Supporting Information
For

Organic Amine Mediated Cleavage of $C_{aromatic}$-C_{α} Bond in Lignin and Its Platform Molecules

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This PDF file includes:

Supplementary Text

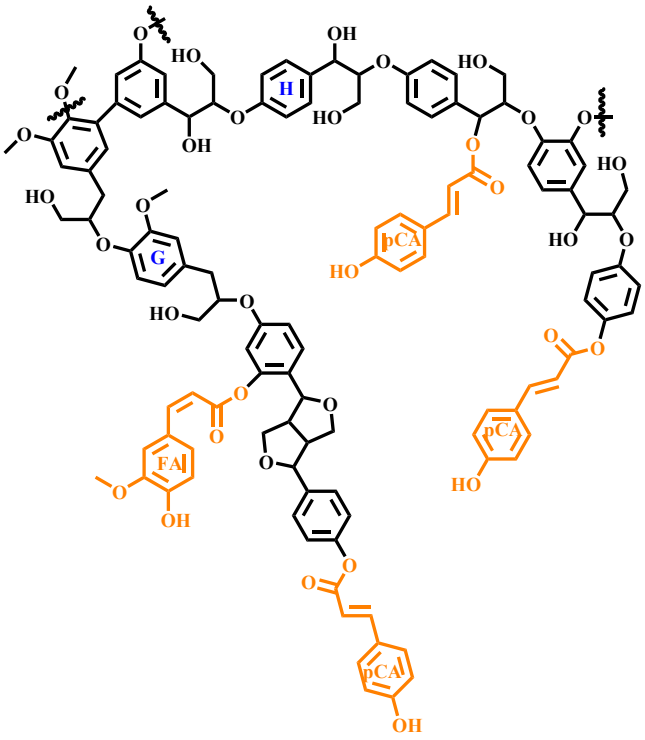


Fig. S1. The structure of bamboo lignin.

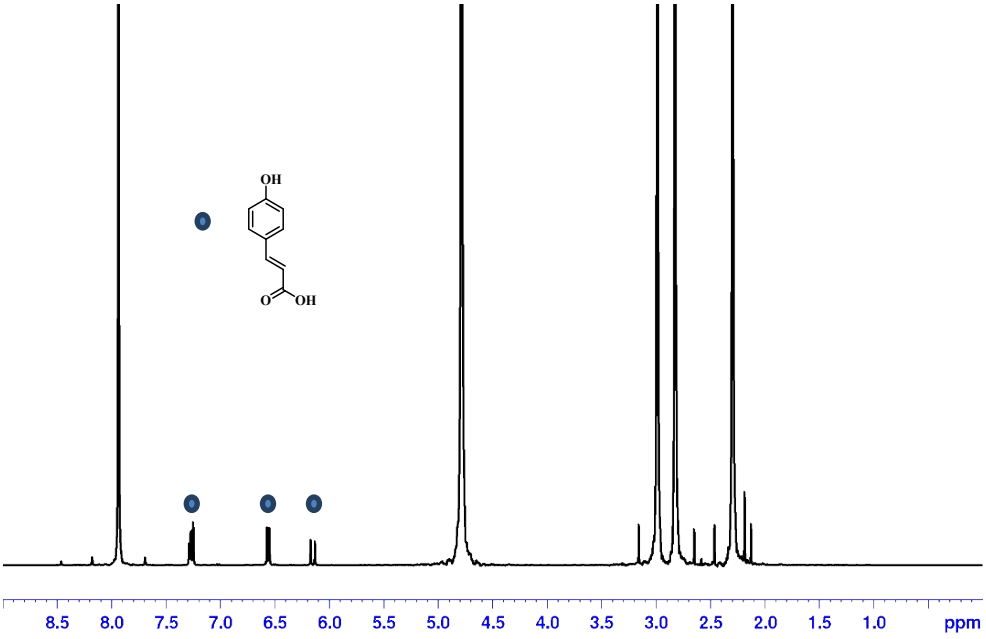


Fig. S2. ^{1}H-NMR spectrum of *p*-coumaric acid in the mixture of water and DMF solvents.

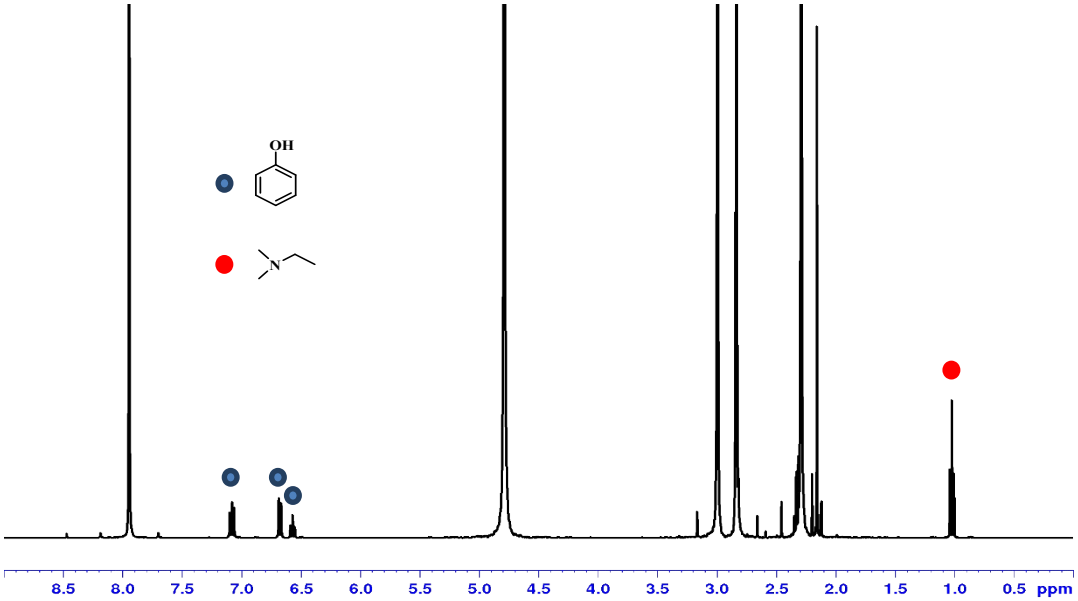


Fig. S3. ^{1}H-NMR spectrum of phenol and N,N-dimethylethylamine in the mixture of water and DMF solvents.

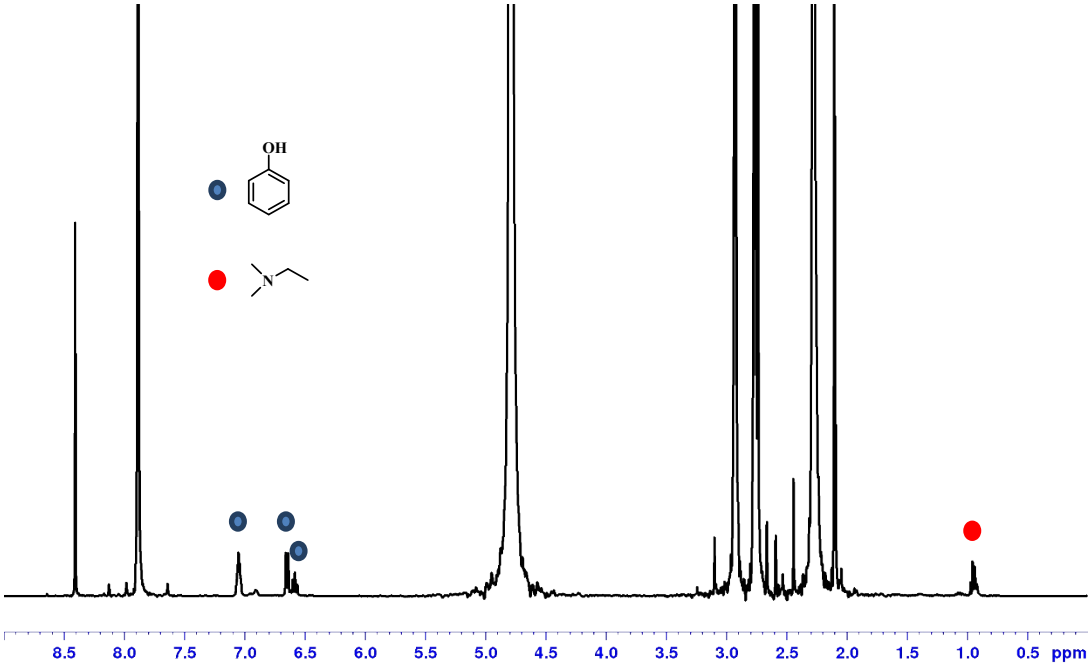


Fig. S4. ^{1}H-NMR spectrum of the product mixture from the reaction of *p*-coumaric acid with DMA in the mixture of water and DMF solvents at 473 K and 1 MPa Ar after 1 h reaction.

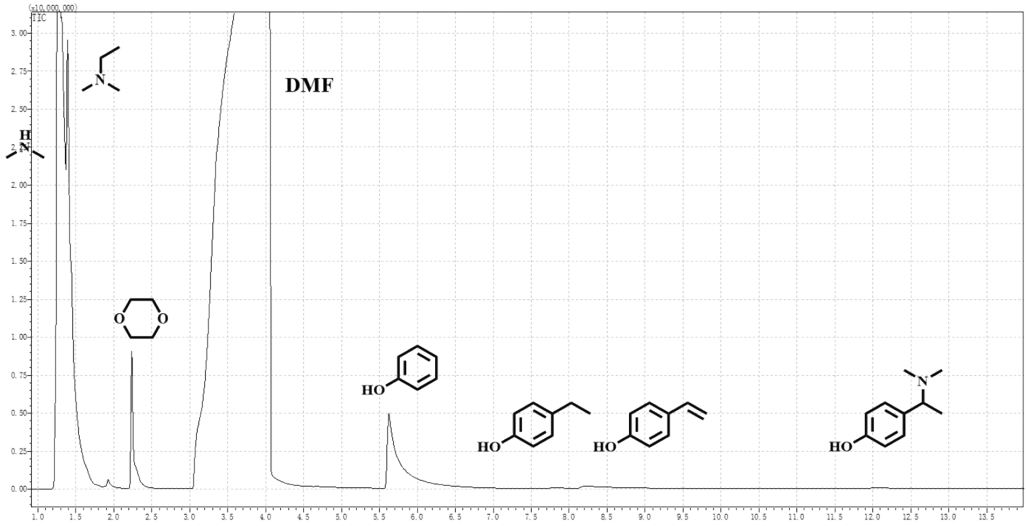


Fig. S5. GC-MS trace of the product mixture from the reaction of *p*-coumaric acid.

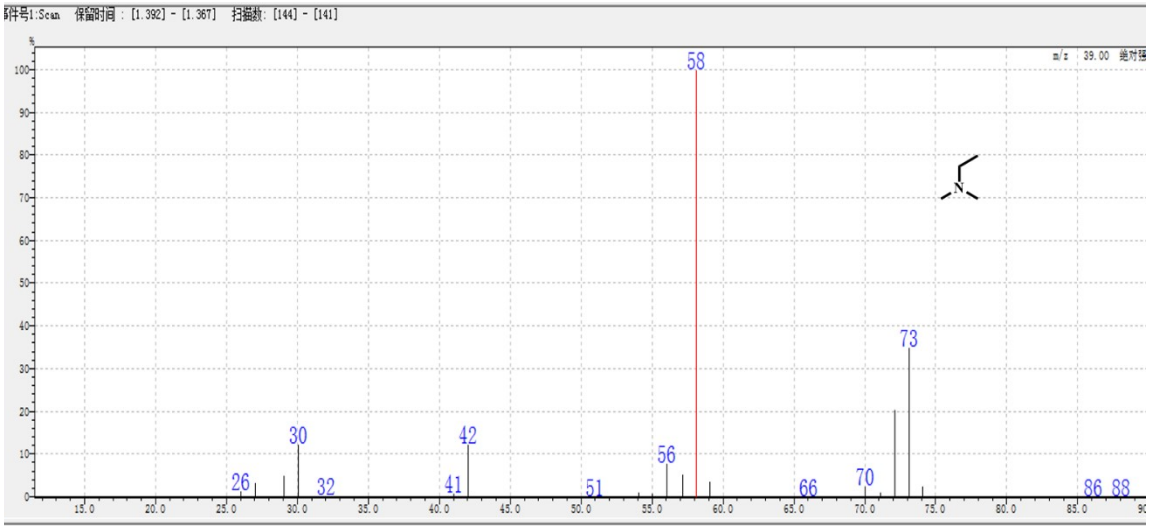


Fig. S6. Mass spectrum of the alkylamine product.

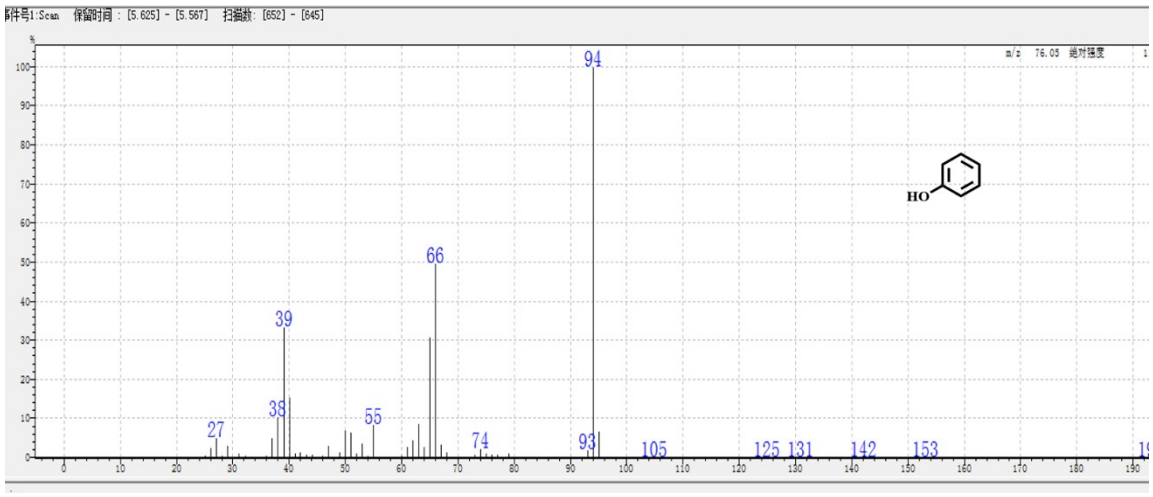


Fig. S7. Mass spectrum of the phenol product.

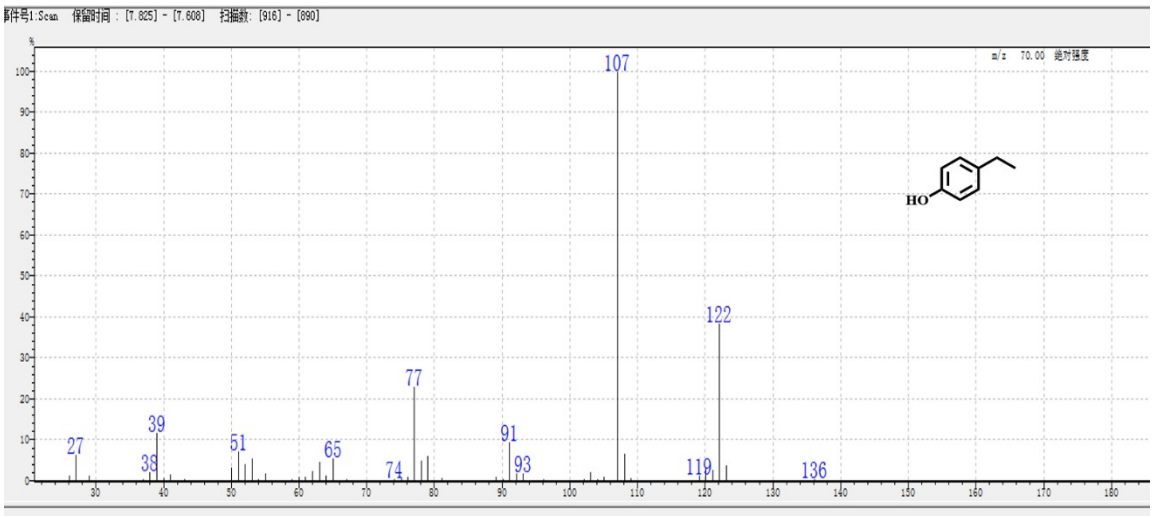


Fig. S8. Mass spectrum of the 4-ethyl phenol product.

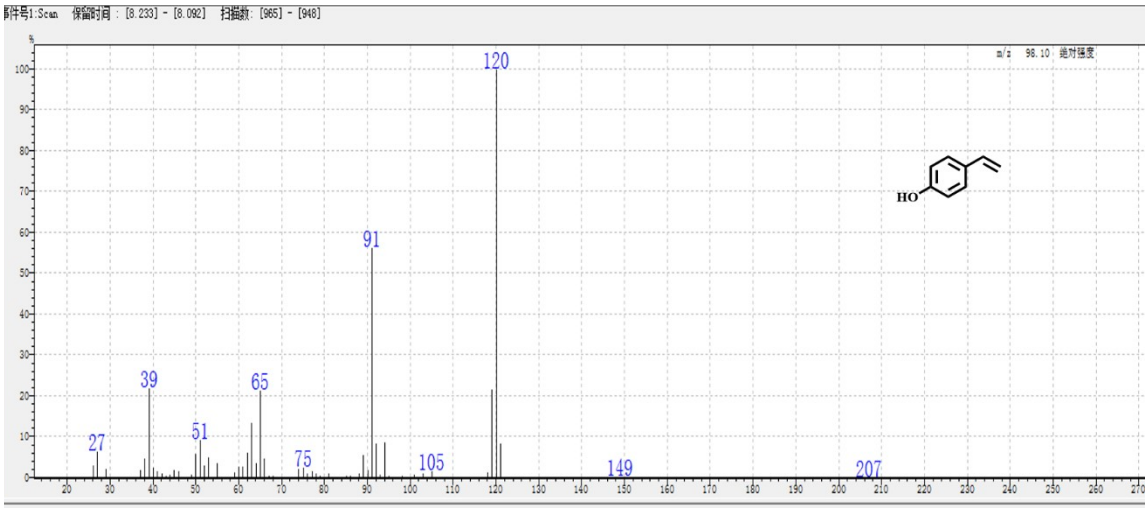


Fig. S9. Mass spectrum of the 4-vinyl phenol product.

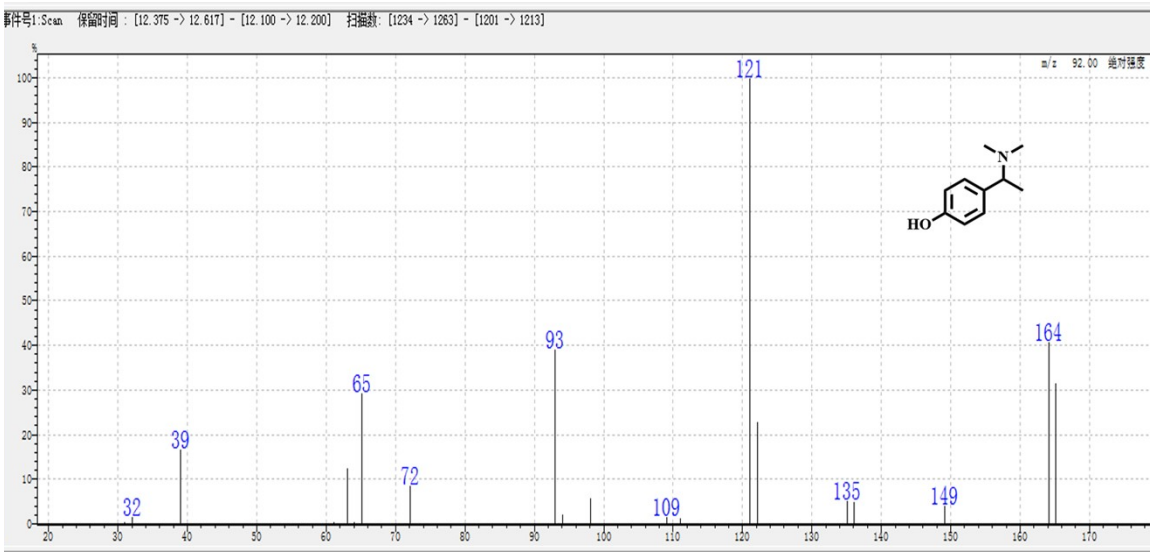


Fig. S10. Mass spectrum of the active amine intermediate.

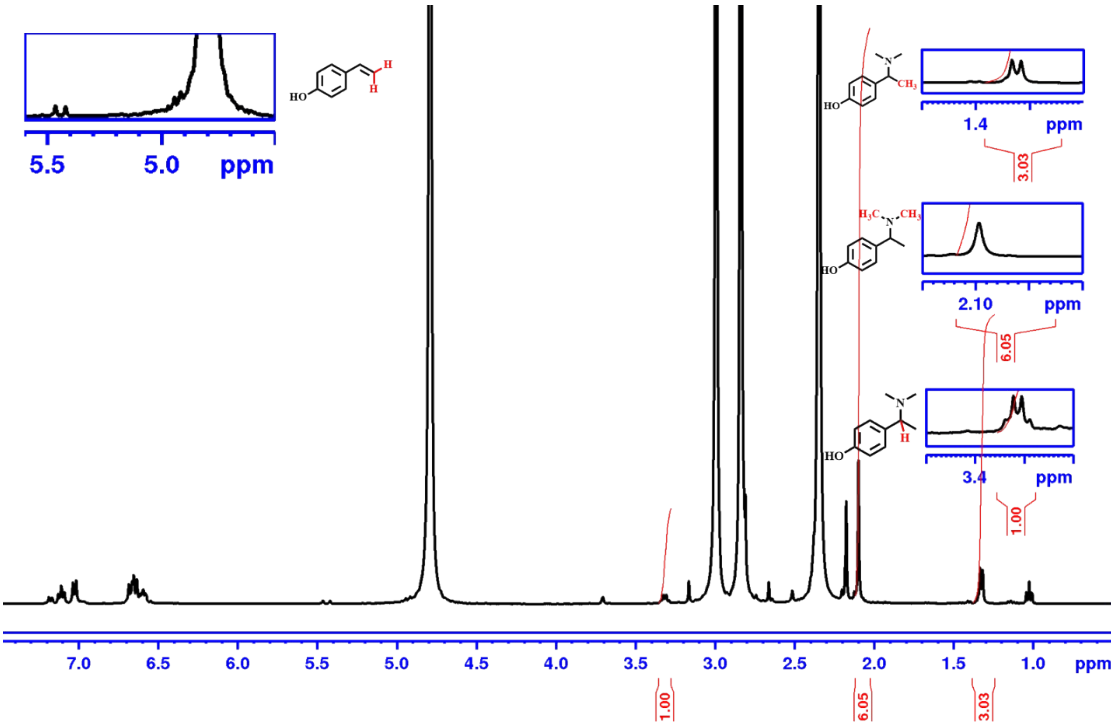


Fig. S11. ^{1}H-NMR spectrum of the product mixture from the reaction of *p*-coumaric acid with DMA in the mixture of water and DMF solvents at 448 K and 1 MPa Ar after 1 h reaction.

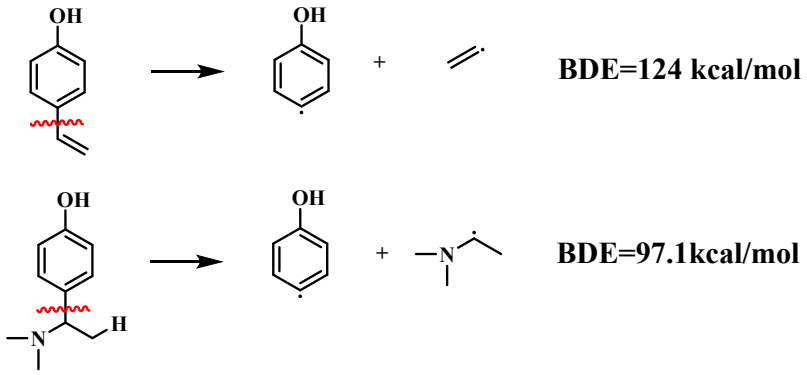


Fig. S12. The bond dissociation energy (BDE) of $C_{aromaic}$-C_{α} in two intermediates.

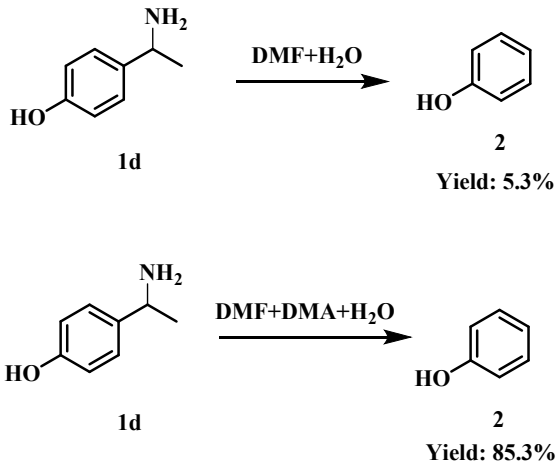


Fig. S13. The cleavage of C-C bond experiments. Reaction conditions: **(1)** 0.6 mmol substrate, 1.5 mL DMF, 2.5 g H_2O, 473 K, 1MPa Ar, 1 h. **(2)** 0.6 mmol substrate, 40 wt% DMA in water (2.5 g), 1.5 mL DMF, 1 MPa Ar, 1 h.

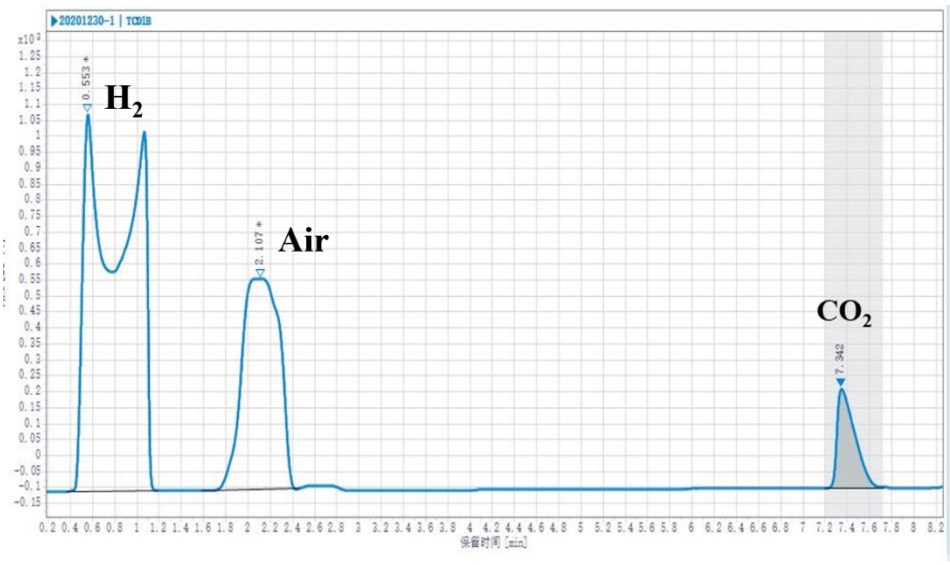


Fig. S14. The GC trace of the gaseous sample after *p*-coumaric acid transformation. Reaction conditions: 0.6 mmol substrate, 1.5 mL DMF, 40 wt% DMA in water (2.5 g), 473 K, 1MPa Ar, 1 h.

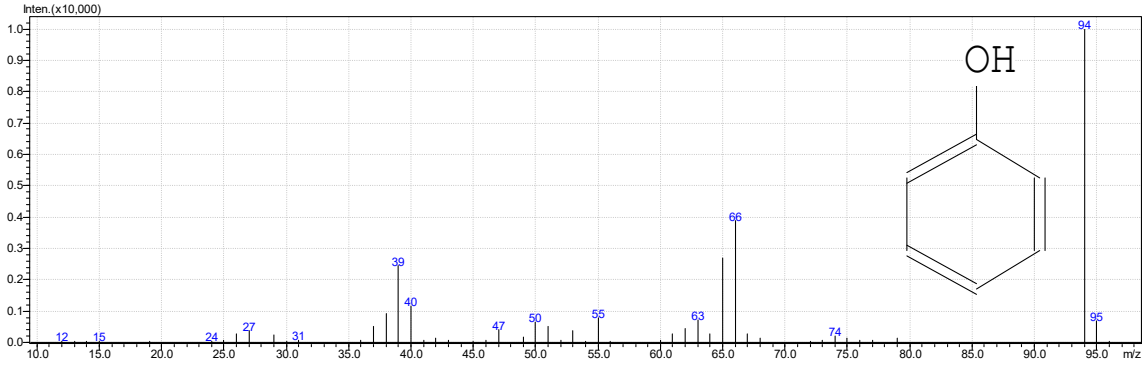


Fig. S15: The GC-MS result of phenol.

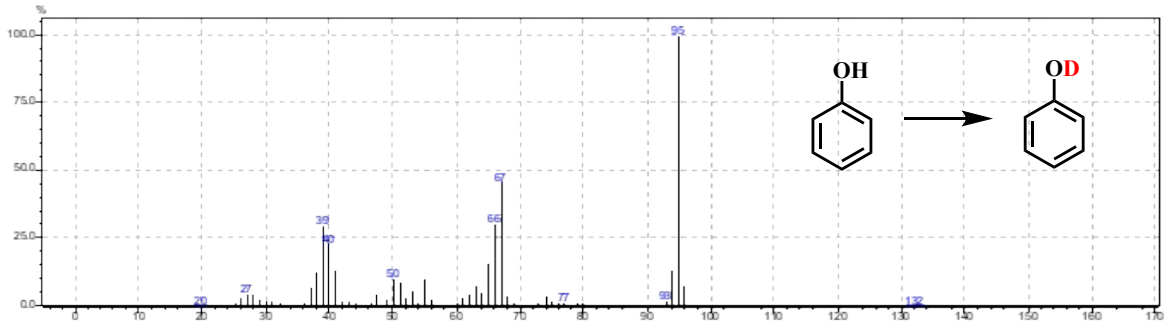


Fig. S16: The GC-MS result of the reaction using D_2O. Reaction condition: 0.6 mmol phenol, 2.5 g 40 wt% DMA in water, 1.5 mL DMF, 1 mL D_2O, 473K, 1 MPa Ar, 1h.

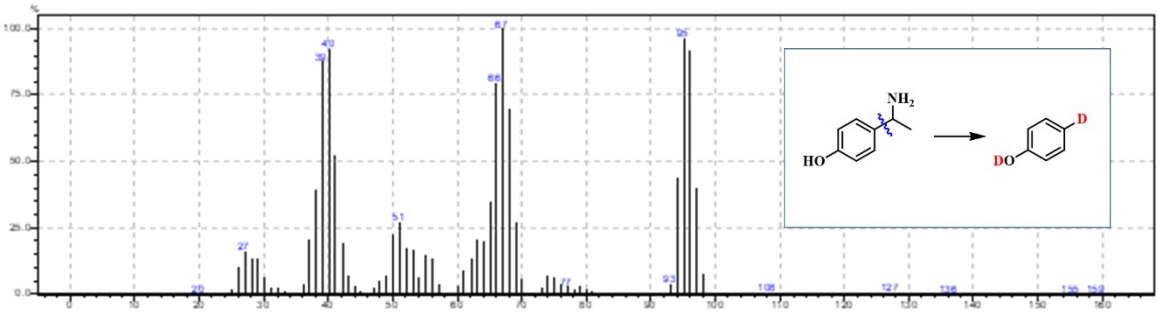


Fig. S17: The GC-MS result of the reaction using D_2O. Reaction condition: 0.6 mmol substrate, 2.5 g 40 wt% DMA in water, 1.5 mL DMF, 1 mL D_2O, 473K, 1MPa Ar, 1h.

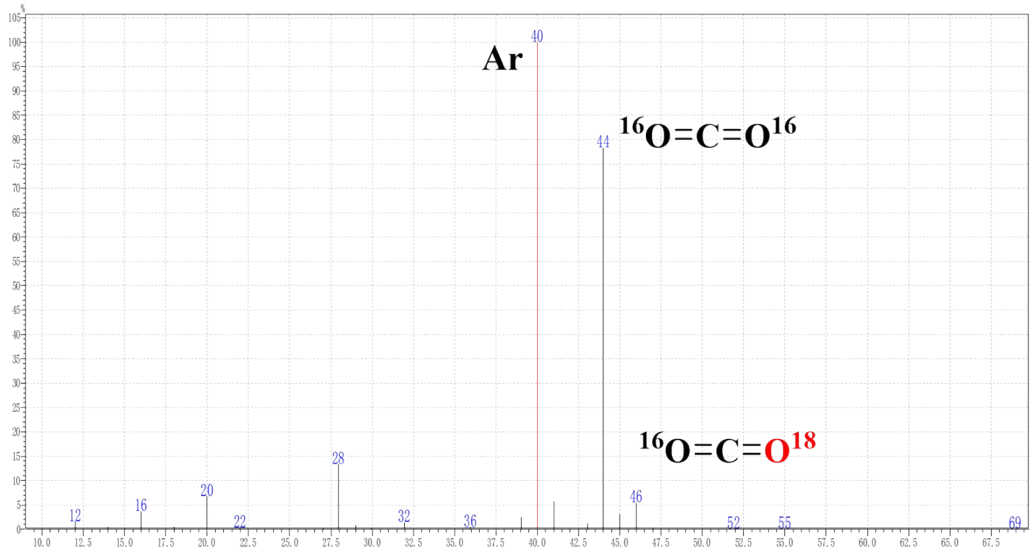


Fig. S18: The GC-MS result of the gaseous sample using $H_2{}^{18}O$. Reaction condition: 0.6 mmol substrate, 2.5 g 40 wt% DMA in water, 1.5 mL DMF, 1 mL $H_2{}^{18}O$, 473K, 1MPa Ar, 1h.

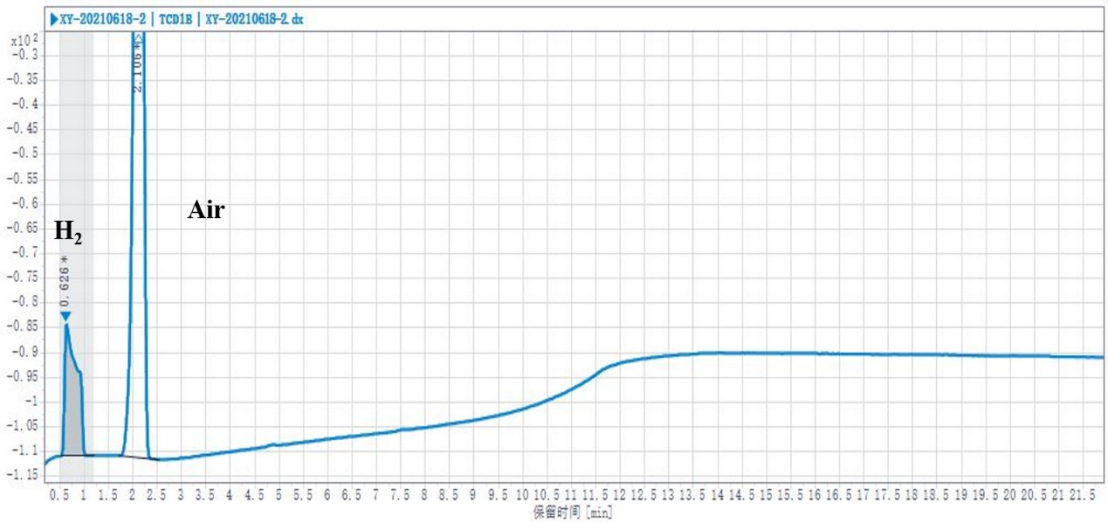
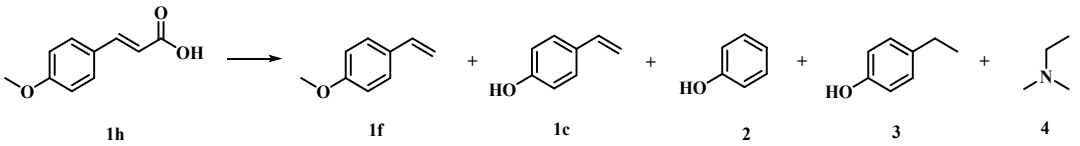


Fig. S19. The GC trace of the gaseous sample after *p*-coumaric acid transformation. Reaction conditions: 0.6 mmol substrate, 1.5 g H_2O, 40 wt% DMA in water (2.5 g), 473 K, 1MPa Ar, 1 h.



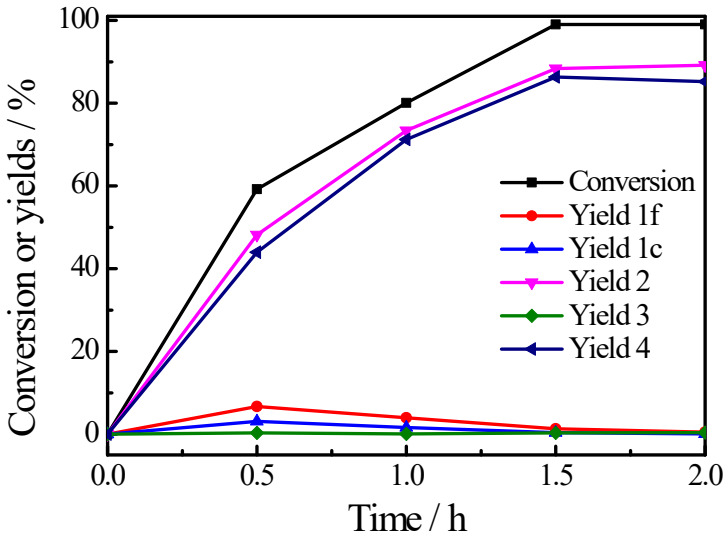


Fig. S20. Product distributions for the conversion of **1h** versus time. Reaction conditions: 0.6 mmol substrate, 1.5 mL DMF, 2.5 g 40 wt% DMA in water, 473 K.

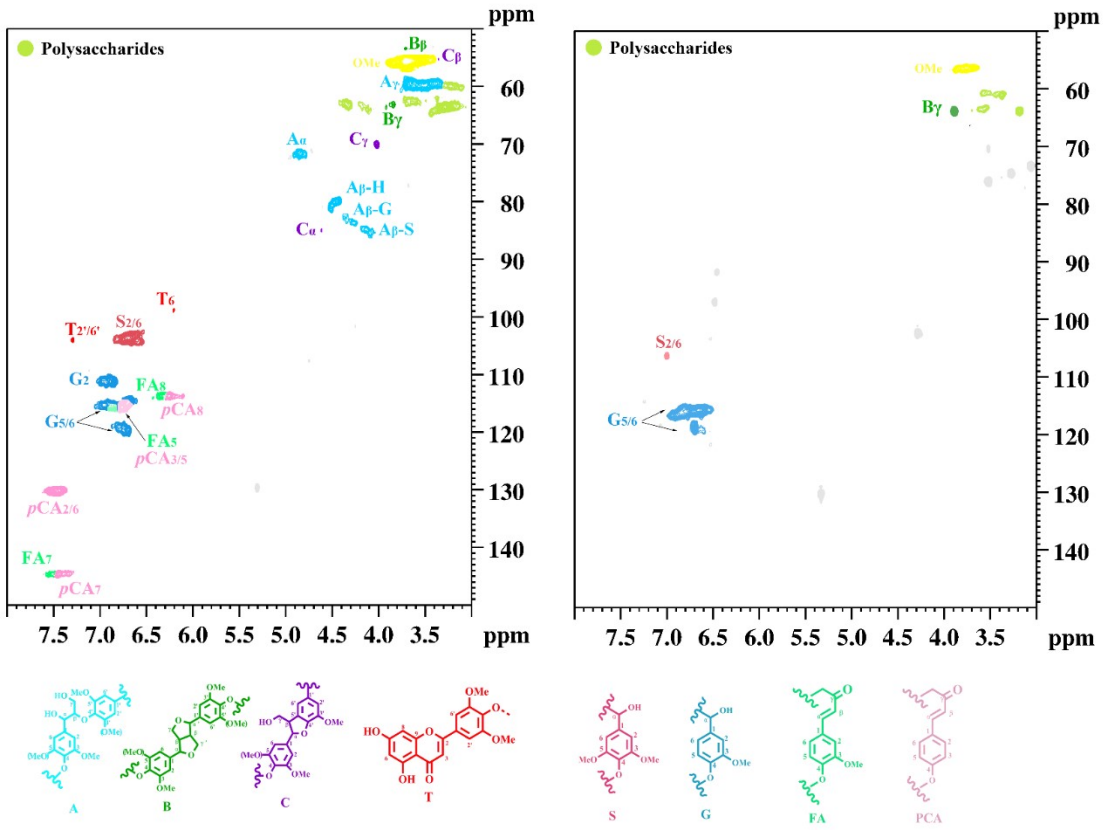
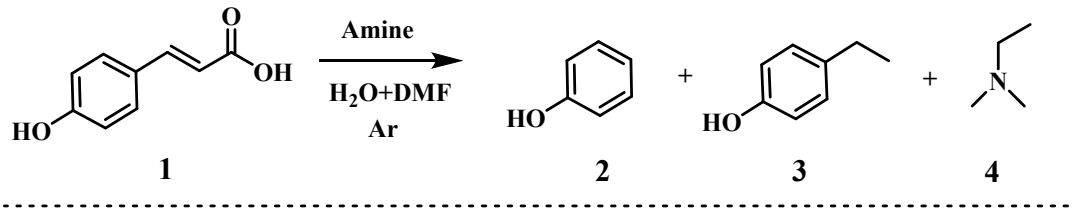
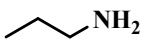


Fig. S21. The 2D-HSQC NMR spectra of the bamboo lignin in deuterated DMSO (DMSO-*d6*) before and after reaction.

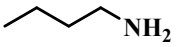
Table S1. The transformation of *p*-coumaric acid in the presence of different amines. [a]



1 2 3 4



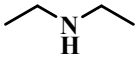
8a: 80.4% 2
6.8% 3
63.7% 4
Conv.: >99%



8b: 81.6% 2
7.2% 3
62.9% 4
Conv.: >99%

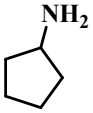
8c: 83.7% 2
6.5% 3
71.4% 4
Conv.: >99%

8d: 85.5% 2
5.1% 3
69.2% 4
Conv.: >99%

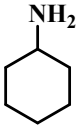


8e: 87.3% 2
4.3% 3
74.5% 4
Conv.: >99%

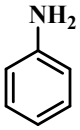
8f: 79.8% 2
9.5% 3
60.1% 4
Conv.: >99%



8g: 73.4% 2
13% 3
56.5% 4
Conv.: >99%



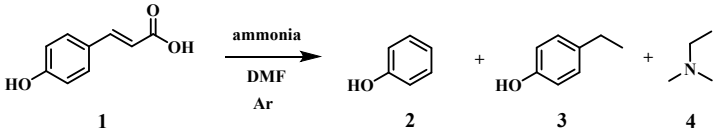
8h: 67.4% 2
19.3% 3
52.7% 4
Conv.: >99%



8i: 60.5% 2
22.4% 3
47.2% 4
Conv.: >99%

[a] Reaction conditions: 0.6 mmol substrate, 24 mmol amines, 1.5 g water, 1.5 mL DMF, 473 K, 1 MPa Ar, 4 h.

Table S2. The transformation of *p*-coumaric acid in the presence of ammonia. [a]



1 2 3 4

The amount of ammonia [g]	Conv. [%]	Yield [%]		
		2	3	4
0	14.5	0.7	12.1	trace
2	52.1	15.5	33.3	12.1

[a] Reaction conditions: 0.6 mmol substrate, 30 wt% ammonia (2 g), 2 mL DMF, 1 MPa Ar, 200 °C, 1 h.

Table S3. Optimization of the reaction parameters. [a]

Entry	DMA:Substrate [mol/mol]	DMF [mL]	Conv. [%]	Y_2 [%]	Y_3 [%]	Y_4 [%]
1	40	0	>99	54.3	3.8	0
2	40	0.5	>99	85.1	4.5	84.2
3	40	1	>99	86.5	3.4	83.1
4	40	1.5	>99	89.3	6.2	85.2

[a] Reaction conditions: 0.6 mmol substrate, 40 wt% DMA in water (2.5 g), 473 K, 1MPa Ar, 1 h.