Supplementary Information for

Domino Lignin Depolymerization and Reconnection to Complex Molecules Mediated by Boryl Radicals

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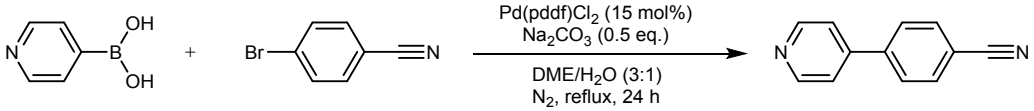
General

All solvents were purchased from Fisher Scientific, Sigma-Aldrich or Acros and were used as received. Technical grade solvents for extraction and column chromatography were bulb-to-bulb distilled prior to usage. Air sensitive reactions were set up using dry glassware and Schlenk technique. ^{1}H- and ^{13}C-NMR experiments were performed at 25 ºC on a Bruker DPX-NMR (400 MHz, 600 MHz) at 25 ºC unless otherwise stated. Chemical shifts are reported in parts per million (ppm) related to solvent peek, coupling constants (*J*) are reported in Hertz (Hz). NMR-solvents were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA) or Deutero GmbH. The multiplicities are written as: s = singlet, d = doublet, t = triplet, m = multiplet and their combinations, such as dd = doublet of a doublet. Multiplets are reported as a span of their middle. Thin layer Chromatography (TLC) was carried out on silica gel 60 F_{254} glass plates with a 0.25 mm layer or Polygram® Alox N/UV_{254} with a 0.2 mm-coating and detected with a CAMAG UV Cabinet dual wavelength, 254/366 nm or stained by *p*-anisaldehyde stain or phosphomolybdic acid (PMA) stain. Column chromatography was performed using silica gel 60 (0.040−0.063 mm). High resolution mass spectrometry (HRMS) was determined with a Thermo Scientific LTQ FT Ultra spectrometer (ESI) using methanol solutions of the respective compounds or a Finnigan MAT95 sectorfield spectrometer (EI). The UV/Vis spectra were recorded with a JASCO V-670 spectrophotometer (spectral range: 190–2500 nm, resolution: ≥ 0.1 nm).

Synthesis of the catalyst and substrates

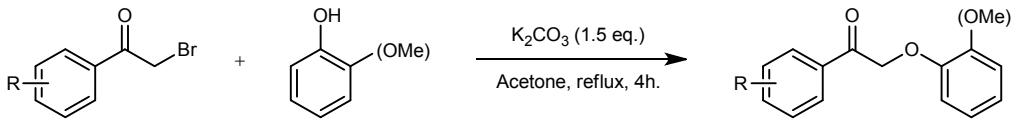
4-(Pyridin-4-yl)benzonitrile[1]



A mixture of 4-bromobenzonitrile (910 mg, 5.00 mmol, 1.00 eq.), pyridin-4-ylboronic acid (738 mg, 6.00 mmol, 1.20 eq.), Pd(pddf)Cl_2 (204 mg, 0.250 mmol, 5.00 mol%), Na_2CO_3 (1.06 g, 10.0 mmol, 2.00 eq.) and 1,2-dimethoxyethane (DME) (15.0 mL) and water (5.0 mL) was stirred at reflux under nitrogen for 40 h. After cooling to rt, the resulting mixture was diluted with 100 mL ethyl ether and then filtered. The filtrate was washed with saturated NaCl solution (75.0 mL). The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was then purified by column chromatography on silica gel to give 4-(pyridin-4-yl)benzonitrile as a white solid (821 mg, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.72 (dd, ^3J = 4.4 Hz, ^4J =1.7 Hz, 2H), 7.78 (dd, ^3J = 6.4 Hz, ^4J = 2.0 Hz, 2H), 7.73 (dd, ^3J = 6.4 Hz, ^4J = 2.0 Hz, 2H), 7.49 (dd, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 2H). Spectroscopic data for the title compound was consistent with the literature.[1]

Synthesis of the model compounds 1aa, 1ab, 1ba, 1bb, 1cb, 1db

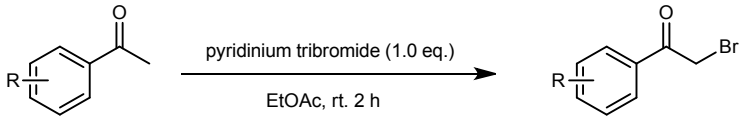
General procedure A: Nucleophilic substitution reaction of 2-bromoacetophenone substrates with phenol compounds.



A 250 mL round bottom flask equipped with a reflux condenser and a dropping funnel was charged with phenol (12.6 mmol, 1.26 eq.) and K_2CO_3 (2.07 g, 15.0 mmol, 1.50 eq.) in acetone (50.0 mL) and stirred at rt. To this solution, 2-bromoacetophenone (10.0 mmol, 1.00 eq.) in acetone (50.0 mL) was added dropwise over 30 min at rt. The resulting suspension was stirred at reflux for 4 h. Afterward the suspension was filtered and concentrated in vacuo. The crude product was purified by recrystallization

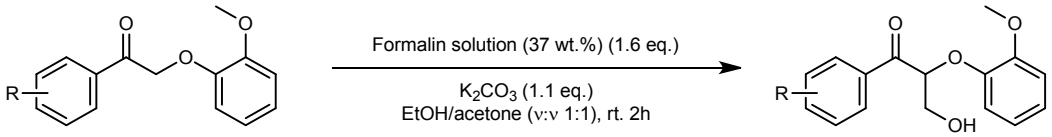
from ethyl acetate/cyclohexane to obtain the product.

General procedure B: Bromination of acetophenone derivatives with pyridinium tribromide.

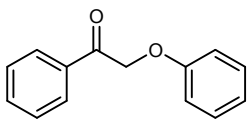


The acetophenone derivative (20.0 mmol, 1.00 eq.) and pyridinium tribromide (20.0 mmol, 1.00 eq.) were dissolved in EtOAc (200 mL). The mixture was stirred for 2 h at rt. Saturated $NaHSO_3$ (200 mL) was used to quench the reaction. The EtOAc layer was separated, dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. Crystallization from ethyl acetate/cyclohexane afforded the brominated product.

General procedure C: Aldol addition of 1-aryl-2-phenoxylethanones with formalin.

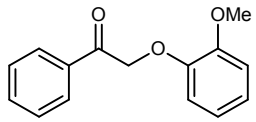


To a solution of 1-aryl-2-phenoxylethanone substrate (1.00 eq.) in EtOH/acetone (v:v 1:1, 0.100 M) containing K_2CO_3 (1.10 eq.) was added formalin solution (37 wt.%, 1.60 eq.). The resulting mixture was stirred at rt for 2 h and then filtered, washed with acetone and concentrated in vacuo to give the crude product as an orange-pink oil. Purification by column chromatography (EtOAc/cyclohexane) was applied to obtain the product.

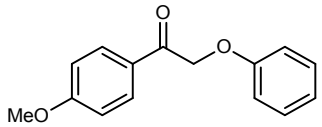


1-Phenyl-2-phenoxylethanone (**1aa**)[2]: According to the *General procedure A*, 1-phenyl-2-phenoxylethanone was obtained as white crystal in 53%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 (dt, ^3J = 8.6 Hz, ^4J = 1.6 Hz, 2H), 7.61 (tt, ^3J = 7.4 Hz, ^4J = 1.4

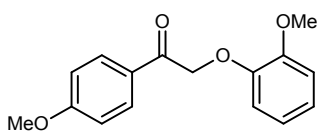
Hz, 1H), 7.51 (dt, ^3J = 7.4 Hz, ^4J = 1.6 Hz, 2H), 7.26–7.32 (m, 2H), 6.94–7.01 (m, 3H), 5.28 (s, 2H). Spectroscopic data for the title compound was consistent with the literature.[2]



1-Phenyl-2-(2-methoxyphenoxy)-ethanone (**1ab**)[2]: According to the *General procedure A*, 1-phenyl-2-(2-methoxyphenoxy)-ethanone was obtained as light-yellow crystalline needles in 85%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 (dt, ^3J = 7.0 Hz, ^4J = 1.6 Hz, 2H), 7.60 (tt, ^3J = 7.3 Hz, ^4J = 1.3 Hz, 1H), 7.49 (dt, ^3J = 7.0 Hz, ^4J = 1.6 Hz, 2H), 6.94–6.99 (m, 1H), 6.90–6.92 (m, 1H), 6.84–6.87 (m, 2H), 5.35 (s, 2H), 3.88 (s, 3H). Spectroscopic data for the title compound was consistent with the literature.[2]

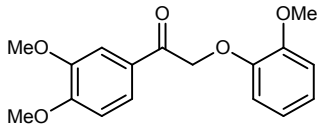


1-(4-Methoxyphenyl)-2-phenoxylethanone (**1ba**)[2]: According to the *General procedure A*, 1-(4-methoxyphenyl)-2-phenoxylethanone was obtained as white crystalline sheets in 66%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00 (dt, ^3J = 8.9 Hz, ^4J = 2.0 Hz, 2H), 7.28 (tt, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 2H), 6.93–7.00 (m, 5H), 5.21 (s, 2H), 3.88 (s, 3H). Spectroscopic data for the title compound was consistent with the literature.[2]

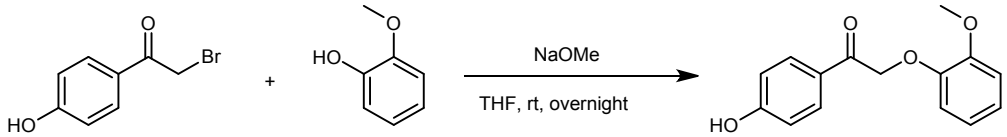


1-(4-Methoxyphenyl)-2-(2-methoxyphenoxy)-ethanone (**1bb**)[2]: According to the

General procedure A, 1-(4-methoxyphenyl)-2-(2-methoxyphenoxy)-ethanone was obtained as light-yellow crystals in 73%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00 (dt, ^3J = 8.9 Hz, ^4J = 2.1 Hz, 2H), 6.92–6.97 (m, 3H), 6.89–6.91 (m, 1H), 6.82–6.86 (m, 2H), 5.27 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H). Spectroscopic data for the title compound was consistent with the literature.[2]

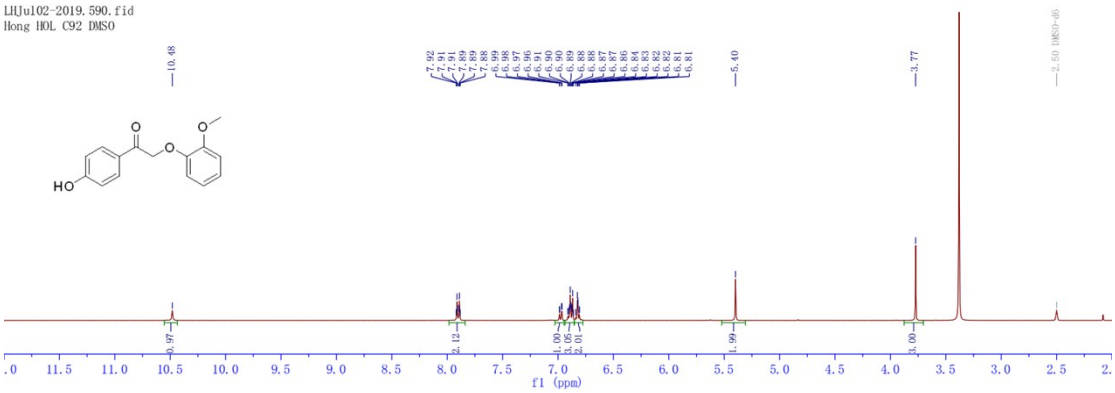


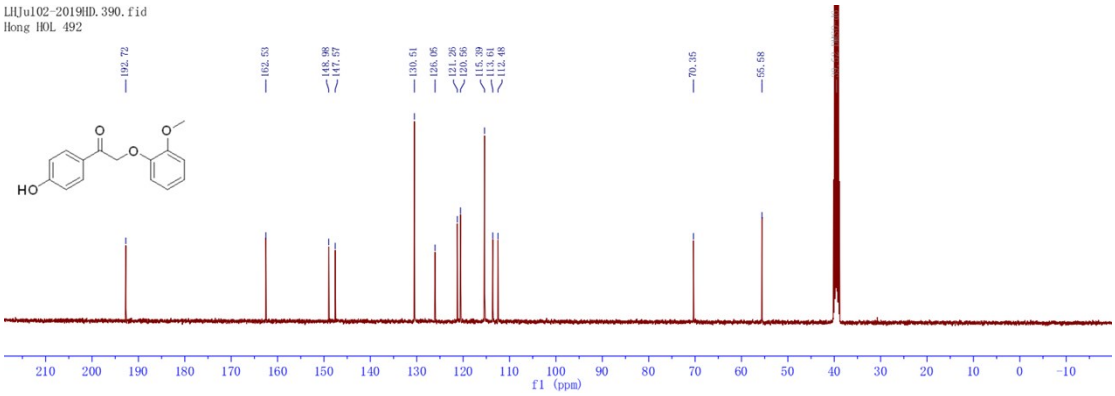
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-ethanone (**1cb**)[2]: According to the *General procedure B & A*, 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-ethanone was obtained as white crystals from 3,4-dimethoxyphenylethanone in 70% overall yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H), 7.60 (d, ^4J = 2.0 Hz, 1H), 6.89–6.98 (m, 3H), 6.84–6.86 (m, 2H), 6.82–6.86 (m, 2H), 5.29 (s, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 3.89 (s, 3H). Spectroscopic data for the title compound was consistent with the literature.[2]



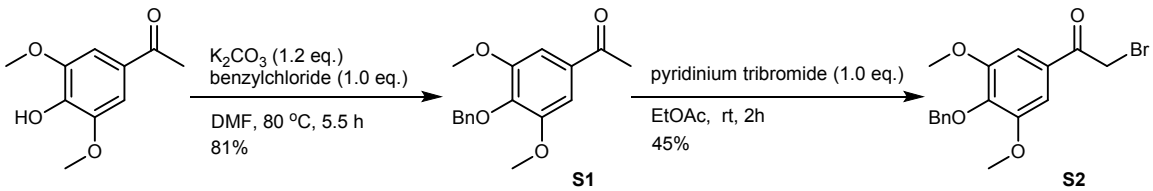
1-(4-Hydroxyphenyl)-2-(2-methoxyphenoxy)-ethanone (**1db**): To a solution of sodium methoxide (0.54 g) in THF (20 mL) was added phenol (0.94 g), the mixture was stirred at rt for 1 h to get sodium phenolate. Then, 2-bromo-1-(4-hydroxyphenyl)-ethanone (2.16 g) was added, and the mixture was stirred for another 5 h. Afterwards, the solvent was removed by evaporation under reduced pressure. The residue was purified by column chromatography over silica gel to obtain the product as a white solid (326 mg, 13%). **^{1}H NMR** (400 MHz, d_6-DMSO): δ 10.48 (s, 1H), 7.90 (dt, ^3J = 8.8 Hz, ^4J = 2.0 Hz, 2H), 6.98 (dd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1H), 6.86–6.91 (m, 3H),

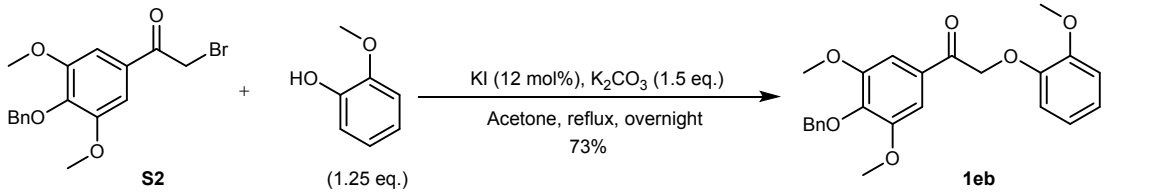
6.81–6.84 (m, 2H), 5.40 (s, 2H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, d_6-DMSO): δ 192.7, 162.5, 149.0, 147.6, 130.5, 126.1, 121.3, 120.6, 115.4, 113.6, 112.5, 70.4, 55.6. **HRMS (ESI)** m/z calcd. for $C_{15}H_{14}O_4$ $[M+Na]^+$ 281.0784, found: 281.0785.





Synthesis of the model compound 1eb

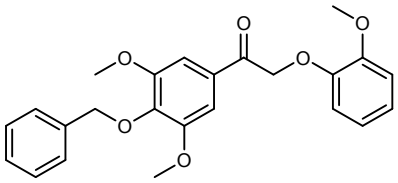




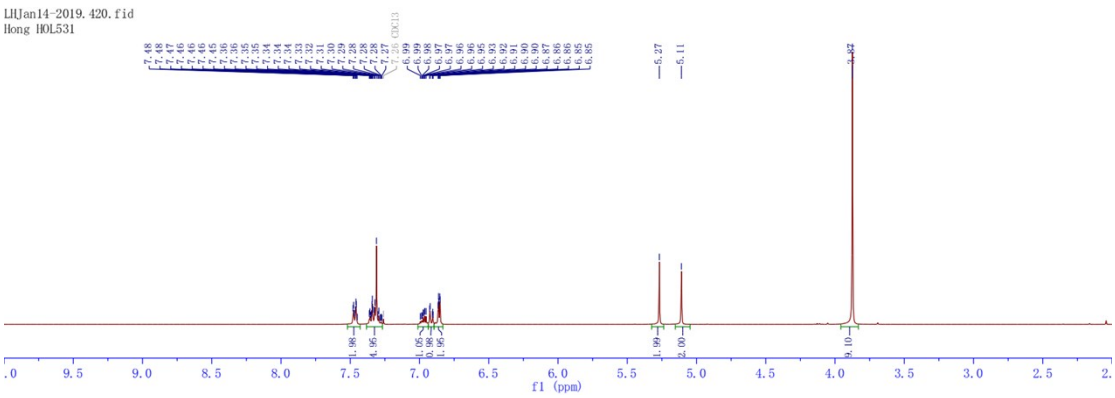
1-(4-Benzyloxy-3,5-dimethoxyphenyl)enthanone (**S1**)[3]: Acetosyringone (5.06 g, 25.0

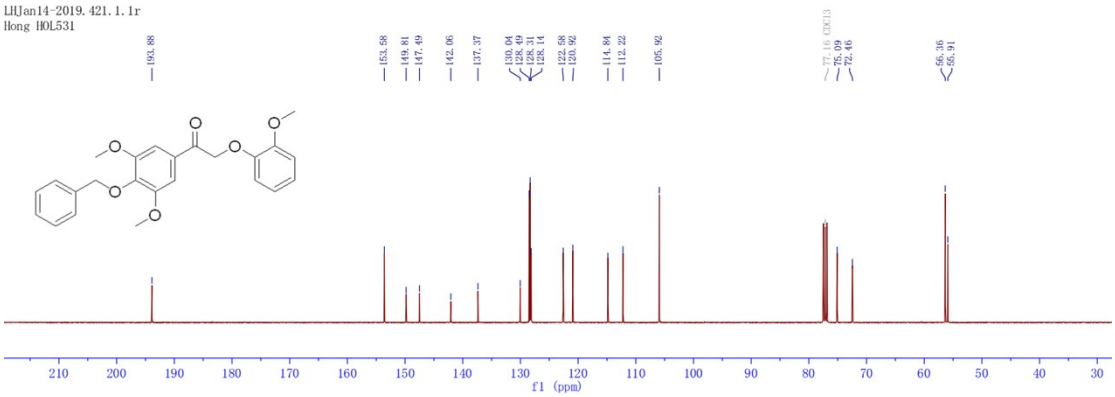
mmol, 1.00 eq.) and benzylchloride (2.9 ml, 25.0 mmol, 1.00 eq.) were dissolved in DMF (25.0 ml). Anhydrous K_2CO_3 (4.15 g, 30.0 mmol, 1.20 eq.) was added, and the mixture was stirred at 70 °C for 5.5 h. The mixture was cooled to rt and poured into water (150 ml), further cooled on an ice bath, and acidified with concentrated HCl. The product was extracted with ethyl acetate. The organic phase was washed with 2 M NaOH, water, and brine and dried over Na_2SO_4. After evaporation of the solvent, the crude product was recrystallized from ethyl acetate/cyclohexane, yielding **S1** as light-yellow crystals (5.80 g, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45–7.48 (m, 2H), 7.27–7.36 (m, 3H), 7.20 (s, 2H), 5.10 (s, 2H), 3.88 (s, 6H), 2.58 (s, 3H). Spectroscopic data for the title compound was consistent with the literature.[3]

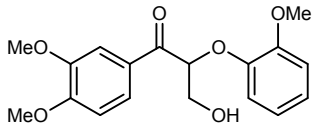
1-(4-(Benzyloxy)-3,5-dimethoxyphenyl)-2-bromoethanone (**S2**)[3]: According to the *General procedure B*, **S2** was obtained as light-yellow crystals from **S1** in 45%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45–7.48 (m, 2H), 7.27–7.36 (m, 3H), 7.22 (s, 2H), 5.12 (s, 2H), 4.41 (s, 2H), 3.88 (s, 6H). Spectroscopic data for the title compound was consistent with the literature.[3]



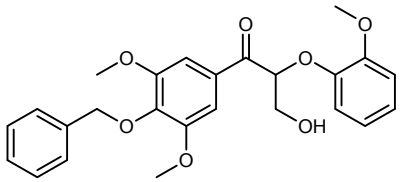
1-(4-Benzyloxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-ethanone (**1eb**): According to the *General procedure A*, **1eb** was obtained as yellow powder from **S2** in 73%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45–7.48 (m, 2H), 7.27–7.36 (m, 5H), 6.94–6.99 (m, 1H), 6.90–6.93 (m, 1H), 6.84–6.87 (m, 2H), 5.27 (s, 2H), 5.11 (s, 2H), 3.87 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.9, 153.6, 149.8, 147.5, 142.1, 137.4, 130.0, 128.5, 128.3, 128.1, 122.6, 120.9, 114.8, 112.2, 105.9, 75.1, 72.5, 56.4, 55.9; **HRMS (ESI)** m/z calcd. for $C_{24}H_{24}O_6$ $[M+Na]^+$ 431.1465, found: 431.1464.



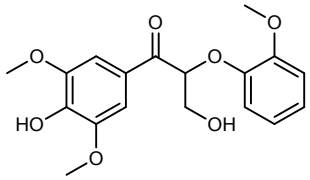




1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-propan-1-one (**1′-cb**)[4]: According to the *General procedure C*, **1′-cb** was obtained as white solid from **1cb** in 79%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (dd, ^3J = 5.6 Hz, ^4J = 1.3 Hz, 1H), 7.61 (d, ^4J = 1.3 Hz, 1H), 6.99 (dt, ^3J = 5.6 Hz, ^4J = 1.3 Hz, 1H), 6.91 (dd, ^3J = 5.4 Hz, ^4J = 1.0 Hz, 1H), 6.87–6.89 (m, 2H), 6.82 (dt, ^3J = 5.0 Hz, ^4J = 1.0 Hz, 1H), 5.40 (t, ^3J = 3.5 Hz, 1H), 4.07 (dd, ^3J = 4.4 Hz, ^3J = 3.5 Hz, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 3.85 (s, 3H), 3.17 (t, ^3J = 4.4 Hz, 1H). Spectroscopic data for the title compound was consistent with the literature.[4]



1-(3,5-Dimethoxy-4-benzyloxy-phenyl)-3-hydroxy-2-(2-methoxyphenoxy)-propan-1-one (**1′-eb**)[5]: According to the *General procedure C*, **1′-eb** was obtained as white solid from **1eb** in 71%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44–7.46 (m, 2H), 7.25–7.34 (m, 5H), 6.98 (dt, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H), 6.89 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H), 6.82 (dt, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1H), 5.36 (t, ^3J = 5.2 Hz, 1H), 5.10 (s, 2H), 4.09 (t, ^3J = 5.7 Hz, 2H), 3.82 (s, 6H), 3.80 (s, 3H), 3.34 (t, ^3J = 6.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 195.7, 153.4, 150.3, 146.8, 142.1, 137.3, 130.2, 128.4, 128.3, 128.1, 123.6, 121.2, 118.0, 112.3, 106.5, 84.3, 75.0, 63.6, 56.3, 55.8. Spectroscopic data for the title compound was consistent with the literature.[5]



1-(3,5-Dimethoxy-4-hydroxy-phenyl)-3-hydroxy-2-(2-methoxyphenoxy)-propan-1-one (**1′-fb**)[5]: According to the literature's method, a solution of compound **1′-eb** (1.58 g, 3.60 mmol, 1.00 eq.) and pentamethylbenzene (1.62 g, 10.8 mmol, 3.00 eq.) in dicholoromethane (15.0 mL) under N_2 was cooled to –78 °C in liquid N_2/acetone bath. To this mixture, BCl_3 (7.2 mL, 1 M solution in DCM, 7.20 mmol, 2.00 eq.) was added dropwise. The mixture was stirred at –78 °C for 30 min upon which the reaction was quenched with MeOH. The organic layer was immediately loaded onto celite and purified by column chromatography on SiO_2 (EtOAc/cyclohexane, 1:1) to obtain the product **1′-fb** (593 mg, 47%) as pale-yellow powder. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 (s, 2H), 6.99 (ddd, ^3J = 8.2 Hz, ^4J = 7.2 Hz, ^5J = 1.6 Hz, 1H), 6.88–6.92 (m, 2H), 6.82 (ddd, ^3J = 8.2 Hz, ^4J = 7.2 Hz, ^5J = 1.6 Hz, 1H), 6.09 (s, 1H), 5.34 (dd, ^3J = 6.2 Hz, ^4J = 4.4 Hz, 1H), 4.05–4.13 (m, 2H), 3.90 (s, 6H), 3.85 (s, 3H); **^{13}C NMR** (100

MHz, $CDCl_3$): δ 195.3, 150.5, 147.0, 146.9, 140.6, 126.5, 123.7, 121.3, 118.1, 112.4, 106.6, 84.6, 63.8, 56.6, 55.9. Spectroscopic data for the title compound was consistent with the literature.[5]

Optimization of reaction conditions

The pyridine catalyst, 4-(pyridin-4-yl)benzonitrile, which has been shown to be most active,[6] was chosen for the optimization. The radical degradation was initially performed with a higher concentration of **1aa** in dry toluene (1.0 M). To our delight, after 18 h, the reaction worked efficiently and the lignin model compound **1aa** was almost completely converted (by ^{1}H NMR spectroscopy, Fig. S1).

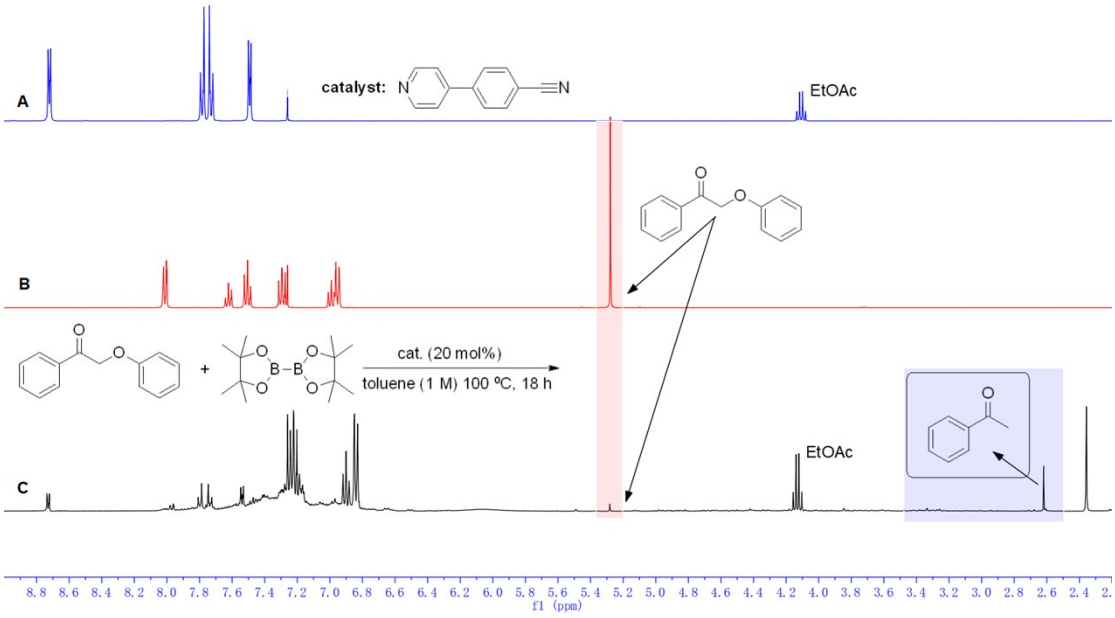


Figure S1. Initial NMR study of the radical process. ^{1}H NMR spectra: 4-(pyridin-4-yl)benzonitrile (**A**), lignin model compound **1aa** (**B**) and the reaction mixture (**C**). The signal highlighted in red originates from substrate **1aa**, while the signal highlighted in blue blanket is from the acetophenone product.

However, the isolated yield of the degraded product acetophenone was about 40% which was significantly lower than the conversion. To determine the reaction yield more reliably, calibration curves for GC-MS analysis have been prepared for lignin model **1aa**, acetophenone, phenol with *n*-undecane as standard (Fig. S2).

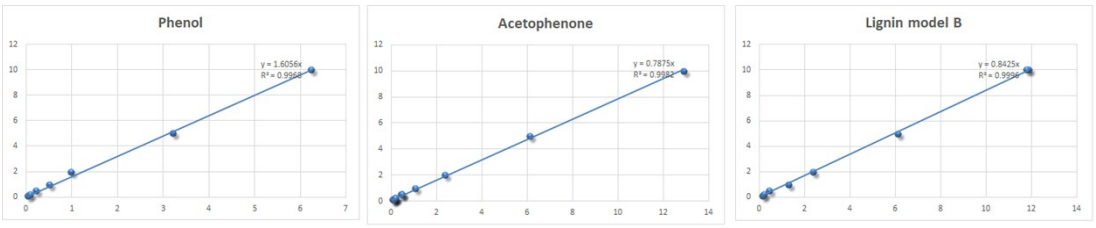
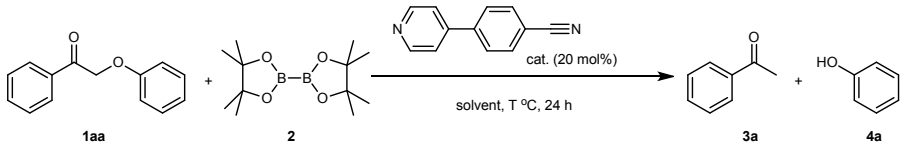


Figure S2. Calibration curves of phenol, acetophenone and lignin model **1aa** using *n*-undecane as standard.

The optimization of the reaction conditions was started by screening the concentration, followed by the solvent and temperature. All results were summarized in Table S1.

Table S1. Optimization of the radical degradation of lignin model compound **1aa**[a].



1aa **2** **3a** **4a**

Entry	Concentration of 1aa (M)	T (°C)	Solvent	Equivalent of 2	Conversion (%)	Yield (%)[b]	
						3a	4a
1	0.1	110	Toluene	1.5	29	14	21
2	0.25	110	Toluene	1.5	52	46	37
3	0.5	110	Toluene	1.5	85	66	35
4	1.0	110	Toluene	1.5	93	52	43
5	0.25	90	Toluene	1.5	48	39	27
6	0.25	130	Toluene	1.5	99	53	38
7	0.25	110	1,4-dioxane	1.5	87	60	37
8	0.25	110	Diglyme	1.5	99	55	47
9	0.25	110	n-octane	1.5	67	37	60
10	0.25	110	DMSO	1.5	10	10	7
11	0.25	110	DMF	1.5	> 99	72 (47)	78 (51)
12	0.25	140	DMF	1.5	> 99	80 (49)	87 (58)
13	0.5	140	DMF	1.5	> 99	83 (53)	91 (60)
14	0.5	140	DMAc	1.5	91	13	66
15	0.5	140	DMF	1.25	74	58	64
16	0.5	140	DMF	2.0	> 99	85	90

[a] Reaction conditions: under N_2, **1aa** (0.4 mmol, 1 eq.), **2** (x equivalent) and catalyst (0.08 mmol) were dissolved in the stated solvent and stirred at the given temperature for 24 h. 1 eq. of *n*-undecane was used as internal standard. [b] The yield was determined by GC-MS using calibration curves; isolated yield was shown in parentheses.

The best reaction conditions obtained are as follows: 1.5 equiv. $B_2(pin)_2$, 20 mol% of catalyst in DMF (0.5 M) at 140 °C for 24 h gave the best GC conversion of > 99% and a GC-yield of 83% and 91% of acetophenone (**3a**) and phenol (**4a**), respectively (entry 13). Yields of 61% and 77% for acetophenone and phenol were obtained via column chromatography without any aqueous work up.

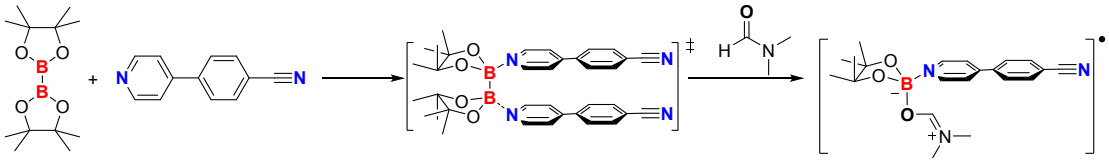


Figure S3. Explanation for the beneficial effect of DMF as solvent: DMF supports formation of the boryl radical.

In addition, the sensitivity of this radical process was evaluated by exposing the reaction to air or H_2O. The test reactions were performed according to the standard procedure and exposed to air and analysed by GC-MS after 24 h. Although, conversion was not as good as under N_2 after 24 h (Fig. S4, Eq. S1 & S2), the observation of the expected acetophenone and phenol degradation products demonstrate that the radical intermediate can survive for a short time in the presence of O_2 and H_2O. To accelerate the transformation, the reaction was tested in the microwave. Although the reaction was not faster, the lignin model compound was almost completely converted after 24 h (85% conversion determined by GC-MS) giving the degradation product acetophenone in a GC yield of 82% (Eq. S3).

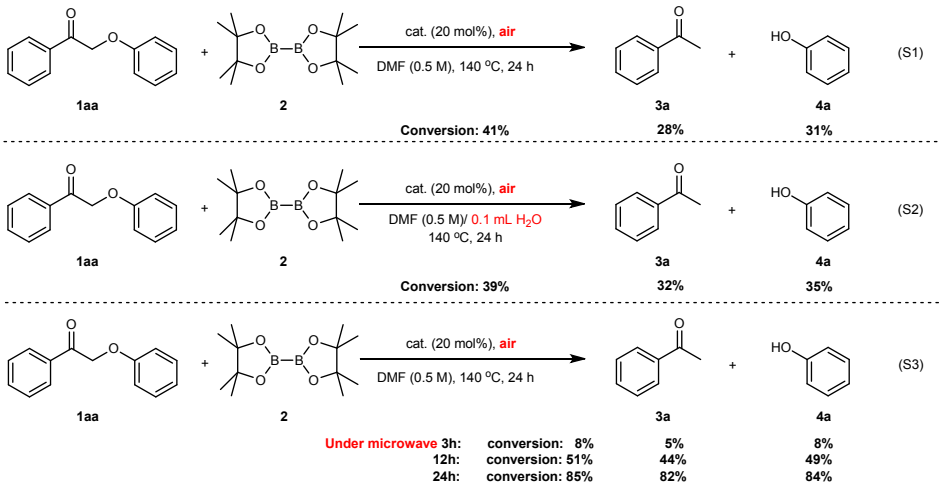
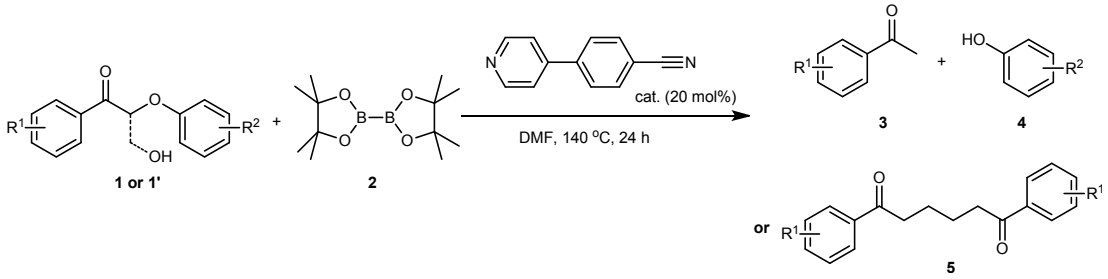


Figure S4. Reaction test under exposure to air and H_2O and in the microwave.

General procedure for the radical cleavage of model compounds



General procedure D: Substrate (1.00 eq.), $B_2(pin)_2$ (1.50 eq. for model compounds **1aa**, **1ba**, **1ab**, **1bb**, **1cb**, **1db**, **1eb**; while 3.00 eq. were used for **1′-cb**, **1′-eb**, **1′-fb**), 4-(4-pyridinyl)benzonitrile (20.0 mol%) were added into a Schlenk tube charged with a magnetic stir bar under N_2. The colour of the solid mixture turned into blue gradually. Then, 1.0 mL of dry DMF was added to dissolve the components. The reaction mixture was then stirred at 140 °C. After 24 h, the reaction mixture was cooled and quenched with aq. 2 M Na_2CO_3 (2.0 mL). The resulted mixture was stirred under air for 1 h, neutralized by aq. HCl (1 M) and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over Na_2SO_4 and then concentrated in vacuo to give the crude product. Purification by column chromatography (EtOAc/cyclohexane) and monitor with TLC and *p*-anisaldehyde stain was applied to obtain the product.

Radical cleavage of 1aa (11.1 mmol scale)**:** Model compound **1aa** (2.36 g, 11.1 mmol, 1.00 eq.), $B_2(pin)_2$ (4.23 g, 16.6 mmol, 1.50 eq.) and 4-(4-pyridinyl)benzonitrile (0.400 g, 2.22 mmol, 20.0 mol%) were subjected to the *General procedure D* described above. The reaction mixture was purified by column chromatography (acetone/cyclohexanes: 1/50) without any work-up obtaining acetophenone **3a** (824 mg, 62%) and phenol **4a** (807 mg, 77%).

Radical cleavage of 1ab (0.5 mmol scale)**:** Model compound **1ab** (121 mg, 0.500 mmol, 1.00 eq.) was subjected to the *General procedure D*. GC-MS analysis showed a conversion of 81%, and yields of 43% and 62% for acetophenone **3a** and guaiacol

4b, respectively. The reaction mixture was worked up and purified by column chromatography (acetone/cyclohexanes: 1/50) giving **3a** (24.0 mg, 40%) and **4b** (35.0 mg, 56%).

Radical cleavage of 1ba (0.5 mmol scale)**:** Model compound **1ba** (121 mg, 0.500 mmol, 1.00 eq.) was subjected to the *General procedure D*. GC-MS analysis showed a conversion of >99%, and yields of 54% and 56% for 1-(*p*-methoxy-phenyl)-ethanone **3b** and phenol **4a**, respectively. The reaction mixture was worked up and purified by column chromatography (acetone/cyclohexanes: 1/50) giving **3b** (36.0 mg, 43%) and **4a** (15.0 mg, 32%).

Radical cleavage of 1bb (0.5 mmol scale)**:** Model compound **1bb** (136 mg, 0.500 mmol, 1.00 eq.) was subjected to the *General procedure D*. GC-MS analysis showed a conversion of 87%, and yields of 47% and 58% for 1-(*p*-methoxy-phenyl)-ethanone **3b** and guaiacol **4b**, respectively. The reaction mixture was worked up and purified by column chromatography (acetone/cyclohexanes: 1/50) giving **3b** (32.0 mg, 43%) and **4b** (29.0 mg, 47%).

Radical cleavage of 1cb (0.5 mmol scale)**:** Model compound **1cb** (151 mg, 0.500 mmol, 1.00 eq.) was subjected to the *General procedure D*. GC-MS analysis showed a conversion of >99%, and yields of 68% and 60% for 1-(3,4-dimethoxy-phenyl)-ethanone **3c** and guaiacol **4b**, respectively. The reaction mixture was worked up and purified by column chromatography (acetone/cyclohexanes: 1/40) giving **3c** (51.0 mg, 57%) and **4b** (30.0 mg, 48%).

Radical cleavage of 1db (0.5 mmol scale)**:** Model compound **1db** (129 mg, 0.500 mmol, 1.00 eq.) was subjected to the *General procedure D*. GC-MS danalysis showed a conversion of 86% after 24h. The reaction mixture was worked up and purified by column chromatography (acetone/cyclohexanes: 1/35) giving 1-(*p*-hydroxy-phenyl)-ethanone **3d** (30.0 mg, 44%).

Radical cleavage of 1eb (0.5 mmol scale)**:** Model compound **1eb** (204 mg, 0.500 mmol, 1.00 eq.) was subjected to the *General procedure D*. GC-MS analysis showed a conversion of 86% after 24h. The reaction mixture was worked up and purified by column chromatography (EtOAc/cyclohexane: 1/10 to 1/4) giving 1-(*p*-benzyloxy-phenyl)-ethanone **3e** (73.0 mg, 44%) and guaiacol **4b** (27.0 mg, 44%).

Radical cleavage of 1′-cb (0.5 mmol scale)**:** Model compound **1′-cb** (151 mg, 0.500 mmol, 1.00 eq.) with 1.50 eq. $B_2(pin)_2$ was subjected to the *General procedure D*. The reaction mixture was worked up and purified by column chromatography (acetone/cyclohexanes: 1/40, then EtOAc/cyclohexane: 1/2 to 1/1) giving **5c** (47.0 mg, 49%) and **4b** (41.0 mg, 66%). Another run of this reaction with 3.0 eq. $B_2(pin)_2$ provided **5c** in 69% yield (67.0 mg).

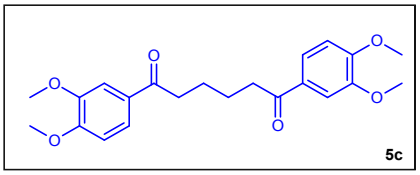
Radical cleavage of 1′-cb (4.0 mmol scale)**:** Model compound **1′-cb** (1.33 g, 4.00 mmol, 1.00 eq.), $B_2(pin)_2$ (3.05 g, 12.0 mmol, 3.00 eq.) and 4-(4-pyridinyl)benzonitrile (144 mg, 0.800 mmol, 20.0 mol%) were subjected to the *General procedure D*. The reaction mixture was purified by column chromatography (EtOAc/cyclohexane: 1/2 to 1/1) giving a light brown crude product, which was then recrystallized from ethyl acetate providing **5c** as white crystals (483 mg, 63%).

Radical cleavage of 1′-eb (1.2 mmol scale)**:** Model compound **1′-eb** (526 mg, 1.20 mmol, 1.00 eq.) with 3.0 equivalent $B_2(pin)_2$ was subjected to the *General procedure D*. The reaction mixture was worked up and purified by column chromatography (EtOAc/cyclohexane: 1/8 to 1/1) giving **5e** (188 mg, 52%) and guaiacol **4b** (91.0 mg, 61%).

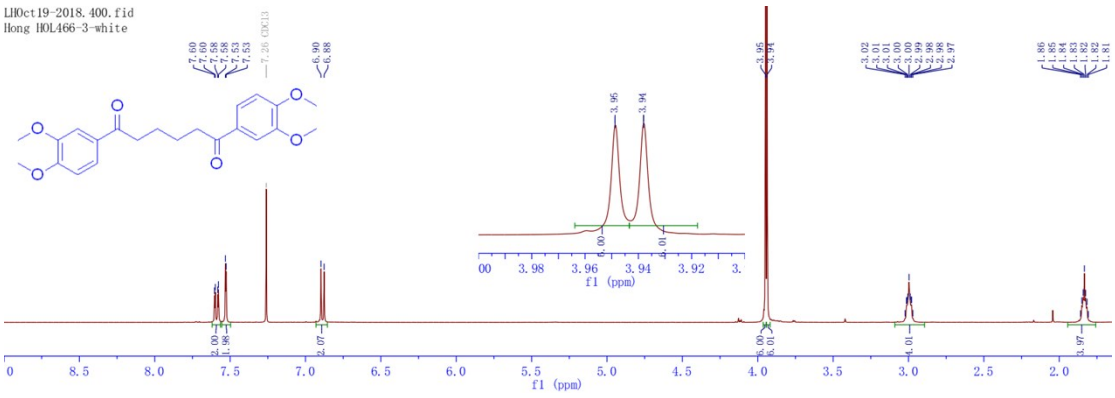
Radical cleavage of 1′-fb (2.0 mmol scale)**:** Model compound **1′-fb** (697 mg, 2.00 mmol, 1.00 eq.) with 3.0 equivalent $B_2(pin)_2$ was subjected to the *General procedure D*. The reaction mixture was worked up and purified by column chromatography (EtOAc/cyclohexane: 1/5 to 3/2) giving the crude product of **5f** (241 mg, 58%), which was not pure enough for the characterization by NMR spectroscopy. Attempts for

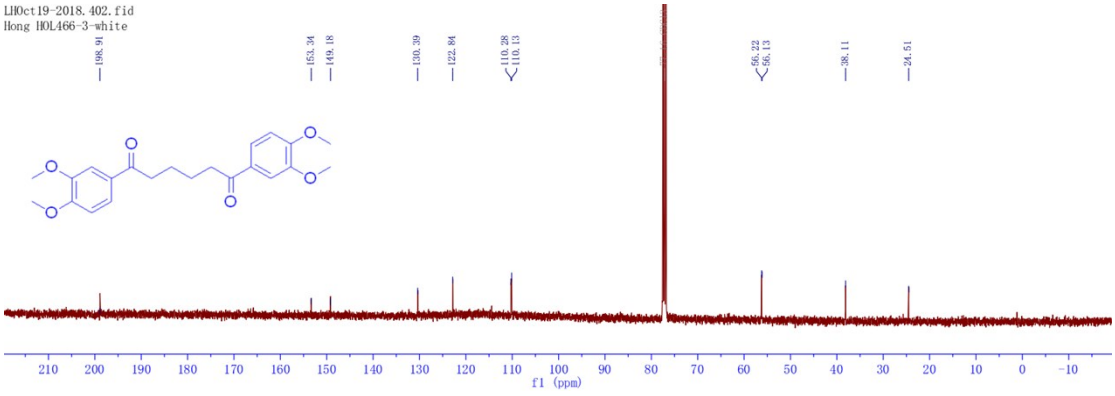
purification by column chromatography or recrystallization did not improve the purity significantly. Finally, some powder (11.0 mg) was obtained in a second recrystallization in EtOAc/cyclohexane with several drops of methanol, which was pure and then characterized by ^{1}H, ^{13}C, HSQC NMR spectroscopy and ESI-MS. In this case, the accurate isolated yield is difficult to determine. Quantification by LC-MS/MS was then performed in the third run of this reaction with a LC-MS yield of **5f** of 77%.

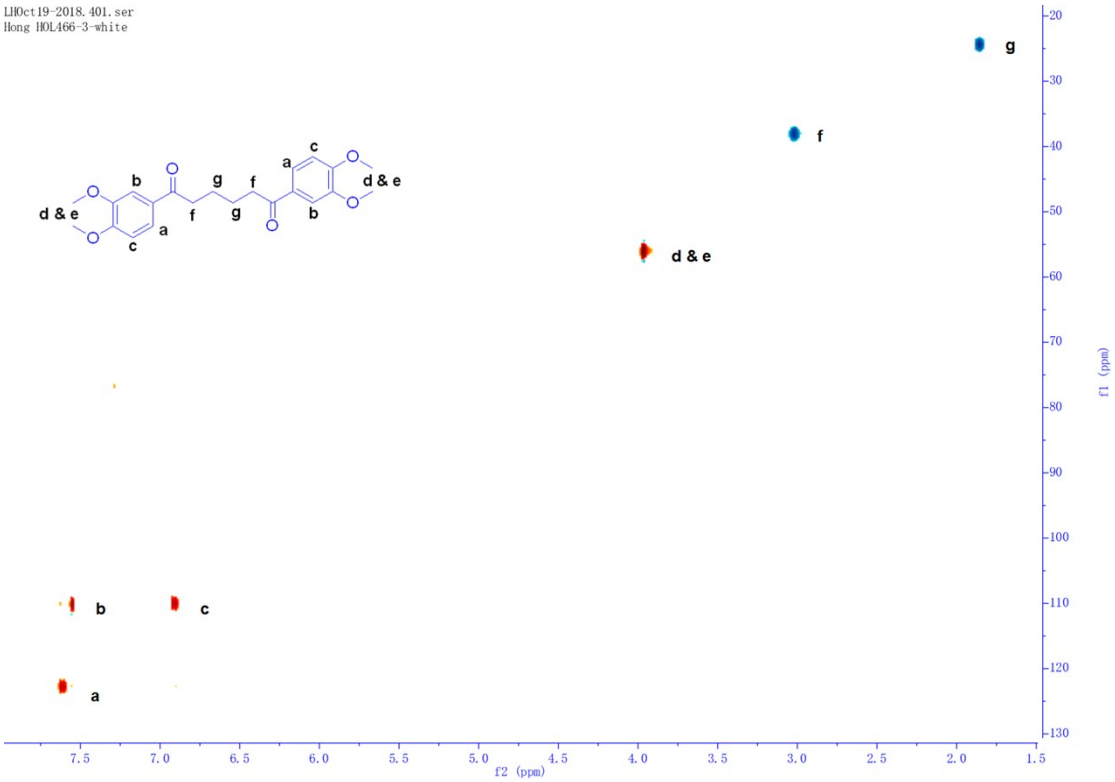
Analytical data of the domino depolymerization/ reconnection products

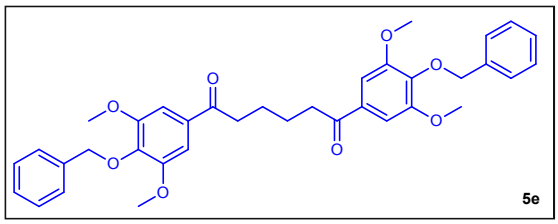


1,6-Bis(3,4-dimethoxyphenyl)-1,6-hexanedione (5c)[7]: White solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (dd, ^3J = 8.3 Hz, ^4J = 2.0 Hz, 2H), 7.53 (d, ^4J = 2.0 Hz, 2H), 6.89 (d, ^3J = 8.3 Hz, 2H), 3.95 (s, 6H), 3.94 (s, 6H), 2.97–3.02 (m, 4H), 1.80–1.87 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.9, 153.3, 149.2, 130.4, 122.8, 110.3, 110.1, 56.2, 56.1, 38.1, 24.5. Spectroscopic data for the title compound was consistent with the literature.[7]

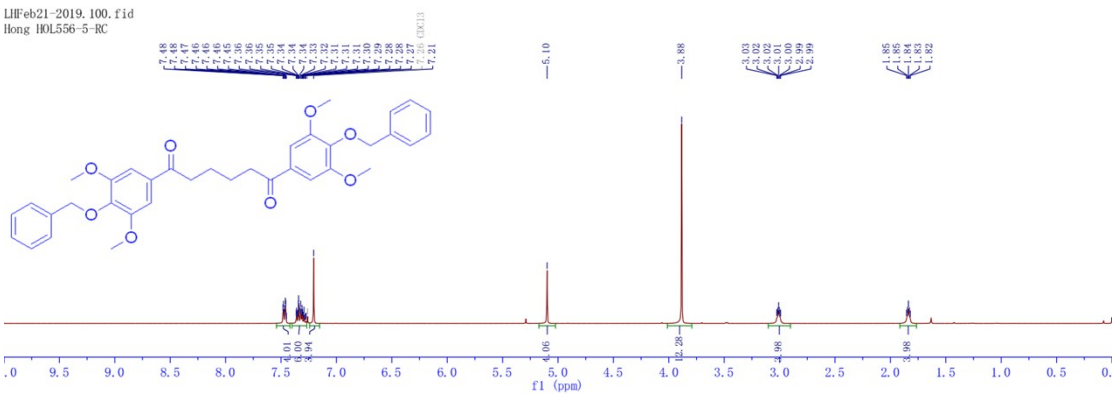








1,6-Bis(3,5-dimethoxy-4-benzyloxy-phenyl)-1,6-hexanedione (5e): White solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45–7.48 (m, 4H), 7.27–7.36 (m, 6H), 7.21 (s, 4H), 5.10 (s, 4H), 3.88 (s, 12H), 2.99–3.03 (m, 4H), 1.82–1.85 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.9, 153.5, 141.5, 137.5, 132.5, 128.6, 128.3, 128.1, 105.7, 75.1, 56.4, 38.3, 24.2; **HRMS (ESI)** m/z calcd. for $C_{36}H_{38}O_8$ $[M+Na]^+$ 621.2459, found: 621.2460.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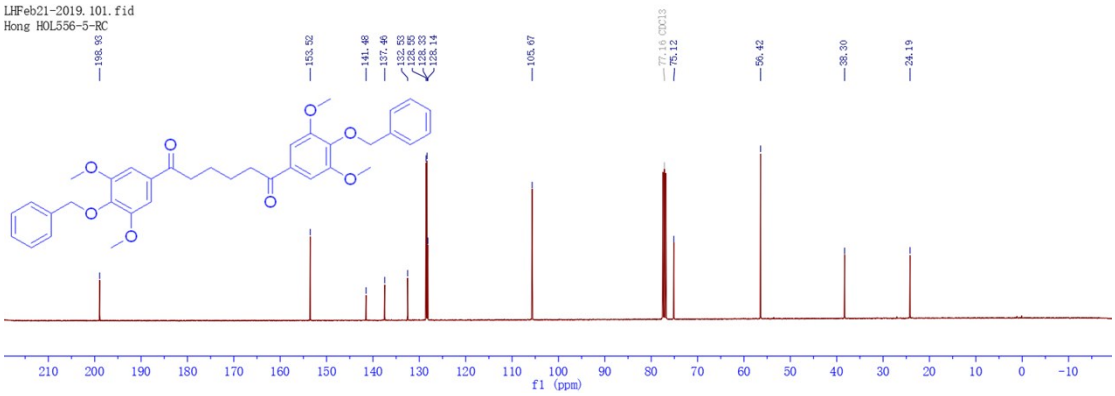
f1 (ppm)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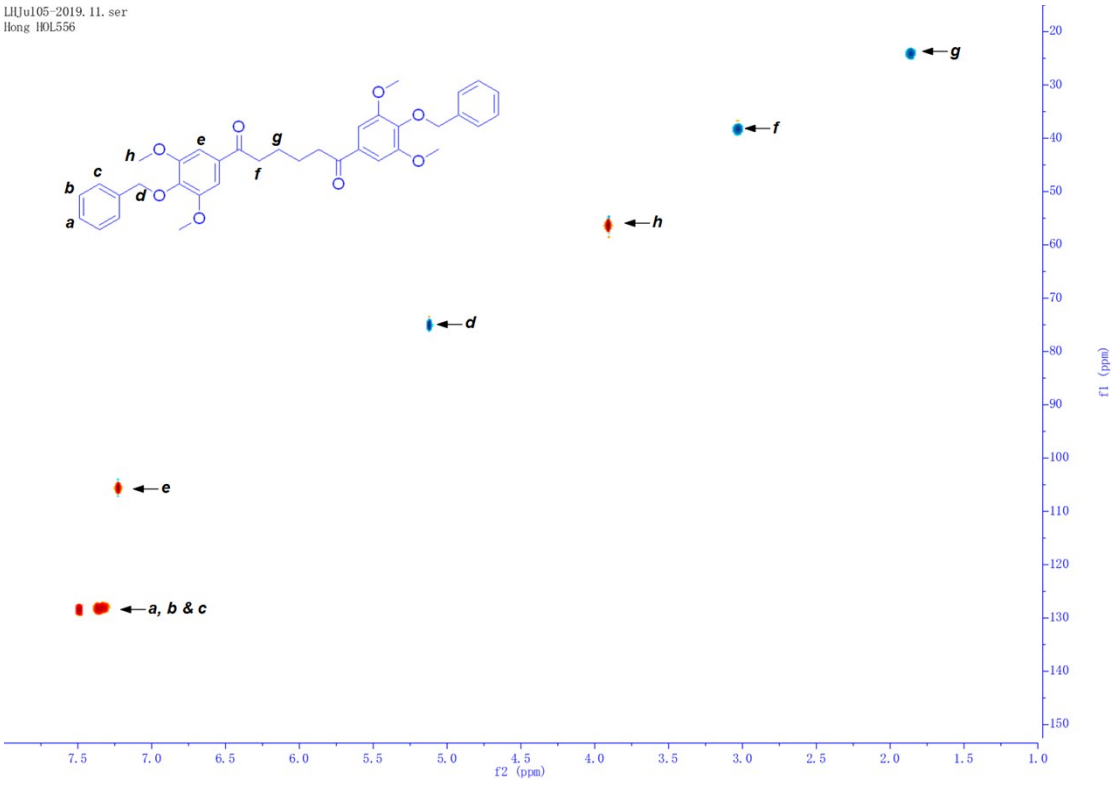
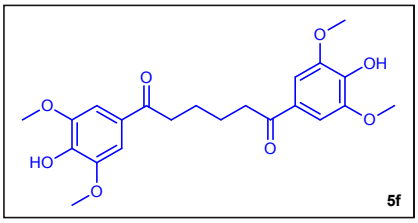
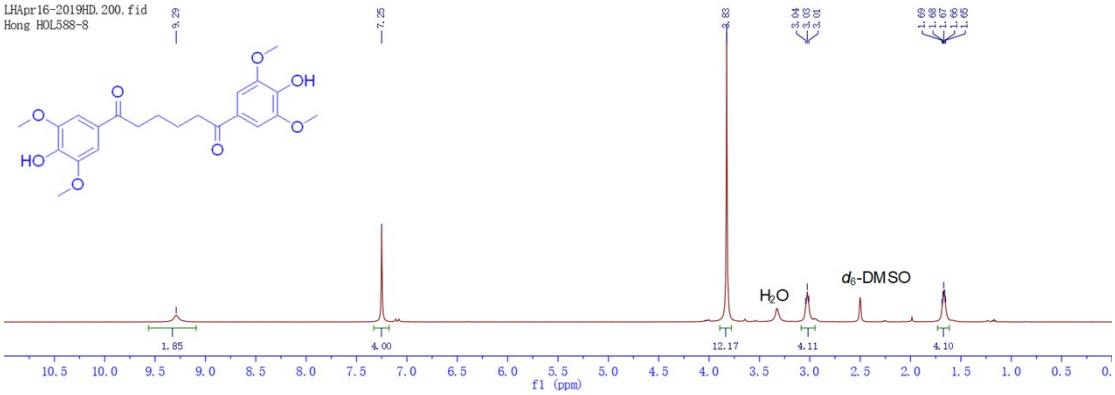
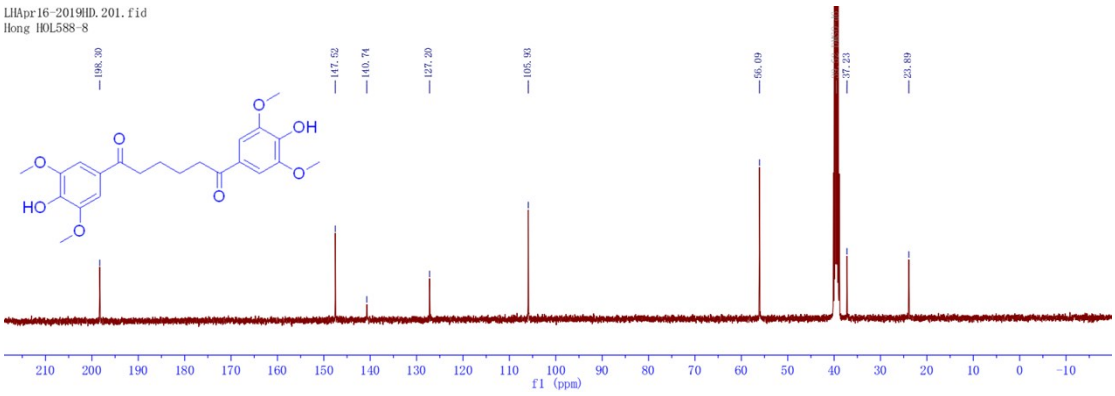
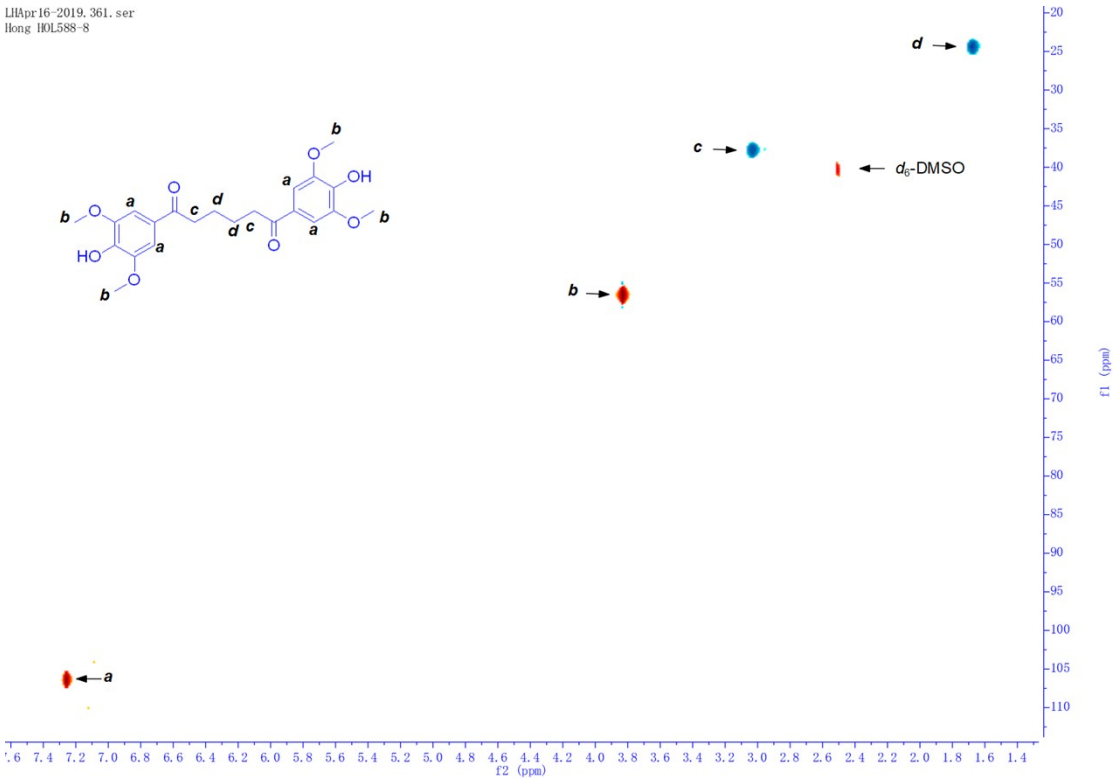

LHJul05-2019.11.ser
Hong HOL556
a
b
c
d
e
f
g
h
a, b & c
f2 (ppm)
f1 (ppm)



1,6-Bis(3,5-dimethoxy-4-hydroxy-phenyl)-1,6-hexanedione (5f)[8]: White powder. **^{1}H NMR** (400 MHz, d_6-DMSO): δ 9.29 (s, 2H), 7.25 (s, 4H), 3.83 (s, 12H), 3.01–3.05 (m, 4H), 1.65–1.69 (m, 4H); **^{13}C NMR** (100 MHz, d_6-DMSO): δ 198.3, 147.5, 140.7, 127.2, 105.9, 56.1, 37.2, 23.9. Spectroscopic data for the title compound was consistent with the literature.[8]

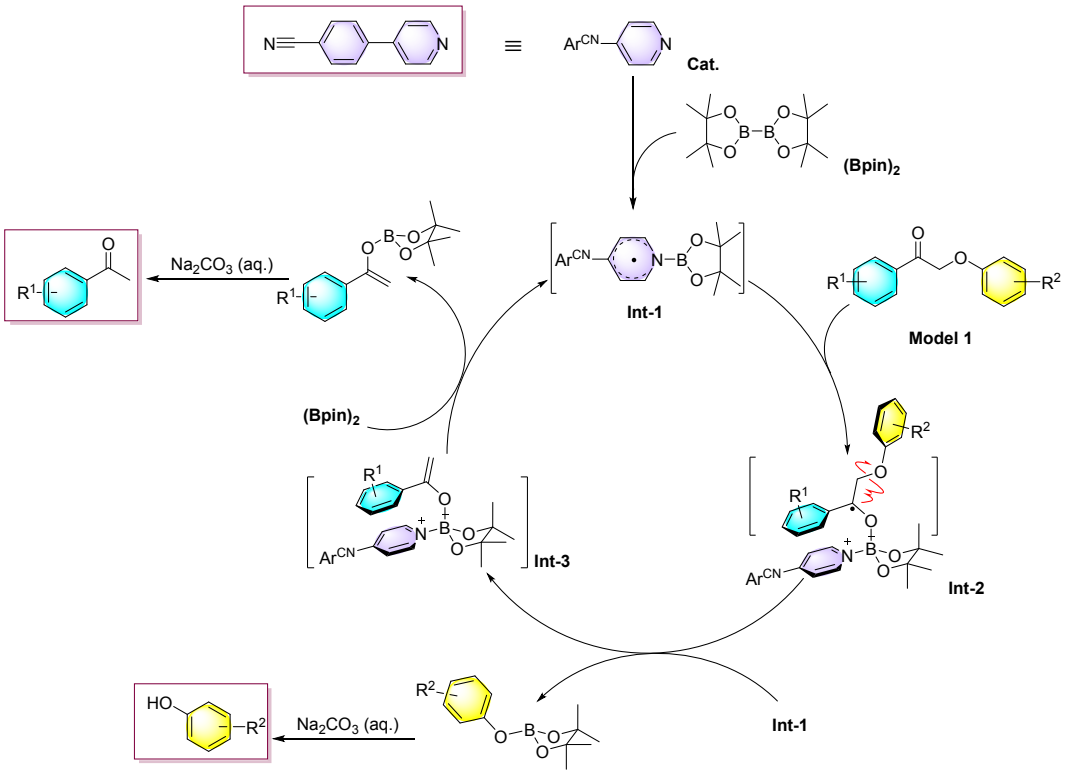





LHApr16-2019.361.ser
Hong HOL588-8
d
c
d6-DMSO
b
a
f2 (ppm)
f1 (ppm)

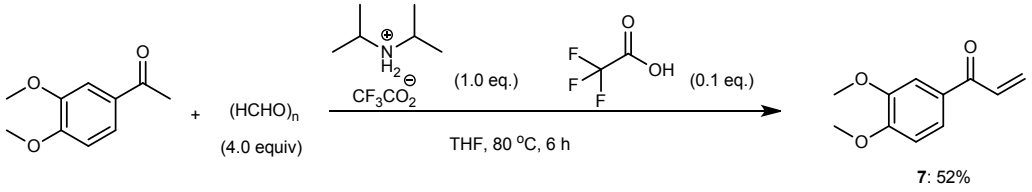
Control experiments and mechanistic discussion

Based on the reported mechanism of pyridine-ligated boryl radical,[6,9,10] a plausible reaction mechanism of the boryl radical cleavage of C–O ether bond in the model compounds was proposed in Scheme S1. The catalytic cycle of boryl radical cleavage of C–O ether bond was initiated by the homolytical cleavage of the B–B bond of $(Bpin)_2$ by 4-(pyridin-4-yl)benzonitrile (**Cat.**). The generated pyridine-ligated boryl radical (**Int-1**) underwent a radical addition with the carbonyl group in the model compounds leading to a ketyl radical intermediate (**Int-2**). Subsequently, an intramolecular single electron transfer (SET) process triggered the cleavage of C–O ether bond. Further radical coupling of the released phenyl oxide radical with another boryl radical formed the pinacol phenolate borate which was finally transformed into corresponding phenol by deborylation with Na_2CO_3 solution. Meanwhile, the generated pinacol enolate borate intermediate (**Int-3**) could release the cleaved product acetophenone in the present of excess amount of $(Bpin)_2$ furnishing the pyridine-ligated boryl radical to the next cycle.



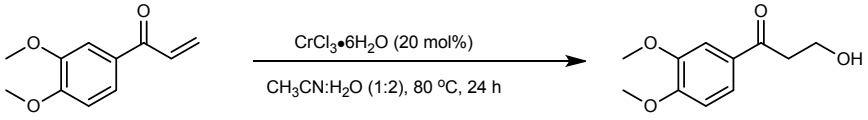
Scheme S1. Proposed mechanism of the boryl radical cleavage of C–O ether bond in oxidized lignin model compounds.

To probe the mechanism of radical dimerization, benzylic alcohol and 3-phenyl-propan-1-ol were selected to evaluate the stability of aliphatic hydroxy groups in the radical process. 1-(3,4-Dimethoxyphenyl)-2-en-1-propone (**7**) and 1-(3,4-dimethoxyphenyl)-3-hydroxy-1-propanone (**6**) were chosen to differentiate between route A-a and A-b (Fig. 6, main manuscript). Benzylic alcohol, 3-phenyl-propan-1-ol were purchased from Fisher Scientific International, Inc. and were used directly as received, **6** and **7** were synthesized according to the literatures' method as described below.[11,12]



1-(3,4-Dimethoxyphenyl)-2-en-1-propone (**7**)[13]: To a mixture of 1-(3,4-dimethoxyphenyl)-ethanone (3.60 g, 20.0 mmol, 1.00 eq.) and paraformaldehyde (1.20 g, 40.0 mmol, 2.00 eq.) in dry THF (30.0 mL) was added the ammonium salt (freshly prepared before use, 4.30 g, 20.0 mmol, 1.00 eq.) and trifluoroacetic acid (154 μL, 2.00 mmol, 10.0 mol%). The reaction mixture was stirred open to the atmosphere at reflux for 2 h. The mixture became clear. The reaction mixture was cooled down to rt and another portion of paraformaldehyde (1.20 g, 40.0 mmol, 2.00 eq.) was added. The reaction mixture was stirred at reflux for an additional 4 h open to the atmosphere. The reaction mixture was cooled down and the solvent was removed under reduced pressure, dissolved in Et_2O and washed with HCl solution (1 M), NaOH solution (1 M), and brine. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography using EtOAc/cyclohexane (1/20) as the eluent giving the product as yellow oil (2.00 g, 52%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (dd, ^3J = 8.3 Hz, ^4J = 2.0 Hz, 1H), 7.50 (d, ^4J = 2.0 Hz, 1H), 7.13 (dd, ^3J = 17.0 Hz, ^3J = 10.5 Hz, 1H), 6.84 (d, ^3J = 8.3 Hz, 1H), 6.36 (dd, ^3J = 17.0 Hz, ^2J = 1.8 Hz, 1H), 5.80 (dd, ^3J = 10.5 Hz, ^2J = 1.8 Hz, 1H), 3.88 (s, 3 H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.0, 153.4, 149.2, 131.9, 130.4, 129.2, 123.4, 110.7, 110.0, 56.0,

56.0. Spectroscopic data for the title compound was consistent with the literature.[13]



7 **6**: 19%

1-(3,4-Dimethoxyphenyl)-3-hydroxy-1-propanone (**6**)[14]: Vinyl ketone **7** (1.49 g, 7.76 mmol, 1.0 equiv) and $CrCl_3 \cdot 6H_2O$ (414 mg, 1.55 mmol, 20.0 mol%) were stirred in CH_3CN/H_2O (8 mL/16 mL) at 80 °C for 24 h. Upon completion of the reaction (as indicated by TLC), the reaction mixture was extracted with ethyl acetate (3 × 100 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The obtained crude residue was purified by silica gel column chromatography using EtOAc/cyclohexane (3/10) as the eluant to afford the product **6** as yellow solid (303 mg, 19%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H), 7.50 (d, ^4J = 2.0 Hz, 1H), 6.88 (d, ^3J = 8.4 Hz, 1H), 4.00 (t, ^3J = 5.4 Hz, 2H), 3.93 (s, 3H), 3.92 (s, 3H), 3.18 (t, ^3J = 5.4 Hz, 2H), 2.80 (br s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 199.2, 153.8, 149.2, 130.1, 123.1, 110.2, 110.0, 58.4, 56.2, 56.1, 40.0. Spectroscopic data for the title compound was consistent with the literature.[14]

The control experiments were then performed according to the *General procedure D* using these four compounds described above as substrates. All results were summarized in Fig. 7 in the main manuscript. As monitored by TLC, both, the reactions of benzylic alcohol and 3-phenyl-propan-1-ol did not lead to any products after the standard workup, which meant that the radical reaction does not occur in the presence of aliphatic hydroxy groups. The reaction of vinyl ketone **7** generated a product which appeared as gel-like polymer after flash column chromatography purification using MeOH/DCM as eluent. However, the low solubility of the product in common solvents caused difficulties in characterization.

These results revealed that the cleavage of the hydroxyl group could not be initiated in the presence of boryl radical and thus excludes the mechanistic routes B and C in Fig. 6 in main manuscript. Both compounds **6** and **7** could undergo a

transformation in the radical process, especially compound **6** could produce the dimer **5f**. That shows the feasibility of route A. As discussed in main manuscript, the radical addition of alcohol **6** would generate an α-ketyl radical intermediate with a hydroxyl group at γ-position, which enables the bidentate complexation with pinacolborane (Fig. S5). The six-member ring could stabilize the carbon radical intermediate and also inhibit dimerization in α-position. The high strain within the spirocycle (six-member ring spiroconnected with the five-member ring of pinalcol borane) would then initiate the intramolecular single electron transfer followed by a dimerization.

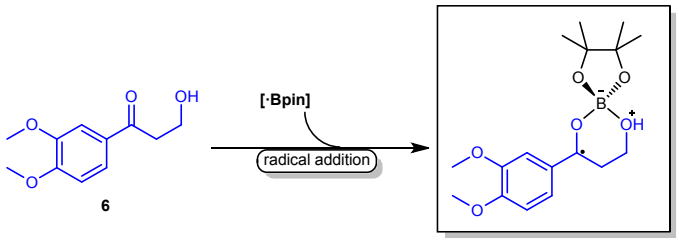


Figure S5. Spiro intermediate via radical addition of β-hydroxyketone **6.** Benzylic position is beneficial for the stabilization of the radical.

Lignin extraction

Organosolv-lignin was chosen in a first proof-of-concept study with lignin to avoid any solubility problems. The organosolv-lignin was extracted with 1,4-dioxane from wood sawdust according to literatures' procedure.[4,14,15] The sawdust of pine wood was obtained from carpenter workshop in our institute, and was then subjected to the literature's lignin extraction process.

10.1 g of wood sawdust was subjected to a Soxhlet extractor with 100 mL of ethanol and 200 mL of toluene overnight. Afterward, the sawdust was dried under reduced pressure and was refluxed by 200 mL of 1,4-dioxane with 8 mL of hydrochloric acid (1.0 M). After 4 h of extraction, the sawdust was filtered, and the filtrate was concentrated to about 60 mL which was then added dropwise into 300 mL of intensively stirred warm deionized water (about 35 °C). The remaining solution of lignin was then left in refrigerator overnight. Afterward, a simple filtration gave 105 mg of brown powder which was then further purified by two precipitations in water and two in diethylether. The obtained light brown powder (74.6 mg) was then analyzed by HSQC spectroscopy and GPC. The signals corresponding to the major structural linkages (A: *β*-O-4, B: *β*-*β* and C: *β*-5) were identified (Figure S6, top), and the abundance was calculated as below based on the integral area corresponding to the α-proton in linkages relative to the aromatic signals while maintaining the same contour level. (Figure S6, bottom). The results of calculation were summarized in Table S1.

$\boldsymbol{I}(\mathrm{C9}) = 0.5\ \boldsymbol{I}(\mathrm{S_{2,6}}) + \boldsymbol{I}(\mathrm{G_2})$ $\boldsymbol{I}(\mathrm{unit}) = \boldsymbol{I}(\mathrm{unit_\alpha}) / \mathbf{n}(\mathrm{H})$ $\boldsymbol{P}(\mathrm{unit}) = [\boldsymbol{I}(\mathrm{unit}) / \boldsymbol{I}(\mathrm{C9})] \times 100\%$	where $\boldsymbol{I}$ is the integral area of characteristic peak; $\mathbf{S_{2,6}}$ is the peak from the two othor-protons of syringyl moiety, while $\mathbf{G_2}$ for the othor-proton of guaiacol moiety and $\mathbf{unit_\alpha}$ for the α-proton of unit; **n(H)** is the number of α-proton in each unit; **P**(unit) is the percentage of unit.

$\boldsymbol{I}(\mathrm{C9}) = 0.5\ \boldsymbol{I}(\mathrm{S_{2,6}}) + \boldsymbol{I}(\mathrm{G_2}) = 0.5 \times 70.1 + 100.0 = 135.1$

$\boldsymbol{P}(\beta\text{-O-4}) = [\boldsymbol{I}(\beta\text{-O-4}_\alpha) / \boldsymbol{I}(\mathrm{C9})] \times 100\% = [40.1 / 135.1] \times 100\% = 29.7\%$

$$\boldsymbol{P}(\beta\text{-}\beta) = [(8.4 / 2) / 135.1] \times 100\% = 3.1\%$$

$$\boldsymbol{P}(\beta\text{-}5) = [(9.4 / 1) / 135.1] \times 100\% = 7.0\%$$

Table S2. Characterisation of lignin analysed with 2D-HSQC NMR.

Lignin sample	**Aromatic units' percentage S, G, H (%)**	**Linkages (per 100 C9 units)**		
		β-O-4	**β-β**	**β-5**
Organosolv-lignin	26, 74, trace	29.7	3.1	7.0

Furthermore, a larger scale extraction was performed starting with 50.0 g wood sawdust to obtain 2.52 g of crude organosolv-lignin which was used later for DDQ-oxidation and depolymerization.

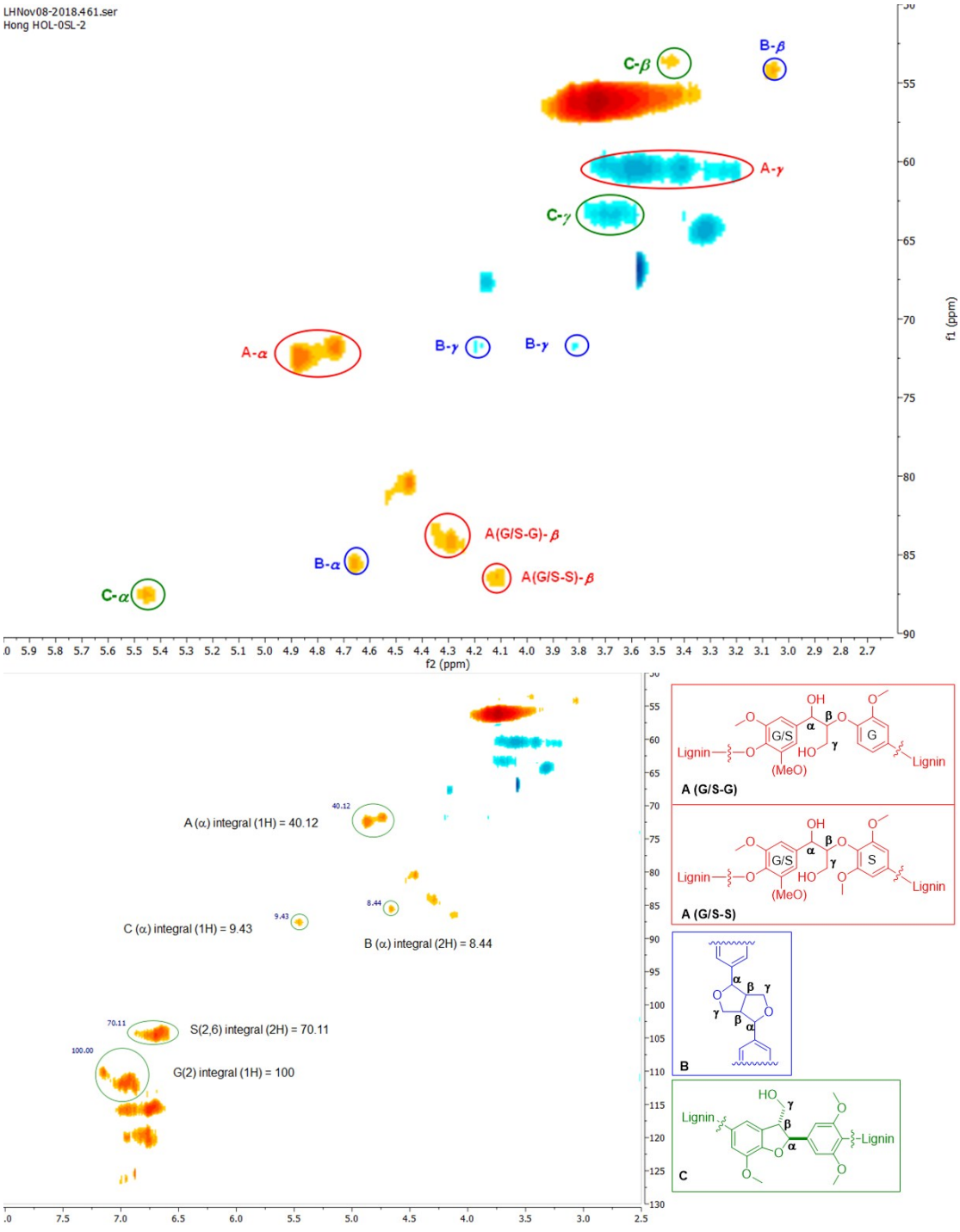


Figure S6. Linkage structure assignment in partial 2D HSQC NMR spectrum (d_6-DMSO) of organosolv-lignin (top); abundance calculation based on the integral area of characteristic peaks (bottom).

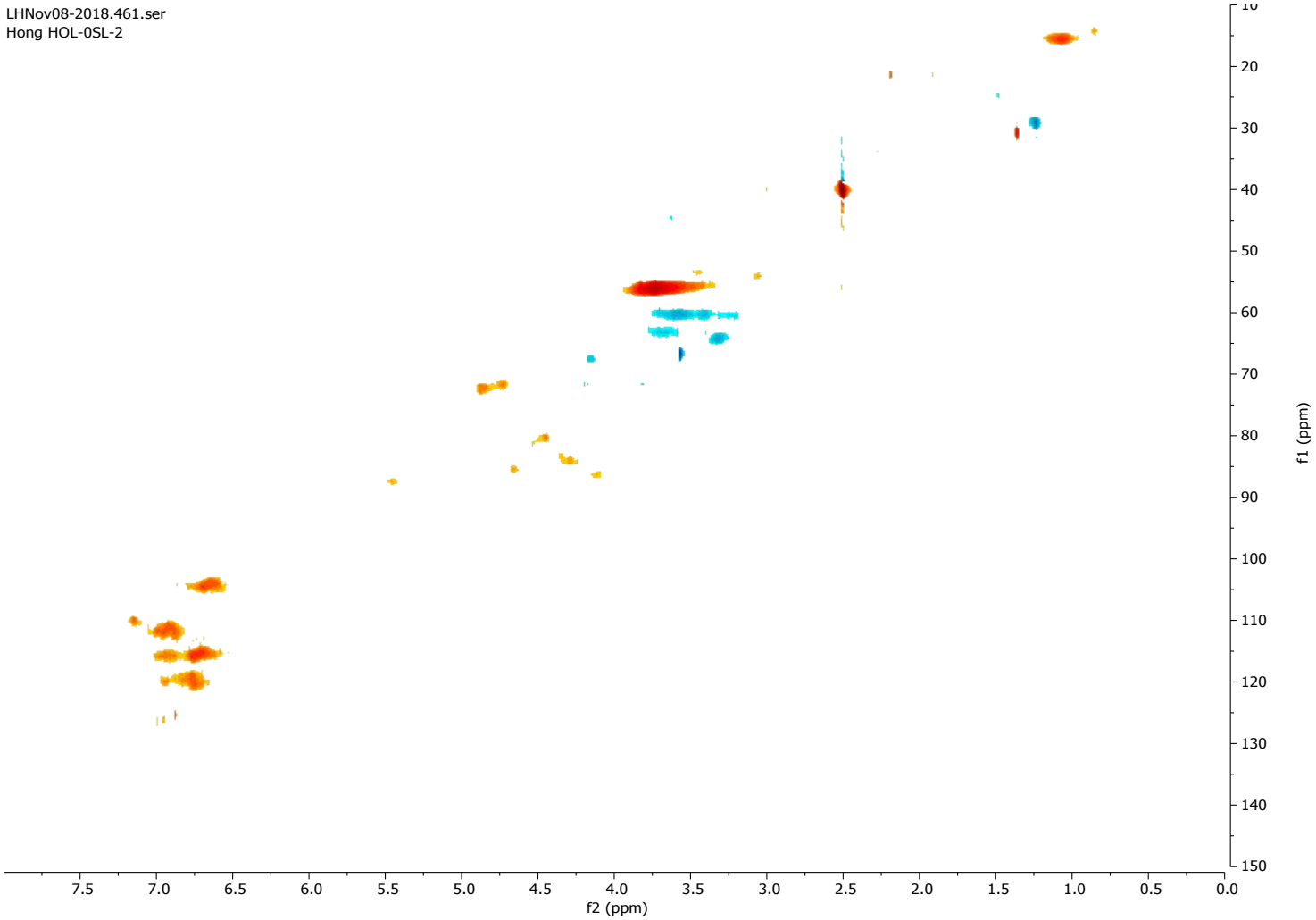


Figure S7. Original HSQC NMR spectrum of organosolv-lignin in d_6-DMSO.

Lignin oxidation

With the organosolv-lignin in hand, oxidation with DDQ was performed according to the well-developed procedure.[16] To a stirred solution of organosolv-lignin (1.2 g, 1.0 wt. eq.) in 1,4-dioxane (30 mL) was added DDQ (1.6 g). The solution was heated to 80 °C for 2 h, cooled, filtered through a pad of celite and washed with 1,4-dioxane (4 mL). The filtrate was added dropwise to Et_2O (300 mL) and the resulting precipitate was filtered and washed with excess Et_2O. The obtained lignin$^{\alpha\text{-ox}}$ (brown powder, 0.76 g) was dried to a constant weight in vacuum overnight prior to analysis and the radical depolymerization.

The oxidized organosolv-lignin was characterized by HSQC-NMR spectroscopy. The signals corresponding to the major structural linkages (A^{ox}: β-O-4$^{\alpha\text{-ox}}$) were identified by comparing with the literatures' value[4,16] (Figure S8, top), and the abundance was calculated as below based on the integral area corresponding to the β-proton in β-O-4$^{\alpha\text{-ox}}$ relative to the aromatic signals while maintaining the same contour level. (Figure S8, bottom). The results of calculation were summarized in Table S2.

$$\boldsymbol{I}(C9) = 0.5\ \boldsymbol{I}(S_{2,6}) + \boldsymbol{I}(G_2) = 0.5 \times (130.1 + 4.2) + 100.0 = 167.2$$

$$\boldsymbol{P}(\beta\text{-O-4}^{\alpha\text{-ox}}) = [\boldsymbol{I}(\beta\text{-O-4}^{\alpha\text{-ox}}{}_{\beta}) / \boldsymbol{I}(C9)] \times 100\% = [(13.5 + 23.7) / 167.2] \times 100\% = 22.2\%$$

Table S3. Characterisation of oxidized-lignin analysed with 2D-HSQC NMR.

Lignin sample	Aromatic units' percentage S, G, H (%)	Linkage (per 100 C9 units) β-O-4$^{\alpha\text{-ox}}$
Oxidized-lignin	40, 60, trace	22.2

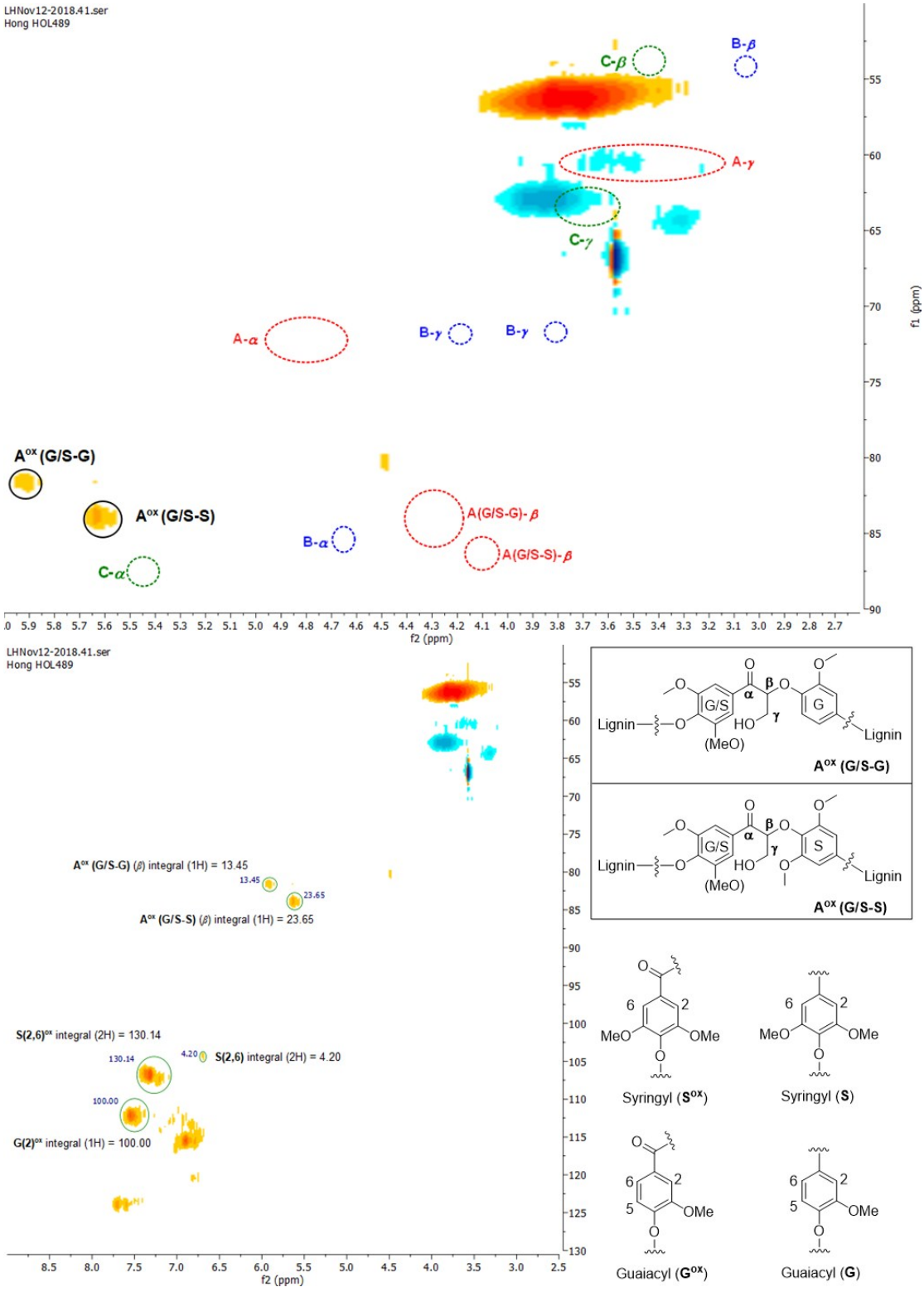


Figure S8. Linkage structure assignment in partial 2D HSQC NMR spectrum (d_6-DMSO) of DDQ-oxidized organosolv-lignin (top); abundance calculation based on the integral area of characteristic peaks (bottom).

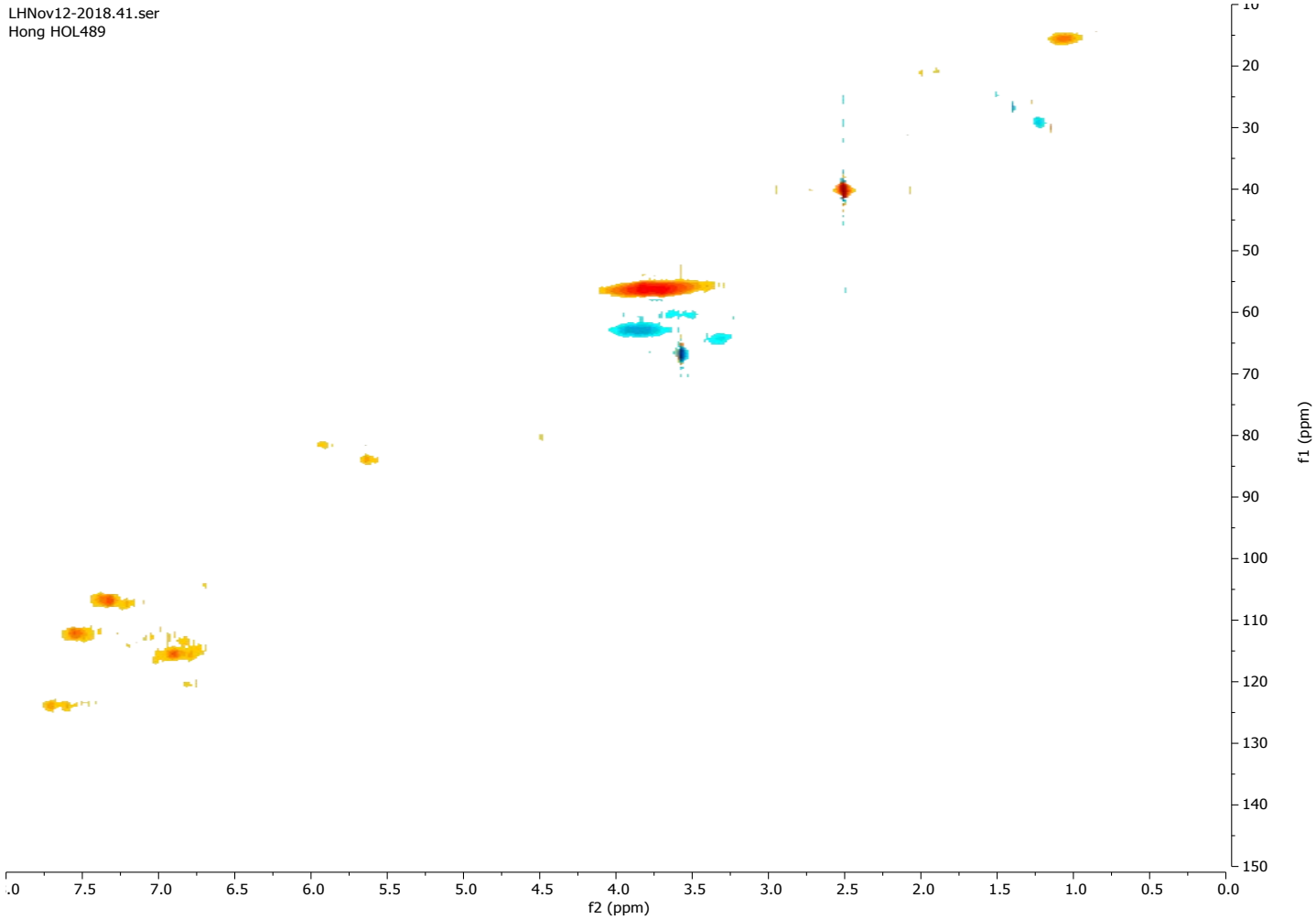


Figure S9. Original HSQC-NMR spectra of DDQ oxidized organosolv-lignin in d_6-DMSO.

Quantitative ^{31}P NMR analysis of lignin and oxidized lignin

The quantitative ^{31}P NMR analysis for the phenolic and the aliphatic hydroxyl groups in the organosolv-lignin, oxidized lignin was conducted on a Brukner 600 MHz spectrometer following previous literature report.[17] In a glovebox, 2.0 mL of $CDCl_3$ and 3.2 mL of pyridine were combined as the solvent-mix for the ^{31}P quantify analysis. 6.1 mg of $Cr(acac)_3$ was dissolved by 1.0 mL of mix-solvent in a vial followed by the addition of NHND (18.5 mg) as the SI solution (1.27 g). 30.2 mg of pre-dried lignin was mixed with 10.0 μL (11.2 mg) of SI solution in a vial, and 0.5 mL of mix-solvent was added to dissolve the sample. The sample solution was taken out from the glovebox and 0.1 mL of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxa-phospholane was added and transferred to an NMR tube for NMR acquisition using 512 scans, 250 ppm sweep width and a relaxation delay of 10 sec. For the oxidized lignin, 10.7 mg of pre-dried oxidized lignin sample was used, and 11.6 mg of SI solution was added.

Table S4. Typical integration regions for organosolv-lignin and oxidized lignin in ^{31}P NMR spectrum.

Lignin functional group	**Chemical shift (p.p.m.)**	**Ratio of the integration of the region of interest over the standard region**	
		Lignin (30.2 mg)	Ox-lignin (10.7 mg)
Aliphatic OH	~145.4–150.0	127.1	10.64
Phenolic OH	~137.6–144.0	41.83	12.07
Guaiacyl OH (G)	~139.0–140.2	27.04	1.80
Syringyl OH (S)	~142.7	7.52	1.06

COOH	~133.6–136.0	7.20	5.40

Table S5. Quantitative ^{31}P NMR calculating of the hydroxyl groups content in lignin and oxidized lignin.

Sample	**OH (mmol/g)**				
	Aliphatic OH	**Phenolic OH**	**Guaiacyl OH (G)**	**Syringyl OH (S)**	**COOH**
Lignin	3.72	1.23	0.79	0.22	0.21
Ox-lignin	0.91	1.03	0.15	0.09	0.46

Lignin degradation

The α-oxidized organosolv-lignin was then subjected to the radical depolymerization procedure: α-oxidized organosolv-lignin (49.7 mg, 1.00 wt. eq.), $B_2(pin)_2$ (163 mg, 3.28 wt. eq.), 4-(4-pyridinyl)benzonitrile (7.9 mg, 0.160 wt. eq.) were placed into a Schlenk tube charged with a magnetic stir bar under N_2. Then, 1.2 mL of dry DMF was added to dissolve the components. The reaction mixture was stirred at 140 °C. After 24 h, the reaction mixture was cooled and quenched with aq. 2 M Na_2CO_3 (2.0 mL). The resulted mixture was stirred under air for another 1 h, and was then neutralized by aq. HCl (1 M), extracted with EtOAc (15 mL × 3). The obtained organic phase was dried over Na_2SO_4. After filtration and removal of the solvent, a brown oil residue was obtained, which was then analyzed by 2D-HSQC NMR spectroscopy, GPC and LC-MS/MS quantification.

The obtained HSQC-NMR spectrum of the degradation mixture (orange-cyan colour) was compared with that of oxidized lignin (grayscale colour). The oxidized β-O-4 linkage disappeared after the treatment with boryl radical conditions (Figure S10).

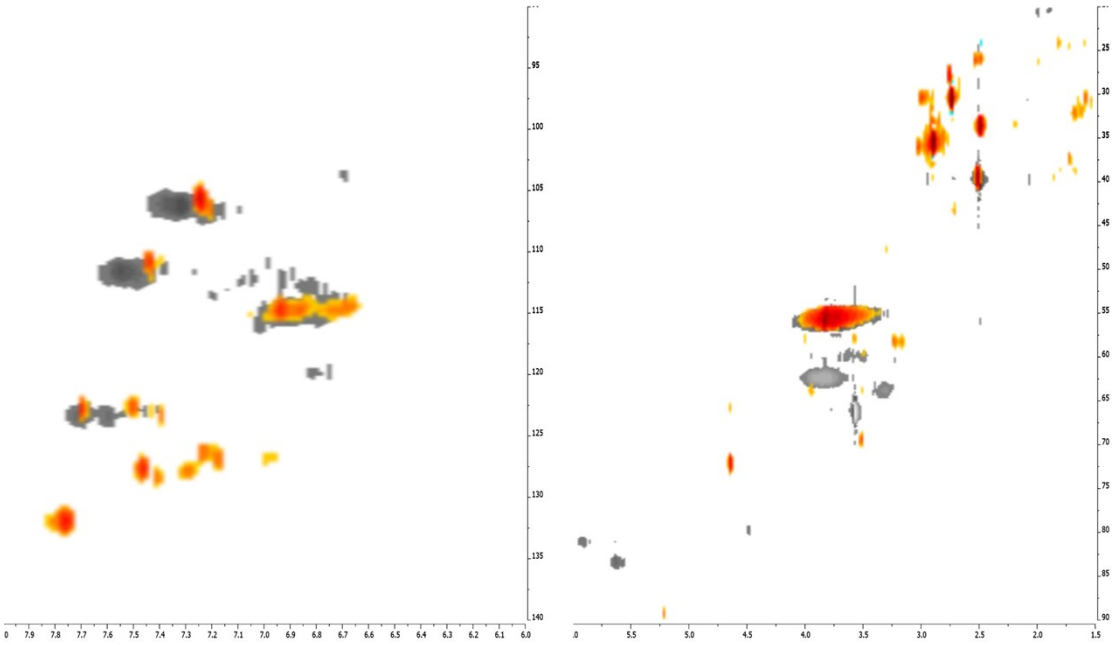


Figure S10. HSQC-NMR spectral overlap of oxidized lignin (grayscale color) with degradation mixture (orange-cyan color) in d_6-DMSO. The left part shows the area of {(8.0–6.0), (140.0–90.0)} while the right part shows the area of {(6.0–1.5), (90.0–20.0)}.

Figure S11. Original HSQC-NMR spectra of degradation mixture in d_6-DMSO.

GPC analysis

The molecular weight distribution profiles of the lignin and the depolymerized product mixture were obtained by GPC performed on an HPLC 2000 system (Jasco, Groß-Umstadt) with a LaChrom Autosampler (Merck-Hitachi, Darmstadt), applying a size-exclusion column (1.000 Å, 5 µm, MCX, PSS, Mainz) fitted with a UV-detector (254 nm). The samples were eluted with 0.1 M NaOH solution with 0.1 wt.% of NaN_3 at a flow rate of 1.0 mL/min. Molecular weight calibration was performed with polystyrene sulfonate standards and 4,4'-Biphenylcarboxylic-acid standards. 7 mg of the samples were diluted in 5 mL of DMSO/pyridine combining solvent (v/v, 5:1) and were used for the GPC measurement.

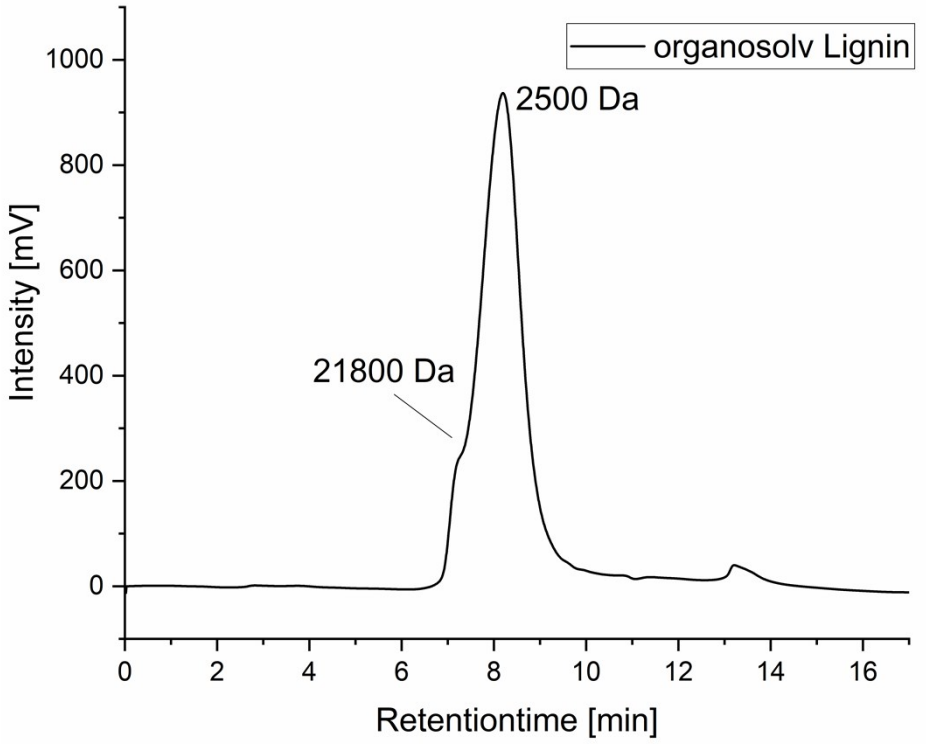


Figure S12. GPC chromatogram of organosolv-lignin.

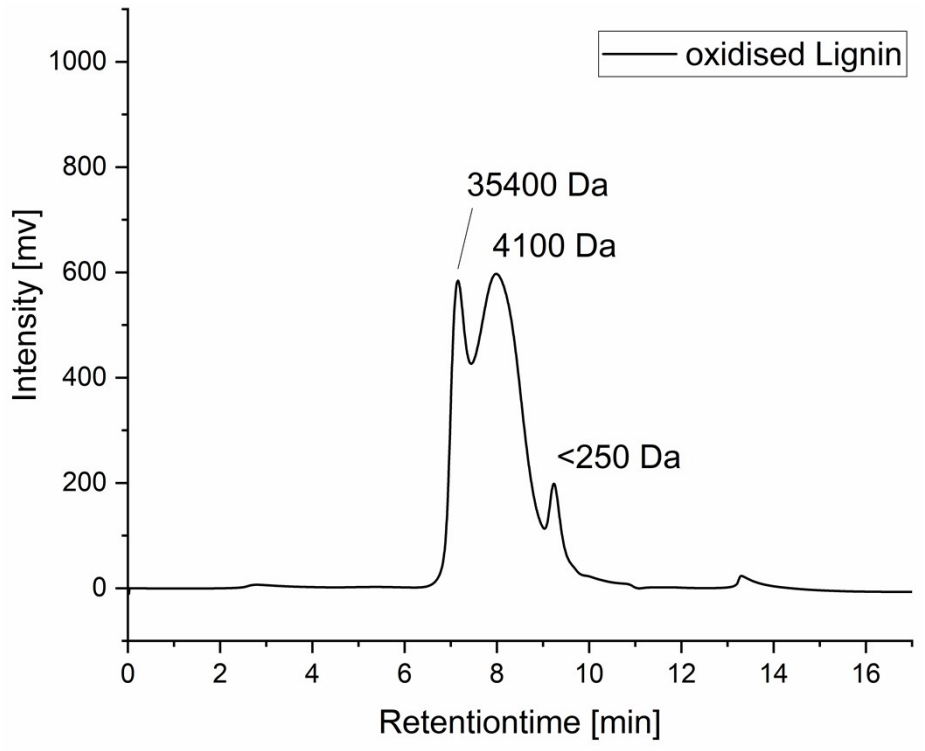


Figure S13. GPC chromatogram of oxidized lignin.

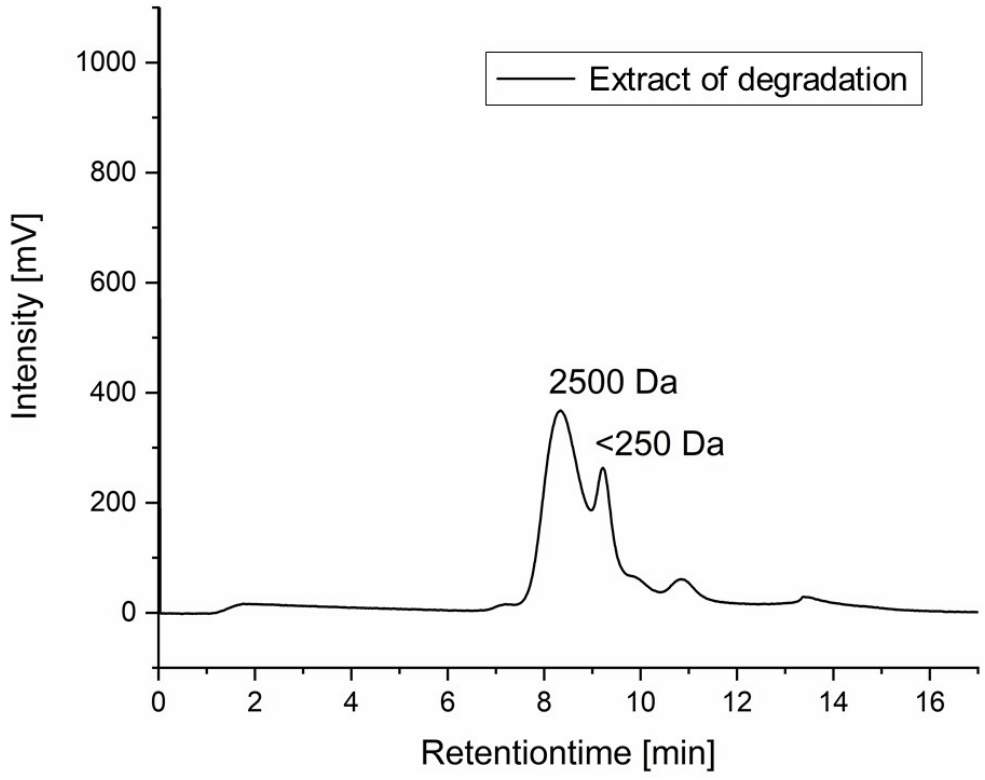


Figure S14. GPC chromatogram of degradation mixture.

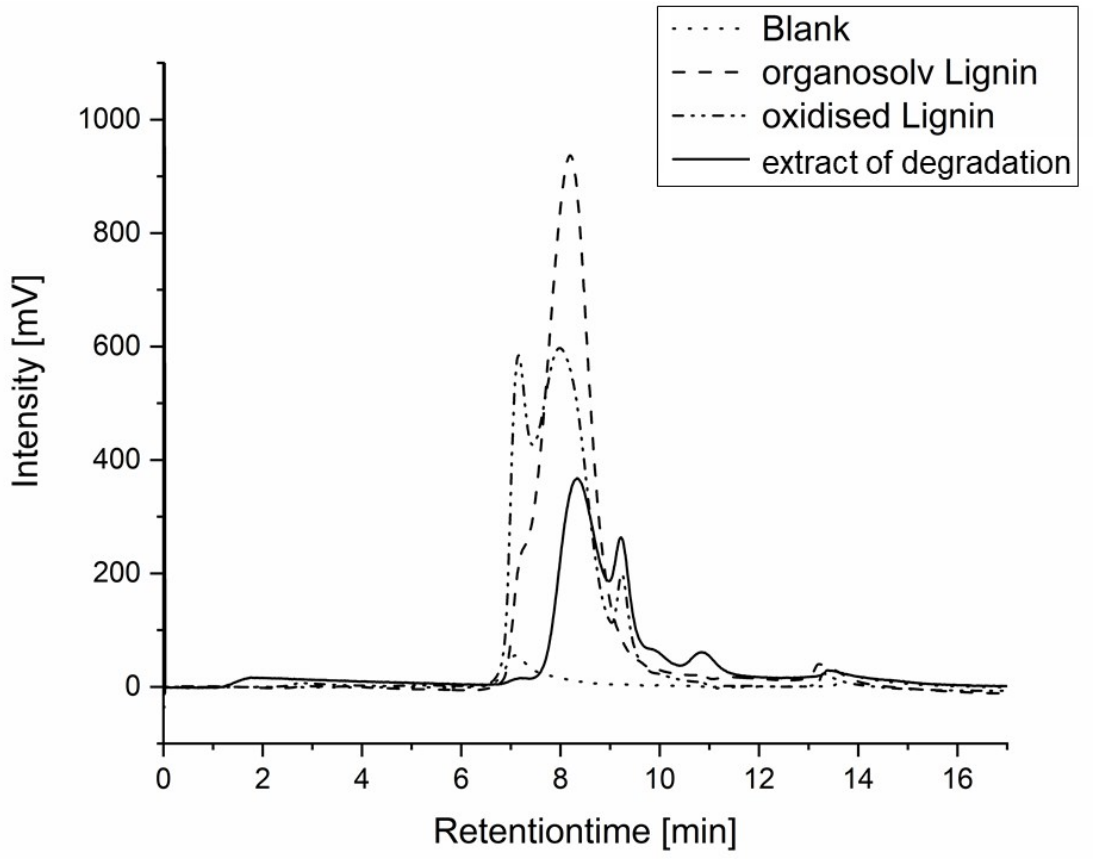


Figure S15. GPC chromatograms comparison.

Quantitative LC-MS/MS analysis

Separation was performed using a Dionex Ultimate RS 3000 UHPLC (Thermo Scientific, Idstein, Germany) which was equipped with an Accucore aq. column (2.1 x 100 mm, 2.6 µm, Thermo Scientific). For gradient elution, 1 mM ammonium acetate + 0.5% formic acid (A) and methanol/acetonitrile (1:1, v/v) (B) were utilized. Separation started with 12% B and this ratio was increased to 99% within 5.5 min. The ratio was kept for 1 min and afterwards set back to 12% within 0.5 min. The column was equilibrated for 1.5 min, resulting in a run time of 8.5 min. Column temperature and injection volume were set to 17 °C and 1 µL, respectively. The system was connected to a QTrap 3200 tandem mass spectrometer (ABSciex, Darmstadt, Germany). Before entering the interface, the flow was split 1:10. Ionization was performed via ESI positive mode (capillary voltage 5000 V, interface temperature 150 °C). For compound detection, the multiple reaction monitoring mode (MRM) was utilized with two transition states per compound. Details are provided in Table S6. Nitrogen was utilized as collision gas. Compounds were considered as unequivocally identified when both transitions states were detectable.

Samples prepared as described in the previous section were dissolved in methanol, acetonitrile with addition of 1% formic acid or in dimethylformamide. For analysis, samples were diluted with methanol/water (1:1, v/v).

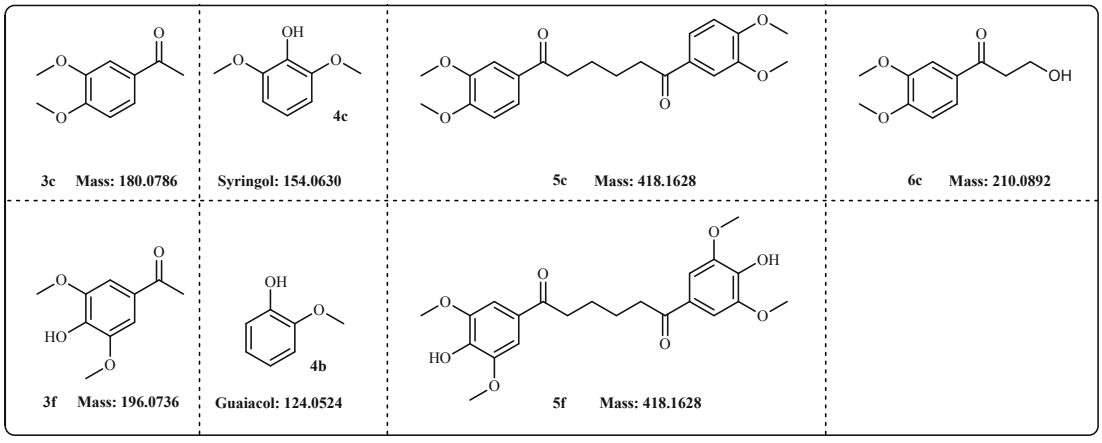


Figure S16. Standard samples prepared for the quantification with LC-MS/MS.

Table S6. Precursor ions and detected fragments of lignin breakdown products.

Compound	Precursor ion	Product ion*	collision energy
	m/z	*m/z*	[V]
3c	181.1	139.1	14
		124.1	24
4c	155.1	123.1	14
		95.1	20
5c	387.1	165.1	20
		203.3	32
6c	211.1	165.1	26
		139.1	15
3f	197.1	155.1	15
		140.1	26
5f	419.1	181.2	21
		219.2	33

* - the more intense fragment ion is mentioned first.

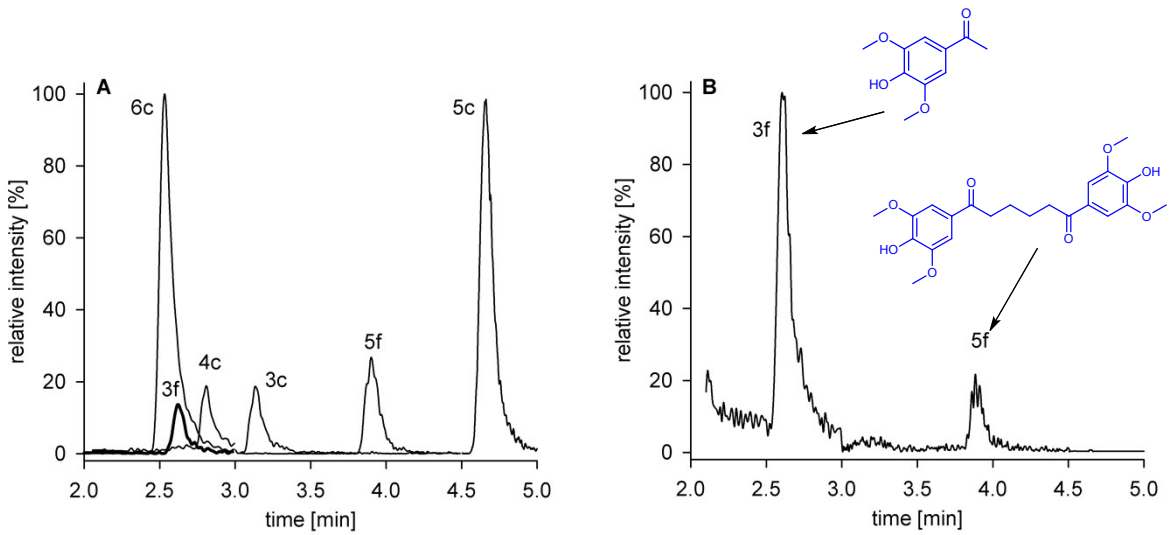
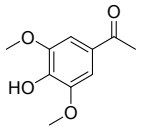
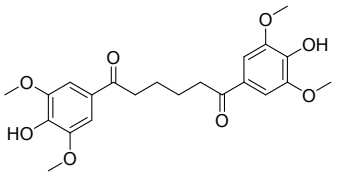


Figure S17. LC-MS/MS chromatogram of A) standard solution (1 mg L^{-1}) and B) depolymerization samples. In case of the standard solution, the ion trace of the more intense fragment is shown (see Table S6), for the degradation sample the total ion count is presented.

In the quantitative analysis, only the syringone **3f** and syringyl dimer **5f** were detected and were quantified with LC-MS/MS for each of the three reactions. The

results were summarized in Table S5. Guaiacol **4b** and syringol **4c** were not detected via LC-MS/MS or via GC/MS. One reason could be the influences of pinacol borylated complexes residues interacting with **4b** and **4c**.

Table S7. Quantification of the 3f and 5f in the degradation mixture.

Sample	**Amount of oxidized lignin (mg)**				
		Absolute amount of 3f (µg)	**Wt % of 3f**	**Absolute amount of 5f (µg)**	**Wt % of 5f**
HOL615-1	46.8	93.0	0.2 wt.%	13.0	0.03 wt.%
HOL615-2	48.3	103.0	0.2 wt.%	15.0	0.03 wt.%
HOL615-3	49.7	187.0	0.4 wt.%	16.0	0.03 wt.%

References

1. J. Tian, C. Yao, W. L. Yang, L. Zhang, D. W. Zhang, H. Wang, F. Zhang, Y. Liu and Z. T. Li, *Chinese Chem. Lett.*, 2017, **28**, 798.
2. M. Dawange, M. V. Galkin and J. S. M. Samec, *ChemCatChem*, 2015, **7**, 401.
3. M. Lahtinen, A. Haikarainen and J. Sipilä, *Holzforschung*, 2013, **67**, 129.
4. C. S. Lancefield, O. S. Ojo, F. Tran and N. J. Westwood, *Angew. Chem., Int. Ed.*, 2015, **54**, 258.
5. J. D. Nguyen, B. S. Matsuura and C. R. Stephenson, *J. Am. Chem. Soc.*, 2014, **136**, 1218.
6. J. Cao, G. Wang, L. Gao, X. Cheng and S. Li, *Chem. Sci.*, 2018, **9**, 3664.
7. Z. Omran and A. Specht, *Tetrahedron Lett.*, 2009, **50**, 2434.
8. B. B. Li, J. L. Li, N. Li, H. S. Lee, X. B. Wang and L. Cui, *Phytochem. Lett.*, 2017, **20**, 123.
9. G. Wang, J. Cao, L. Gao, W. Chen, W. Huang, X. Cheng and S. Li, *J. Am. Chem. Soc.*, 2017, **139**, 3904.
10. G. Wang, H. Zhang, J. Zhao, W. Li, J. Cao, C. Zhu and S. Li, *Angew. Chem., Int. Ed.*, 2016, **55**, 5985.
11. A. Bugarin, K. D. Jones and B. T. Connell, *Chem. Commun.*, 2010, **46**, 1715.
12. J. J. Yun, X. Y. Liu, W. Deng, X. Q. Chu, Z. L. Shen and T. P. Loh, *J. Org. Chem.*, 2018, **83**, 10898.
13. S. Dabral, J. Engel, J. Mottweiler, S. S. M. Sppehrle, C. W. Lahive and C. Bolm, *Green Chem.*, 2018, **20**, 170.
14. I. Bosque, G. Magallanes, M. Rigoulet, M. D. Karkas and C. R. J. Stephenson, *ACS Cent. Sci.*, 2017, **3**, 621.
15. S. Bauer, H. Sorek, V. D. Mitchell, A. B. Ibanez and D. E. Wemmer, *J. Agric. Food. Chem.*, 2012, **60**, 8203.
16. H. Guo, Daniel M. Miles-Barrett, A. R. Neal, T. Zhang, C. Li and N. J. Westwood, *Chem. Sci.*, 2018, **9**, 702.
17. X. Meng, C. Crestini, H. Ben, N. Hao, Y. Pu, A. J. Ragauskas and D. S. Argyropoulos, *Nat. Protoc.*, 2019, **14**, 2627.