Supporting materials:

Revealing structural modifications of lignin in acidic γ-valerolactone-H_2O pretreatment

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1. The reported mechanism of β-O-4 and β-5 substructures during acid treatment 3

2. Determination of Products from **GG** under acidic GVL solvent system..... 3

3. NMR data of products obtained from β-O-4 5

3.1 Synthesis and NMR Spectra of 1,3-dioxane structures (**1a, 1b**)..... 5
3.2 NMR Spectra of phenyl dihydrobenzofuran **3** 7
3.3 NMR Spectra of condensation product trimer **4** 8
3.4 Synthesis and NMR Spectra of enol ether compounds (**5a, 5b**)..... 9
3.5 NMR Spectra of Hibbert's Ketone **10** 10
3.6 TIC (total ion chromatogram) of the products obtained from β-O-4 10
3.7 TIC (total ion chromatogram) of the products obtained from 1,3-dioxane compounds 11

4. Synthesis and NMR Spectra of products obtained from β-5 11

4.1 phenylcoumarone **24**.....11
4.2 stilbene **25** 12
4.3 coumaran **27**..... 13
4.4 phenylcoumarone **29**..... 14
4.5 stilbene **30** 15

5. Products obtained from syringaresinol (β-β)..... 16

5.1 syringaresinol..... 16
5.2 epi-syringaresinol..... 16
5.3 dia-syringaresinol..... 16
5.4 GC-MS of the products obtained from β-β..... 18

1. The reported mechanism of β-O-4 and β-5 substructures during acid treatment

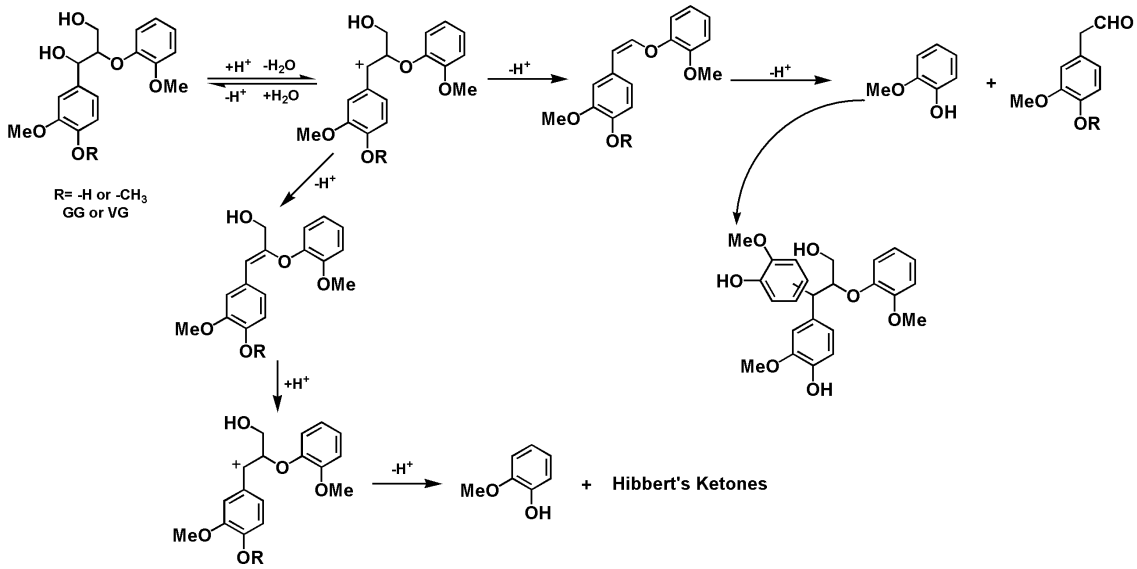

Fig.S1 The reported mechanism of β-O-4 substructure during acid treatment[1-10]

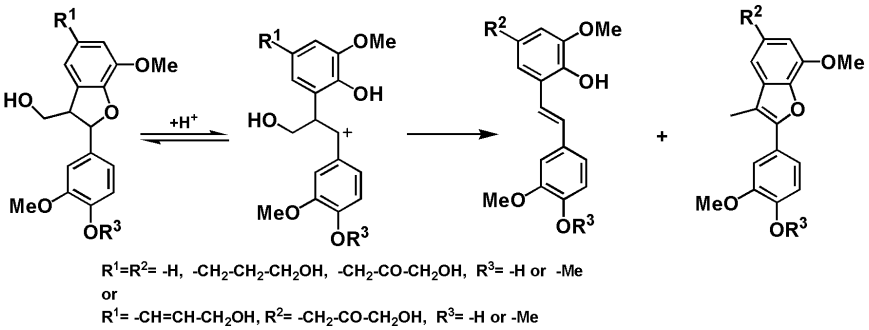

Fig.S2 The reported mechanism of β-5 substructure during acid treatment[11-15]

2. Determination of Products from GG under acidic GVL solvent system

The yields of products from GG were determined by GC-MS with internal standard (VG-dimer). Therefore, yields of each product were calculated by the following Eq.

$$Y = \frac{m_{AP} \times M_{IS}}{m_{IS} \times M_L} \times 100\%$$

Y: Yield of product (%);

m_{Ap}: Mass weight of product for GC-MS analysis;

m_{IS} : Mass weight of internal standard for GC-MS analysis;

$M_{IS.}$: Mass weight of internal standard added;

M_L: Mass of lignin model.

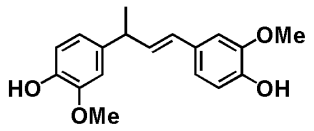

Fig.S3 Internal standard compound

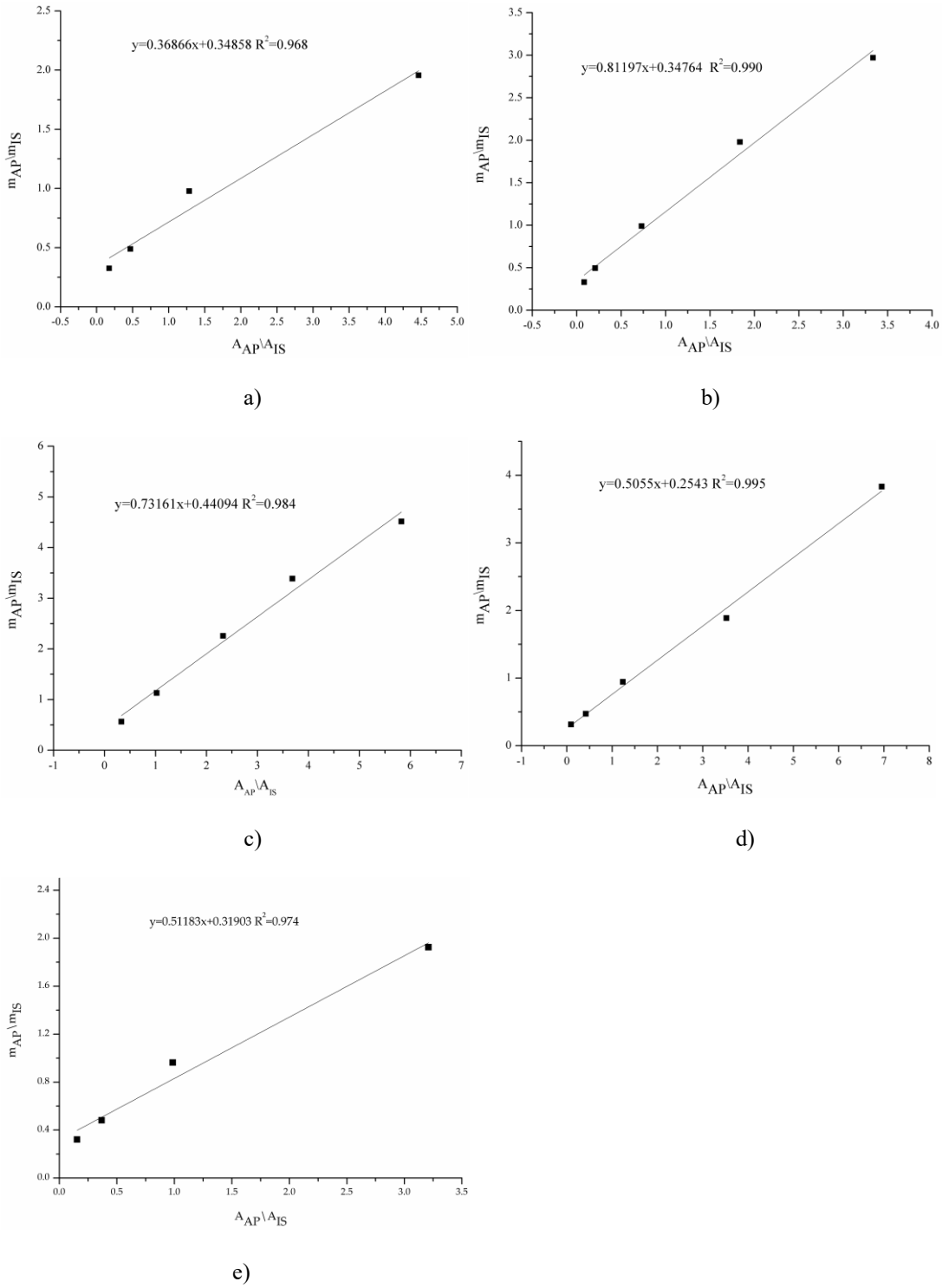

Fig.S4 The standard curve of different product a)product 3, b)product 1, c)product 7, d)product 4, and e)product 8. A_{AP}: peak area of product; A_{IS}: peak area of internal standard.

3. NMR data of products obtained from β-O-4

3.1 Synthesis and NMR Spectra of 1,3-dioxane structures (1a, 1b)

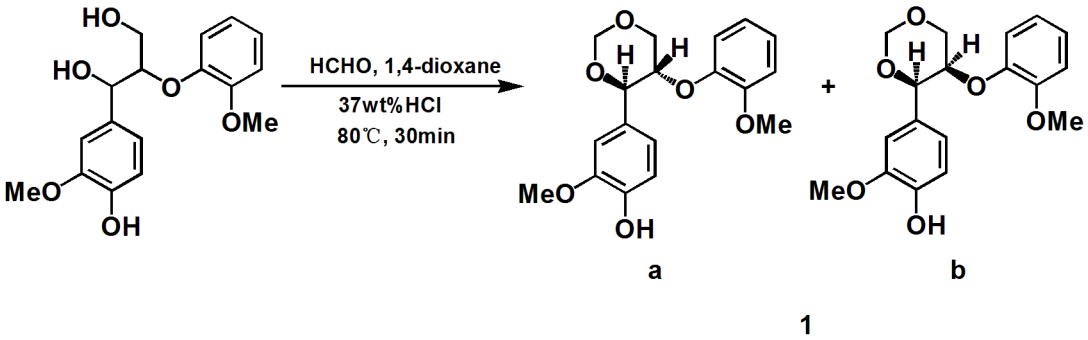

Fig.S5 Synthesis route of 1,3-dioxane structures (GG)[16]

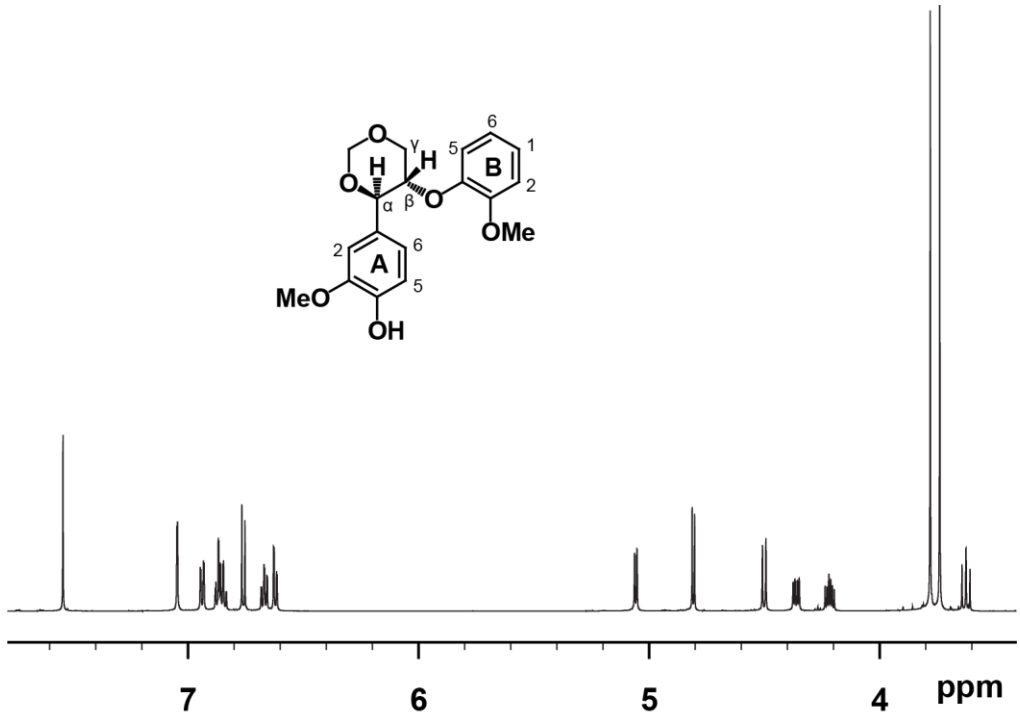

Fig.S6 ^{1}H NMR of trans-isomer of 1,3-dioxane structure, *trans*

1a, *trans*-isomer: ^{1}H-NMR (acetone-d6, 600MHz): δ 7.54 (s, 1H; ArOH), 7.05 (d, J=1.9 Hz, 1H; A2), 6.94 (dd, J=1.9, 8.1 Hz, 1H; A6), 6.87 (dd, J=1.9, 8.1Hz, 1H; B2), 6.85 (ddd, J=1.5, 6.9, 8.1Hz, 1H; B1), 6.76 (d, J=8.1 Hz, 1H; A5), 6.67 (m, 1H; B6), 6.62 (dd, J=1.5, 8.1Hz, 1H; B5), 5.06 (d, J=6.2 Hz, 1H; acetal-H), 4.81 (d, J=6.2 Hz, 1H; acetal-H), 4.50 (d, J=9.1 Hz, 1H; α-H), 4.36 (dd, J=5.0, 10.4 Hz, 1H; γ-H), 4.22 (ddd, J=5.0, 9.1, 10.4 Hz, 1H; β-H), 3.78 (s, 3H; OCH_3), 3.74 (s, 3H; OCH_3), 3.62 (t, J=10.4 Hz, 1H; γ-H).

^{13}C NMR (acetone-d6, 600MHz): δ151.69 (C-B3), 148.10 (C-A3), 147.97 (C-B4), 147.44 (C-A4), 131.20 (C-A1), 123.58 (C-B1), 121.57 (C-A6), 121.46 (C-B6), 118.80 (C-B5), 115.22 (C-A5), 113.61 (C-B2), 112.14 (C-A2), 94.15 (C-acetal), 83.34 (C-α), 75.66 (C-β), 70.07 (C-γ), 56.31 (C-OCH_3), 56.12 (C-OCH_3).

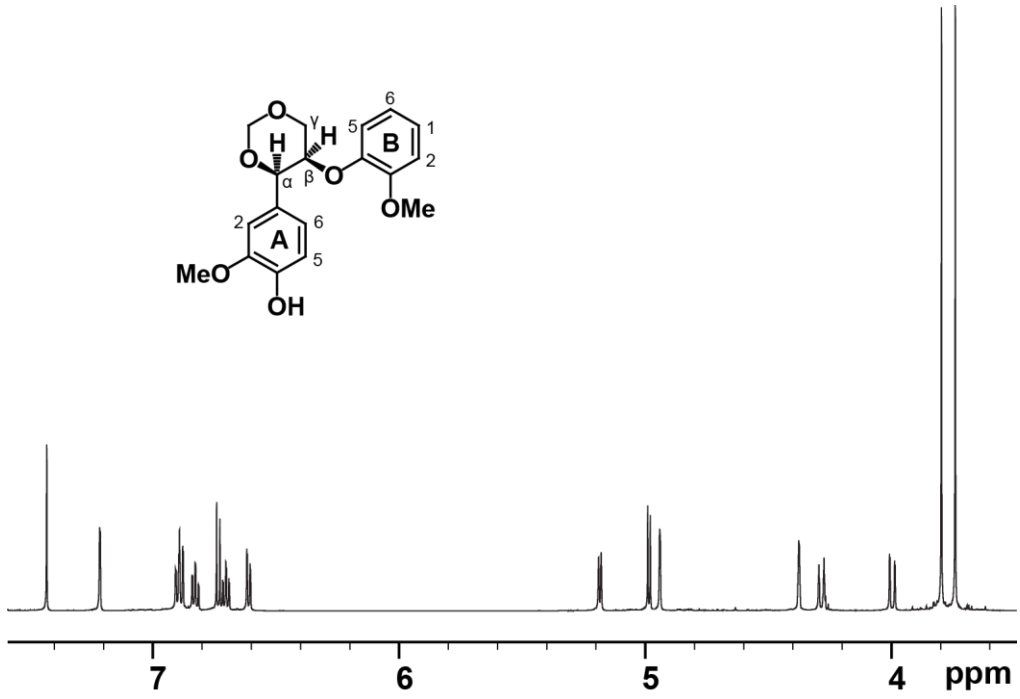

Fig.S7 ^{1}H NMR of cis-isomer of 1,3-dioxane structure, *cis*

1b, *cis*-isomer: ^{1}H-NMR (acetone-d6, 600MHz): δ 7.43 (s, 1H; ArOH-H), 7.21 (d, J=1.8 Hz, 1H; A2), 6.90 (dd, J=1.6, 8.2 Hz, 1H; A6), 6.88 (dd, J=1.5, 8.1Hz, 1H; B2), 6.83 (dt, J=1.5, 7.5, 8.1Hz, 1H; B1), 6.73 (d, J=8.2 Hz, 1H; A5), 6.70 (dt, J=1.6, 7.5, 8.0Hz, 1H; B6), 6.61 (dd, J=1.5, 8.0Hz, 1H; B5), 5.18 (d, J=6.3 Hz, 1H; acetal-H), 4.98 (d, J=6.3 Hz, 1H; acetal-H), 4.94 (d, J=1.5 Hz, 1H; α-H), 4.37 (d, J=1.5 Hz, 1H; β-H), 4.28 (dt, 1H; γ-H), 4.00 (dd, J=1.5, 12.4 Hz, 1H; γ-H), 3.80 (s, 3H; OCH_3), 3.74 (s, 1H; OCH_3).

^{13}C NMR (acetone-d6, 600MHz): δ151.85 (C-B3), 148.45 (C-B4), 147.85 (C-A3), 146.88 (C-A4), 131.24 (C-A1), 122.77 (C-B1), 121.63 (C-B6), 120.44 (C-A6), 118.15 (C-B5), 114.88 (C-A5), 114.25 (C-B2), 112.18 (C-A2), 94.48 (C-acetal), 80.82 (C-α), 75.02 (C-β), 68.71 (C-γ), 56.41 (C-OCH_3), 56.24 (C-OCH_3).

3.2 NMR Spectra of phenyl dihydrobenzofuran 3

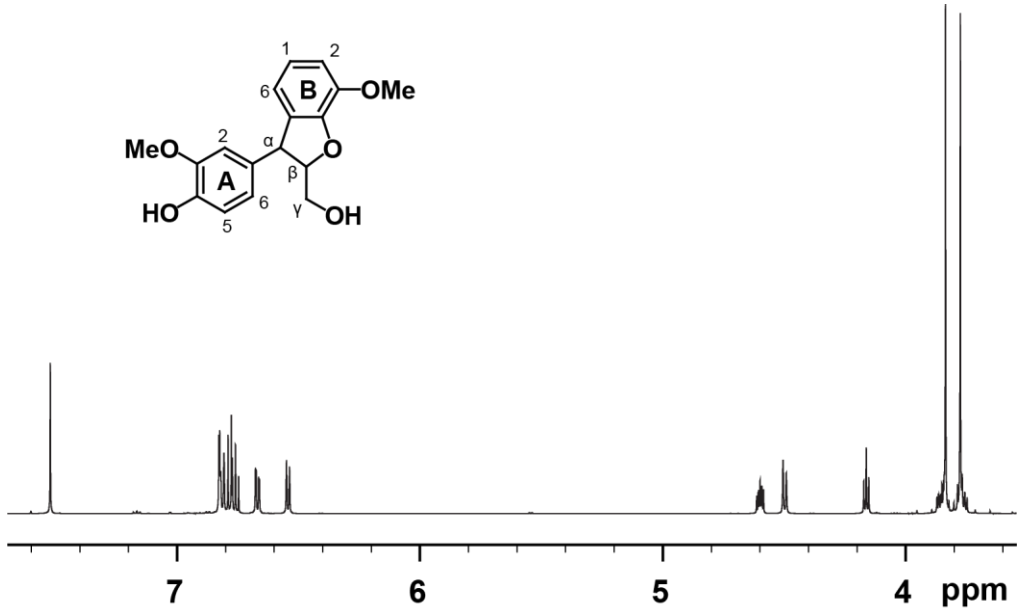

Fig.S8 ^{1}H NMR of phenyl dihydrobenzofuran **3** [17]

3, ^{1}H-NMR (acetone-d6, 600MHz): δ 7.52 (s, 1H; ArOH-H), 6.83 (d, J=2.0 Hz, 1H; A2), 6.81 (d, J=8.0 Hz, 1H; B2), 6.78 (d, J=8.1 Hz, 1H; A5), 6.76 (dd, J=8.0,7.6 Hz, 1H; B1), 6.67 (dd, J=8.1, 2.0 Hz, 1H; A6), 6.54 (dt, J=7.6Hz, 1H; B6), 4.61-4.58 (m, 1H; β-H), 4.50 (d, J=8.1 Hz, 1H; α-H), 4.16 (t, 1H; γOH-H), 3.86 (m, 1H; γ-H), 3.84 (s, 3H; OCH_3), 3.77 (s, 3H; OCH_3), 3.77 (m, 1H; γ-H).

^{13}C NMR (acetone-d6, 600MHz): δ 149.26 (C-B4), 148.49 (C-A3), 146.49 (C-A4), 145.44 (C-B3), 134.88 (C-A1), 133.03 (C-B5), 121.83 (C-B1), 121.48 (C-A6), 118.07(C-B6), 115.93 (C-A5), 112.73 (C-B2), 112.34 (C-A2), 93.49 (C-β), 63.40 (C-γ), 56.20 (C-OCH_3), 56.14 (C-OCH_3), 50.74 (C-α).

3.3 NMR Spectra of condensation product trimer 4

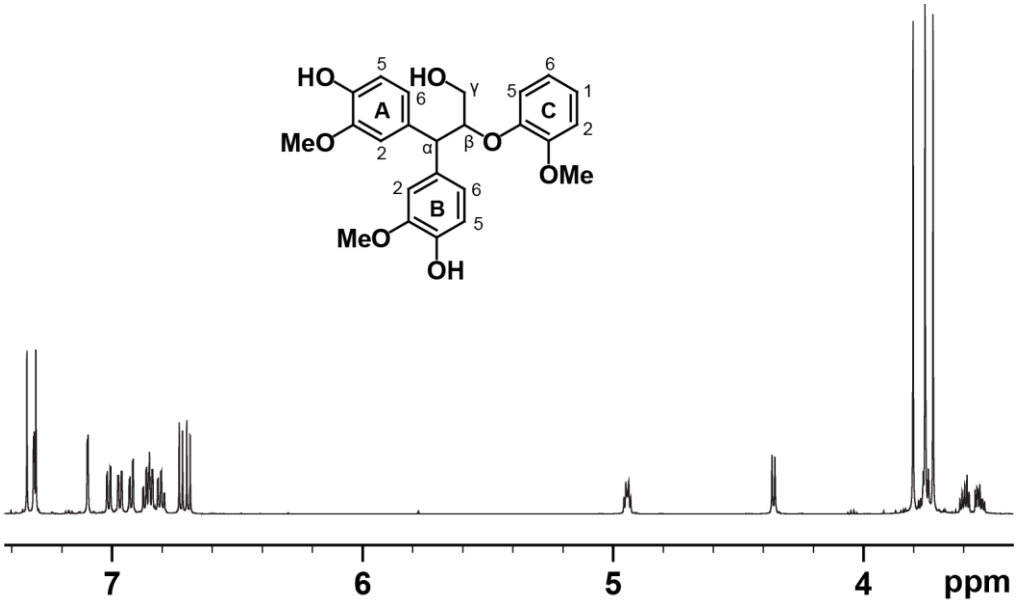

Fig.S9 ^{1}H NMR of trimer **4**

4, ^{1}H-NMR (acetone-d6, 600MHz): δ7.34 (s, 1H; ArOH-H), 7.31 (d, J=2.0 Hz, 1H; A2), 7.30 (s, 1H; ArOH-H), 7.10 (d, J=2.0 Hz, 1H; B2), 7.01 (dd, J=1.5, 8.0 Hz, 1H; C5), 6.97 (dd, J=2.0, 8.0 Hz, 1H; A6), 6.92 (dd, J=1.5,8.0Hz, 1H; C2), 6.86 (dt, 1H; C1), 6.84 (dd, J=2.0,6.5 Hz, 1H; B6), 6.80 (dt, J=1.6,7.8Hz, 1H; C6), 6.72 (d, J=8.0 Hz, 1H; A5), 6.69 (d, J=8.0 Hz, 1H; B5), 4.97-4.93 (m, 1H; β-H), 4.36 (d,J=6.9Hz, 1H; α-H), 3.80 (s, 3H; OCH_3), 3.75 (s, 3H; OCH_3), 3.72 (s, 3H; OCH_3), 3.62-3.57(m, 1H; γ-H), 3.77-3.51 (m, 1H; γ-H).

^{13}C NMR (Acetone-d6, 600MHz): δ 151.43 (C-C3), 149.18 (C-C4), 148.02 (C-B3), 147.86 (C-A3), 145.80 (C-B4), 145.76 (C-A4), 135.54 (C-B1), 134.44 (C-A1), 122.85 (C-A6), 122.40 (C-C1), 121.89 (C-B6), 121.75 (C-C6), 117.30 (C-C5), 115.47 (C-B5), 115.16 (C-A5), 113.81 (C-A2), 113.39 (C-C2), 112.94 (C-B2), 84.13 (C-β), 62.12 (C-γ), 56.26 (C-OCH_3), 56.17 (C-OCH_3), 56.07 (C-OCH_3), 52.56 (C-α).

3.4 Synthesis and NMR Spectra of enol ether compounds (5a, 5b)

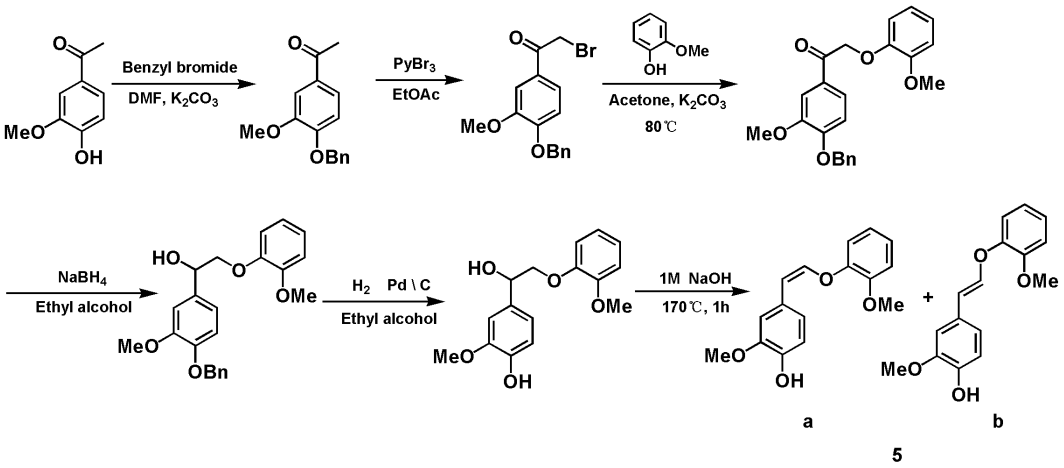

Fig.S10 Synthesis route of (E/Z)-4-hydroxy-3-methoxy-β-(2-methoxyphenoxy)styrene (enol ether compounds **5a-b**)

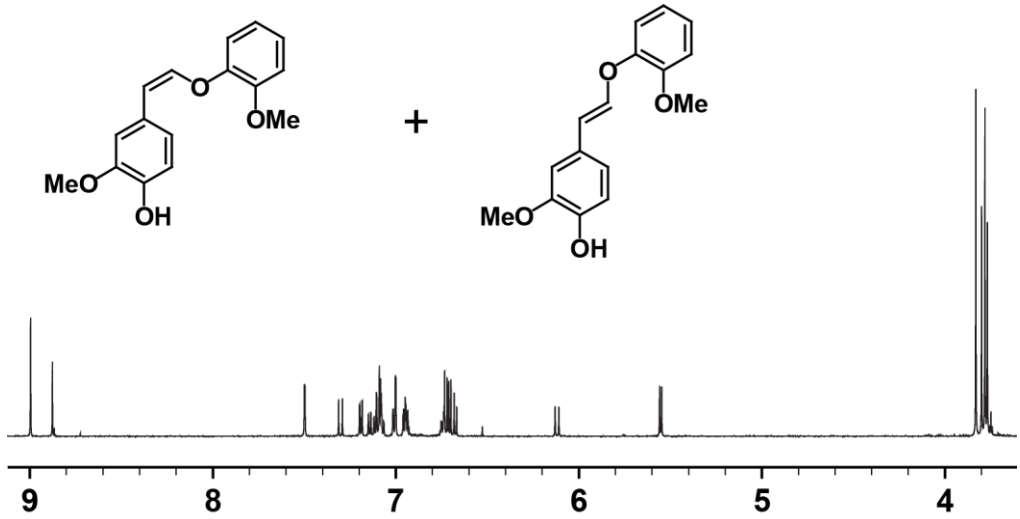

Fig.S11 ^{1}H NMR of enol ether compounds **5a-b**

5a, Z-isomer: ^{1}H NMR (DMSO-d6, 600MHz): δ 8.99 (s, 1H; ArOH-H), 7.50 (d, 1H; Ar-H), 7.18 (dd, 1H; Ar-H), 7.11 (dd, 1H; Ar-H), 7.07 (td, 1H; Ar-H), 7.01 (dd, 1H; Ar-H), 6.94 (td, 1H; Ar-H), 6.72 (d, 1H; Ar-H), 6.69 (d, 1H; β-H), 5.55 (d, 1H; α-H), 3.83 (s, 3H; OCH_3), 3.78 (s, 3H; OCH_3).

5b, E-isomer: ^{1}H NMR (DMSO-d6, 600MHz): δ 8.87 (1H, s, H-ArOH), 7.30 (1H, d, H-βH), 7.14 (1H, d, H-ArH), 7.09 (1H, dd, H-ArH), 7.08 (1H, td, H-ArH), 7.01 (1H, dd, H-ArH), 6.94 (1H, td, H-ArH), 6.74 (1H, dd, H-ArH), 6.67 (1H, d, H-ArH), 6.12 (1H, d, H-αH), 3.80 (3H, s, H-OCH_3), 3.77 (3H, s, H-OCH_3).

3.5 NMR Spectra of Hibbert's Ketone 10

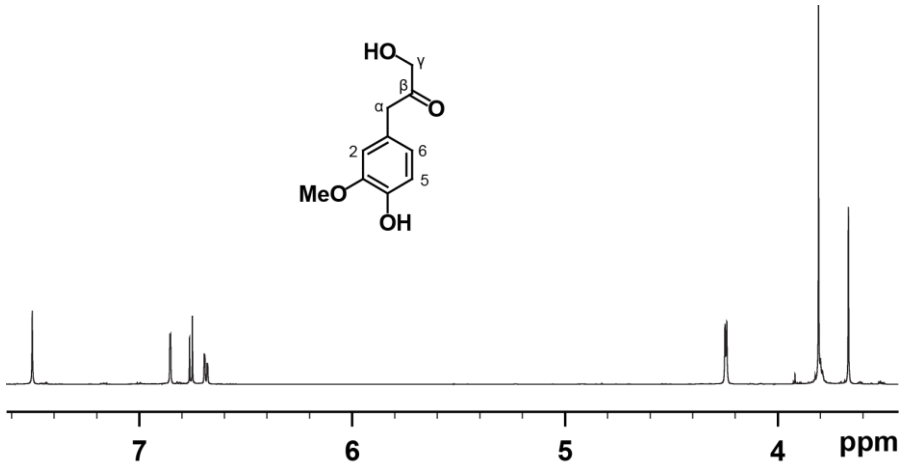

Fig.S12 ^{1}H NMR of Hibbert's Ketone **10**

10, ^{1}H-NMR (acetone-d6, 600MHz): δ 7.54 (s, 1H; ArOH-H), 6.85 (d, J=2.0 Hz, 1H; 2-H), 6.75 (d, J=8.0Hz, 1H; 5-H), 6.68 (dd, J=2.0, 8.0Hz, 1H; 6-H), 4.24 (s, 1H; γ-H), 3.87-3.81 (m, 1H; OH-H), 3.81 (s, 1H; OCH_3), 3.67 (s, 1H; α-H).

^{13}C NMR (acetone-d6, 600MHz): δ 208.68 (C-β), 148.29 (C-3), 146.45 (C-4), 126.24 (C-1), 122.92 (C-6), 115.77 (C-5), 113.86 (C-2), 68.08 (C-γ), 45.35 (C-α), 56.18 (C-OCH_3).

3.6 TIC (total ion chromatogram) of the products obtained from β-O-4

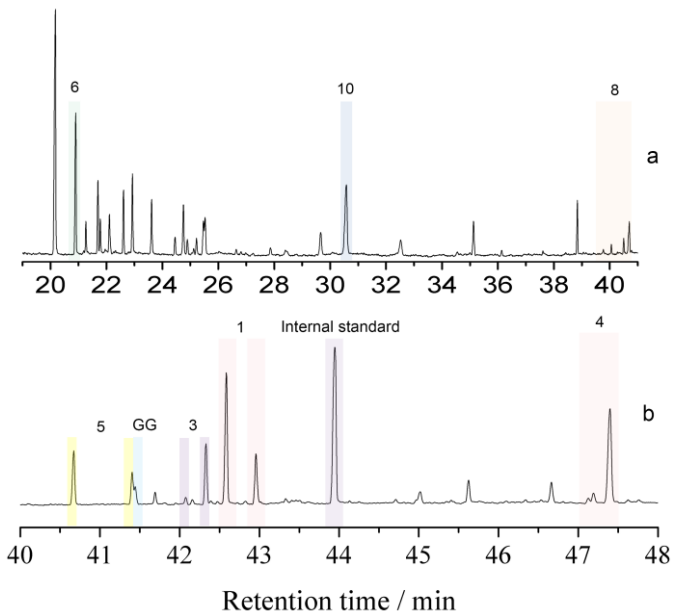

Fig.S13 GC-MS of the products obtained from β-O-4 at 170°C after GVL-H_2O-H_2SO_4 treatment a) to show products **6**, **8** and **10** were produced in 10 min reaction; b) to show products **1**, **3**, **4** and **5** were produced in 5 min reaction.

3.7 TIC (total ion chromatogram) of the products obtained from 1,3-dioxane compounds

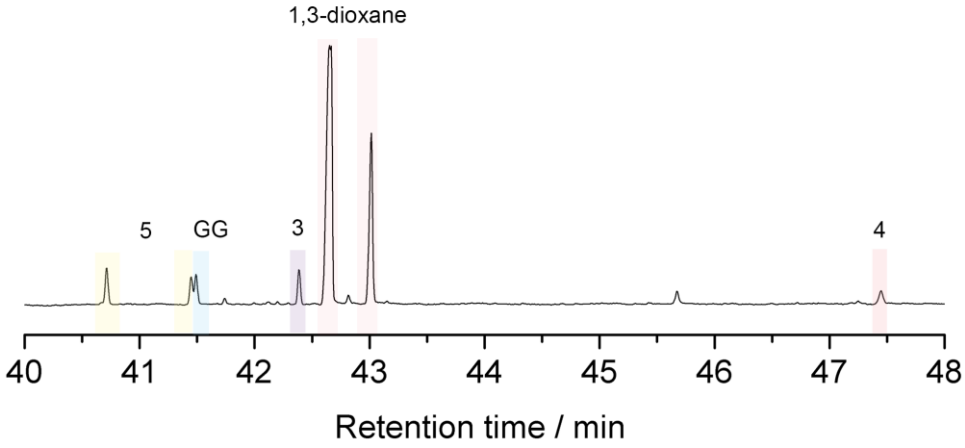

Fig.S14 GC-MS of the products obtained from 1,3-dioxane structures at 170°C in 5 min after GVL-H_2O-H_2SO_4 treatment

4. Synthesis and NMR Spectra of products obtained from β-5

4.1 Phenylcoumarone 24

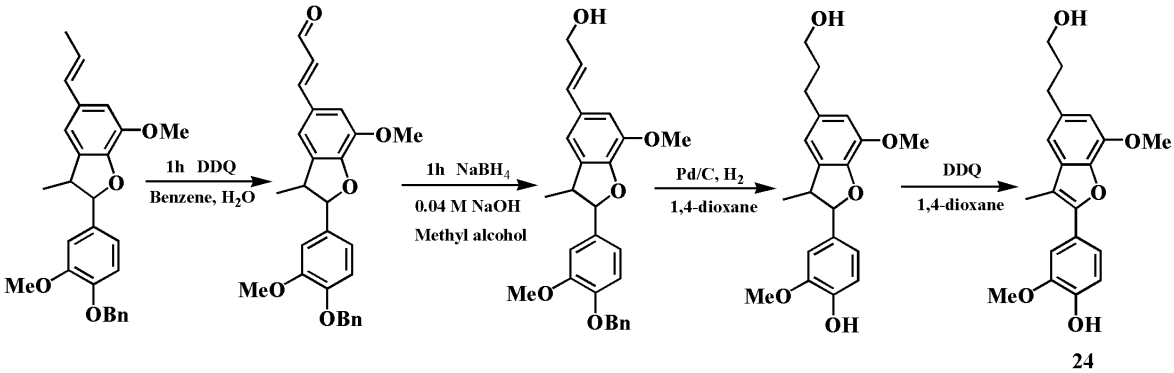

Fig.S15 Synthesis route of phenylcoumarone **24**

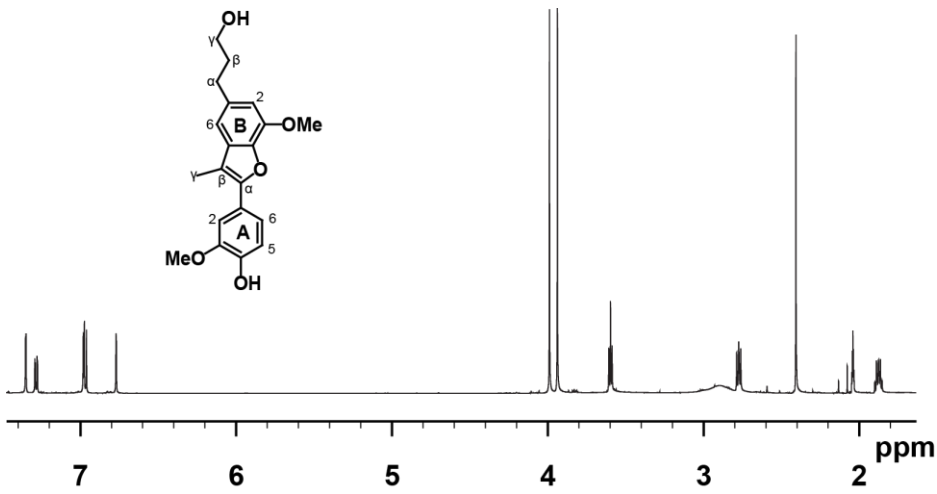

Fig.S16 ^{1}H NMR of phenylcoumarone **24**

24, ^{1}H-NMR (acetone-d6, 600MHz): δ 7.35 (d, J=2.0 Hz, 1H; A2), 7.28 (dd, J=2.0, 8.2 Hz, 1H; A6), 6.98 (t, J=1.2 Hz, 1H; B6), 6.97 (d, J= 8.2 Hz, 1H; A5), 6.77 (d, J=1.2Hz, 1H; B2), 3.99 (s, 3H; OCH_3), 3.94 (s, 3H; OCH_3), 3.60 (t, J=6.4Hz, 1H; Bγ-H), 2.77 (t, J=7.8Hz, 1H; Bα-H), 2.41 (s, 1H; Aγ-H), 1.91-1.85 (m, 1H; Bβ-H).

^{13}C NMR (acetone-d6, 600MHz): δ 151.98 (C-Aα), 148.52 (C-A3), 147.80 (C-A4), 145.64 (C-B3), 141.96 (C-B4), 138.65 (C-B1), 133.77 (C-B5), 124.04 (C-A1), 120.94 (C-A6), 116.16 (C-A5), 111.43 (C-B6), 110.87 (C-A2), 110.38 (C-Aβ), 108.55 (C-B2), 61.78(C-Bγ), 56.33 (C-OCH_3), 56.27 (C-OCH_3), 36.05 (C-Bβ), 33.21 (C-Bα), 9.64 (C-Aγ).

4.2 Stilbene 25

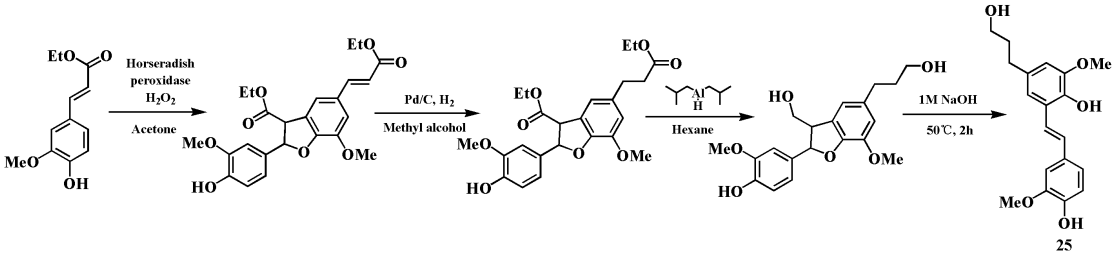

Fig.S17 Synthesis route of stilbene **25**

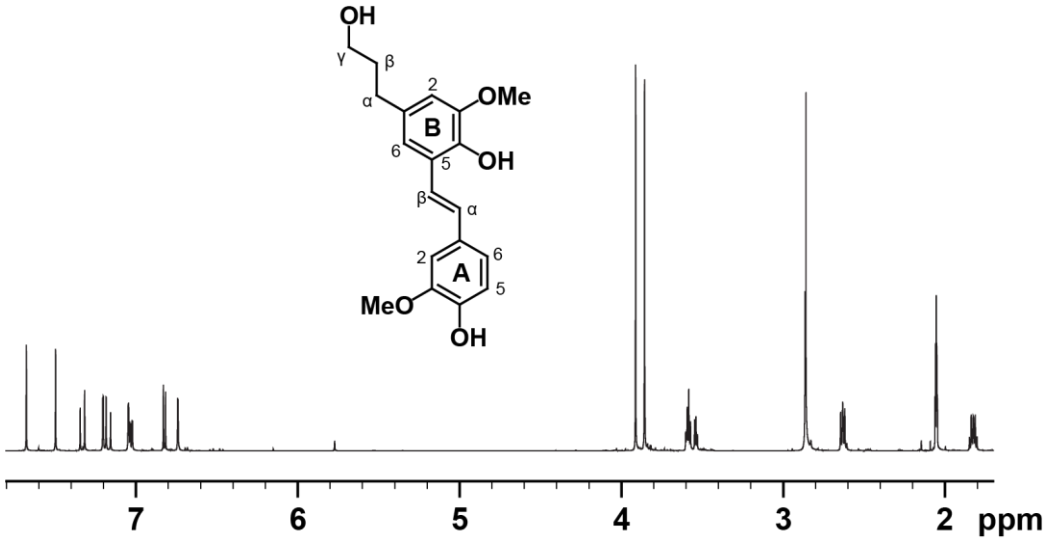

Fig.S18 ^{1}H NMR of stilbene **25**

25, ^{1}H-NMR (acetone-d6, 600MHz): δ 7.32 (d, J=16.5Hz, 1H; Aβ-H), 7.19 (d, J=1.9 Hz, 1H; A2), 7.16 (d, J=16.5Hz, 1H; Aα-H), 7.03 (d, J=1.7 Hz, 1H; B6), 7.01 (dd, J=1.9, 8.1 Hz, 1H; A6), 6.81 (d, J= 8.1 Hz, 1H; A5), 6.73 (1H, d, J=1.7Hz, H-B2), 3.90 (3H, s, H-OCH_3), 3.84 (3H, s, H-OCH_3), 3.60-3.55 (1H, m, H-Bγ), 2.62 (t, J=7.51Hz, 1H; Bα-H), 1.84-1.78 (m, 1H; Bγ-H).

^{13}C NMR (acetone-d6, 600MHz): δ 148.56 (C-A3), 148.24 (C-B3), 147.31 (C-A4), 142.85 (C-B4), 133.96 (C-B1), 131.19 (C-A1), 129.40 (C-Aα), 124.71 (C-B5), 121.72 (C-Aβ), 120.82 (C-A6), 118.58 (C-B6), 115.94 (C-A5), 111.04 (C-B2), 110.0 (C-A2), 61.78 (C-Bγ), 56.34 (C-OCH_3), 56.21 (C-OCH_3), 35.78 (C-Bβ), 32.65 (C-Bα).

4.3 Coumaran 27

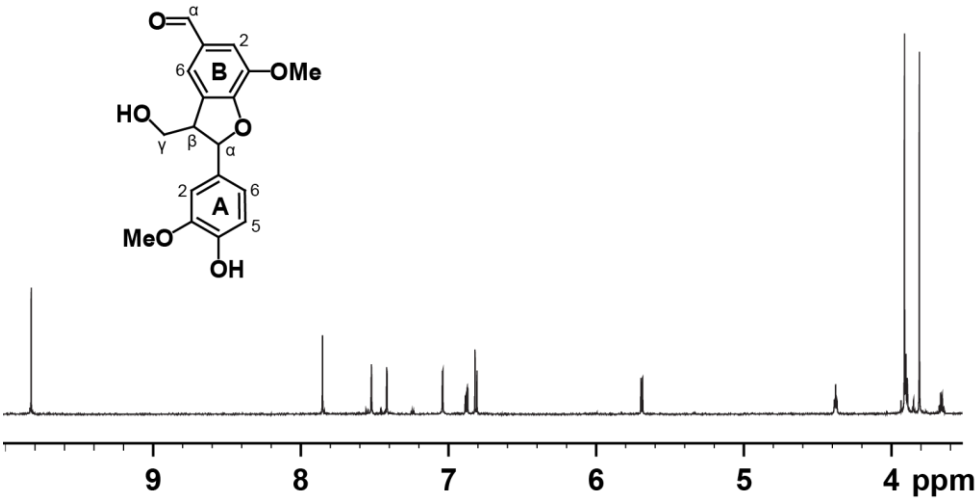

Fig.S19 ^{1}H NMR of benzoaldehyde coumaran **27**

27, ^{1}H-NMR (acetone-d6, 600MHz): δ 9.82 (s, 1H; Bα-H), 7.86 (s, 1H; ArOH-H), 7.52 (t, J=1.2 Hz, 1H; B6), 7.42 (d, J=1.4 Hz, 1H; B2), 7.04 (d, J=2.0 Hz, 1H; A2), 6.88 (dd, J=2.0, 8.1 Hz, 1H; A6), 6.81 (d, J=8.1Hz, 1H; A5), 5.69 (d, J=6.8Hz, 1H; Aα-H), 4.38 (t, 1H; γOH-H), 3.91 (s, 3H; OCH_3), 3.91-3.87 (m, 1H; Aγ-H), 3.81 (s, 3H; OCH_3), 3.68-3.63 (m, 1H; Aβ-H).

^{13}C NMR (acetone-d6, 600MHz): δ 191.05 (C-Bα), 154.83 (C-B4), 148.51 (C-A3), 147.67 (C-A4), 145.76 (C-B3), 133.31 (C-A1), 132.32 (C-B1), 131.14 (C-B5), 121.47 (C-B6), 119.74 (C-A6), 115.80 (C-A5), 113.34 (C-B2), 110.64 (C-A2), 89.85 (C-Aα), 64.15 (C-Aγ), 56.32 (C-OCH_3), 56.25 (C-OCH_3), 53.79 (C-Aβ).

4.4 Phenylcoumarone 29

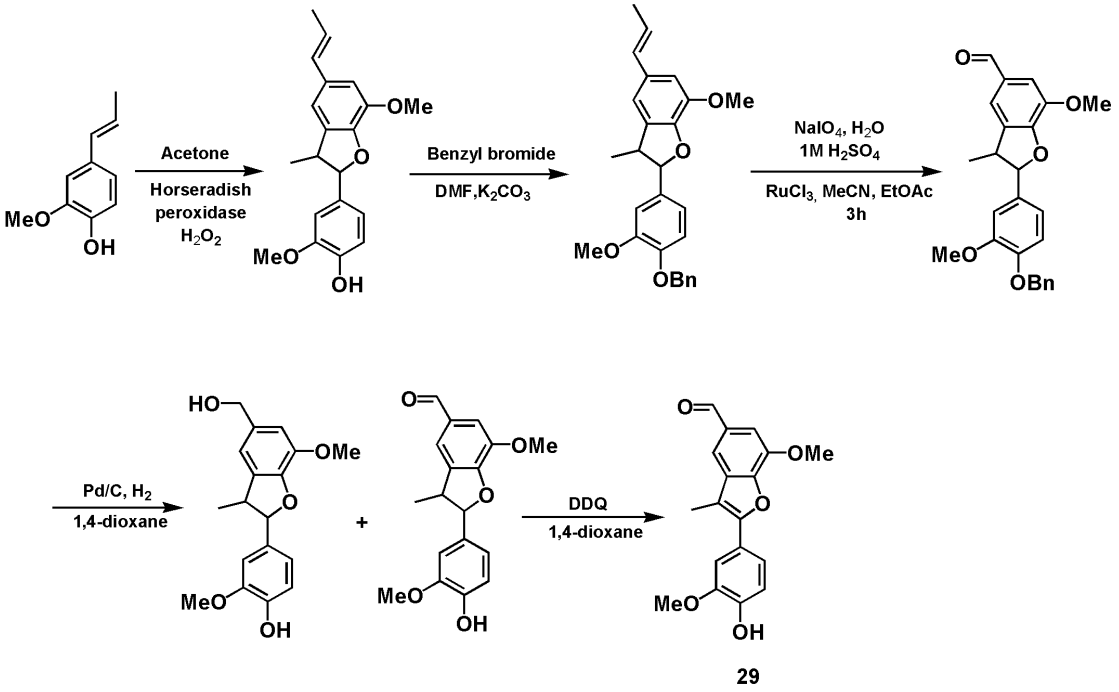

Fig.S20 Synthesis route of phenylcoumarone **29**

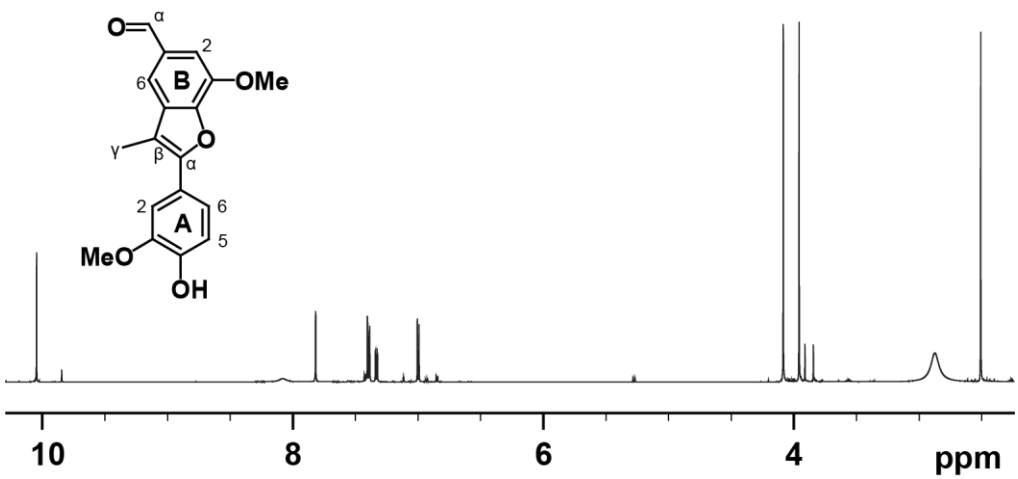

Fig.S21 ^{1}H NMR of phenylcoumarone **29**[18]

29, ^{1}H-NMR (acetone-d6, 600MHz): δ 10.05 (s, 1H; Bα-H), 7.82 (d, J=1.28 Hz, 1H; B6), 7.40 (d, J=1.2 Hz, 1H; B2), 7.38 (d, J=2.0 Hz, 1H; A2), 7.33 (dd, J=8.20, 2.0Hz, 1H; A6), 7.00 (d, J=8.2 Hz, 1H; A5), 4.08 (s,3H; OCH_3), 3.96 (s, 3H; OCH_3), 2.50 (s, 3H; CH_3).

4.5 Stilbene 30

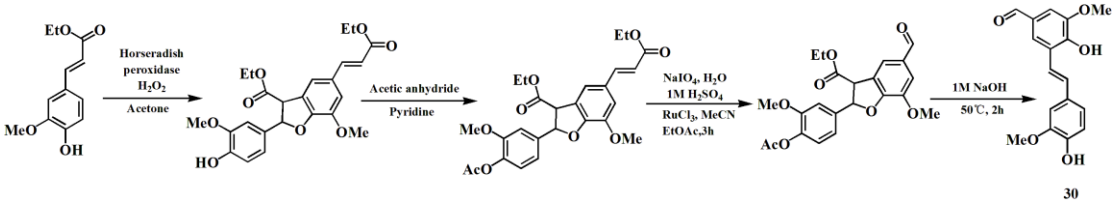

Fig.S22 Synthesis route of stilbene **30**

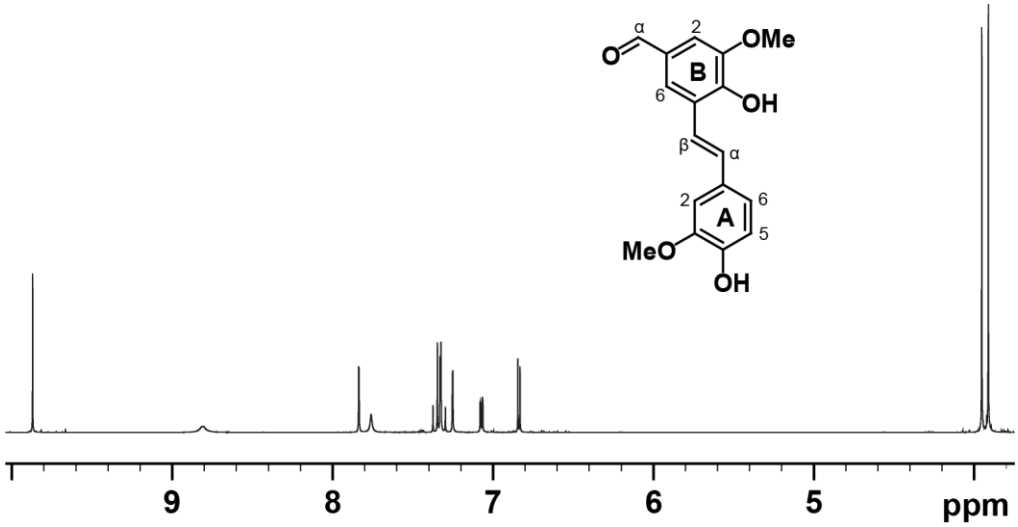

Fig.S23 ^{1}H NMR of stilbene **30**[18]

30, ^{1}H-NMR (acetone-d6, 600MHz): δ 9.87 (s, 1H; Bα-H), 7.83 (d, J=1.7 Hz, 1H; B6), 7.36 (d,

J=16.5 Hz, 1H; Aβ-H), 7.33 (d, J=1.9 Hz, 1H; B2), 7.31 (d, J=16.5 Hz, 1H; Aα-H), 7.25 (d, J=1.7 Hz, 1H; A2), 7.07 (dd, J=8.1, 1.9Hz, 1H; A6), 6.84 (d, J=8.13 Hz, 1H; A5), 3.95 (s, 3H; OCH_3), 3.91 (s, 3H; OCH_3).

^{13}C NMR (acetone-d6, 600MHz): δ 191.52 (C-Bα), 150.30 (C-B4), 149.07 (C-B3), 148.66 (C-A3), 147.80 (C-A4), 131.19 (C-Aα), 130.53 (C-A1), 130.00 (C-B1), 125.58 (C-B5), 124.06 (C-B6), 121.21 (C-A6), 120.07 (C-Aβ), 116.03 (C-A5), 110.22 (C-A2), 108.38 (C-B2), 56.50 (C-OCH_3), 56.22 (C-OCH_3).

5. Products obtained from syringaresinol (β-β)

5.1 Syringaresinol

31, ^1H-NMR (acetone-d6, 600MHz): δ 6.67 (s, 4H; A\B2\6), 4.66 (d, J=4.2 Hz, 2H; A\Bα-H), 4.21 (dd, J=6.9, 8.9 Hz, 2H; A\Bγ-H), 3.87-3.76 (m, 2H; A\Bγ-H), 3.87-3.76 (s,12H; OCH_3), 3.12-3.04 (m, 2H; Aβ-H).

^{13}C NMR (Acetone-d6, 600MHz): δ148.61 (C-A\B-3\5), 136.07 (C- A\B-4), 133.13 (C-A\B-1), 104.30 (C-A\B-2\6), 86.74 (C- A\B-α), 72.29 (C-A\B-γ), 56.55 (C-OCH_3), 56.53 (C-OCH_3), 55.26 (C- A\B-β).

5.2 Epi-syringaresinol

32, ^1H-NMR (acetone-d6, 600MHz): δ 6.68 (s, 4H; A\B2\6), 4.81 (d, J=6.0 Hz, 1H; Bα-H), 4.34 (d, J=7.0 Hz, 1H; Aα-H), 4.12 (m, 1H; Bγ-H), 3.87-3.76 (m, 2H; A\Bγ-H), 3.87-3.76 (s, 12H; OCH_3), 3.23-3.18 (m, 1H; Aγ-H), 3.51-3.47 (m, 1H; Aβ-H), 2.93-2.82 (m, 1H; Bβ-H).

^{13}C NMR (Acetone-d6, 600MHz): δ 148.59 (C-A\B-3\5), 148.49 (C-A\B-3\5), 136.13 (C-A\B-4), 135.56 (C-A\B-4), 133.24 (C-A\B-1), 130.32 (C-A\B-1), 104.29 (C-A\B-2\6), 103.89 (C-A\B-2\6), 88.65 (C-A\B-α), 82.74 (C-A\B-α), 71.43 (C-A\B-γ), 70.10 (C-A\B-γ), 56.55 (C-OCH_3), 56.53 (C-OCH_3), 55.65 (C- A\B-β), 50.19 (C- A\B-β).

5.3 Dia-syringaresinol

33, ^{1}H-NMR (acetone-d6, 600MHz): δ 6.69 (s, 4H; A\B2\6), 4.86 (d, J=4.9 Hz, 2H; A\Bα-H), 3.87-3.76 (s, 12H; OCH_3), 3.61-3.53 (m, 2H; A\Bγ-H), 3.51-3.47 (m, 2H; A\Bγ-H), 3.43-3.35 (m, 2H; Aβ-H).

^{13}C NMR (Acetone-d6, 600MHz): δ 147.03 (C-A\B-3\5), 135.70 (C-A\B-4), 130.85 (C-A\B-1), 104.54 (C-A\B-2\6), 84.77 (C-A\B-α), 69.23 (C-A\B-γ), 56.55 (C-OCH_3), 56.53 (C-OCH_3), 50.19 (C- A\B-β).

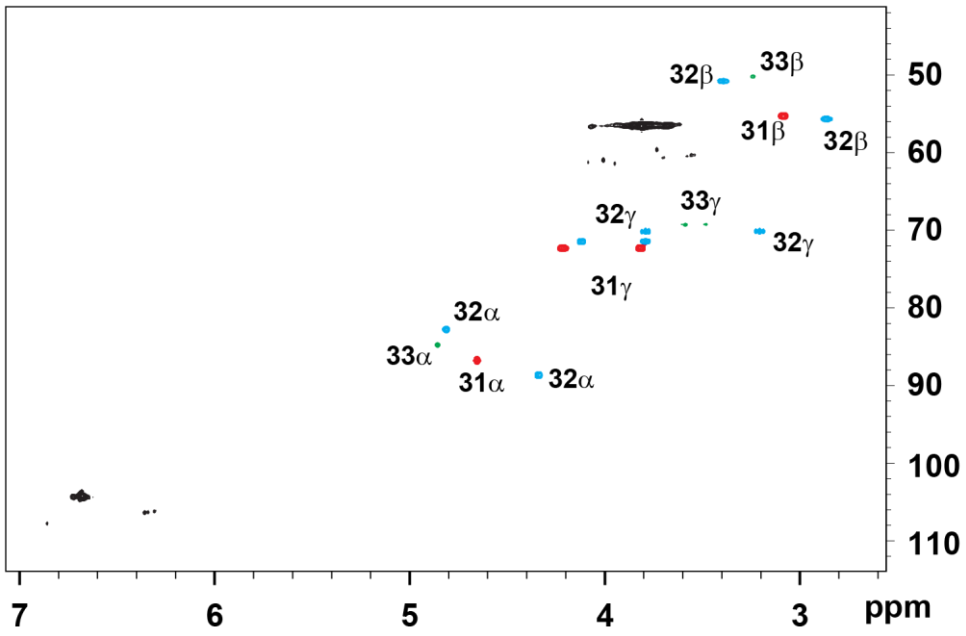

Fig.24 2D HSQC NMR spectrum of products of β-β after GVL-H_2O-H_2SO_4 treatment[19, 20]

5.4 GC-MS of the products obtained from β-β

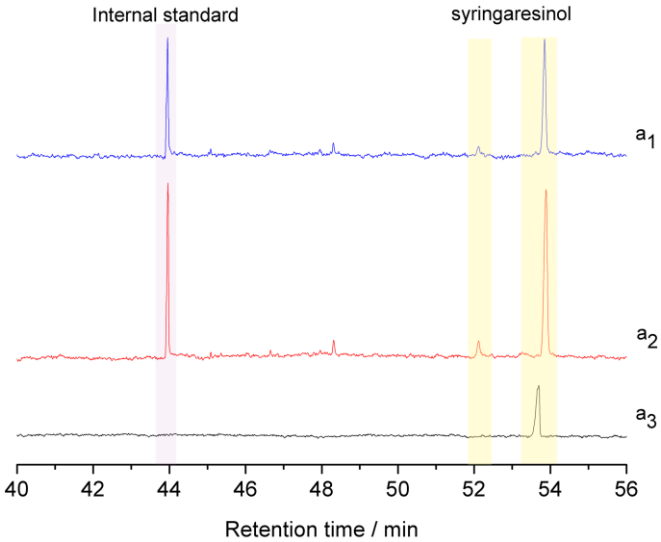

Fig.S25 GC-MS of the products obtained from β-β at 170°C after GVL-H_2O-H_2SO_4 treatment

a_1: products obtained from β-β in 60min; a_2: products obtained from β-β in 40min; a_3: β-β lignin model compound.

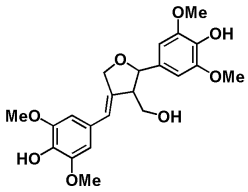

Fig.S26 The possible structure of the product eluted at retention time of 48.43 min

Based on the TMS-derived molecular ion of 632 for the peak at 48.43 (Fig.S24), we speculated the structure of the product is as showed in Fig.S26.

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