in boiling water bath for 1 h. After heating, the mixture was filtered by G2 funnel. The solid was extracted until the filtrate was colorless, and washed by fresh nitric acid-ethanol solution and hot water until the filtrate was neutral. The residue in the G2 funnel was dryer in a 105 °C oven. The content of cellulose was calculated following the equation (2):

$$Cellulose = \frac{m_1 - m_2}{m_0 \times (1 - w)} \times 100 \quad (2)$$

where, m_1 is the weight of the residue and G2 funnel after drying; m_2 is the weight of the G2 funnel; m_0 is the weight of the samples; w is the moisture content in the samples.

The content of lignin (Klason and acid-soluble lignin) was performed according to the TAPPI standard. 0.500 ± 0.002 g samples were fully mixed with 7.5 mL 72% H_2SO_4 in a flask placed in an ice water bath and then reacted for 2 h at room temperature. After that, the mixture was diluted by MillQ water until the concentration of H_2SO_4 to 3%, and boiling for 4h. The mixture was filtered by G3 glass sinter funnel, and the filtrate was collected. The residue in G3 funnel was washed by hot water until the filtrate was neutral. The residue in the G3 funnel was dryer in a 105 °C oven. The content of Klason lignin was calculated according to the equation (3):

$$Klason\ lignin = \frac{m_1 - m_2}{m_0} \times (100 - Extractives) \quad (3)$$

where, m_0 is the weight of the extracted samples; m_1 is the weight of the residue and G3

funnel; m_2 is the weight of the G3 funnel. The content of acid-soluble lignin was calculated by using UV to detect the absorbance of filtrate.

The hemicellulosic sugars were measured according to the previous method.[2] Briefly, 2-4 mg of the samples were weighed in a 10 mL pear-shaped flask equipped with a hermetically sealing Teflon-coated screw cap. HCl in methanol (2 mL, 2 M) was added to the flask, which was then hermetically screwed and heated in an oven at 105 °C for 5 h. During the reaction, the flask was carefully shaken 2 times. After that, the flask was cooled down in the air, and the residual acid was neutralized with 200 μL of pyridine. 1.0 mL of the internal standard (0.1 mg/mL of resorcinol in methanol) was added to the samples and evaporated the solvent. The residual in the pear-shaped flask was additionally dried in a vacuum-desiccator at 40 °C for 40 min and silylated overnight. The TMS-derivatives of sugars and uronic acids were analyzed with the GC method using a Shimadzu GC-2010AF instrument equipped with a capillary columns HP-1 (25 m×0.20 mm; film thickness 0.11 μm) and HP-5 (25 m×0.20 mm; film thickness 0.11 μm.

3.2 Identification and quantification of model compounds after amination

The identification of the model compounds after amination was realized by Liquid Chromatography-Electrospray Ionization-Mass Spectrometry (LC-ESI-MS) combined with Nuclear magnetic resonance (NMR). Before the analysis, the mixture was separated by a column filled with silica. The organic solution (n-hexane: MTBE, 1:4, v/v) was used as eluent. The liquid was collected in tubes and verified by TLC plates coated with silica using the same eluent. The same compounds were collected, concentrated, and dried. The purity of the collect compounds was measured by HPLC equipped with UV/Vis detector using C18 column (2.1

× 100 mm, 4.6 μm). The MillQ-water-formic acid (99.9:0.1, v/v) as eluent A and methanol-formic acid (99.9:0.1, v/v) as eluent B. The gradient of the eluent was: 30%B at the beginning, then changed to 50% B in 7 min, and then to 70% B in 3 min, which was held for 3 min, then changed to 95% B in 1 min, which was held for 1 min, finally changed to 30% B in 1 min, which was held for 5 min. The total running time was 21 min, and the flow rate of eluent was 0.8 mL/min. Samples were introduced to the ToF-MS using an electrospray source in negative ion mode, with dual spray for the reference mass solution. The nebulizer gas flow rate (nitrogen) was 7 L/min at 15 psi. The ESI source settings were in negative mode (with dual spray for reference mass solution); gas temperature 300 °C; skimmer voltage 35 V, and fragmenter voltage 140 V. Ions were analyzed over a mass range of 100–1,000 m/z. The pure compounds were characterized by GC-MS, LC-MS and NMR. The quantification of the identified model compounds was performed on a HPLC equipped with UV/Vis detector using C18 column (2.1× 100 mm, 4.6 μm) using the same conditions with LC-MS.

GC-MS: 1 mg pure compound was mixed with 1 mL silylation reagent (pyridine: BSTFA: TMCS, 1:4:1, v/v/v), then silylated at 70 °C for 45 min. The silylated sample was analyzed with an Agilent GC-MS equipped with a HP 6890 GC (Hewlett-Packard., USA) and a HP 5973 quadrupole mass selective detector (EI, 70 eV) using a HP-1 capillary column (25 m x 0.2 mm i.d., 0.11 μm film thickness). Helium was used as the carrier gas with a flow rate of 0.8 mL/min and a split flow rate of 15 mL/min. The temperature of column was raised from 80 to 300 °C at a speed of °C/min. The temperatures of injector, GC-MS transmission line and ion source are 260, 290 and 230 °C respectively. NMR: 3–5 mg pure compounds was dissolved in 0.6 mL DMSO-d_6, then the solution was transferred into 5 mm NMR tube. The ^{1}H, ^{13}C, COSY, HSQC

and HMBC spectrums of sample were recorded by an AVANCE III 500 MHz spectrometer (Bruker Ltd, Switzerland) equipped with a 5 mm Z gradient broadband observation cryoprobe.

3.3 Characterization of aminated lignin properties

The chemical compositions of aminated lignin followed the same protocols as the Section 3.1.

The chemical structural characteristics of aminated were investigated by Nuclear Magnetic Resonance (NMR) spectroscopy (^{1}H, ^{13}C ^{1}H-^{13}C HSQC and ^{31}P NMR), and the experiment details were according to literature.[2]

The molecular weight of aminated lignin was analyzed using HPLC system equipped with a differential refractive index (RI) concentration detector and a multi-angle light scattering detector (MALS) in DMSO/LiBr (0.05 M) eluent. The dried aminated lignin was dissolved in DMSO/LiBr eluent to 5 mg/mL and filtered over a 0.45 μm Nylon syringe filter prior to analysis. The separation was performed with a Jordi X-stream H_2O 10^3Å (10 × 250 mm, I.D. × L) at 60 °C. The HPLC system was operated under the following conditions: 0.5 mL/min flow rate; 0.15 mL/g dn/dc, 75 μL injection volume. Data evaluation used ASTRA software, version 7.3.2.

The element content of the aminated lignin was analyzed by an organic elemental analyzer (Thermo Scientific FLASH 2000).

3.4 Characterization of amino lignin micro/mano-particles (LMNPs)

The morphology of amino LMNPs was analyzed by transmission electron microscopy (TEM, Jeol JEM-1400 plus). For the sample preparation, 100 μL of LNPs suspension was diluted to

1 mL with MilliQ water. 5 μL of diluted amino LMNPs suspension (about 0.1 mg/mL) was added on the carbon film supporting grid. After deposited for 3 min, the excess water was carefully absorbed by blotting a sharp end of filter paper on the edge of the copper grid. In addition, differential light scattering (DLS, Zetasizer nano series, Malvern) was used to detect the Zeta potential of amino LMNPs.

4. Calculation for sustainability evaluation

4.1 General information

Different green metrics (E-factor, Mass intensity (MI), and Reaction mass efficiency (RME)) were calculated based on the laboratory data to evaluate the sustainability of the whole preparation process (*in-situ* amination, LMNP formation, and deformylation) of amino lignin macro/nanoparticles from bamboo. The other amination methods in the literature were used as controls. Considering that this work starts from biomass, other modification methods using technical lignin as raw materials also start from biomass.

E_{simple} is used to define simple E-factor, which is calculated without any solvent other than the reaction medium. Ecomplex is used to define complex E-factor, which is calculated with solvent (considering the technical lignin preparation and LMNPs formation need a large amount of water). Mass intensity (MI) is used to describe the total mass consumed per unit of product mass in a particular process. Reaction Mass Efficiency (RME) is used to express the mass of the target product relative to the total mass of all reactants.

Regarding the calculation of green metrics in the literature, if some key parameters are not reported, the ideal values or the same values as in this work were used. For example, if the

yield of aminated lignin was missing, the theoretical yield was used, which is calculated by assuming that the reaction sites are 100% converted to the main reaction.[3] The yield of LMNPs was the same as that in this work.

4.2 Calculation

This work:

1) *In-situ* amination of lignin from biomass

Starting materials: 100 g bamboo, 900 mL 85% formic acid (933.3 g formic acid+ 135 g H_2O), 100 mL aniline (102.17 g), 4 L 85% formic acid (washing, 4148 g formic acid + 600 g H_2O).

Recycle solvents: 5786.2 g formic acid/H_2O (4898.34 g formic acid+ 887.86 H_2O), 115.16 g formanilide.

Aminated lignin: 46.51 g

2) Formation of aminated LMNPs

Starting materials: 1 g aminated lignin, 100 mL THF, 900 mL acidic H_2O (HCl solution, pH 2.5).

Recycle solvents: 90 mL THF.

Aminated LMNPs: 0.9 g (yield 90%).

3) **Deformylation**

Starting materials: 0.9 g aminated LMNPs (10 mg/mL in H_2O), 8.9 g 37% HCl solution, 150 mL H_2O (washing).

Recycle solvents: 90 mL HCl solution.

Amino LMNPs: 0.765 g (5 mg/mL in H_2O) (yield 85%).

4) Calculation

$$E_{simple} = \frac{\sum staring\ materials - desired\ product}{desired\ product} = 6.58$$

$$E_{complex} = \frac{\sum staring\ materials(+solvent) - \sum recycle\ solvents - desired\ product}{desired\ product} = 1385.19$$

$$MI = \frac{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)}{desired\ product} = 33.73$$

$$RME = \frac{desired\ product}{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)} = 30.38$$

Reference 1: G. J. Jiao, P. Peng, S. L. Sun, Z. C. Geng and D. She, *Int. J. Biol. Macromol.*, 2019, **127**, 544–554.[4]

1) Fractionation of lignin from biomass (Biorefinery process: dilute acid +dilute alkaline)

Starting materials: 10 g corncob, 100 g 1 wt% H_2SO_4 solution (1 g H_2SO_4 +99 g H_2O), 1 g NaOH, 100 mL H_2O (for dilute alkaline), 600 mL H_2O (washing).

Technical lignin: 1 g

2) Modification of lignin (phenolation + amination)

a) Phenolation

Starting materials: 1 g technical lignin, 2 g phenol, 1 g NaOH, 0.92 g H_2SO_4, 20 mL acidic H_2O (HCl solution, pH 2.0).

Phenolated lignin: 2.4 g (80% based on the total weight of technical lignin and phenol)

b) Mannich amination

Starting materials: 2.4 g phenolated lignin, 9.6 g formaldehyde (319.68 mmol in 37% aq. solution, 25.92 g total weight considering water), 7.2 g ethylenediamine (120 mmol, in 40%

aq. solution, 18 g total weight considering water), 0.16 g sodium hydroxide (1.92 mmol, 0.4 mol/L, 4.81 g total weight considering water), 500 ml H_2O (dialysis).

Aminated lignin: 3.75 g (theoretical yield)

3) Formation of aminated LMNPs

Starting materials: 1 g aminated lignin, 100 mL THF, 900 mL acidic H_2O (HCl solution, pH 2.5).

Recycle solvents: 90 mL THF.

Aminated LMNPs: 0.9 g (yield 90%).

4) Calculation

$$E_{simple} = \frac{\sum staring\ materials - desired\ product}{desired\ product} = 8.40$$

$$E_{complex} = \frac{\sum staring\ materials(+solvent) - \sum recycle\ solvents - desired\ product}{desired\ product} = 1431.06$$

$$MI = \frac{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)}{desired\ product} = 31.65$$

$$RME = \frac{desired\ product}{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)} = 10.61$$

Reference 2: X. Du, J. Li and M. E. Lindström, *Ind. Crop. Prod.*, 2014, **52**, 729–735.[5]

1) Fractionation of lignin from biomass (Kraft pulping)

Starting materials: 1 kg spruce, 193.55 g NaOH, 62.90 g Na_2S, 4 L H_2O, 8 L H_2O (washing).

Technical lignin: 180 g

2) Lignin Amination and LNP formation

Starting materials: 1 g technical lignin, 1.65 g formaldehyde (55 mmol, in 37% aq. solution, 4.46 g total weight considering water), 2.48 g dimethylamine (55 mmol, in 40% aq. solution,

6.2 g total weight considering water), 2.1 g acetic acid (35 mmol), 10.24 g (80% solution of 1,4-dioxane in water), 3 L H_2O (dialysis, for LNPs formation)

Aminated LNPs: 1.08 g (theoretical yield)

3) Calculation

$$E_{simple} = \frac{\sum staring\ materials - desired\ product}{desired\ product} = 11.14$$

$$E_{complex} = \frac{\sum staring\ materials(+solvent) - \sum recycle\ solvents - desired\ product}{desired\ product} = 2857.53$$

$$MI = \frac{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)}{desired\ product} = 21.88$$

$$ME = \frac{desired\ product}{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)} = 8.44$$

Reference 3: M. Kollman, X. Jiang, S. J. Thompson, O. Mante, D. C. Dayton, H. Chang and H. Jameel, *Green Chem.*, 2021, **23**, 7122–7136.[6]

1) Fractionation of lignin from biomass (Kraft pulping)

Starting materials: 1 kg pine, 193.55 g NaOH, 62.90 g Na_2S, 4 L H_2O, 8 L H_2O (washing).

Technical lignin: 180 g

2) Lignin Amination and LNP formation

Starting materials: 1 g technical lignin, 1.50 g formaldehyde (50 mmol in 37% aq. solution, 4.06 g total weight considering water), 2.254 g dimethylamine (50 mmol), 10.3 g 1,4-dioxane, 1 L H_2O (dialysis, for aminated lignin purification).

Aminated LNPs: 1.19 g (theoretical yield).

3) Formation of aminated LMNPs

Starting materials: 1 g aminated lignin, 100 mL THF, 900 ml acidic H_2O (HCl solution, pH 2.5).

Recycle solvents: 90 mL THF.

Aminated LMNPs: 0.9 g (yield 90%).

4) Calculation

$$E_{simple} = \frac{\sum staring\ materials - desired\ product}{desired\ product} = 9.00$$

$$E_{complex} = \frac{\sum staring\ materials(+solvent) - \sum recycle\ solvents - desired\ product}{desired\ product} = 2133.86$$

$$MI = \frac{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)}{desired\ product} = 41.83$$

$$RME = \frac{desired\ product}{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)} = 9.99$$

Reference 4: J. Chen, L. An, J. H. Bae, J. W. Heo, S. Y. Han and Y. S. Kim, *Ind. Crop. Prod.*, 2021, **173**, 114102.[7]

1) Fractionation of lignin from biomass (Kraft pulping)

Starting materials: 1 kg hardwood chips, 193.55 g NaOH, 62.90 g Na_2S, 4 L H_2O, 8 L H_2O (washing).

Technical lignin: 180 g

2) Lignin Amination and LNP formation

Starting materials: 1 g technical lignin, 3.22 g 2-chloroethylamine hydrochloride (27.76 mmol), 6 g sodium hydroxide (150 mmol, 106 g of total solution considering water), 1 L H_2O (dialysis, for aminated lignin purification).

Aminated LNPs: 0.77 g (77%).

3) Formation of aminated LMNPs

Starting materials: 1 g aminated lignin, 100 mL THF, 900 mL acidic H_2O (HCl solution, pH 2.5).

Recycle solvents: 90 mL THF.

Aminated LMNPs: 0.9 g (yield 90%).

4) Calculation

$$E_{simple} = \frac{\sum staring\ materials - desired\ product}{desired\ product} = 22.38$$

$$E_{complex} = \frac{\sum staring\ materials(+solvent) - \sum recycle\ solvents - desired\ product}{desired\ product} = 2455.29$$

$$MI = \frac{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)}{desired\ product} = 45.60$$

$$RME = \frac{desired\ product}{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)} = 8.02$$

Reference 5: L. Liu, X. Wan, S. Chen, P. Boonthamrongkit, M. Sipponen and S. Renneckar, *ChemSusChem*, 2023, **16**, e202300276.[8]

1) Fractionation of lignin from biomass (Kraft pulping)

Starting materials: 1 kg softwood chips, 193.55 g NaOH, 62.90 g Na_2S, 4 L H_2O, 8 L H_2O (washing).

Technical lignin: 180 g

2) Lignin Amination and LNP formation

Starting materials: 1 g technical lignin, 3.08 g 2-oxazolidinone (35.4 mmol), 0.06 g sodium hydroxide (1.475 mmol), 1 L HCl solution (0.01 mol/L)

Aminated LNPs: 1.01 g.

3) Formation of aminated LMNPs

Starting materials: 1 g aminated lignin, 100 mL THF, 900 mL acidic H_2O (HCl solution, pH 2.5).

Recycle solvents: 90 mL THF.

Aminated LMNPs: 0.9 g (yield 90%).

4) Calculation

$$E_{simple} = \frac{\sum staring\ materials - desired\ product}{desired\ product} = 10.13$$

$$E_{complex} = \frac{\sum staring\ materials(+solvent) - \sum recycle\ solvents - desired\ product}{desired\ product} = 1672.25$$

$$MI = \frac{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)}{desired\ product} = 33.36$$

$$RME = \frac{desired\ product}{\sum staring\ materials(no\ H_2Osolvent) - \sum recycle\ solvents(no\ H_2O)} = 6.11$$

5. Results

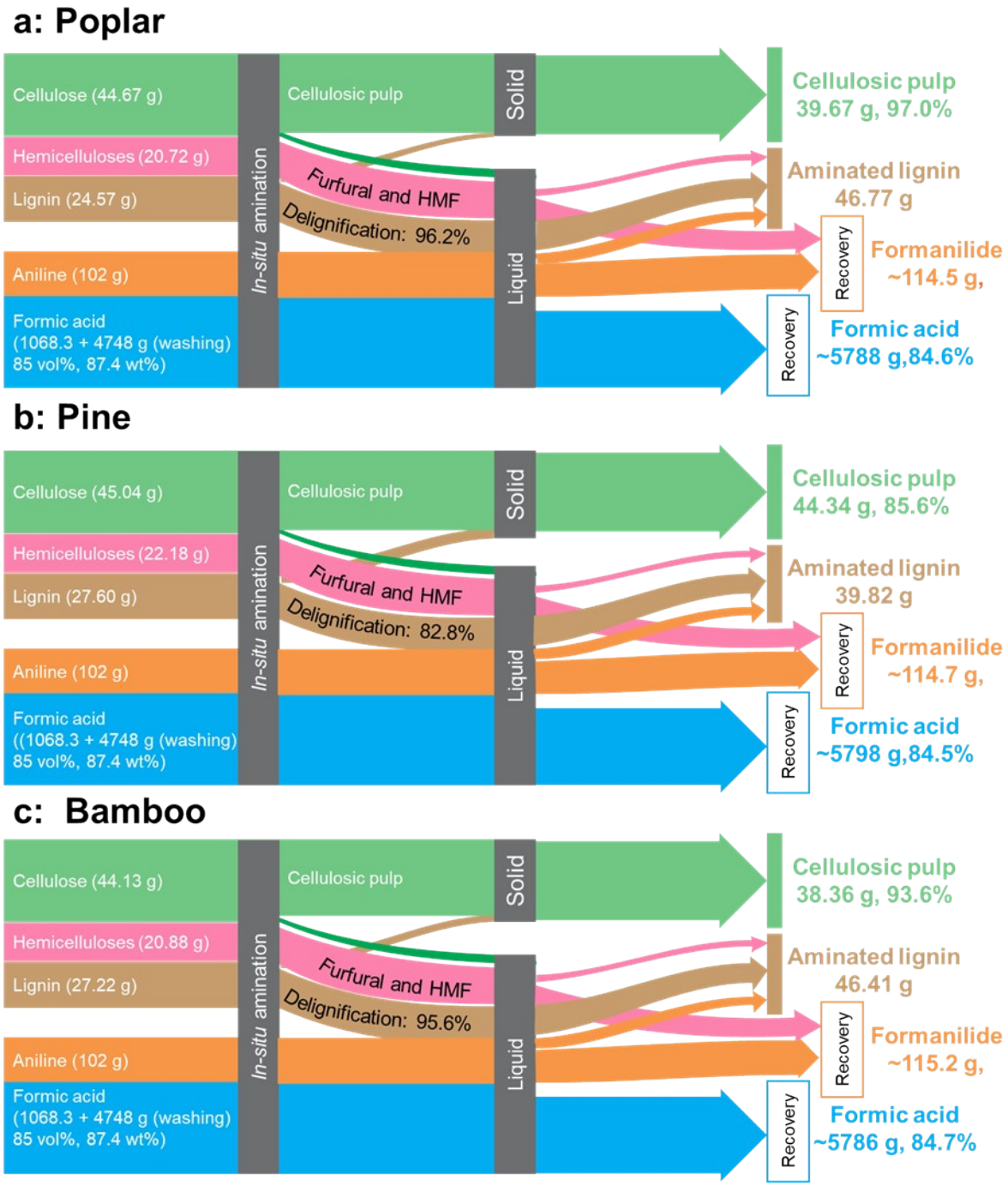

Fig. S1. Sankey diagram of mass flow and solvent recovery for *in-situ* reactive fractionation of biomass.

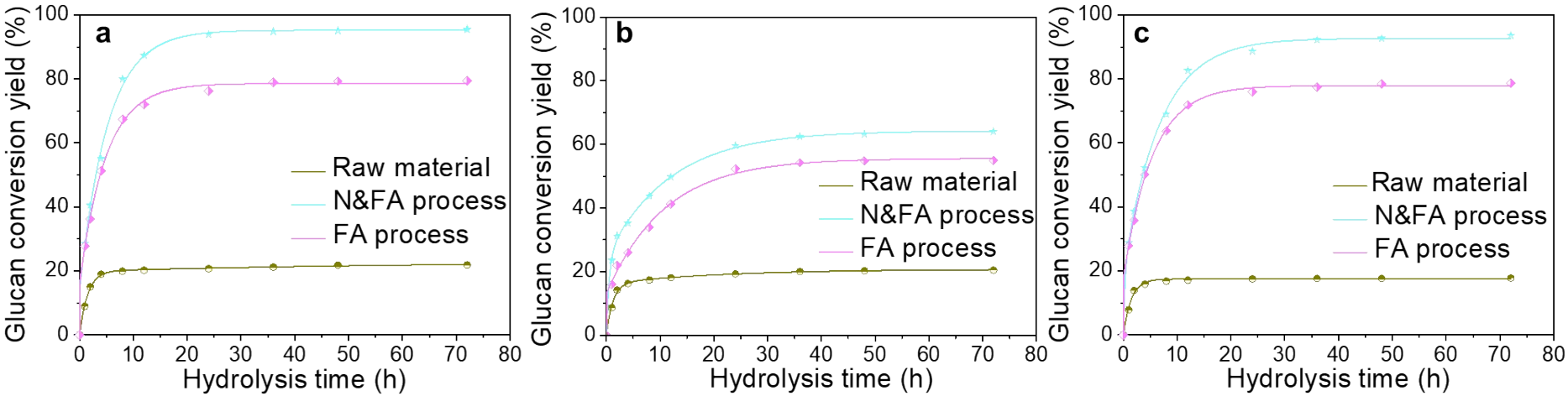

Fig. S2. Enzymatic hydrolysis efficiency of the starting materials and cellulose fractions after delignification using aniline-formic acid solvent system (N&FA) and formic acid (FA). Different starting materials were used in: a: poplar; b: pine; c: bamboo.

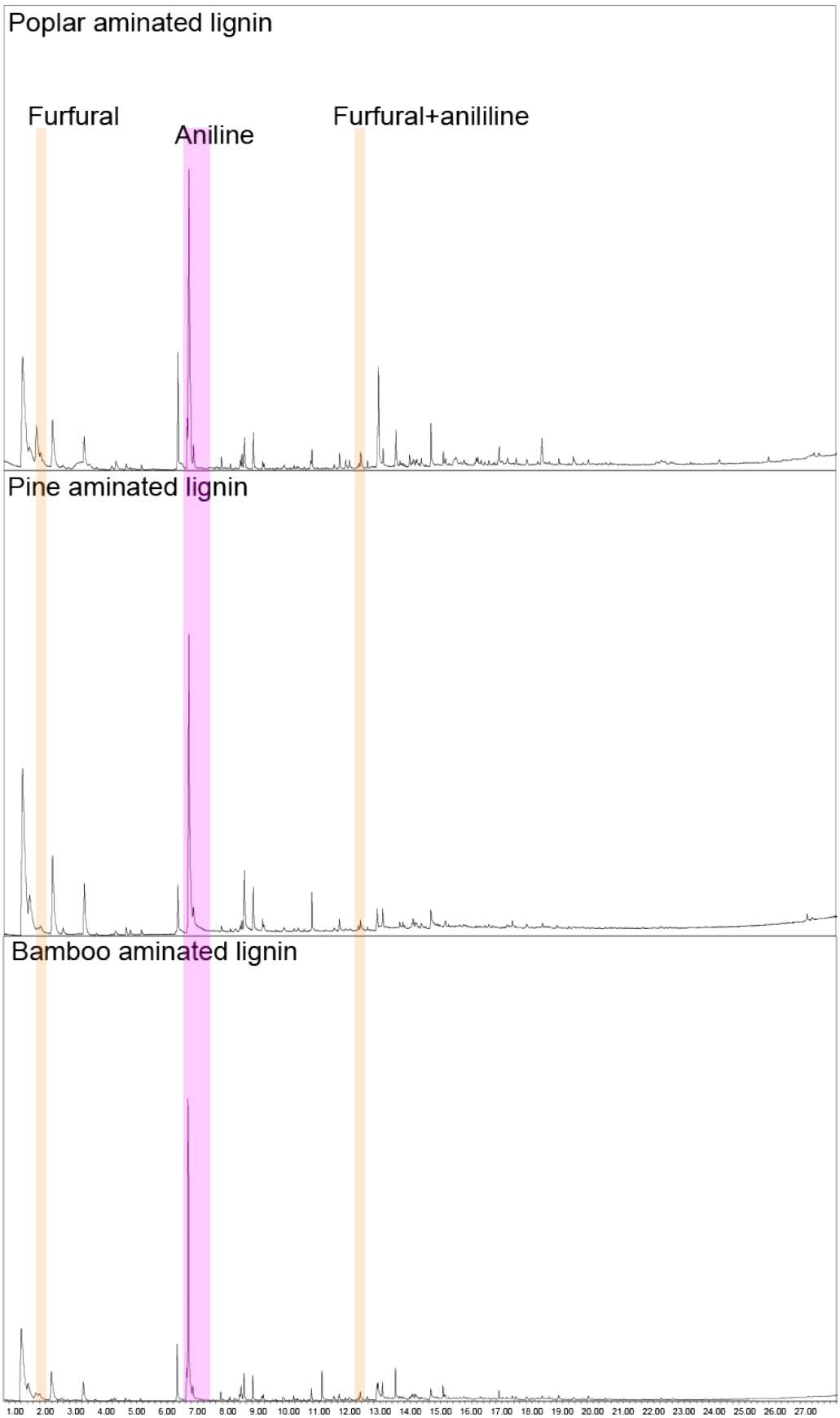

Fig. S3. Py GC-MS chromatograms of different aminated lignins.

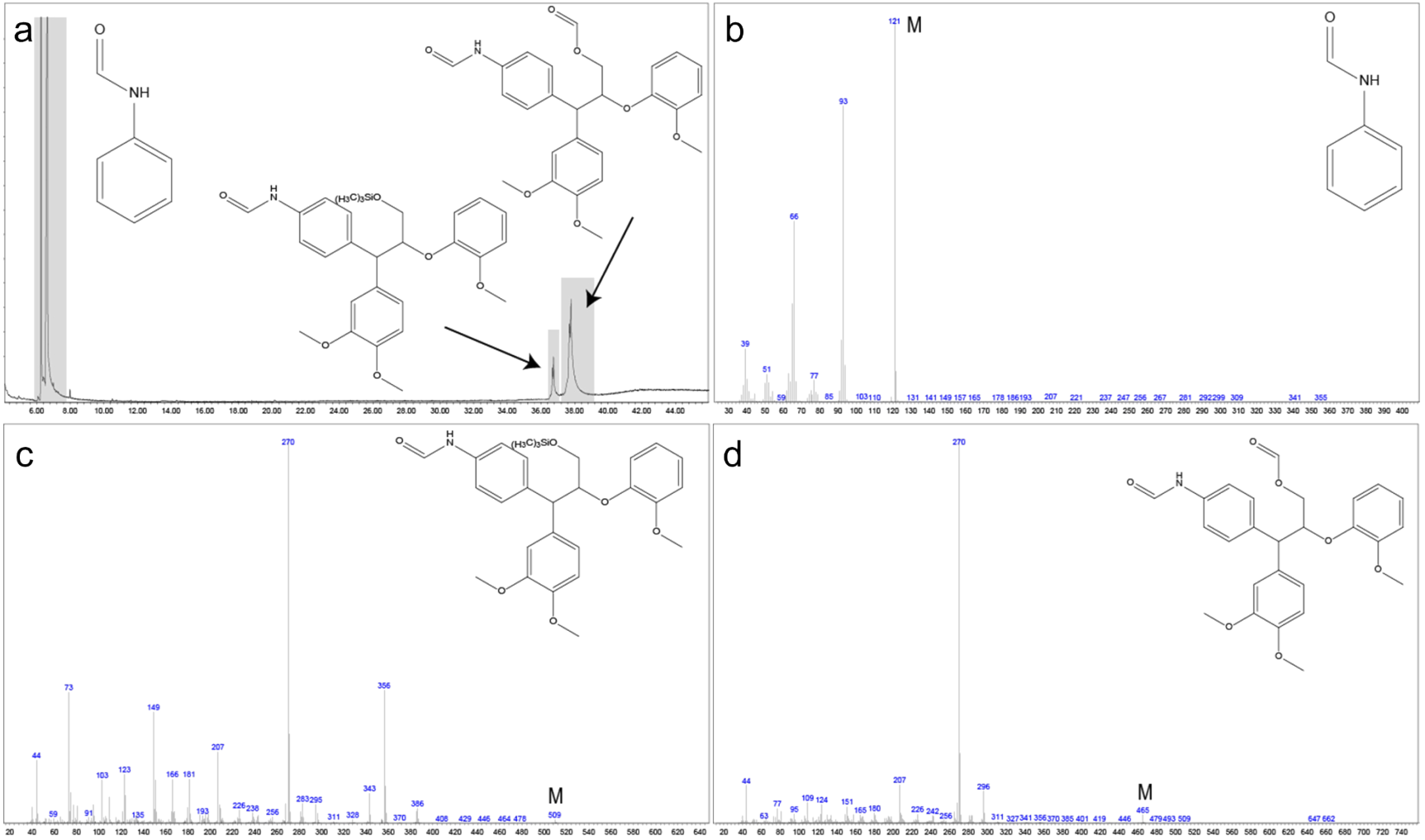

Fig. S4. *In-situ* amination of lignin dimer model (VG) by aniline-formic acid solvent system (at 140 °C for 2 h). (a) GC chromatogram of the reaction products; (b-d) MS spectra of different reaction products.

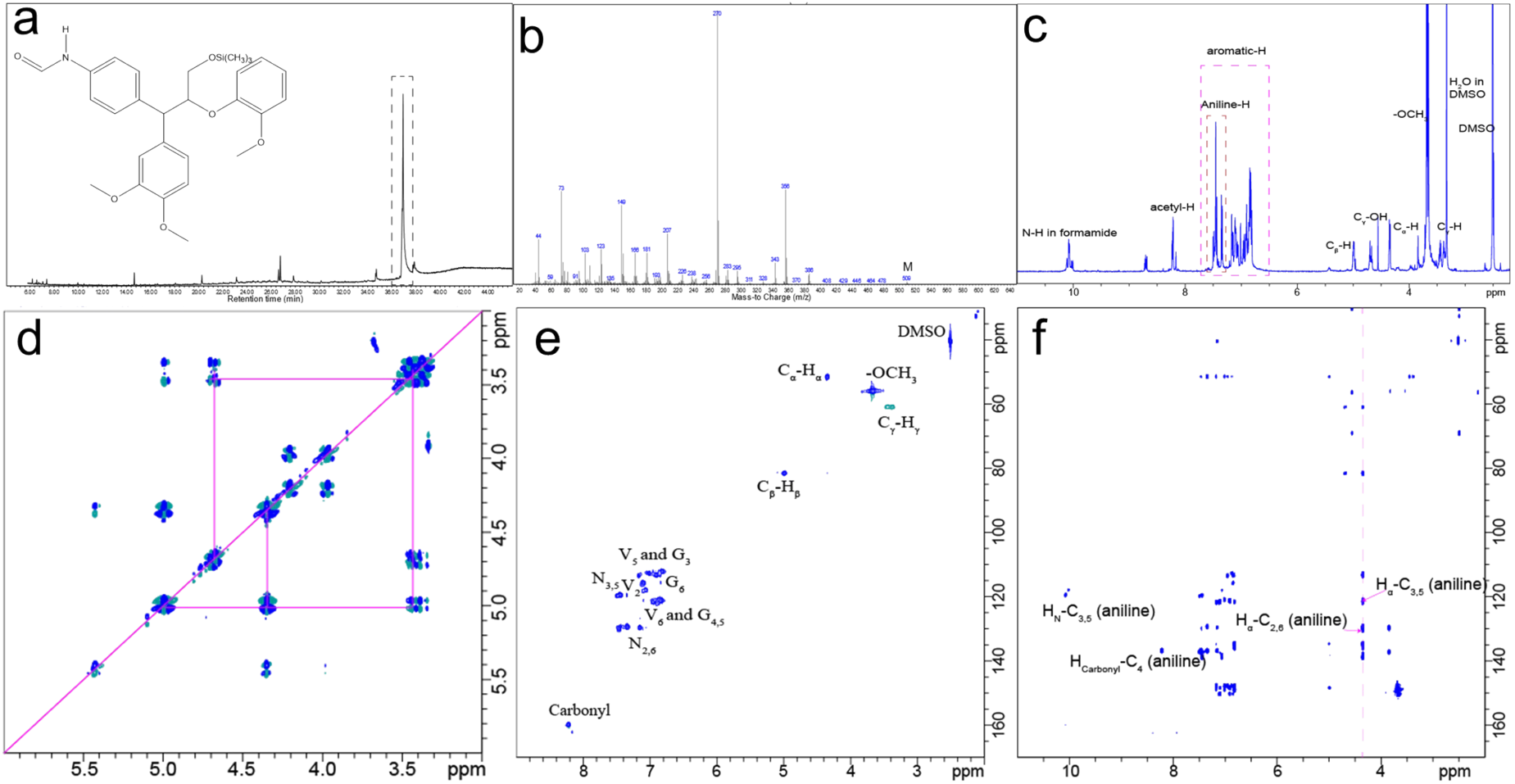

Fig. S5. Identification of product 2 (separated from reaction products by TLC column filled with silica). (a) GC chromatogram of product 2; (b) MS spectrum of product 2; (c) ^{1}H NMR spectrum of product 2; (d) 2D ^{1}H-^{1}H COSY NMR spectrum of product 2; (e) 2D ^{1}H-^{13}C HSQC NMR spectrum of product 2; (f) 2D ^{1}H-^{13}C HMBC NMR spectrum of product 2.

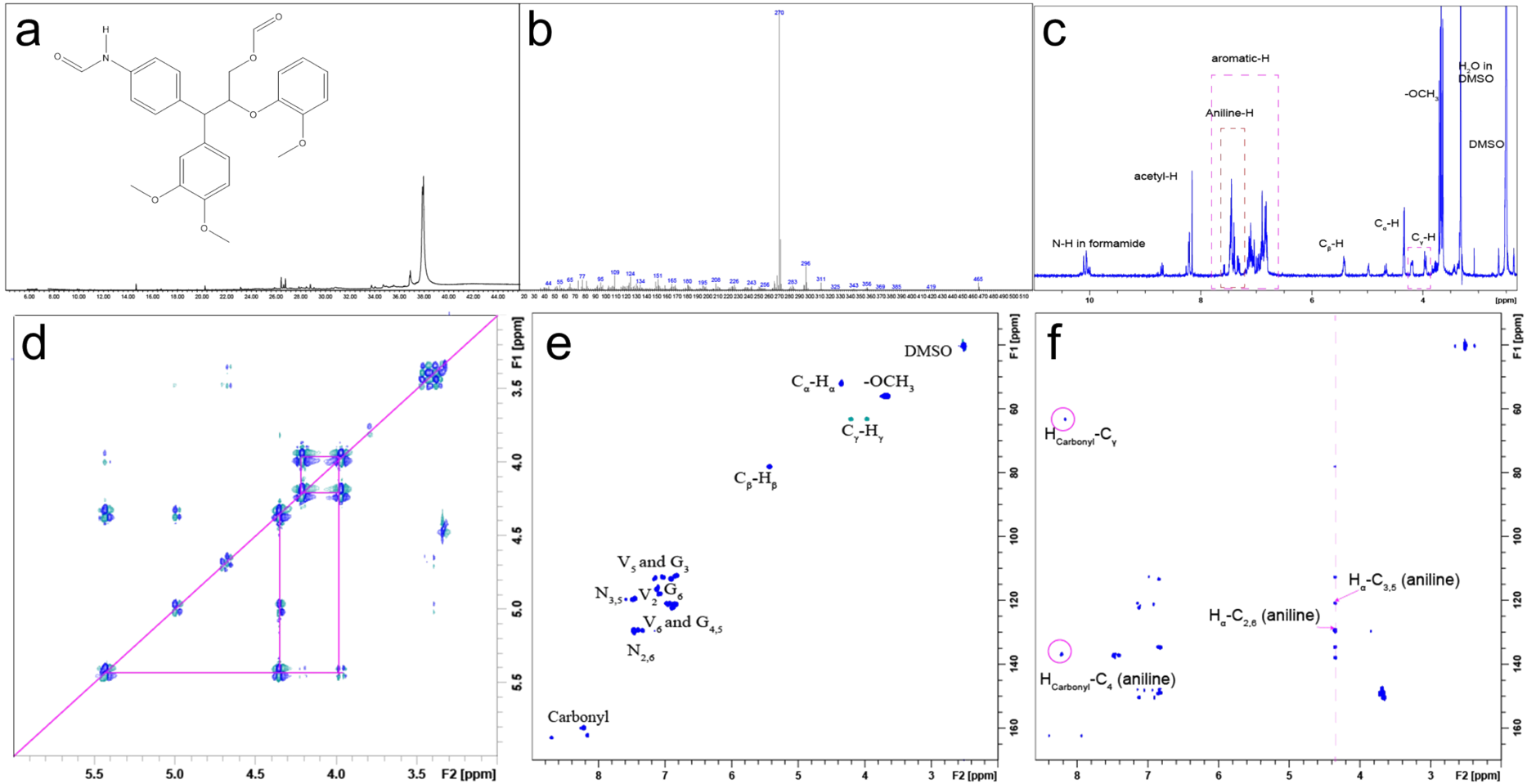

Fig. S6. Identification of product 3 (silylated, separated from reaction products by TLC column filled with silica). (a) GC chromatogram of product 3; (b) MS spectrum of product 3; (c) 1H NMR spectrum of product 3; (d) 2D ^{1}H-^{1}H COSY NMR spectrum of product 3; (e) 2D ^{1}H-^{13}C HSQC NMR spectrum of product 3; (f) 2D ^{1}H-^{13}C HMBC NMR spectrum of product 3.

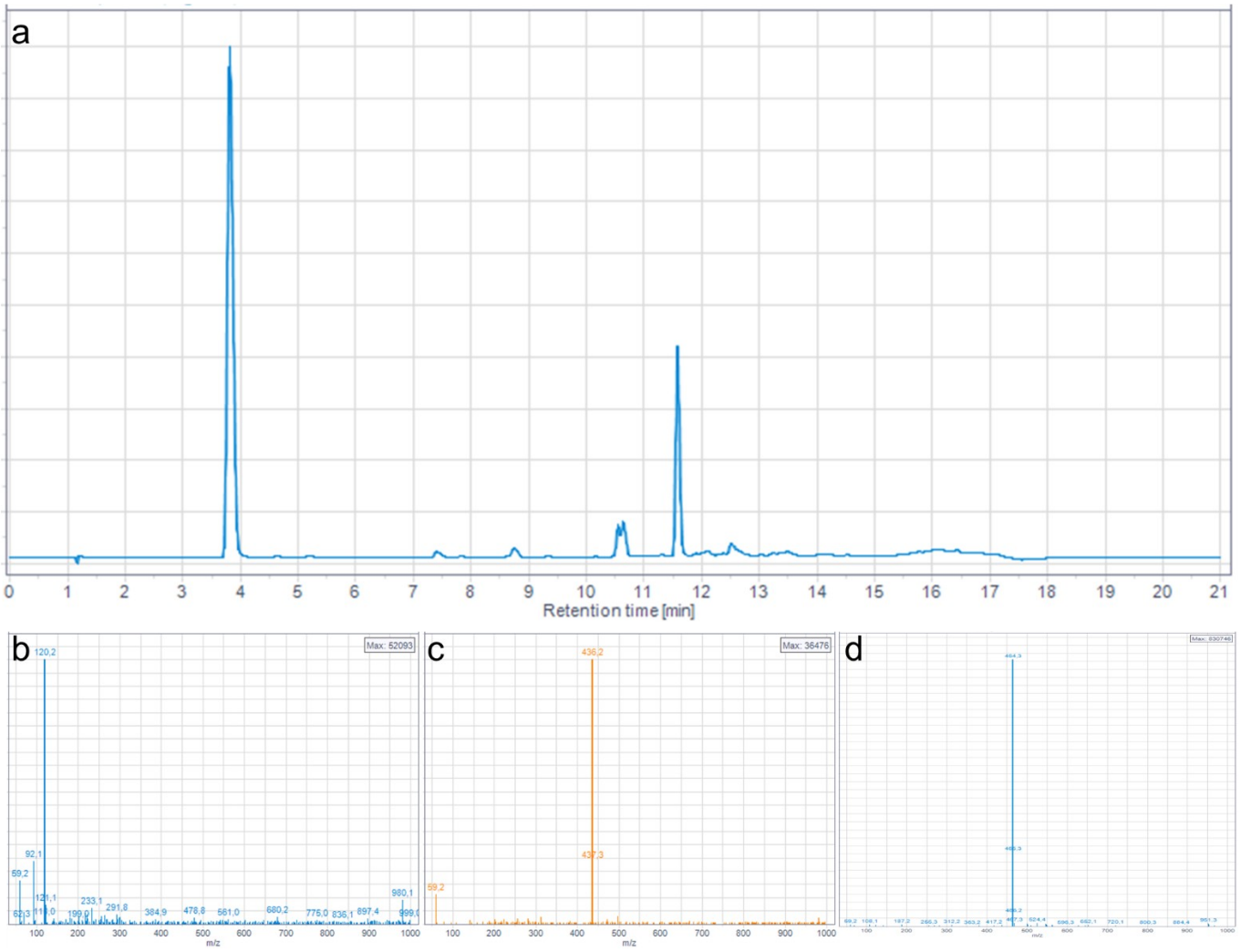

Fig. S7. Identification of model compounds after amination by LC-MS. a: UV signal spectrum at 280 nm; b: MS spectrum of formanilide at RT 3.9 min; c: MS spectrum of product 3 at RT 10.6 min; d: MS spectrum of product 2 at RT 11.6 min.

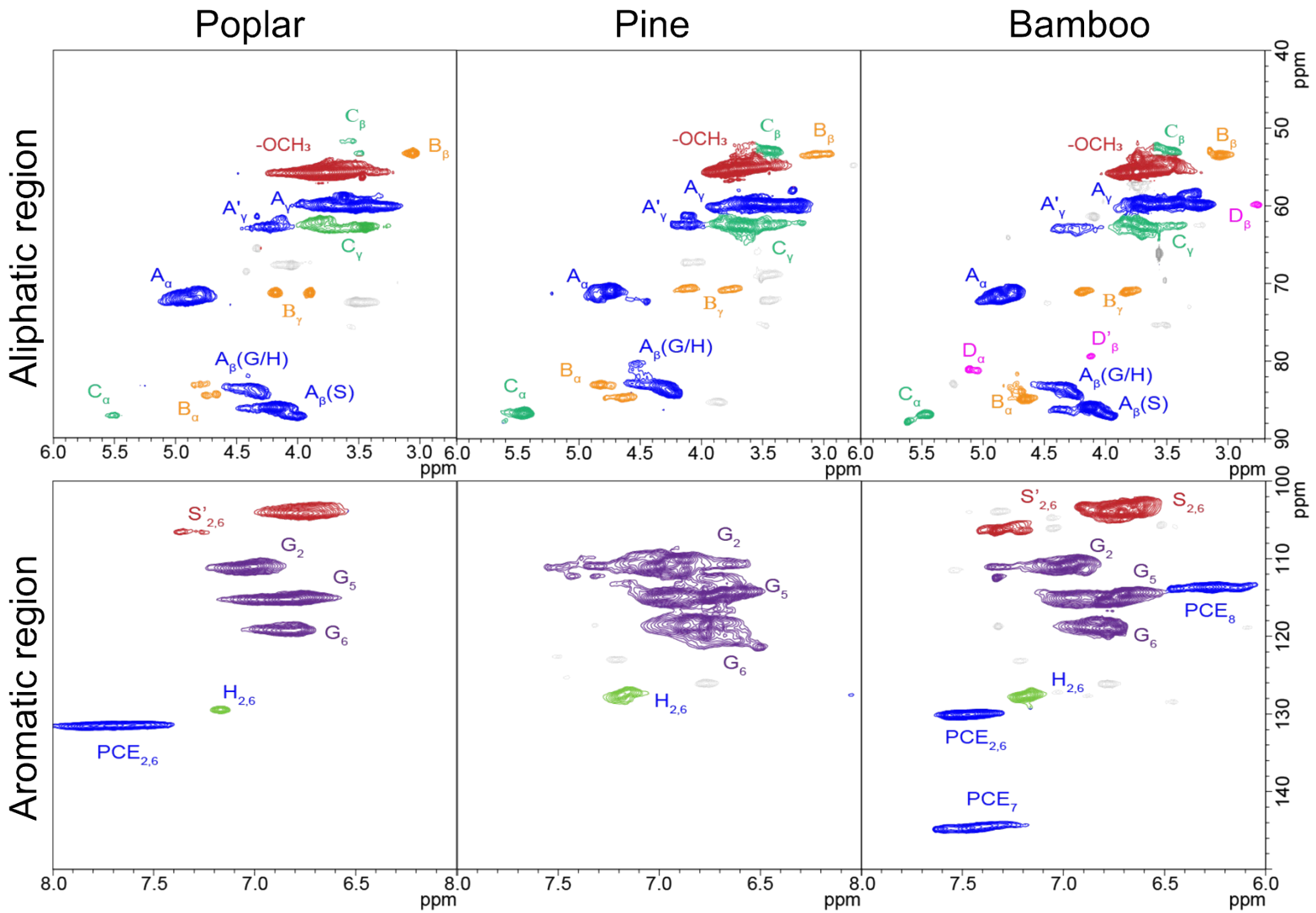

Fig. S8. 2D HSQC NMR spectra of milled wood lignin (MWL) from different biomass resources

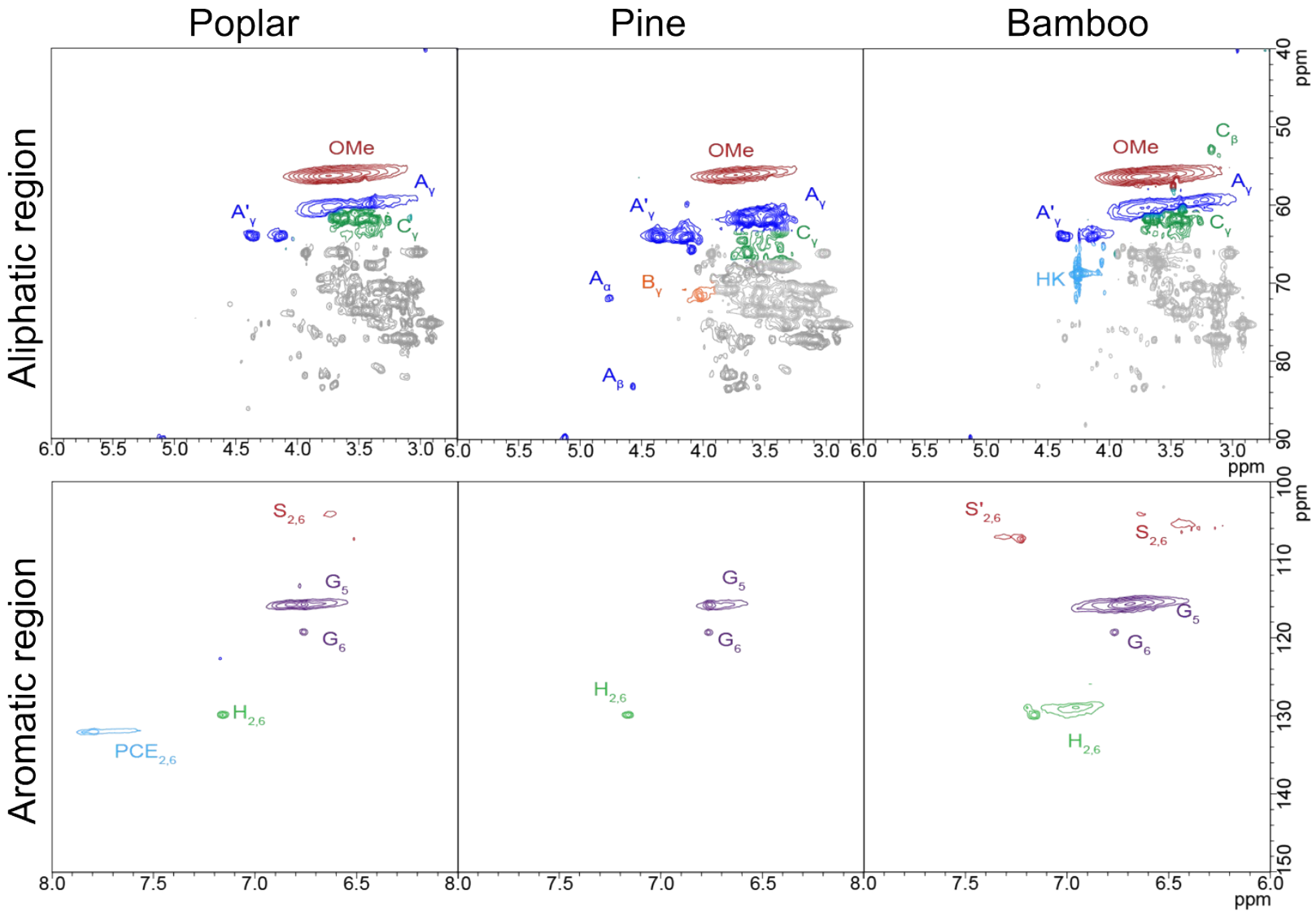

Fig. S9. 2D HSQC NMR spectra of formic acid lignin from different biomass resources.

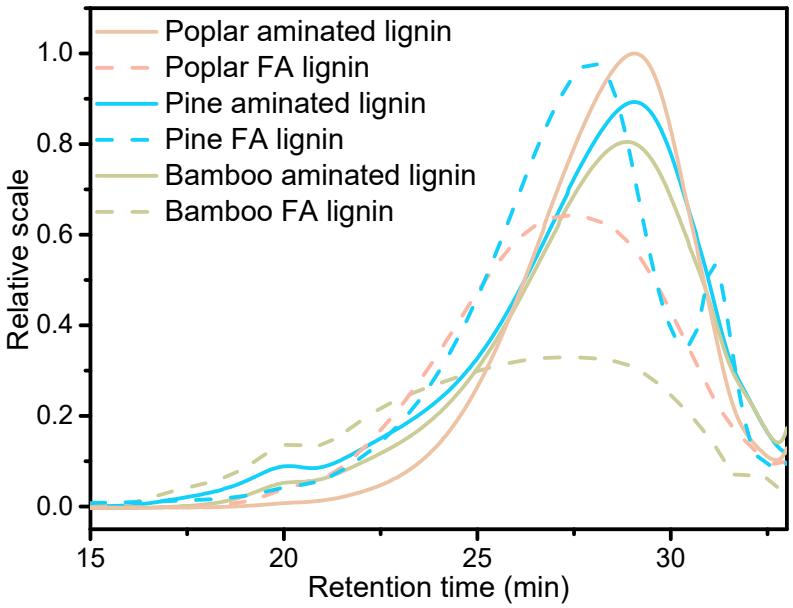

Fig. S10. SEC-MALS chromatography of different lignins

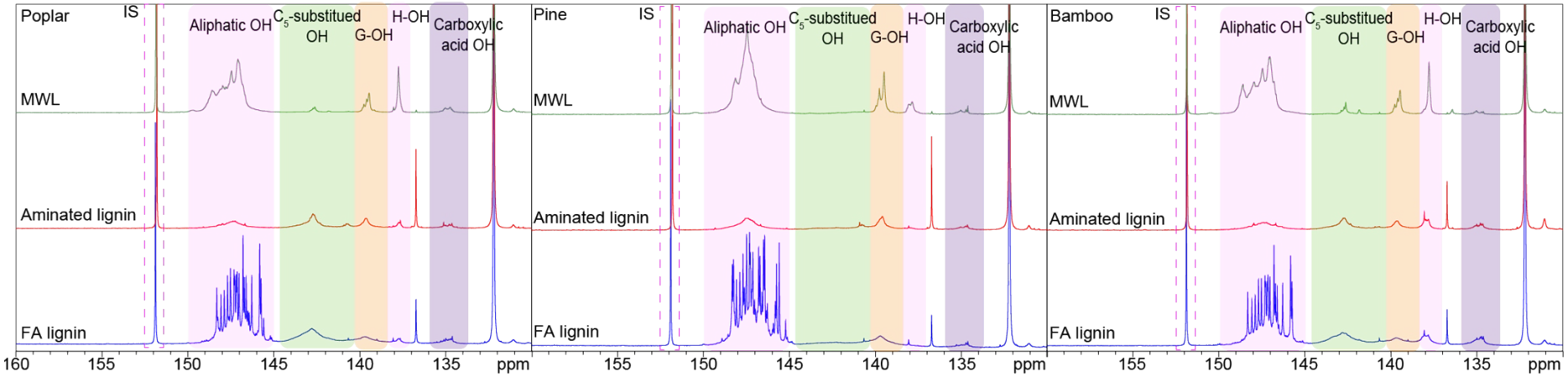

Fig. S11. ^{31}P NMR spectra of milled wood lignin (MWL), aminated and FA lignins from different biomass resources.

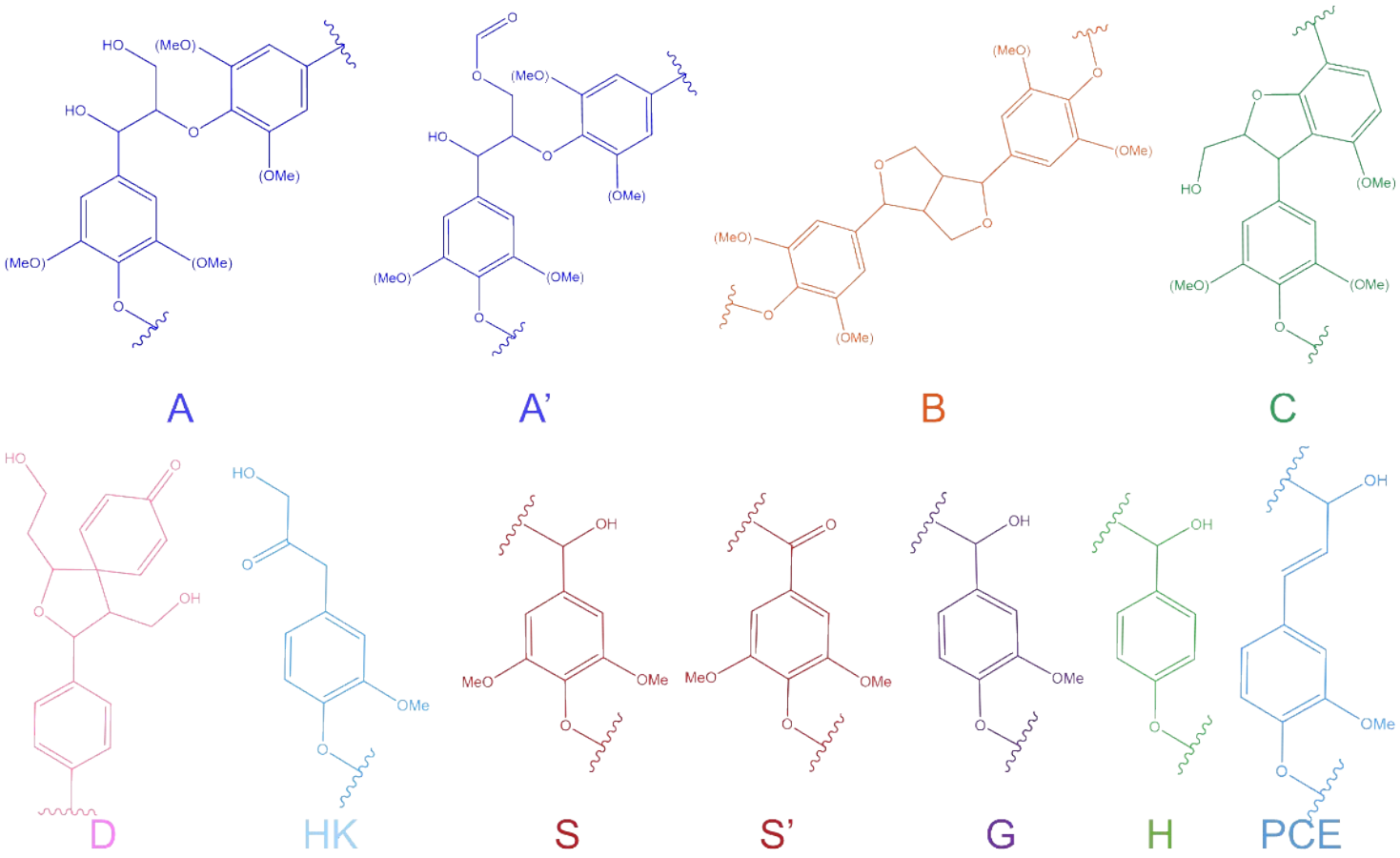

Fig. S12. Common structure of lignin.

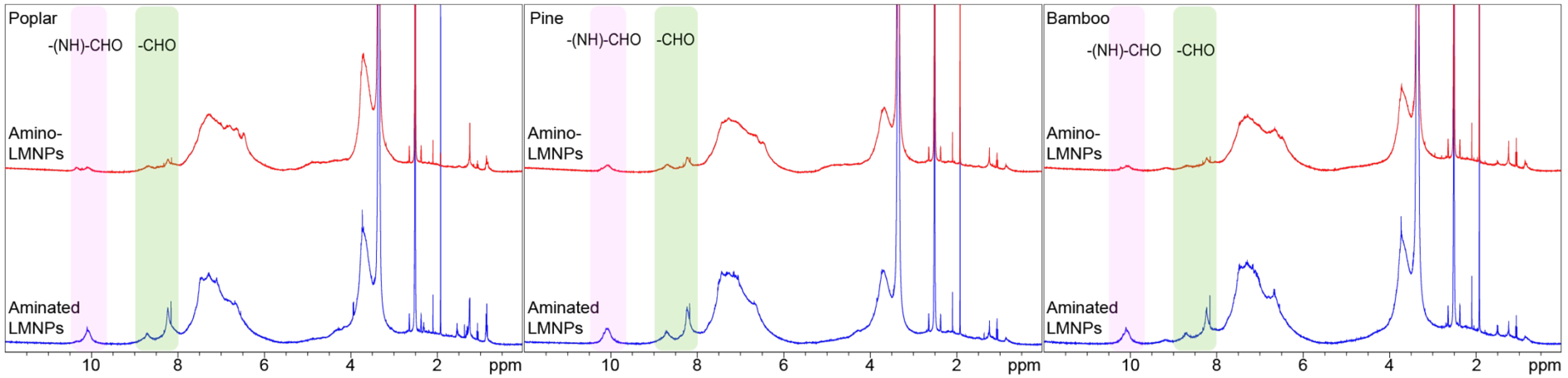

Fig. S13. ^{1}H NMR spectra of LMNPs before and after deformylation.

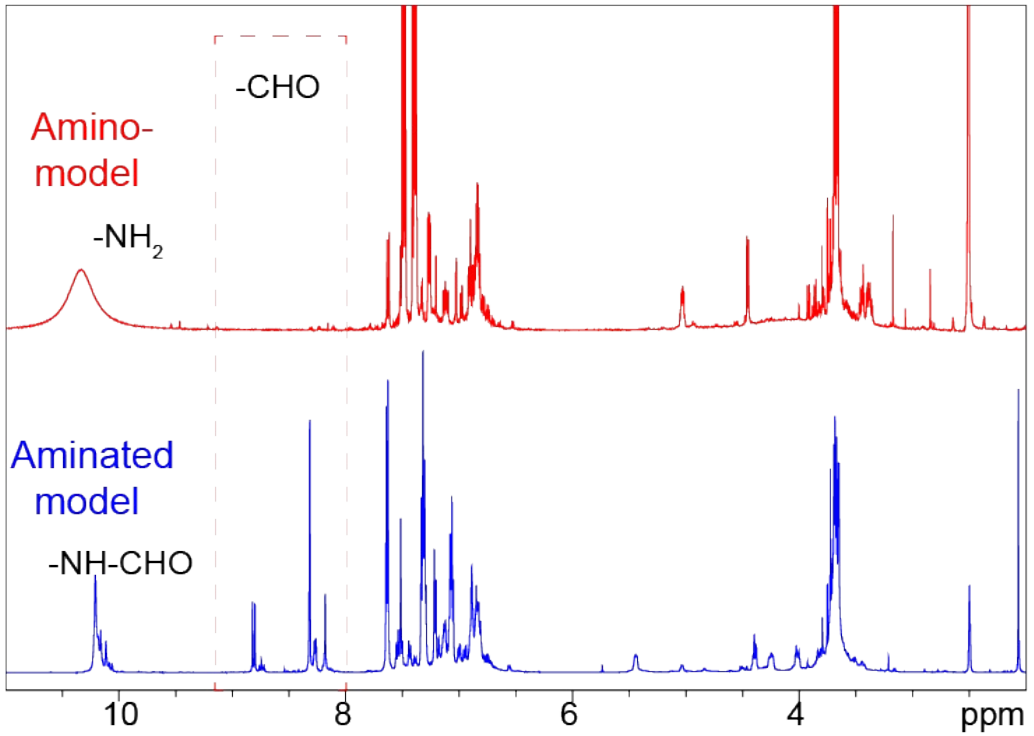

Fig. S14. ^{1}H NMR spectrum of lignin aminated model compounds before and after deformylation.

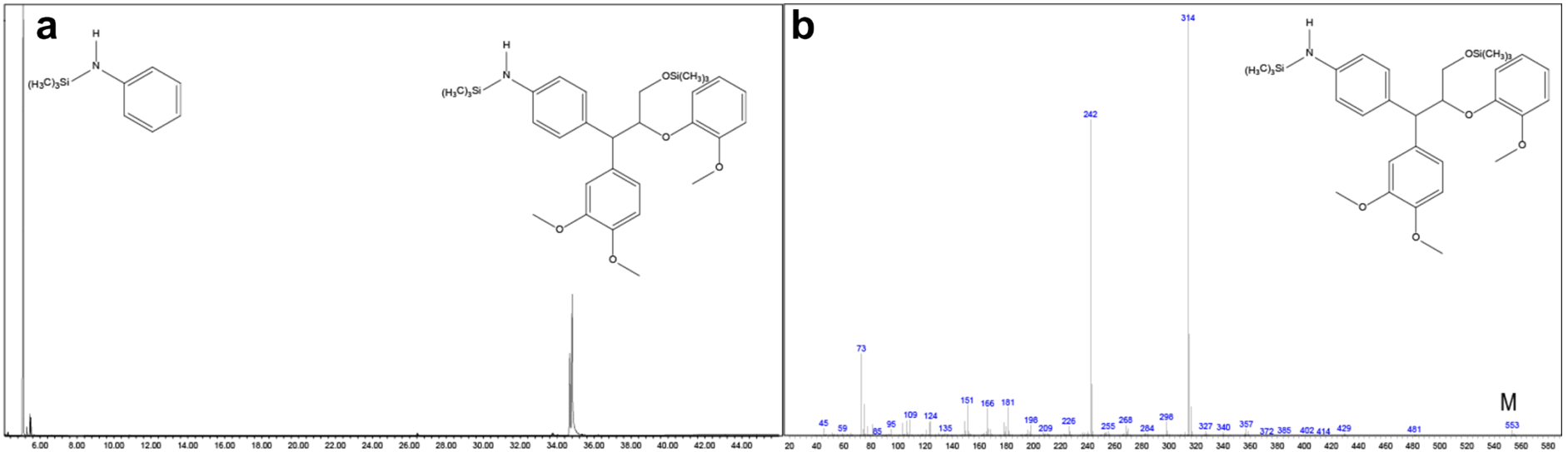

Fig. S15. GC-MS chromatography of aminated lignin dimer model after deformylation. (a) GC chromatogram of the aminated lignin dimer model after deformylation; (b) MS spectrum of aminated lignin dimer model after deformylation

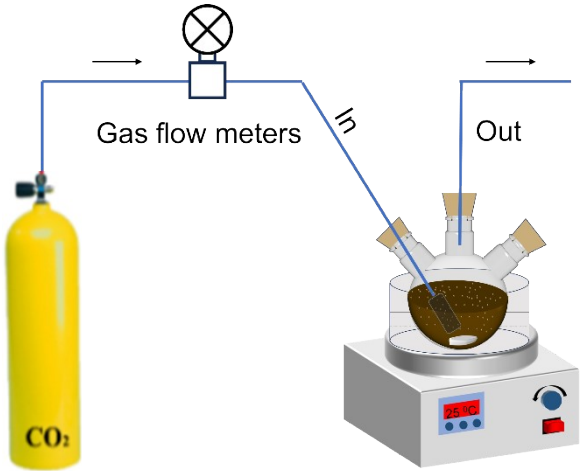

Fig. S16. Schematic diagram of the CO_2 capture using amino-LMNPs colloidal suspension

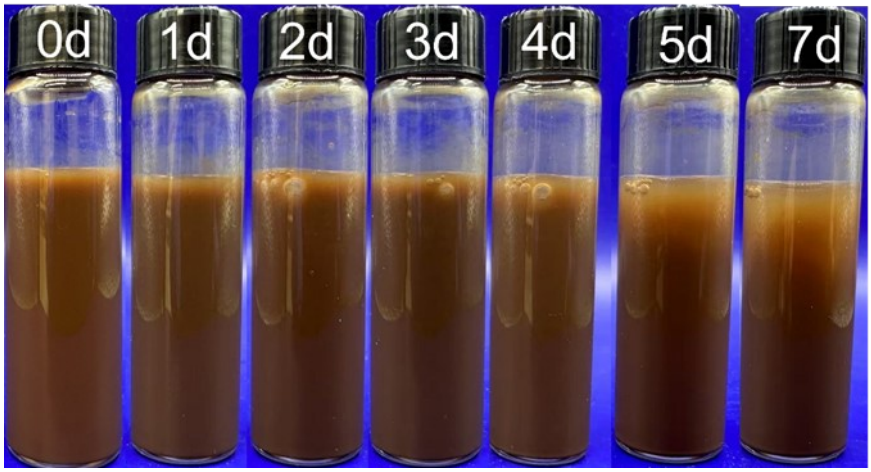

Fig. S17. Long-term stability of aminated LNP in a size range of 339 ± 72 nm derived from the bamboo-biomass

Table S1 Chemical composition of starting materials and solid fractions after fractionation

	Poplar			Pine			Bamboo		
		N&FA	FA		N&FA	FA		N&FA	FA
Yield (wt%)	100	39.67	37.22	100	44.34	42.15	100	38.36	35.07
Cellulose (wt%)	44.67	96.95	94.95	45.04	85.55	76.01	44.13	93.64	92.41
Xyl (wt%)	15.01	--	--	4.02	1.46	0.92	17.23	--	--
Man (wt%)	1.28	--	--	10.53	0.75	--	--	--	--
Glc (wt%)	2.08	--	--	3.14	--	--	2.63	--	--
Ara (wt%)	0.52	--	--	0.99	--	--	1.02	--	--
Rha (wt%)	0.36	--	--	0.35	--	--	--	--	--
GalA (wt%)	1.47	--	--	1.39	0.76	--	--	--	--
Gal (wt%)	--	--	--	2.76	--	--	--	--	--
Total Hemi (wt%)	20.72	--	--	22.18	2.97	0.92	20.88	--	--
Klason lignin (wt%)	23.22	1.67	2.08	25.97	9.50	21.15	25.97	2.16	2.05
Soluble lignin (wt%)	1.35	0.69	0.68	1.63	1.24	0.66	1.25	0.96	0.89
Total lignin (wt%)	24.57	2.36	2.76	27.60	10.74	21.81	27.22	3.12	2.94
Delignification (%)	--	96.19	95.82	--	82.75	66.69	--	95.60	96.21
Extractives (wt%)	1.35	--	--	1.96	--	--	3.33	--	--

Table S2 The content of hemicellulosic sugars and degradation products in the liquid phase

		Poplar		Pine		Bamboo	
		N&FA	FA	N&FA	FA	N&FA	FA
Hemicellulosic sugars	Anhydrous sugars (polymeric form)						
	4-O-Me-GlcA (mg/g)	--	6.36	--	3.14	4.16	0.84
	Xyl (mg/g)	--	20.25	--	14.55	--	15.16
	Man (mg/g)	--	7.88	34.70	54.11	--	--
	Glu (mg/g)	21.99	20.14	34.67	36.09	22.88	45.17
	Ara (mg/g)	--	--	--	5.12	--	--
	Gal (mg/g)	--	3.26	13.50	--	--	--
	GalA (mg/g)	19.88	3.32	34.74	--	--	--
	Monomer sugars						
	Rhamnose (mg/g)	--	2.31	--	1.95	--	--
	Xylose (mg/g)	--	56.14	--	16.97	--	45.95
	Mannose (mg/g)	--	9.28	--	29.58	--	--
	Glucose (mg/g)	--	19.98	--	16.38	--	20.88
	Arabinose (mg/g)	--	1.76	--	3.55	--	4.51
	Galactose (mg/g)	--	2.41	--	10.68	--	1.56
	Total (mg/g)	41.87	153.09	117.61	192.12	27.04	134.08
Degradation products	Furfural (mg/g)	--	16.72	--	9.65	--	40.13
	HMF (mg/g)	--	1.11	--	1.94	--	1.72
	Acetic acid (mg/g)	35.62	36.25	11.16	23.92	45.64	46.92

Table S3 The yield and chemical compositions of lignins

	Poplar		Pine		Bamboo	
	Aminated lignin	FA lignin	Aminated lignin	FA lignin	Aminated lignjn	FA lignin
Recovery (g/100 g RM*)	46.77	25.09	39.82	16.91	46.41	26.13
Klason lignin (%)	88.36	86.53	87.34	87.84	85.29	85. 96
Soluble lignin (%)	6.09	2.16	4.96	0.77	5.90	3.16
Total lignin (%)	94.45	88.69	92.30	88.61	91.19	89.12
Xyl (%)	--	1.55	--	1.43	--	2.98
Glc (%)	2.58	4.39	2.01	1.28	3.21	4.09
Man (%)	0.38	1.63	1.19	4.62	--	0.19
4-O-MeGlcA (%)	0.66	0.53	0.19	0.19	0.37	0.17
Gal (%)	--[c]	--	--	2.19	--	--
Rha (%)	0.11	0.12	--	--	--	--
GalA	0.75	0.66	0.31	0.12	--	--
Total sugar (%)	4.48	8.88	3.70	9.83	3.58	7.35

*RM: raw material

Table S4. Quantification of chemical structure of lignins

	Poplar			Pine			Bamboo		
	MWL	Aminated lignin	FA lignin	MWL	Aminated lignin	FA lignin	MWL	Aminated lignin	FA lignin
Nitrogen content	--	5.05	0.31	--	5.36	0.15	--	5.31	0.59
Lignin interunit linkage (100Ar)									
β−O−4	48.52	10.25	--	48.72	9.04	--	48.61	7.11	--
β−*β*	8.01	--	--	6.17	--	--	12.12	--	--
β−5	3.88	--	--	20.21	--	--	5.90	--	--
β−1	--	--	--	--	--	--	2.40	--	--
Lignin hydroxyl groups (mmol/g)									
Aliphatic OH	4.60	0.67	7.09	4.99	1.02	8.81	4.32	0.78	5.29
C_5-substitued OH	0.26	0.79	1.03	--	0.47	0.52	0.29	0.72	1.35
G-OH	0.47	0.53	0.29	0.87	0.51	0.73	0.44	0.48	0.57
H-OH	0.56	0.16	0.07	0.34	0.12	0.06	0.55	0.41	0.44
Total phenolic OH	1.29	1.48	1.39	1.11	1.10	1.19	1.38	1.61	2.36
Carboxylic acid OH	0.20	0.16	0.33	0.16	0.19	0.29	0.09	0.27	0.15

Table S5. Quantification details of *β*−O−4 linkage

		Poplar			Pine			Bamboo		
		MWL	Aminated lignin	FA lignin	MWL	Aminated lignin	FA lignin	MWL	Aminated lignin	FA lignin
2D HSQC NMR										
	δC/δH	90-78/6-2.5	90-78/6-2.5	90-78/6-2.5	90-78/6-2.5	90-78/6-2.5	90-78/6-2.5	90-78/6-2.5	90-78/6-2.5	90-78/6-2.5
	Integral	1.00	1	1	1	1	1	1	1	1
A_α	δC/δH	71.6/4.8	51.6/4.3	--	71.6/4.8	51.2/4.3	--	71.6/4.8	51.3/4.3	--
	Integral	0.55	0.22	--	0.40	0.20	--	0.48	0.18	--
A_β	δC/δH	84.4/4.3, 86.7/4.1	77.7/5.3, 80.9/5.0	--	84.5/4.3	77.6/5.3, 80.9/5.0	--	84.0/4.3, 86.1/4.1	77.6/4.3, 80.1/4.9	--
	Integral	0.52	0.21	--	0.39	0.21	--	0.46	0.17	--
Aγ	δC/δH	59.5/3.7-2.8	59.5/3.7-2.8	--	59.5/3.7-2.8	60.0/3.5	--	59.5/3.7-2.8	59.6/3.8-3.2	--
	Integral	1.42	0.65	--	0.96	0.26	--	0.70	1.23	--
^{13}C NMR										
I (163.0-100.0)		600	600	--	600	600	600	600	600	600
I (90.0-78)		93.42	46.56	--	124.92	45.18	--	100.68	41.82	--
β−O−4		48.52	10.25	--	48.72	9.04	--	48.61	7.11	--

Table S6. The CO_2 uptake of amino LMNPs from different biomass using wet method

Species	Methods	CO_2 uptake		
		Mass (mg/g lignin)	Volume (cc/g)	Molar (mmol/g)
Poplar	M1	139.75	70.58	3.18
	M2	165.60	83.63	3.76
	M3	200.20	101.11	4.55
	M4	175.13	88.45	3.98
Pine	M1	156.49	79.04	3.56
	M2	226.11	114.20	5.14
	M3	280.52	141.68	6.38
	M4	320.58	161.91	7.29
Bamboo	M1	159.14	80.37	3.62
	M2	247.20	124.85	5.62
	M3	324.12	163.70	7.37
	M4	386.51	195.20	8.78

Note: the adsorption temperature was 25 °C, the CO_2 flow rate was 100 mL/min at 1 bar, and the lignin concentration was 2 mg/mL.

Table S7. The CO_2 uptake of amino LMNPs with different concentrations by wet method

Species	Methods	Concentration (mg/mL)	CO_2 uptake		
			Mass (mg/g lignin)	Volume (cc/g)	Molar (mmol/g)
Bamboo	M3	1	315.36	159.27	7.18
		2	324.12	163.70	7.37
		3	304.13	153.60	6.91
		5	277.68	140.24	6.31

Note: The adsorption temperature was 25 °C, the CO_2 flow rate was 100 mL/min at 1 bar, and the amino LMNPs were prepared from bamboo using method 3.

Table S8. The CO_2 uptake of LMNPs prepared by different lignin using wet method

Species	Methods	Lignin	CO2 adsorption capacity		
			Mass (mg/g lignin)	Volume (cc/g)	Molar (mmol/g)
Bamboo	M3	FA	84.76	42.81	1.93
		Aminated lignin	268.87	135.80	6.11
		Amino lignin	324.12	163.70	7.37

Note: the adsorption temperature was 25 °C, the CO_2 flow rate was 100 mL/min at 1 bar, the lignin concentration was 2 mg/mL, and the amino LMNPs were prepared from bamboo using method 3.

Table S9. The regeneration performance of amino lignin by wet method

Lignin	Cycle	CO_2 adsorption capacity		
		Mass (mg/g lignin)	Volume (cc/g)	Molar (mmol/g)
Amino lignin	1st	324.12	163.70	7.37
	2nd	321.64	162.45	7.31
	3rd	319.34	161.28	7.25
	4th	314.16	158.67	7.14
	5th	313.68	158.43	7.13

Note: the adsorption temperature was 25 °C, the CO_2 flow rate was 100 mL/min at 1 bar, the lignin concentration was 2 mg/mL, and the amino LMNPs were prepared from bamboo using method 3.

Table S10. The CO_2 adsorption capacity of amino lignin by TGA (25 °C, 100 mL/min CO_2, 1 bar)

Species	Methods	CO2 adsorption capacity (mg/g lignin)					CO_2/N_2 selectivity
		1st	2nd	3rd	4th	5th	
Poplar	M1	12.69	12.08	11.80	11.69	11.62	14.59
	M2	11.69	11.28	11.12	11.01	10.91	12.85
	M3	11.43	11.21	11.22	11.15	11.13	13.45
	M4	11.03	11.10	11.16	11.12	11.19	14.90
Pine	M1	12.25	12.03	11.86	11.77	11.69	16.78
	M2	11.77	11.49	11.36	11.25	11.19	13.37
	M3	13.38	13.12	12.95	12.86	12.78	17.15
	M4	11.95	11.80	11.78	11.82	11.82	16.86
Bamboo	M1	15.35	15.01	14.87	14.77	14.67	15.62
	M2	14.80	14.30	14.10	13.91	13.82	18.05
	M3	13.22	13.08	13.01	12.91	12.92	12.88
	M4	12.89	12.77	12.67	12.64	12.64	12.89

Note: the adsorption temperature was 25 °C, the CO_2 flow rate was 100 mL/min at 1 bar, and the lignin dosage was 10 mg.

Reference

1 R. Wu, X. Wang, Y. Zhang, Y. Fu and M. Qin, *Bioresource Technol.*, 2022, **345**, 126533.

2 L. Wang, L. Tan, L. Hu, X. Wang, R. Koppolu, T. Tirri, B. Van Bochove, P. Ihalainen, L. S. Seleenmary Sobhanadhas, J. V. Seppälä, S. Willför, M. Toivakka and C. Xu, *ACS Sustain. Chem. Eng.*, 2021, **9**, 8770–8782.

3 C. Libretti, L. S. Correa and M. A. Meier, *Green Chem.*, 2024, **26**, 4358–4386.

4 G. J. Jiao, P. Peng, S. L. Sun, Z. C. Geng and D. She, *Int. J. Biol. Macromol.*, 2019, **127**, 544–554.

5 X. Du, J. Li and M. E. Lindström, *Ind. Crop. Prod.*, 2014, **52**, 729–735.

6 M. Kollman, X. Jiang, S. J. Thompson, O. Mante, D. C. Dayton, H. Chang and H. Jameel, *Green Chem.*, 2021, **23**, 7122–7136.

7 J. Chen, L. An, J. H. Bae, J. W. Heo, S. Y. Han and Y. S. Kim, *Ind. Crop. Prod.*, 2021, **173**, 114102.

8 L. Liu, X. Wan, S. Chen, P. Boonthamrongkit, M. Sipponen and S. Renneckar, *ChemSusChem*, 2023, **16**, e202300276.