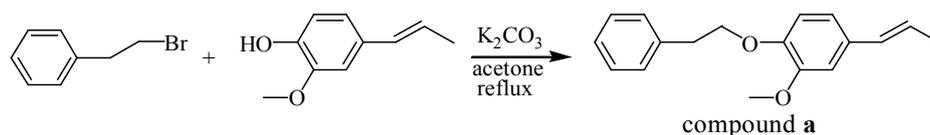


Electronic Supplementary Information

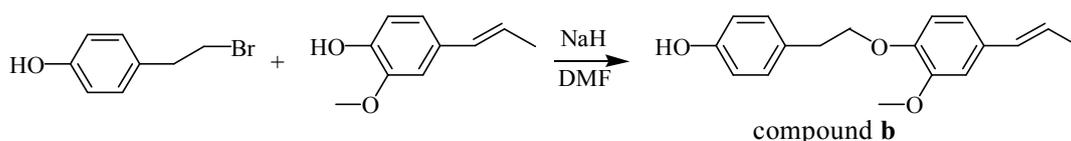
The preparation methods of lignin model compound **a** and **b** were as follows:

Lignin model compound **a**:



Under a nitrogen atmosphere, a mixture of (2-bromoethyl)benzene (3.70 g, 20.0 mmol), isoeugenol (3.61 g, 22.0 mmol) and potassium carbonate (4.18 g, 30.0 mmol) in 50 mL of acetone was stirred and heated to reflux for 4 h. After being cooled to atmospheric temperature, it was filtered and concentrated under reduced pressure to give crude compound **a**. The resulting product was further purified by column chromatography on silica gel (ethyl acetate-hexane 1: 4, v: v) to give compound **a** (4.23 g, 80%). 1H -NMR (400MHz, $DMSO-d_6$): 7.27-7.37 (m, 4H), 7.23 (t, $J = 6.4Hz$, 1H), 7.00 (s, 1H), 6.89 (d, $J = 8.2 Hz$, 1H), 6.83 (d, $J = 8.2Hz$, 1H), 6.33 (d, $J = 15.8Hz$, 1H), 6.08-6.24 (m, 1H), 4.15 (t, $J = 6.9Hz$, 2H), 3.76 (s, 3H), 3.03 (t, $J = 6.9Hz$, 2H), 1.84 (t, $J = 12.0Hz$, 3H); ^{13}C -NMR (400MHz, $DMSO-d_6$): 149.10, 147.13, 138.31, 130.72, 130.59, 128.95, 128.24, 126.21, 123.22, 118.58, 113.31, 109.34, 68.98, 55.55, 35.06 and 18.11. The m/z (%) as detected by EI-MS were 268 (42), 164 (30), 105 (100), 103 (11), 79 (15) and 77 (14).

Lignin model compound **b**:



Under a nitrogen atmosphere, a mixture of isoeugenol (3.61 g, 22.0 mmol) and sodium hydride (0.80 g, 20.0 mmol) in 80 mL of N,N-dimethylformamide (DMF) was stirred at room temperature for 0.5 h, then 4'-hydroxyphenethyl bromide (4.02g, 20.0 mmol) was added and stirred at room temperature for 5.0 h. After the reaction, the pH of reaction mixture was adjusted to 2-3 with 1N HCl. Then 80 mL of saturated NaCl solution was added and extracted three times with ethyl acetate (120 mL). The organic extracts were combined, washed twice with brine, dried over MgSO₄, filtered and concentrated under reduced pressure to give crude compound **b**. The resulting product was further purified by column chromatography on silica gel (ethyl acetate-hexane 1: 4, v: v) to give compound **b** (4.66 g, 82%).

¹H-NMR (400MHz, DMSO-d₆): 9.19 (s, 1H), 7.10 (d, J = 7.4Hz, 2H), 6.99 (s, 1H), 6.84 (dd, J = 19.4Hz, 7.8Hz, 2H), 6.68 (d, J = 7.6Hz, 2H), 6.31 (d, J = 15.7Hz, 1H), 6.15 (m, 1H), 4.05 (t, J = 6.8Hz, 2H), 3.75 (s, 3H), 2.89 (t, J = 6.4Hz, 2H), 1.81 (d, J = 6.0Hz, 3H); ¹³C-NMR (400MHz, DMSO-d₆): 155.73, 149.00, 147.13, 130.57, 129.84, 128.18, 123.19, 118.57, 115.03, 113.12, 109.20, 69.29, 55.50, 34.21 and 18.12. The m/z (%) as detected by EI-MS were 284 (16), 165 (11), 164 (100), 121 (87), 103 (18), 93 (10), 91 (23) and 77 (26).

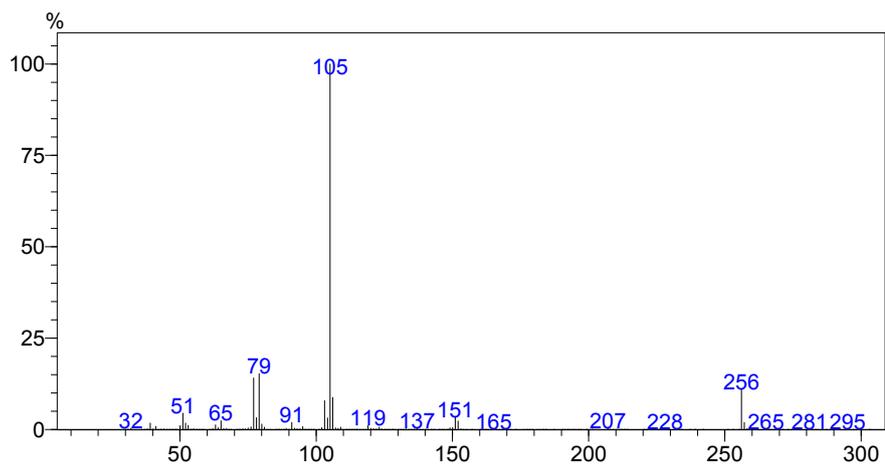


Fig. S1 MS spectrum of product 1

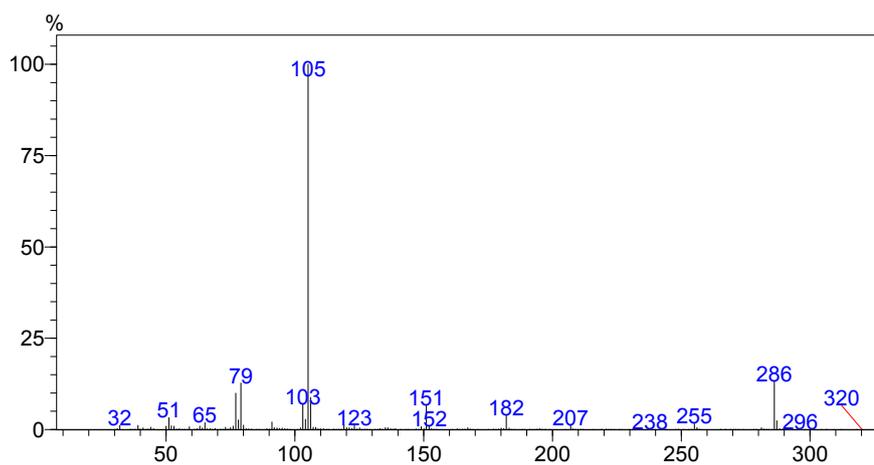


Fig. S2 MS spectrum of product 2

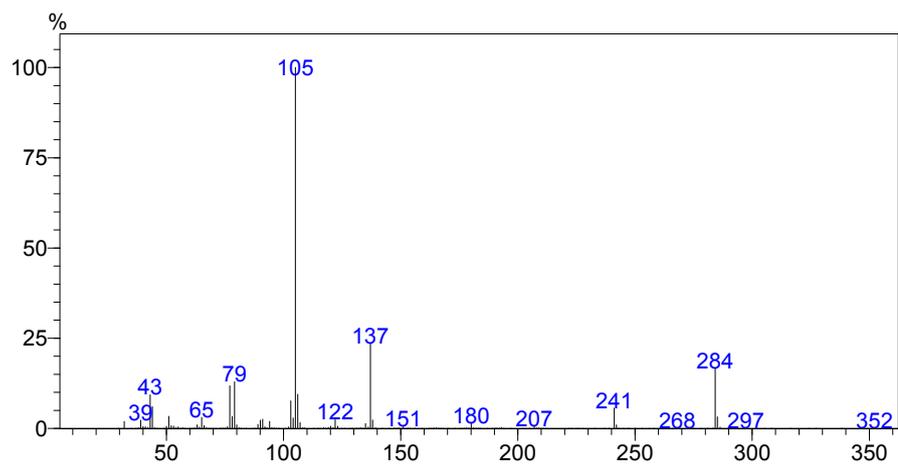


Fig. S3 MS spectrum of product 3

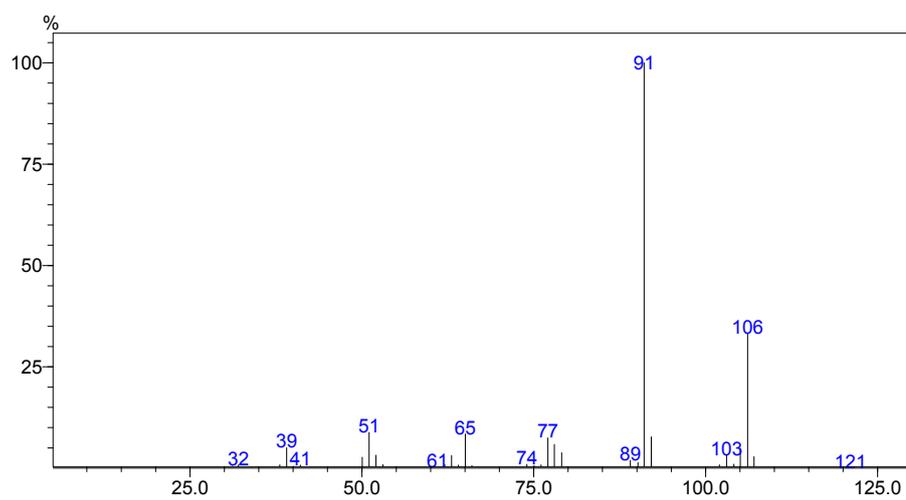


Fig. S4 MS spectrum of product 4

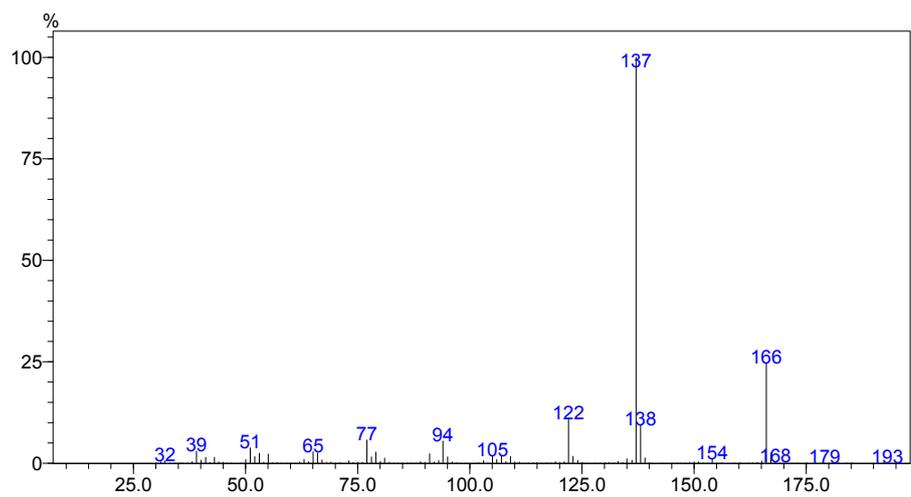


Fig. S5 MS spectrum of product 5

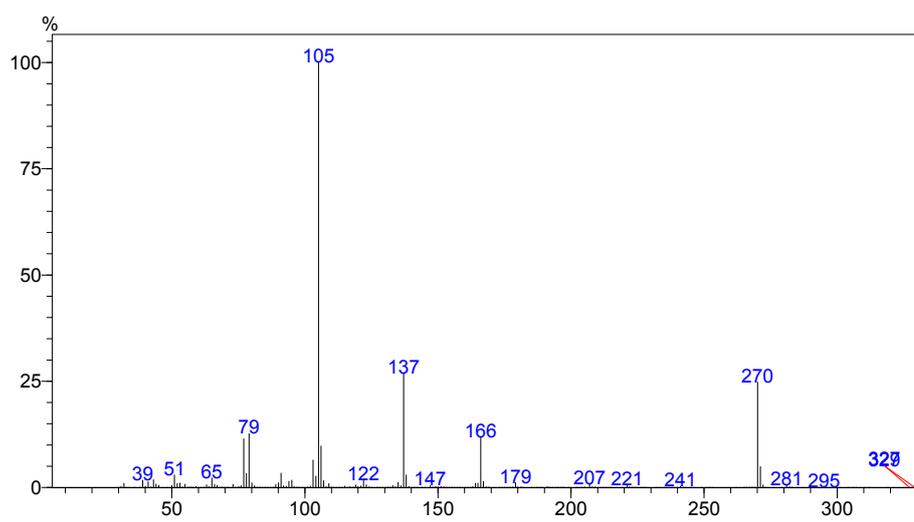


Fig. S6 MS spectrum of product 6

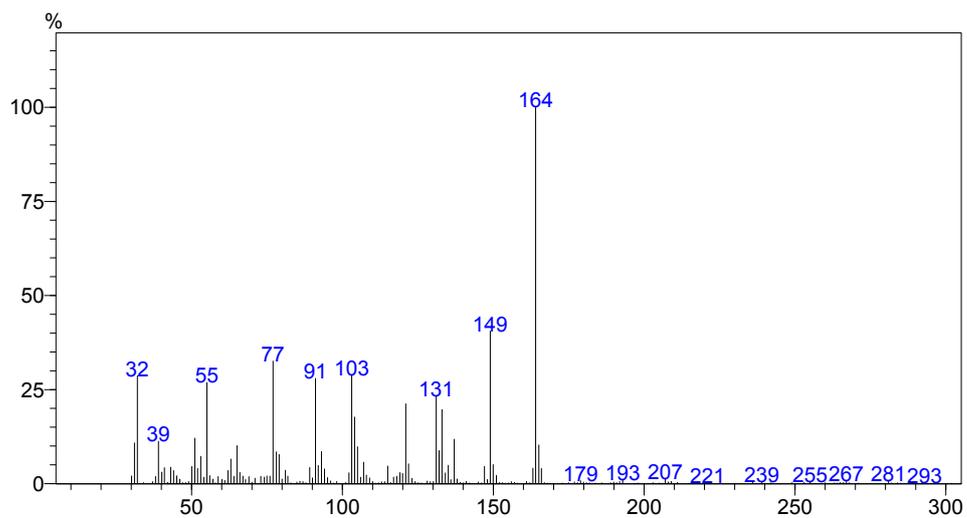


Fig. S7 MS spectrum of product 7

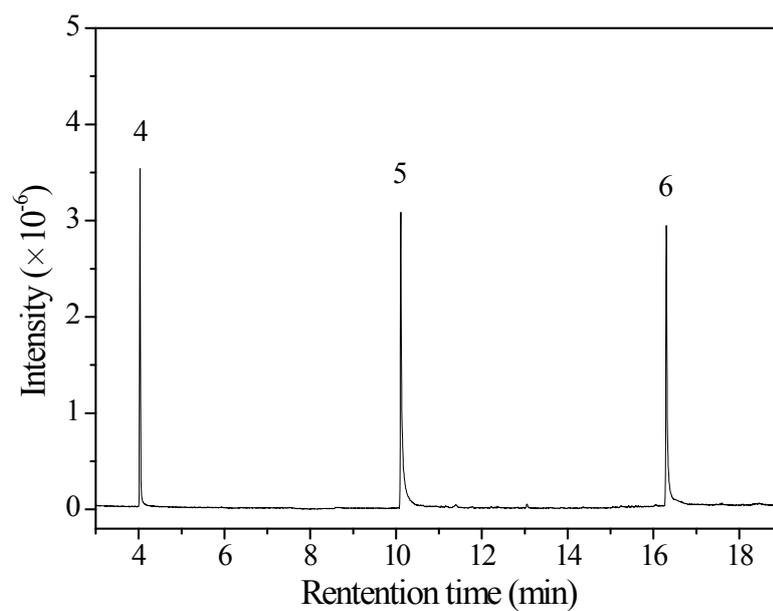


Fig. S8 GC chromatogram of decomposed products carried out at 140°C for 50 min

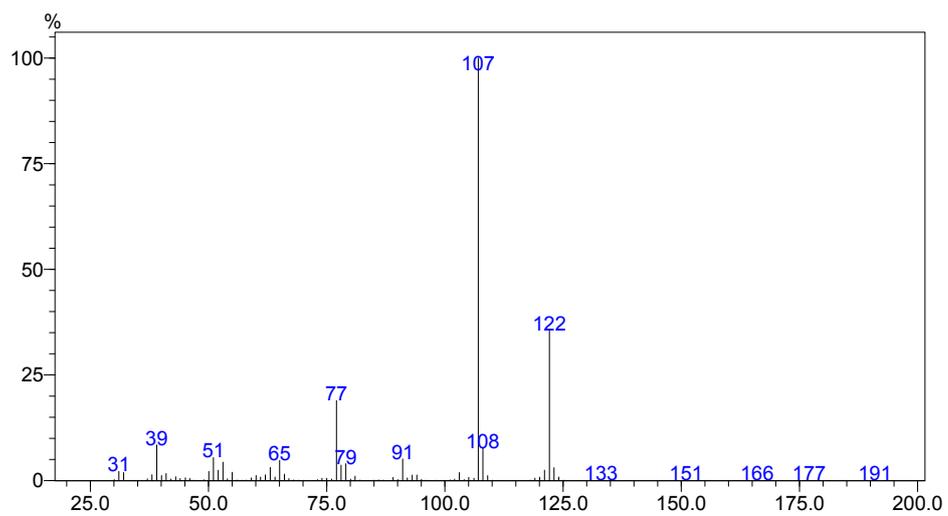


Fig. S9 MS spectrum of product 8

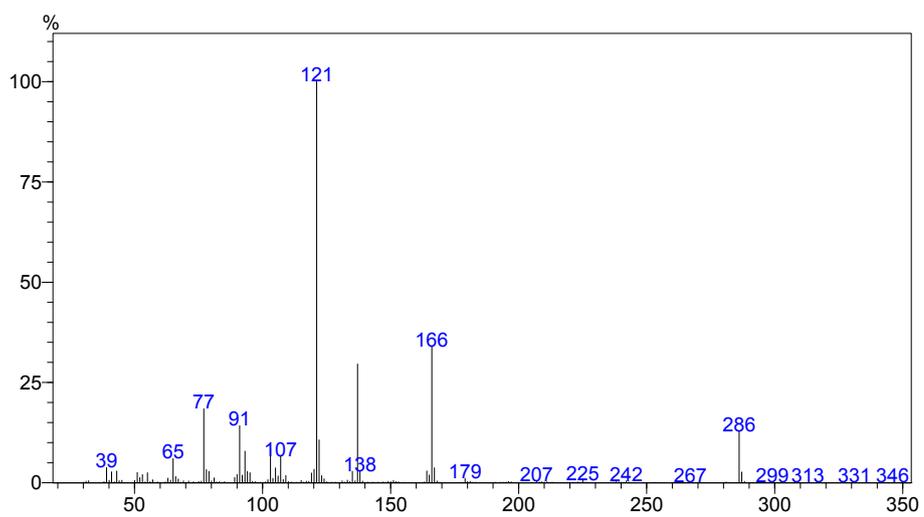


Fig. S10 MS spectrum of product 9