Supporting Information

Direct Production of Jet Fuel-Range Bicyclic Alkanes from Native Lignin via a Two-Step Pre-arylation and Hydrodeoxygenation Strategy

Ni Han, Zhaolin Dou, Min Ji*, Min Wang*

School of Chemistry, Dalian University of Technology, Dalian, 116024, Liaoning China.

*Corresponding author: wangmin@dlut.edu.cn, jimin@dlut.edu.cn

Table of contents

Experimental procedures

Reagents

All commercial chemicals were analytical reagents and were used without any further purification. Formic acid (88 wt%), guaiacol and syringol were purchased from Aladdin Chemistry Co., Ltd. TiO_2 was purchased from Alfa Aesar. CuO, Al_2O_3, ZrO_2, SiO_2, CeO_2) were purchased from Shanghai Macklin Biochemical Co., Ltd. MoO_3 and phenol were purchased from Tianjin DAMAO Chemical Reagent Factory. $PdCl_3$/HCl was purchased from CNMC Shenyang Research Institute of Nonferrous Metals Co., Ltd. Ethanol was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. All wood raw materials are purchased from Taobao Teana Forest Wood Industry

Catalyst preparation

Preparation of other supported catalyst

The Pd/x (x = TiO_2, CuO, Al_2O_3, ZrO_2, MoO_3, SiO_2, CeO_2) catalyst was prepared by the deposition-precipitation method. Typically, 0.5 g of x was dissolved in 20 mL of water in a 100 mL beaker and magnetically stirred at room temperature. Then, 25 mg of Pd (4.136 mL $PdCl_3$/HCl solution) was added into the above suspension and stirred for 24 h at room temperature. Subsequently, the suspension evaporated at 120 °C. The final samples were obtained by reduction in H_2 flow at 400 °C for 4h.

Experiment process

Phenol arylated lignin (P-lignin). Wood power (1.0 g, dry weight) was mixed with phenol (0.8 g) and 10 mL FA (88 wt%) in 75-mL pressure bottle. The bottle was immersed in an oil bath at 100 °C with magnetic stirring. After quenching the reaction at a pre-set time, the pulp was isolated by filtration through a filter paper, and further washed sequentially with 88wt% FA, ethanol and H_2O. The filtrate was concentrated by rotary evaporation and subsequently precipitated in deionized water to isolate arylated lignin.

Guaiacol arylated lignin (G-lignin). Wood power (1.0 g, dry weight) was mixed with guaiacol (1.05 g) and 10 mL FA (88 wt%) in 75-mL pressure bottle. The bottle was immersed in an oil bath at 100 °C with magnetic stirring. After quenching the reaction at a pre-set time, the pulp was isolated by filtration through a filter paper, and further washed sequentially with 88wt% FA, ethanol and H_2O. The filtrate was concentrated by rotary evaporation and subsequently precipitated in deionized water to isolate arylated lignin.

Syringol arylated lignin (S-lignin). Wood power (1.0 g, dry weight) was mixed with guaiacol (1.31 g) and 10 mL FA (88 wt%) in 75-mL pressure bottle. The bottle was immersed in an oil bath at 100 °C with magnetic stirring. After quenching the reaction at a pre-set time, the pulp was isolated by filtration through a filter paper, and further washed sequentially with 88wt% FA, ethanol and H_2O. The filtrate was concentrated by rotary evaporation and subsequently precipitated in deionized water to isolate arylated lignin.

Phenol arylated lignin (A-lignin). Wood power (1.0 g, dry weight) was mixed with 10 mL FA (88 wt%) in 75-mL pressure bottle. The bottle was immersed in an oil bath at 100 °C with magnetic stirring. After quenching the reaction at a pre-set time, the pulp was isolated by filtration through a filter paper, and further washed sequentially with 88wt% FA, ethanol and H_2O. The filtrate was concentrated by rotary evaporation and subsequently precipitated in deionized water to isolate arylated lignin.

Phenol arylated lignin (F-lignin). Wood power (1.0 g, dry weight) was mixed with 10 mL formaldehyde solution in 75-mL pressure bottle. The bottle was immersed in an oil bath at 100 °C with magnetic stirring. After quenching the reaction at a pre-set time, the pulp was isolated by filtration through a filter paper, and further washed sequentially with 88 wt% FA, ethanol and H_2O. The filtrate was concentrated by rotary evaporation and subsequently precipitated in deionized water to isolate arylated lignin.[1]

HDO reaction of lignin model compounds. The catalytic HDO reactions were performed in a 50-mL autoclave reactor with internal Teflon insert. Typically, 50 mg of reactant, 20 mg of catalyst and 6 mL cyclohexane were added into the stainless-steel autoclave with an internal Teflon insert, and a certain amount of hydrogen was charged and then heated to the desired temperature under magnetic stirring. After reaction, the reaction mixture was diluted by ethanol, and the catalyst was filtered. A certain amount of decane was added into the above solution as internal standard. And then, the products were analysed by gas chromatography−mass spectrometry (GC-MS) using an Agilent 7890A/5975C instrument equipped with an HP-5 MS column (30 m in length, 0.25 mm in diameter) and quantified by GC using an Agilent 7890 instrument equipped with an HP-5 column (30 m in length, 0.25 mm in diameter).[2]

Catalytic conversion of phenol arylated lignin to jet fuel. The catalytic reactions were performed in a 50 ml autoclave reactor with an internal Teflon insert. Typically, 20 mg of phenol arylated lignin, 50 mg of catalyst and 6 mL cyclohexane were added into the stainless-steel autoclave with an internal Telon insert. After charged with 3 MPa of H2, the reactor was heated to 300 °C for 16 h under magnetic stirring. And then, the products were analysed by gas chromatography−mass spectrometry (GC-MS) using an Agilent 7890A/5975C instrument equipped with an HP-5 MS column (30 m in length, 0.25 mm in diameter) and quantified by GC using an Agilent 7890 instrument equipped with an HP-5 column (30 m in length, 0.25 mm in diameter). The yield was determined using Effective Carbon Number (ECN). The detailed calculation was shown in the monomer quantification and yield calculation.

Compositional analysis of lignin and carbohydrates. Lignin and carbohydrates in wood powders and cellulose pulp were quantified using the procedure of two-stage sulfuric acid hydrolysis following the National Renewable Energy Laboratory (NREL) standard protocol.[3] In brief, 0.3 g biomass (weighed to the nearest 0.1 mg) was treated in 72 wt% H_2SO_4 at 30 °C for 60 min. The slurry was diluted to 4 wt% H_2SO_4 and autoclaved at 121 °C for 60 min. After filtration, the acid insoluble lignin and the acid-soluble lignin were measured

gravimetrically and spectrophotometrically, respectively. The carbohydrates were analysed by the HPLC-RID as noted above.

Analytical methods and quantitative caclulations

Liquid chromatography for carbohydrates

High-performance liquid chromatography (HPLC, Shimadzu Prominence LC-20AD) equipped with an ultraviolet-visible detector (UV) and differential refractive index detector (RID) was used to analyse the concentration of substrates and products in the liquid phase. Chromatographic column used a ROA-Organic Acid H^+ column (8 %, 300 × 7.8 mm), the mobile phase was H_2SO_4 (0.05 wt%) solution with the flow rate of 0.5 mL min^{-1}, the column temperature was 313.15 K, and the UV wavelength was set to 210 nm. And 10 μL of diluent was injected by an autosampler. The molar amount of liquid phase products was quantified by standard curves. [4]

NMR analysis

Heteronuclear single-quantum coherence NMR analysis. Two-dimensional heteronuclear single-quantum coherence (HSQC) NMR spectra were recorded on Bruker 600 MHz spectrometers equipped with either a 5-mm TCI Z-gradient (53.0 G cm−1) cryoprobe or a 5-mm BBO probe (for most samples). Arylation lignin were dissolved in 0.5 ml DMSO-d_6. HSQC spectra were recorded at 298 K using Bruker's standard hsqcetgpsisp 2.2 pulse programme (acquisition times 100 ms and 8 ms in ^1H and ^{13}C dimensions, respectively; inter-scan relaxation delay 1 s).[5]

Monomer quantification and yield calculations

Due to the difficulty in obtaining or producing a large quantity of monomers, we used a quantification based on an internal standard (decane) and the effective carbon number (ECN) method. HDO monomer ECN in Table S1. Add 100 μL of internal standard solution (10 mg decane dissolved in 1 mL acetonitrile) to the

solution to be analyzed. The resulting solution was analyzed by GC-FID. The monomer yield was calculated based on the area of the monomer and the area of decane in the GC chromatogram. The detailed calculation was as follows:

$$n_{decane} = \frac{W_{decane\ in\ sample}}{MW_{decane}}$$

$$n_{monomer} = \frac{A_{monomer\ in\ sample}}{A_{decane\ in\ sample}} \times \frac{ECN_{decane}}{ECN_{monomer}}$$

$$W_{monomer} = n_{monomer} \times MW_{monomer}$$

$$Y_{monomer} = \frac{W_{monomer}}{W_{lignin}} \times 100\%$$

In the equations,

$W_{decane\ in\ sample}$ (mg): the weight of decane used as an internal standard in each analysed sample;

MW_{decane} (mg mmol^{-1}): the molecular weight of decane (142 mg mmol^{-1});

n_{decane} (mmol): the molar amount of decane in each analyzed sample;

$n_{monomer}$ (mmol): the molar amount of monomer in each analyzed sample;

$A_{monomer\ in\ sample}$: the peak area of monomer in the GC-FID chromatogram;

$A_{decane\ in\ sample}$: the peak area of decane in the GC-FID chromatogram;

ECN_{decane}: the effective carbon number (10) of decane;

$ECN_{monomer}$: the effective carbon number of the lignin monomer molecule;

$W_{monomer}$ (mg): the molecular weight of hydrodeoxygenation monomer in the sample was analyzed.

$Y_{monomer}$: the yield of monomer based on the weight of lignin

W_{lignin} (mg): the weight of lignin;

Supplementary figures and tables

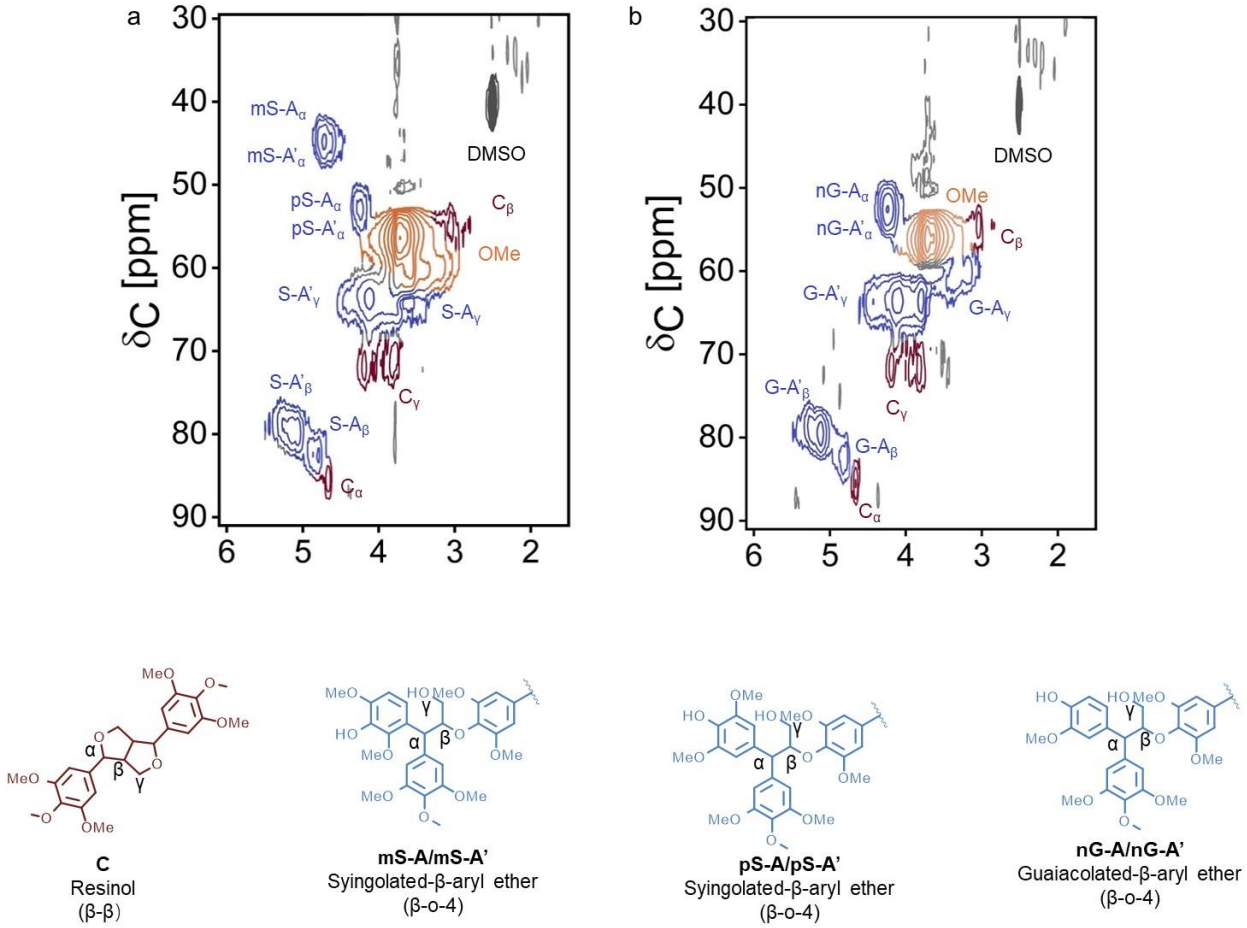


Figure S1. (a) The ^{1}H-^{13}C correlation (heteronuclear single quantum coherence) spectra of S-lignin. (b) The ^{1}H-^{13}C correlation (heteronuclear single quantum coherence) spectra of G-lignin. Extraction conditions: 100 °C, 2 h.

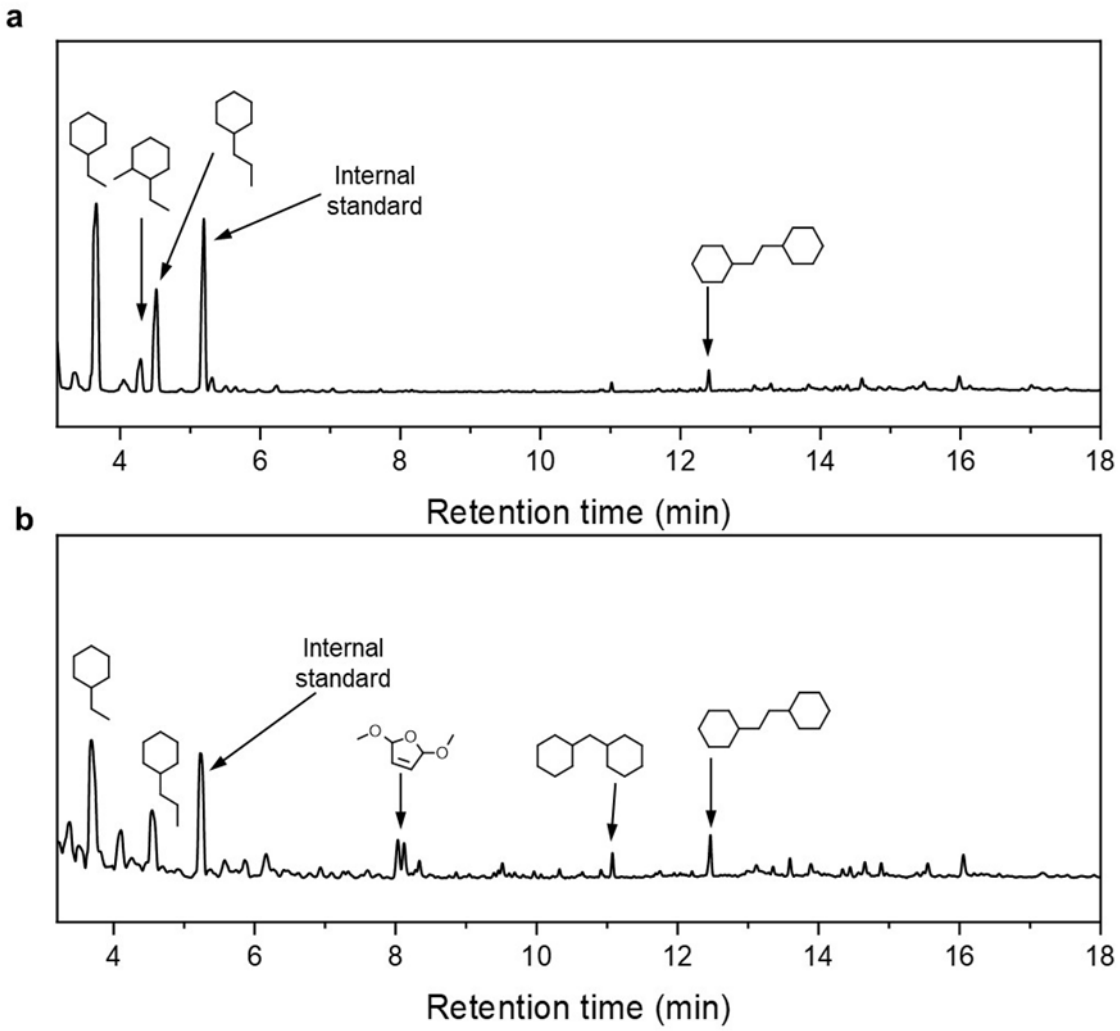


Figure S2. (a) Gas chromatogram of the conversion of F-lignin extracted from beech powder into cycloalkanes. (b) Gas chromatogram of native beech wood converted into cycloalkanes. Extraction conditions: 100 °C, 2 h; HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

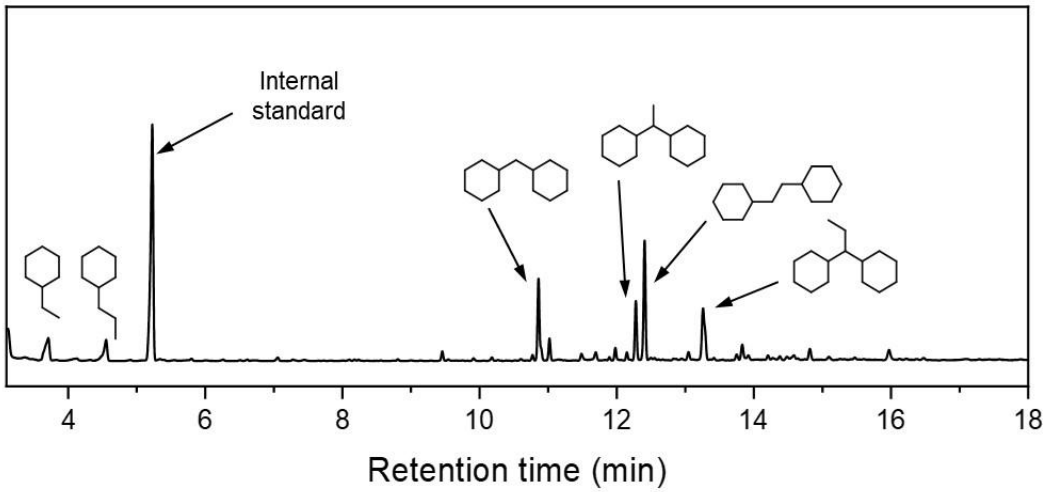


Figure S3. Gas chromatogram of the conversion of P-lignin extracted from pine powder into cycloalkanes. Extraction conditions: 100 °C, 2 h; HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

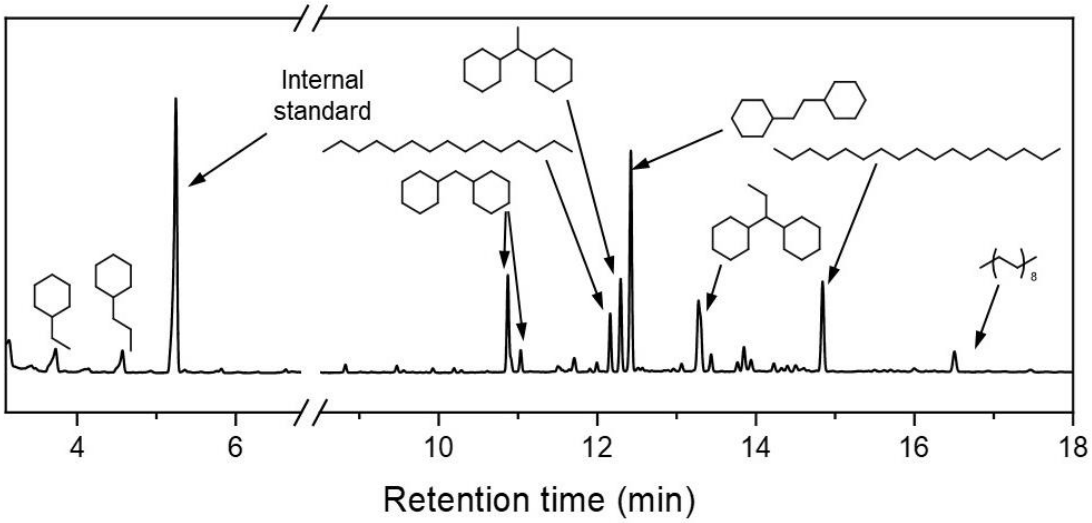


Figure S4. Gas chromatogram of the conversion of P-lignin extracted from peanut shell powder into cycloalkanes. Extraction conditions: 100 °C, 2 h; HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

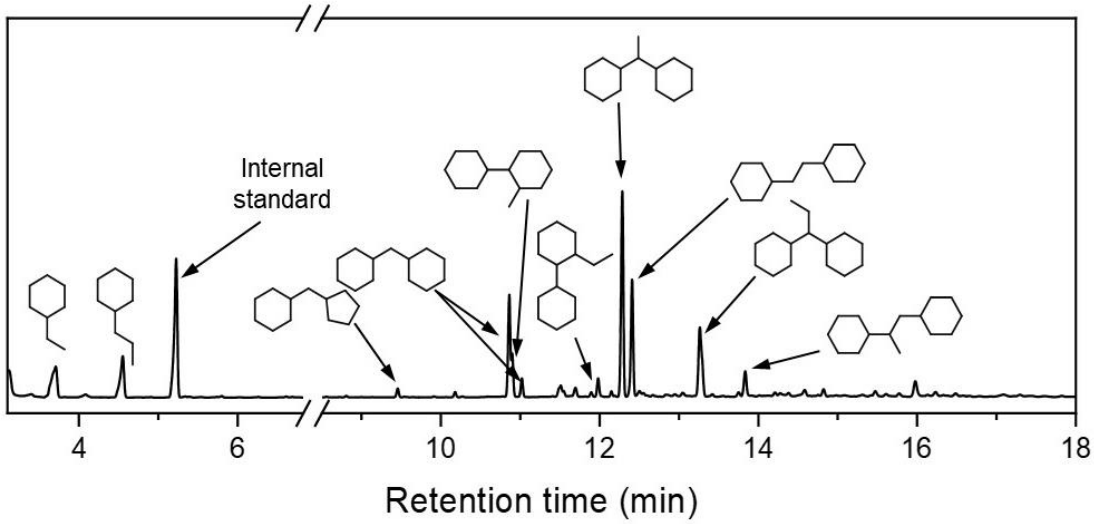


Figure S5. Gas chromatogram of the conversion of P-lignin extracted from poplar powder into cycloalkanes. Extraction conditions: 100 °C, 2 h; HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

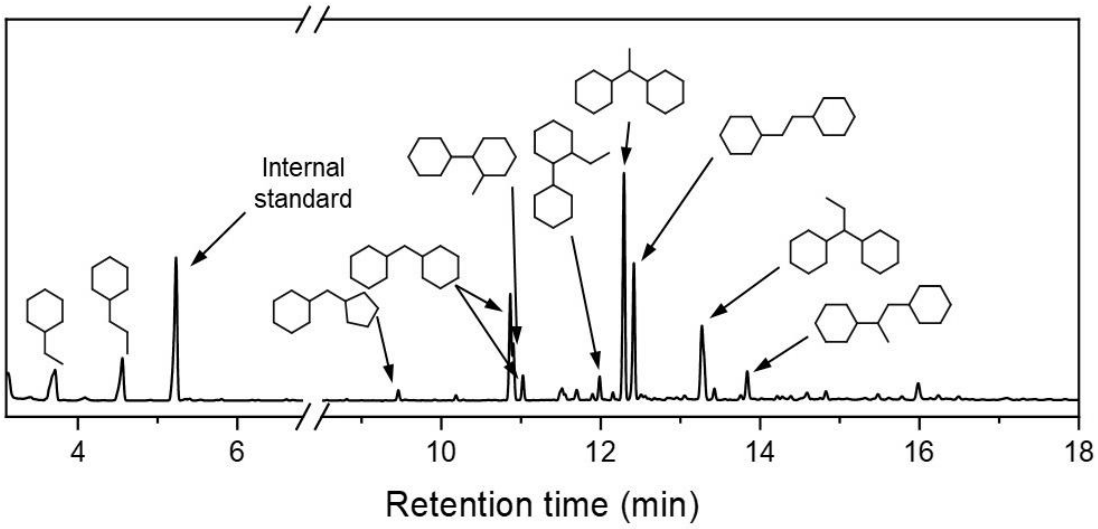


Figure S6. Gas chromatogram of the conversion of P-lignin extracted from elm powder into cycloalkanes. Extraction conditions: 100 °C, 2 h; HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

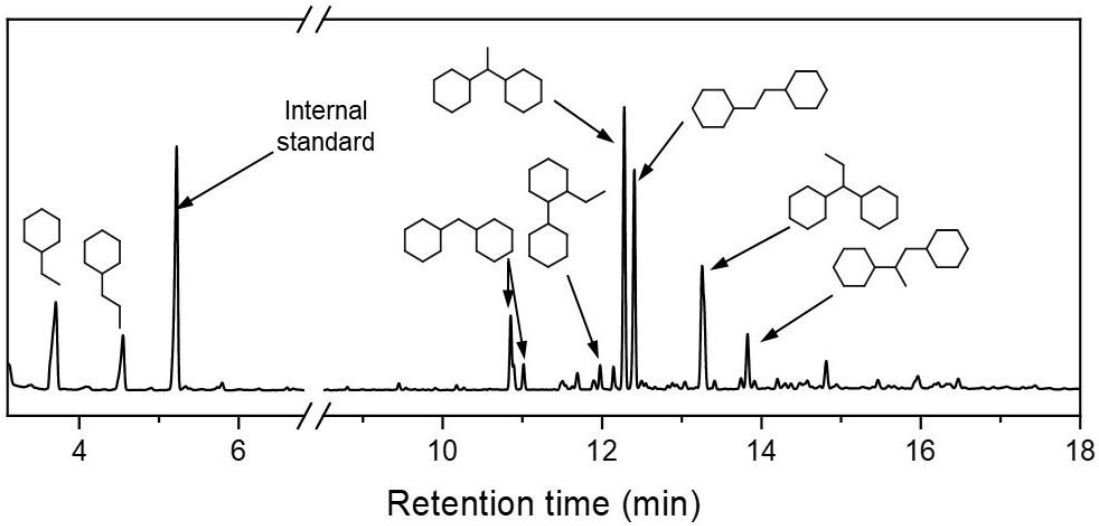


Figure S7. Gas chromatogram of the conversion of P-lignin extracted from sorghum powder into cycloalkanes. Extraction conditions: 100 °C, 2 h; HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

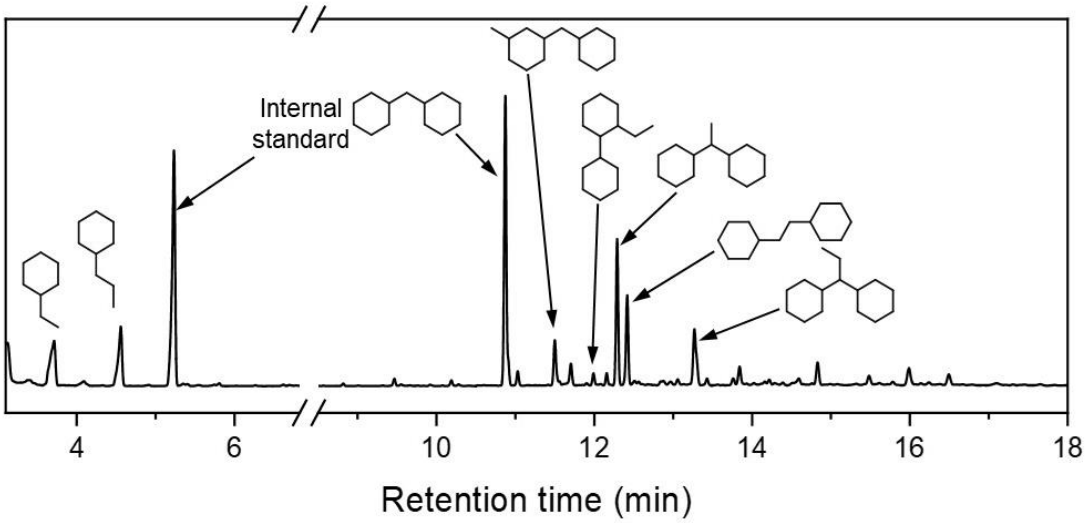


Figure S8. Gas chromatogram of the conversion of P-lignin extracted from cypress powder into cycloalkanes. Extraction conditions: 100 °C, 2 h; HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

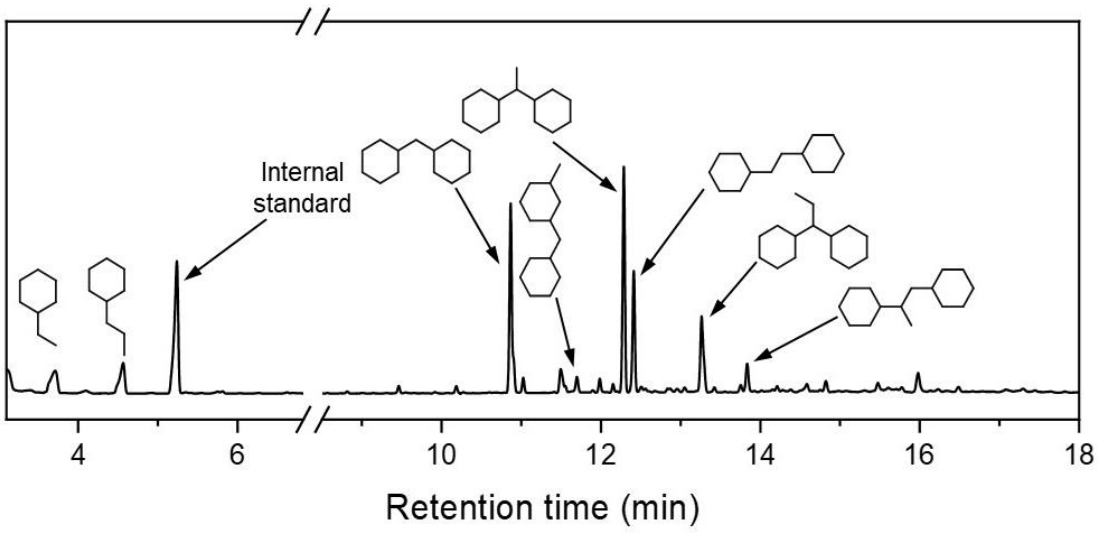


Figure S9. Gas chromatogram of the conversion of P-lignin extracted from birch powder into cycloalkanes. Extraction conditions: 100 °C, 2 h; HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

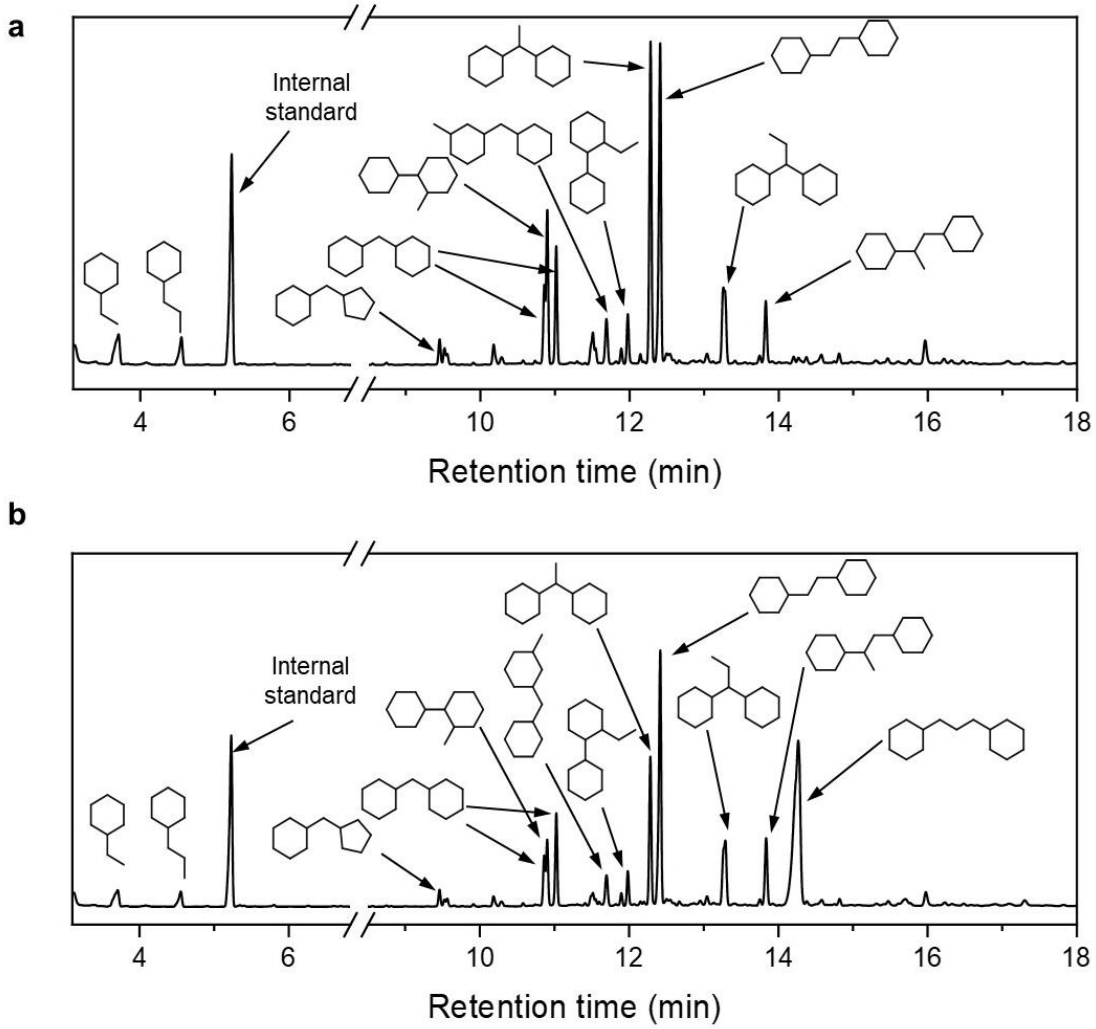


Figure S10. (a) Gas chromatogram of the conversion of G-lignin extracted from beech powder into cycloalkanes. (b) Gas chromatogram of the conversion of S-lignin extracted from beech powder into cycloalkanes. Extraction conditions: 100 °C, 2 h; HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

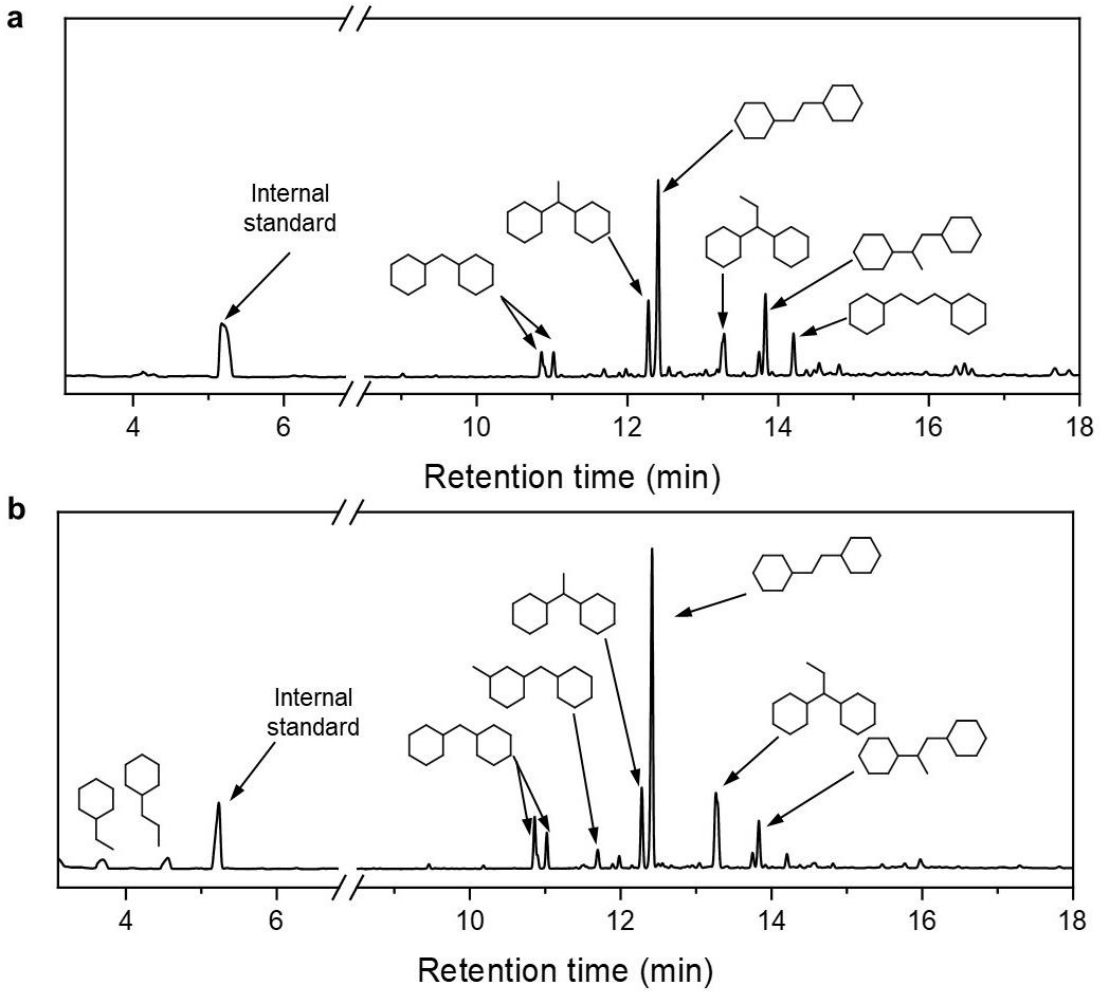


Figure S11. Gas chromatogram of the conversion of P-lignin extracted from beech powder into cycloalkanes. (a) hydrodeoxygenation reaction using Pd/TiO_2. (b) hydrodeoxygenation reaction using Pt/C. HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

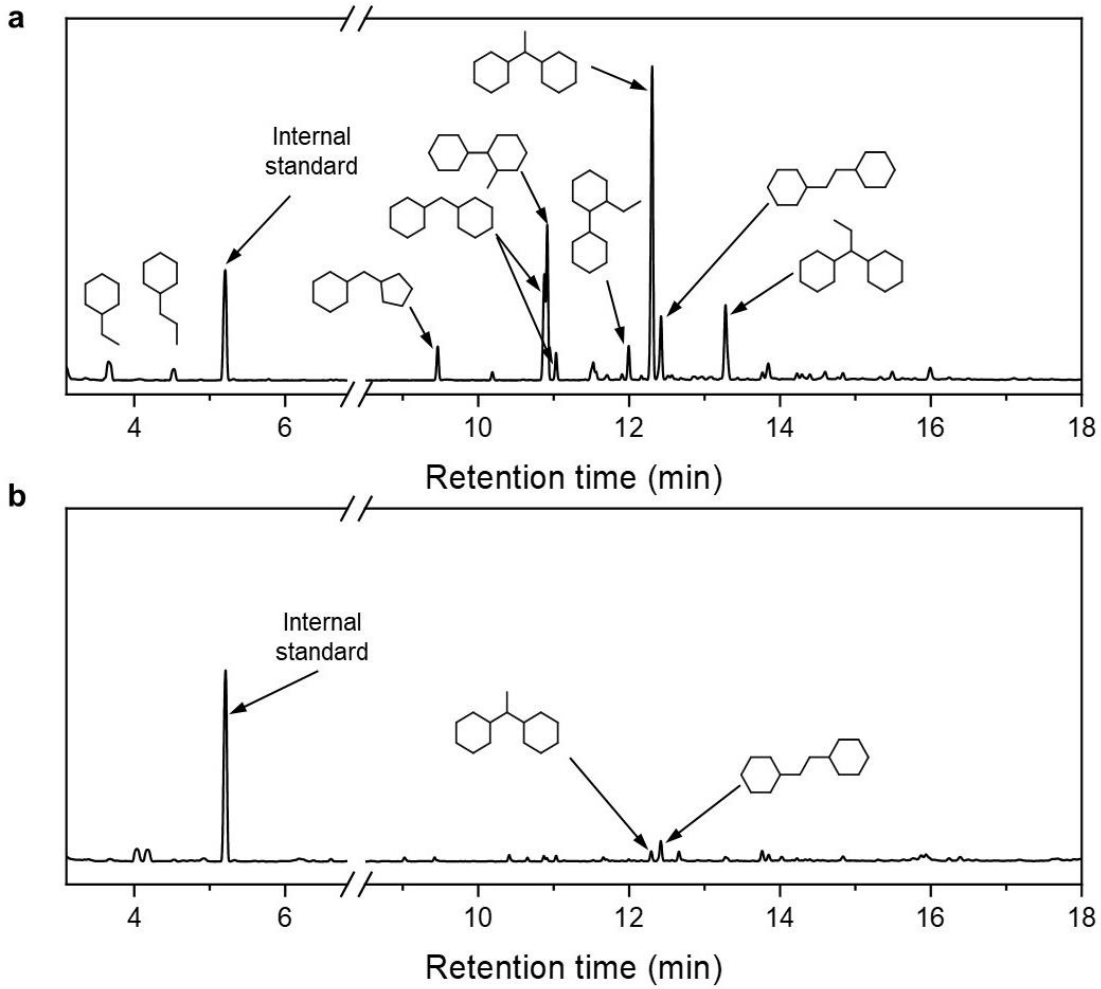


Figure S12. Gas chromatogram of the conversion of P-lignin extracted from beech powder into cycloalkanes. (a) hydrodeoxygenation reaction using Pd/ZrO_2. (b) hydrodeoxygenation reaction using Pd/SiO_2. HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

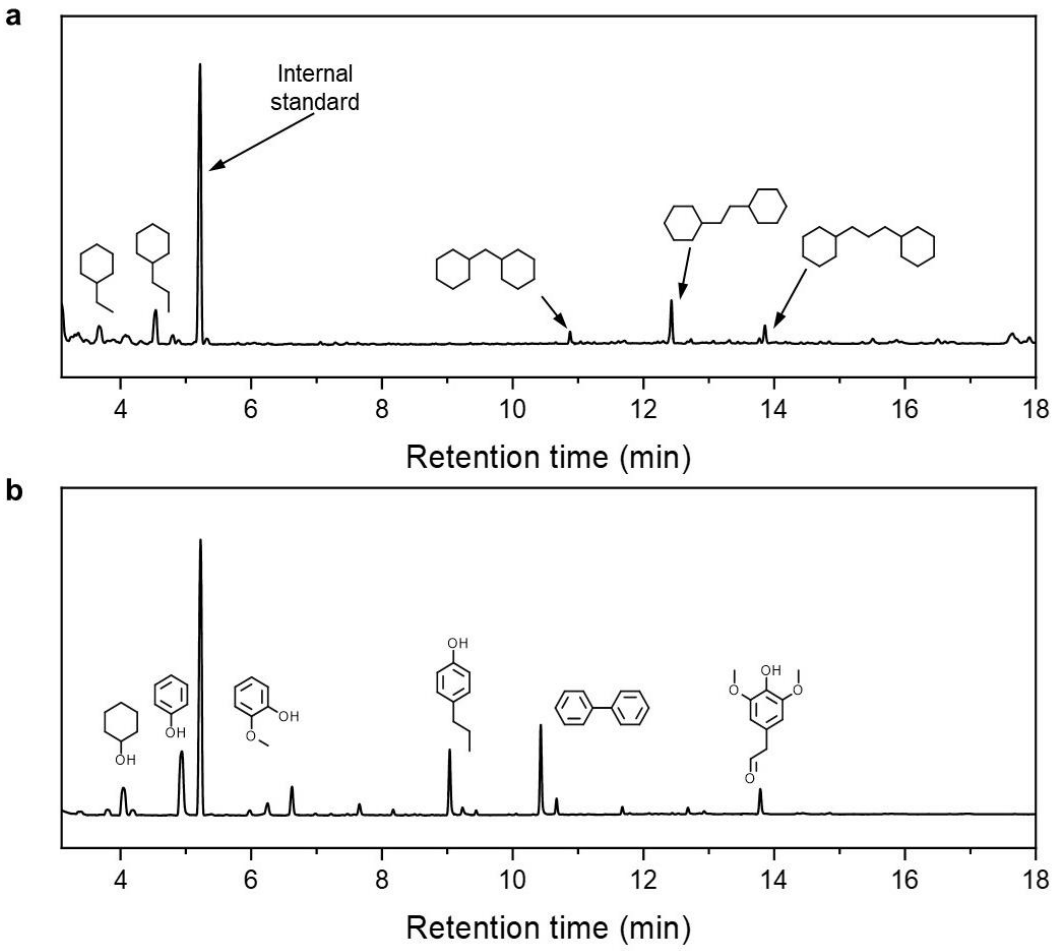


Figure S13. Gas chromatogram of the conversion of P-lignin extracted from beech powder into cycloalkanes. (a) hydrodeoxygenation reaction using Pd/MoO_3. (b) hydrodeoxygenation reaction using Pd/CuO. HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

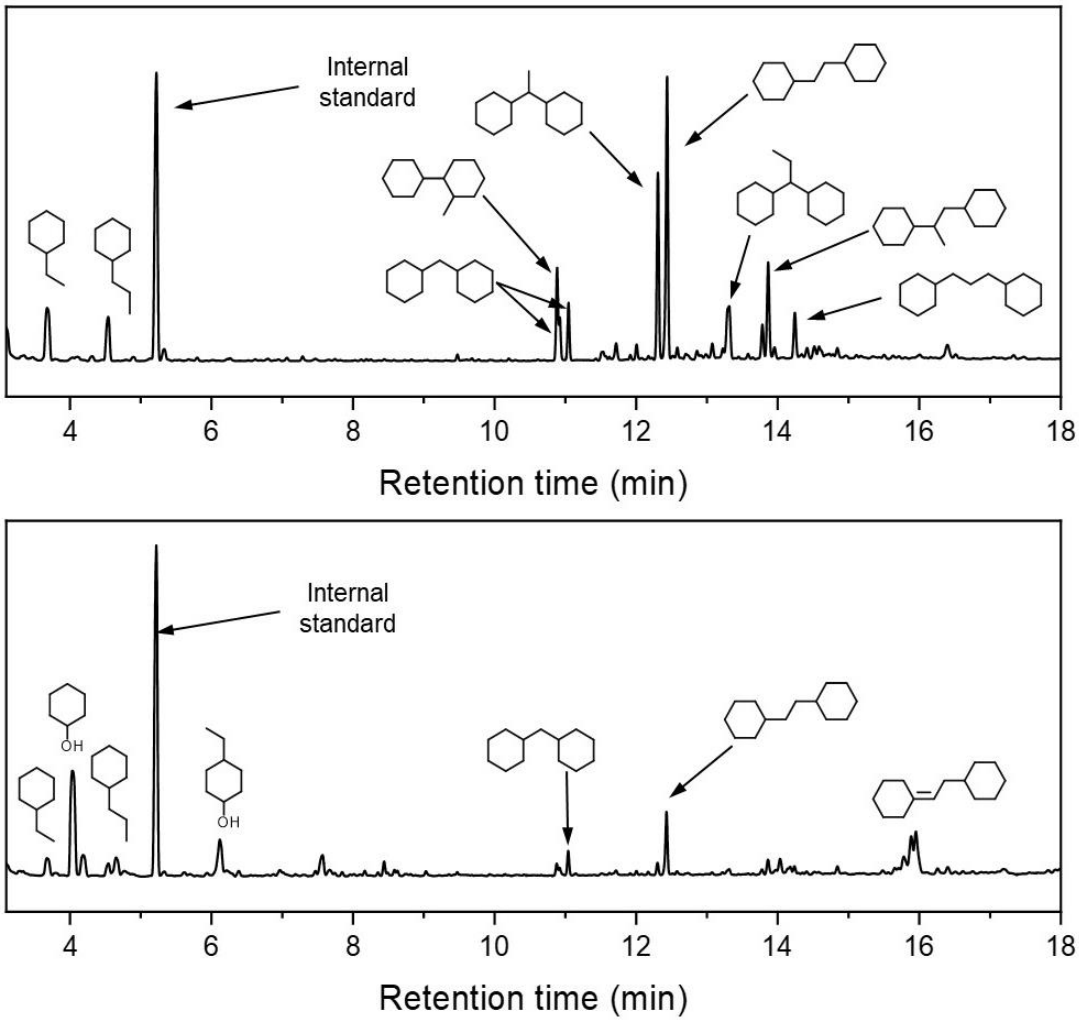


Figure S14. Gas chromatogram of the conversion of P-lignin extracted from beech powder into cycloalkanes. (a) hydrodeoxygenation reaction using Pd/Al_2O_3. (b) hydrodeoxygenation reaction using Pd/CeO_2. HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

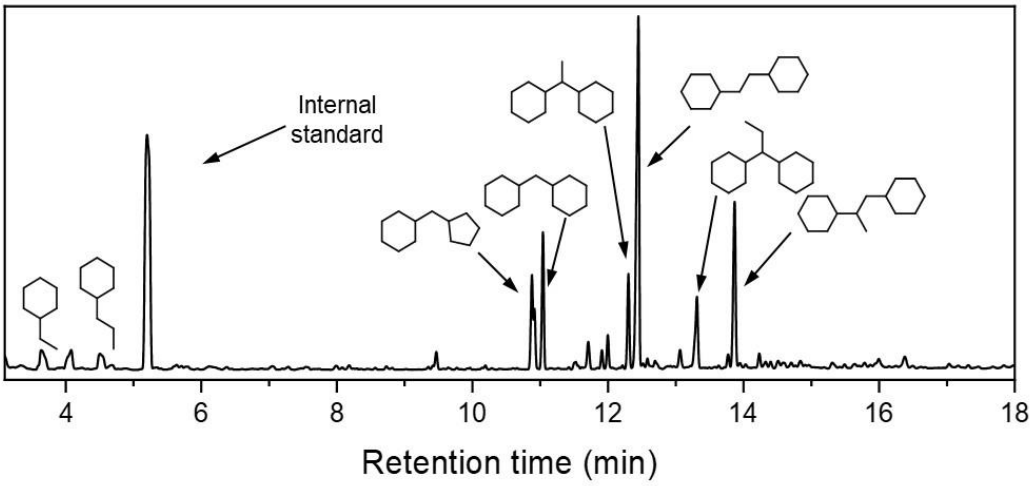


Figure S15. Analysis of P-lignin HDO extracted from beech wood powder by gas chromatography in a scale-up experiment. HDO conditions: lignin 2.5 g, Pd/C 2.5 g, cyclohexane 30 mL, 3 MPa H_2, 300 °C, 24 h.

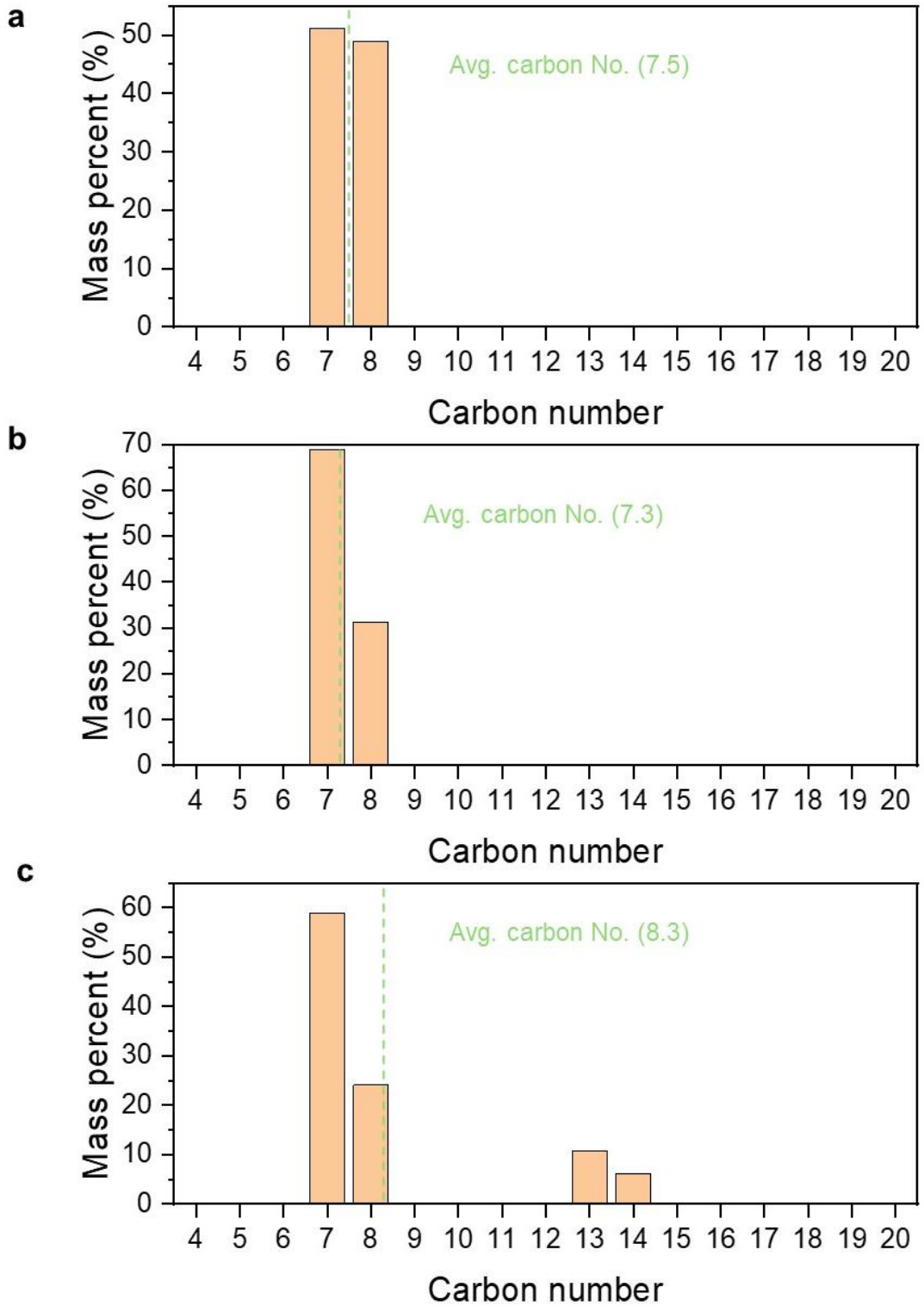


Figure S16. (a) Carbon distribution of A-lignin oil. (b) Carbon distribution of F-lignin oil. (c) Carbon distribution of N-lignin oil. HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

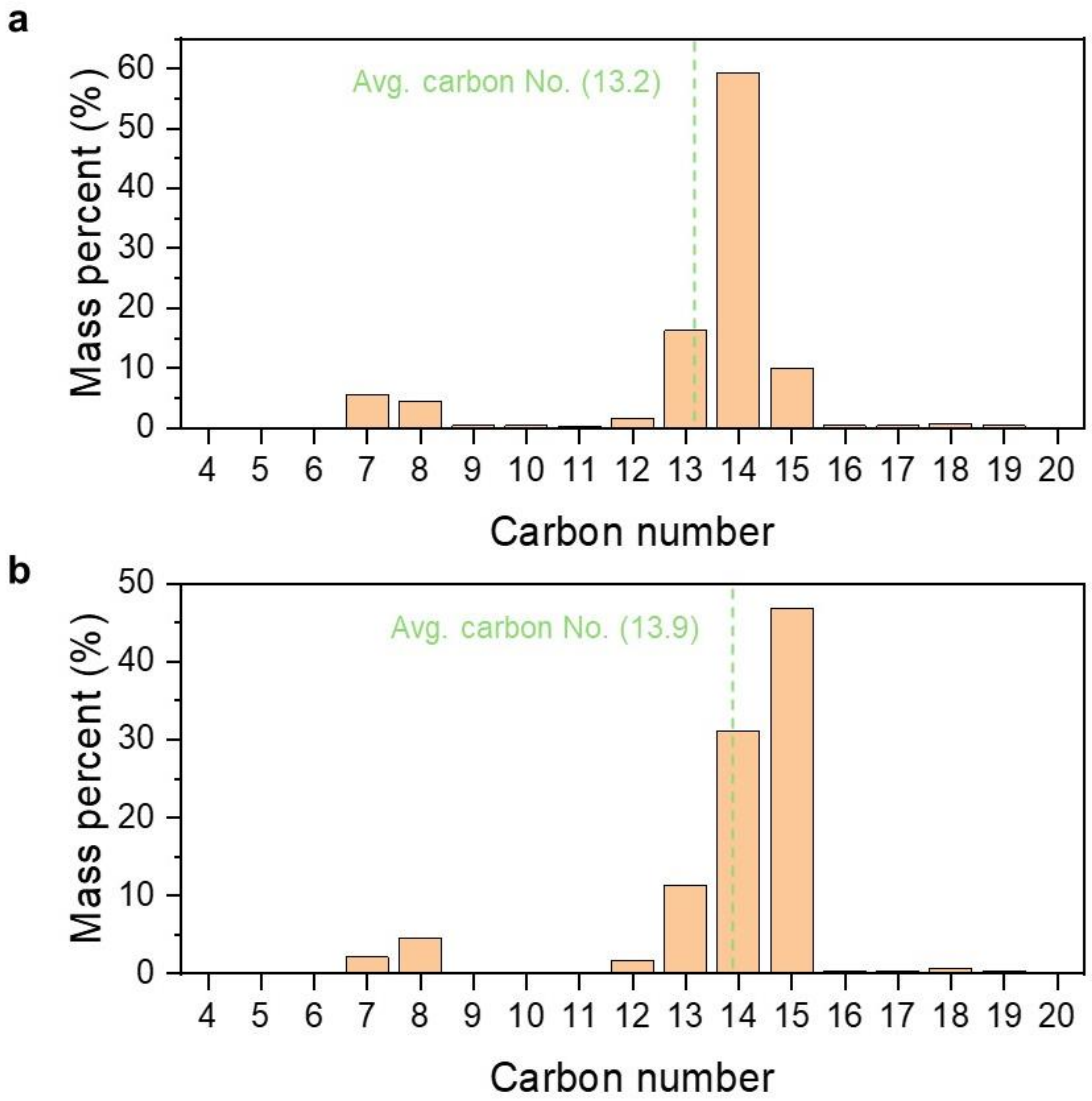


Figure S17. (a) Carbon distribution of G-lignin oil. (b) Carbon distribution of S-lignin oil. HDO conditions: lignin 20 mg, Pd/C 50 mg, cyclohexane 6 mL, 3 MPa H_2, 300 °C, 16 h.

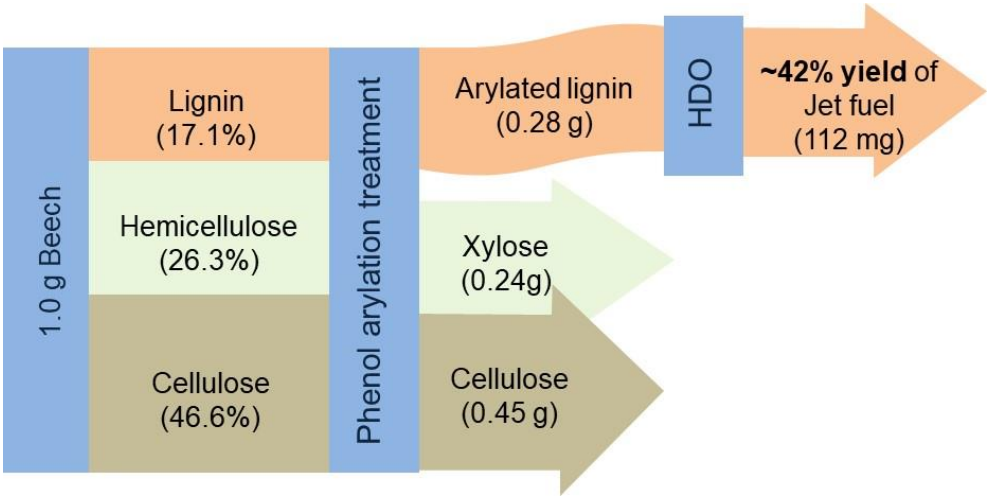


Figure S18. Analysis of beech raw materials and arylation products: Initial composition: The contents of lignin, hemicellulose and cellulose were determined by Klason method.

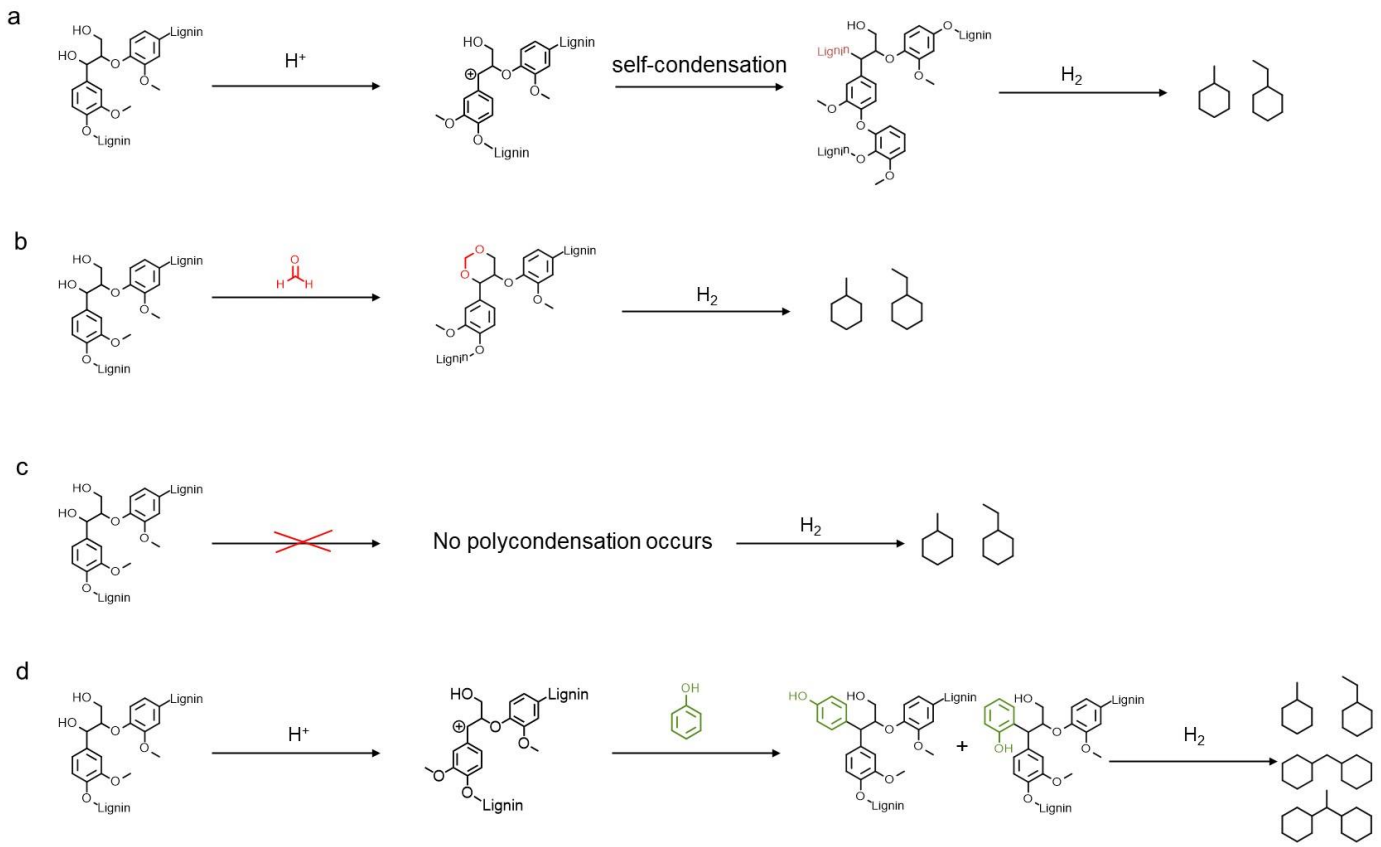


Figure S19. Different lignin reaction mechanism diagrams. (a) A-lignin, (b) F-lignin, (c) N-lignin, (d) P-lignin.

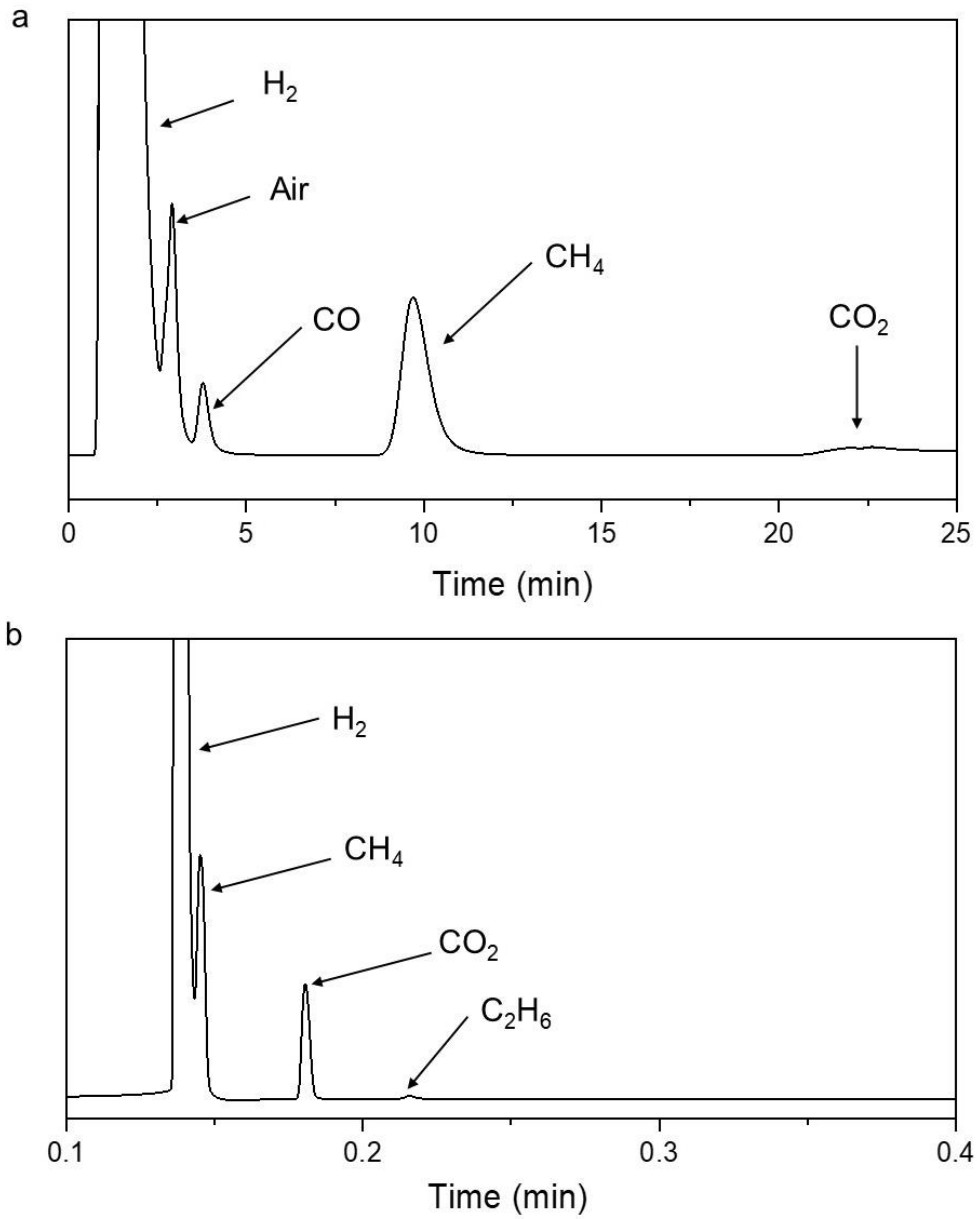


Figure S20. (a) Gas chromatogram of P-lignin gas phase products, (b) Micro gas chromatogram of P-lignin gas phase products.

Tables

Table S1. Effective carbon number (ECN) for lignin monomers used in this study.

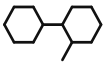
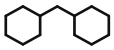
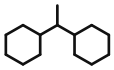
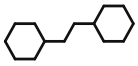
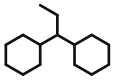
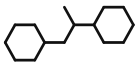
Entry	Compounds	ECN
1		8
2		9
3		13
4		13
5		14
6		14
7		15
8		15

Table S2. Main product properties of P-lignin HDO.[6, 7]

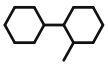
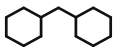
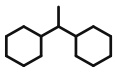
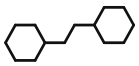
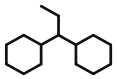
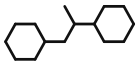
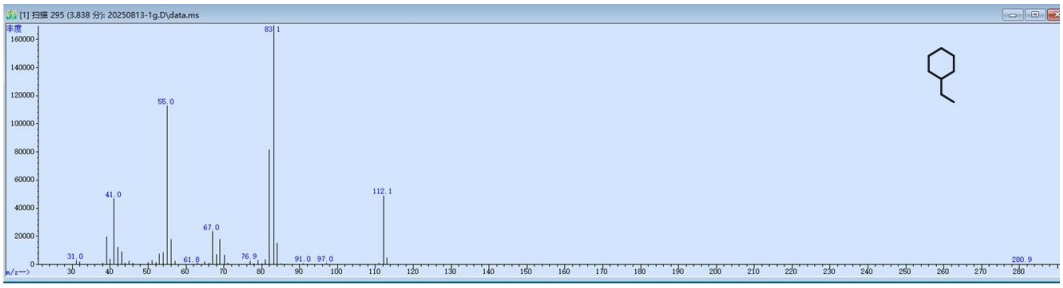
Entry	Compounds	Density (20 °C, g/mL)	Freezing point (°C)
1		0.772	-111.3
2		0.754	-94.9
3		0.884	-26.4
4		0.88	-20
5		0.89	-22.2
6		0.874	11.5
7		0.893	-23.5
8		0.882	-22

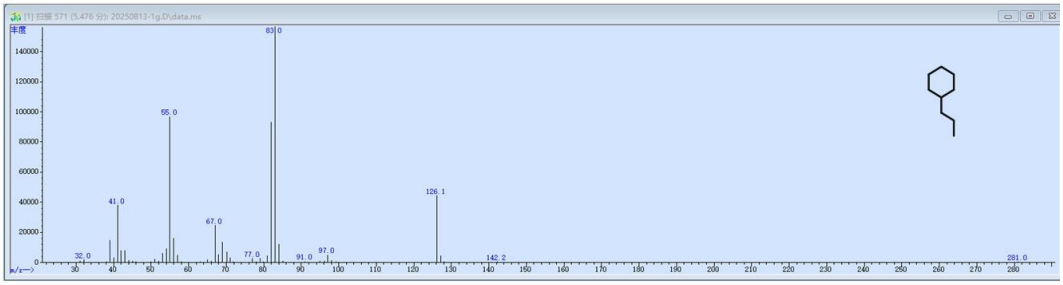
Table S3. The contents of cellulose, hemicellulose, and lignin in various raw materials, along with the contents of arylated lignin, hemicellulose, and xylose derived from arylation treatment.

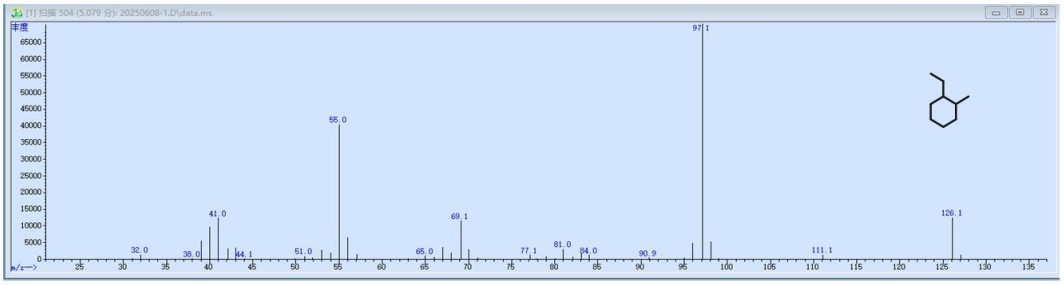
Entry	Feedstock	Cellulose (wt%) [a]	Hemicellulose (wt%) [a]	Lignin (wt%) [a]	Arylation lignin (wt%) [b]	Cellulose (wt%) [b]	Xylose (wt%) [b]
1	Beech	46.6	26.3	17.1	28.1	45.0	15.3
2	Birch	42.7	21.4	27.5	25.5	58.5	8.2
3	Cypress	42.3	16.5	25.9	24.5	44.4	4.4
4	Elm	44.3	18.1	34.3	25.3	50.7	10.8
5	Poplar	40.1	16.1	26.6	22.1	49.5	8.7
6	Pine	39.4	20.0	32.7	28.1	55.3	11.1
7	Peanut shell	33.2	16.8	32.8	16.4	57.9	10.6
8	sorghum	39.6	26.1	26.4	15.8	45.7	12.1

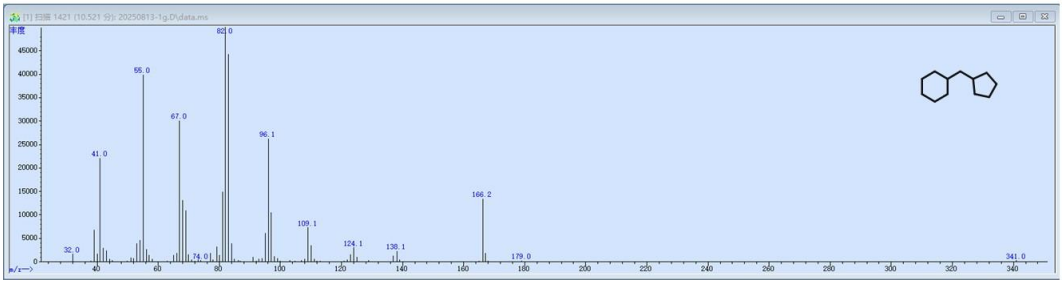
(a) The contents of lignin cellulose, hemicellulose and lignin were determined by Klason method. Methods: 0.3 g biomass (weighed to the nearest 0.1 mg) was treated in 72 wt% H_2SO_4 at 30 °C for 60 min. The slurry was diluted to 4 wt% H_2SO_4 and autoclaved at 121 °C for 60 min. (b) The content of cellulose, hemicellulose and arylated lignin in the arylation strategy. Extraction conditions: 100 °C, 2h.

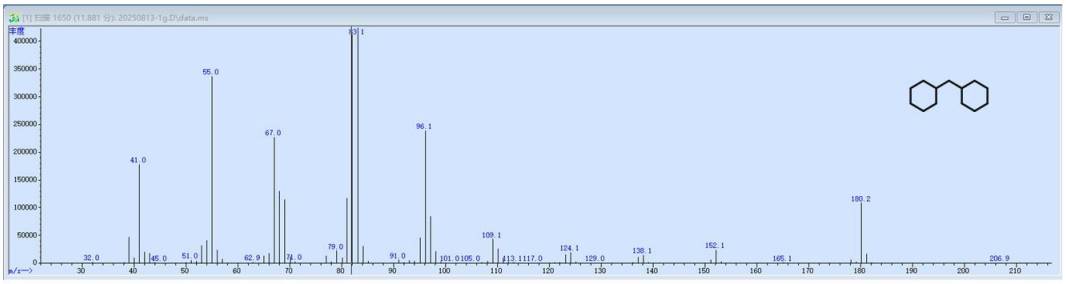
Mass spectra

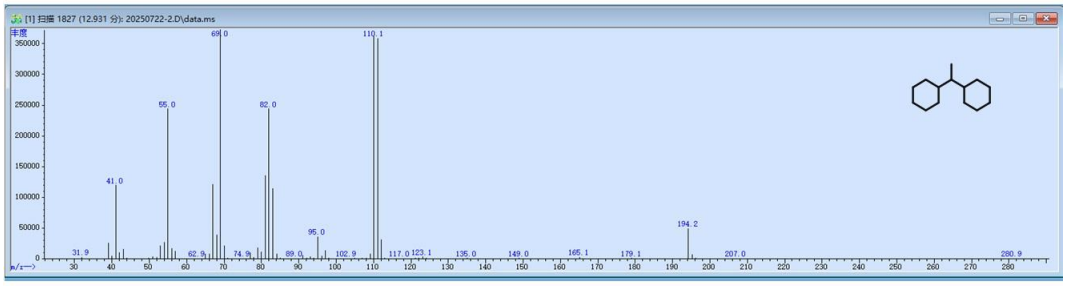


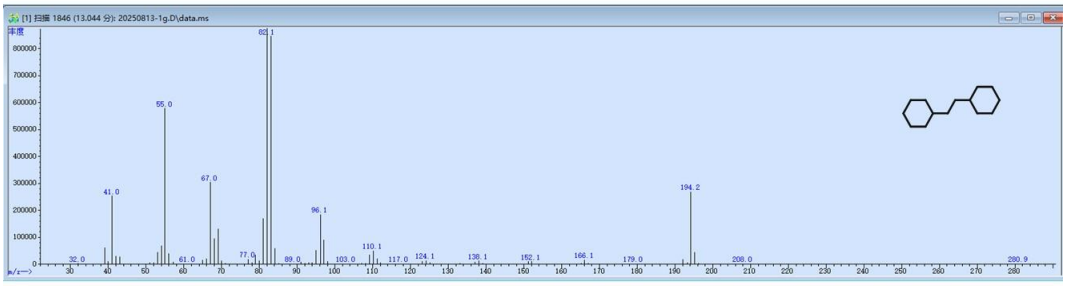


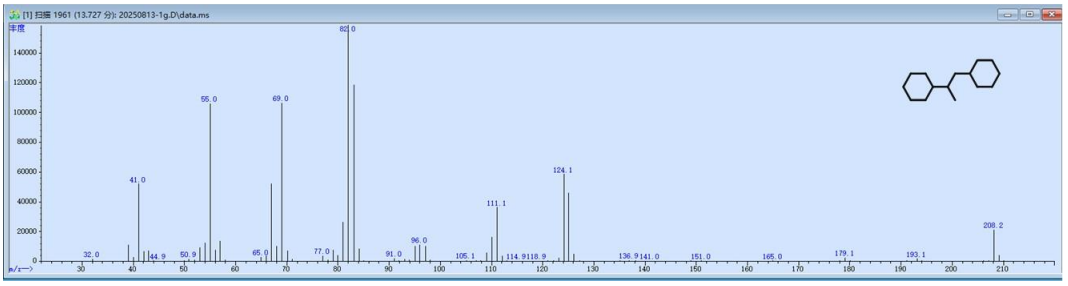


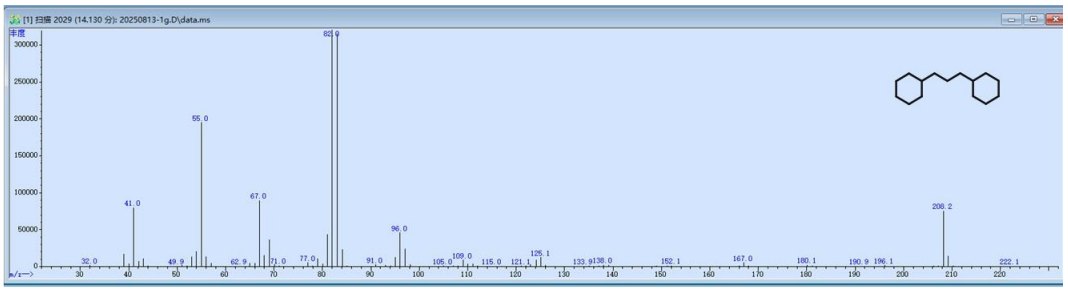


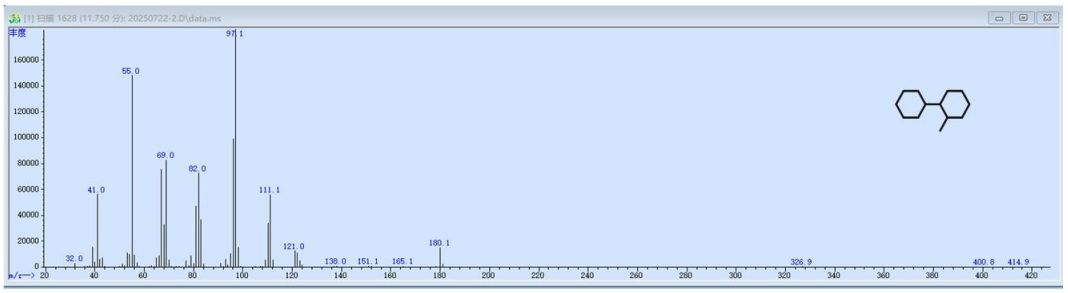

[1] 扫描 1650 (11.881 分): 20250813-1g.D\data.ms
丰度
m/z-->

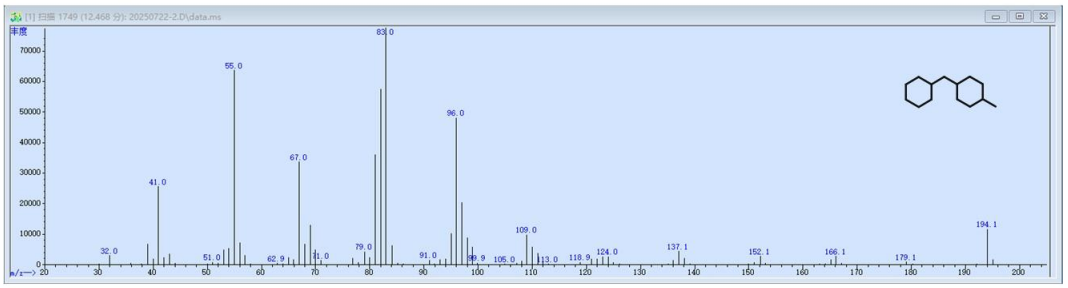

[1] 扫描 1827 (12.931 分): 20250722-2.D\data.ms
丰度
m/z-->

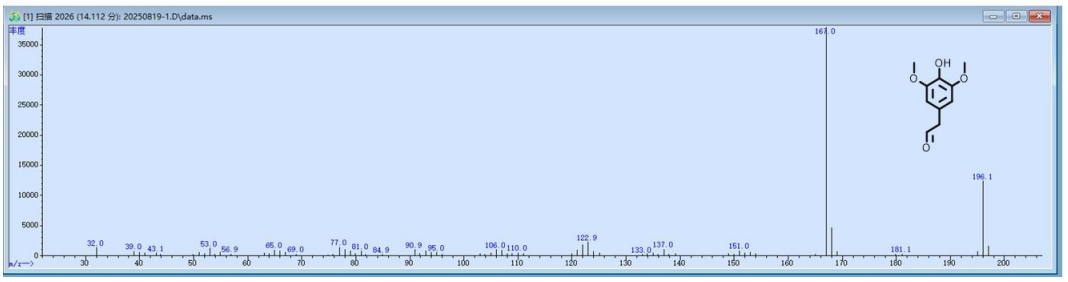

[1] 扫描 1846 (13.044 分): 20250813-1g.D\data.ms
丰度
m/z-->

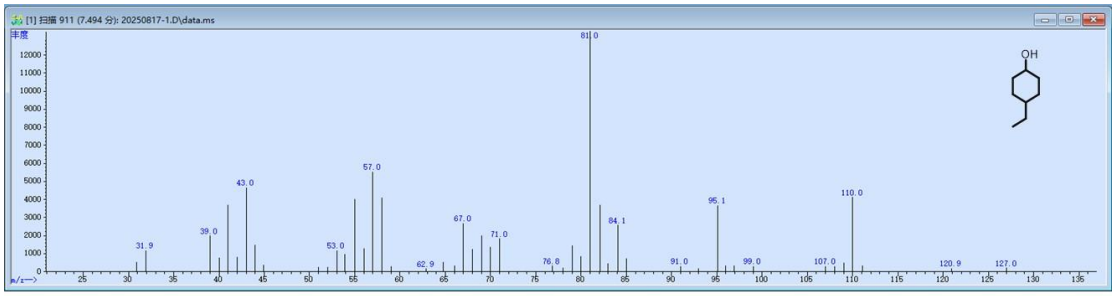

[1] 扫描 1961 (13.727 分): 20250813-1g.D\data.ms
丰度
m/z-->

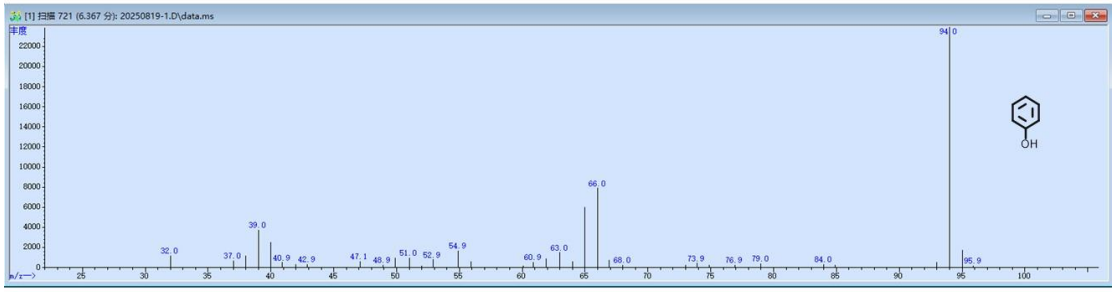

[1] 扫描 2029 (14.130 分): 20250813-1g.D\data.ms
丰度
m/z-->

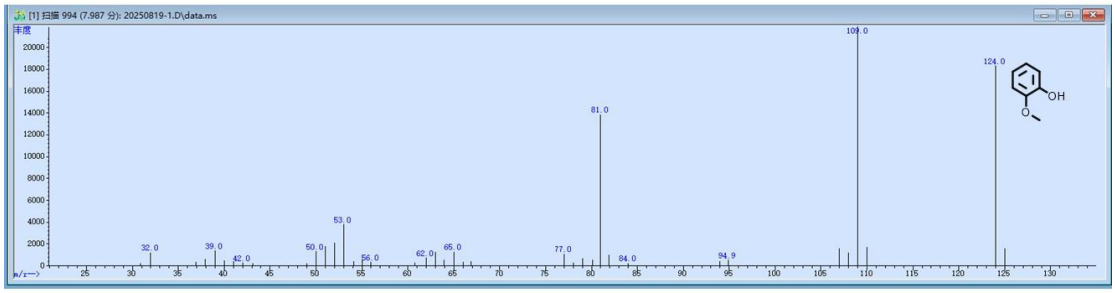

[1] 扫描 1628 (11.750 分): 20250722-2.D\data.ms
丰度
m/z-->

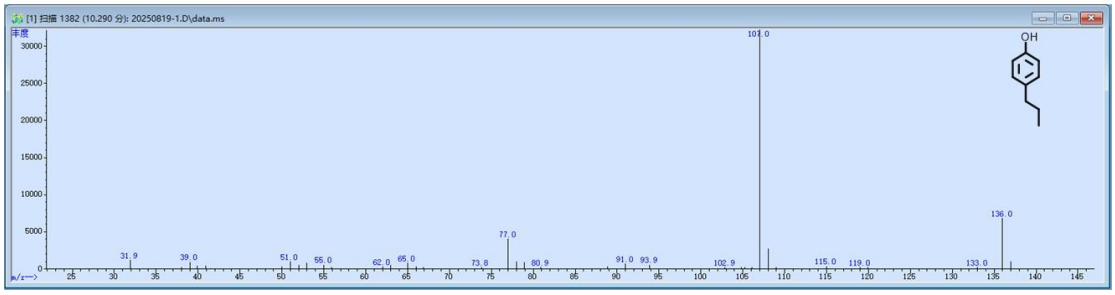

[1] 扫描 1749 (12.468 分): 20250722-2.D\data.ms
丰度
m/z-->

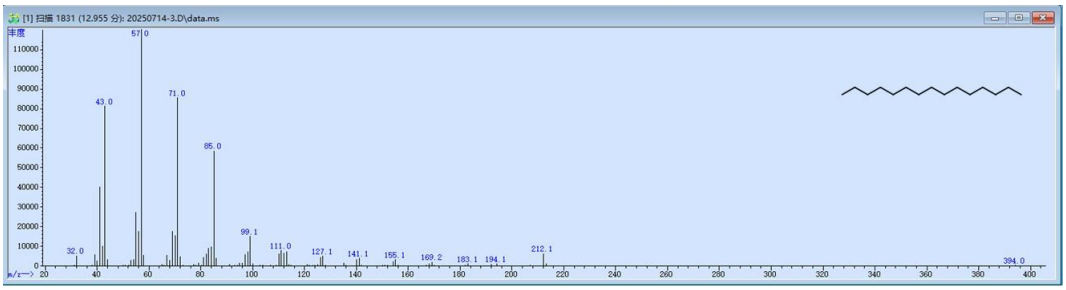

[1] 扫描 2026 (14.112 分): 20250819-1.D\data.ms
丰度
m/z-->

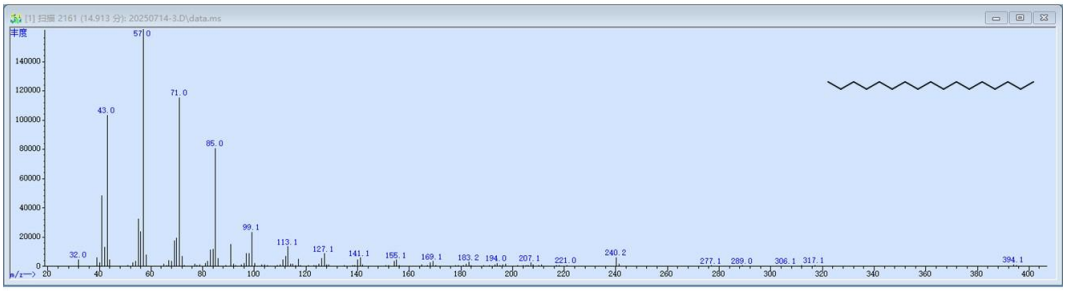

[1] 扫描 911 (7.494 分): 20250817-1.D\data.ms
丰度
m/z-->
81.0
57.0
43.0
110.0
95.1
84.1
67.0
71.0
39.0
31.9
53.0
OH

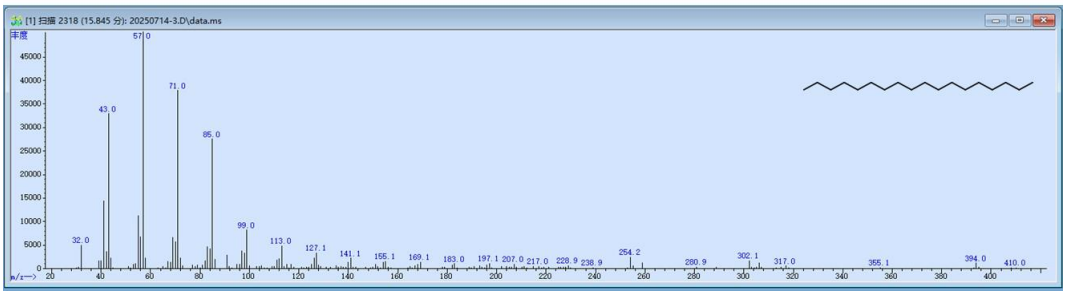

[1] 扫描 721 (6.367 分): 20250819-1.D\data.ms
丰度
m/z-->
94.0
66.0
39.0
32.0
OH


[1] 扫描 994 (7.987 分): 20250819-1.D\data.ms
丰度
m/z-->
109.0
124.0
81.0
53.0
OH
O


[1] 扫描 1382 (10.290 分): 20250819-1.D\data.ms
丰度
m/z-->
107.0
136.0
77.0
OH


[1] 扫描 1831 (12.955 分): 20250714-3.D\data.ms
丰度
m/z-->


[1] 扫描 2161 (14.913 分): 20250714-3.D\data.ms
丰度
m/z-->


[1] 扫描 2318 (15.845 分): 20250714-3.D\data.ms
丰度
m/z-->

References

1. W. Lan, M. T. Amiri, C. M. Hunston and J. S. Luterbacher, Protection Group Effects During α,γ-Diol Lignin Stabilization Promote High-Selectivity Monomer Production, *Angew. Chem. Int. Edit.*, 2018, **57**, 1356-1360.
2. Z. L. Dou, Z. Zhang, H. R. Zhou and M. Wang, Photocatalytic Upgrading of Lignin Oil to Diesel Precursors and Hydrogen, *Angew. Chem. Int. Edit.*, 2021, **60**, 16399-16403.
3. L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Heroguel, Y. D. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph and J. S. Luterbacher, Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization, *Science*, 2016, **354**, 329-333.
4. F. Kong, H. Zhou, Z. Chen, Z. Dou, M. Ji and M. Wang, Stepwise electro-photocatalytic decomposition of biomass to CO and H2 in acidic media, *J Catal*, 2025, **442,** 115928.
5. N. Li, K. Yan, T. Rukkijakan, J. Liang, Y. Liu, Z. Wang, H. Nie, S. Muangmeesri, G. Castiella-Ona, X. Pan, Q. Zhou, G. Jiang, G. Zhou, J. Ralph, J. S. M. Samec and F. Wang, Selective lignin arylation for biomass fractionation and benign bisphenols, *Nature*, 2024, **630**, 381-386.
6. X. Lv, C. Zhao, N. Yan, X. Ma, S. Feng and L. Shuai, Sustainable aviation fuel (SAF) from lignin: Pathways, catalysts, and challenges, *Bioresour. Technol.*, 2025, **419,** 132039.
7. H. Tang, Y. Hu, G. Li, A. Wang, G. Xu, C. Yu, X. Wang, T. Zhang and N. Li, Synthesis of jet fuel range high-density polycycloalkanes with polycarbonate waste, *Green Chem.*, 2019, **21**, 3789-3795.

Author Contributions

N.H. conducted most of the experiments and data analysis of the project; Z.L.D. conducted thermal catalytic data analysis. M.W. and M.J designed the experiments, supervised the research and revised the manuscript. All authors discussed the results.