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Supporting Information

The highly selective conversion of lignin models and organosolv lignin to amines over Ru/C catalyst

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^{1}H NMR of lignin models

Reference

General information

All chemical reagents are obtained from commercial suppliers and used without further purification. 5% Ru/C (wetted with ca. 50% Water), 5% Pd/C (wetted with ca. 50% Water), 5% Pt/C (wetted with ca. 50% Water), and 5% Rh/C (wetted with ca. 50% Water) were purchased from Alfa Aesar. The quantitative analysis of product distribution was conducted by gas chromatography (GC), which was performed on an Agilent 8890 Gas chromatograph with a flame ionization detector equipped with OV-1701 capillary columns (30 m × 320 μm). The XRD results were collected on a Rigaku Ultima IV X-Ray diffractometer operating in Bragg-Brentano focusing geometry and using CuKα radiation from a generator operating at 40 kV and 40 mA. The transmission electron microscopy (TEM) images, high-resolution (HR) TEM images, and STEM-EDX mapping images were collected on an FEI Talos F200S. ^{1}H NMR spectra were taken on Varian Inova 600 with TMS as an internal standard and $CDCl_3$ as solvent. HSQC NMR spectra were measured on a Bruker Avance NEO 600 MHz spectrometer with CD_3OD as solvent.

Extraction of birch lignin

The birch sawdust (40-80 mesh, 30 g) was added into an autoclave reactor and charged with MeOH (200 mL), and the mixture was heated at 180°C under Ar atmosphere for 3 h. The mixture was cooled and filtrated. The filtrate was concentrated in vacuo, and the residue was precipitated by THF/n-hexane (150 mL). The fine lignin was obtained through drying in vacuo at 40^{o}C as a brown solid (2.7 g).

The conversion of realistic ogranosolv birch lignin to amine monomers

Organosolv birch lignin (100 mg), 5% Ru/C (25 mg), and THF (5 mL) were added to an autoclave reactor. The autoclave reactor was flushed with H_2 5 times, and 0.8 MPa

and 4.2 MPa H_2 were charged into the autoclave reactor. The reaction was conducted at 220°C for 72 hours. Then the reactor was cooled to room temperature. The mixture was filtered using a filter membrane and the solution was analyzed by GC-MS. The solvent was removed in vacuo. Residues were dissolved in CD_3OD and filtered using a filter membrane. The filtrate was analyzed by 2D ^{13}C-^{1}H HSQC NMR.

Catalyst Evaluation

The catalytic reaction was carried out in an autoclave reactor, and 2.5 mmol lignin model compounds, catalyst, and 5 mL n-hexane were charged into the reactor. After the reactor was flushed with H_2 5 times, the autoclave reactor was charged with 0.8 MPa ammonia and 2.2 MPa H_2, and the reaction was conducted at 200°C for 2 hours with a stirring speed of 600 rpm. After the reaction, the reactor was cooled to room temperature with ice water, and the reaction solution was diluted with CH_2Cl_2 and analyzed by gas chromatography (GC) analysis on an Agilent 8890 Gas chromatograph with flame ionization detector equipped with OV-1701 capillary columns (30 m × 320 μm). n-Hexadecane was used as an internal standard to calibrate the organic product concentrations and carbon balances. The carbon balances for all of the reported experiments were better than 90%.

For the kinetic data, the results were collected at time durations.

Calculation of conversion, yield, and selectivity:

$$Conv.(\%) = \frac{(n_{lignin\ model})_0 - (n_{lignin\ model})_{end}}{(n_{lignin\ model})_0} * 100\%$$

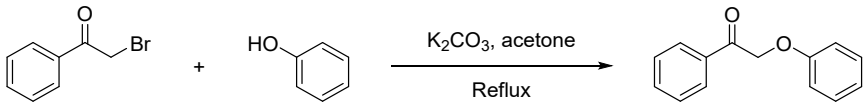
$$Sel.(xi)(\%) = \frac{n_{xi}}{n_{x1} + n_{x2} + n_{x3} + \ldots + n_{xn}} * 100\%$$

$$Yield(xi)(\%) = \frac{n_{xi}}{(n_{lignin\ model})_0} * 100\%$$

Synthesis of β-O-4 linkage model compounds.

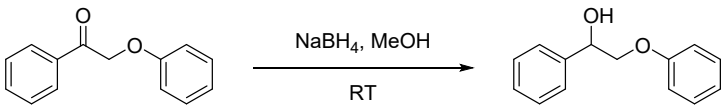
All substrates have been prepared according to literature procedures with minor modifications.[1]

Synthesis of 2-phenoxy-1-phenylethan-1-one



A 1 L three-necked round-bottomed flask equipped with a reflux condenser and a dropping funnel was charged with phenol (5.2 g, 55 mmol) and K_2CO_3 (10.4 g, 76 mmol) in acetone (250 mL) and stirred at RT. To this suspension, 2-bromoacetophenone (10.0 g, 50 mmol) in acetone (50 mL) was added dropwise over 45 min at RT. The resulting suspension was stirred at reflux for 4 h, then the suspension was filtered out and the filtrate was concentrated in vacuo. The crude product was purified by recrystallization from petroleum ether to give 2-phenoxy-1-phenylethanone as a white solid (7.47 g, 4.9 mmol) in 71% yield. 1H NMR (600 MHz, CDCl3) δ 8.01-7.98 (m, 2H), 7.62-7.58 (m, 1H), 7.50-7.47 (m, 2H), 7.29-7.26 (m, 2H), 6.99-6.96 (m, 1H), 6.96-6.93 (m, 2H), 5.26 (s, 2H).

Synthesis of 2-phenoxy-1-phenylethan-1-ol



A 500 mL round bottom flask was charged with 2-phenoxy-1-phenylethanone (4.25 g, 20.0 mmol) and methanol (100 mL). Sodium borohydride (0.83 g, 22.0 mmol) was added to the solution in small portions at 0°C, the suspension was stirred at 0°C until the reaction is finished. After the reaction is completed, 100 mL of saturated aqueous NH_4Cl was charged into the reaction flask, followed by the addition of ethyl acetate (250 mL). After separation, the organic phase was washed with H_2O (100 mL X 2) and saturated with aqueous NaCl (100 mL), and dried over anhydrous Na_2SO_4, filtered and the organic phase was evaporated in vacuum. The crude product was purified by recrystallization from hexane to give 3.91 g white crystalline in 90% yield. ^1H

NMR (600 MHz, CD_3OD) δ 7.46-7.44 (m, 2H), 7.37-7.34 (m, 2H), 7.30-7.27 (m, 1H), 7.25-7.22 (m, 2H), 6.91-6.89 (m, 3H), 5.02 (t, J = 6.0 Hz, 1H), 4.04 (d, J = 6.0 Hz, 2H).

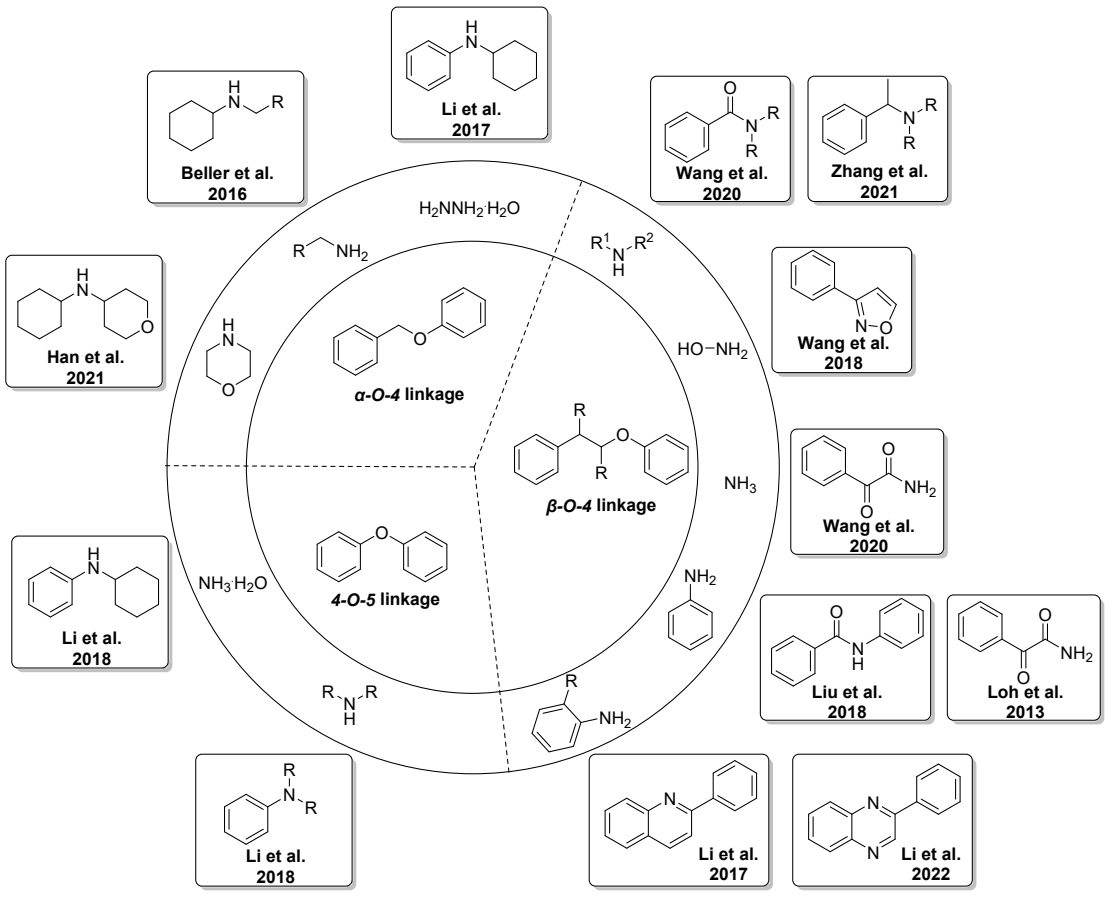


Figure S1. Representative examples of the transformation from lignin models to amines and amides.

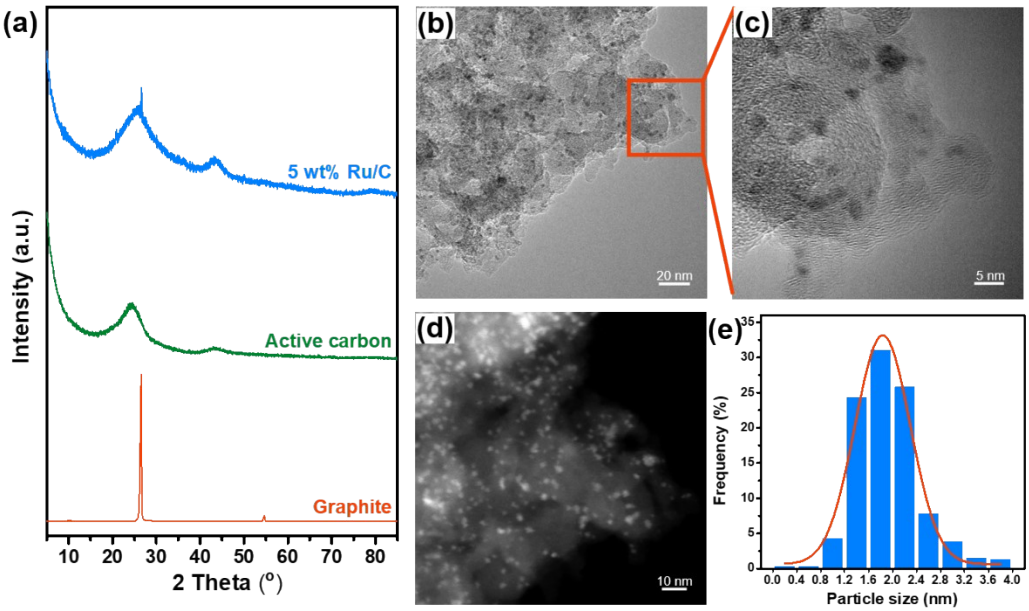


Figure S2. Characterizations of 5 wt% Ru/C. (a) X-Ray Diffraction image; (b and c) High-resolution transmission electron microscopy images of 5 wt% Ru/C; (d) High-angle annular dark-field scanning transmission electron microscopy image of 5 wt% Ru/C; (e) Ru particle diameter distribution of Ru/C.

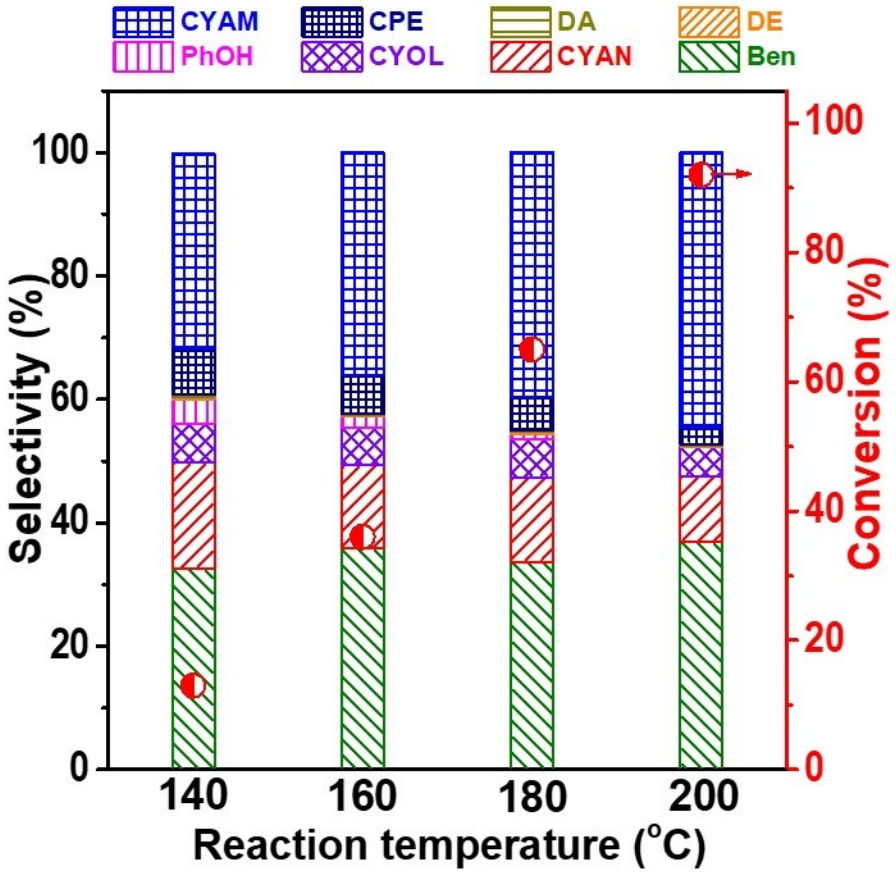


Figure S3. The optimization of reaction temperature.

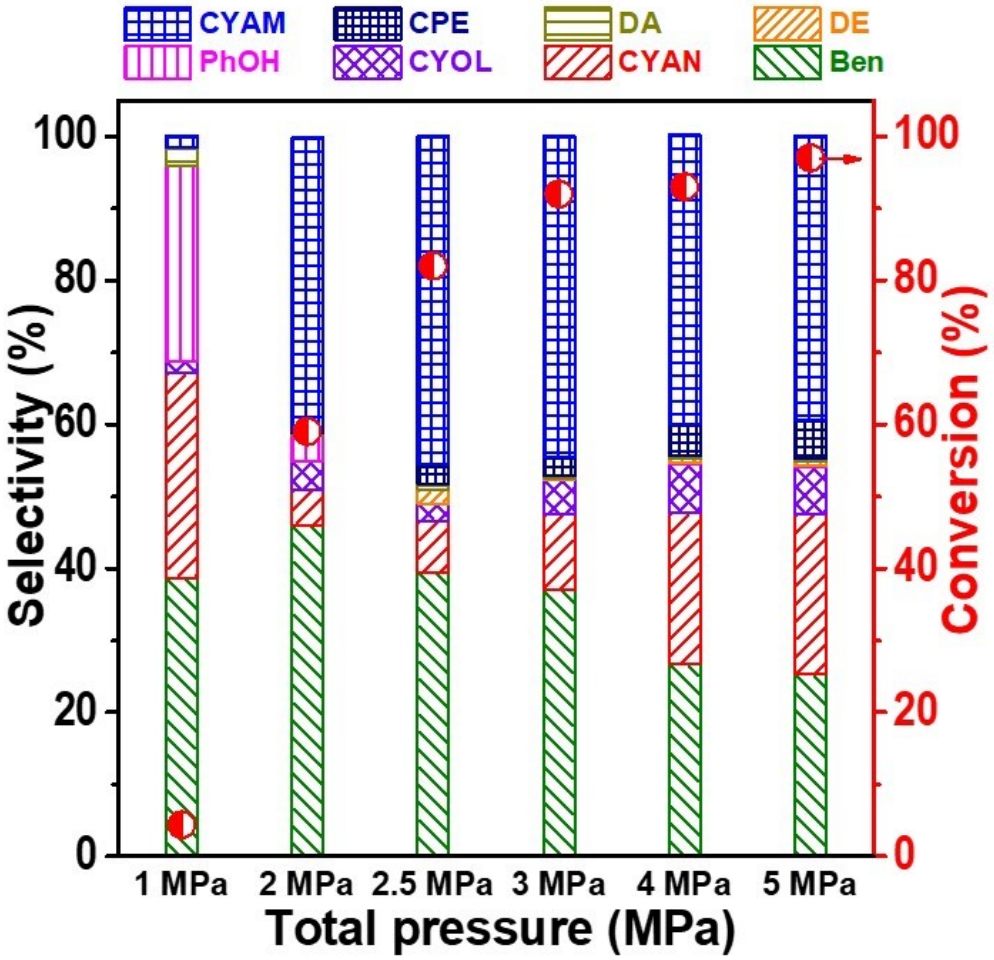
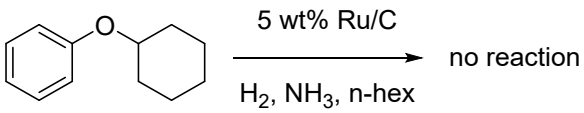


Figure S4. The optimization of total pressure. The H_2-NH_3 mixture always contains 0.8 MPa NH_3.



Scheme S1. The control reaction for the conversion of CPE to amine.

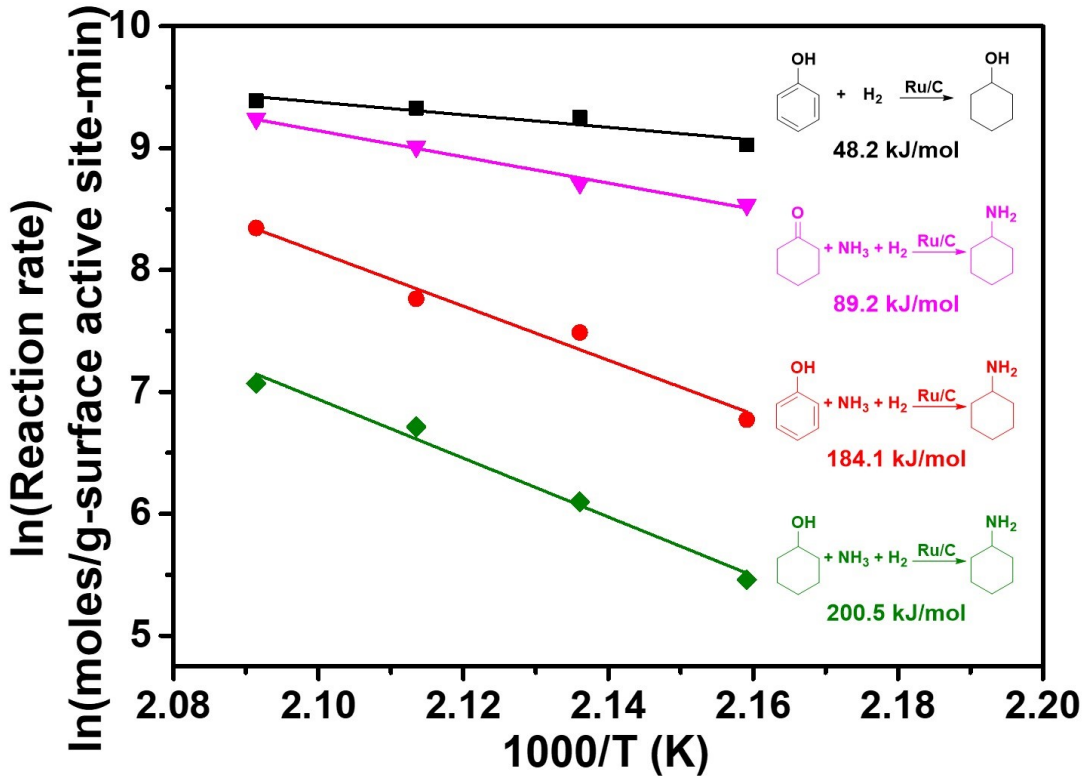


Figure S5. Arrhenius plots for the transformation of the oxygen-contained intermediates during the DPE transformation catalyzed by 5 wt% Ru/C at the temperature range of 463-478 K.

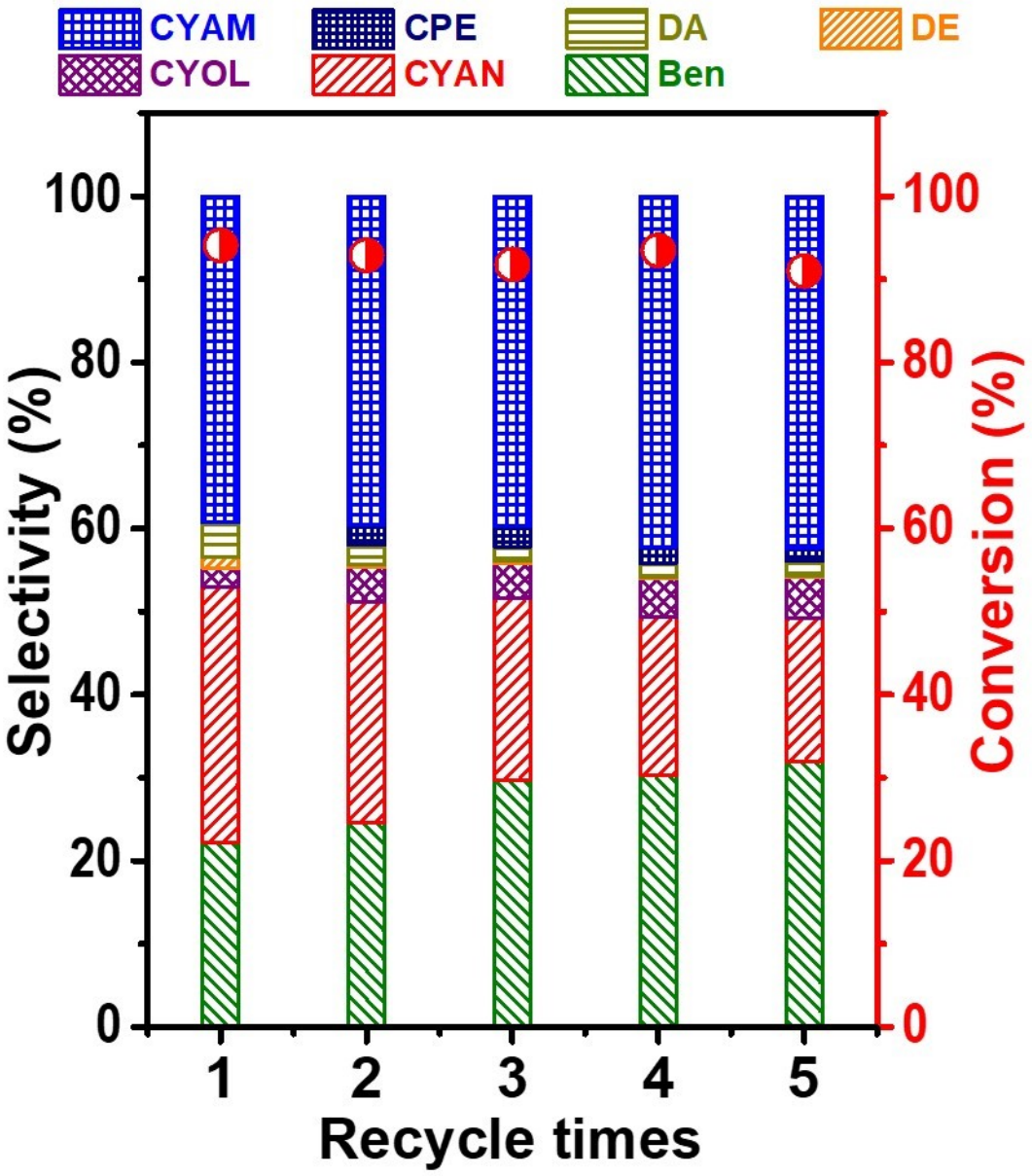


Figure S6. The recycle stability of Ru/C for the conversion of DPE to amines.

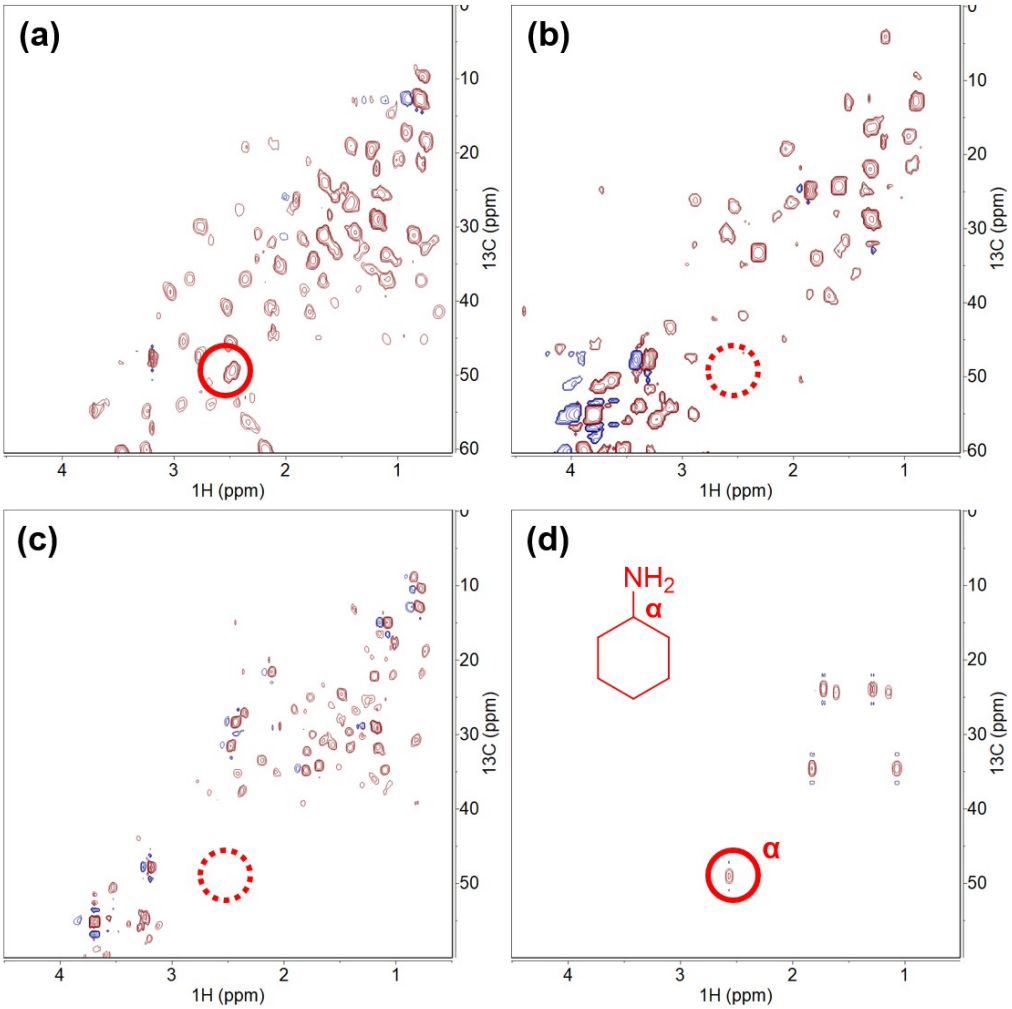


Figure S7 2D ^{13}C-^{1}H HSQC spectra of (a) organosolv birch lignin after depolymerization with Ru/C-H_2-NH_3 for 72 h, (b) organosolv birch lignin before reaction, (c) organosolv birch lignin after depolymerization with Ru/C-H_2 for 72 h, and (d) cyclohexylamine. All spectra were obtained in CD_3OD.

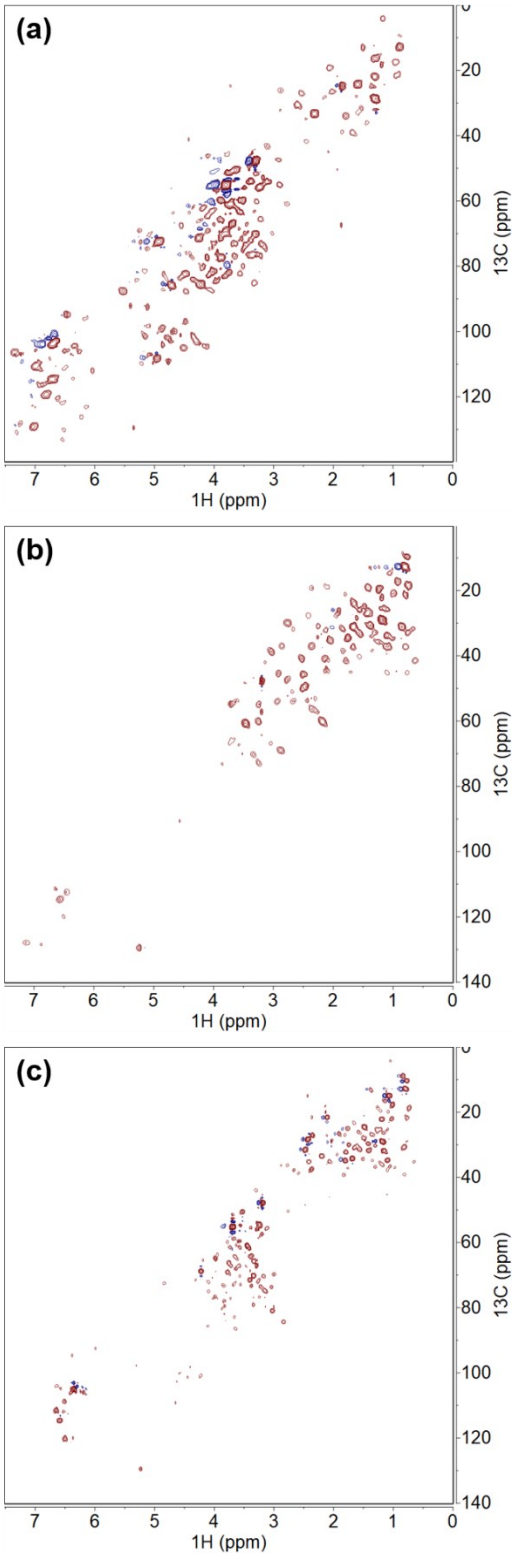


Figure S8 2D ^{13}C-^{1}H HSQC spectra of (a) organosolv birch lignin before reaction, (b) organosolv birch lignin after depolymerization with Ru/C-H_2-NH_3 for 72 h, and (c) organosolv birch lignin after depolymerization with Ru/C-H_2 for 72 h. All spectra were obtained in CD_3OD.

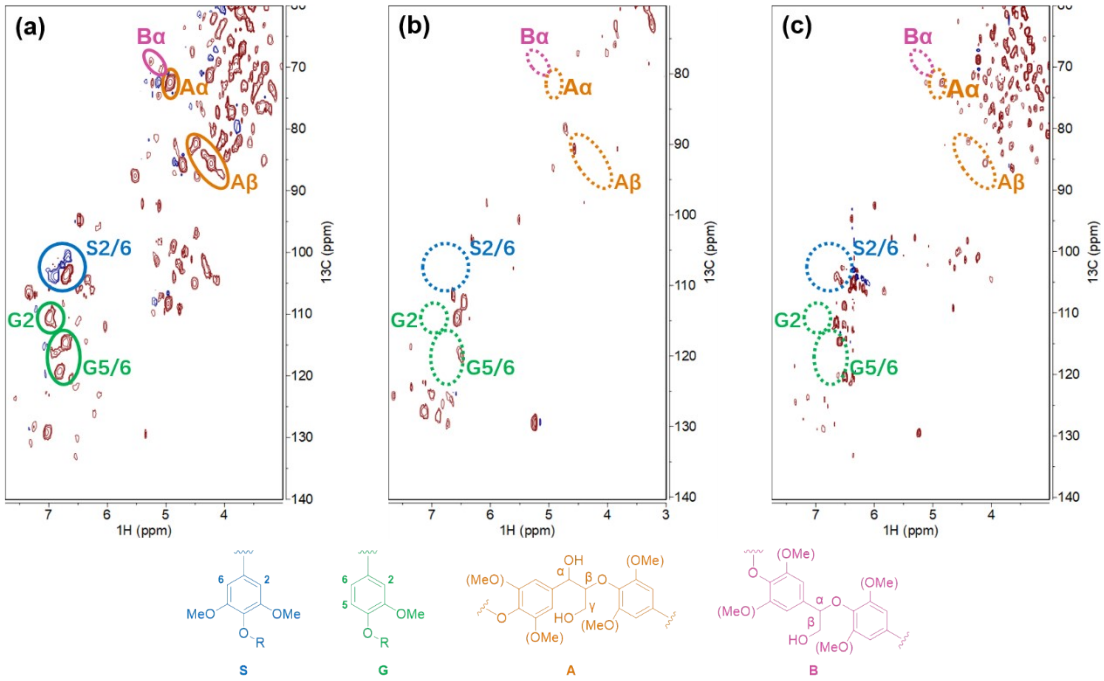


Figure S9 2D ^{13}C-^{1}H HSQC spectra of (a) organosolv birch lignin before reaction, (b) organosolv birch lignin after depolymerization with Ru/C-H_2-NH_3 for 72 h, and (c) organosolv birch lignin after depolymerization with Ru/C-H_2 for 72 h. All spectra were obtained in CD_3OD.

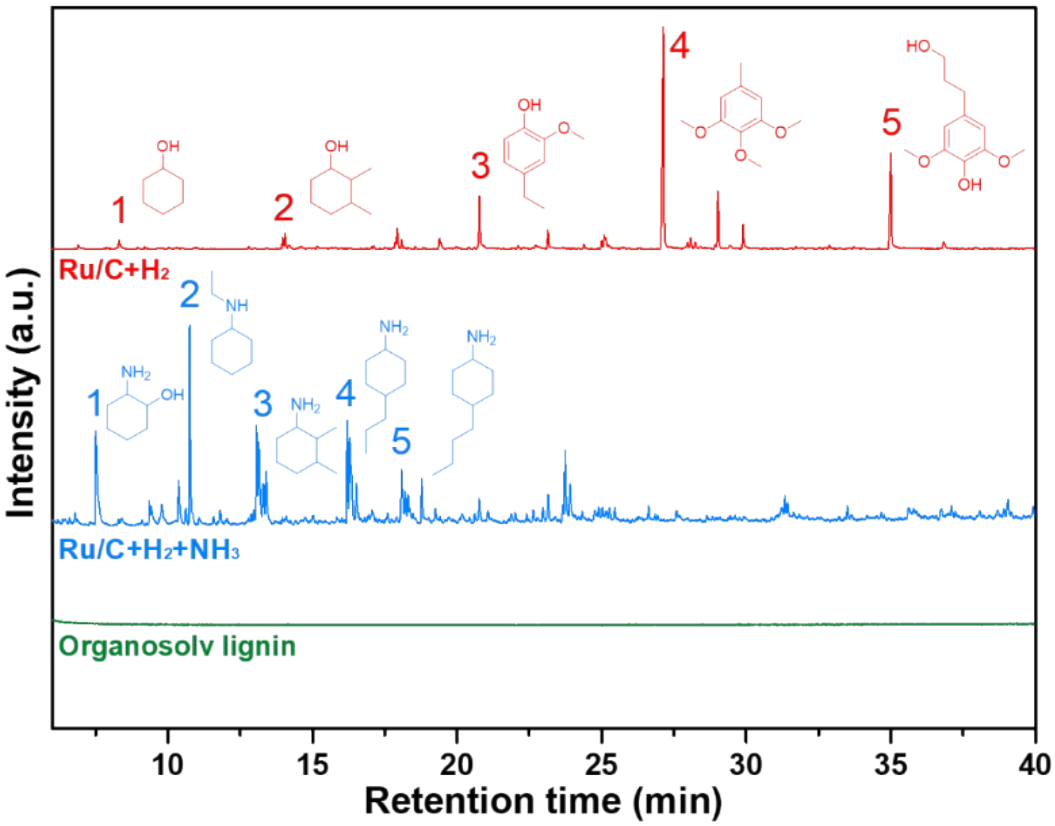


Figure S10. GC-MS analysis of organosolv lignin depolymerization mixture with Ru/C-H_2 system and Ru/C-H_2-NH_3 system and organosolv lignin.

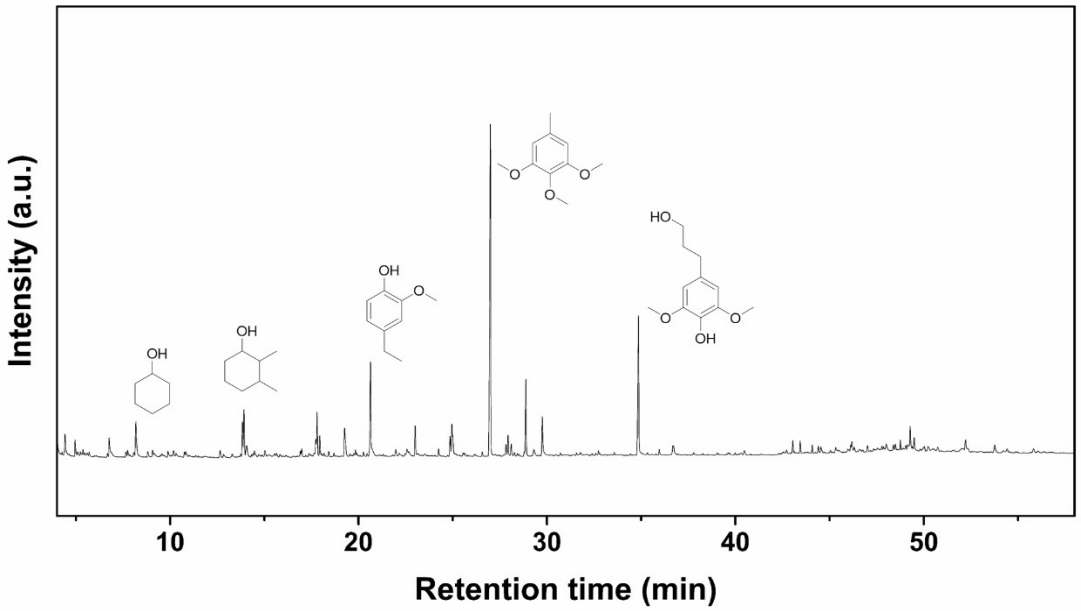


Figure S11. GC spectra of the depolymerization mixture of organosolv birch lignin with Ru/C-H_2 system.

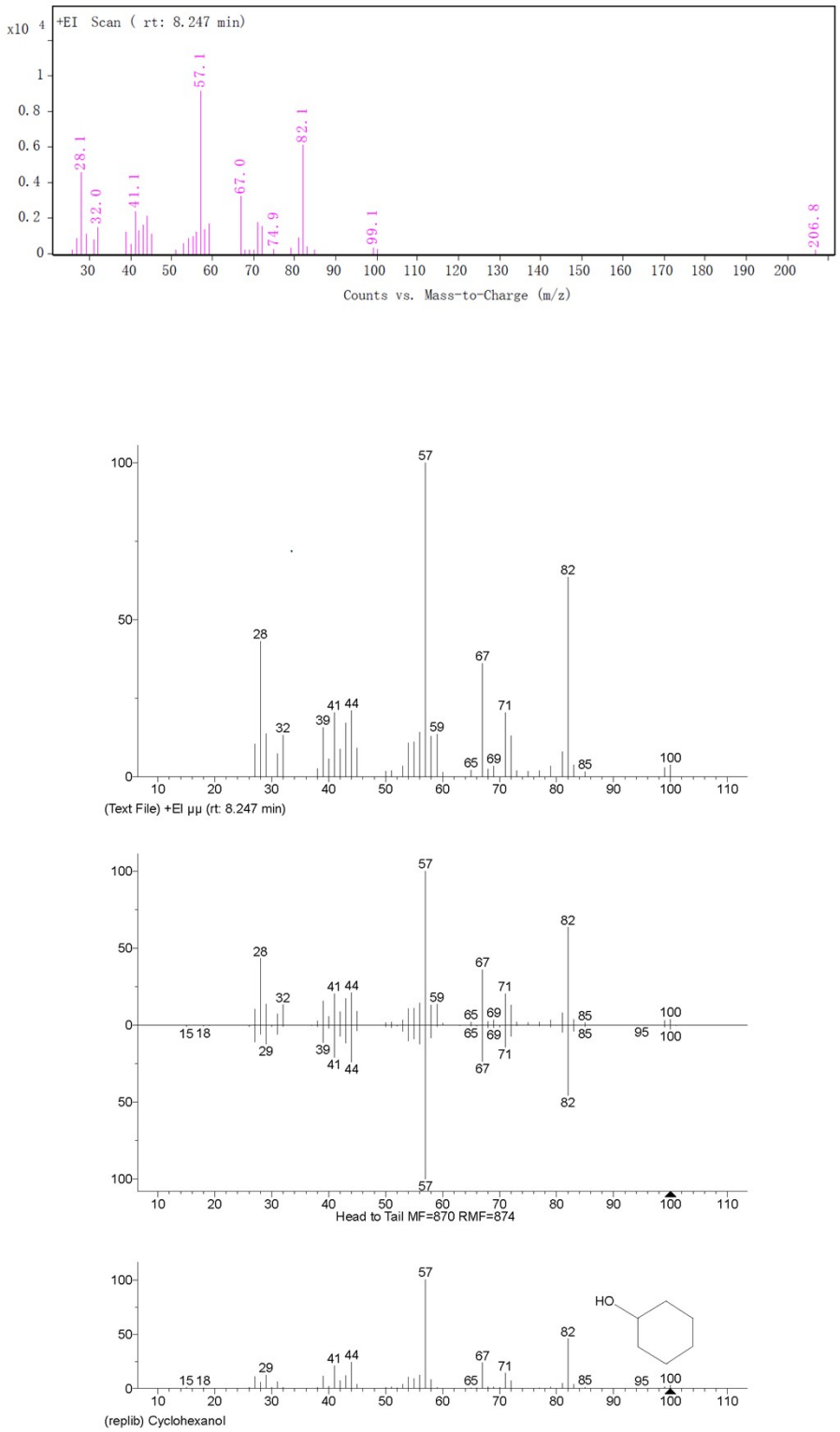


Figure S12. Fragment information of ion at the retention time of 8.25 min of organosolv lignin depolymerization with Ru/C-H_2 system.

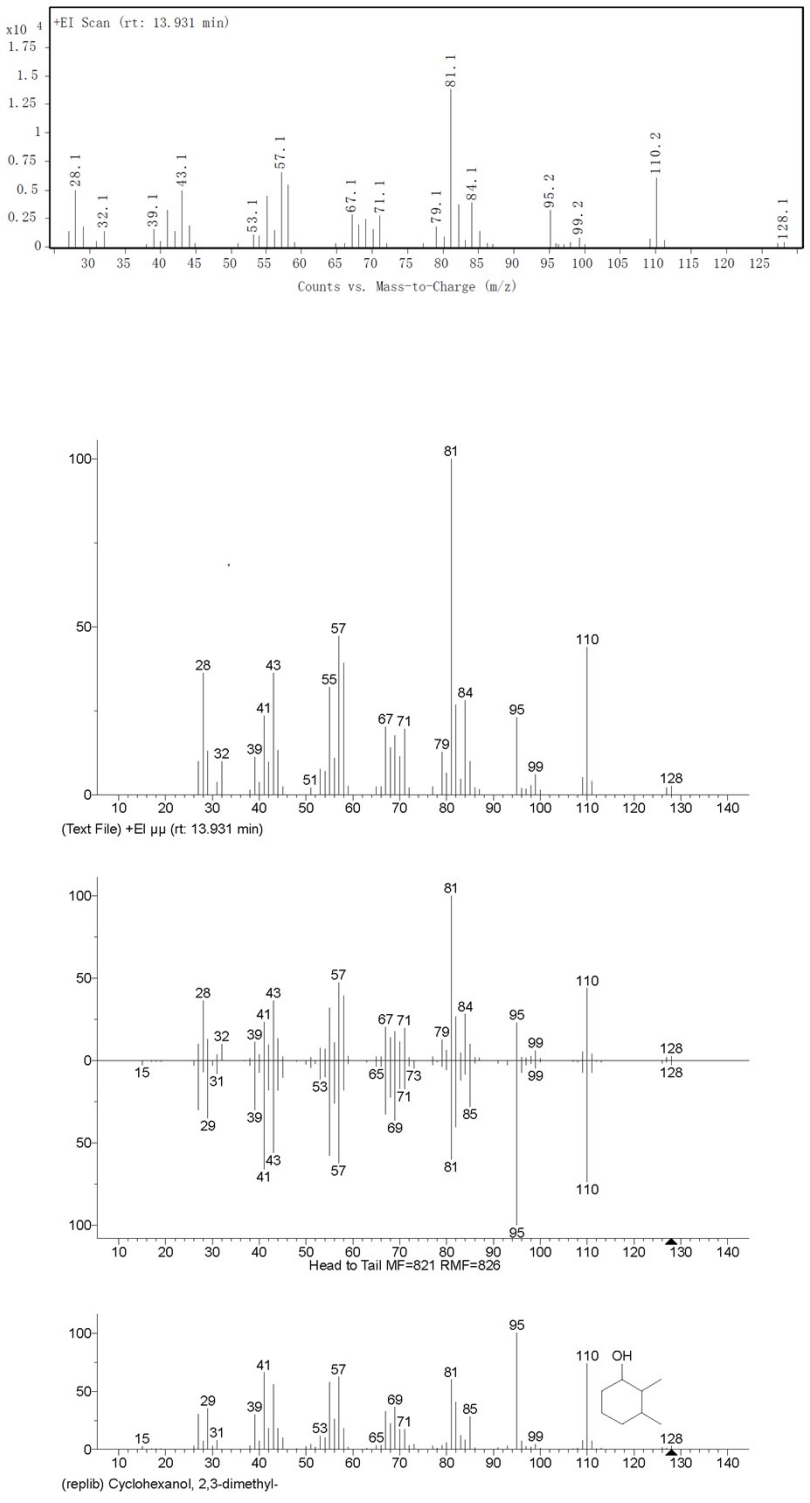


Figure S13. Fragment information of ion at the retention time of 13.93 min of organosolv lignin depolymerization with Ru/C-H_2 system.

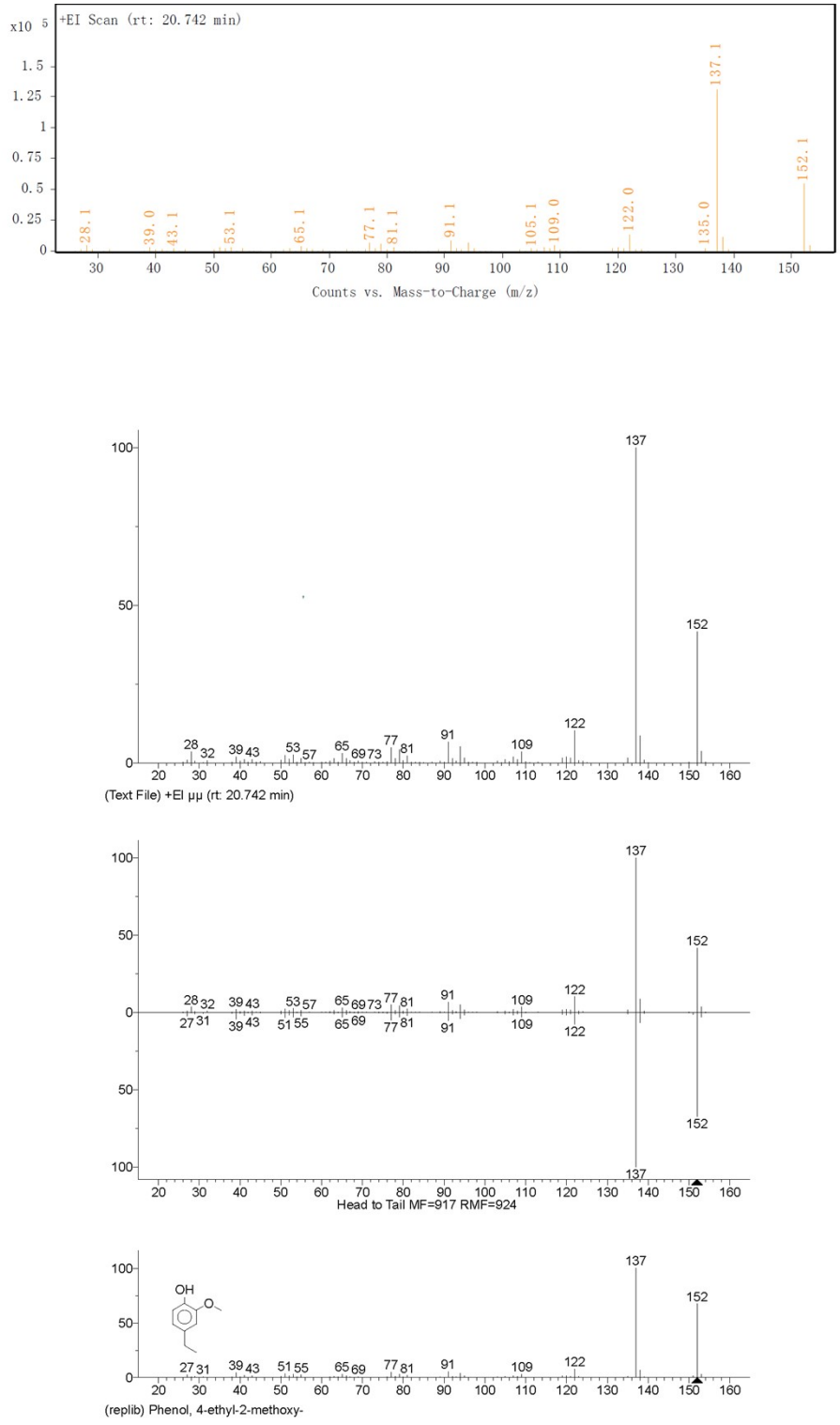


Figure S14. Fragment information of ion at the retention time of 20.74 min of organosolv lignin depolymerization with Ru/C-H_2 system.

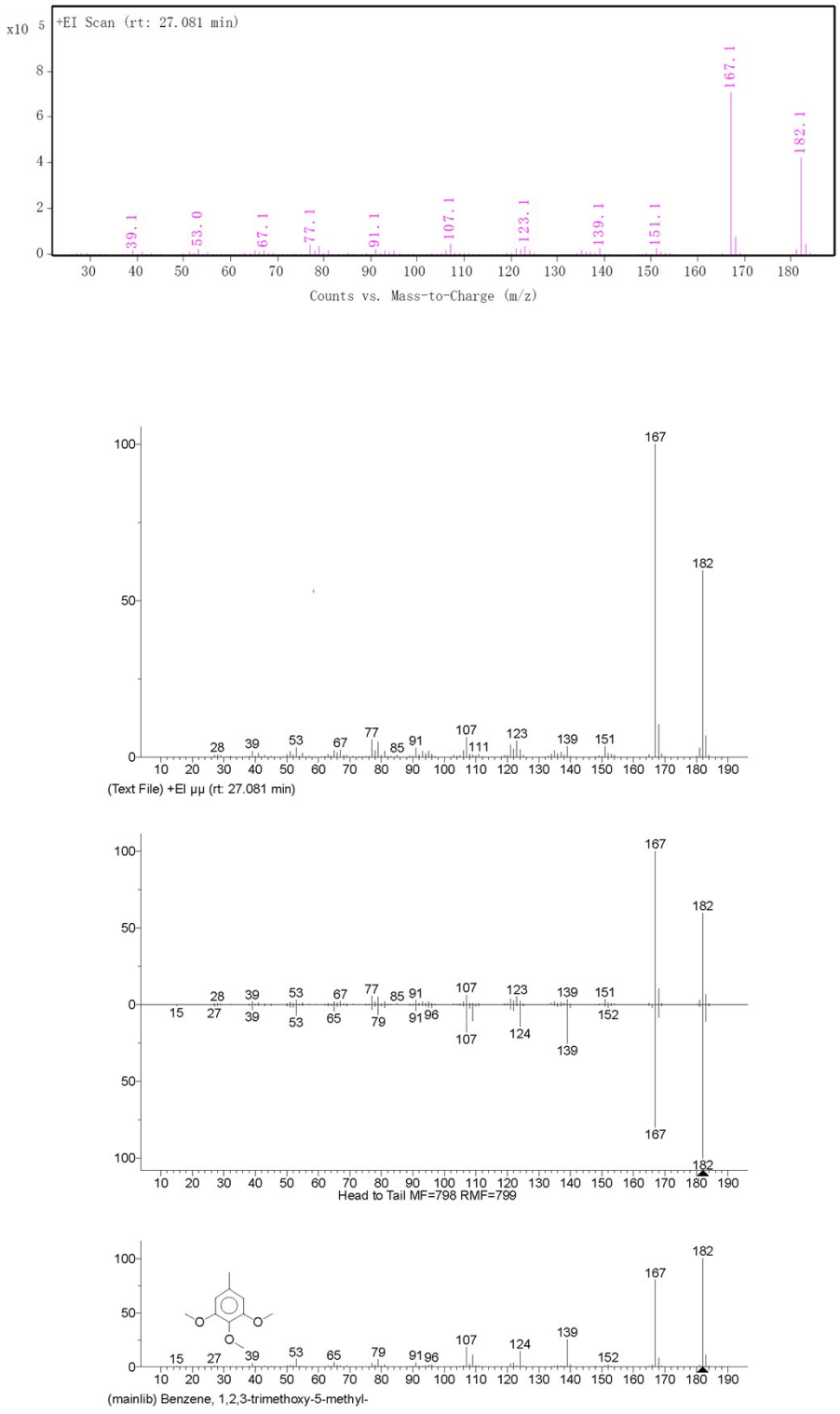


Figure S15. Fragment information of ion at the retention time of 27.08 min of organosolv lignin depolymerization with Ru/C-H_2 system.

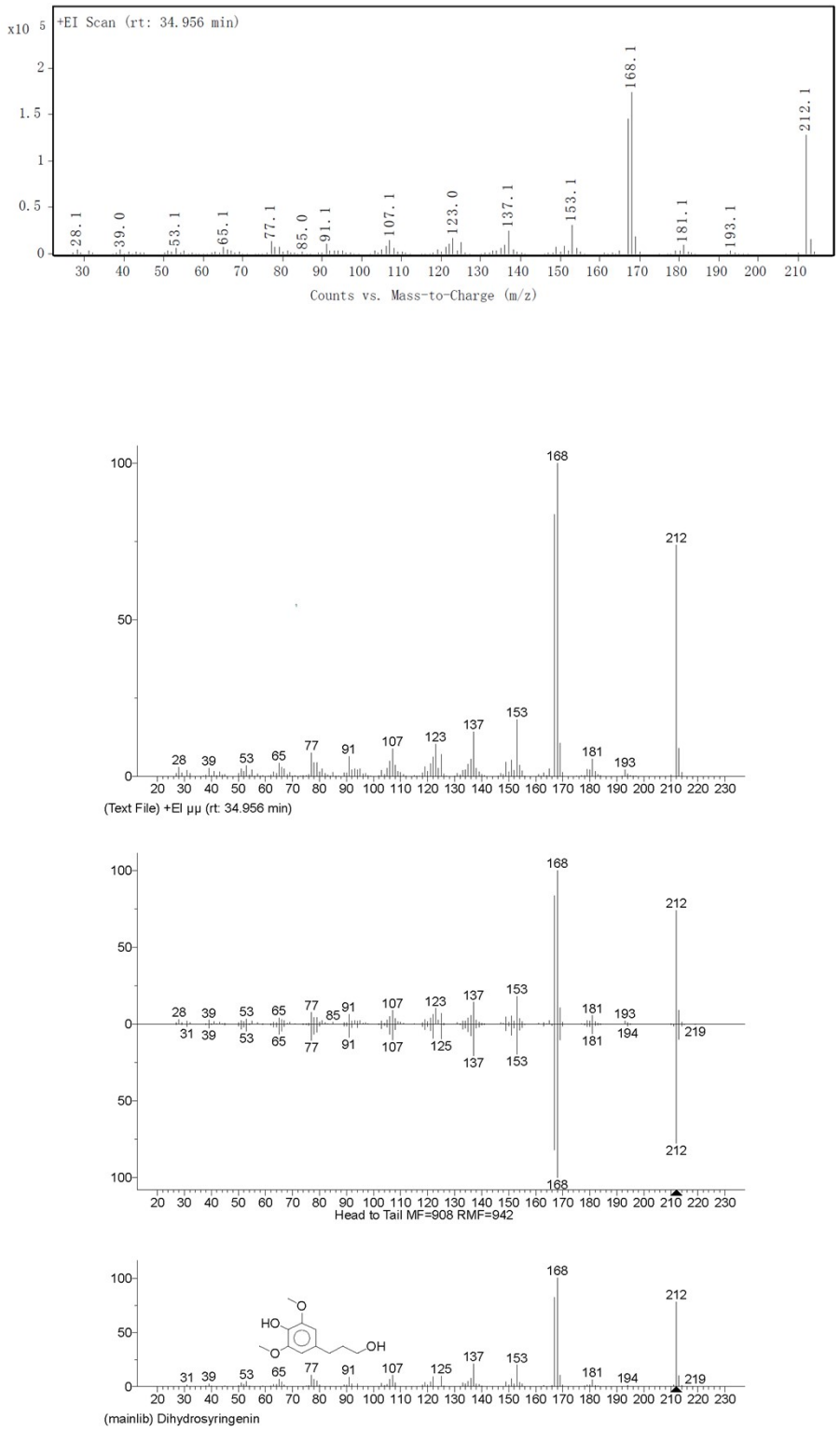


Figure S16. Fragment information of ion at the retention time of 34.96 min of organosolv lignin depolymerization with Ru/C-H_2 system.

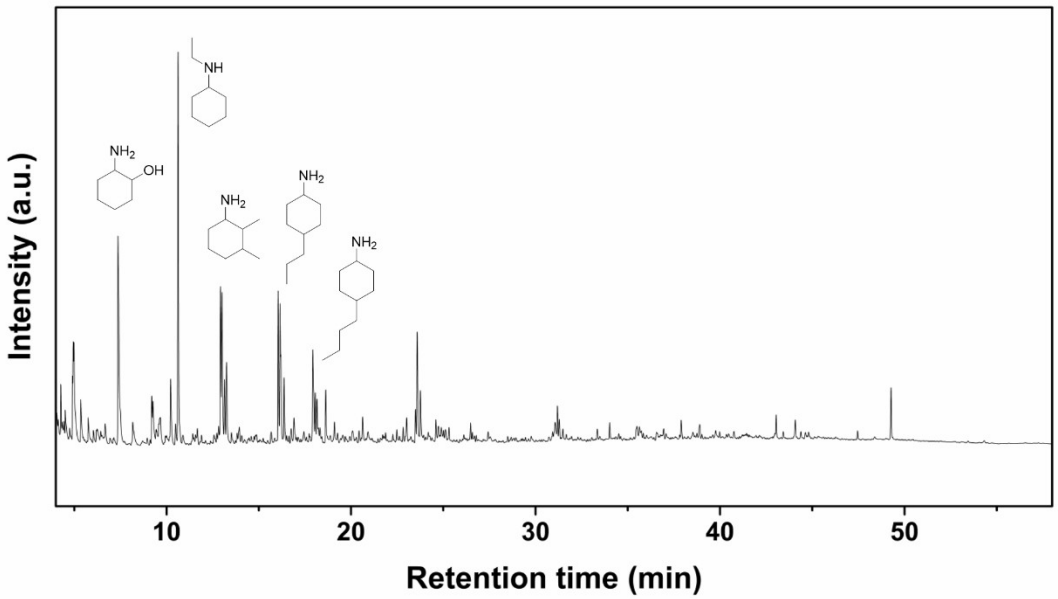


Figure S17. GC spectra of the depolymerization mixture of organosolv birch lignin with Ru/C-H_2-NH_3 system.

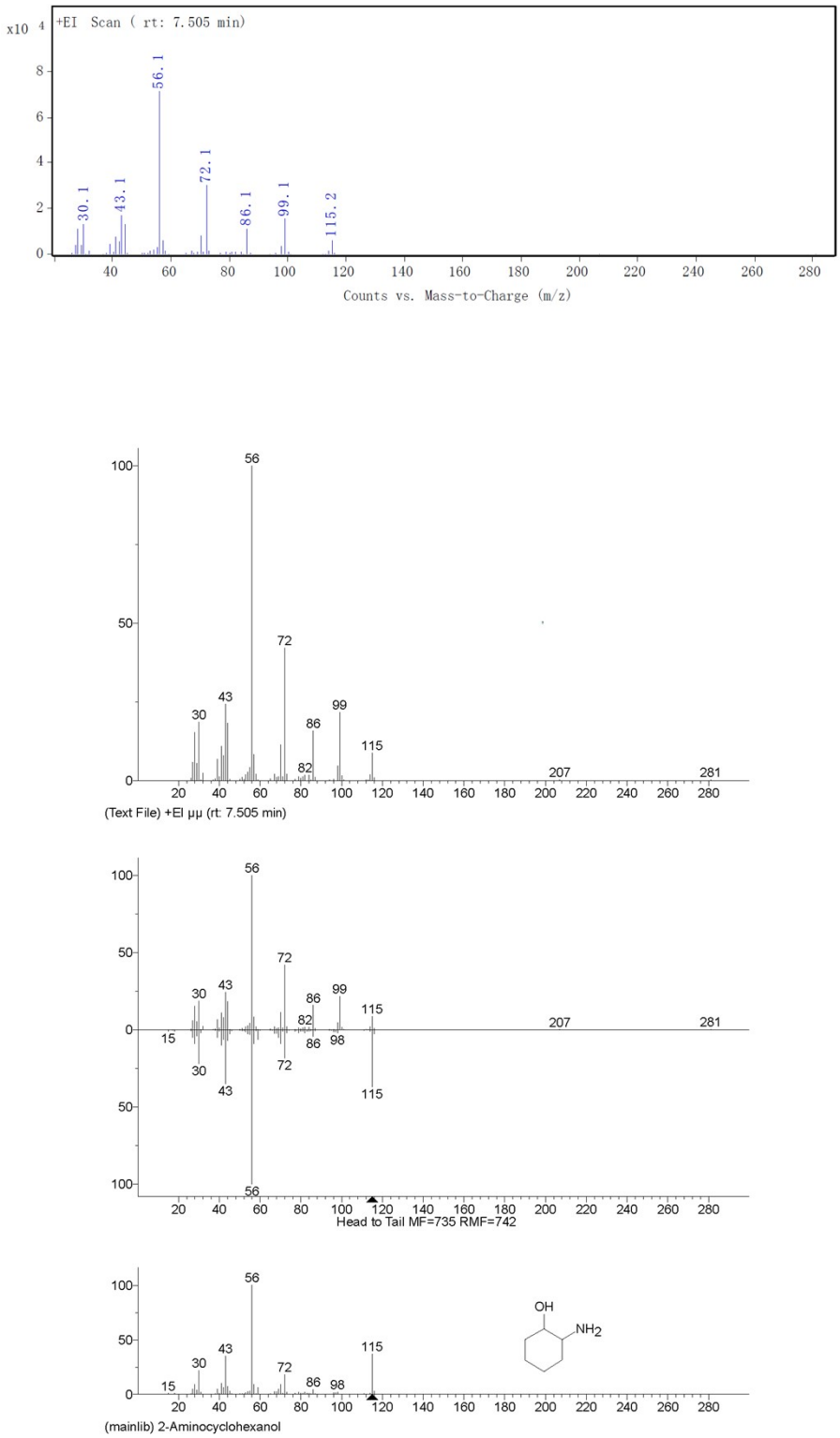


Figure S18. Fragment information of ion at the retention time of 7.51 min of organosolv lignin depolymerization with Ru/C-H_2-NH_3 system.

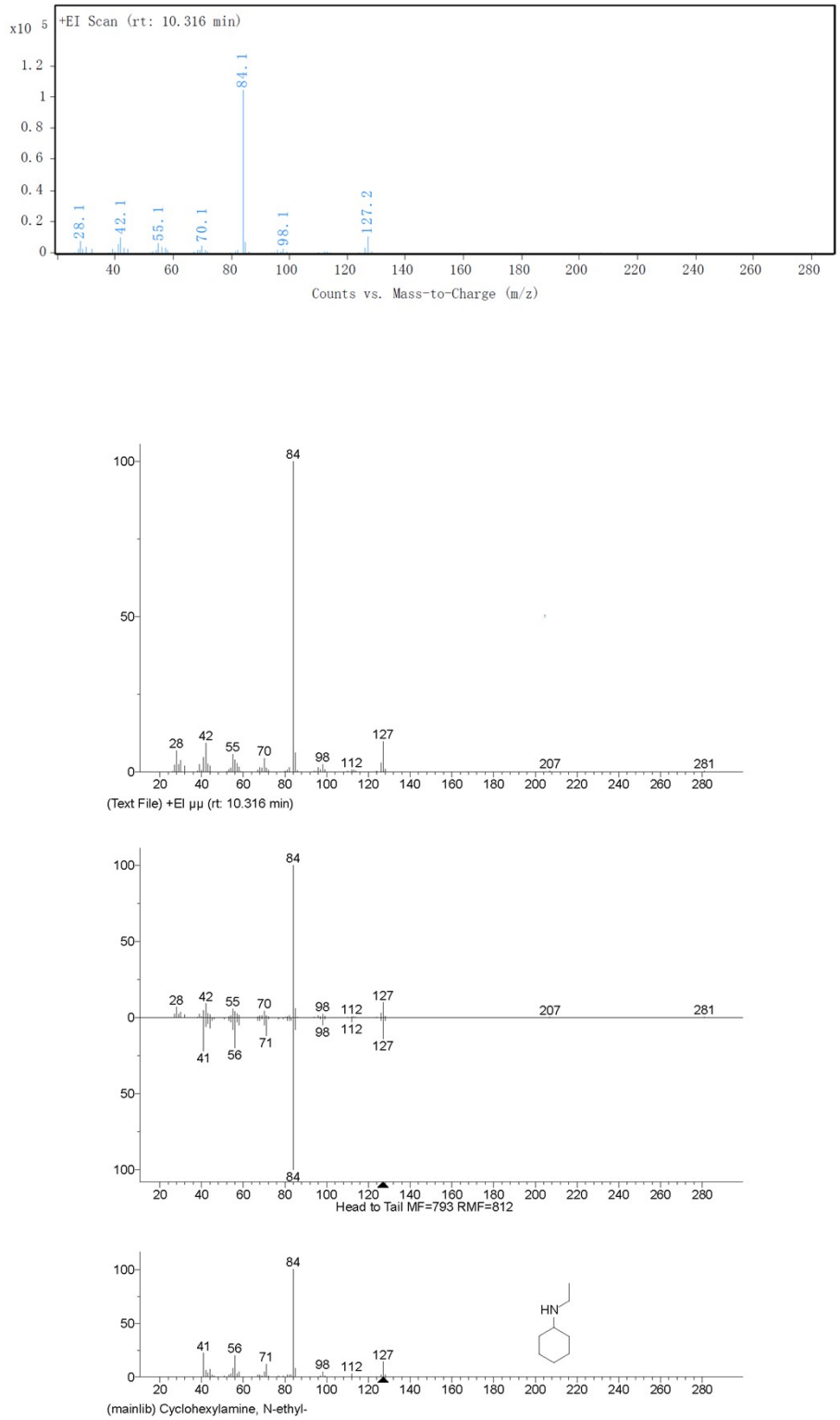


Figure S19. Fragment information of ion at the retention time of 10.32 min of organosolv lignin depolymerization with Ru/C-H_2-NH_3 system.

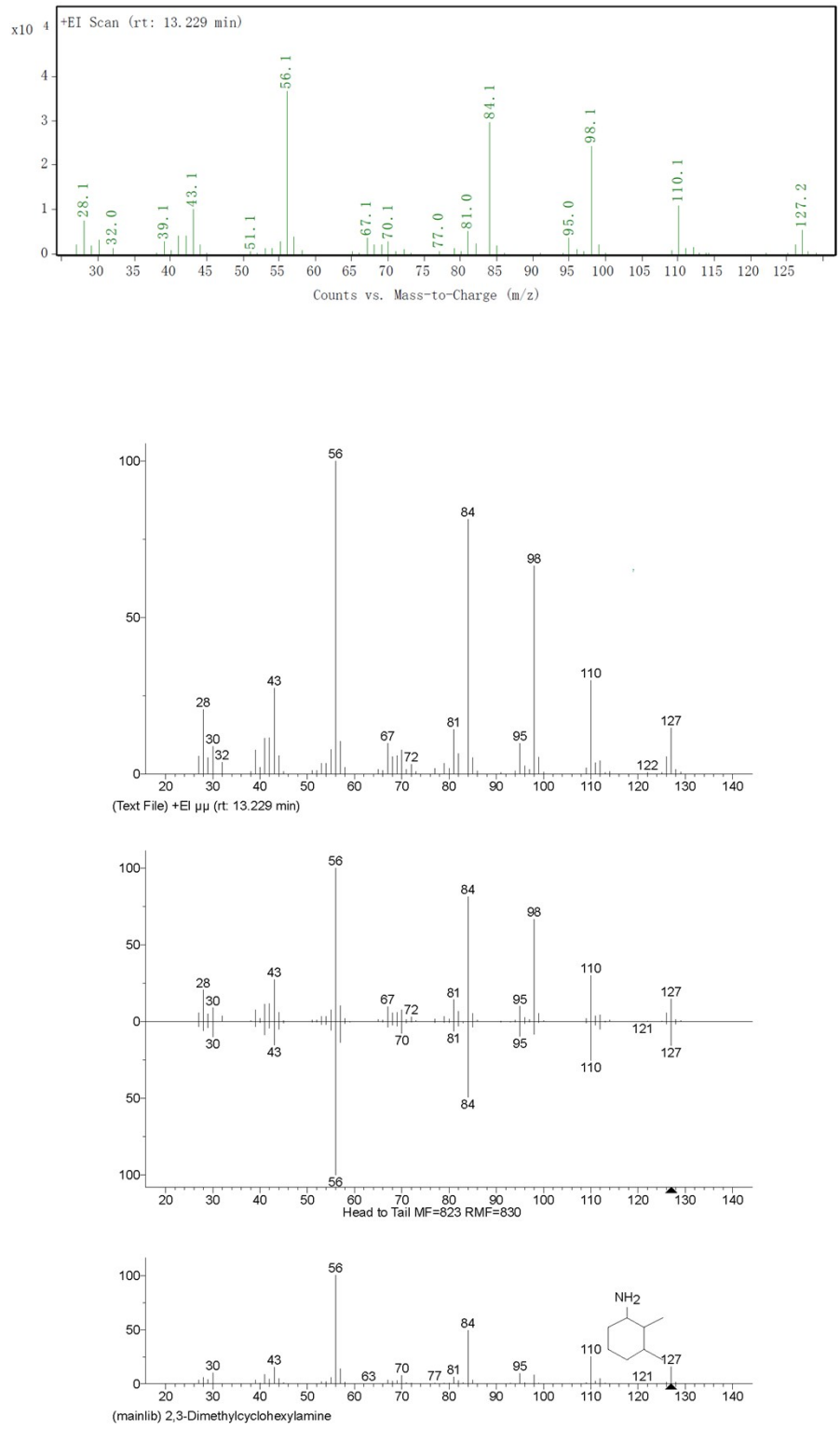


Figure S20. Fragment information of ion at the retention time of 13.23 min of organosolv lignin depolymerization with Ru/C-H_2-NH_3 system.

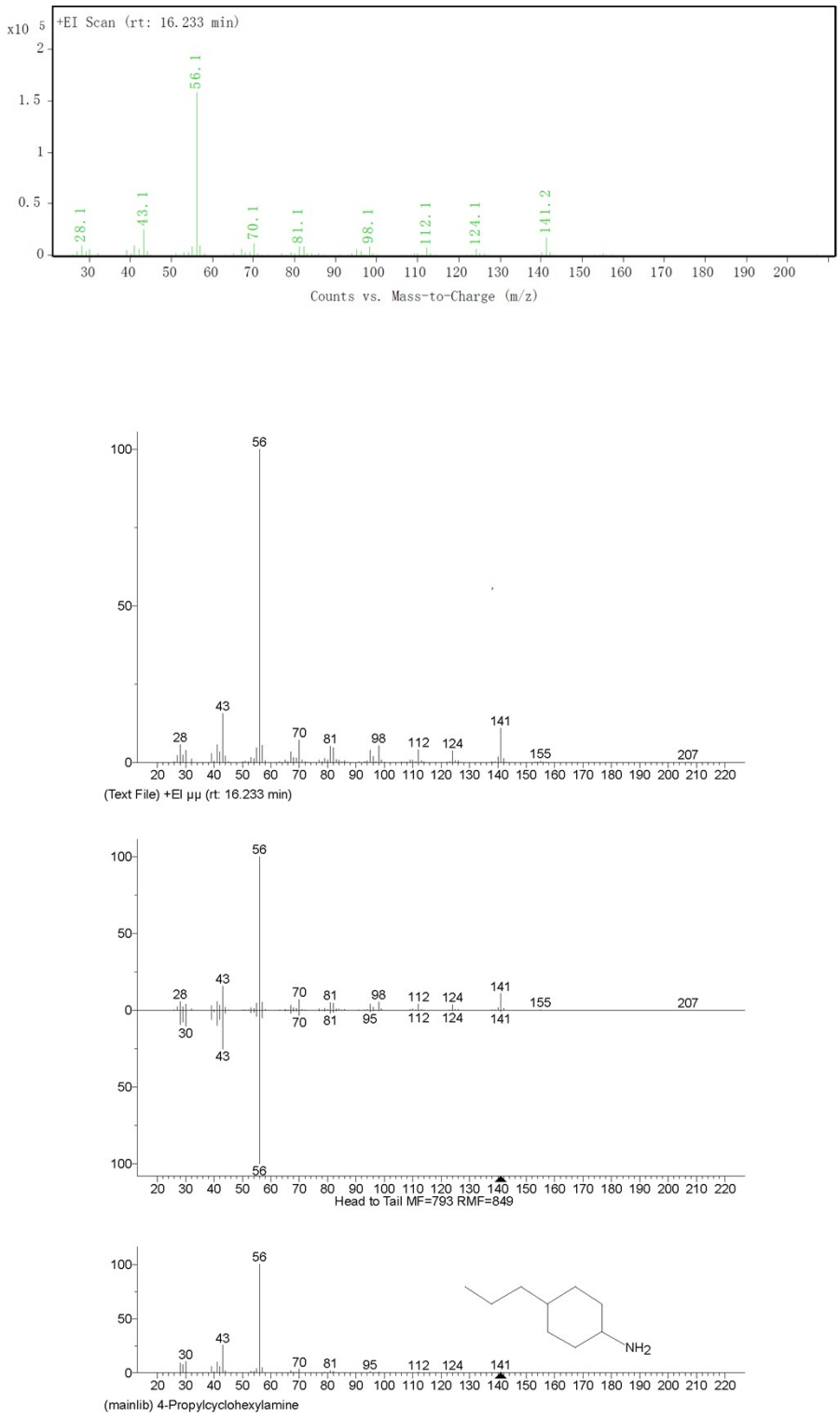


Figure S21. Fragment information of ion at the retention time of 16.23 min of organosolv lignin depolymerization with Ru/C-H_2-NH_3 system.

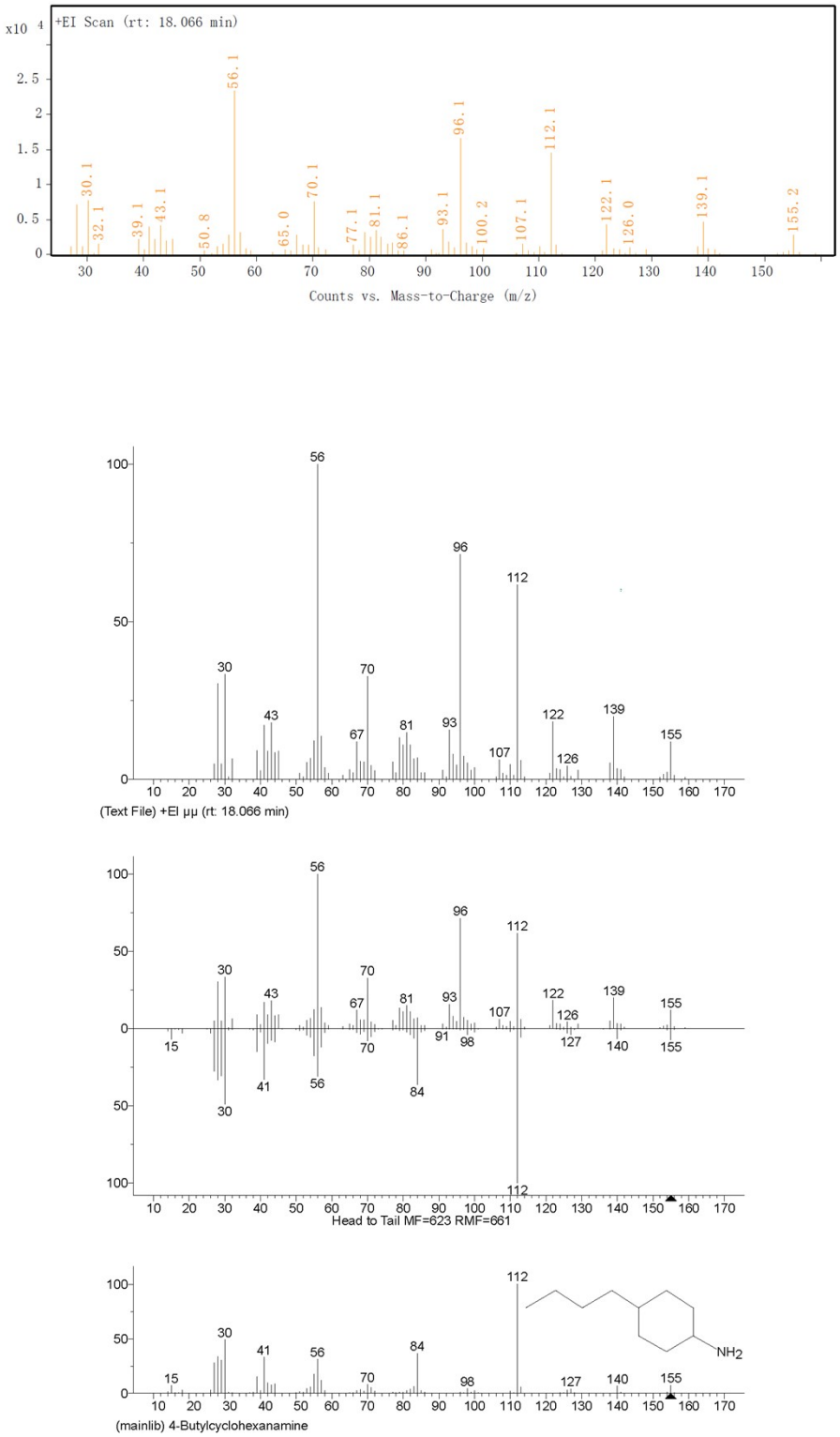
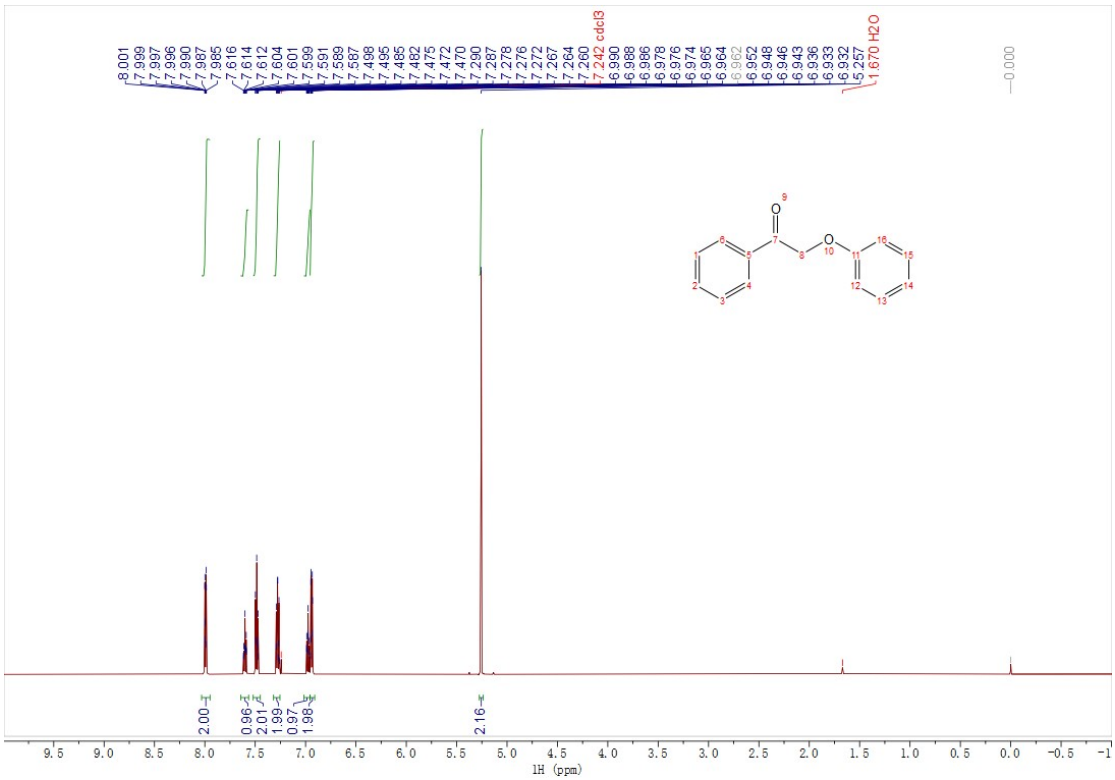


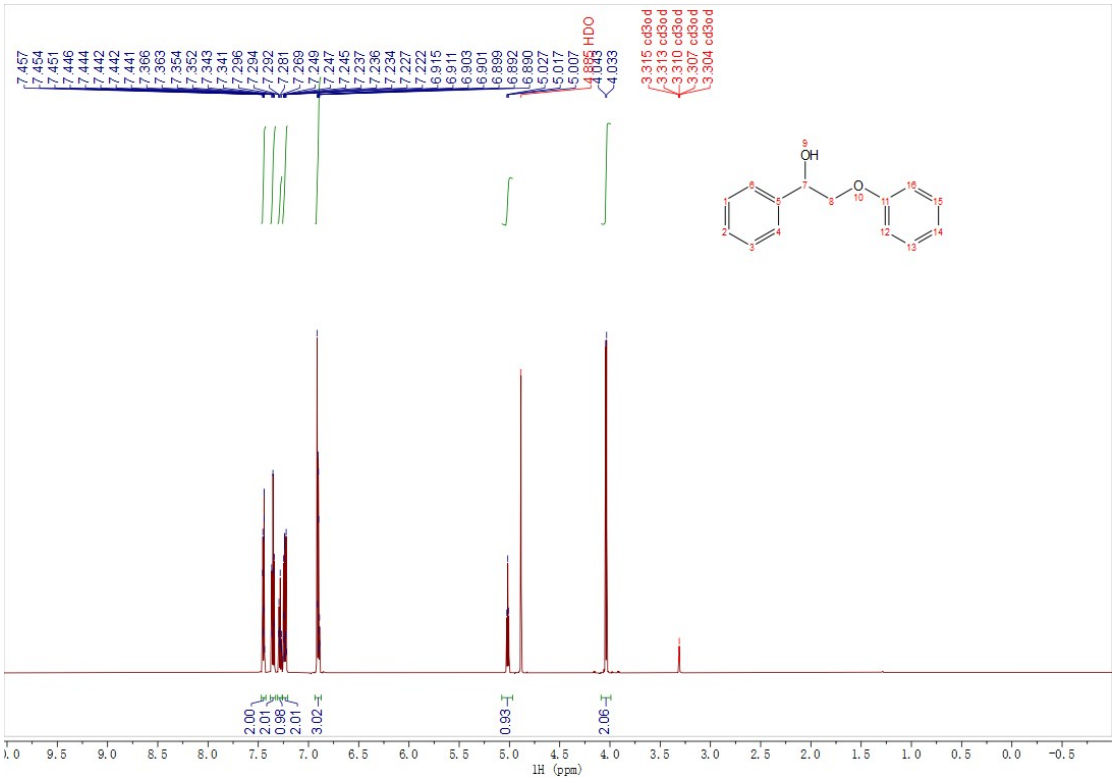
Figure S22. Fragment information of ion at the retention time of 18.07 min of organosolv lignin depolymerization with Ru/C-H_2-NH_3 system.

6. ^{1}H NMR of lignin models

2-phenoxy-1-phenylethan-1-one



2-phenoxy-1-phenylethan-1-ol



Reference

1. J.-w. Zhang, G.-p. Lu, C. Cai, *Green Chemistry* **2017**, *19*, 4538-4543.