Synthesis of model compounds

General methods

All chemicals were purchased from Sigma-Aldrich and used as received. Solvents were purchased from Fischer Scientific and used as received. Tetrahydrofuran (THF) was dried using an MBraun MB-SPS solvent purification system. All glassware was pre-dried in an oven at 120°C then cooled in a desiccator prior to use. ^{1}H and ^{13}C spectra were recorded on Varian Innova 400MHz spectrometer with an Oxford magnet operating at 9.4T. All NMR chemical shifts are reported as δ in parts per million (ppm) relative to the residual solvent signal.

Benzyl phenol ether (**BPE**) was synthesized according to the following method: 5 mL of benzyl bromide (33 mmol), phenol (3.1023 g, 33 mmol), K_2CO_3 (8.29 g, 60 mmol), and KI (0.8295 g, 5 mmol) were combined together is 45 mL acetone heated to reflux and stirred overnight. The mixture was filtered and the resultant solution concentrated *in vacuo*. Deionized water (50 mL) was added. The reaction mixture was extracted with ethyl acetate (40 mL) three times. The combined ethyl acetate layers were washed with a brine solution, dried over $MgSO_4$, and filtered. The solution was concentrated *in vacuo* and **BPE** was crystallized from a cold ethanol solution and obtained as a white solid (84% yield). ^{1}H-NMR (400MHz, $CDCl_3$): δ 5.05 (2H, s, Hα), 6.93-7.36 (10H, m, Aromatic H). ^{13}C-NMR (100MHz, $CDCl_3$) δ 70.11 (Cα), 115.07 (C3', C5'), 121.14 (C1'), 127.67 (C2, C6), 128.12 (C4), 128.77 (C3, C5), 129.68 (C2', C6'), 137.30 (C1), 159.01 (C4').

1-(phenoxyethyl)benzene (**PEB**) was synthesized according to the following method: phenol (2.6 g, 27.7 mmol) and K_2CO_3 (5.74 g, 41.5 mmol) were combined in acetone (30 mL), the mixture was stirred for 30 min at room temperature. 1-bromoethyl benzene (7.68 g, 41.5 mM) and KI (0.46g, 2.77mM) were added and the mixture was refluxed for 24 h. The solution was filtered to remove excess K_2CO_3 and the filter cake was washed with acetone. Solvent was removed in *vacuo*. The obtained oil was diluted with deionized water (40 mL) and extracted with ethyl acetate (40 mL) three times. Combined ethyl acetate layers were washed with brine, dried over $MgSO_4$ and filtered. Ethyl acetate *in vacuo* gave a slightly yellow oil which was purified by silica gel column chromatography developed with *n*-hexane:ethyl acetate (4:1) to obtain a pure compound (1.18 g, yield 66.4%). ^{1}H-NMR (400MHz, $CDCl_3$): δ 1.577 (3H, d, *J*=6.4, Hβ), 5.239 (1H, dd, *J*=6.4, 12.8, Hα), 6.79-7.33 (10H, m, Aromatic H). ^{13}C-NMR (100MHz, $CDCl_3$) δ 24.38 (Cβ), 75.75 (Cα), 115.85 (C3', C5'), 120.56 (C1'), 125.43 (C2, C6), 127.29 (C4), 128.50 (C3, C5), 129.22 (C2', C6'), 143.17 (C1), 157.91 (C4').

2-phenoxy-1-phenylethanol (**PPE**) was synthesized in a two-step manner. Step 1: synthesis of 2-Phenoxy-1-phenylethanone precursor: 2-bromoacetophenone (1.1942 g, 60 mmol) and phenol (7.0582 g, 75 mmol) were dissolved in 250 mL of acetone, to which K_2CO_3 (12.3000 g, 89 mmol) was added. The mixture was heated to reflux and stirred for 18 h, after which it was filtered and concentrated *in vacuo*. 2-Phenoxy-1-phenylethanone was crystallized from cold

ethanol (250 mL) (85% yield). Step 2: 2-Phenoxy-1-phenylethanone (1.1089 g, 5.2 mmol) was dissolved in 35 mL of methanol. Sodium borohydride (0.3534 g, 10.4 mmol) was added portion-wise. After addition the mixture was stirred at room temperature for 2 h. Excess sodium borohydride was quenched with careful addition of saturated aqueous NH_4Cl solution (30 mL). The resultant solution was extracted with 20 mL diethyl ether three times. The combined ether layers were dried with 50 mL saturated brine solution, dried over $MgSO_4$, and filtered. The ether was removed *in vacuo* yielding an off white solid of 2-phenoxy-1-phenylethanol (80% yield). The solid was dried overnight in a vacuum desiccator. ^1H NMR (400 MHz, CDCl3) δ 7.45 (d, J = 7.1 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.27 (t, J = 7.5 Hz, 2H), 6.96 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 5.12 (dt, J = 8.9, 2.8 Hz, 1H), 4.10 (dd, J = 9.6, 3.2 Hz, 1H), 3.99 (t, J = 9.2 Hz, 1H), 2.76 (d, J = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 158.4, 139.6, 128.3, 127.9, 126.6, 126.1, 119.3, 113.4, 74.0, 71.3. Data are consistent with previously reported yields and NMR characterization. GC-MS (EI): Calcd for ($C_{14}H_{14}O_2$) m/z 214.1; found 214.0.

1-phenyl-2-phenoxy-1,3-propanediol (**PPPD**) was synthesized in the following multistep manner. Step 1, synthesis of methyl phenoxyacetate: methyl bromoacetate (10 mL, 105.6 mmol) and phenol (9.9380 g, 105.6 mmol) were dissolved in 250 mL of acetone; K_2CO_3 (21.89 g, 158 mmol) and KI (5 g, 30 mmol) were added and the mixture heated to reflux with stirring overnight. The mixture was filtered and the resultant solution concentrated *in vacuo*. Deionized water (200 mL) was added. The reaction mixture was extracted with 50 mL ethyl acetate three times. The combined ethyl acetate layers were washed with brine, dried over $MgSO_4$, and filtered. All ethyl acetate was removed *in vacuo*, resulting in a slightly yellow liquid () (80% yield). Step 2: A lithium diisopropylamide solution was prepared by combining diisopropyl amine (10.5 mL, 75 mmol) with n-butyl-lithium (30 mL of 2.5 M soln in THF, 75 mmol) in 50 mL dry THF at 0°C. The solution was stirred for 2 h after which the temperature was reduced to and maintained at -78°C. Methyl phenoxyacetate (7.3 mL, 50 mmol) was added drop wise to this solution and allowed to react for 30 min. Freshly distilled benzaldehyde (50 mL, 50 mmol) was added and the resultant solution allowed to react for an additional 2 h at -78^o C, after which time the reaction was quenched with the addition of 100 mL saturated aqueous NH_4Cl solution and warmed to room temperature. The solution was extracted with 50 mL diethyl ether three times. The combined ether layers were washed with brine, dried over $MgSO_4$, and filtered. The evaporation of the ether in *vacuo* gave a slightly yellow oil of 2-phenoxy-3-phenyl-methyl-3-hydroxypropanoate. Step 3, reduction of ester: 2-phenoxy-3-phenyl-methyl-3-hydroxypropanoate (2.2048 g, 8 mmol) was dissolved in 50 mL of methanol. Sodium borohydride (1.2106 g, 32 mmol) was added portion-wise, after addition the reaction mixture was stirred at room temperature for 4 h. The excess sodium borohydride was carefully quenched with a saturated aqueous NH_4Cl (30 mL) solution. The resultant solution was extracted with 25 mL diethyl ether three times. The combined ether layers were dried with 50 mL saturated brine solution, dried over $MgSO_4$, and filtered. The evaporation of the ether *in vacuo* gave a slightly yellow oil which was purified by silica gel column chromatography developed with *n*-

hexane:ethyl acetate (4:1) to obtain a pure compound (yield 58%). ^{1}H NMR (400 MHz, CDCl3) δ 7.45 (d, *J* = 7.1 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.10 (d, *J* = 5.1 Hz, 1H), 4.42 (q, *J* = 4.6 Hz, 1H), 3.94 (dd, *J* = 12.1, 4.7 Hz, 1H), 3.84 (dd, *J* = 12.1, 4.0 Hz, 1H), 2.84 (s, 1H), 2.2 (s, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 156.5, 139.7, 128.4, 128.4, 127.7, 127.7, 127.0, 127.0, 125.9, 119.2, 113.3, 113.3, 89.7, 71.4, 60.0. GC-MS (EI): Calcd for ($C_{15}H_{16}O_3$) m/z 244.1; found 244.0.

1-(4-hydroxyphenyl)-2-phenoxy-1,3-propanediol (**HH**) was synthesized in the following multistep manner. Step 1: a lithium diisopropylamide solution was synthesized by combining diisopropyl amine (3.62 mL, 25 mmol) with n-butyl-lithium (25 mmol) in 50 mL dry THF at 0°C. The solution was stirred for 2 h after which the temperature was reduced to and maintained at -78°C. Previously prepared methyl phenoxyacetate (3.95 g, 23.45 mmol) was added drop wise to this solution and allowed to react for 30 min. Benzyloxy benzaldehyde (4.9770 g, 23.45 mmol) was added and the resultant solution allowed to react for an additional 2 h at -78^{o}C, after which time the reaction was quenched with the addition of 25 mL saturated aqueous NH_4Cl solution. The solution was extracted with 50 mL diethyl ether three times. The combined ether layers were washed with brine, dried over $MgSO_4$, and filtered. The evaporation of the ether in *vacuo* gave a slightly yellow waxy solid of 2-phenoxy-3-benzyloxyphenyl-methyl-3-hydroxypropanoate which was purified by silica gel column chromatography developed with *n*-hexane:ethyl acetate (4:1) to obtain a pure compound (yield 70%). Step 2, reduction of ester: 2-phenoxy-3-benzyloxyphenyl-methyl-3-hydroxypropanoate (1.8921 g, 5 mmol) was dissolved in 50 mL of methanol. Sodium borohydride (20 mmol) was added portion-wises, after addition the reaction mixture was stirred at room temperature for 4 h. The excess sodium borohydride was quenched with a saturated aqueous NH_4Cl (30 mL) solution. The resultant solution was extracted with 25 mL diethyl ether three times. The combined ether layers were dried with 50 mL saturated brine solution, dried over $MgSO_4$, and filtered. The evaporation of the ether in *vacuo* gave an off-white oil of 2-phenoxy-1-[4-(phenylmethoxy)phenyl]-1,3-propanediol. Step 3, debenzylation: 2-phenoxy-1-[4-(phenylmethoxy)phenyl]-1,3-propanediol (0.6512 g, mmol) and 10% Pd/C (50 mg) were combined in 25 mL methanol. The air in the flask was removed under vacuum and replaced with H_2. The mixture was stirred under H_2 at room temperature for 4 h after which the mixture was filtered over a bed of celite, removing the catalyst. All methanol was removed *in vacuo* yielding a clear oil of pure 1-(4-hydroxyphenyl)-2-phenoxy-1,3-propanediol (57% yield). ^{1}H NMR (400 MHz, acetone d6) δ 8.23 (s, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 2H), 4.90 (d, *J* = 5.3 Hz, 1H), 4.41 (q, *J* = 4.9, 4.5 Hz, 1H), 3.94 – 3.70 (m, 2H), 2.88 (s, 1H). ^{13}C NMR (30.6 MHz, acetone d6) δ 156.5, 154.7, 132.3, 128.4, 128.4, 127.3, 127.3, 115.0, 115.0, 113.3, 113.3, 89.7, 71.4, 60.0. GC-MS (EI): Calcd for ($C_{15}H_{16}O_4$) m/z 260.1; found 242.0 (-HOH).

1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)-1,3-propanediol (**SS**) was synthesized in the following multistep manner. Step 1, synthesis of benzyl protected **SS**: To

diisopropylamine (1.6 mL, 11 mmol) in 15 mL of dry THF under N_2 was added a solution of 2.5M *n*-BuLi in hexanes (4.5 mL, 11 mmol) dropwise at 0°C. The solution was cooled to -78°C and a solution of 3,5-dimethoxyphenol acetate in THF (2.26 g, 10 mmol) was added dropwise over 20 minutes. The solution was stirred at -78°C for 30 minutes and then a solution of benzyl protected syringaldehyde (2.72 g, 10 mmol) in THF was added dropwise over 20 minutes. The solution was stirred at -78°C for 3 hours and then allowed to warm to room temperature. The reaction was quenched with saturated NH_4Cl, extracted with ethyl acetate (50 mL) thee times. The combined ethyl acetate layers were, dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The benzyl protected **SS** ester (2-(2,6-dimethoxyphenoxy)-3-(4-benzyloxy-3,5-dimethoxyphenyl)-methyl-3-hydroxypropanoate) was isolated as a white solid after column chromatography with hexanes/ethylEtOAc (4:1 to 1:1). NMR shows that the *erythro* isomer was isolated. Yield 79%. Step 2, reduction of benzyl protected **SS** ester: To a solution of benzyl protected **SS** dimer (3.96 g, 7.9 mmol) in 30 mL of MeOH was added sodium borohydride (0.65 g, 1.6 mmol) portion-wise. The reaction was stirred at room temperature and monitored by TLC (developing solvent: hexanes/ethylEtOAc (4:1)). Once compete the excess sodium borohydride reaction was quenched with aqueous NH_4Cl solution and extracted with ether (50 mL) three times. The combined ether layers were washed with brine (50mL), dried with $MgSO_4$, filtered, and concentrated in *vacuo*. The isolated product was used in the next step without further purification. Yield 80%. Step 3, debenzylation: 2-(2,6-dimethoxyphenoxy)-1-[4-benzyloxy-3.5-dimethoxyphenyl)-1,3-propanediol (2.21 g, 4.7 mmol) and 10% Pd/C (200 mg) were combined in 20 mL methanol. The air in the flask was removed under vacuum and replaced with H_2. The mixture was stirred under H_2 at room temperature for 3 h after which the mixture was filtered over a bed of celite, removing the catalyst. All methanol was removed in *vacuo* yielding a white crystalline solid of **SS** in quantitative yield. and the ^{1}H NMR (400 MHz, acetone d6) δ 7.04 (t, J = 8.4 Hz, 1H), 6.73 (d, J = 8.4 Hz, 2H), 6.70 (s, 2H), 4.97 (d, J = 3.7 Hz, 1H), 4.16 (m, 1H), 3.88 (m, 1H), 3.85 (s, 6H), 3.8 (s, 6H), 3.41 (m, 1H). ^{13}C NMR (30.6 MHz, acetone d6) δ 153.2 (2C), 146.9 (2C), 135.2, 134.3, 131.0, 124.5, 105.2 (2C), 103.9 (2C), 89.2, 74.4, 60.0, 56.3 (2C), 56.1 (2C).

((1-phenylethane-1,2-diyl)bis(oxy))dibenzene was synthesized in the following multistep manner. To a stirred solution of PE (2.68g) in dry tetrahydrofuran (40 mL) at 0°C was added n-butyl lithium (1.1eq, 5.5 mL) dropwise via addition funnel under an N_2 atmosphere. The solution was allowed to stir at 0°C for 1 hour. After 1 hour, chlorodiphenyl phosphine was added dropwise via addition funnel and the solution was allowed to warm from 0°C to room temperature. After 1 hour, the solution was concentrated *in vacuo* and diluted with 10 mL of 8:1 hexanes:ethyl acetate. This solution was first passed through a pad of alumina basic (26g) and then through a pad of celite (8g). The filtered solution was concentrated *in vacuo* and used directly in the next step without further purification. To a solution of crude alkoxy-diphenylphosphine (1.5 eq, 4.52g) in 10 mL of dry methylene chloride was added a solution of 2,6-dimethyl benzoquinone (1.03g) in 5 mL of dry methylene chloride via syringe under an N_2 atmosphere. A solution of phenol (0.712g) in 5 mL of dry methylene chloride was added

immediately after via syringe. The solution was allowed to stir overnight at room temperature. The reaction was quenched with water (50 mL), extracted with methylene chloride (3 X 25 mL), dried over sodium sulfate, and then concentrated *in vacuo*. The resulting pale yellow oil was purified using flash chromatography (10:1 hexanes:ethyl acetate) to afford the product as a clear oil.

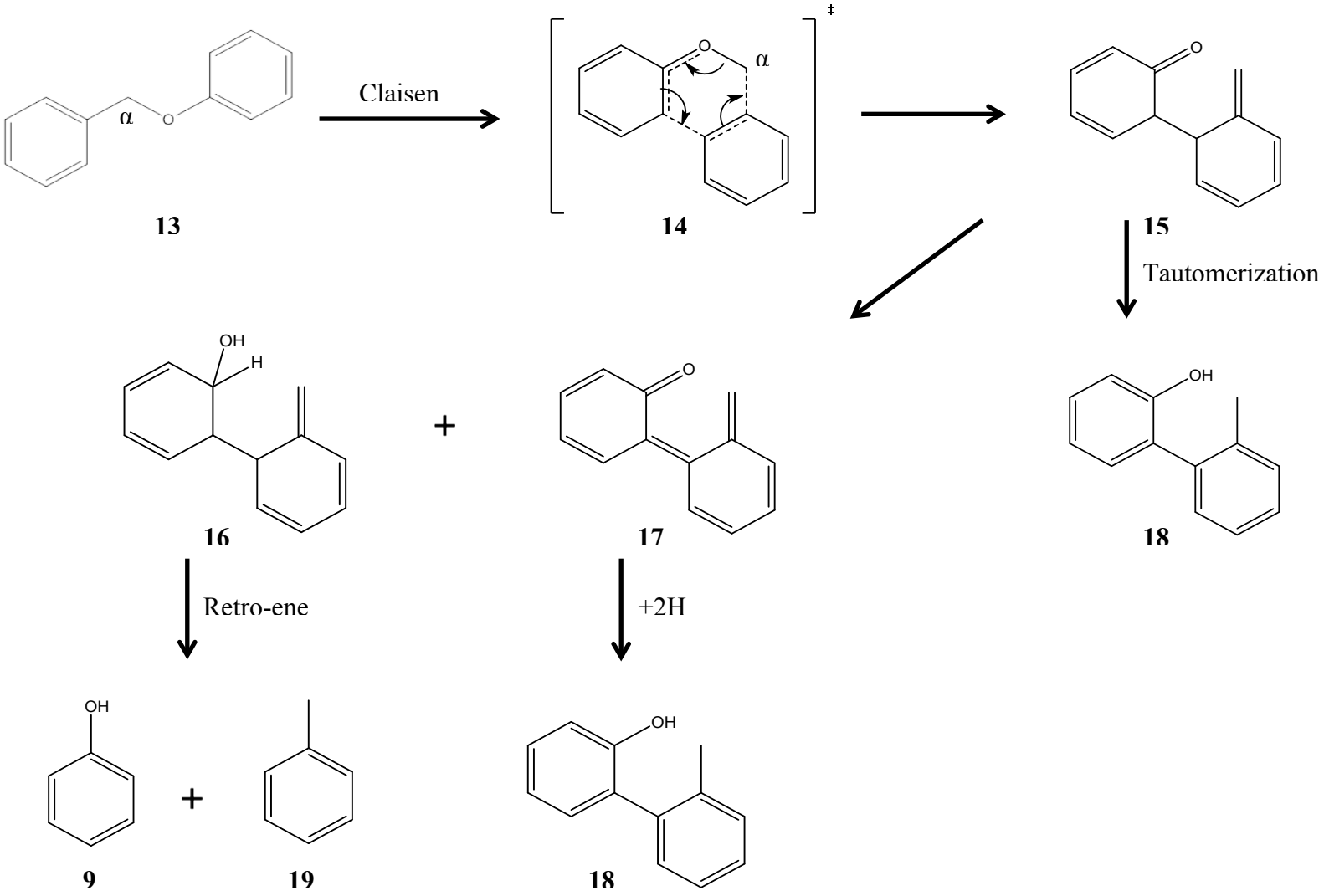


Figure S1. Pericyclic reaction network for BPE pyrolysis[44]

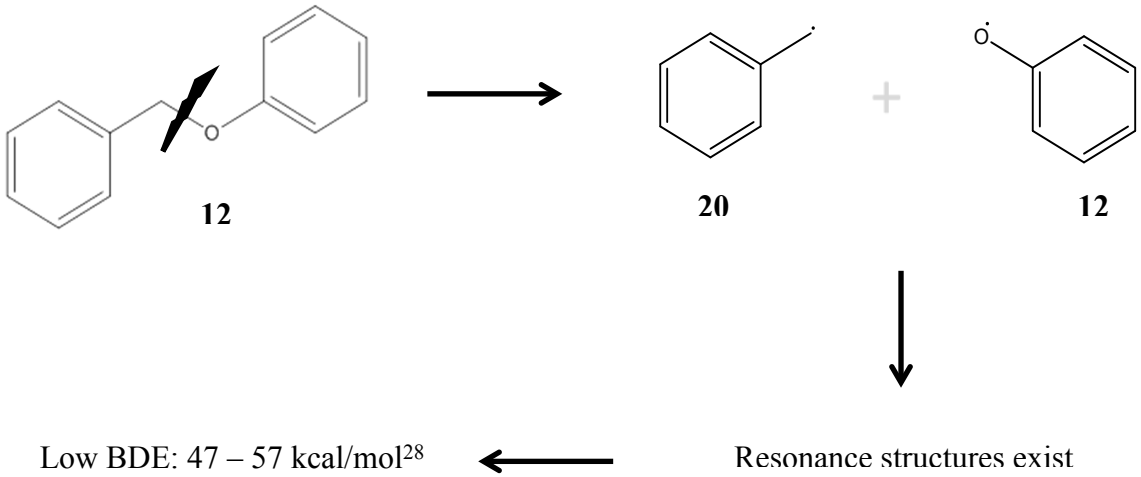
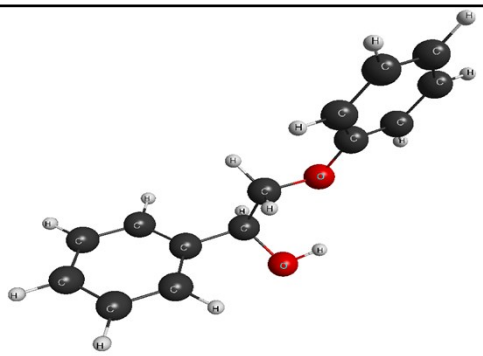
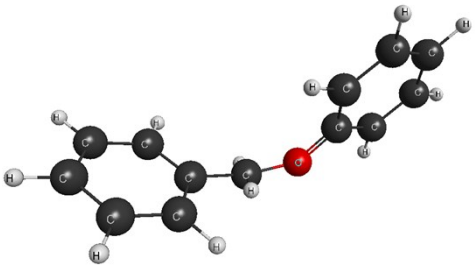
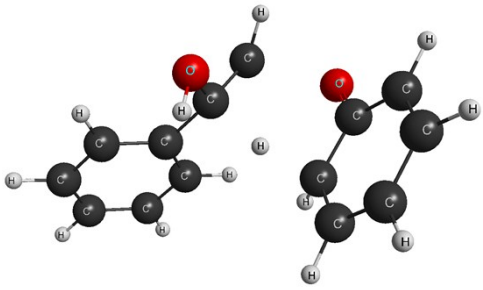
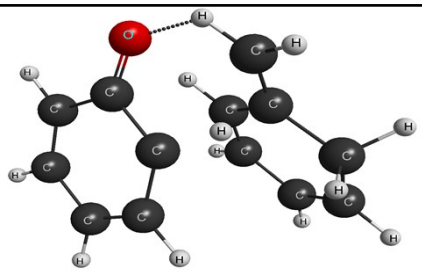
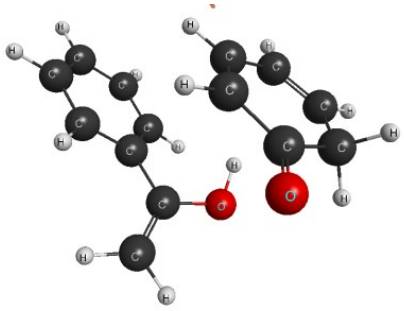
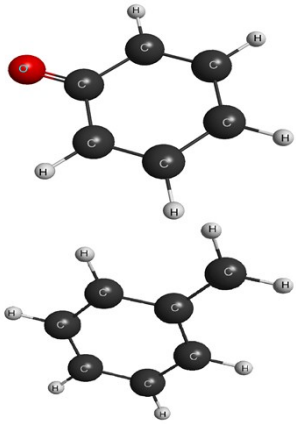


Figure S2 Homolytic cleavage for BPE

Figure S3. The optimized structures of transition states of concerted reaction of PPE and homolysis of BPE as obtained from DFT calculations.

	PPE	BPE
Reactant		
Transition state		
Product		

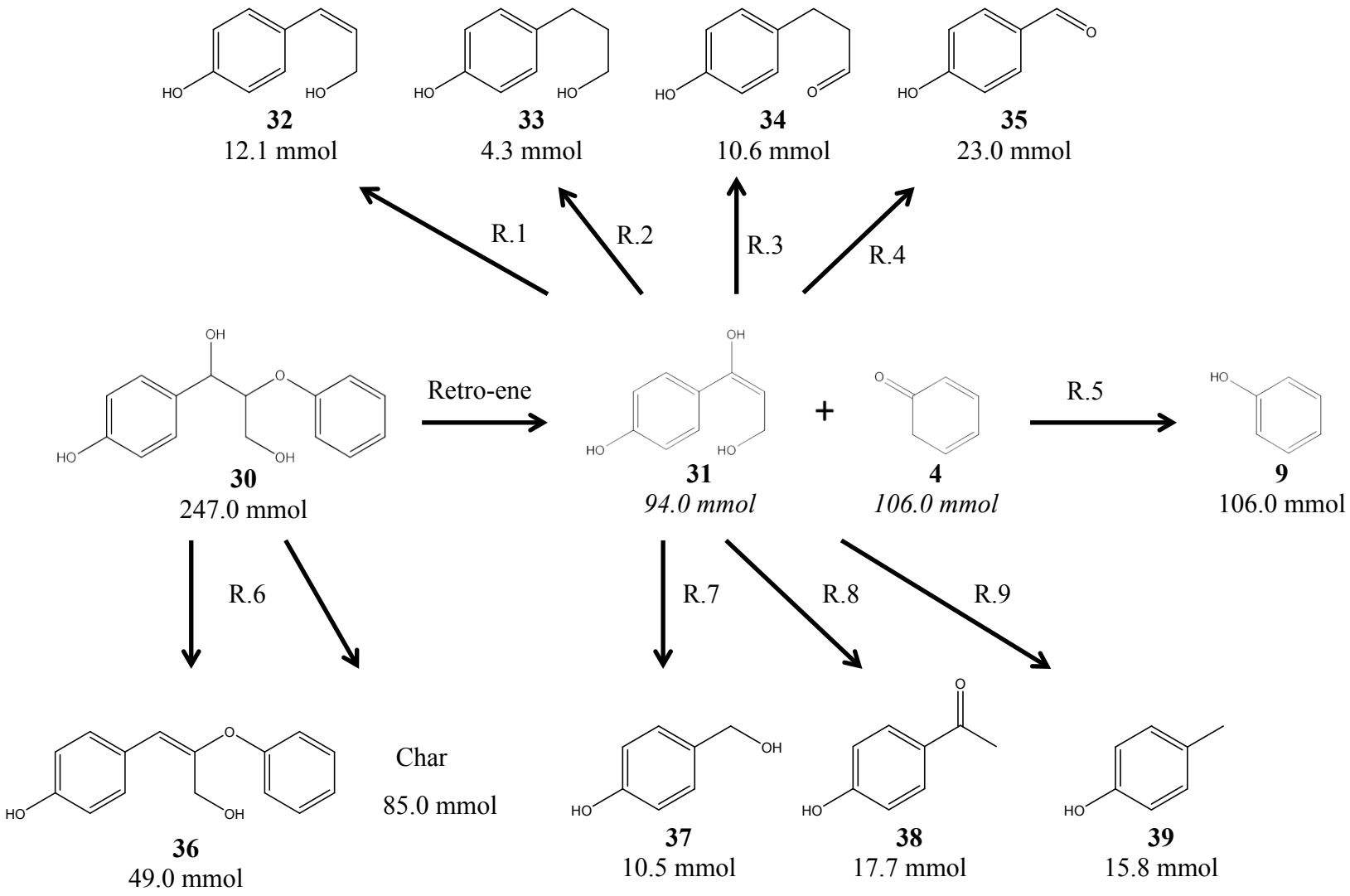


Figure S4. Proposed pericyclic reaction network for HH pyrolysis

Possible reaction pathways (HH pyrolysis)

R.1: Dehydration and hydrogenation

R.2: Dehydration and hydrogenation

R.3: Dehydration, hydrogenation and tautomerization

R.4: Tautomerization and deacetylation

R.5: Tautomerization

R.6: Dehydration

R.7: Deacetylation

R.8: Tautomerization and deformylation

R.9: Dehydration, hydrogenation and deacetylation

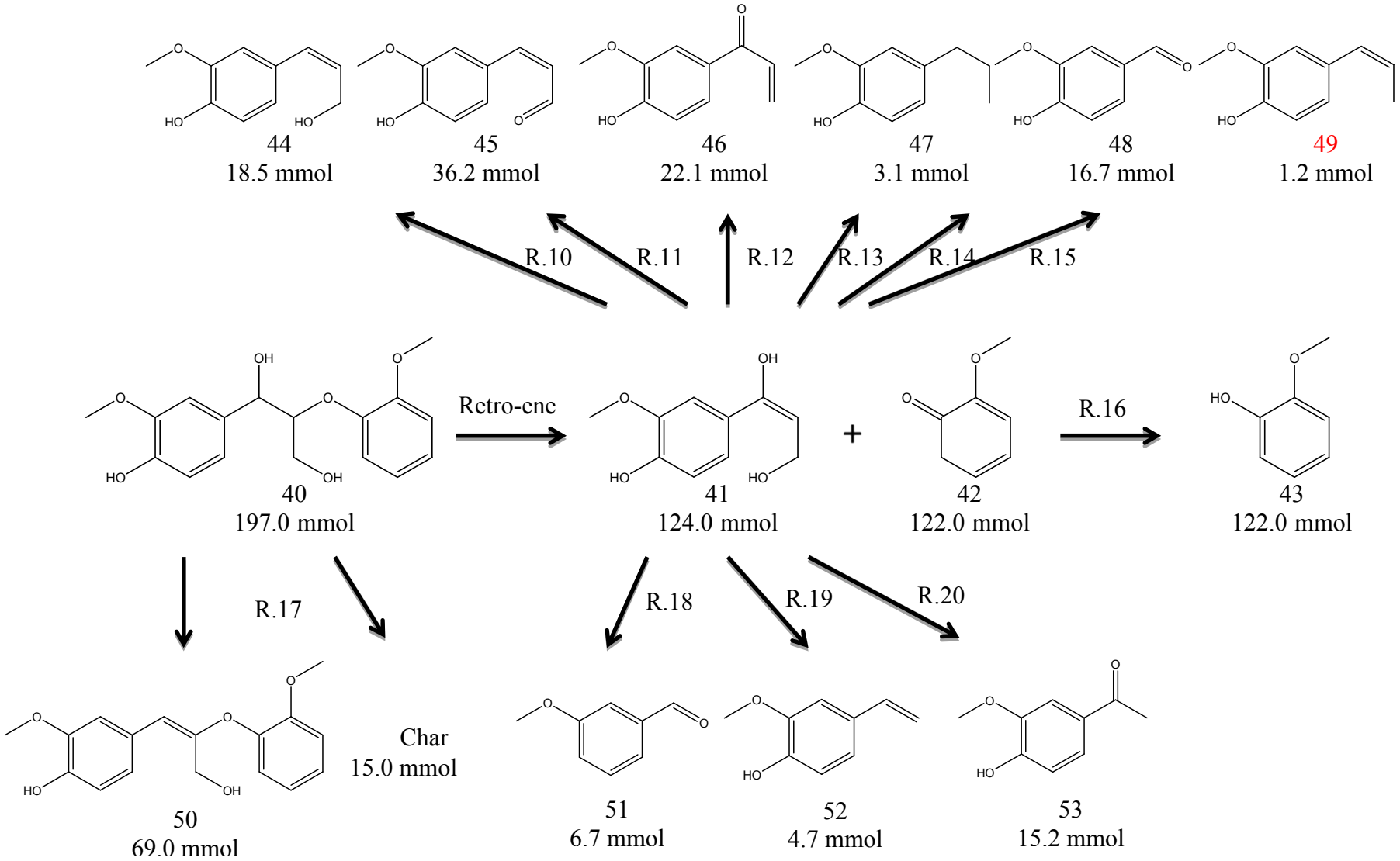


Figure S5. Proposed pericyclic reaction network for GG pyrolysis

Possible reaction pathways (GG pyrolysis)

R.10: Dehydration and hydrogenation

R.11: Dehydration, hydrogenation and tautomerization

R.12: Dehydration, hydrogenation and tautomerization

R.13: Dehydrations and hydrogenation

R.14: Tautomerization and deacetylation

R.15: Dehydrations and hydrogenations

R.16: Tautomerization

R.17: Dehydration

R.18: Dehydroxylation, tautomerization and deacetylation

R.19: Deformylation and dehydration

R.20: Tautomerization and deformylation

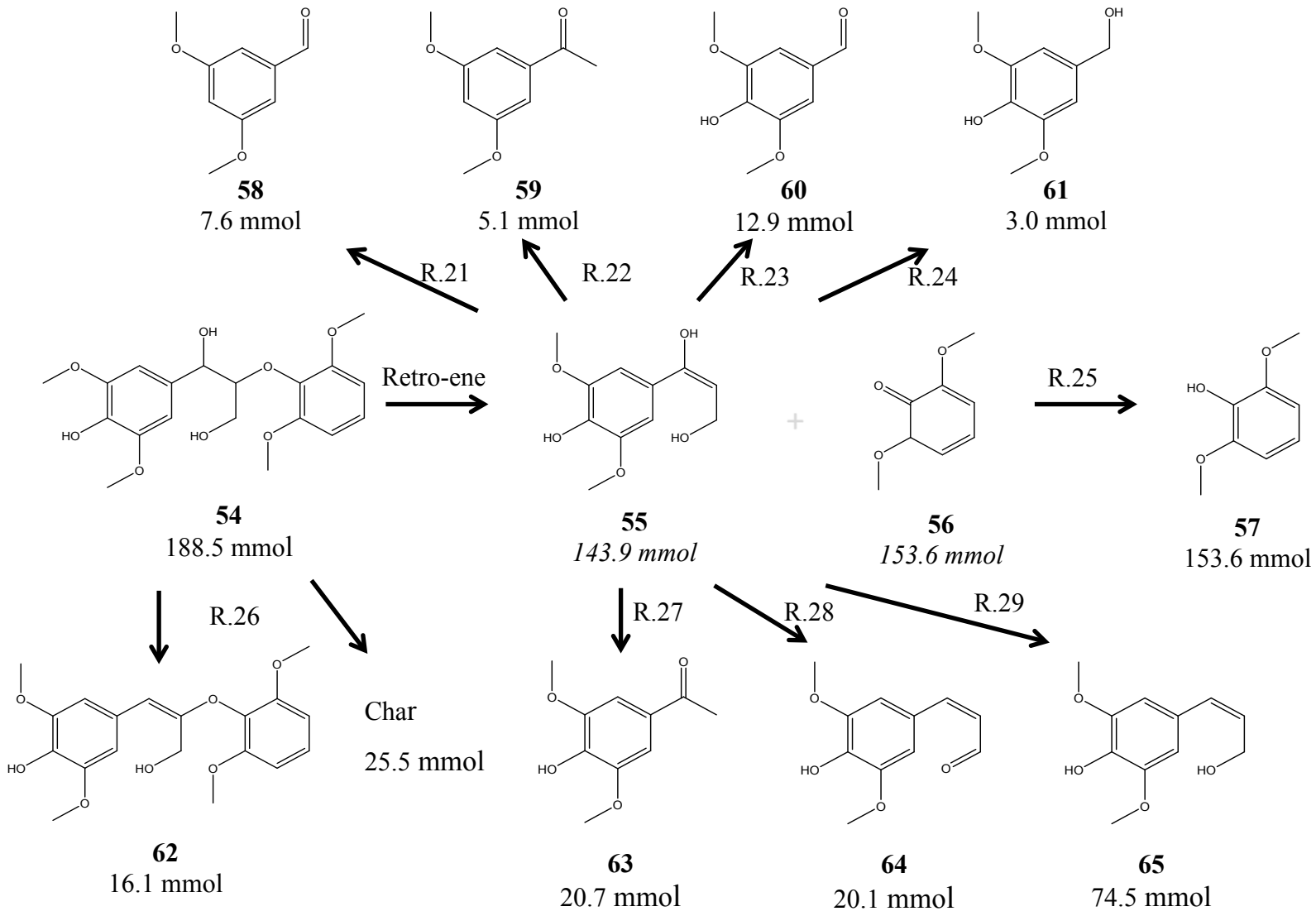


Figure S6. Proposed pericyclic reaction network for SS pyrolysis

Possible reaction pathways (SS pyrolysis)

R.21: Tautomerization, deacetylation and dehydroxylation

R.22: Tautomerization, deformylation and dehydroxylation

R.23: Tautomerization and deacetylation

R.24: Deacetylation

R.25: Tautomerization

R.26: Dehydration

R.27: Tautomerization and deformylation

R.28: Dehydration, hydrogenation and tautomerization

R.29: Dehydration and hydrogenation

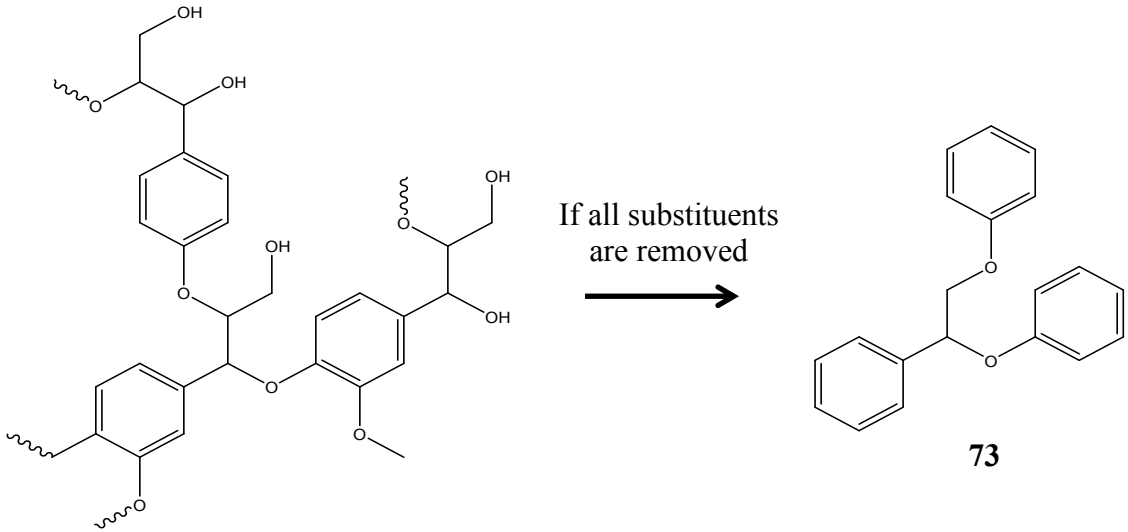


Figure S7. Synthesized trimer model compound, **73**, to simulate native lignin

Table S1. Product distribution of PPE pyrolysis

Compound	Yield, %	STD
Benzaldehyde	0.1	0.0
Benzeneacetaldehyde	0.8	0.0
Acetophenone	0.5	0.0
Phenol	0.9	0.1
(2-phenoxyvinyl)benzene	0.2	0.0
Styrene	0.0	0.0
PPE, converted	2.5	

Table S2. Product distribution of BPE pyrolysis

Compound	Yield, %	STD
Toluene	0.1	0.0
Phenol	2.9	0.1
Bibenzyl	2.9	0.0
2-benzylphenol	1.9	0.1
4-benzylphenol	1.2	0.0
Benzene	0.1	0.0
Benzaldehyde	0.3	0.0
CO_2	0.1	0.0
BPE, converted	9.8	

Table S3. Product distribution of PPPD pyrolysis

Compound	Yield, %	STD
Benzaldehyde	8.8	0.0
Benzeneacetaldehyde	3.7	0.1
Acetophenone	4.0	0.4
Phenol	18.6	0.1
Cinnamyl alcohol	0.4	0.0
2-phenoxy-3-phenylprop-2-en-1-ol	47.6	1.2
Formaldehyde	4.6	0.0
Acetaldehyde	2.9	0.1
Ethyl acetate	0.1	0.0
Benzene	0.1	0.0
Styrene	0.1	0.0
Char	0.5	0.0
CO	0.2	0.1
CO_2	0.3	0.1
PPPD, converted	98.1	

Table S4. Product distribution of HH pyrolysis

Compound	Yield, %	STD
Formaldehyde	2.3	0.2
Phenol	10.0	0.5
p-cresol	1.7	0.0
4-hydroxybenzaldehyde	2.8	0.0
3-(p-hydroxyphenyl)-1-propanol	0.6	0.0
p-coumaryl alcohol	1.8	0.1
3-(p-hydroxyphenyl)-propanol	1.6	0.1
4-hydroxybenzyl alcohol	1.3	0.0
4-hydroxyacetophenone	2.4	0.0
4-(3-hydroxy-2-phenoxyprop-1-en-1-yl)phenol	11.9	0.2
Methanol	0.8	0.1
Diethyl ether	1.6	0.3
o-cresol	0.4	0.0
2-(1-phenylethyl)phenol	0.1	0.0
4-(1-phenylethyl)phenol	0.3	0.0
Char	22.2	0.9
CO	0.2	0.0
CO_2	2.2	0.3
HH, converted	64.2	

Table S5. Product distribution of GG pyrolysis

Compound	Yield, %	STD
4-hydroxybenzaldehyde	0.2	0.0
p-cresol	0.1	0.0
Guaiacol	15.1	0.7
2-methoxy-4-methylphenol	0.1	0.0
3-methoxybenzaldehyde	0.9	0.1
2-methoxy-4-vinylphenol	0.2	0.0
Vanillin	2.6	0.1
4'-hydroxy-3'-methoxyacetophenone	2.5	0.2
Coniferyl alcohol	3.3	0.2
Coniferyl aldehyde	6.5	0.7
4-(oxy-allyl)-guaiacol	3.9	0.1
4-propylguaiacol	0.5	0.1
Isoeugenol	0.2	0.0
4-(3-hydroxy-2-(2-methoxyphenoxy)prop-1-en-1-yl)-2-methoxyphenol	20.6	3.2
Methanol	0.4	0.0
Ethyl acetate	0.2	0.0
Anisole	0.0	0.0
Phenol	0.1	0.0
Char	4.7	0.7
CO	0.3	0.0
CO_2	0.6	0.1
GG, converted	63.0	

Table S6. Product distribution of SS pyrolysis

Compound	Yield, %	STD
Acetaldehyde	1.1	0.2
2,6-dimethoxyphenol	23.7	1.0
3,5-dimethoxybenzaldehyde	1.3	0.0
3',5'-dimethoxyacetophenone	0.9	0.1
4-hydroxy-3,5-dimethoxybenzaldehyde	2.4	0.2
3,5-dimethoxy-4-hydroxybenzyl alcohol	0.5	0.0
4-hydroxy-3,5-dimethoxyacetophenone	4.1	0.6
3,5-dimethoxy-4-hydroxycinnamaldehyde	4.2	0.4
Sinapyl alcohol	15.7	3.2
4-(2-(2,6-dimethoxyphenoxy)-3-hydroxyprop-1-en-1-yl)-2,6-dimethoxyphenol	5.8	1.9
Char	9.7	0.5
CO	0.7	0.0
CO_2	1.8	0.1
SS, converted	71.6	

Table S7. Product distribution of PEB pyrolysis

Compound	Yield, %	STD
Ethyl benzene	0.0	0.0
Styrene	0.1	0.0
Phenol	5.8	0.7
2-(1-phenylethyl)phenol	12.5	0.1
4-(1-phenylethyl)phenol	31.9	0.3
2,4-bis(1-phenylethyl)phenol	31.2	0.7
PEB, converted	88.2	