Supporting information

The effect of acidic ternary deep eutectic solvent treatment on native lignin

Zhiwen Wang, [†] *Yongzhuang Liu,* [§,‡] *Katalin Barta,* [¶,§] *Peter. J. Deuss*[†,*]

[†] *Department of Chemical Engineering (ENTEG), University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands; p.j.deuss@rug.nl*

[‡] *Key Laboratory of Bio-Based Material Science and Technology, Ministry of Education, Northeast Forestry University, Harbin 150040, P. R. China.*

[§] *Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands.*

[¶] *Karl-Franzens University of Graz, Heinrichstrasse 28, Graz, Austria; The Netherlands.*

Table of Contents

Number of pages: 53, Number of schemes: 1, Number of figures: 50, Number of tables: 10

Supplementary experiment sections

Materials

Chemicals such as choline chloride and ethylene glycol, oxalic acid, Ru/C (5%), Ctec2, acetic acid, sodium acetate and solvents as well as standard compounds including 4-n-propylguaiacol and 4-n-ethylguaiacol (G3) and 4-n-propylphenol were all purchased from Sigma-Aldrich. Trifluoromethanesulfonic acid (HOTf), 4-n-propanolphenol (H1) and 4-n-ethylphenol (H2) were acquired from Fluorochem. 4-n-propylguaiacol (G1) was ordered from Tokyo Chemical Industry (TCI). Octadecane was bought from Fisher Scientific. All these chemicals were used without further purification. Biomass from birch, pine, reed and walnut shell were pretreated according to our previous work.[1] Biomass was firstly smashed by a Willey mill and then extracted by ethanol/toluene (1:2, v/v) for 8 h. The dewaxed biomasses were ball milled for 6 h according to one of our previously published paper.[1] Some standard chemicals including 4-(3-hydroxypropyl)- 2,6-dimethoxyphenol (S1), 2,6-dimethoxy-4-propylphenol (S2), 4-ethyl-2,6-dimethoxyphenol (S3), methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate (FMA), methyl (E)-3-(4-hydroxy-3-methoxyphenyl) acrylate (FAMe), methyl 3-(4-hydroxyphenyl)propanoate (PMA) and hydroxycyclohexyl)propanoate (OHP)were synthesized, isolated and calibrated in our previous study.[2]

Residual enzyme lignin (REL) isolation

The REL was isolated according to our previous publication.[1] 20 g biomass with 6 h ball milled sample was used for the first enzymatic hydrolysis, after the treatment, the solid product was separated by centrifugation and freeze-dried using a lyophilizer (ALPHA 2-4 LD, Appropriate Technical Resources), and then the dried residue was further milled 6 h before the second enzymatic hydrolysis treatment. The enzyme cocktail (Ctec2, Novozymes) dosage for hydrolysis was 0.25 mL_{enzyme} /$g_{biomass}$. Accordingly, the solid lignin samples obtained are labeled Birch_REL, Pine_REL, Reed_REL and Walnut_REL. 2D HSQC NMR spectra of these lignins were collected, and the main linkages are provided in Table S6.

Carbohydrate content analysis of lignin

The carbohydrate content analysis of lignin was performed according to NREL method in a smaller scale with some modification.[3] 10 mg lignin sample was put into a 4 mL scale glass vial with screws, and 100 µL 72% H_2SO_4 was added. The vials were incubated in a water bath at 30°C for 1 h. After that, 2.8 mL MillQ-water was added, before putting the cap for the vials, the glass screw fit was taped with two rings of Teflon tape. The vials were placed into an autoclave and further hydrolyzed for 1 h at 121°C. At the same time, 10 mg of glucose, xylose, and arabinose were hydrolyzed by following the same procedures with the lignin to correct the influence of the monosaccharide degradation for the quantification. The hydrolysate was diluted 10 times before injection for the quantification of the monosaccharides. The amount of monosaccharides in the resulting solution was determined by HPLC

(1200 Agilent Technologies, USA) with a refractive index detector (RID). An aminex column HPX-87H (Bio- Rad, USA) was used to separate the monosaccharides at 50°C with 5 mM sulfuric acid at a flow rate of 0.6 mL/min. Under these conditions, xylose, mannose and galactose were eluted at the same retention time which were integrated as a single peak. Since xylan is the main hemicellulose constituent and the calibration constant among these three monosaccharides showed no large differences, the overlapped peak was directly quantified by using the calibration curve of xylose. Thus, the hemicellulose content of the samples was represented as the total amount of xylan, mannan, galactan and arabinan.

Catalytic hydrogenolysis of DES fractionated lignins

The reductive catalytic hydrogenolysis of the fractionated lignin was performed by using an optimized parameter from a published paper[33] with minor modification using a Ru/C catalyst in methanol. For each reaction, a 10 mL volume homemade batch reactor was loaded with 50 mg treated lignin, 4 mL methanol, 25 mg of 5wt% Ru/C and a magnetic stirring bar. The reactor was sealed and charged with 40 bar H_2 at room temperature. After 10 minutes, once the pressure of H_2 remained constant at 40 bar, the reactor was placed into a preheated oil bath at 250°C and stirred at 300 rpm. 3 h later, the reactor was cooled with tap water for over 15 mins to below room temperature, and then the gas was released before opening the reactor. 4 mL methanol with a concentration of 0.004 mmol/mL octadecane as GC internal standard was added to the reactor for quantitation and dilution before filtration. 1 mL filtrate was filtered using a 0.45 μm PTFE filter and transferred to a GC vial and injected into GC-FID. GC-FID was used for the quantitation of monomers using a Agilent 8860 equipped with a flame ionization detector and a HP-5 column (30 m length, 0.320 mm diam, 0.25 µm film). The following operating conditions were used: injection volume, 1 µL, injection temperature, 280°C, column temperature program: 40 °C (5min),10°C /min to 320°C, 320°C (5 min), detection temperature 320°C. The monomers were calibrated by following the method in our previous publication.[34]

Recycling of ChCl/EG/HOTf

The recycling of ChCl/EG/HOTf started from mixing 21 g ChCl, 18 g EG and 5.55 g HOTf, after a clear liquid appeared, 500 mg REL_Birch lignin was added under 500 rpm stirring. The mixture was stirred at 25 °C for 18 h. Then, the mixture was precipitated in 10 times volume of water under stirring. After 1 h precipitation without stirring, the precipitation was recovered by centrifugation (12000 rpm, Thermal Scientific Sorvall Legend X1R Centrifuge) and freeze dried (ALPHA 2-4 LD, Appropriate Technical Resources) to yield a powder was labeled Residual_L_$R_{\text{number of recycling}}$. The liquid fraction was extracted by 100 mL 2-methytetrahydrofuran for three times, and then evaporated under rotary evaporator at 70 °C for several hours (until there is no liquid condensation on the neck of the flask) to yield a mixture with mild red liquid named by Mixutre_$R_{\text{number of recycling}}$. Fresh lignin was directly charged in the mixture for next recycling without any new DES components addition. The recycling data is listed in **Table S9**.

General Characterization

The NMR analysis was performed according to the methods presented in our previous publication.[4] For REL, 40 mg lignin sample was dissolved in 0.6 mL DMSO-d_6/pyridine-d_5 (4:1, v/v), and the mixture was sonicated for 1-4 hour until a gel state appeared. For lignin after treatment, 40 mg lignin sample was dissolved in 0.65 mL DMSO-d_6 and then sonicated for 15 min in a 4 mL vial. Bruker standard pulse sequence 'hsqcetgpsisp.2' was used for the ^{13}C-^{1}H correlation experiment. A set of reported parameters with minor modification was used for the analysis: spectra were acquired using 2048 data points from 11 to 0 ppm in F2 (^{1}H) (acquisition time 130 ms), 160 to 0 ppm in F1 (^{13}C) with 256 increments (acquisition time 6 ms) of 64 scans with 1 s internal delay; the d_{24} delay was set to 86 ms. The total acquisition time was 1.2 h. The signal of the solvent was used as internal reference (δ_C 39.5, δ_H 2.49 ppm). Volume integration of the contours in HSQC spectra was performed by MestReNova (12.0.4), and the integration was used for relative comparisons, and the data was based on the total integration of S, G and H. Molar percentages of the linkages were calculated from 2D HSQC NMR spectra by using the integration of corresponding signal for the C-H at the α position divided by the integration of the total C-H's of the aromatic units according to Eq. S1..

$$No.of\ linkages = \frac{I\alpha}{\frac{S2{,}6 + S'2{,}6 + H2{,}6}{2} + G2 + G'2} \qquad \text{(Eq.S1)}$$

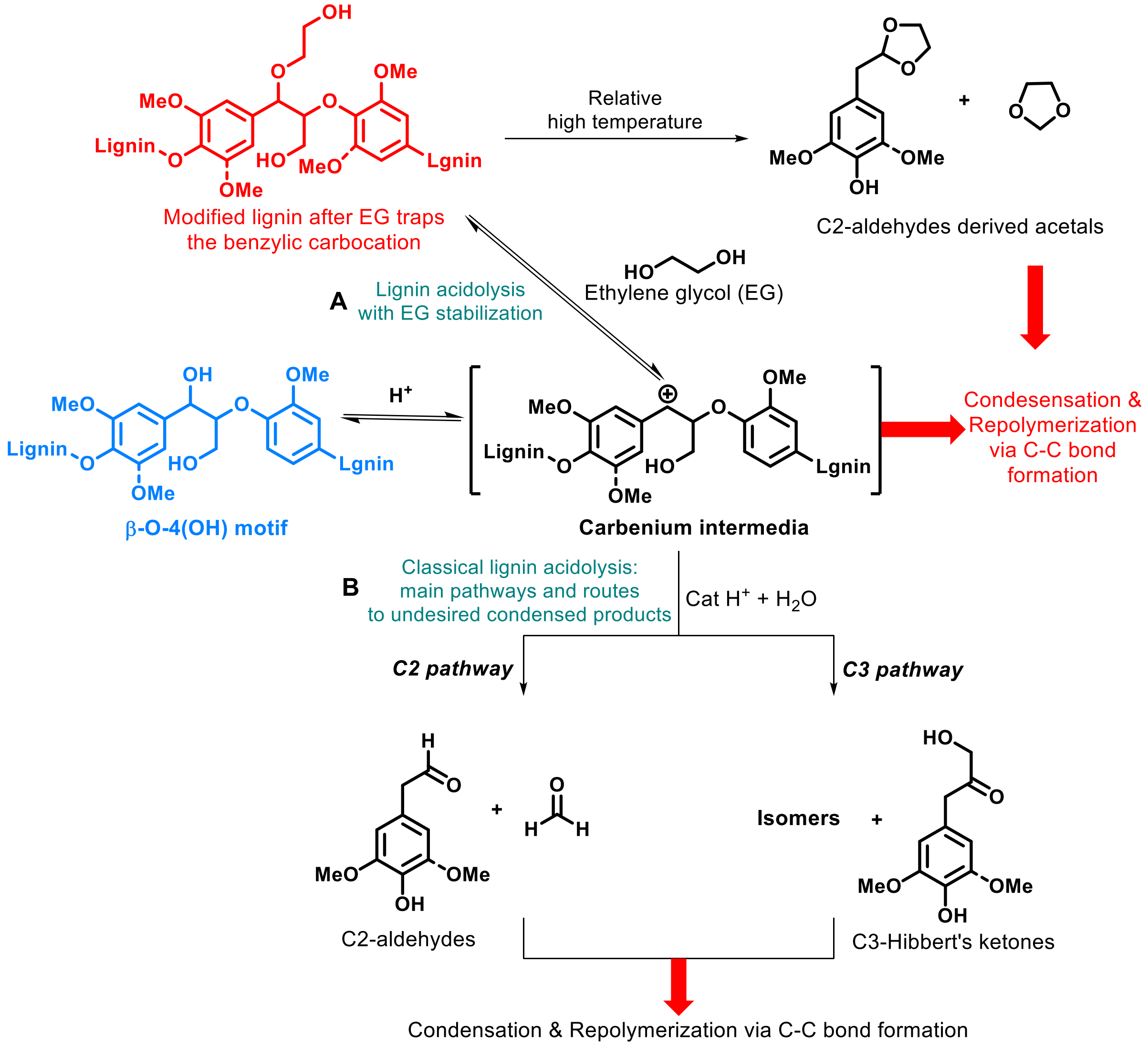
In the formula, ($S_{2,6}$+S'2,6+H2,6)/2+G2+G'2) is the total integration. S/G ratio obtained by (S2,6+S'2,6)/(G2+G'2); S = syringyl units, S' = syringyl with an α-ketone structure; G = guaiacyl structure; G' = guaiacyl units with an α-ketone structure; H = *p*-hydroxylphenyl units. S/G ratio obtained by (S2,6+S'2,6)/(G2+G'2); S = syringyl units, S' = syringyl with an α-ketone structure; G = guaiacyl structure; G' = guaiacyl units with an α-ketone structure; H = *p*-hydroxylphenyl units. Iα is the integration of α $^{13}C/^{1}H$ of the linkages; S2,6 is the integration of $^{13}C/^{1}H$ at position of 2 and 6 on the aromatic ring of syringyl units; S'2,6 is the integration of $^{13}C/^{1}H$ at position of 2 and 6 on the aromatic ring of syringyl units with a an α-ketone structure; H2,6 is the integration of $^{13}C/^{1}H$ at position of 2 and 6 on the aromatic ring of *p*-hydroxylphenyl units; G2 is the integration of $^{13}C/^{1}H$ at position of 2 on the aromatic ring of guaiacyl units; G2 is the integration of $^{13}C/^{1}H$ at position of 2 on the aromatic ring of guaiacyl units with a an α-ketone structure.

GPC was performed with DMF (containing 0.01 M LiBr) as mobile phase on a Viscotek GPC max equipped with a RID detector, a PSS, GRAM, 3 × analytical linear column (10 µm, 8× 300 mm with precolumn) and a flow rate of 1.0 mL·min^{-1}. The calibration standards were polystyrene with a calibrated range of 380- 380000 Da. Toluene was added as internal reference. The columns and detectors were held at 70°C. Data acquisition and calculations were performed using PSS WinGPC UniChrom, Build 4815, WKS024233. The samples were filtered over a 0.2 µm PTFE filter prior to injection, and a 200 µL sample with a concentration of 2.0 mg/mL was injected.

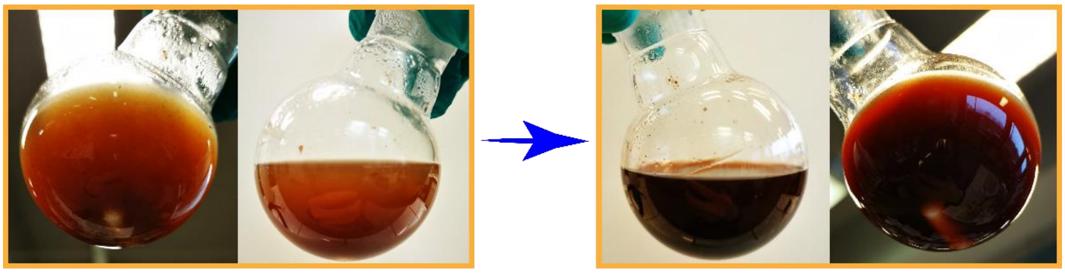
Supplementary results and discussion

Reductive catalytic hydrogenolysis (RCH) of lignin before and after ChCl/EG/OA treatment

With detailed structural information in hand of the recovered lignins, reductive catalytic hydrogenolysis (RCH) was performed before and after the treatment of ChCl/EG/OA in order to evaluate the influence of structure alteration induced by DES treatment on the monomers yields and distributions. Monomer yields from RCH can be used to evaluate the structural alteration of lignin as it specifically targets aryl ether linkages. RCH was performed according to previously established conditions,[5] and the monomer yields and distribution as well as ratios between products from S units and G units were quantified (**Figure S2**).[5,6] In total, the monomer yields before the DES treatment were higher than that after DES treatment for lignins from all the four biomasses. This decrease did not correlate with the total aryl ether linkages determined by 2D HSQC NMR analysis before and after treatment. This indicated that the lower monomer yield was not only due to the degradation of lignin, implying the EG incorporation also affects the formation of monomers. More S monomers than G monomers are released from the hydrogenolysis than expected based on the established S/G ratios. This is because C-C linking motifs such as β-5 and 5-5 are more prominently presence in high G containing lignin and these lead to dimers in hydrogenolysis.[2,5,7] Apart from monomers released from ferulate/ferulic acid and *p*-coumarate/*p*-coumaric acid (only appeared in grass samples),[2,5] the total monomer yield of these lignins followed by birch > walnut shell > reed> pine for not only REL but also DEL. This sequence does roughly correlate with their sequence of total aryl ether linkage. So overall, the benzylic alkoxylation of EG with REL prevented it from serious degradation, even though the DES treatment does partly degrade the lignin, which resulted the decreased of the total monomer yield from reductive catalytic hydrogenolysis.



Scheme S1. Schematic overview of lignin β-O-4 motif cleavage and the main pathways involved. (A) Scheme for the acidolysis of lignin β-O-4 motif with ethylene glycol stabilization. (B) Scheme representation of main paths of lignin β-O-4 motif in classical lignin acidolysis.



Reaction: 5 mins

Patially suspend in the DES

Reaction: 18 h

Completly homogenous

Figure S1. Pictures of the reaction at initial 5 mins and 18. Reaction time: reaction condition: 12.6 g (90 mmol) ChCl, 10.8 g (180 mmol) EG, 500 mg REL from walnut shell, 2.11 g oxalic acid (9%, based on the total mass of ChCl and EG) at 80°C for 18 h.

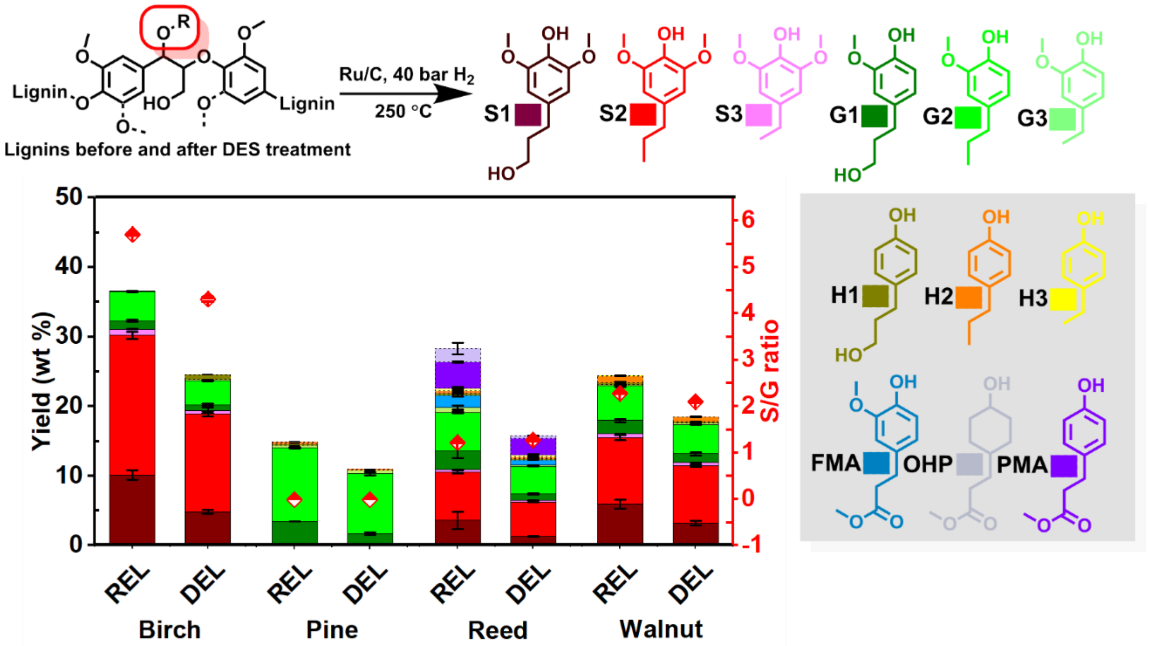


Figure S2. The yields, distribution and the S/G ratios of monomers obtained from the reductive catalytic hydrogenolysis; REL, residual enzyme lignin; DEL, REL from treatment of ChCl/EG/OA; DES reaction condition: 12.6 g (90 mmol) ChCl, 10.8 g (180 mmol) EG, 300 mg REL (from four biomasses), 2.11 g oxalic acid (9%, based on the total mass of ChCl and EG) at 80°C for 36 h; RCH conditions: 50 mg REL or DEL, 25 mg Ru/C, 4 mL methanol, 250°C, 3 h and 40 bar H_2; the monomer yield was based on the weight of lignin after correcting for the saccharide impurities and EG incorporation. Detailed data and calculation method are attached in **Table S7**.

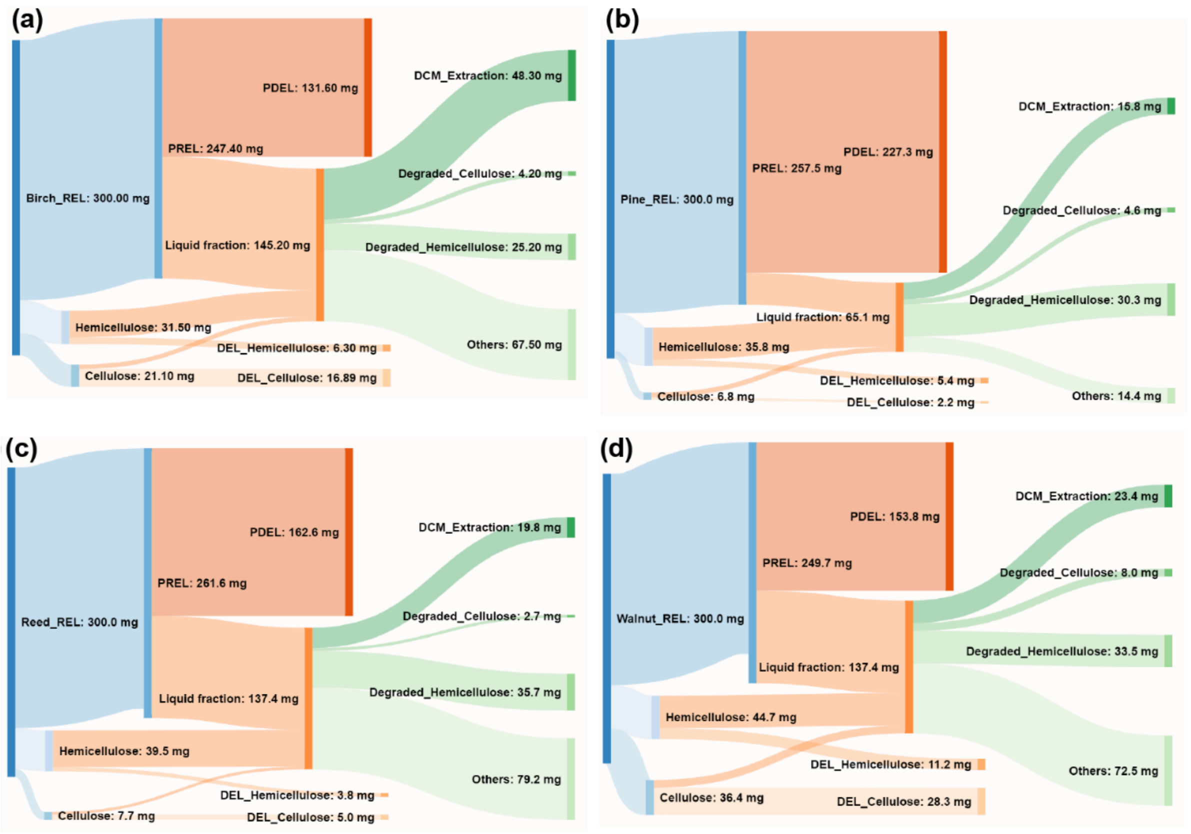


Figure S3. A rough mass balance of all the fractions tracked from the treatment of REL in acidified DES; (a), (b), (c) and (d) are fractions of REL of Birch, Pine, Reed and Walnut shell obtained from acidified DES treatment. REL, residual enzyme lignin; DEL, REL obtained from acidified DES; PREL, REL after subtracting saccharide impurity; PDES, DEL after subtracting saccharide impurity. Liquid fraction, the fraction after subtracting DEL from the REL. DCM_Extraction, weight of oil obtained from DCM extraction. DEL_Hemicellulose and cellulose are hemicellulose and cellulose of DEL. Degraded_Hemicellulose and cellulose are content of hemicellulose and cellulose obtained from the difference between REL and DEL. Others, the other components after subtracting DCM_Extraction and degraded_Hemicellulose and cellulose from the total liquid fractions, including small (oligomeric) lignin fragments.

S1 2D HSQC NMR and integration

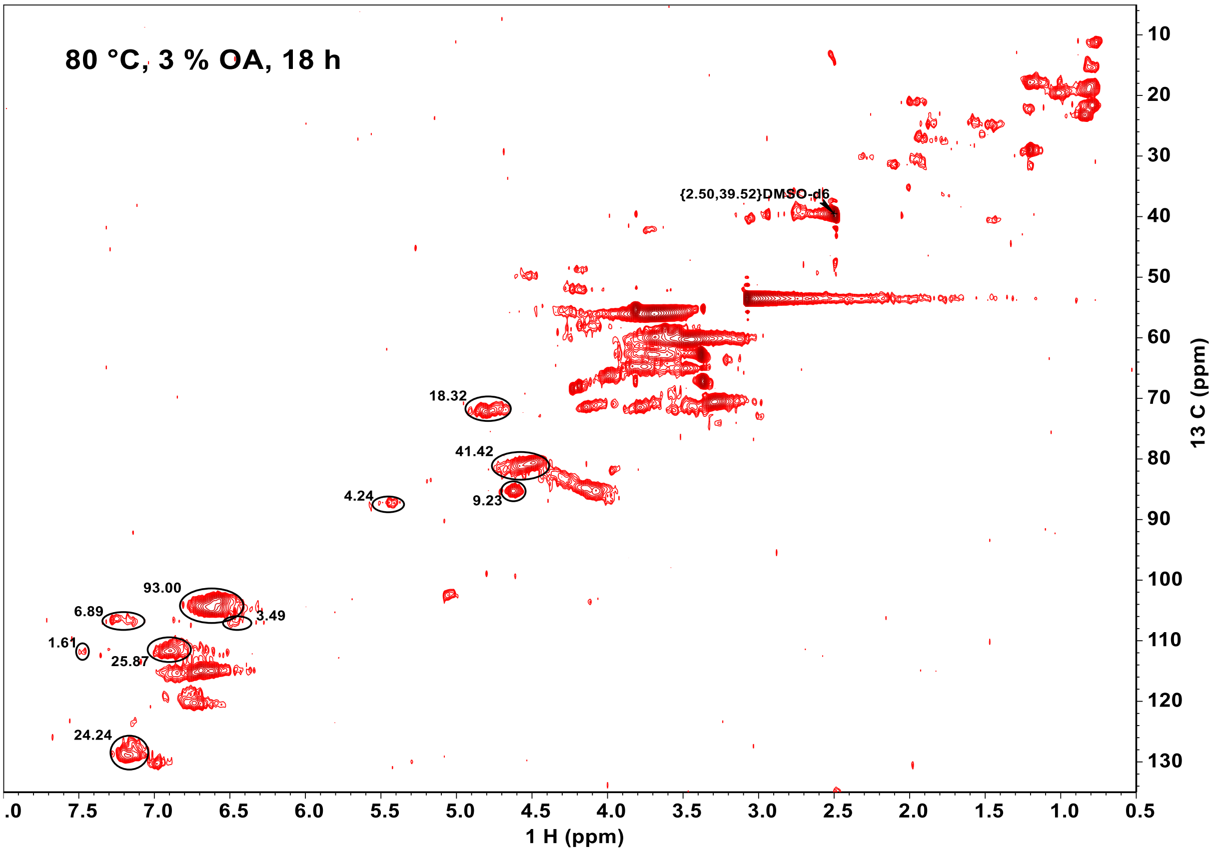


Figure S4. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating in the ChCl/EG with 3% oxalic acid at 80°C for 18 h. Reaction condition: 100 mg REL_Walnut, 4.2 g ChCl, 3.6 g ethylene glycol, 0.234 g oxalic acid, 80°C for 18 h (see detailed data in **Table S1**, **E1** and **E6**).

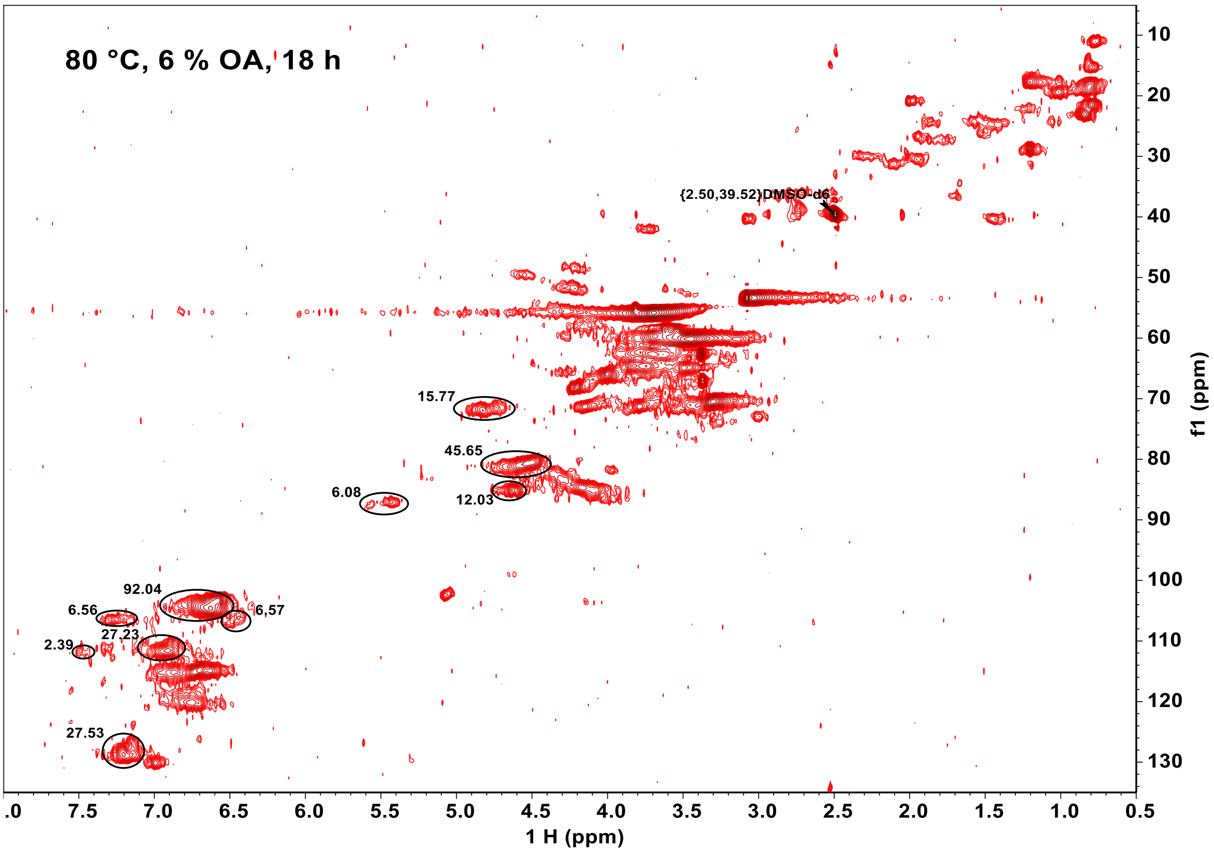


Figure S5. The 2D HSQC NMR (600 Hz, DMSO-*d*$_6$) and integration of lignin obtained from treating in the ChCl/EG with 6% oxalic acid at 80°C for 18 h. Reaction condition: 100 mg REL_Walnut, 4.2 g ChCl, 3.6 g ethylene glycol, 0.468 g oxalic acid, 80°C for 18 h (see detailed data in **Table S1**, **E2**).

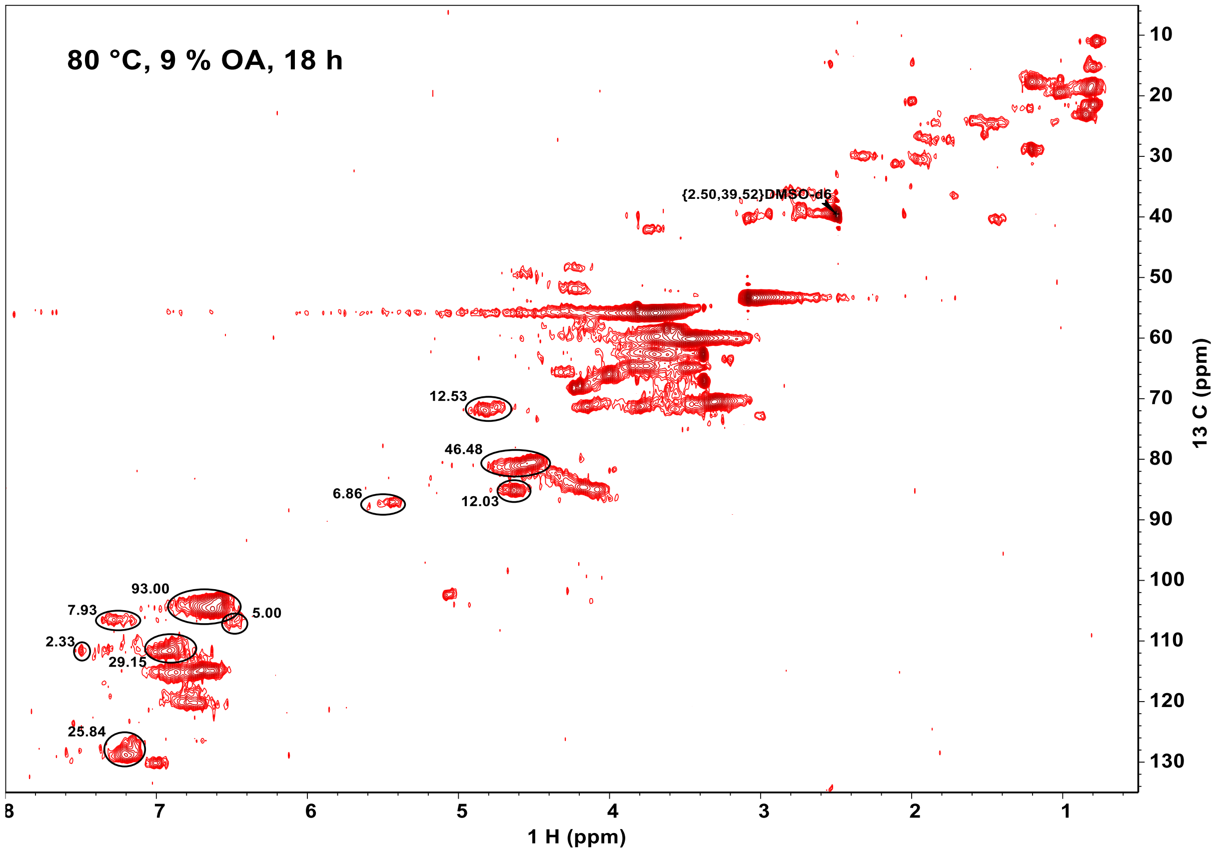


Figure S6. The 2D HSQC NMR (600 Hz, DMSO-*d*$_6$) and integration of lignin obtained from treating in the ChCl/EG with 9% oxalic acid at 80°C for 18 h. Reaction condition: 100 mg REL_Walnut, 4.2 g ChCl, 3.6 g ethylene glycol, 0.702 g oxalic acid, 80°C for 18 h (see detailed data in **Table S1**, **E3**).

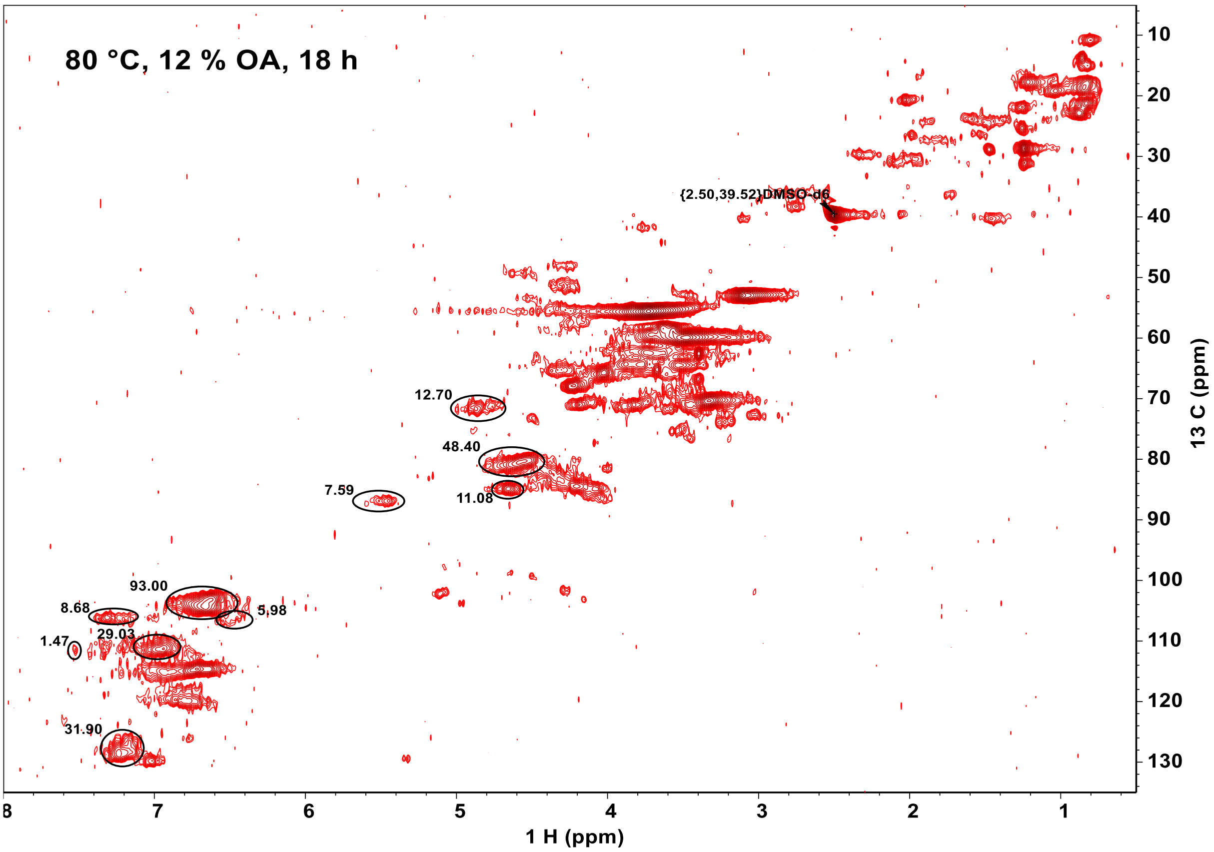


Figure S7. The 2D HSQC NMR (600 Hz, DMSO-*d*$_6$) and integration of lignin obtained from treating in the ChCl/EG with 12% oxalic acid at 80°C for 18 h. Reaction condition: 100 mg REL_Walnut, 4.2 g ChCl, 3.6 g ethylene glycol, 0.702 g oxalic acid, 80°C for 18 h (see detailed data in **Table S1**, **E4**).

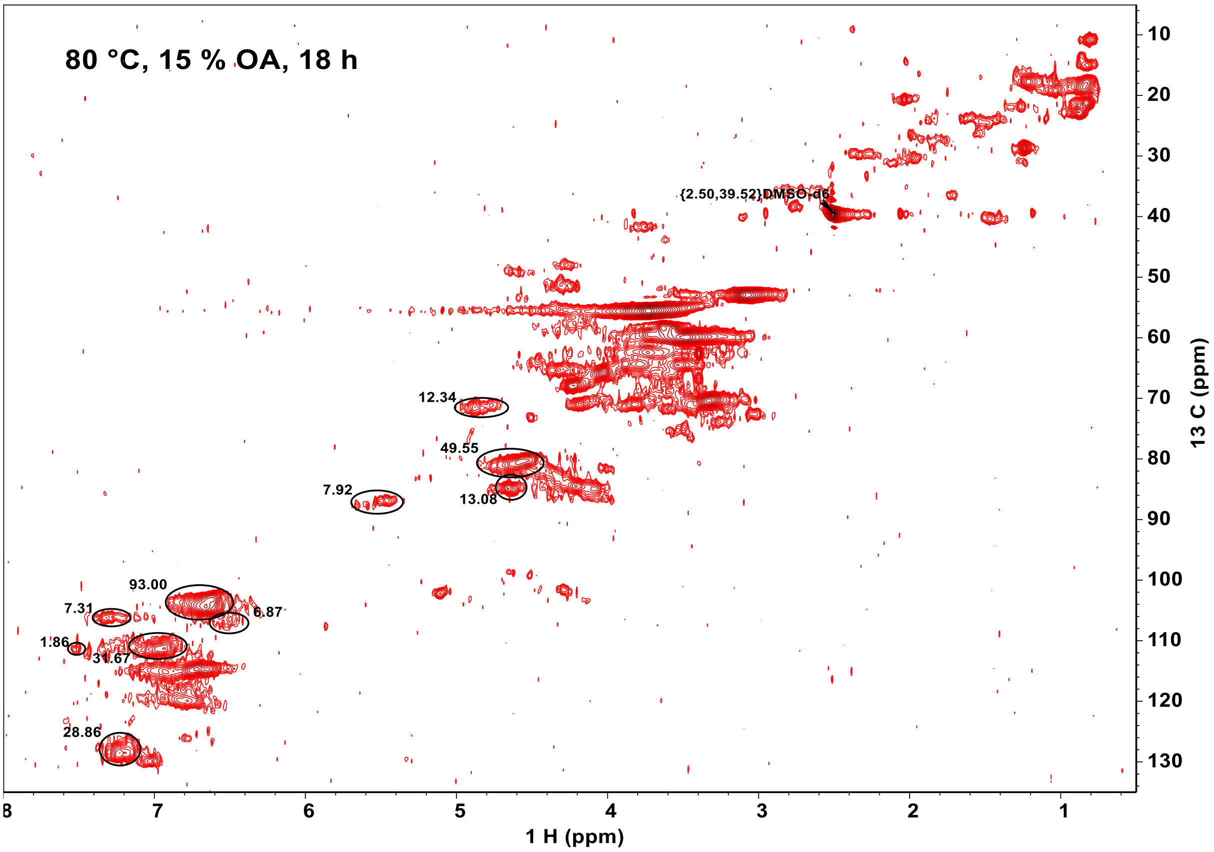


Figure S8. The 2D HSQC NMR (600 Hz, DMSO-*d*$_6$) and integration of lignin obtained from treating in the ChCl/EG with 15% oxalic acid at 80°C for 18 h. Reaction condition: 100 mg REL_Walnut, 4.2 g ChCl, 3.6 g ethylene glycol, 1.17 g oxalic acid, 80°C for 18 h (see detailed data in **Table S1**, **E5**).

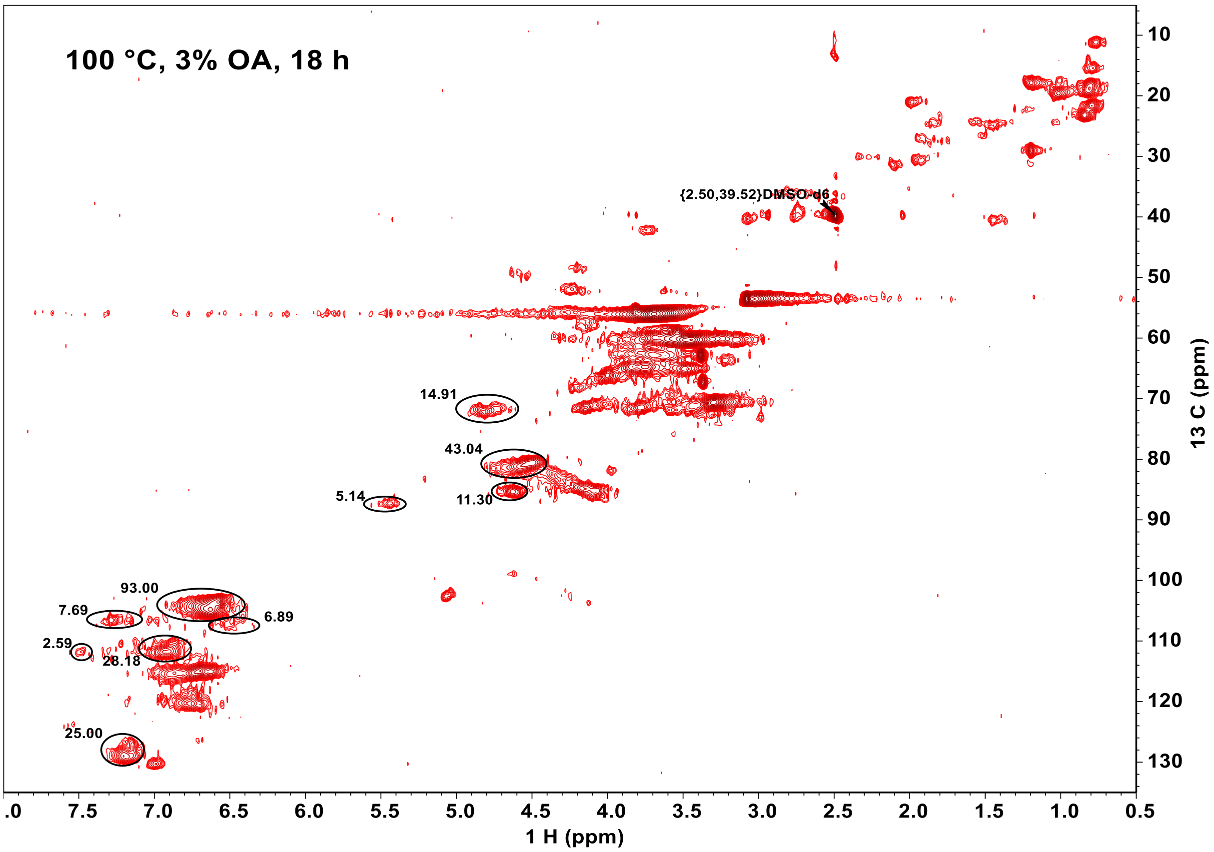


Figure S9. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating in the ChCl/EG with 3% oxalic acid at 80°C for 18 h. Reaction condition: 100 mg REL_Walnut, 4.2 g ChCl, 3.6 g ethylene glycol, 0.234 g oxalic acid, 100°C for 18 h (see detailed data in **Table S2**, **E7**).

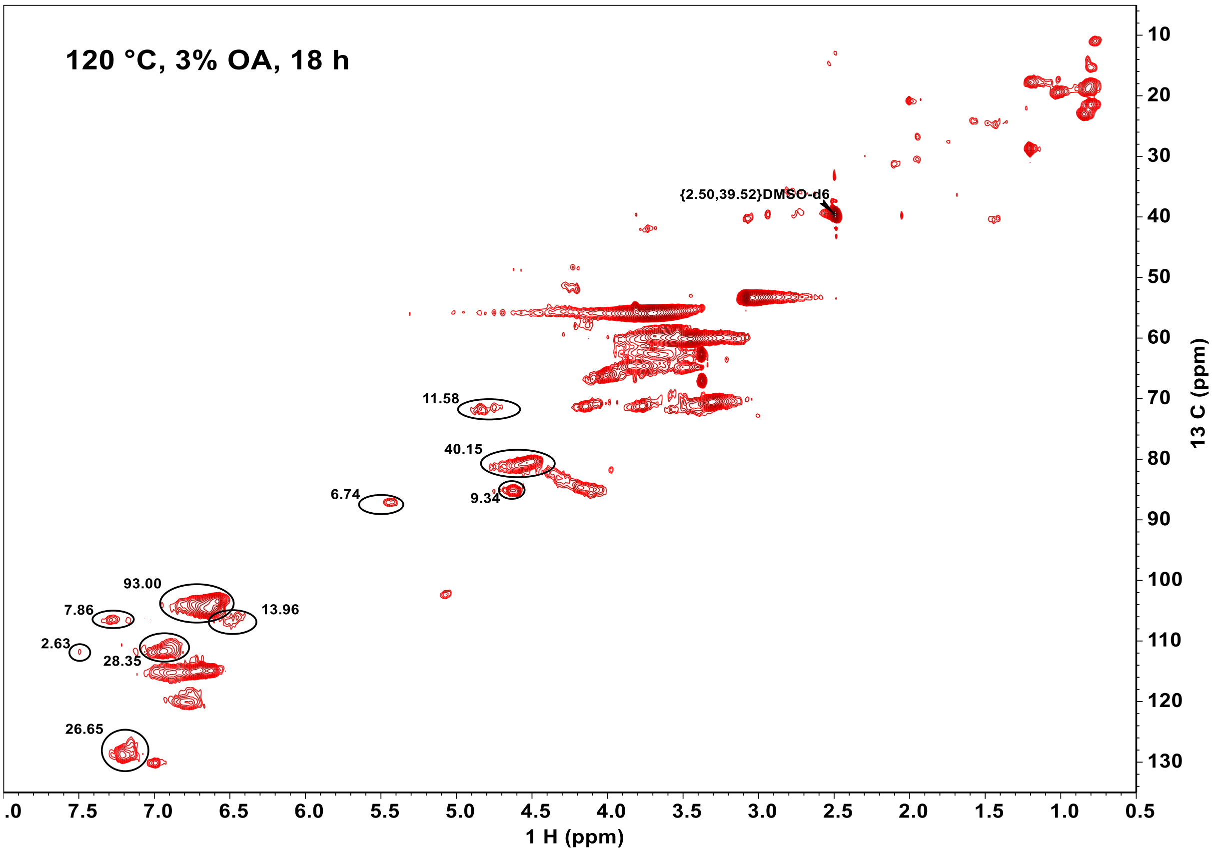


Figure S10. The 2D HSQC NMR (600 Hz, DMSO-*d*$_6$) and integration of lignin obtained from treating in the ChCl/EG with 3% oxalic acid at 80°C for 18 h. Reaction condition: 100 mg REL_Walnut, 4.2 g ChCl, 3.6 g ethylene glycol, 0.234 g oxalic acid, 120°C for 18 h (see detailed data in **Table S2**, **E8**).

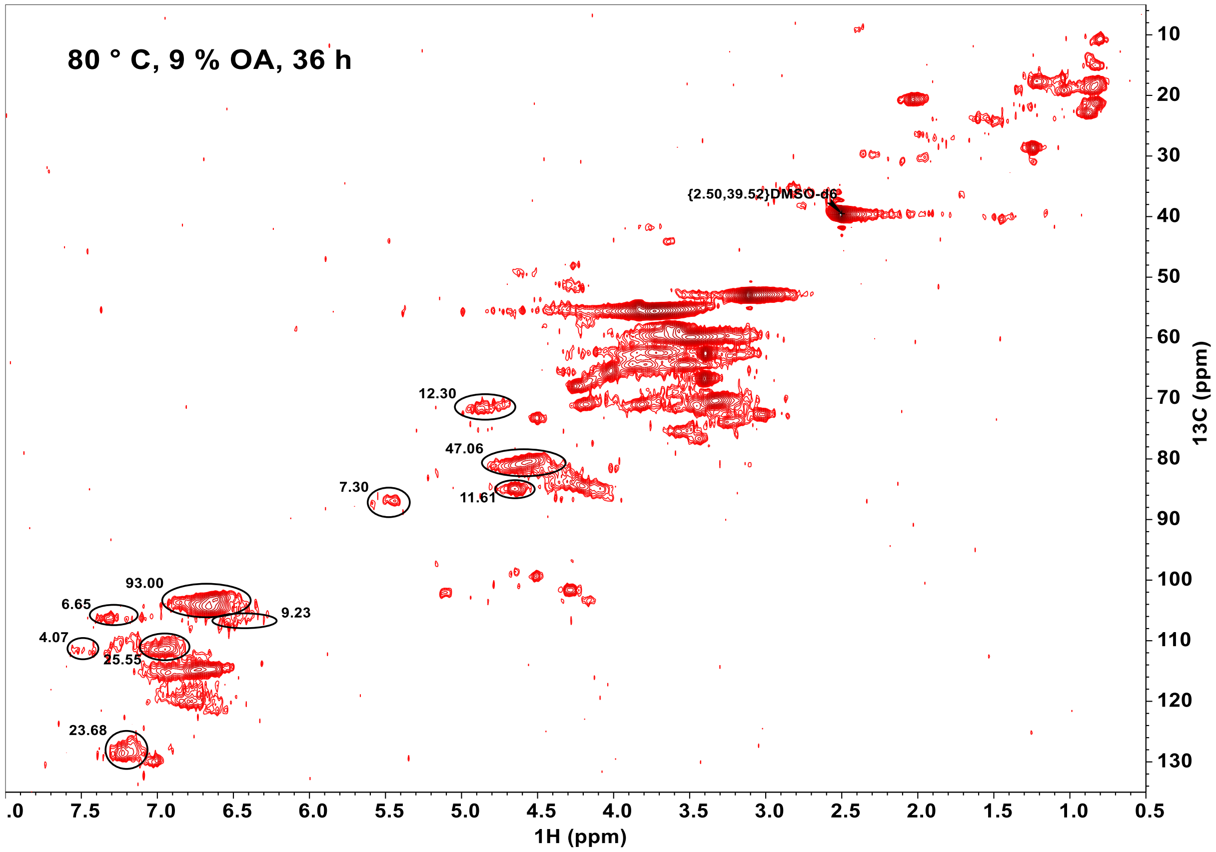


Figure S11. The 2D HSQC NMR (600 Hz, DMSO-*d*$_6$) and integration of lignin obtained from treating in the ChCl/EG with 9% oxalic acid at 80°C for 36 h. Reaction condition: 100 mg REL_Walnut, 21 g ChCl, 18 g ethylene glycol, 0.351 g oxalic acid, 80°C for 36 h (see detailed data in **Table S2**, **Ec**).

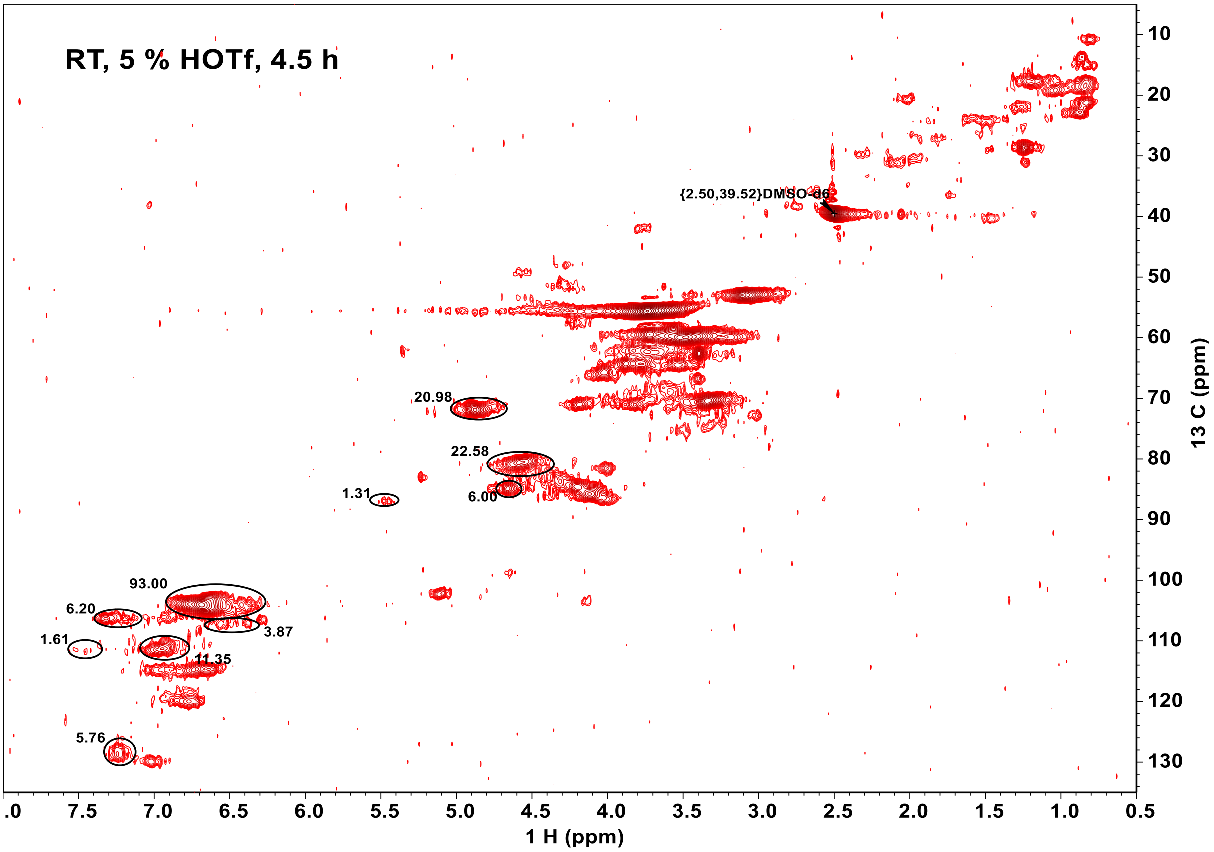


Figure S12. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating in the ChCl/EG with 5% HOTf at RT for 4.5 h. Reaction condition: 100 mg REL_Birch, 2.1 g ChCl, 1.8 g ethylene glycol, 0.195 g HOTf, RT for 4.5 h (see detailed data in **Table S3**, **E9**).

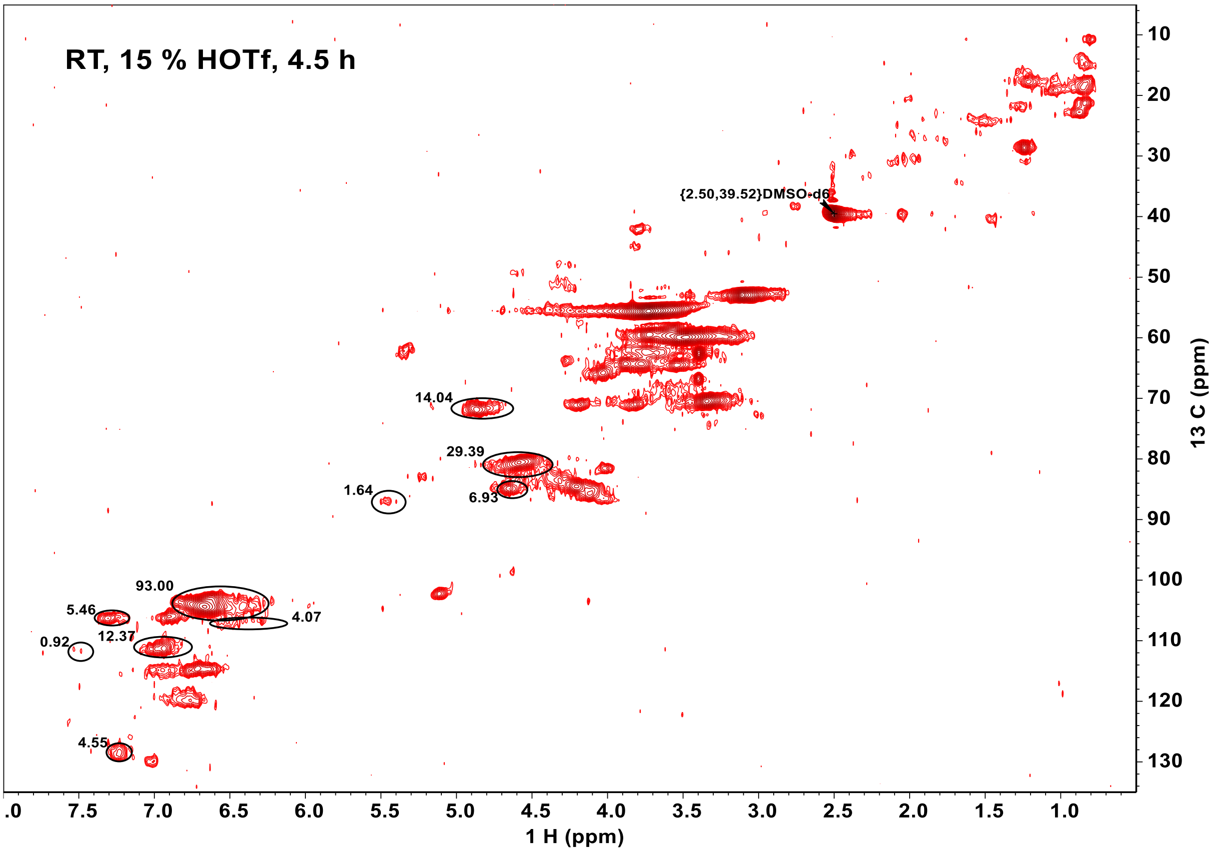


Figure S13. The 2D HSQC NMR (600 Hz, DMSO-*d*$_6$) and integration of lignin obtained from treating in the ChCl/EG with 15% HOTf at RT for 4.5 h. Reaction condition: 100 mg REL_Birch, 2.1 g ChCl, 1.8 g ethylene glycol, 0.585 g HOTf, RT for 4.5 h (see detailed data in **Table S3**, **E10** and **E 12**).

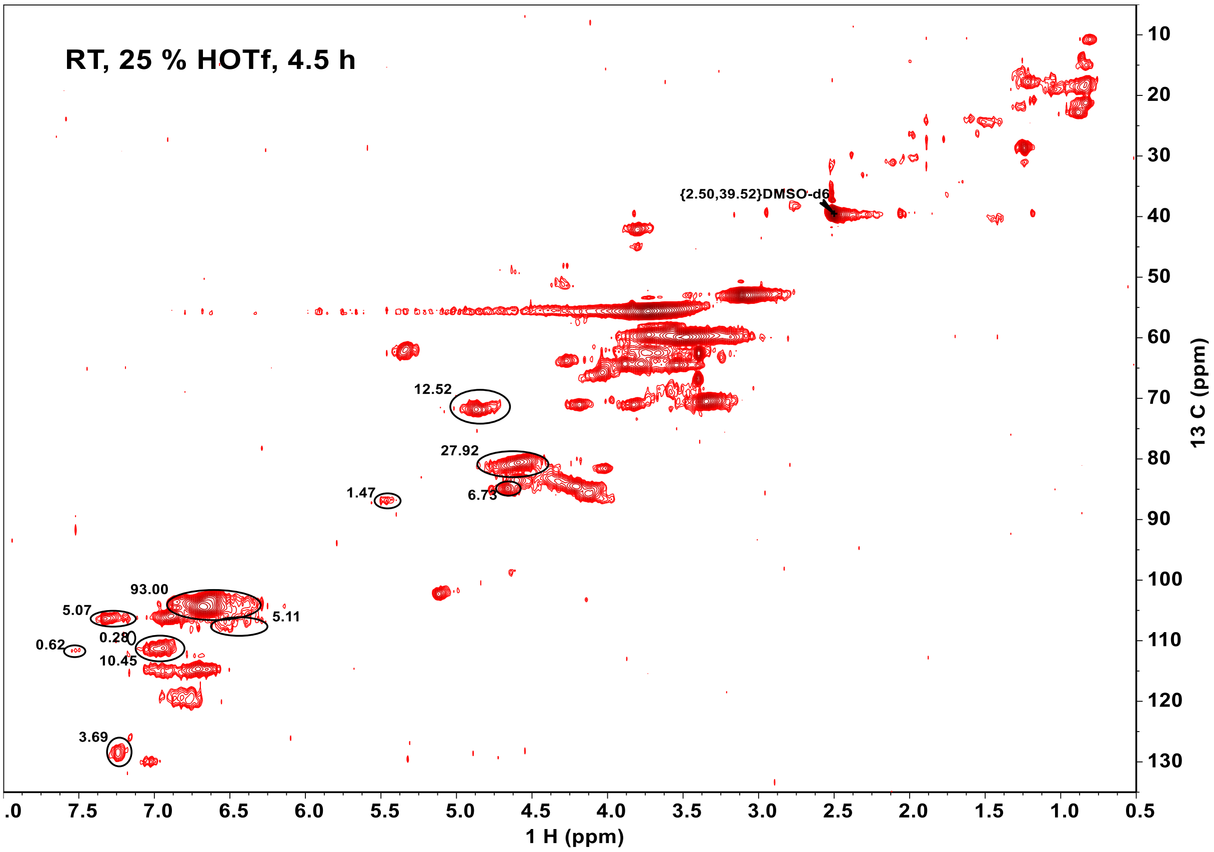


Figure S14. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating in the ChCl/EG with 25% HOTf at RT for 4.5 h. Reaction condition: 100 mg REL_Birch, 2.1 g ChCl, 1.8 g ethylene glycol, 0.975 g HOTf, RT for 4.5 h (see detailed data in **Table S3**, **E11**).

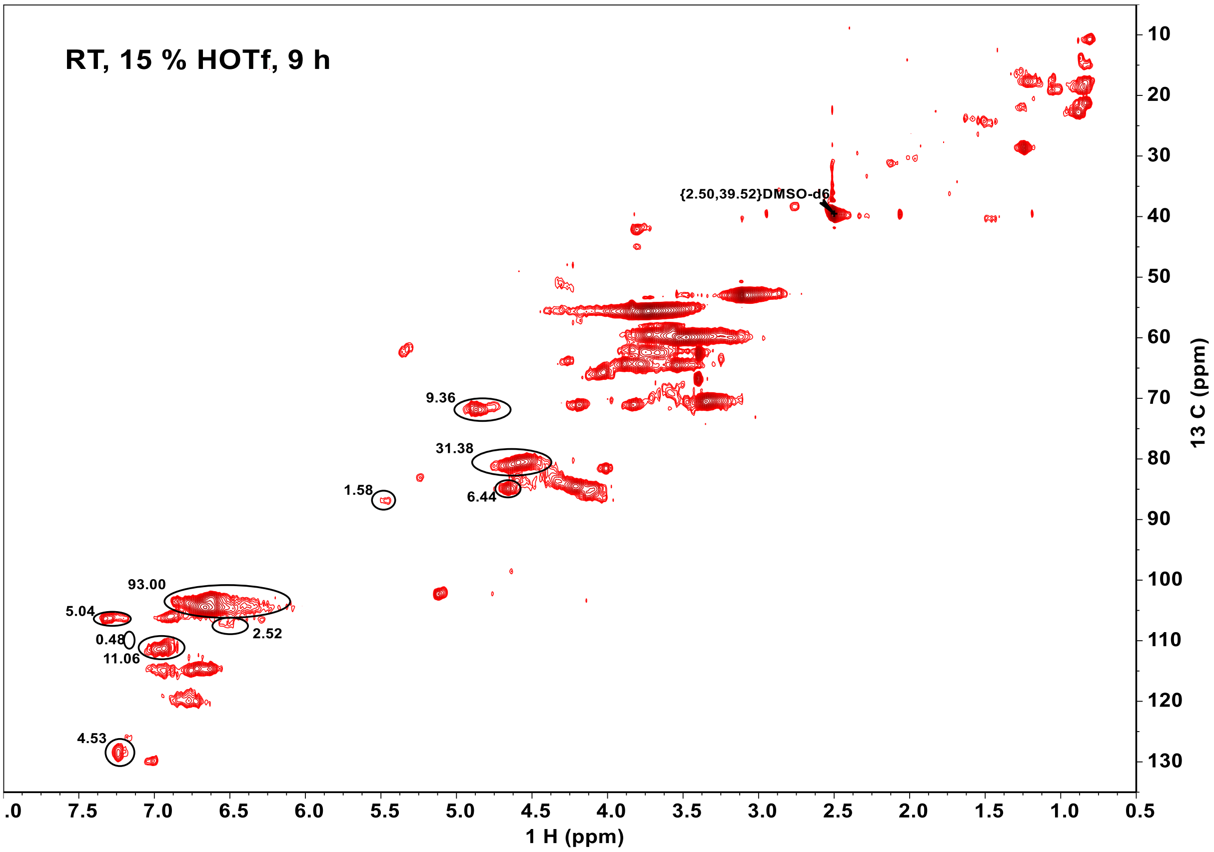


Figure S15. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating in the ChCl/EG with 15% HOTf at RT for 9 h. Reaction condition: 100 mg REL_Birch, 2.1 g ChCl, 1.8 g ethylene glycol, 0.585 g HOTf, RT for 9 h (see detailed data in **Table S4**, **E13**).

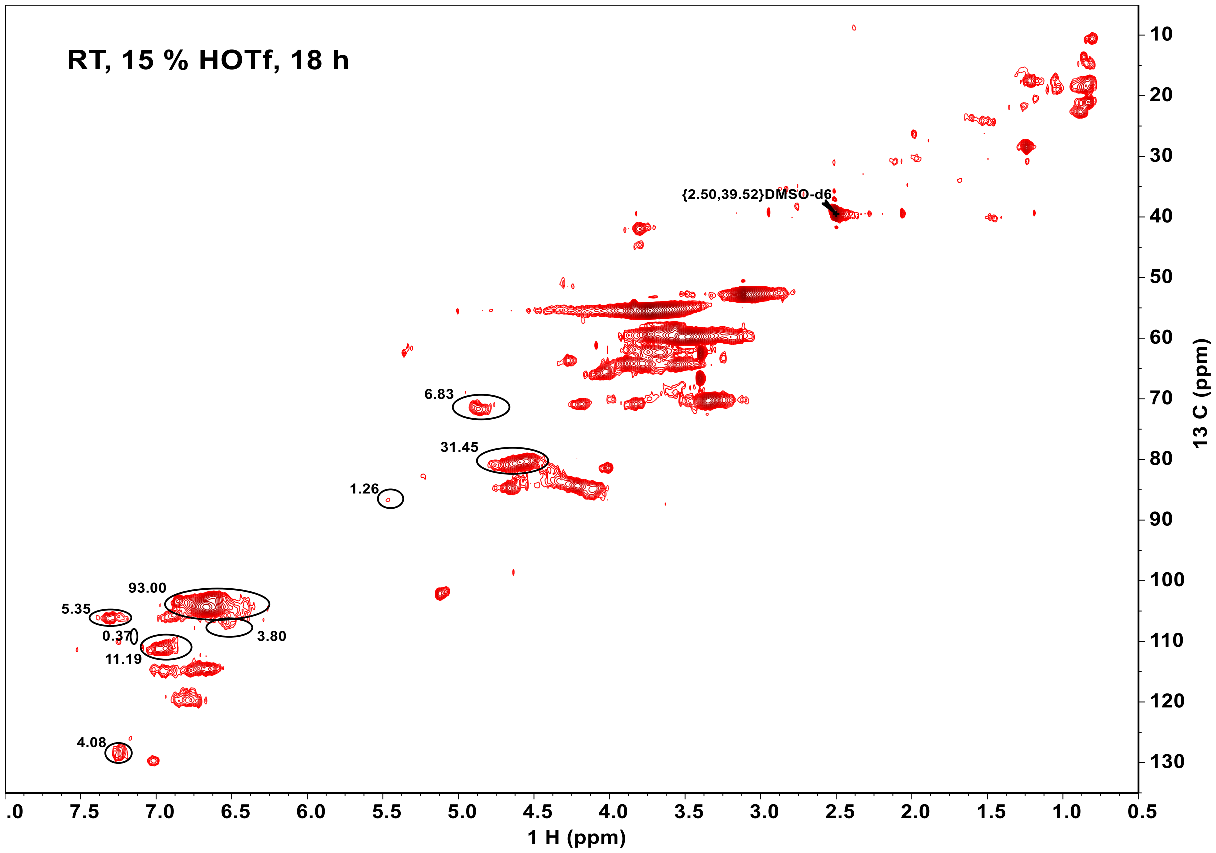


Figure S16. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating in the ChCl/EG with 15% HOTf at RT for 18 h. Reaction condition: 100 mg REL_Birch, 2.1 g ChCl, 1.8 g ethylene glycol, 0.585 g HOTf, RT for 18 h (see detailed data in **Table S4**, **E14**).

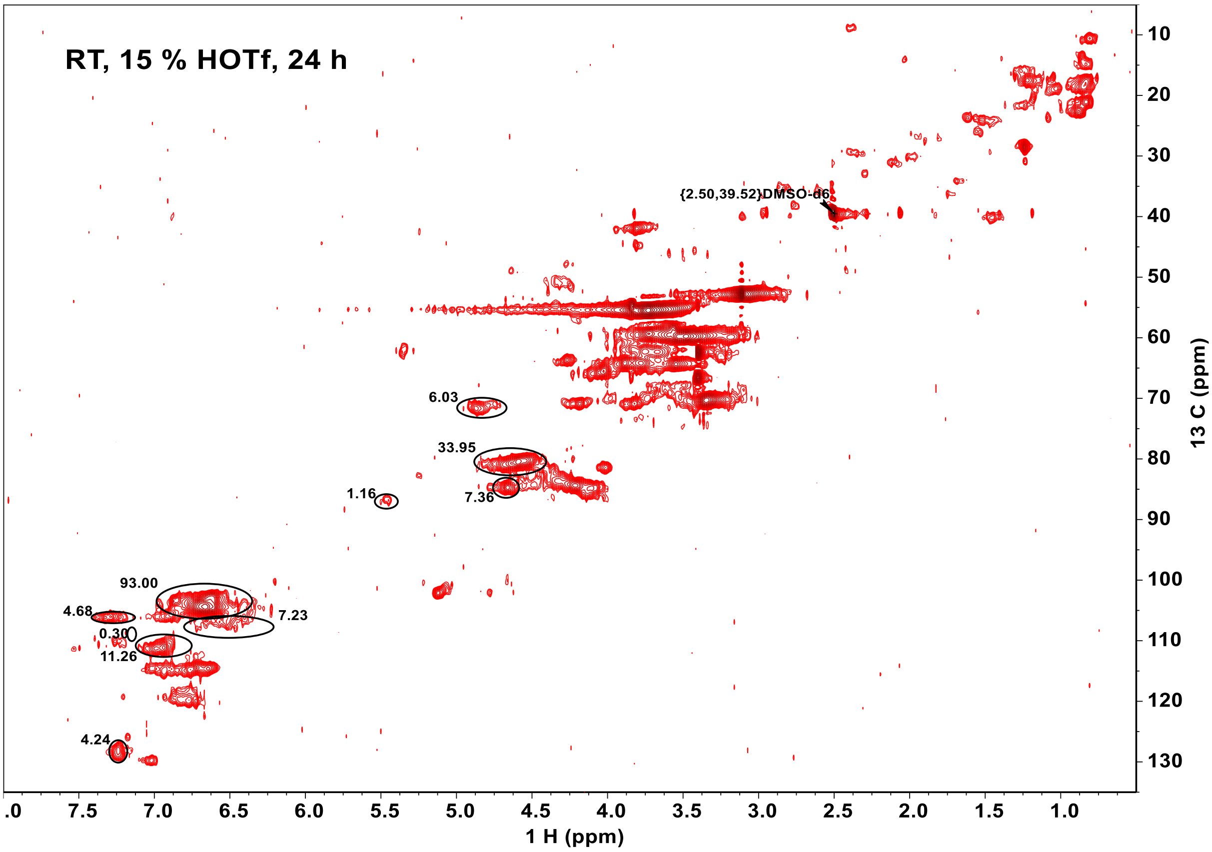


Figure S17. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating in the ChCl/EG with 15% HOTf at RT for 24 h. Reaction condition: 100 mg REL_Birch, 2.1 g ChCl, 1.8 g ethylene glycol, 0.585 g HOTf, RT for 24 h (see detailed data in **Table S4**, **E15**).

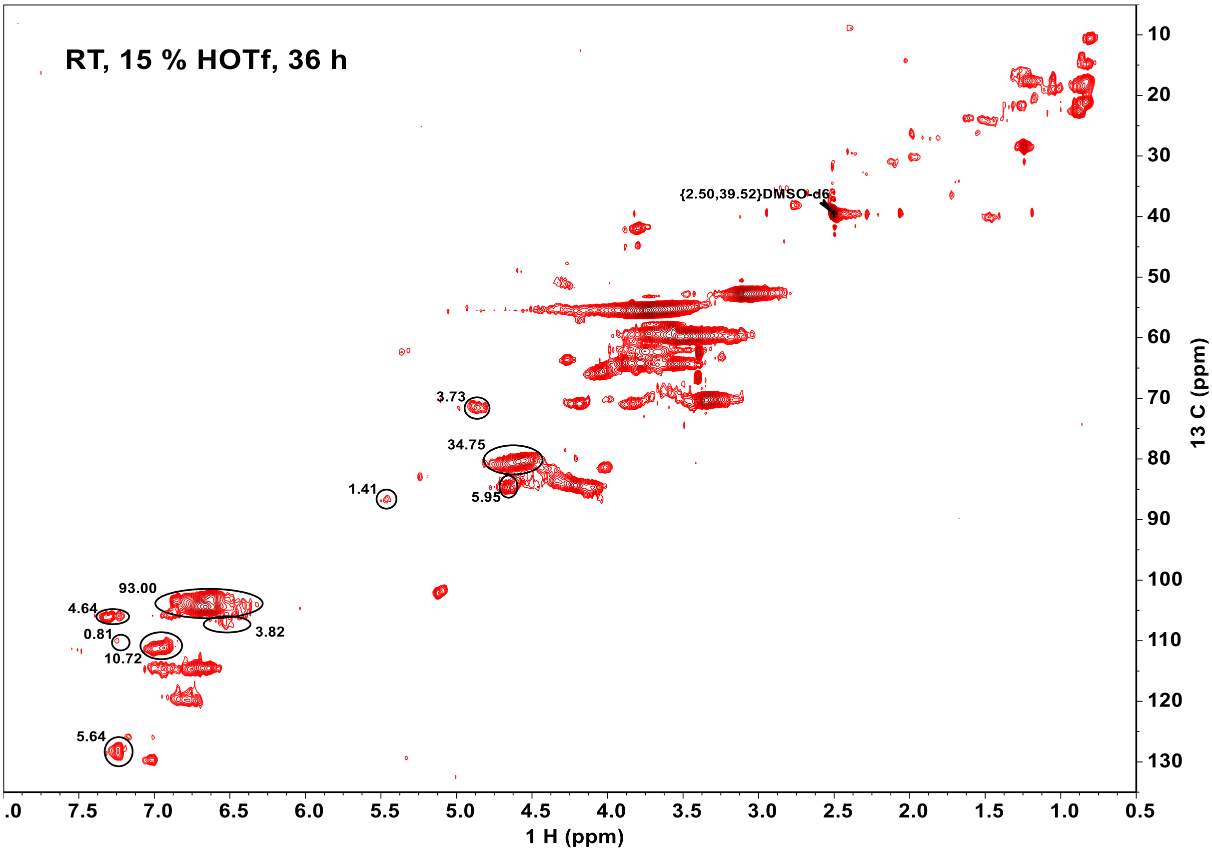


Figure S18. The 2D HSQC NMR (600 Hz, DMSO-*d*$_6$) and integration of lignin obtained from treating in the ChCl/EG with 15% HOTf at RT for 36 h. Reaction condition: 100 mg REL_Birch, 2.1 g ChCl, 1.8 g ethylene glycol, 0.585 g HOTf, RT for 36 h (see detailed data in **Table S4**, **E16**).

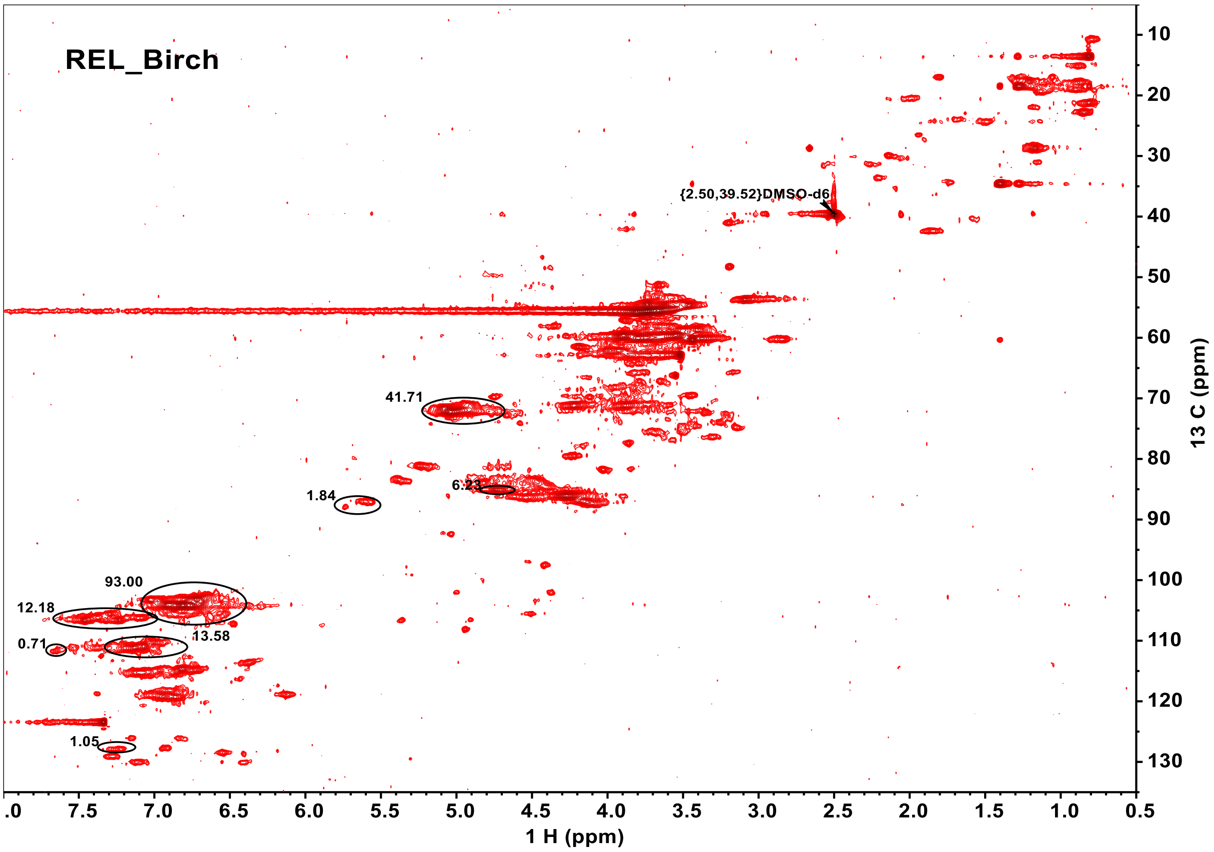


Figure S19. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of residual enzyme lignin from birch (see detailed data in **Table S3**, **STMB**, or **Table S6**).

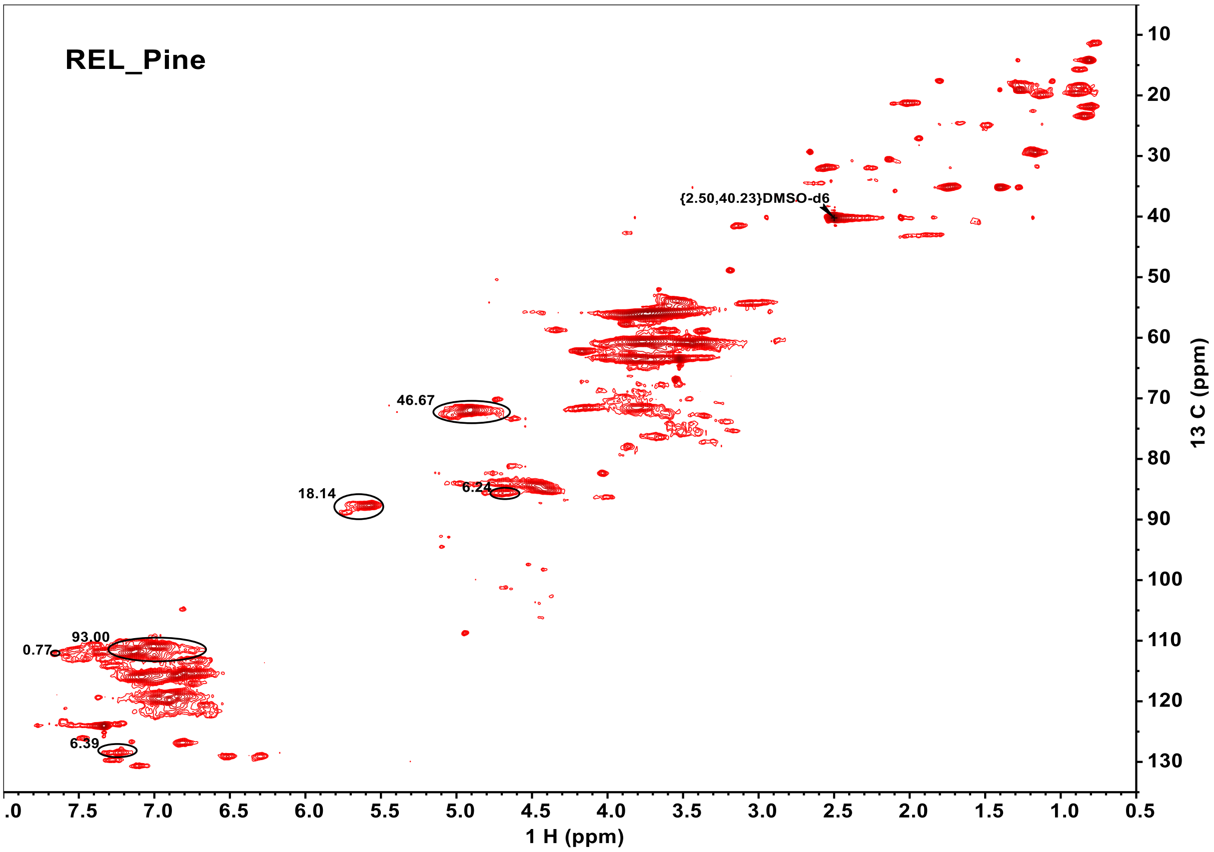


Figure S20. The 2D HSQC NMR (600 Hz, DMSO-*d*$_6$) and integration of residual enzyme lignin from pine (see detailed data in **Table S6**).

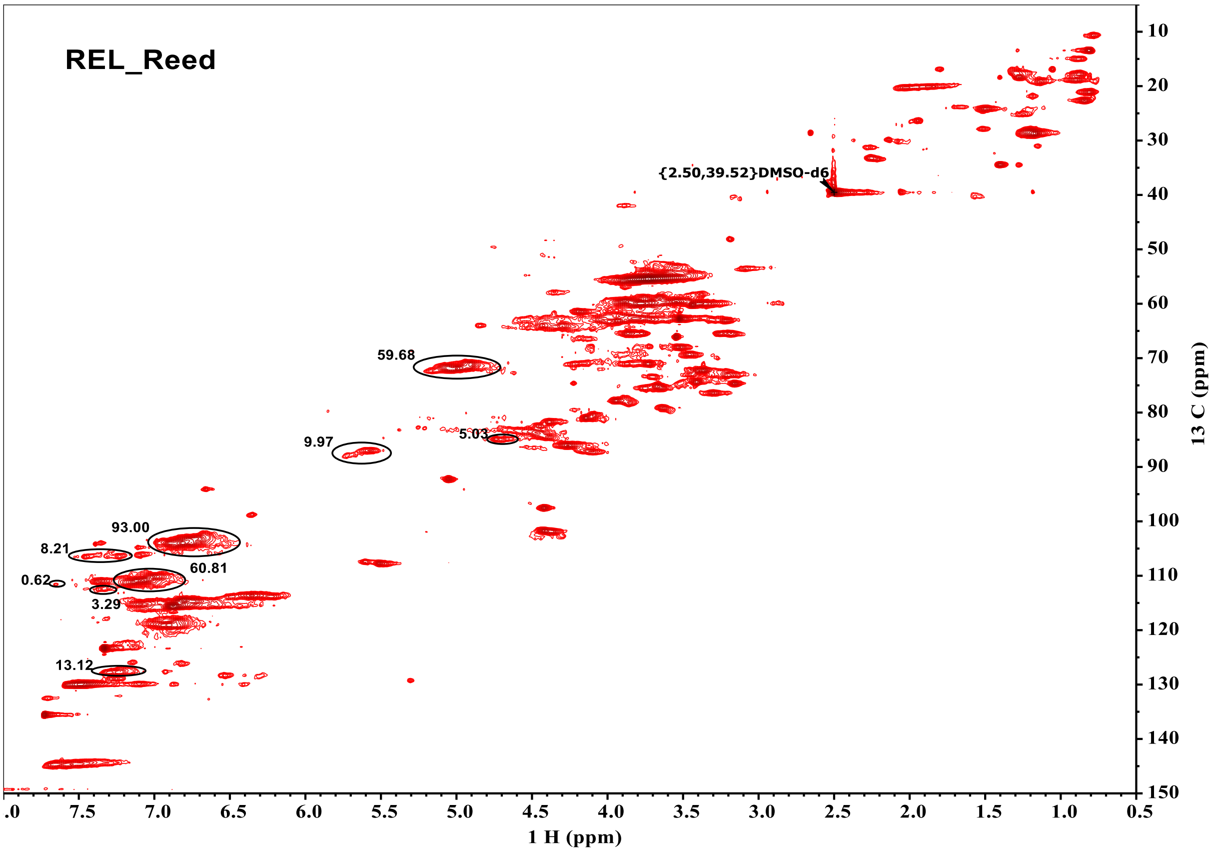


Figure S21. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of residual enzyme lignin from reed (see detailed data in **Table S6**).

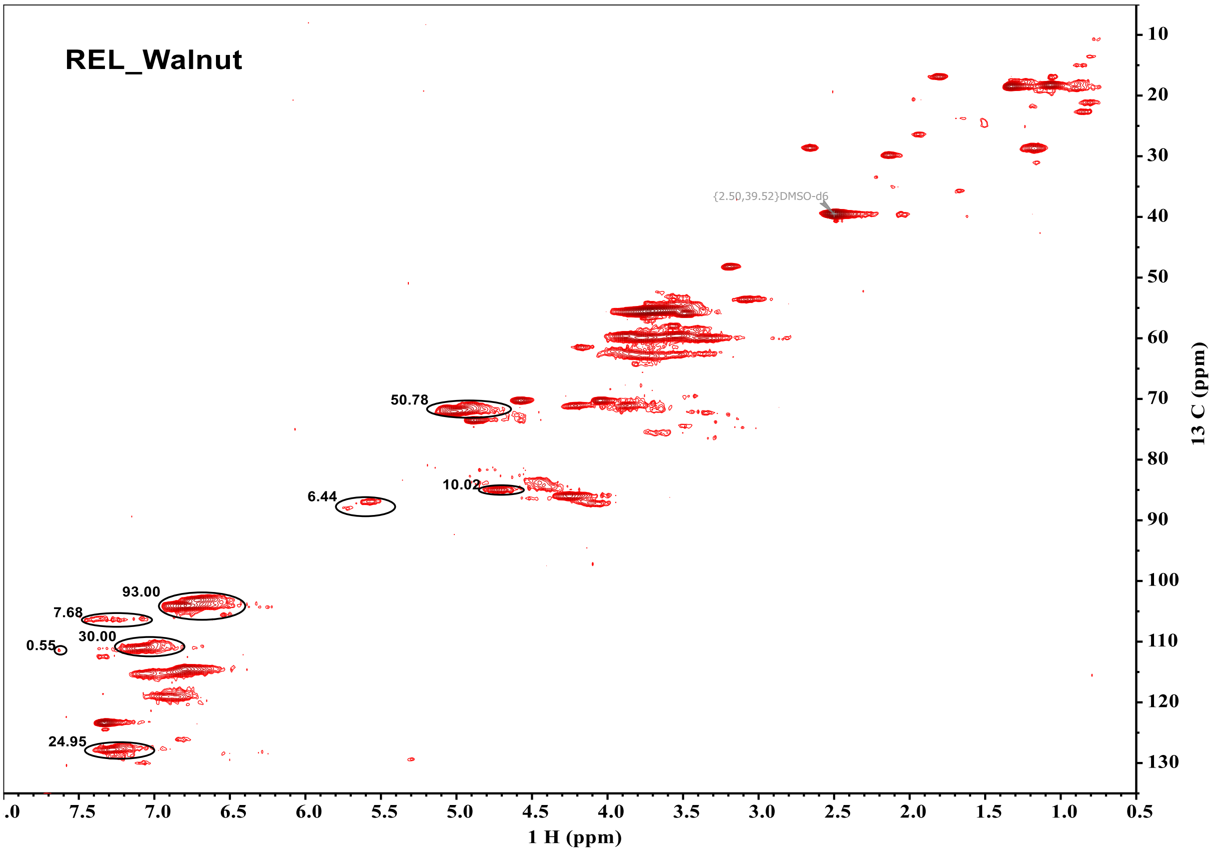


Figure S22. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of residual enzyme lignin from birch (see detailed data in **Table S1**, **STMW**, or **Table S6**).

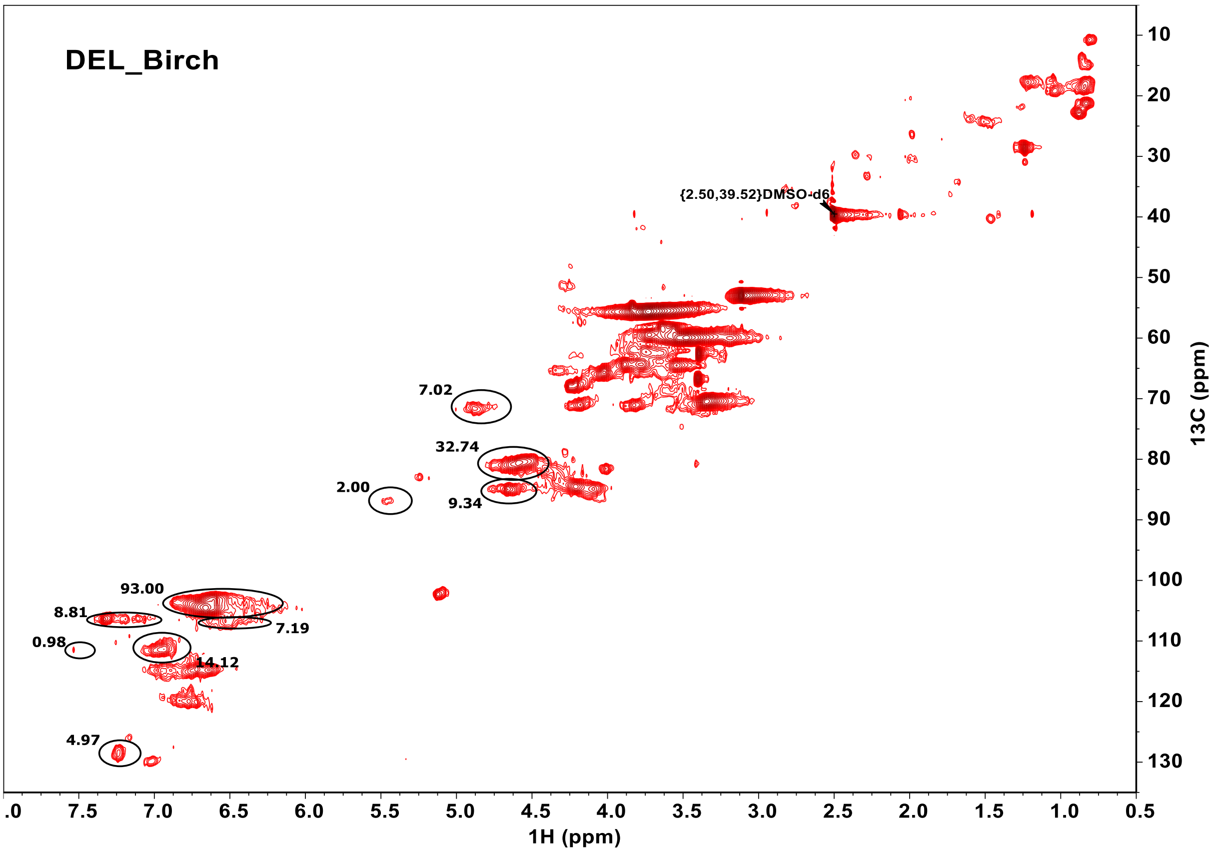


Figure S23. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating REL_Birch at ChCl/EG/OA with 9% oxalic acid at 80°C for 36 h. Reaction condition: 300 mg REL_Birch, 12.6 g ChCl, 10.8 g ethylene glycol, 2.106 g oxalic acid, RT for 36 h (see detailed data in **Table S6**).

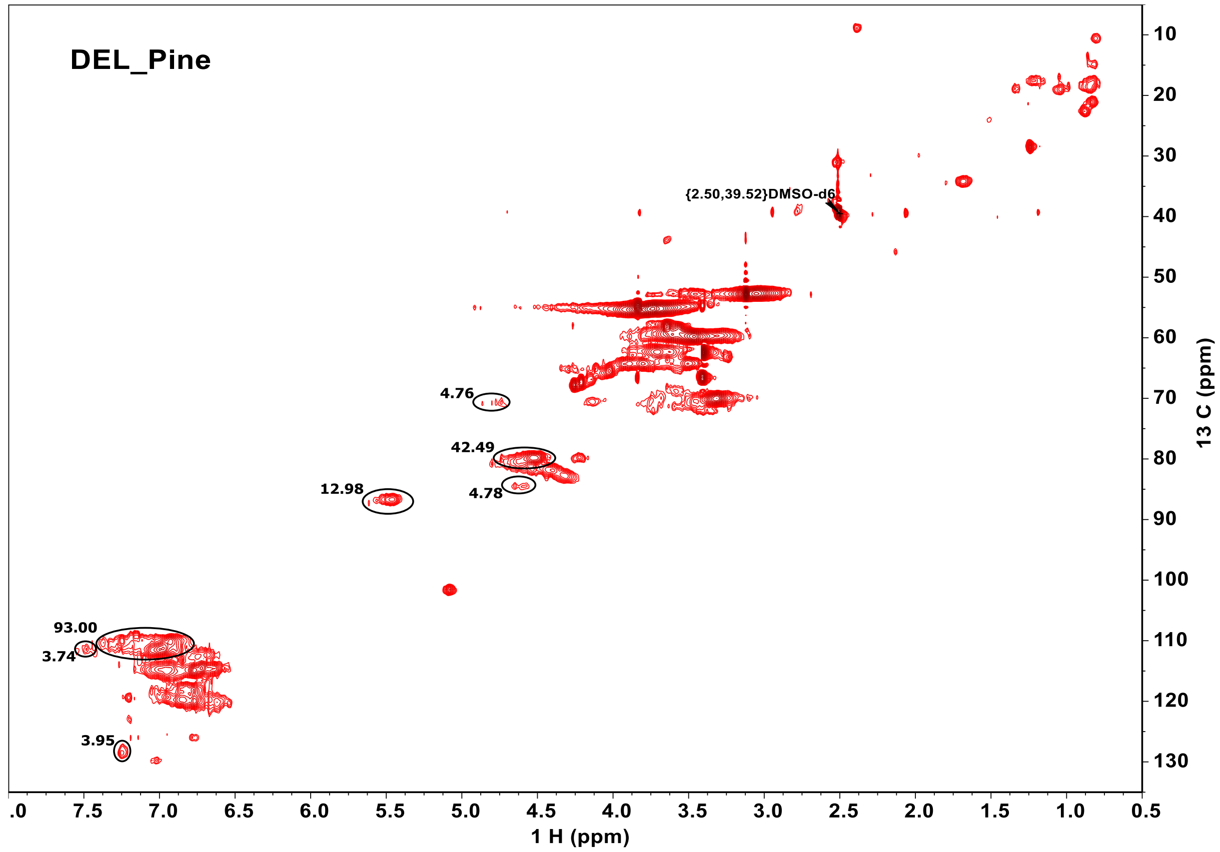


Figure S24. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating REL_Pine at ChCl/EG/OA with 9% oxalic acid at 80°C for 36 h. Reaction condition: 300 mg REL_Pine, 12.6 g ChCl, 10.8 g ethylene glycol, 2.106 g oxalic acid, RT for 36 h (see detailed data in **Table S6**).

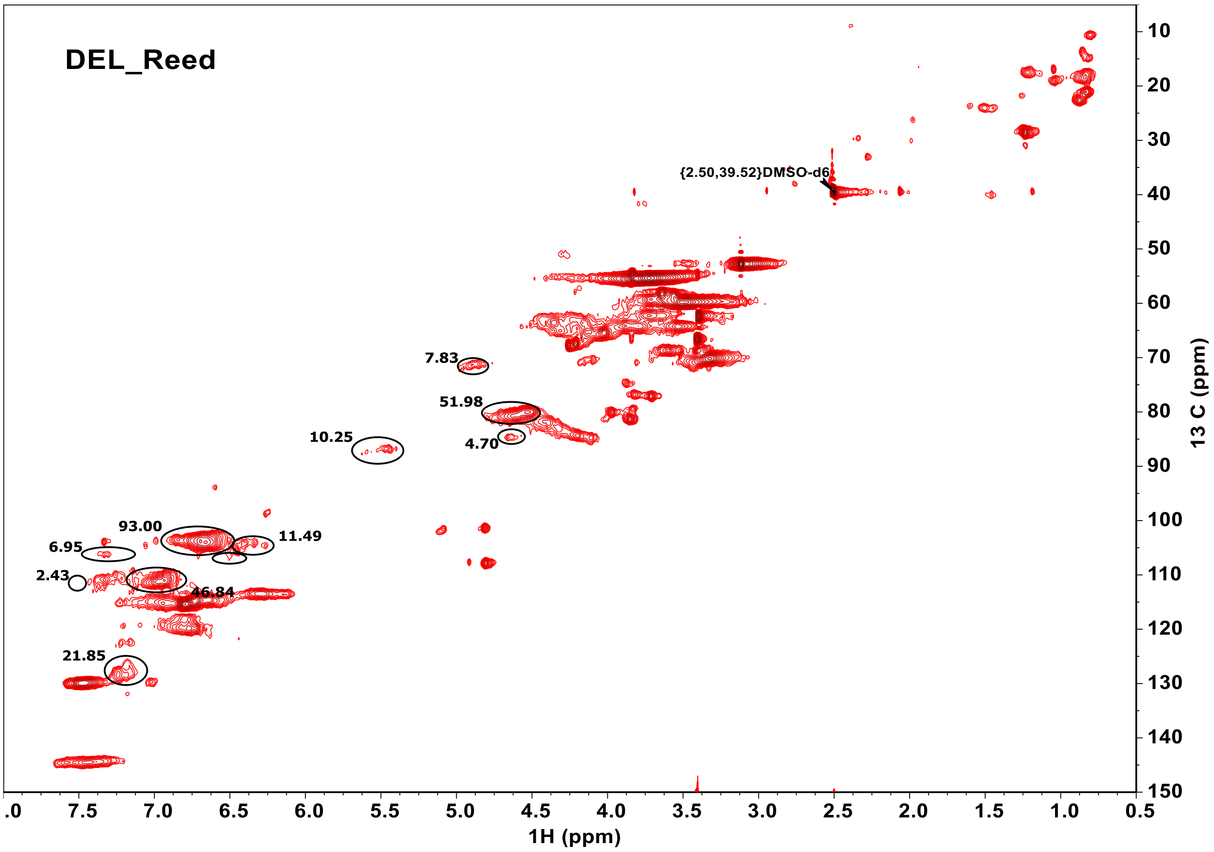


Figure S25. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating REL_Reed at ChCl/EG/OA with 9% oxalic acid at 80°C for 36 h. Reaction condition: 300 mg REL_Reed, 12.6 g ChCl, 10.8 g ethylene glycol, 2.106 g oxalic acid, RT for 36 h (see detailed data in **Table S6**).

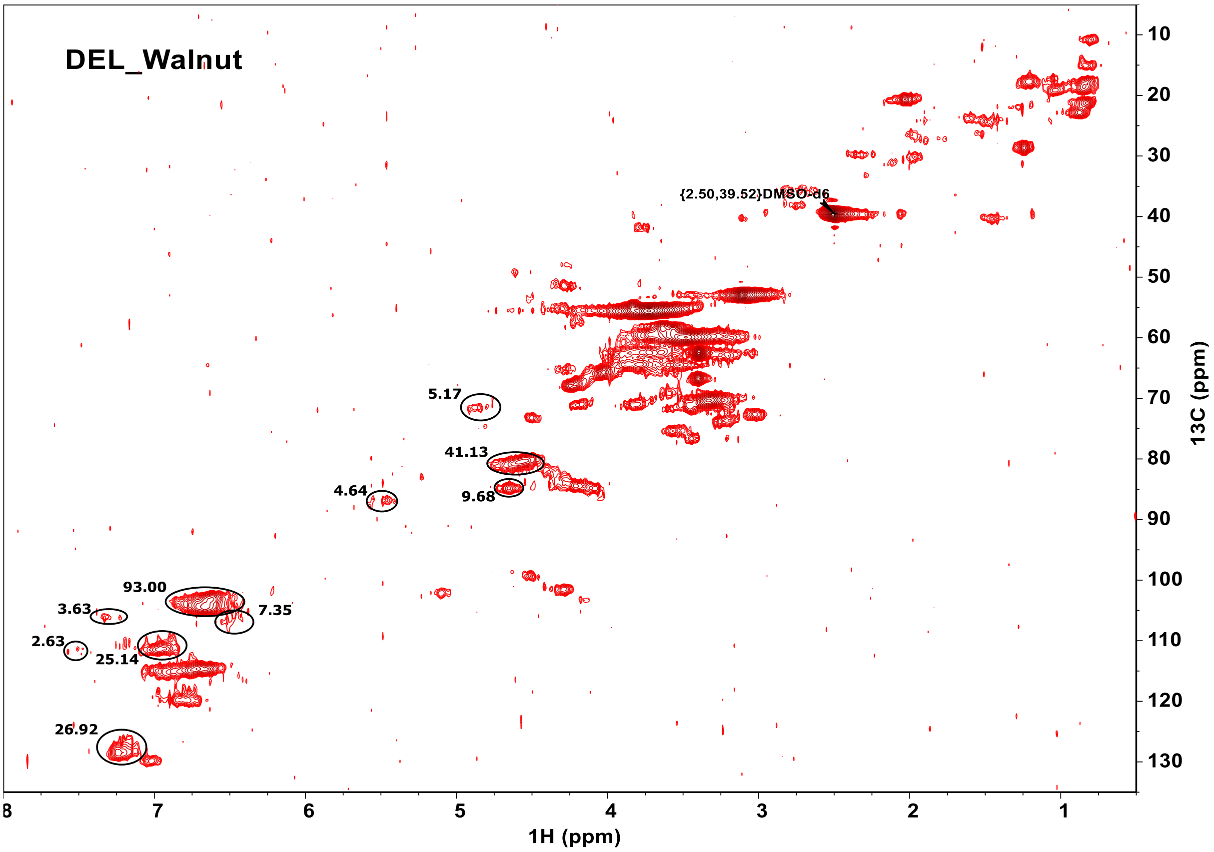


Figure S26. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating REL_Walnut at ChCl/EG/OA with 9% oxalic acid at 80°C for 36 h. Reaction condition: 300 mg REL_Walnut, 12.6 g ChCl, 10.8 g ethylene glycol, 2.106 g oxalic acid, RT for 36 h (see detailed data in **Table S6**).

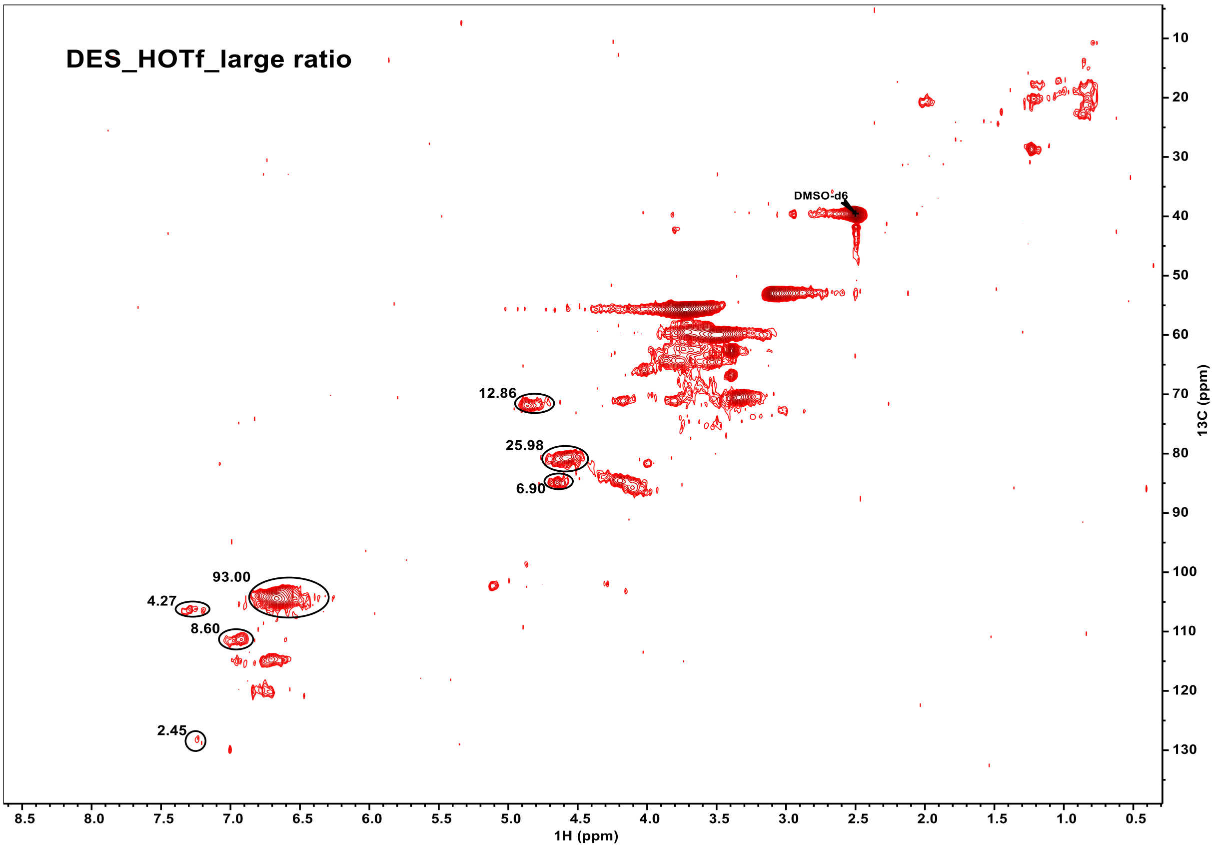


Figure S27. The 2D HSQC NMR (600 Hz, DMSO-d_6) and integration of lignin obtained from treating REL_Birch at ChCl/EG/HOTf with 15 % oxalic acid at 25 °C for 18 h. Reaction condition: 100 mg REL_Birch, 4.2 g ChCl, 3.6 g ethylene glycol, 1.17 g HOTf, 25 °C for 18 h (see detailed data in **Table S4**).

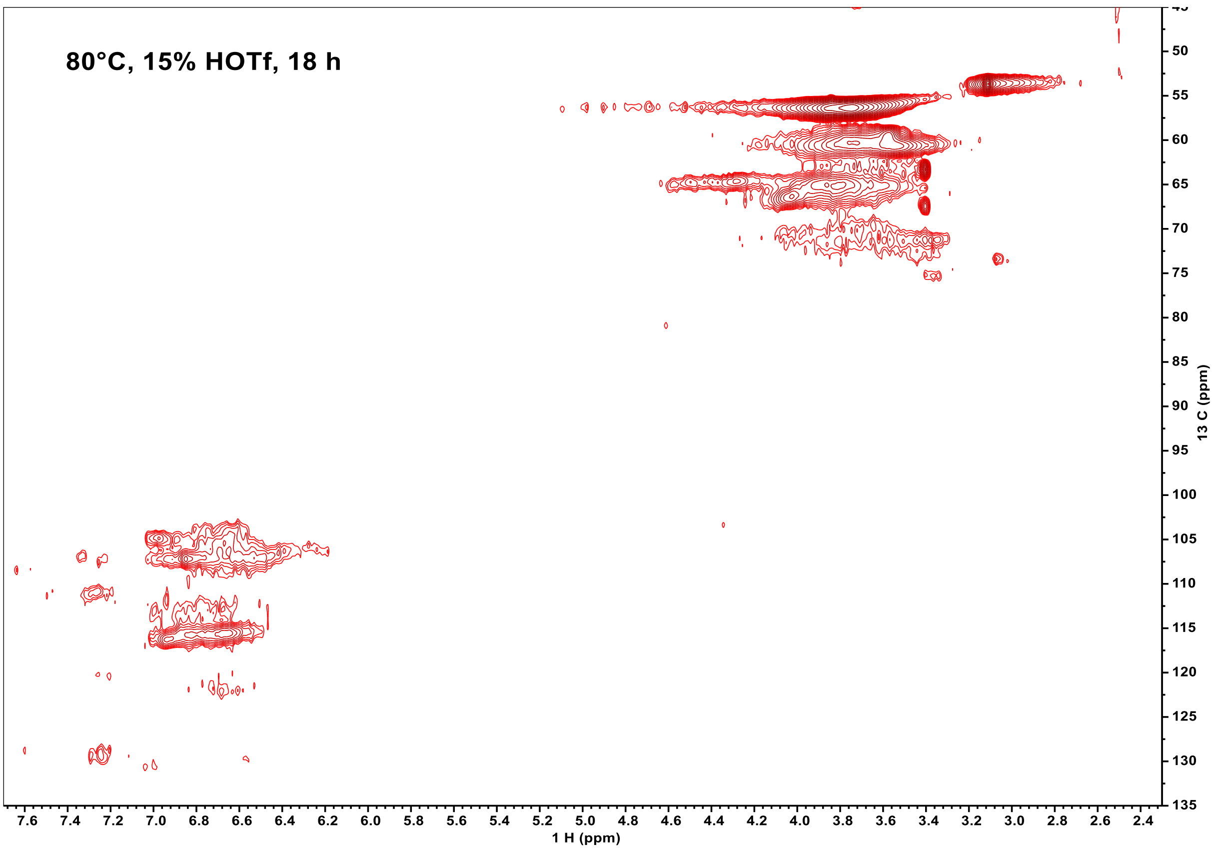


Figure S28. The 2D HSQC NMR (600 Hz, DMSO-d_6) lignin obtained from treating REL_Birch at ChCl/EG/HOTf with 15% HOTf at 80°C for 18 h. Reaction condition: 200 mg REL_Birch, 8.4 g ChCl, 7.2 g ethylene glycol, 2.346 g HOTf, 80°C for 18 h (see detailed data in **Table S8**).

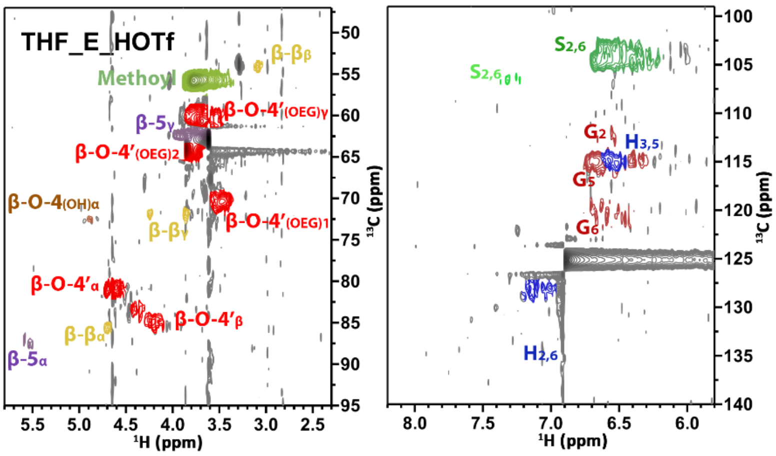


Figure S29. The 2D HSQC NMR (600 Hz, DMSO-*d*$_6$) of the oil obtained from THF extraction of the filtrate obtained after precipitation; DES reaction condition: 1 g Walnut_REL, 42 g (0.30 mol) ChCl, 36 g (0.6 mol) EG and 7.02 g (9% based on the total weight of ChCl and EG) HOTf under 30°C for 18 h (see detailed data in **Table S8**).

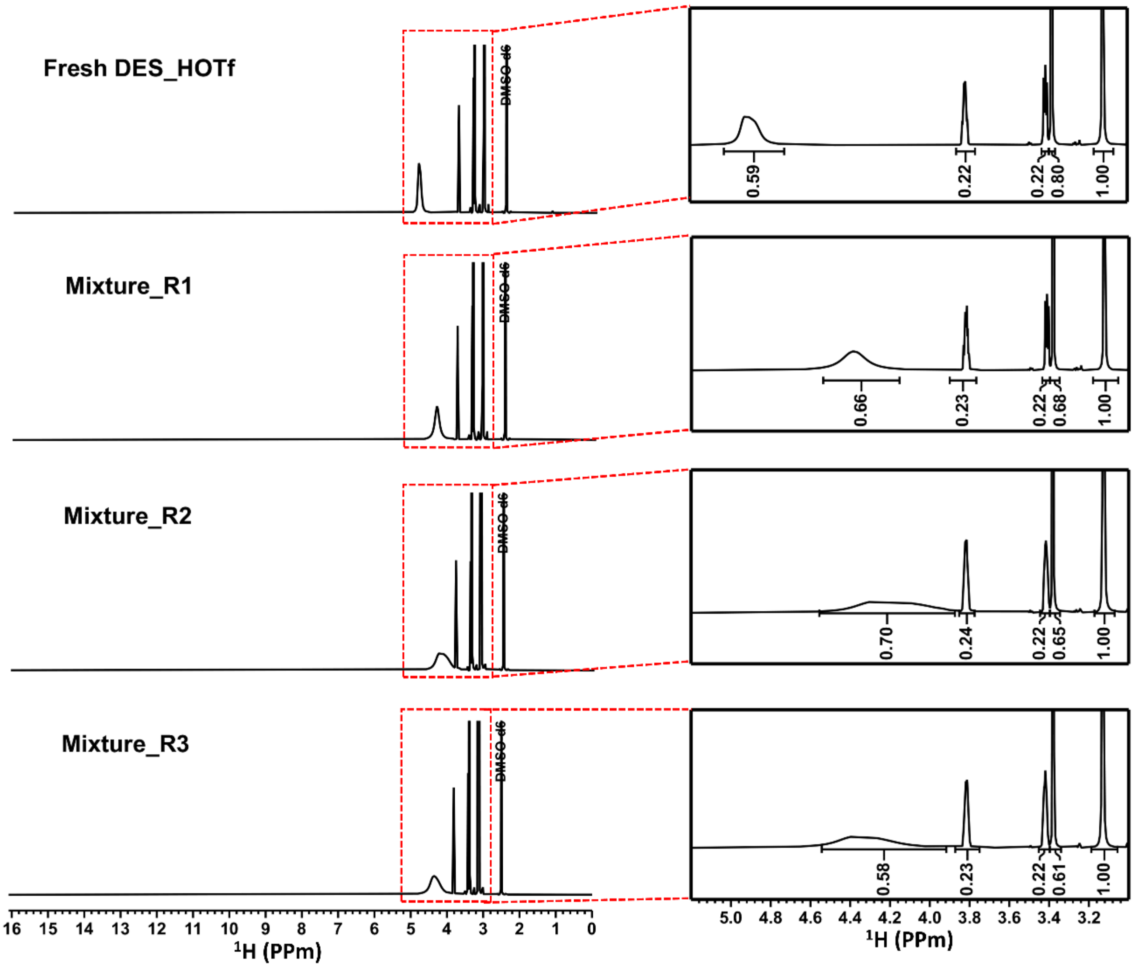


Figure S30. The proton NMR (600 Hz, DMSO-*d₆*) of the ChCl/EG/HOTf before and after recycling; DES reaction condition, ChCl, 21 g (0.15 mol), EG, 18 g (0.30 mol), HOTf 5.55g (15% based on the total weight of ChCl and EG), birch lignin, 500 mg, 25 ºC, 18 h. Detailed recycling parameters were attached in **Table S10**.

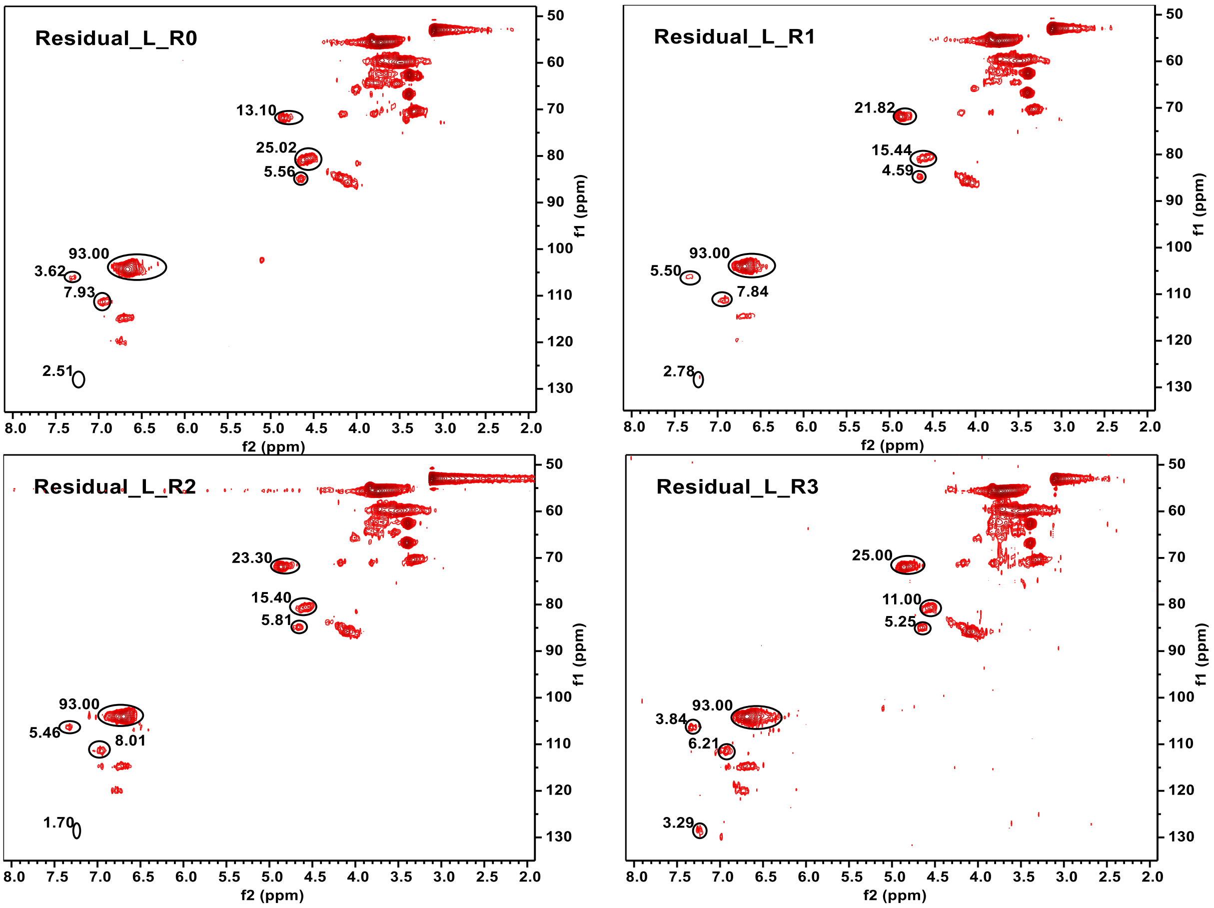


Figure S31. The 2D HSQC NMR (600 Hz, DMSO-d_6) of the residual lignin obtained from recycling of ChCl/EG/HOTf; DES reaction condition, ChCl, 21 g (0.15 mol), EG, 18 g (0.30 mol), HOTf 5.55g (15% based on the total weight of ChCl and EG), birch lignin, 500 mg, 25 ºC, 18 h. Detailed data from semi-quantification were attached in **Table S9**.

.

S2 Mass spectra of products obtained from DCM extraction

Figure S32. Product: 1 (3.530 min)

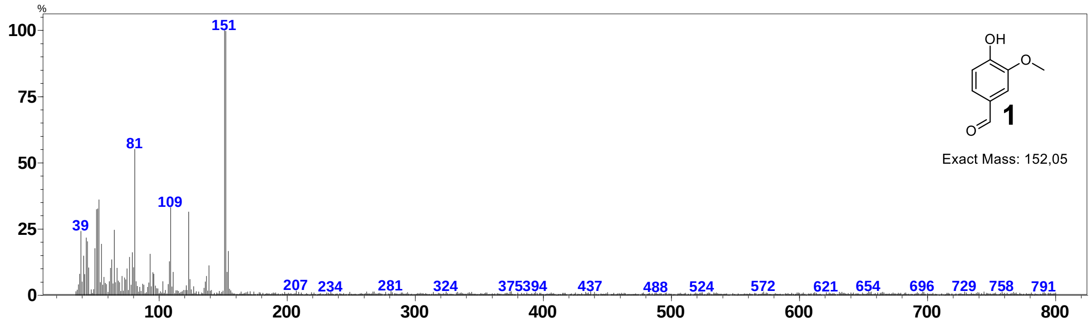


Figure S33. Product: 2 (5.410 min)

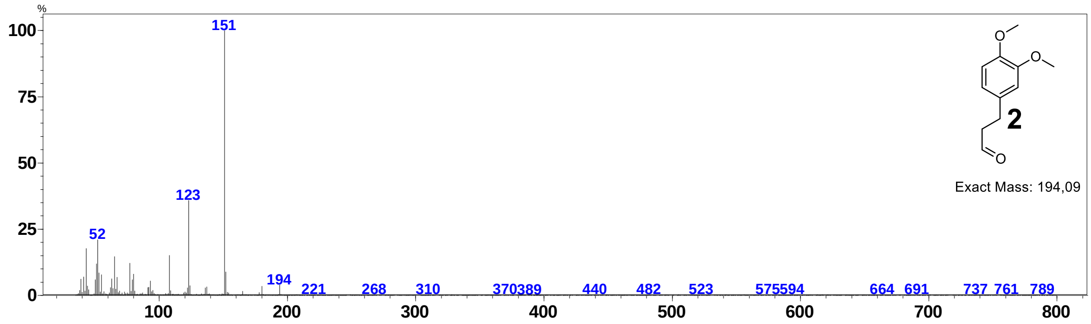


Figure S34. Product: 3 (6.315 min)

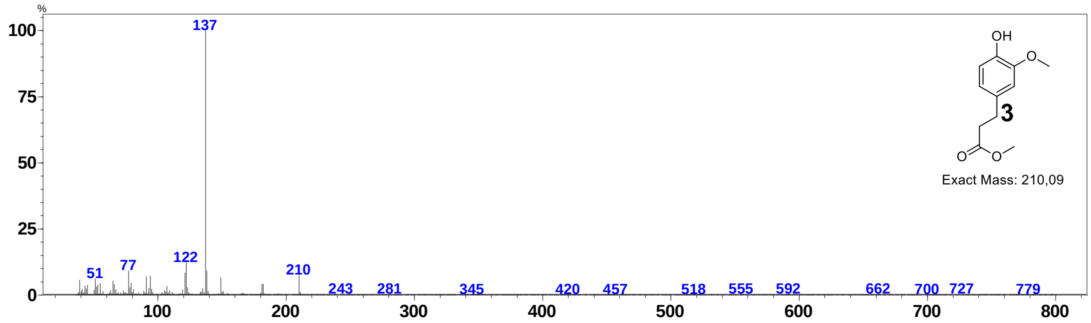


Figure S35. Product: 4 (6.365 min)

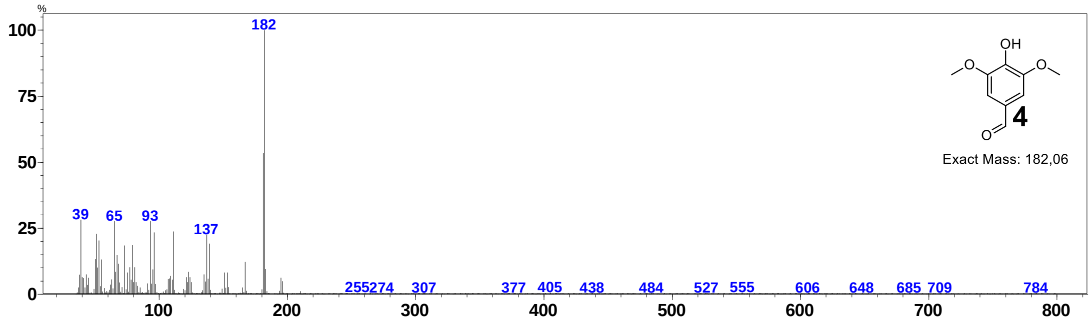


Figure S36. Product: 5 (7.207 min)

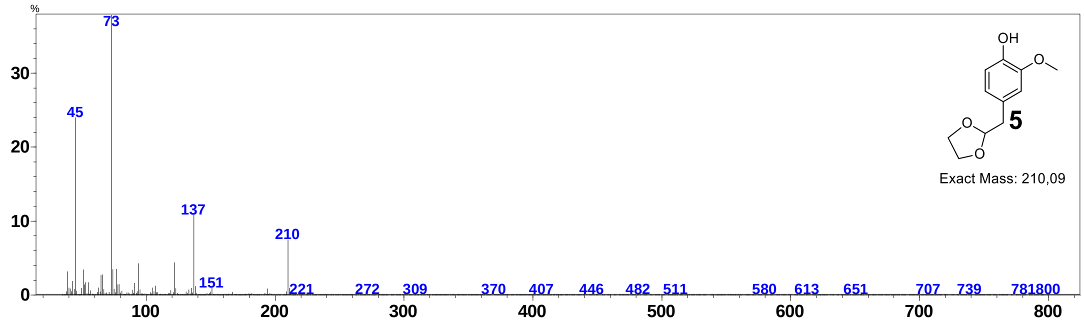


Figure S37. Product: 6 (7.335 min)

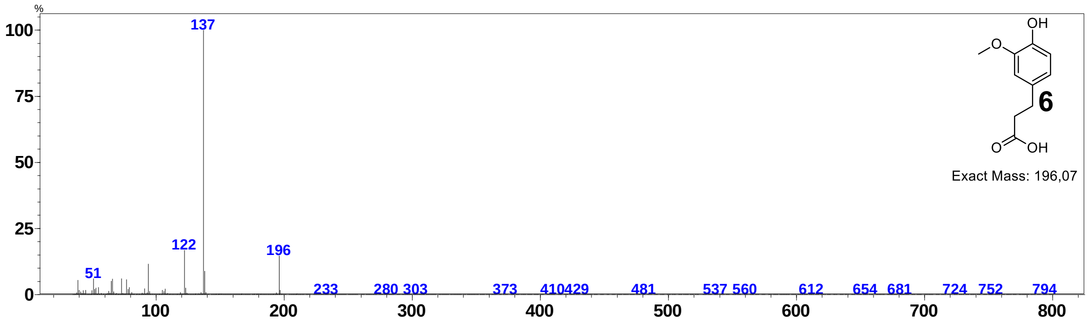


Figure S38. Product: 7 (7.515 min)

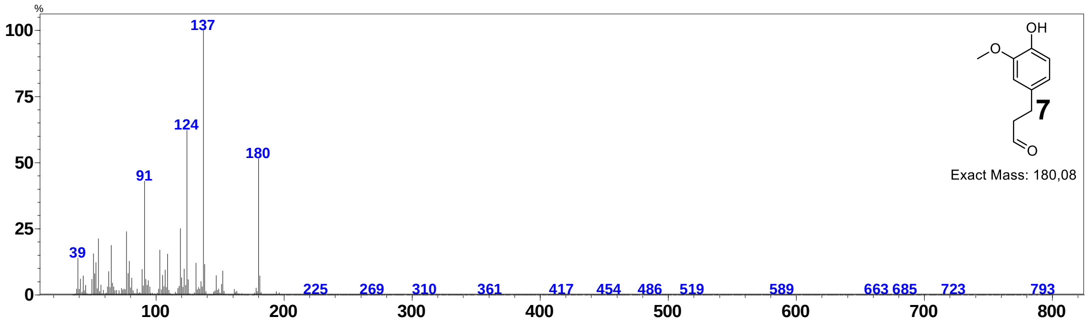


Figure S39. Product: 8 (8.840 min)

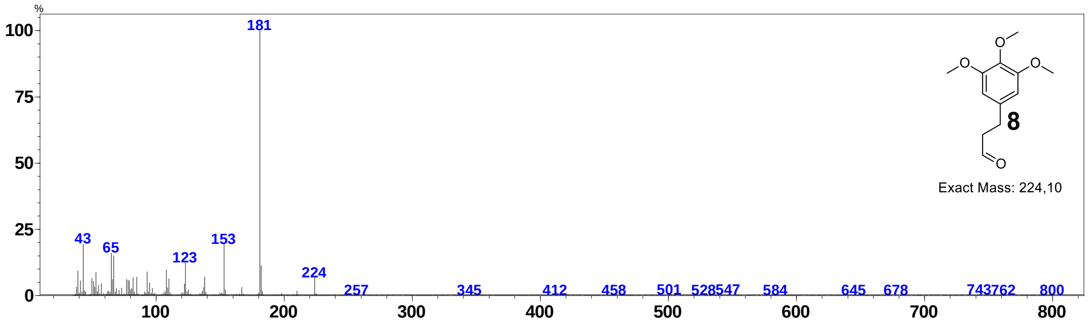


Figure S40. Product: 9 (9.115 min)

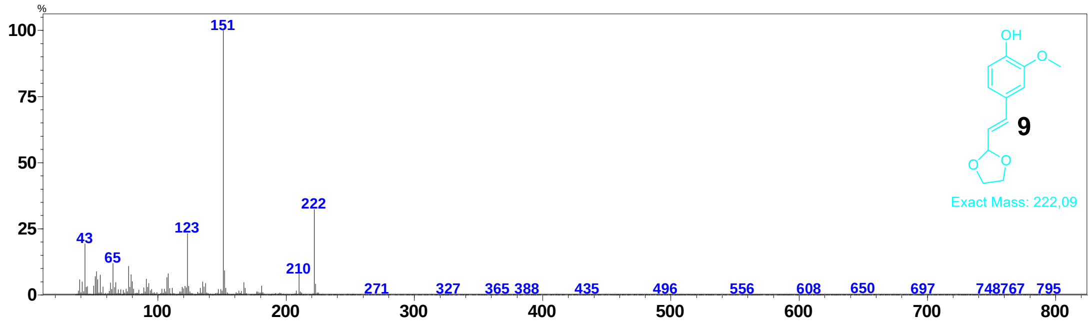


Figure S41. Product: 10 (9.545 min)

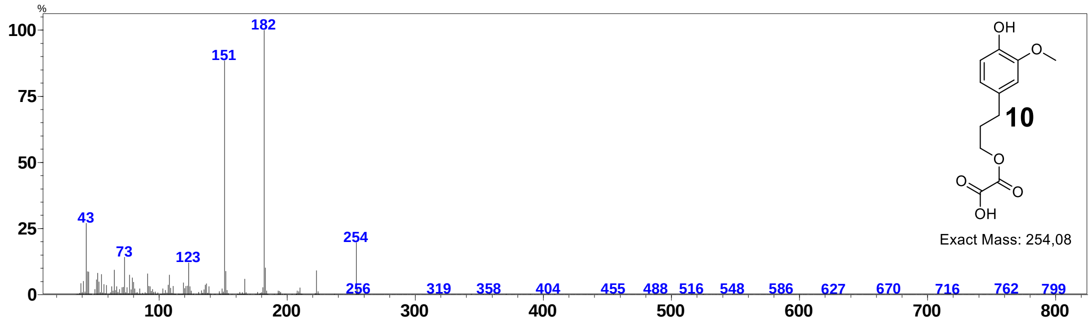


Figure S42. Product: 11 (9.870 min)

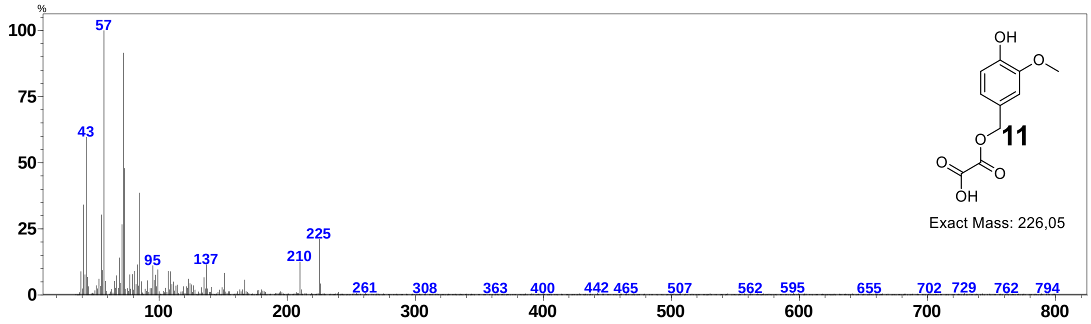


Figure S43. Product: 12 (10.105 min)

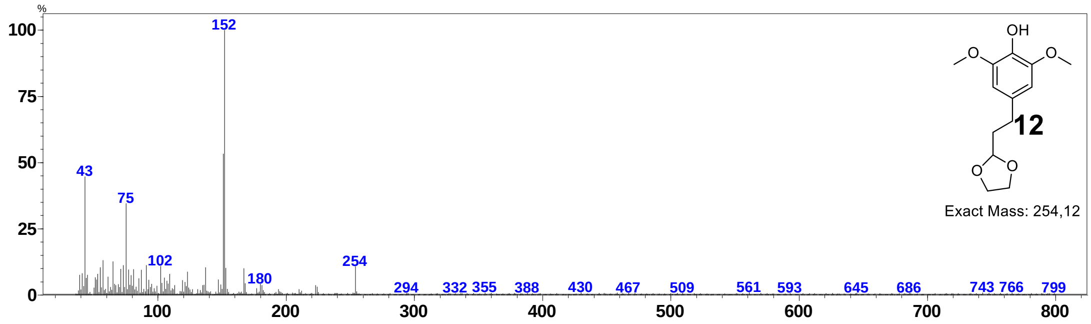


Figure S44. Product: 13 (10.340 min)

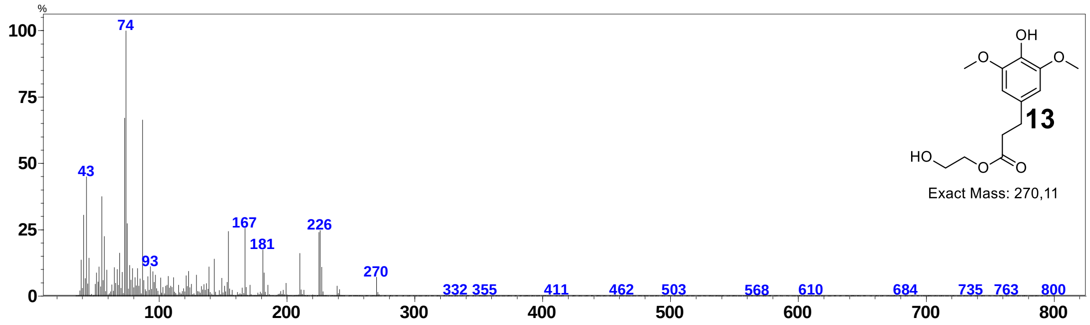


Figure S45. Product: 14. (10.770 min)

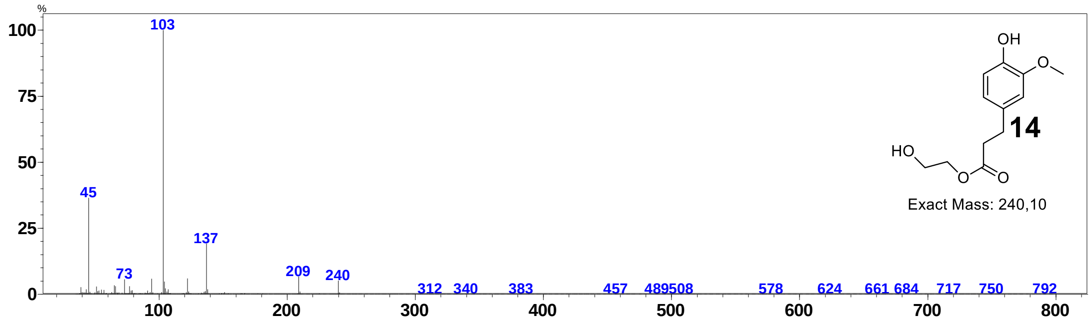


Figure S46. Product: 15 (11.215 min)

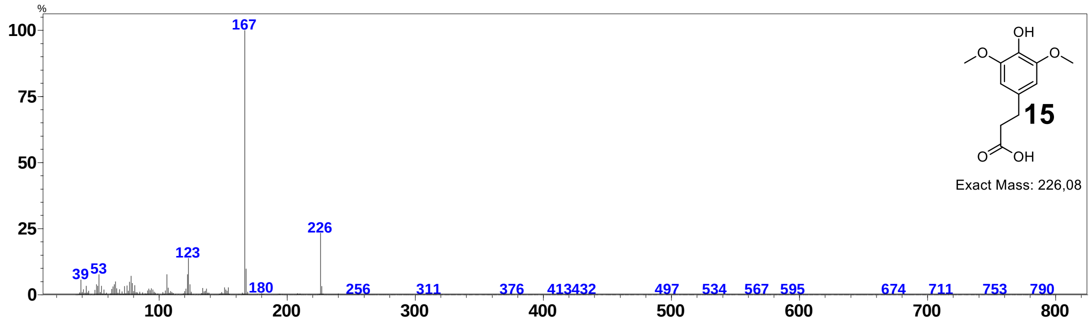


Figure S47. Product: 16 (11.260 min)

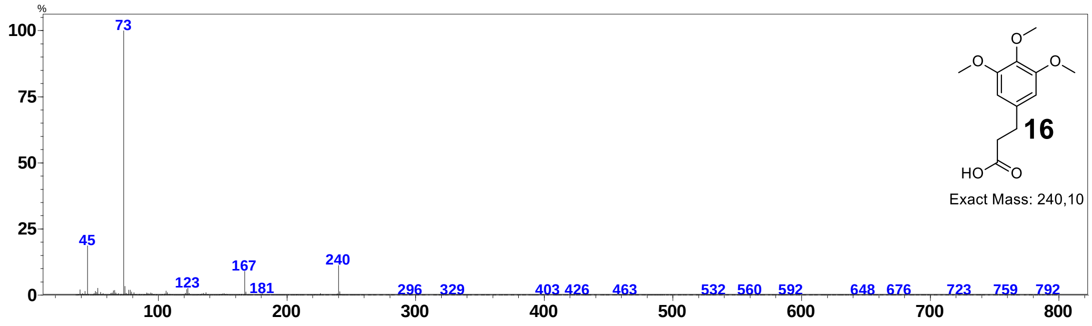


Figure S48. Product: 17 (11.485 min)

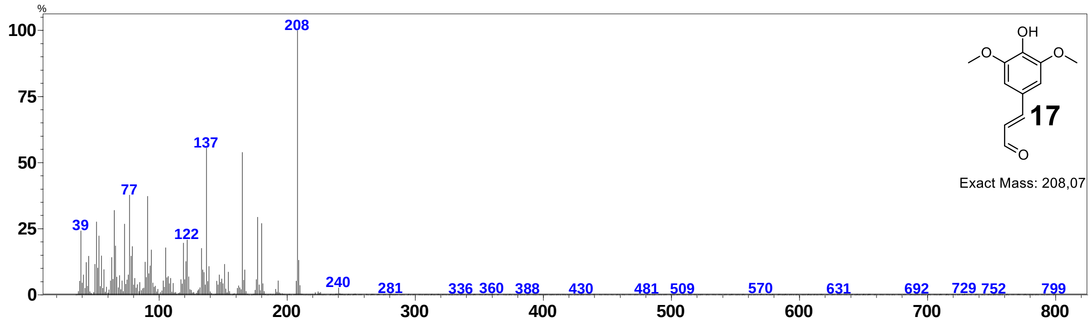


Figure S49. Product: 18 (11.765 min)

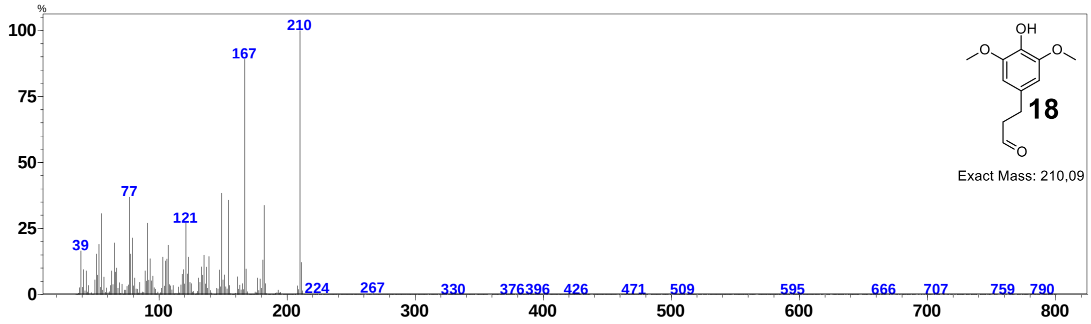
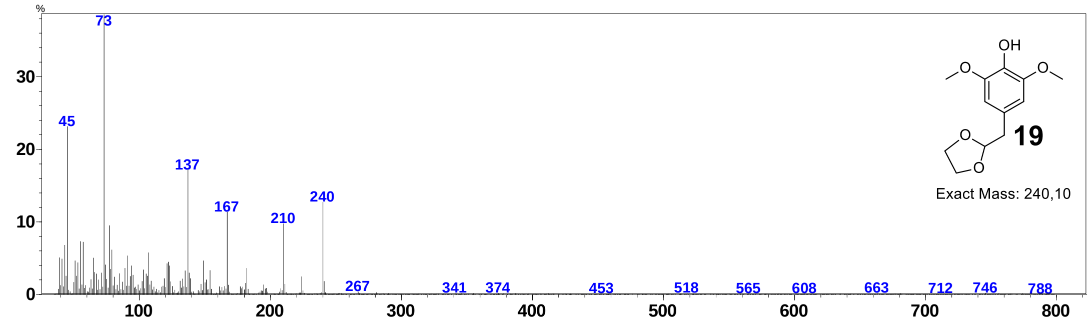


Figure S50. Product: 19 (12.165 min)



Supplementary tables

Table S1. The experimental conditions and lignin recover yield as well as semi-quantification of 2D HSQC NMR of REL before and after treating at ChCl/EG/OA system with different acid load at 80 °C (**Figure 2a**).

Samples	S[a]	S'[a]	Sc[a]	G[a]	G'[a]	H[a]	Aa[b]	Aa'[b]	Ca[b]	Ba[b]	TA[b]	Total L[b]	Yield (%)[c]	LOR/ALOH[b]	S/G[b]	Tem (ºC)	Time (h)	OA[f](%)	ChCl	EG[f]	Lignin
STMW[e]	49,8	4,1	0,0	32,1	0,6	13,4	52,3	0,0	6,9	10,7	52,3	69,9	100,0	0,0	1,6	NA[e]	NA	NA	NA	NA	NA
E1	50,0	3,7	3,8	27,8	1,7	13,0	19,7	44,5	4,6	9,9	64,2	78,7	76,0	2,1	1,9	80	18	3	4,2	3,6	STMW(100mg)
E2	47,9	3,4	4,1	27,9	2,5	14,2	16,3	47,0	6,3	12,4	63,3	82,0	63,0	2,8	1,8	80	18	6	4,2	3,6	STMW (100mg)
E3	46,6	4,0	5,0	29,2	2,3	12,9	12,5	46,6	6,9	12,1	59,1	78,0	58,0	3,7	1,8	80	18	9	4,2	3,6	STMW(100mg)
E4	45,0	4,2	5,8	28,1	1,4	15,4	12,3	46,9	7,3	10,7	59,2	77,2	58,0	3,9	1,9	80	18	12	4,2	3,6	STMW(100mg)
E5	44,3	3,5	6,5	30,2	1,8	13,7	11,8	47,2	7,5	12,5	59,0	79,0	59,0	4,2	1,7	80	18	15	4,2	3,6	STMW (100mg)
Ec[e]	46,3	3,3	9,2	25,4	4,0	11,8	12,2	46,8	7,3	11,6	59,1	77,9	55,0	3.9	1,7	80	36	9	21	18	STMW (500mg)

[a] S, syringyl units, S’ syringyl units with a α-ketone structures, Sc, condenced syrinyl units G, guaiacyl structure, G’, guaiacyl units with a α-ketone structures, H, p-hydroxylphenyl units. Percentage of the units was caculated from the intergration of one ^{13}C-^{1}H cross signals of the units at the aromatic region of the total intergration of the units. Among them, S unit = integration of $S_{2,6}$/2/total units integration, S’ unit = integration of $S'_{2,6}$/2/total units integration, G unit = integration of G_2/total units integration, G’ unit = integration of G'_2/total units integration, H unit = integration of $H_{2,6}$/2/total units integration.

[b] Molar percentages of the linkage was caculated from the integration of correspdonding α position divide the intergratuon of the total intergradtion of aromatic units; Total unit intergration= $(S_{2,6}+S'_{2,6}+H_{2,6})/2+G_2+G'_2)$; S/G ratio obtained by $(S_{2,6}+S'_{2,6}+Sc)/(G_2+G'_2)$; Ta=Aa+Aa’. Total L= Aa + Aa’ + Ca + Ba, Aa, aryl-alkyl ether [β-O-4(OH)], Aa’, aryl-alkyl ether with benzylic alkoxylation of α hydroxyl [β-O-4(OEG)], Ca, phenylcoumaran (β-5), Ba, resinols (β- β).

[c] The yield was caculated by the weigh of the lignin recoverved from DES treatment dividing the weight of starting material, NA, not aviliable.

[e] STMW, starting material (residual enzyme lignin from walnut shell); Ec, Treatment under extra long reaction time.

[f] EG, ethylene glycol, The percentage of oxilic acid was based on the total weight of EG and ChCl.

Table S2. The experimental conditions and lignin recover yield as well as semi-quantification of 2D HSQC NMR of REL before and after treating at ChCl/EG/OA system with 3% oxalic acid at different temperature (**Figure 2b**).

Samples	S[a]	S'[a]	Sc[a]	G[a]	G'[a]	H[a]	Aa[b]	Aa'[b]	Ca[b]	Ba[b]	TA[b]	Total L[b]	Yield (%)[c]	Aa'/Aa	S/G[b]	Tem (ºC)	Time (h)	OA (%)[f]	ChCl	EG[f]	Lignin
E6	50,0	3,7	3,8	27,8	1,7	13,0	19,7	44,5	4,6	9,9	64,2	78,7	76,0	2,1	1,9	80	18	3	4,2	3,6	STMW(100mg)
E7	46,3	3,8	6,9	28,0	2,6	12,4	14,8	42,8	5,1	11,2	57,7	74,0	50,0	2,9	1,9	100	18	3	4,2	3,6	STMW(100mg)
E8	42,8	3,6	12,8	26,1	2,4	12,3	10,7	36,9	6,2	8,6	47,6	62,4	44,0	3,8	2,1	120	18	3	4,2	3,6	STMW(100mg)

[a] S, syringyl units, S' syringyl units with a α-ketone structures, Sc, condenced syrinyl units G, guaiacyl structure, G', guaiacyl units with a α-ketone structures, H, p-hydroxylphenyl units. Percentage of the units was caculated from the intergration of one ^{13}C-^{1}H cross signals of the units at the aromatic region of the total intergration of the units. Among them, S unit = integration of $S_{2,6}$/2/total units integration, S' unit = integration of $S'_{2,6}$/2/total units integration, G unit = integration of G_2/total units integration, G' unit = integration of G'_2/total units integration, H unit = integration of $H_{2,6}$/2/total units integration.

[b] Molar percentages of the linkage was caculated from the integration of correspdonding α position divide the intergratuon of the total intergradtion of aromatic units; Total unit intergration= $(S_{2,6}+S'_{2,6}+H_{2,6})/2+G_2+G'_2)$; S/G ratio obtained by $(S_{2,6}+S'_{2,6}+Sc)/(G_2+G'_2)$; Ta=Aa+Aa'. Total L= Aa + Aa' + Ca + Ba, Aa, aryl ether [β-O-4(OH)], Aa', aryl ether with benzylic alkoxylation of α hydroxyl [β-O-4(OEG)], Ca, phenylcoumaran (β-5), Ba, resinols (β- β).

[c] The yield was caculated by the weigh of the lignin recoverved from DES treatment dividing the weight of starting material, NA, not aviliable.

[e] STM, starting material (residual enzyme lignin from walnut shell);

[f] EG, ethylene glycol, The percentage of oxilic acid was based on the total weight of EG and ChCl.

Table S3. The experimental conditions and lignin recover yield as well as semi-quantification of 2D HSQC NMR of REL before and after treating at ChCl/EG/HOTf system with different acid load (**Figure 3a**).

Samples	S[a]	S'[a]	Sc[a]	G[a]	G'[a]	H[a]	Aa[b]	Aa'[b]	Ca[b]	Ba[b]	TA[b]	Total L[b]	Yield (%)[c]	Aa'/Aa[b]	S/G[b]	Tem (ºC)	Time (h)	HOTf (%)[f]	ChCl	EG[f]	Mw[g]	Mn[g]	Mw/Mn[g]	Lignin
STMB[e]	69	8,8	0	1,1	0	0,8	58,8	0	2,7	9,2	58,8	70,8	100	NA[c]	3,7	NA	NA	NA	NA	NA	12930	6120	2,1	Birch(100mg)
E9	67,1	4,5	5,6	16,4	2,3	4,2	30,3	32,6	1,9	8,7	62,8	73,4	59	0,7	4.1	RT	18	5	2,1	1,8	10480	3040	3,4	Birch(100mg)
E10	67,	4	5,9	18	1,3	3,3	20,4	42,7	2,4	10,1	63,1	75,5	56	1,4	4.0	RT	18	15	2,1	1,8	9750	3340	2,9	Birch(100mg)
E11	69,3	3,8	7,6	15,6	0,9	2,8	18,7	41,6	2,2	10	60,3	72,5	54	1,5	4,9	RT	18	25	2,1	1,8	9230	3350	2,8	Birch(100mg)

[a] S, syringyl units, S' syringyl units with a α-ketone structures, Sc, condenced syrinyl units G, guaiacyl structure, G', guaiacyl units with a α-ketone structures, H, p-hydroxylphenyl units. Percentage of the units was caculated from the intergration of one ^{13}C-^{1}H cross signals of the units at the aromatic region of the total intergration of the units. Among them, S unit = integration of $S_{2,6}$/2/total units integration, S' unit = integration of $S'_{2,6}$/2/total units integration, G unit = integration of G_2/total units integration, G' unit = integration of G'_2/total units integration, H unit = integration of $H_{2,6}$/2/total units integration.

[b] Molar percentages of the linkage was caculated from the integration of correspdonding α position divide the intergratuon of the total intergradtion of aromatic units; Total unit intergration= $(S_{2,6}+S'_{2,6}+H_{2,6})/2+G_2+G'_2)$; S/G ratio obtained by $(S_{2,6}+S'_{2,6}+Sc)/(G_2+G'_2)$; Ta=Aa+Aa'. Total L= Aa + Aa' + Ca + Ba, Aa, aryl ether [β-O-4(OH)], Aa', aryl ether with benzylic alkoxylation of α hydroxyl [β-O-4(OEG)], Ca, phenylcoumaran (β-5), Ba, resinols (β- β).

[c] The yield was caculated by the weigh of the lignin recoverved from DES treatment dividing the weight of starting material, NA, not aviliable.

[e] STMW, starting material (residual enzyme lignin from birch);

[f] EG, ethylene glycol, The percentage of HOTf was based on the total weight of EG and ChCl.

[g] Mw, weight molecular size, Mn, number molecular size, Mw/Mn, polydispersity.

Table S4. The experimental conditions and lignin recover yield as well as semi-quantification of 2D HSQC NMR of REL before and after treating at ChCl/EG/HOTf system with different reaction time (**Figures 3b** and **S27**).

Samples	S[a]	S'[a]	Sc[a]	G[a]	G'[a]	H[a]	Aa[b]	Aa'[b]	Ca[b]	Ba[b]	TA[b]	Total L[b]	Yield (%)[c]	Aa'/Aa[b]	S/G[b]	Tem (ºC)	Time (h)	HOTf (%)[e]	ChCl	EG[e]	Mw[f]	Mn[f]	Mw/Mn[f]	Lignin
E12	69,4	4,1	3,1	18,2	0,6	4,5	20,6	43	1,7	10,4	63,6	75,8	56	1,4	4.1	30	4,5	15	2,1	1,8	9750	3340	2,9	STMB(100mg)
E13	69,9	3,7	3,8	17,9	1	3,8	15,2	47,6	2,1	9,3	62,7	74,2	51	2,1	4.1	30	9	15	2,1	1,8	11720	3780	3,1	STMB(100mg)
E14	69,6	3,9	5,7	17,2	0,7	2,9	12,3	45,9	2,1	8,2	58,2	68,6	49	2,5	4.4	30	18	15	2,1	1,8	9270	3260	2,8	STMB(100mg)
E15	69,2	2,9	6,7	17,6	0,6	2,9	9,5	48,3	1,6	9,4	57,8	68,7	44	3,4	4.3	30	24	15	2,1	1,8	9430	3580	2,6	STMB(100mg)
E16	66,4	3,8	7,3	17,5	0,6	4,5	5,8	51,1	1,9	8,6	56,9	67,5	41	6,1	4.3	30	36	15	2,1	1,8	11690	3850	3,0	STMB(100mg)
EL	79.5	3.7	0	14.7	0	2.9	22.0	44.4	0.0	11.8	66.4	78.2	55	2.0	5.7	25	18	15	4.2	3.6	NA	NA	NA	NA

[a] S, syringyl units, S’ syringyl units with a α-ketone structures, Sc, condenced syrinyl units G, guaiacyl structure, G’, guaiacyl units with a α-ketone structures, H, p-hydroxylphenyl units. Percentage of the units was caculated from the intergration of one ^{13}C-^{1}H cross signals of the units at the aromatic region of the total intergration of the units. Among them, S unit = integration of $S_{2,6}$/2/total units integration, S’ unit = integration of $S'_{2,6}$/2/total units integration, G unit = integration of G_2/total units integration, G’ unit = integration of G'_2/total units integration, H unit = integration of $H_{2,6}$/2/total units integration.

[b] Molar percentages of the linkage was caculated from the integration of correspdonding α position divide the intergratuon of the total intergradtion of aromatic units; Total unit intergration= ($S_{2,6}$+$S'_{2,6}$+$H_{2,6}$)/2+G_2+G'_2); S/G ratio obtained by ($S_{2,6}$+$S'_{2,6}$+Sc)/(G_2+G'_2); Ta=Aa+Aa’. Total L= Aa + Aa’ + Ca + Ba, Aa, aryl ether [β-O-4(OH)], Aa’, aryl ether with benzylic alkoxylation of α hydroxyl [β-O-4(OEG)], Ca, phenylcoumaran (β-5), Ba, resinols (β- β).

[c] The yield was caculated by the weigh of the lignin recoverved from DES treatment dividing the weight of starting material.

[e] EG, ethylene glycol, The percentage of HOTf was based on the total weight of EG and ChCl.

[f] Mw, weight molecular size, Mn, number molecular size, Mw/Mn, polydispersity.

[9] EL = Extraction at double REL/DES ratio (**Figure S27**)

Table S5. Saccharide analysis of the lignin before and after ChCl/EG/OA treatment as well as mass loss track from saccharide removal, DCM extraction.

Biomass	Lignin[a]	Cellulose[b]	Hemicellulose[b]	Total[c]	RSD[c]	YL[c] (%)	TM[e]	MCY[e]	YOTHF[e] (%)	TM of SO[e] (%)	MT of SO[e] (%)
Birch	REL	7,04±0,077	10,51±0,11	17,55	0	100	0	0	NA	NA	NA
	DEL	10,91±0,035	4,10±0,38	15,01	55,87	51,6±3,7	48,4	9,81	16,1	25,91	53,53
Pine	REL	2,26±0,084	11,92±0,021	14,18	0	100	0	0	NA	NA	NA
	DEL	0,92±0,138	2,33±0,11	3,25	82,05	78,3±1,7	21,7	11,63	5,2	16,83	77,56
Reed	REL	2,58±0,067	13,15±0,14	15,73	0	100	0	0	NA	NA	NA
	DEL	3,08±0,088	2,32±0,12	5,4	81,39	54,2±5,8	45,8	12,8	6,6	19,4	42,36
Walnut	REL	12,11±0,34	14,91±0,026	27,02	0	100	0	0	NA	NA	NA
	DEL	17,42±0,25	6,88±0,27	24,3	51,26	54,2±5,8	45,8	13,85	7,8	21,65	47,27

[a] REL, residual enzyme lignin, the starting lignin before the ChCl/EG/OA treatment, DEL, lignin obtained from the ChCl/EG/OA treatment;

[b] Cellulose was represent by the glucan determinted from the composition analysis, Hemicellulose represent the total value of xylan and arabinan determinted from the compostion analysis;

[c] Total= % of cellulose + % of hemicellulose; YL, the yield of lignin recovered from treating in the ChCl/EG/OA system; RSD, the saccharide removal yield after the ChCl/EG/OA treatment, and RSD was caculated by (Total*YL of REL-Total*YL of DEL)/ Total*YL of REL.

[e] TM, the total percentage of mass loss by subtracting the YL; MCY, the mass loass contributed by the degradation of saccharide impuritis and was caculated by Total of REL*RSD of DEL/100; YOTHF; the yield of oil obtained from DCM extraction of the liquid phased recovered from the treating in the ChCl/EG/OA system. TM of SO, the total percentage of MCY and YOTHF; MT of SO, the tracking percentage of mass loss by taking account MCY and YOTHF, and caculated by TMSO divide TM.

Table S6. The experimental conditions and lignin recover yield as well as semi-quantification of 2D HSQC NMR of REL before and after treating at ChCl/EG/OA system for **Figure 4**.

Biomass	Lignin	S[a]	S'[a]	Sc[a]	G[aa]	G'[a]	H[a]	Aa[b]	Aa'[b]	Ca[b]	Ba[b]	Ta[b]	Total L[b]	Aa'/Aa	S/G[b]	Tem (ºC)	Time (h)	OA(%)c	ChCl	EG[c]c	Lignin (g)
Birch	REL	69,0	9,0	0,0	20,1	1,1	0,8	61,9	0,0	2,7	9,2	61,9	73,9	NA[c]	3,7	NA	NA	NA	NA	NA	NA
	DEL	61,4	5,9	9,5	18,6	1,3	3,3	9,3	43,2	2,6	12,3	52,5	67,4	3,5	3,9	80	36h	0,09	12,6	10,8	0,3
Pine	REL	0,0	0,0	0,0	95,9	0,8	3,3	48,1	0,0	18,7	6,4	48,1	73,3	NA	0,0	NA	NA	NA	NA	NA	NA
	DEL	0,0	0,0	0,0	94,2	3,8	2,0	4,8	43,0	13,1	4,8	47,9	65,9	8,8	0,0	80	36h	0,09	12,6	10,8	0,3
Reed	REL	39,2	3,5	0,0	51,3	0,5	5,5	49,3	0,0	8,3	4,2	49,3	61,8	NA	0,8	NA	NA	NA	NA	NA	NA
	DEL	37,1	2,8	12,2	37,3	2,0	8,7	6,2	41,4	8,4	3,7	47,7	59,8	8,3	1,3	80	36h	0,09	12,6	10,8	0,3
Walnut	REL	49,8	4,1	0,0	32,1	0,6	13,4	54,4	0,0	6,9	10,7	54,4	72,0	NA	1,6	NA	NA	NA	NA	NA	NA
	DEL	48,0	1,9	7,6	25,9	2,7	13,9	5,3	42,4	4,8	10,0	47,8	62,6	7,7	2,0	80	36h	0,09	12,6	10,8	0,3

[a] S, syringyl units, S’ syringyl units with a α-ketone structures, Sc, condenced syrinyl units G, guaiacyl structure, G’, guaiacyl units with a α-ketone structures, H, p-hydroxylphenyl units. Percentage of the units was caculated from the intergration of one ^{13}C-^{1}H cross signals of the units at the aromatic region of the total intergration of the units. Among them, S unit = integration of $S_{2,6}$/2/total units integration, S’ unit = integration of $S'_{2,6}$/2/total units integration, G unit = integration of G_2/total units integration, G’ unit = integration of G'_2/total units integration, H unit = integration of $H_{2,6}$/2/total units integration.

[b] Molar percentages of the linkage was caculated from the integration of correspdonding α position divide the intergratuon of the total intergradtion of aromatic units; Total unit intergration= $(S_{2,6}+S'_{2,6}+H_{2,6})/2+G_2+G'_2)$; S/G ratio obtained by $(S_{2,6}+S'_{2,6}+Sc)/(G_2+G'_2)$; Ta=Aa+Aa’. Total L= Aa + Aa’ + Ca + Ba, Aa, aryl ether [β-O-4(OH)], Aa’, aryl ether with benzylic alkoxylation of α hydroxyl [β-O-4(OEG)], Ca, phenylcoumaran (β-5), Ba, resinols (β- β).

[c] EG, ethylene glycol, The percentage of OA was based on the total weight of EG and ChCl, NA, not avialiable.

Table S7. Monomer yield correction from sugar impurity and incorporation of EG for **Figure S2** based on **Table S6**.

Biomass	Lignin[a]	Aa'[a]	NoEGL[a]	TS[a]	TG[a]	H a	MwaOH[b]	MwaOEG[b]	Mwta[c]	M0(g)[d]	Purity (%)[d]	NSL (g)[d]	ML[e]	POS (%)[i]	LFC[l]	S1[p]	S2[p]	S3[p]	G1[p]	G2[p]	G3[p]	FCA[p]	H1[p]	H2[p]	H3[p]	PCA[p]	Oh[p]	S/G[p]	TM[p]
	REL	0,00	100,00	78,02	21,20	0,78	219,40	263,45	219,40	0,05	0,82	0,04	0,000188	100,00	0,04	10,14	20,06	0,90	1,20	4,17	0,07	0,00	0,03	0,00	0,00	0,00	0,00	5,71	36,58
Birch	DEL	43,21	56,79	76,79	19,93	3,28	218,28	262,33	237,31	0,05	0,85	0,04	0,000179	95,30	0,04	4,85	14,08	0,47	0,85	3,47	0,18	0,00	0,65	0,01	0,01	0,00	0,00	4,31	24,27
	REL	0,00	100,00	0,00	96,70	3,30	195,21	239,27	195,21	0,05	0,86	0,04	0,000220	100,00	0,04	0,00	0,00	0,00	3,50	10,61	0,33	0,00	0,25	0,24	0,02	0,00	0,00	0,00	14,95
Pine	DEL	43,04	56,96	0,00	98,00	2,00	195,60	239,66	214,56	0,05	0,97	0,05	0,000225	102,57	0,04	0,00	0,00	0,11	1,61	8,67	0,45	0,00	0,08	0,10	0,00	0,00	0,00	0,00	11,02
	REL	0,00	100,00	42,71	51,83	5,46	207,39	251,44	207,39	0,05	0,84	0,04	0,000203	100,00	0,04	3,64	6,93	0,32	2,67	5,58	0,69	1,80	0,25	0,35	0,41	3,70	1,97	1,22	20,85
Reed	DEL	41,42	58,58	52,01	39,28	8,71	209,21	253,26	227,45	0,05	0,95	0,05	0,000208	102,34	0,04	1,29	4,94	0,26	0,95	3,99	0,17	0,69	0,23	0,23	0,34	2,32	0,40	1,27	12,39
	REL	0,00	100,00	53,92	32,72	13,36	208,38	252,43	208,38	0,05	0,73	0,04	0,000175	100,00	0,04	5,94	9,57	0,57	1,91	4,94	0,21	0,00	0,28	0,95	0,05	0	0	2,28	24,42
Walnut	DEL	42,45	57,55	57,45	28,66	13,89	209,28	253,33	227,98	0,05	0,76	0,04	0,000166	94,81	0,03	3,23	8,22	0,51	1,23	4,22	0,25	0,00	0,18	0,65	0,01	0,00	0,00	2,10	18,50

[a] Aa', mol percentage of aryl ether linkage with benzylic alkylation of α hydroxyl (Table S6); NoEGL, mol percentage without benzylic of α hydroxyl =100-Aa'; TS, total S units=S+S'; TG, total G units=G+G'; S, syringyl units, S', syringyl, G, guaiacyl structure, G', guaiacyl units with a α-ketone structures, H, *p*-hydroxylphenyl units (Table S6);

[b] MwaOH=(S_{OH}*TS+G_{OH}*TG+H_{OH}*H)/100; MwaOR= (S_{OEH}*TS+G_{OEH}*TG+H_{OEH}*H)/100;

[c] Mwta=(MwaOH*NoEGL+MwaOR*Aa')/100;

[d] M_0=the weight of starting lignin before the pretreatment; Purity, purity of lignin=from sugar analysis of lignin before and after treatment (Table S5), NSL, weigt of lignin after substracting suagar impurities=100-purity.

[e] ML, Mol of lignin=NSL/Mwta; [f] mol of Birch_REL; [g] mol of Birch_REL_EH; [h] mol of Birch_REL_EG;

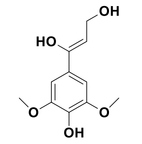
[i] POS, mol pertentage of Birch_REL_EH and Birch_REL_EG based on Birch_REL;

[j] mol percentage of Birch_REL_EH based on Birch_REL=$^{g}/^{f}$, [k] mol percentage of Birch_REL_EG based on Birch_REL = $^{h}/^{f}$;

[l] LFC, weight of lignin used for calcualtion of monomer yield. [m] weight used for caclulation of the monomer of Birch_REL=NSL;

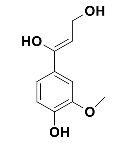
[n] weight used for caclulation of the monomer of Birch_REL_EH=$^{m}*^{j}$/100; [o] weight used for caclulation of the monomer of Birch_REL_EGH=$^{m}*^{k}$/100;

[p] S1, 4-(3-hydroxypropyl)-2,6-dimethoxyphenol, S2, 2,6-dimethoxy-4-propylphenol, S3, 4-ethyl-2,6-dimethoxyphenol, G1, 4-(3-hydroxypropyl)-2-methoxyphenol, G2, 2-methoxy-4-propylphenol, G3, 4-ethyl-2-methoxyphenol, TM, total monomers =S1+S2+S3+G1+G2+G3.



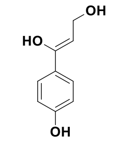
Molecular Weight: 226,23

S_{OH}



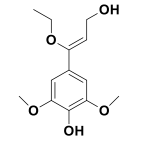
Molecular Weight: 196,20

G_{OH}



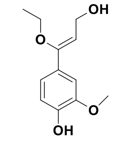
Molecular Weight: 166,18

H_{OH}



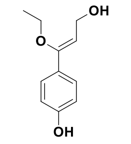
Molecular Weight: 254,28

S_{OEH}



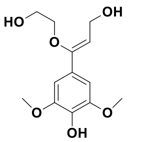
Molecular Weight: 224,26

G_{OEH}



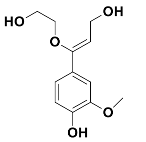
Molecular Weight: 194,23

H_{OEH}



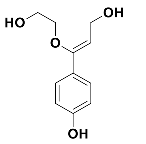
Molecular Weight: 270,28

S_{OEG}



Molecular Weight: 240,26

G_{OEG}



Molecular Weight: 210,23

H_{OEG}

Table S8. The experimental conditions and semi-quantification of 2D HSQC NMR of oil obtained from THF extraction of liquid fraction collecting from treatment of REL_Walnut in ChCl/EG/OA and ChCl/EG/HOTf system.

Sample	S[a]	S'[a]	Sc[a]	G[a]	G'[a]	H[a]	Aa[b]	Aa'[b]	Ca[b]	Ba[b]	Ta[b]	Total L	Aa'/Aa	S/G[b]	Tem (ºC)	Time (h)	Acid[c]	ChCl (g)	EG (g)	Lignin (mg)
THF_E	39,7	6,0	26,8	16	6,7	4,7	0,0	22,6	3,1	7,7	22,6	33,3	0,0	3,2	80,0	36,0	OA (3,5 g, 9%)	21,0	18	500
THF_HOTf_E	79,1	3,4	0,0	9,2	0,0	8,4	13,4	59,0	11,3	12,8	72,5	96,5	2,6	9,0	30,0	18,0	HOTf (7,0 g, 9%)	42,0	36	1000

[a] S, syringyl units, S' syringyl units with a α-ketone structures, Sc, condenced syrinyl units G, guaiacyl structure, G', guaiacyl units with a α-ketone structures, H, *p*-hydroxylphenyl units. Percentage of the units was caculated from the intergration of one ^{13}C-^{1}H cross signals of the units at the aromatic region of the total intergration of the units. Among them, S unit = integration of $S_{2,6}$/2/total units integration, S' unit = integration of $S'_{2,6}$/2/total units integration, G unit = integration of G_2/total units integration, G' unit = integration of G'_2/total units integration, H unit = integration of $H_{2,6}$/2/total units integration.

[b] Molar percentages of the linkage was caculated from the integration of correspdonding α position divide the intergratuon of the total intergradtion of aromatic units; Total unit intergration= ($S_{2,6}$+$S'_{2,6}$+$H_{2,6}$)/2+G_2+G'_2); S/G ratio obtained by ($S_{2,6}$+$S'_{2,6}$+Sc)/(G_2+G'_2); Ta=Aa+Aa'. Total L= Aa + Aa' + Ca + Ba, Aa, aryl ether [β-O-4(OH)], Aa', aryl ether with benzylic alkoxylation of α hydroxyl [β-O-4(OEG)], Ca, phenylcoumaran (β-5), Ba, resinols (β- β).

[c] EG, ethylene glycol, The percentage of acid was based on the total weight of EG and ChCl.

Table S9. The experimental conditions and semi-quantification of 2D HSQC NMR of lignin obtained from the recycling of ChCl/EG/HOTf system.

Sample	S[a]	S'[a]	Sc[a]	G[a]	G'[a]	H[a]	Aa[b]	Aa'[a]	Ca[b]	Ba[b]	Ta[b]	Total L[b]	Aa'/Aa[b]	S/G[b]	Tem (ºC)	Time (h)
Residual_L_R0	80,88	3,15	0,00	13,79	0,00	2,18	22,78	43,52	0,00	9,67	66,30	75,97	1,91	6,09	25	18
Residual_L_R1	79,51	4,70	0,00	13,41	0,00	2,38	37,31	26,40	0,00	7,85	63,71	71,56	0,71	6,28	25	18
Residual_L_R2	80,05	4,70	0,00	13,79	0,00	1,46	40,11	26,51	0,00	10,00	66,62	76,62	0,66	6,15	25	18
Residual_L_R3	82,63	3,41	0,00	11,04	0,00	2,92	44,42	19,55	0,00	9,33	63,97	73,30	0,44	7,80	25	18

[a] S, syringyl units, S’ syringyl units with a α-ketone structures, Sc, condenced syrinyl units G, guaiacyl structure, G’, guaiacyl units with a α-ketone structures, H, *p*-hydroxylphenyl units. Percentage of the units was caculated from the intergration of one ^{13}C-^{1}H cross signals of the units at the aromatic region of the total intergration of the units. Among them, S unit = integration of $S_{2,6}$/2/total units integration, S’ unit = integration of $S'_{2,6}$/2/total units integration, G unit = integration of G_2/total units integration, G’ unit = integration of G'_2/total units integration, H unit = integration of $H_{2,6}$/2/total units integration.

[b] Molar percentages of the linkage was caculated from the integration of correspdonding α position divide the intergratuon of the total intergradtion of aromatic units; Total unit intergration= $(S_{2,6}+S'_{2,6}+H_{2,6})/2+G_2+G'_2)$; S/G ratio obtained by $(S_{2,6}+S'_{2,6}+Sc)/(G_2+G'_2)$; Ta=Aa+Aa’. Total L= Aa + Aa’ + Ca + Ba, Aa, aryl ether [β-O-4(OH)], Aa’, aryl ether with benzylic alkoxylation of α hydroxyl [β-O-4(OEG)], Ca, phenylcoumaran (β-5), Ba, resinols (β- β).

[c] EG, ethylene glycol, The percentage of acid was based on the total weight of EG and ChCl.

Table S10. The yield of DES and lignin before and after DES recycling.

Sample	Mixture(g), (recycling yield, %)	Fresh lignin (mg)	Recovered lignin (mg), (Lignin yield, %)
Fresh DES_HOTf	44,6 (100%)	500	Residual_L_R0 (390), (78)
Mixture_R1	41,7 (93,6%)	467	Residual_L_R1 (397), (85)
Mixture_R2	37,9 (90,7%)	423	Residual_L_R2 (394), (88)
Mixture_R3	35,5 (93,6%)	396	Residual_L_R3 (356), (90)

Reaction condition: starting DES, ChCl, 21 g, EG, 18 g, HOTf 5.55g, birch lignin, 500 mg, 25 ºC, 18 h.

References

(1) Wang, Z.; Zhu, X.; Deuss, P. J. The Effect of Ball Milling on Birch, Pine, Reed, Walnut Shell Enzymatic Hydrolysis Recalcitrance and the Structure of the Isolated Residual Enzyme Lignin. Ind. Crops Prod. 2021, 167, 113493. https://doi.org/10.1016/j.indcrop.2021.113493.

(2) Deuss, P. J.; Wang, Z. Catalytic Hydrogenolysis of Lignin: The Influence of Minor Units and Saccharides. *ChemSusChem* **2021**. https://doi.org/10.1002/cssc.202101527.

(3) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. Determination of Structural Carbohydrates and Lignin in Biomass. *Lab. Anal. Proced.* **2008**, *1617* (1), 1–16.

(4) Liu, Y.; Deak, N.; Wang, Z.; Yu, H.; Hameleers, L.; Jurak, E.; Deuss, P. J.; Barta, K. Tunable and Functional Deep Eutectic Solvents for Lignocellulose Valorization. *Nat. Commun.* **2021**, *12* (1), 1–15. https://doi.org/10.1038/s41467-021-25117-1.

(5) Van den Bosch, S.; Schutyser, W.; Vanholme, R.; Driessen, T.; Koelewijn, S.-F.; Renders, T.; De Meester, B.; Huijgen, W. J. J.; Dehaen, W.; Courtin, C. M. Reductive Lignocellulose Fractionation into Soluble Lignin-Derived Phenolic Monomers and Dimers and Processable Carbohydrate Pulps. *Energy Environ. Sci.* **2015**, *8* (6), 1748–1763. https://doi.org/10.1039/C5EE00204D.

(6) Liao, Y.; Koelewijn, S.-F.; Van den Bossche, G.; Van Aelst, J.; Van den Bosch, S.; Renders, T.; Navare, K.; Nicolaï, T.; Van Aelst, K.; Maesen, M. A Sustainable Wood Biorefinery for Low–Carbon Footprint Chemicals Production. *Science (80).* **2020**, *367* (6484), 1385–1390. https://10.1126/science.aau1567.

(7) Anderson, E. M.; Stone, M. L.; Katahira, R.; Reed, M.; Muchero, W.; Ramirez, K. J.; Beckham, G. T.; Román-Leshkov, Y. Differences in S/G Ratio in Natural Poplar Variants Do Not Predict Catalytic Depolymerization Monomer Yields. *Nat. Commun.* **2019**, *10* (1), 1–10. https://10.1038/s41467-019-09986-1.