Supplementary Information

Pyrolysis-assisted catalytic conversion of wood in hot-compressed water for the production of aromatic monomers and syngas without external hydrogen addition

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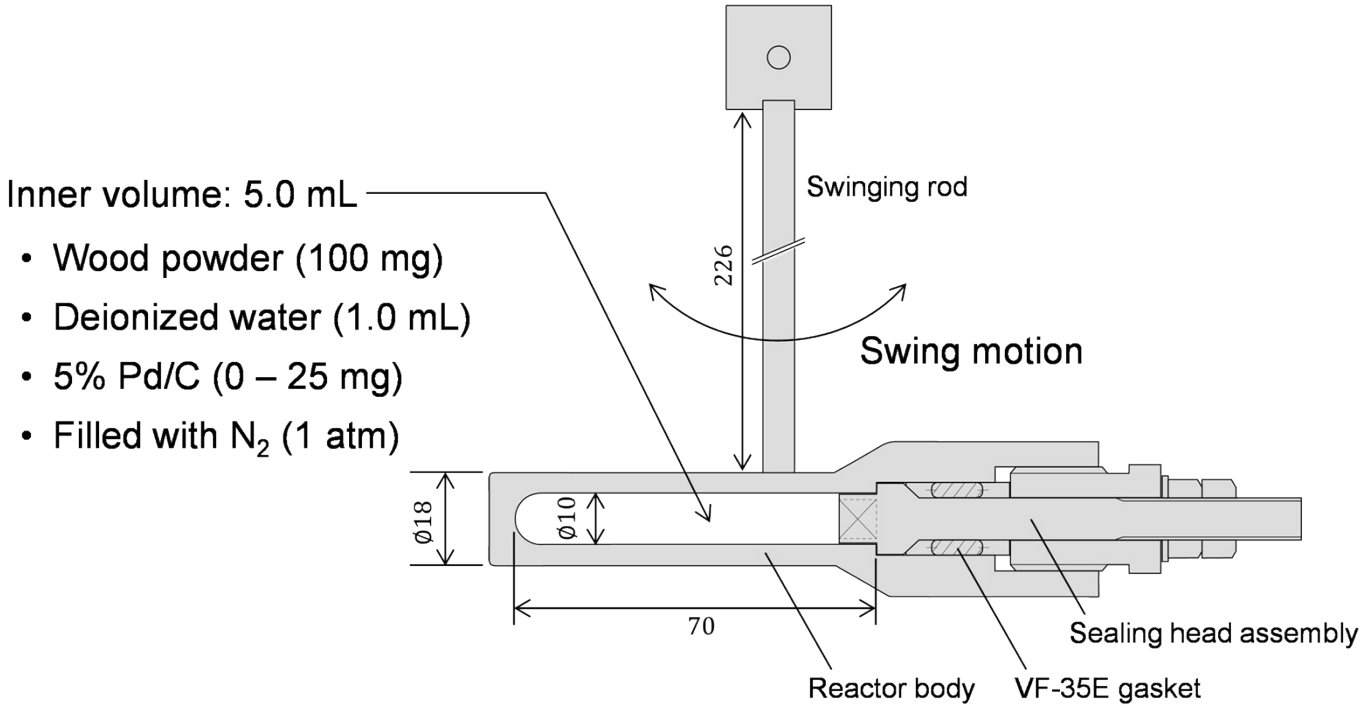


Fig. S1 Schematic diagram of the Inconel 625 batch reactor used for the conversion.

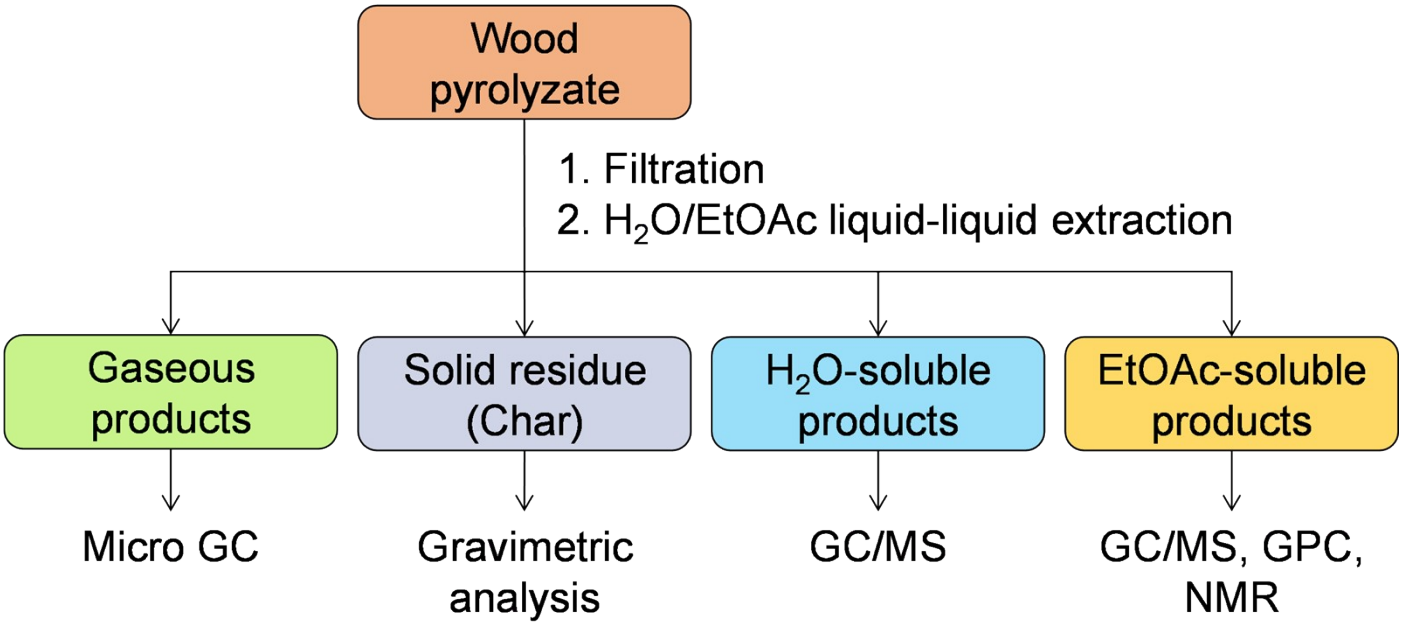


Fig. S2 Fractionation and analytical methods of the products.

Table S1 Yields of solid residue (char), gaseous products and lignin-derived monomers from wood at various pyrolysis conditions.

Reaction conditions					Japanese beech			Japanese cedar		
Temperature (°C)	Reaction time (min)	Pd/C catalyst (mg)	Solvent	Solvent volume (mL)	Solid residue (wt.%)	Gas yield (C-mol%)	Monomer yield (mol%)	Solid residue (wt.%)	Gas yield (C-mol%)	Monomer yield (mol%)
300	60	25	H_2O	1	4.1	40.9	69.7	8.9	28.9	42.9
350	60	25	H_2O	1	0.9	43.6	70.0	4.8	36.7	51.2
375	60	25	H_2O	1	4.9	46.3	77.1	7.4	41.0	58.0
400	60	25	H_2O	1	6.0	43.9	68.9	1.8	48.0	59.4
450	60	25	H_2O	1	10.4	58.0	23.1	ND*	53.6	46.3
350	60	0	H_2O	1	6.3	14.3	39.8	13.3	9.6	20.3
350	5	25	H_2O	1	4.6	23.2	43.0	4.7	43.2	29.4
350	15	25	H_2O	1	2.6	51.8	44.6	12.6	48.4	34.0
350	30	25	H_2O	1	ND	41.4	76.1	6.7	47.2	51.5
400	5	25	H_2O	1	1.5	30.4	66.7	3.4	31.3	38.3
400	15	25	H_2O	1	5.4	27.3	74.3	3.3	36.3	42.3
400	30	25	H_2O	1	6.7	35.5	69.3	ND	35.2	50.2
350	60	25	H_2O	2	1.9	35.4	81.6	-	-	-
400	60	25	H_2O	2	1.2	38.5	50.6	-	-	-
450	5	25	H_2O	1	8.8	60.6	55.9	ND	60.5	57.7
300	5	25	H_2O	1	8.0	33.6	23.1	9.6	34.2	25.7

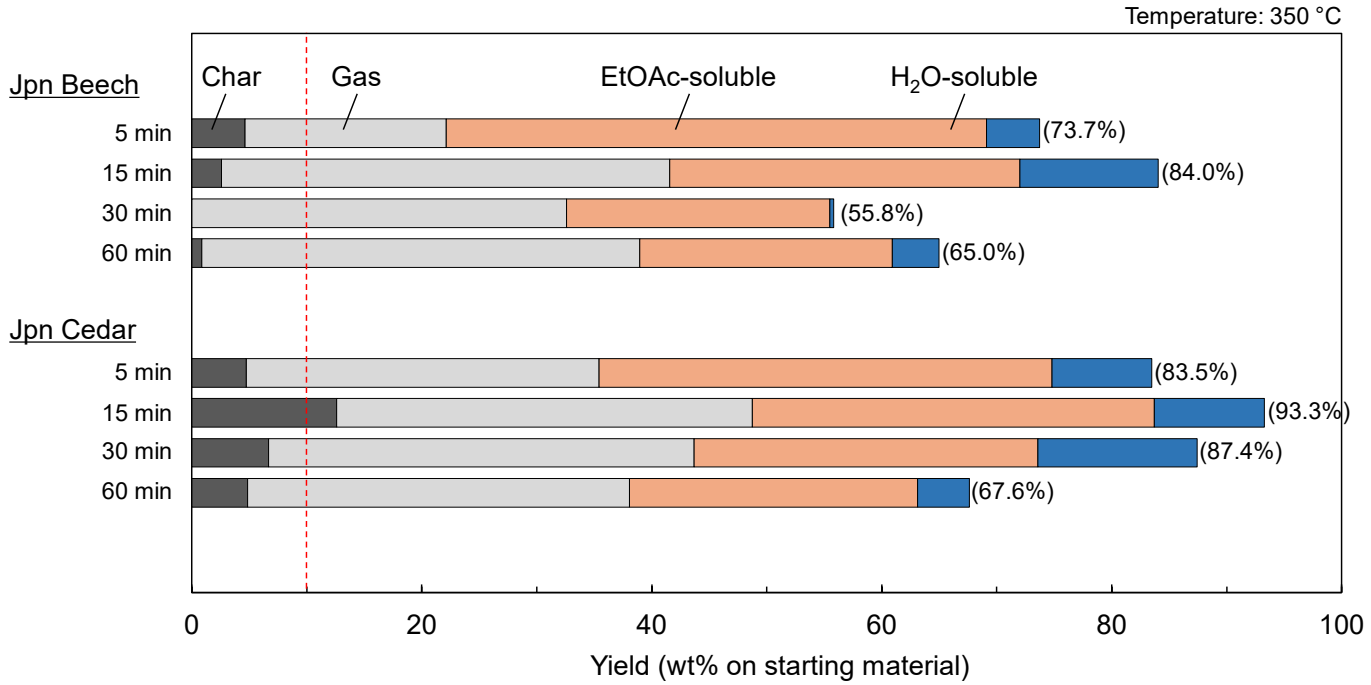


Fig. S3 Yields of char, gas, EtOAc-soluble and water-soluble products from Japanese beech and Japanese cedar (100 mg) treated at 350 °C for various reaction times in H_2O (1 mL) under N_2 (1 atm, prior to heating) over Pd/C (25 mg). Values in parentheses indicate the total yield of the products.

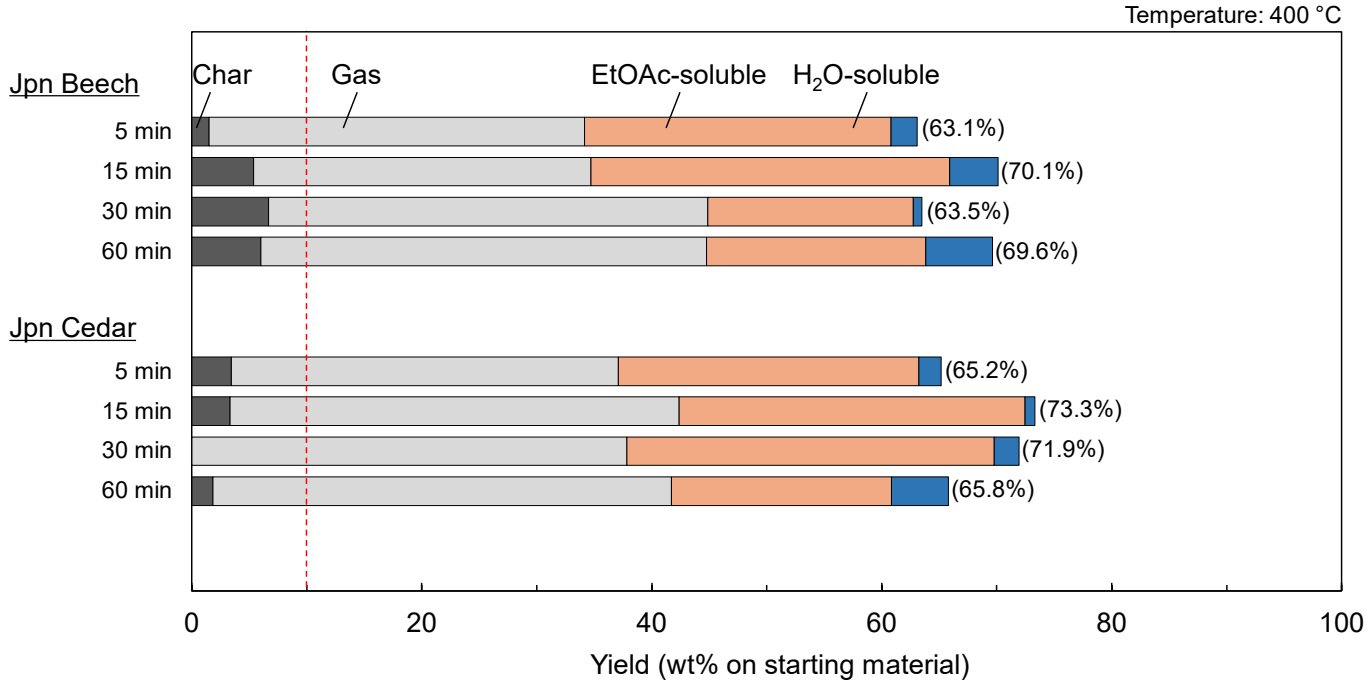


Fig. S4 Yields of char, gas, EtOAc-soluble and water-soluble products from Japanese beech and Japanese cedar (100 mg) treated at 400 °C for various reaction times in H_2O (1 mL) under N_2 (1 atm, prior to heating) over Pd/C (25 mg). Values in parentheses indicate the total yield of the products.

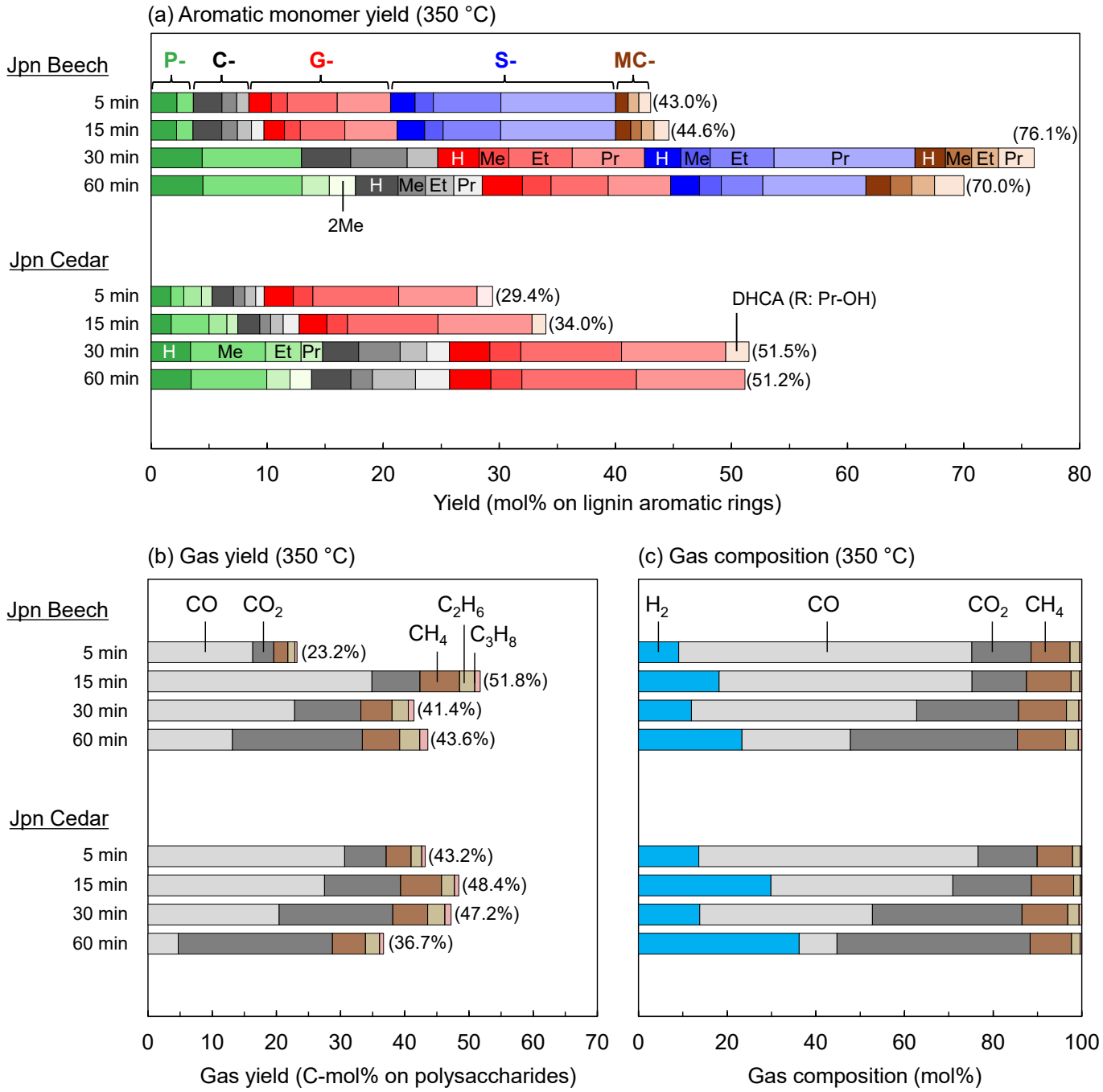


Fig. S5 Yields of (a) aromatic monomers, (b) gaseous products, and (c) gas composition from Japanese beech and Japanese cedar (100 mg) treated at 350 °C for various reaction times in H_2O (1 mL) under N_2 (1 atm, prior to heating) over Pd/C (25 mg). Values in parentheses indicate the total yield of aromatic monomers or gases.

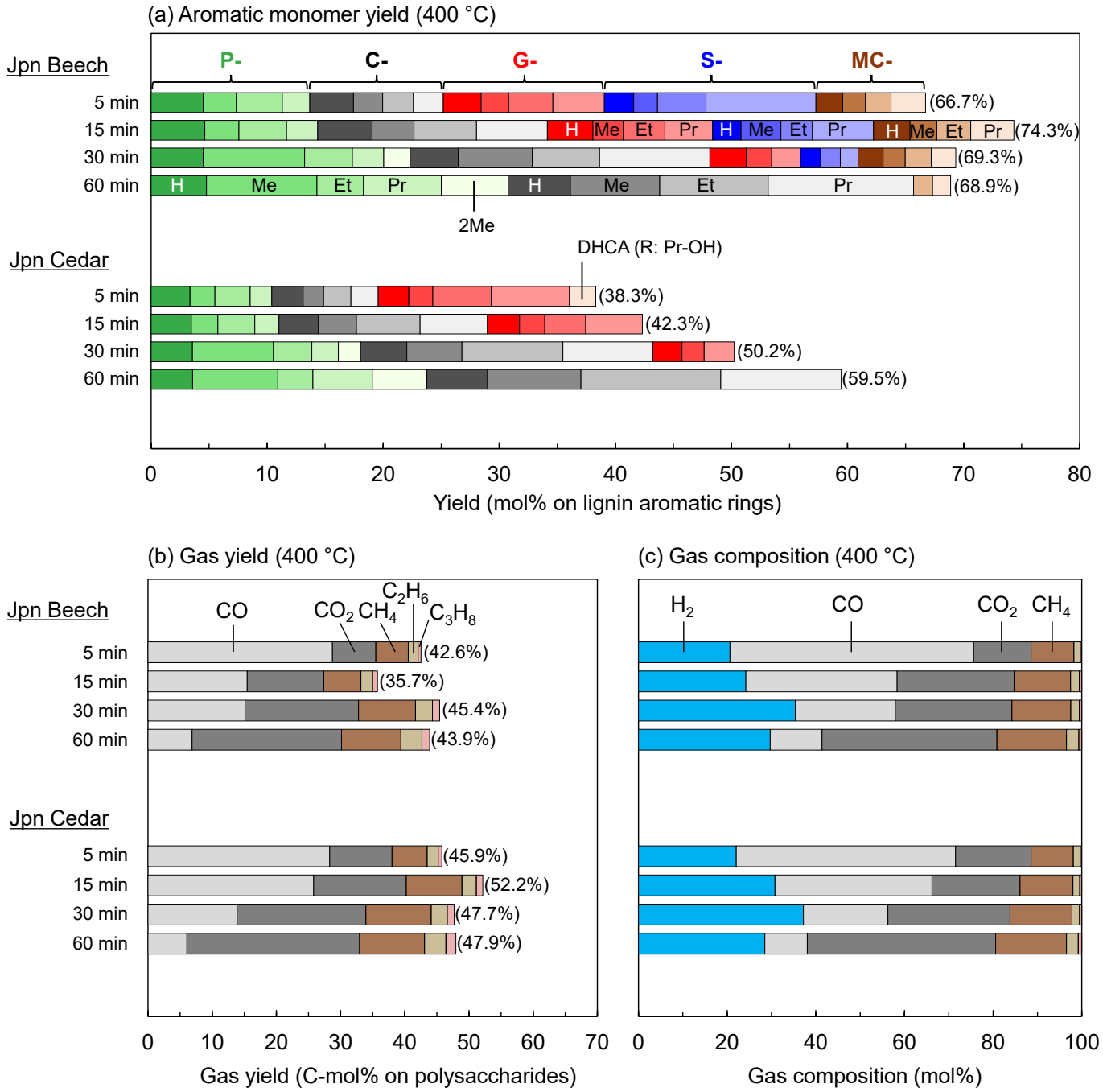


Fig. S6 Yields of (a) aromatic monomers, (b) gaseous products, and (c) gas composition from Japanese beech and Japanese cedar (100 mg) treated at 400 °C for various reaction times in H_2O (1 mL) under N_2 (1 atm, prior to heating) over Pd/C (25 mg). Values in parentheses indicate the total yield of aromatic monomers or gases.

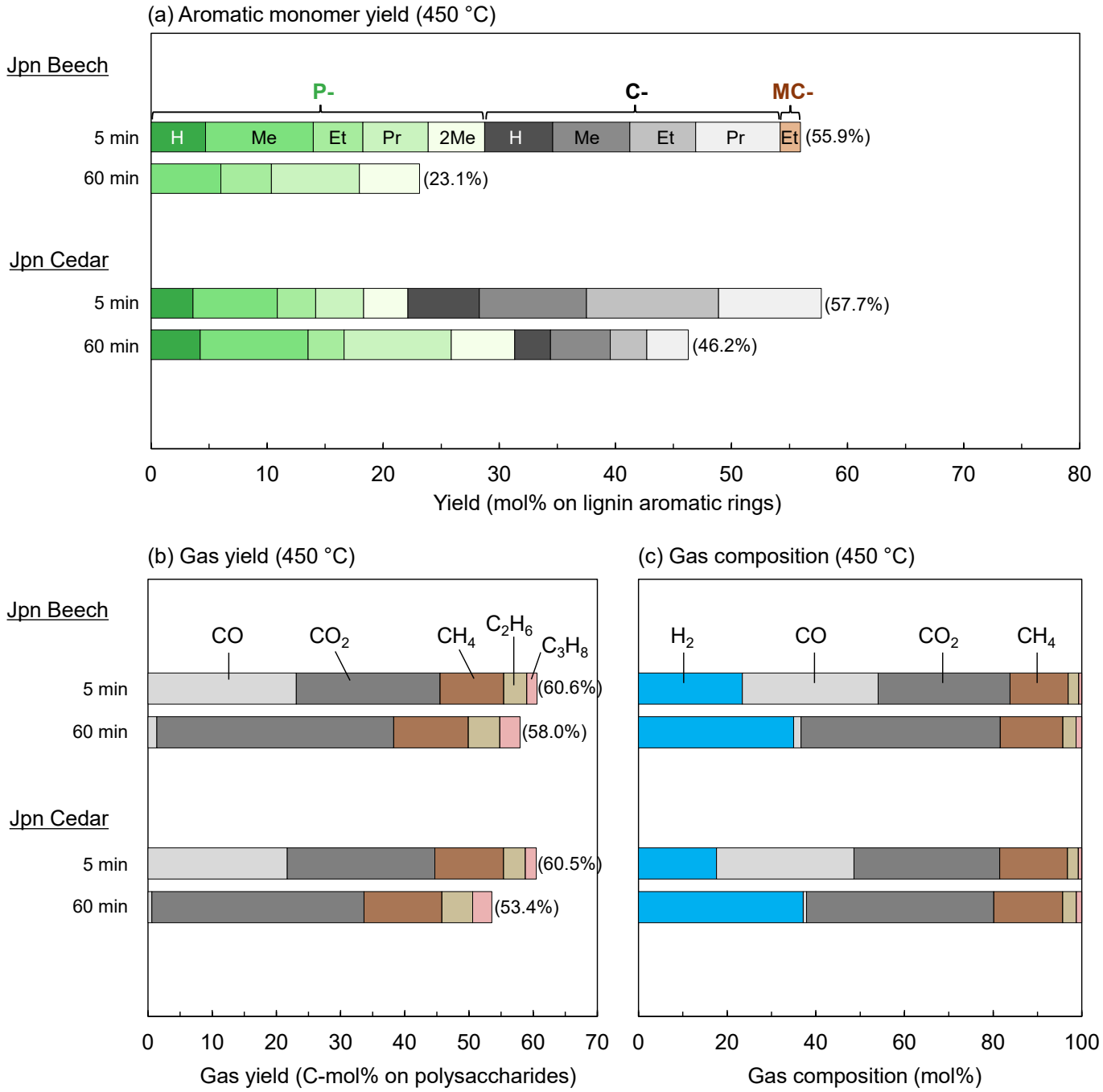


Fig. S7 Yields of (a) aromatic monomers, (b) gaseous products, and (c) gas composition from Japanese beech and Japanese cedar (100 mg) treated at 450 °C for various reaction times in H_2O (1 mL) under N_2 (1 atm, prior to heating) over Pd/C (25 mg). Values in parentheses indicate the total yield of aromatic monomers or gases.

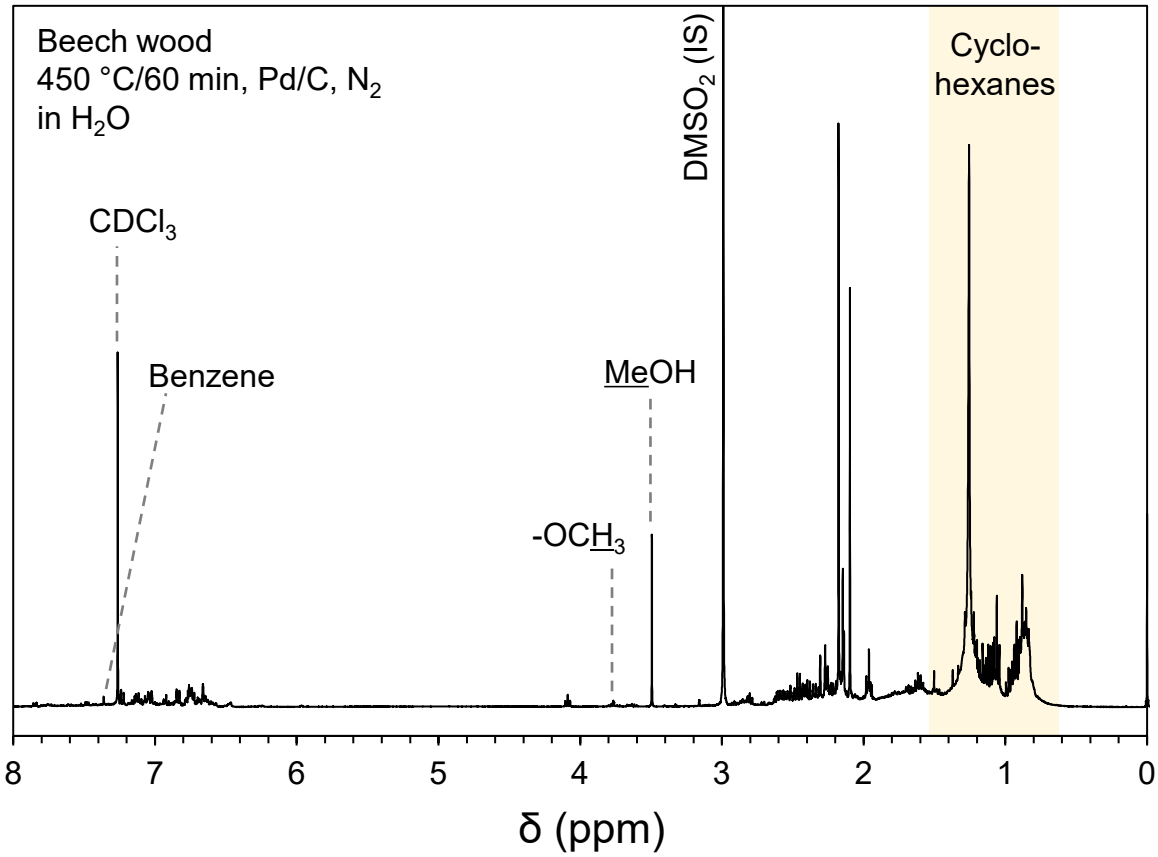


Fig. S8 ^{1}H-NMR spectrum (400 MHz) of $CDCl_3$-soluble products obtained from Japanese beech (100 mg) over Pd/C (25 mg) in H_2O (1 mL) under N_2 atmosphere (1 atm, prior to heating) at 450 °C for 60 min. Internal standard (IS): dimethyl sulfone ($DMSO_2$).

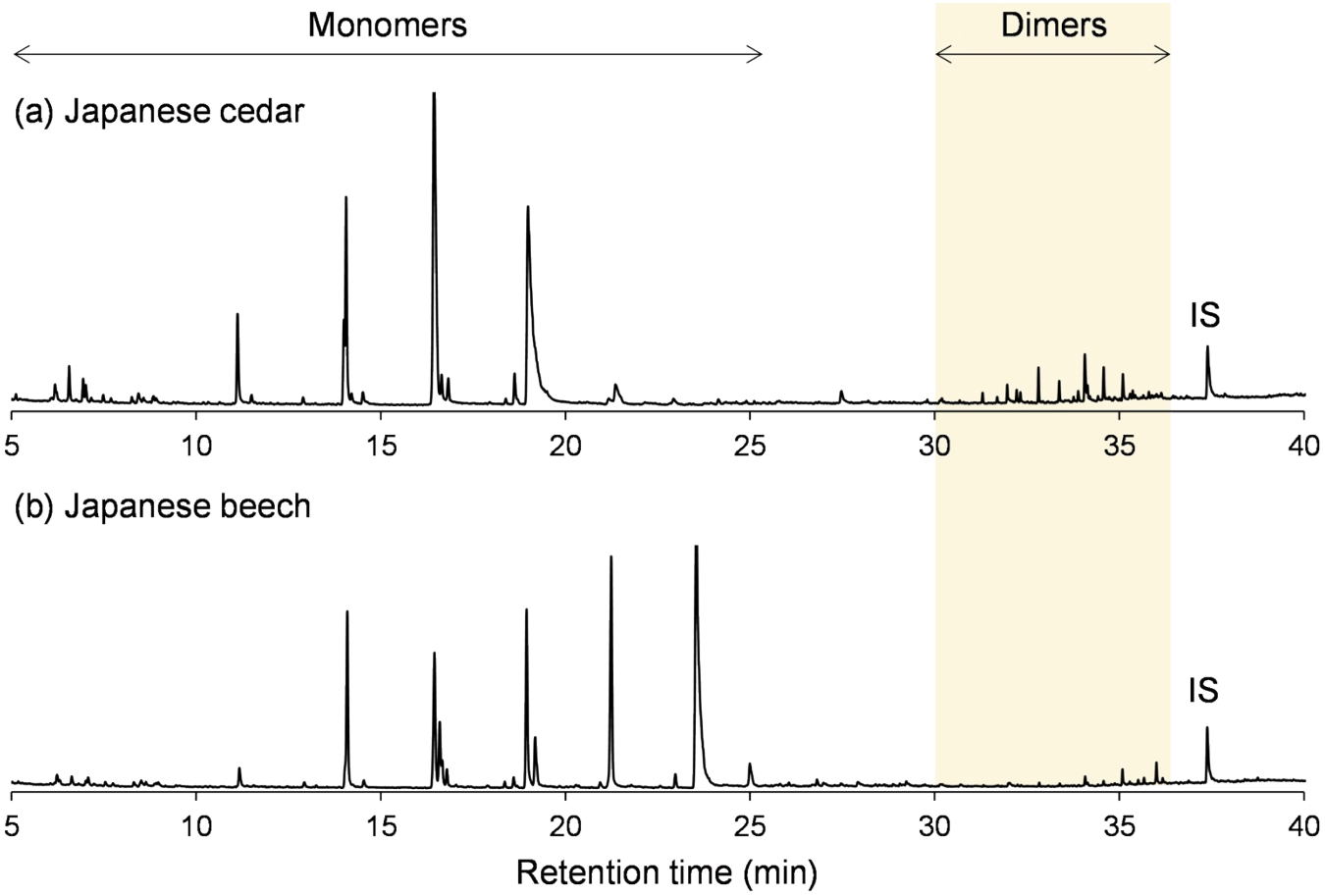
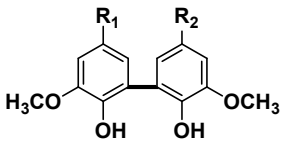


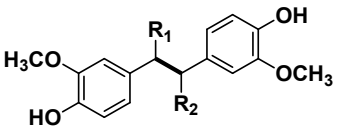
Fig. S9 Assignment of dimeric products on the GC/MS total-ion chromatogram of EtOAc-soluble products after trimethylsilylation obtained from Japanese cedar wood (100 mg) in H_2O (1 mL) under N_2 atmosphere (1 mL, prior to heating) over Pd/C (25 mg) at 350 °C for 5 min. Internal standard (IS): 1,3,5-triphenylbenzene.

(a) 5-5 dimers



Compound	m/z (TMS)	R_1	R_2
1	418	Me	Me
2	432	H (Me)	Pr (Et)
3	446	Me (Et)	Pr (Et)
4	460	Et	Pr
5	474	Pr	Pr

(b) Diarylethanes



Compound	m/z (TMS)	R_1	R_2
6	418	H	H
7	432	H	Me
8	446	Me	Me
9	460	Et	Me

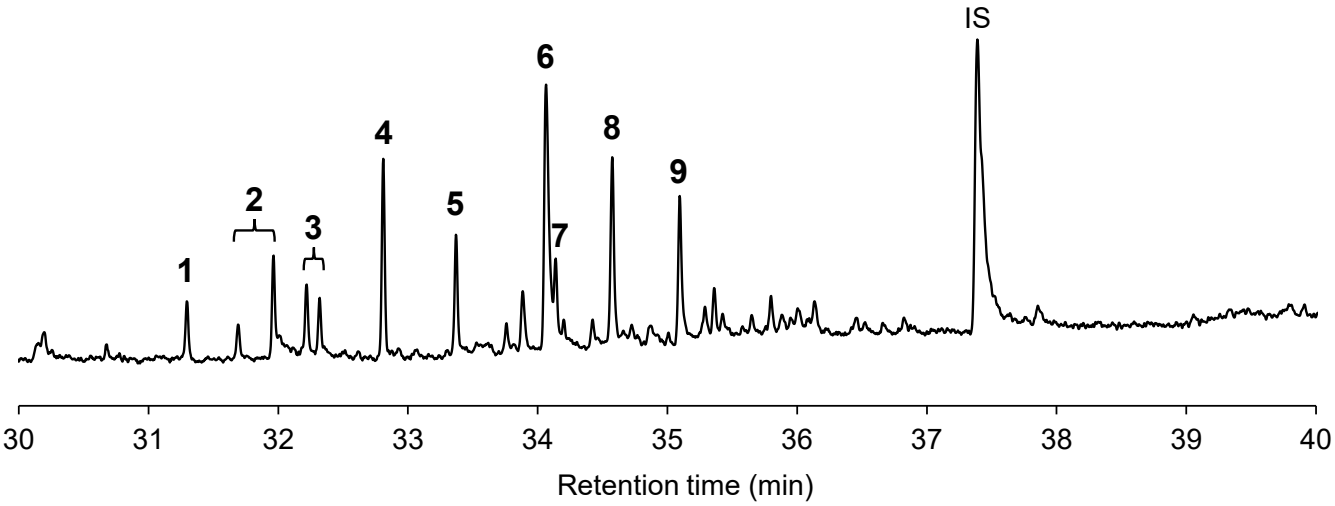
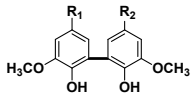


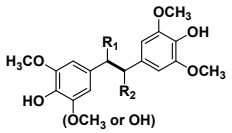
Fig. S10 Assignment of dimeric products on the GC/MS total-ion chromatogram of EtOAc-soluble products after trimethylsilylation obtained from Japanese cedar wood (100 mg) in H_2O (1 mL) under N_2 atmosphere (1 mL, prior to heating) over Pd/C (25 mg) at 350 °C for 5 min. Internal standard (IS): 1,3,5-triphenylbenzene.

(a) 5-5 dimers



Compound	m/z (TMS)	R_1	R_2
4	460	Et	Pr
5	474	Pr	Pr

(b) Diarylethanes



Compound	m/z (TMS)	Type	R_1	R_2
6	418	G-G	H	H
7	432	G-G	H	Me
8	446	G-G	Me	Me
10	448	S-G	H	H
11	506	MC-G	H	H
12	476	C-G	H	H
13	492	C-G	Me	H
14	478	S-S	H	H
15	536	MC-S	H	H

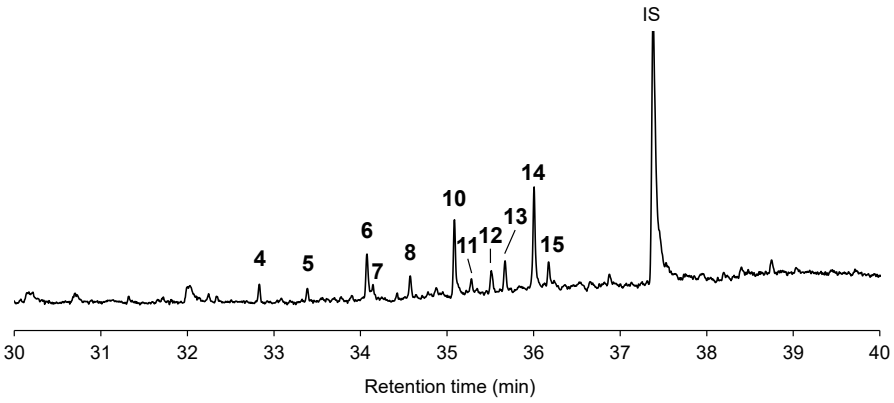


Fig. S11 Assignment of dimeric products on the GC/MS total-ion chromatogram of EtOAc-soluble products after trimethylsilylation obtained from Japanese beech wood (100 mg) in H_2O (1 mL) under N_2 atmosphere (1 mL, prior to heating) over Pd/C (25 mg) at 350 °C for 5 min. Internal standard (IS): 1,3,5-triphenylbenzene.

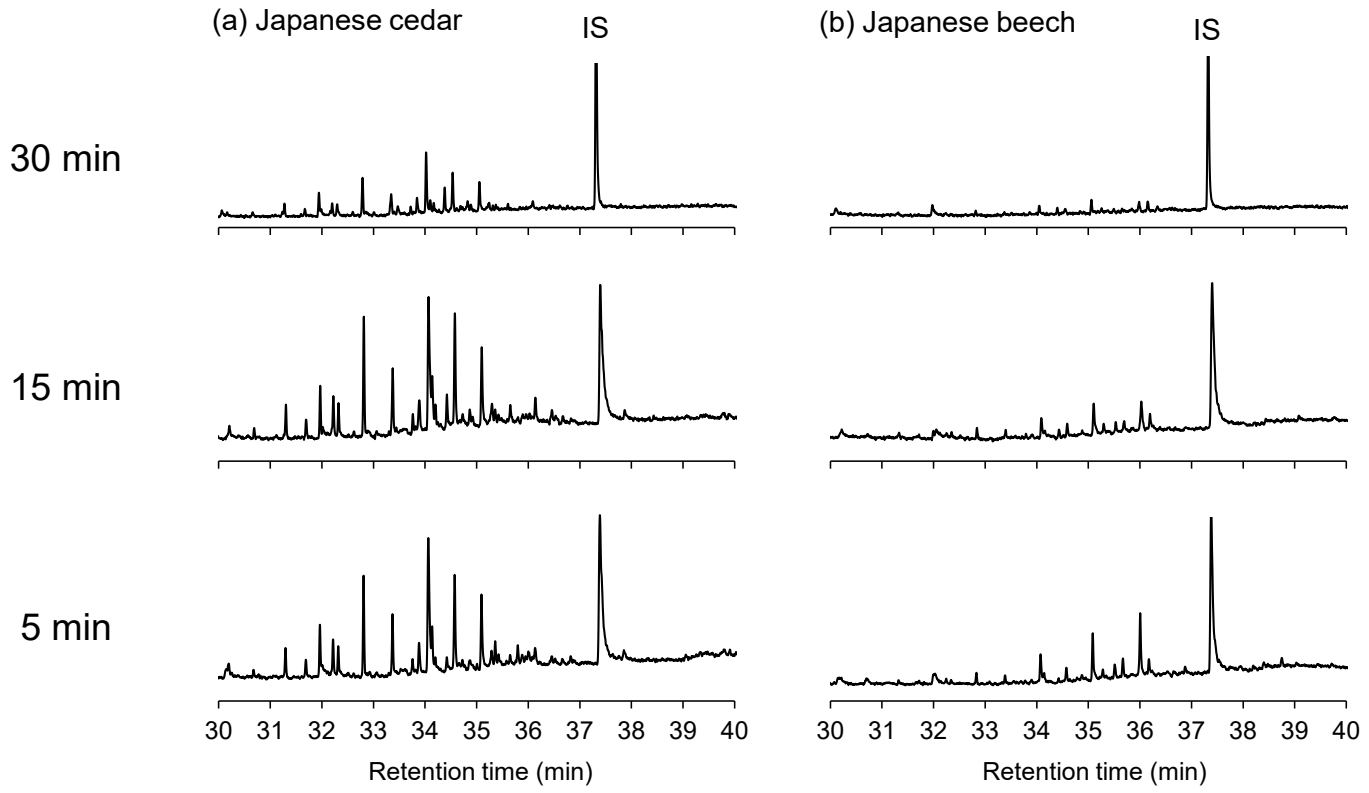


Fig. S12 Assignment of dimeric products on the GC/MS total-ion chromatograms of EtOAc-soluble products after trimethylsilylation obtained from (a) Japanese cedar wood (100 mg) and (b) Japanese beech wood in H_2O (1 mL) under N_2 atmosphere (1 mL, prior to heating) over Pd/C (25 mg) at 350 °C for 5, 15 and 30 min. Internal standard (IS): 1,3,5-triphenylbenzene.

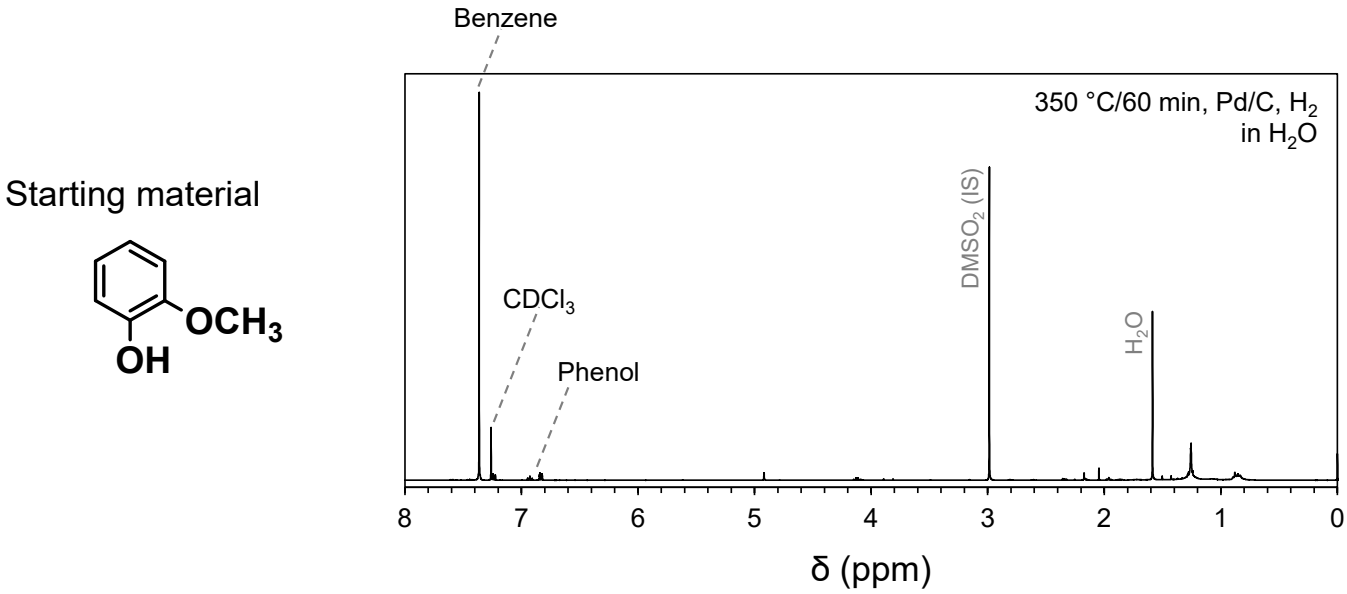


Fig. S13 ^{1}H-NMR spectrum (400 MHz) of $CDCl_3$-soluble products obtained from guaiacol (20 mg) over Pd/C (20 mg) in H_2O (1 mL) under N_2 atmosphere (1 atm, prior to heating) at 350 °C for 60 min. Internal standard (IS): dimethyl sulfone ($DMSO_2$, 1.50 mg).

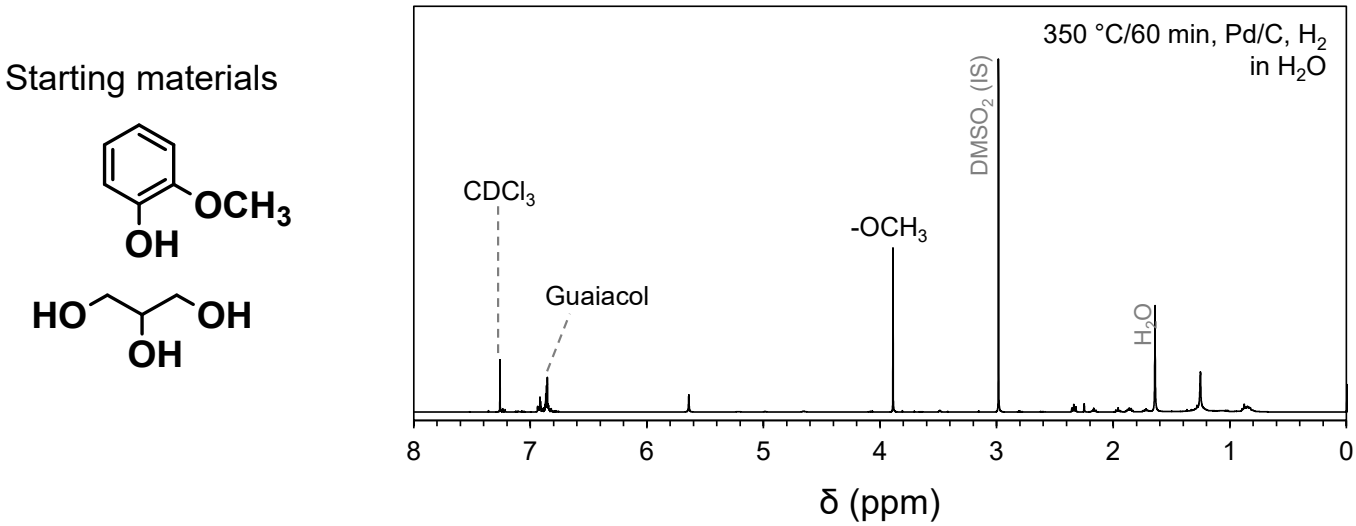


Fig. S14 ^{1}H-NMR spectrum (400 MHz) of $CDCl_3$-soluble products obtained from a mixture of guaiacol (20 mg) and glycerol (20 mg) over Pd/C (20 mg) in H_2O (1 mL) under N_2 atmosphere (1 atm, prior to heating) at 350 °C for 60 min. Internal standard (IS): dimethyl sulfone ($DMSO_2$, 1.72 mg).

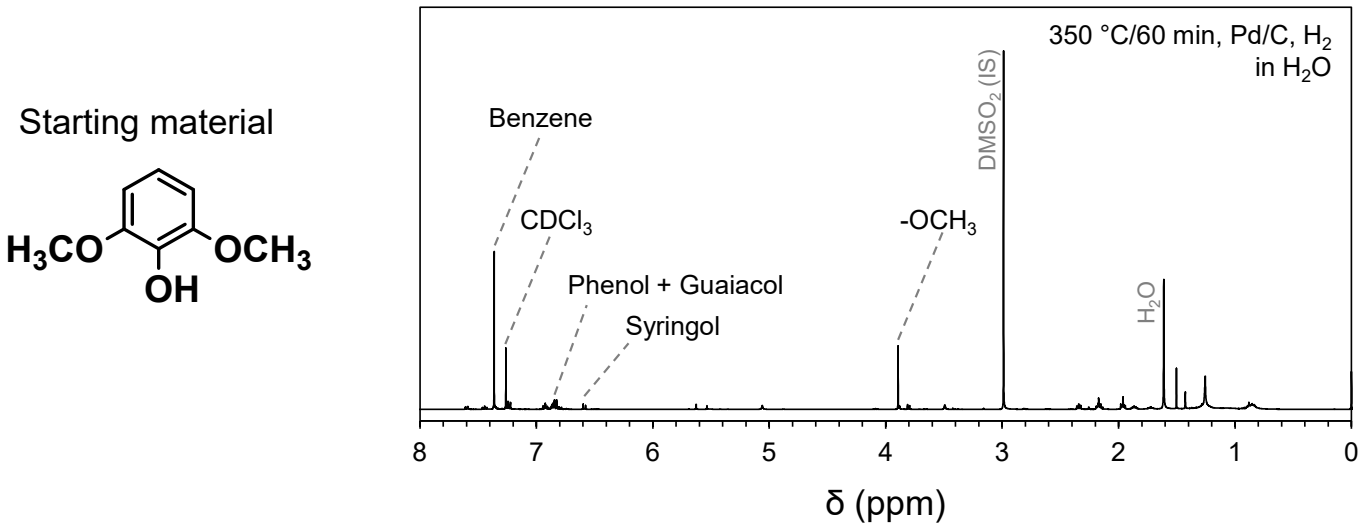


Fig. S15 ^{1}H-NMR spectrum (400 MHz) of $CDCl_3$-soluble products obtained from syringol (20 mg) over Pd/C (20 mg) in H_2O (1 mL) under N_2 atmosphere (1 atm, prior to heating) at 350 °C for 60 min. Internal standard (IS): dimethyl sulfone ($DMSO_2$, 1.70 mg).

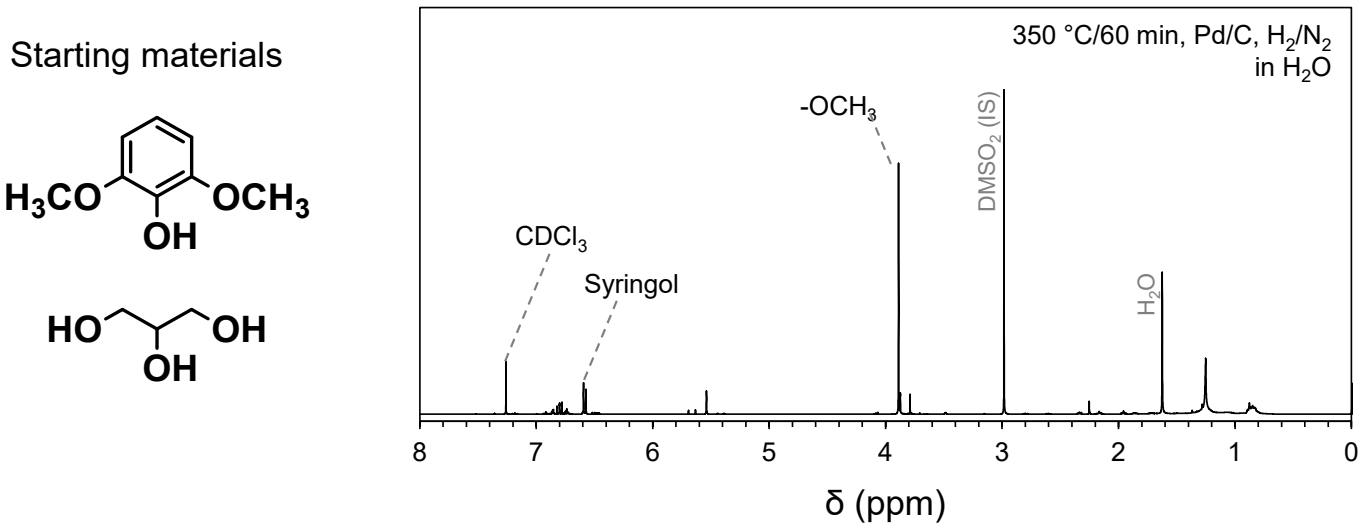


Fig. S16 ^{1}H-NMR spectrum (400 MHz) of $CDCl_3$-soluble products obtained from a mixture of syringol (20 mg) and glycerol (20 mg) over Pd/C (20 mg) in H_2O (1 mL) under N_2 atmosphere (1 atm, prior to heating) at 350 °C for 60 min. Internal standard (IS): dimethyl sulfone ($DMSO_2$, 1.72 mg).

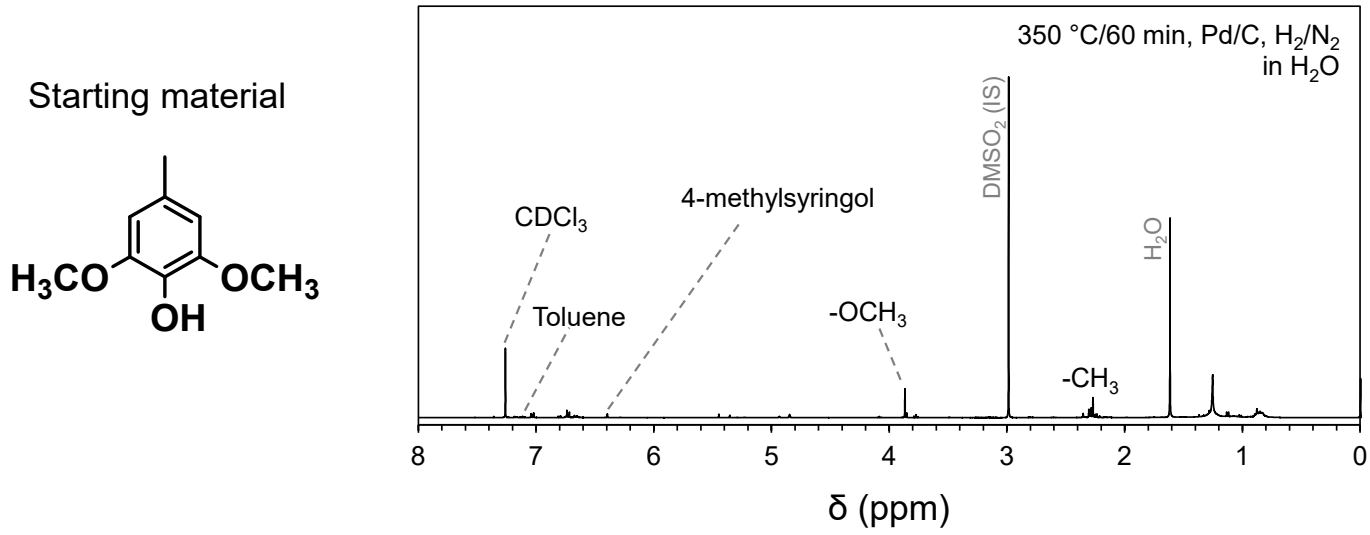


Fig. S17 ^{1}H-NMR spectrum (400 MHz) of $CDCl_3$-soluble products obtained from 4-Methylsyringol (20 mg) over Pd/C (20 mg) in H_2O (1 mL) under N_2 atmosphere (1 atm, prior to heating) at 350 °C for 60 min. Internal standard (IS): dimethyl sulfone ($DMSO_2$, 1.22 mg).

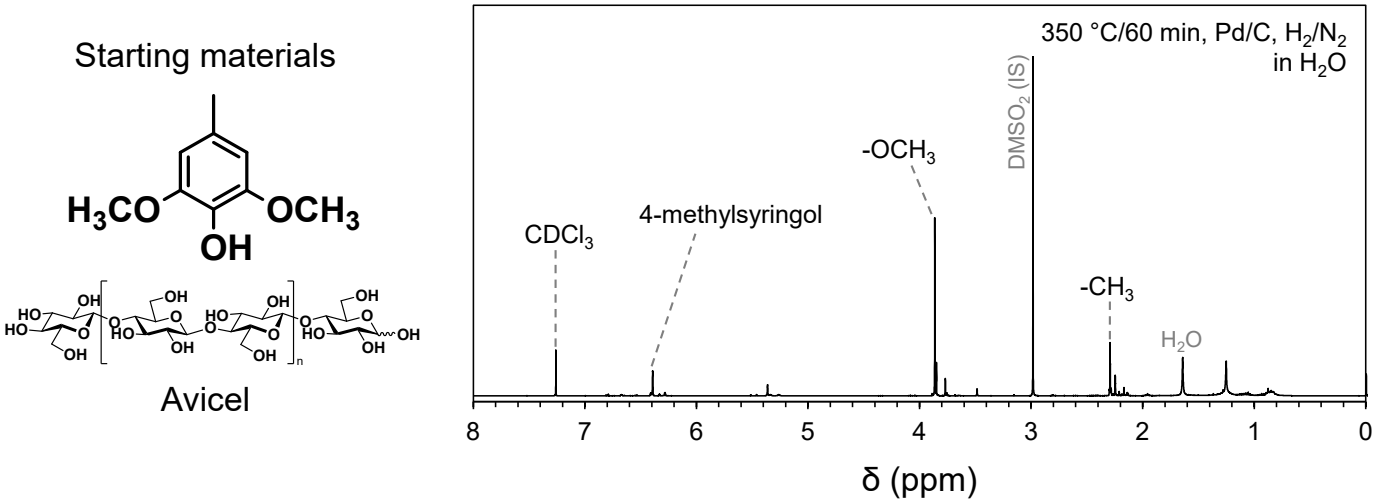


Fig. S18 ^{1}H-NMR spectrum (400 MHz) of $CDCl_3$-soluble products obtained from a mixture of 4-Methylsyringol (20 mg) and Avicel (20 mg) over Pd/C (20 mg) in H_2O (1 mL) under N_2 atmosphere (1 atm, prior to heating) at 350 °C for 60 min. Internal standard (IS): dimethyl sulfone ($DMSO_2$, 1.93 mg).

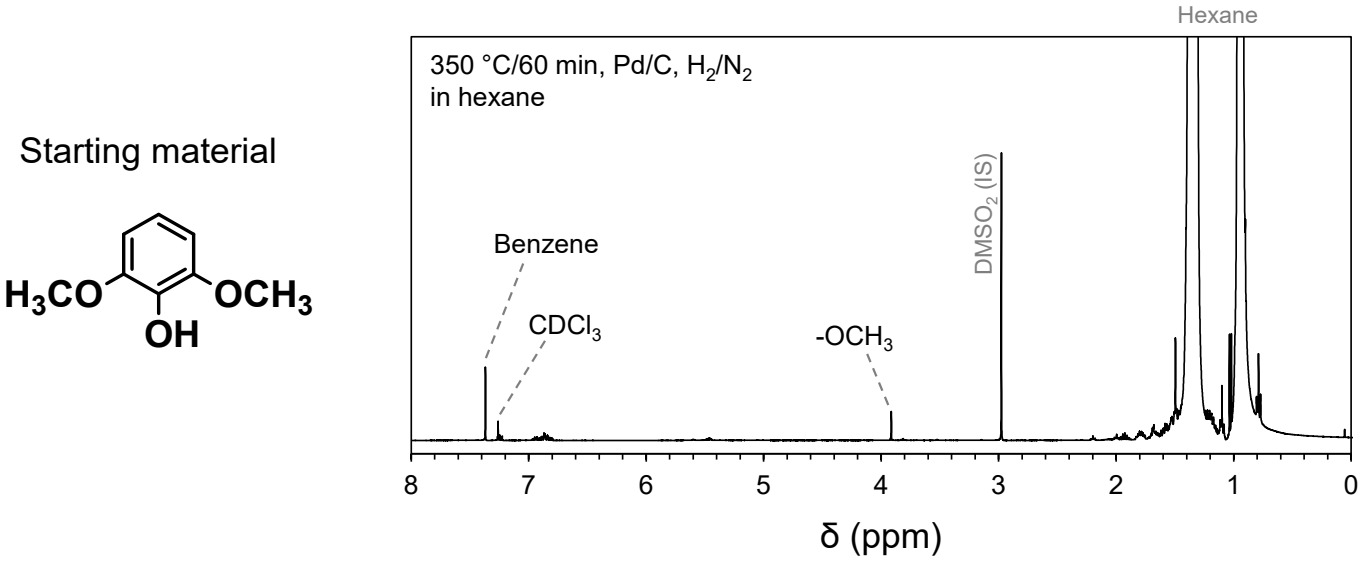


Fig. S19 ^{1}H-NMR spectrum (400 MHz) of $CDCl_3$-soluble products obtained from syringol (20 mg) over Pd/C (20 mg) in hexane (1 mL) under a H_2:N_2 atmosphere (1 atm, 1:1 v/v, prior to heating) at 350 °C for 60 min. Internal standard (IS): dimethyl sulfone ($DMSO_2$, 1.50 mg).

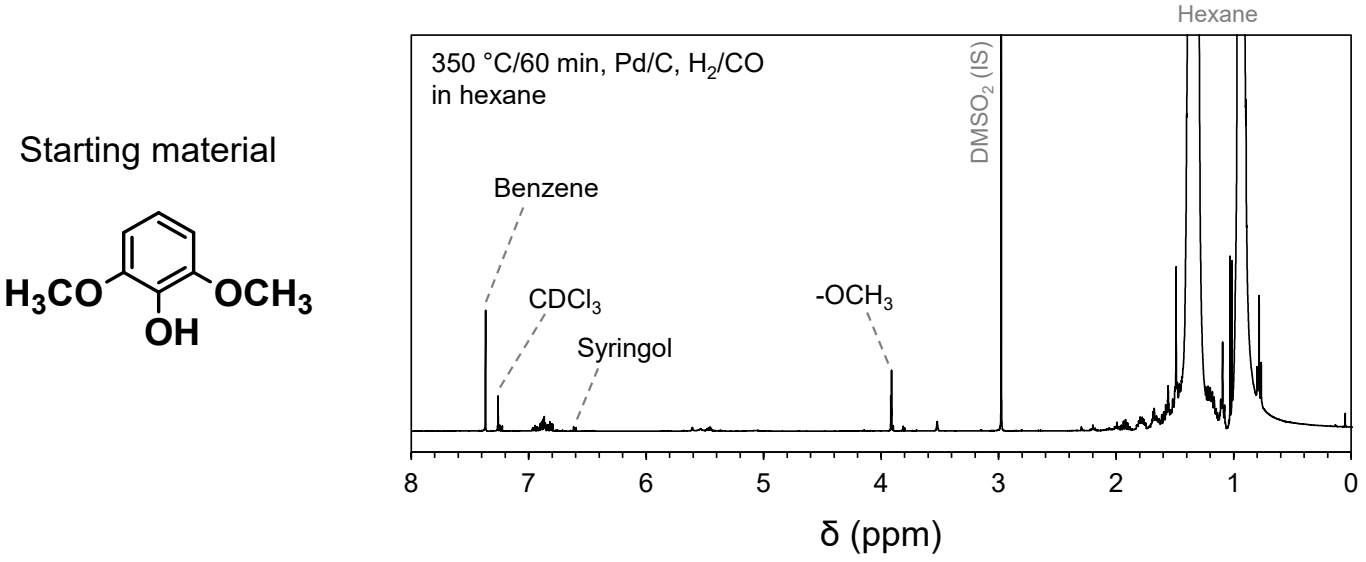


Fig. S20 ^{1}H-NMR spectrum (400 MHz) of $CDCl_3$-soluble products obtained from syringol (20 mg) over Pd/C (20 mg) in hexane (1 mL) under a H_2:CO atmosphere (1 atm, 1:1 v/v, prior to heating) at 350 °C for 60 min. Internal standard (IS): dimethyl sulfone ($DMSO_2$, 1.46 mg).

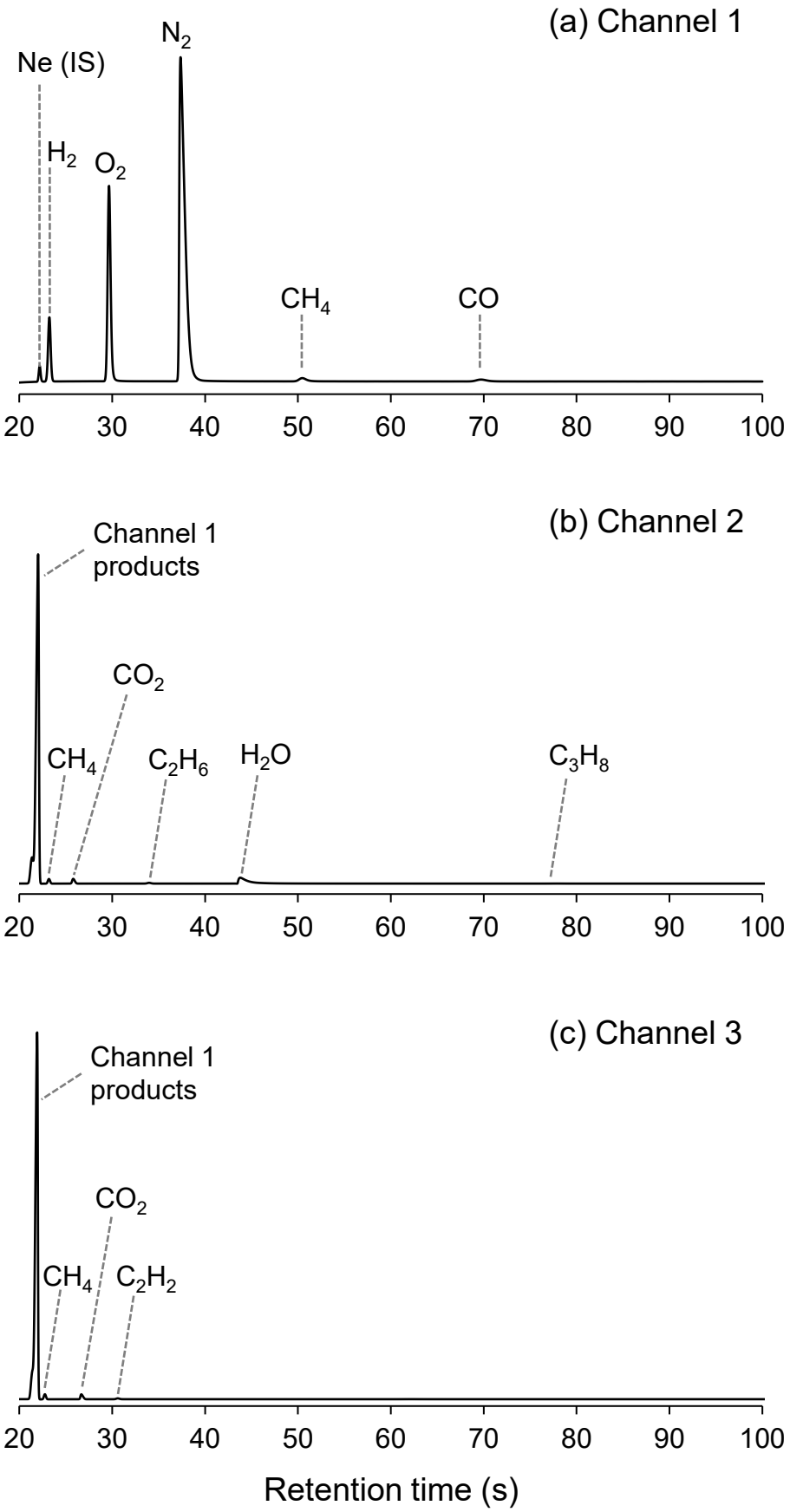


Fig. S21 Representative GC chromatograms of gaseous products obtained from Japanese beech wood (100 mg) in H_2O (1 mL) under N_2 atmosphere (1 mL, prior to heating) over Pd/C (25 mg) at 350 °C for 60 min. Internal standard (IS): Ne (5 mL, 25 °C, 0.1 MPa).

Table S2 Single-point response factors obtained during Micro GC calibration

Standard	Channel #	Response factor (relative to Ne)	Correction factor (relative to N_2 in air)
Ne	1	1.0	-
H_2	1	3.65	-
O_2	1	0.662	0.33426
N_2	1	-	1.0
CH_4	1	1.33	-
CO	1	0.47	-
CO_2	2	3.5	0.019
C_2H_n (*)	2, 3	9.44	-
C_2H_6	2	11.2	-
C_3H_6	2	7.75	-
C_3H_8	2	9.26	-

*: includes both C_2H_2 and C_2H_4.

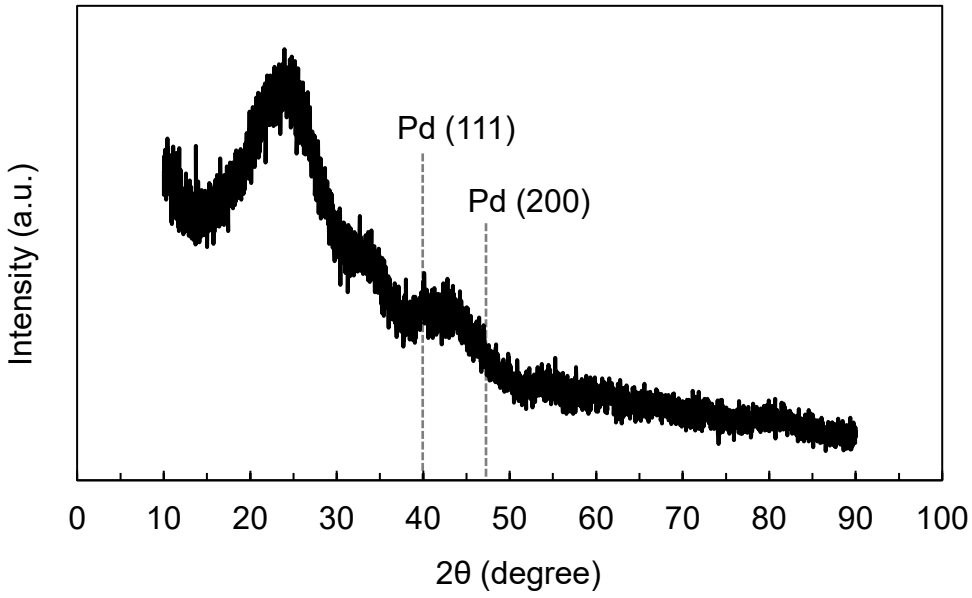


Fig. S22 XRD pattern of the 5% Pd/C catalyst used in the present study.

nacalai tesque
The quality for certainty.

CERTIFICATE OF ANALYSIS

April 19 2024

NACALAI TESQUE, INC.
Kyoto Factory
17 Ishibashi, Kaide-cho,
Muko, Kyoto 617-0004
TEL : +81- (0) 75-251-1730

Product number	Grade	Lot number	Package size
25910-36	EP	V4F5246	10G

Product name
Palladium Carbon

Test Item	Unit	Specification	Result
Loss on drying	%	max. 10.0	0.5
Assay (Pd)	%	4.0 - 5.5	5.0

Remarks

k. Goya
SIGNATURE

Fig. S23 Composition of the Pd/C catalyst as informed by the manufacturer.