---Supporting Information---

Lignin C−C Bond Cleavage Induced by Consecutive Two-Photon Excitation of a Metal-Free Photocatalyst

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Contents

Experimental Section

Materials

Reagents required for the experiments were obtained from commercial sources in high purity and used as received. N-phenylphenothiazine (PTH), acetonitrile-D_3 (CD_3CN), and tetrabutylammonium perchlorate ($TBAClO_4$) were purchased from TCI Development Co., Ltd. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), $AgNO_3$, Chloroform-D ($CDCl_3$), 1,4-benzoquinone, and 2,6-lutidine were purchased from Aladdin Reagent Co., Ltd. Triethanolamine (TEOA), formic acid (HCOOH), dimethyl sulfoxide (DMSO), acetone, and methanol (MeOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. Acetonitrile (CH_3CN) was purchased from B&J Co., Ltd.

UV−vis−NIR Absorption

The UV−vis−NIR absorption spectrum of PTH was measured by an Agilent Cary 60 spectrometer. Briefly, PTH was dissolved in 2 mL anhydrous CH_3CN solution at a working concentration of 7.5 mM and placed in a 1 cm quartz cuvette to measure its absorption spectrum.

Steady State Fluorescence

PTH steady state fluorescence was determined by an Agilent Cary Eclipse fluorimeter. 2 mL PTH (7.5 mM) CH_3CN solution was prepared, and the fluorescence under excitation at 395 nm was tested as well as fluorescence titration of different concentrations of 1a (1, 10, 25, 50 and 100 mM).

UV-vis-NIR Spectrum of Photo-oxidized PTH

Changes in the photo-oxidation absorption spectra of PTH were recorded by an Agilent Cary 60 spectrometer. 2 mL PTH (20 mM) aerated CH_3CN solution was placed in a 1 cm quartz cuvette, irradiated with a blue LED (λ_{ex} = 390 nm) under magnetic stirring, and then the steady state absorption spectrum of the solution was tested at 10 min interval.

Electrochemical Characterization

The spectroelectrochemistry of PTH was measured by a combination of a CHI 1232C electrochemical workstation and an Agilent Cary 60 spectrometer. A typical three-electrode cell system consisted of Pt mesh as the working electrode, Ag/AgCl as the pseudo reference electrode and Pt wire as the counter electrode. The three electrodes were placed in a long-necked quartz cuvette. The UV−vis−NIR absorption spectral changes of PTH (300 μM) and PTH (300 μM) + 1a (20 mM) were recorded with increasing potentials in 4 mL 100 mM $TBAClO_4$ CH_3CN solution with stirring.

Cyclic voltammetry (CV) was performed on a CHI 760E electrochemical workstation. Cyclic voltammograms were recorded using a typical three-electrode cell system consisting of glassy carbon (GC) as the working electrode, Ag/AgCl as the pseudo reference electrode, and Pt wire as the counter electrode. The Cyclic voltammograms of 5 mM 1a, 5 mM PTH and 5 mM 1a + 5 mM PTH were obtained with 100 mM $TBAClO_4$ CH_3CN solution as the electrolyte at a scan rate of 50 mV s^{-1}. Cyclic voltammograms for other substrates were also obtained using the same method described above.

The Ag/AgCl pseudo reference electrode potential was corrected with ferrocene before and after all electrochemical measurements and were further converted into a normal hydrogen electrode (NHE) (ferrocenium/ferrocene: $E^0(Fc^+/Fc)$ = 0.63 V vs NHE).

Nanosecond Transient Absorption Spectroscopy

All nanosecond transient absorption spectroscopy data were acquired on a TSP-2000 (Unisoku) laser flash photolysis system. Briefly, a Q-switched frequency-triple pulsed Nd:YAG laser (Quantel Q-Smart 450, 10 Hz) was used as the excitation source to output a 355 nm pulsed laser (5−8 nm full width at half-maximum). A 75 W xenon arc lamp was used as a probe beam aligned orthogonal to the pulsed laser beam and focused on a 1 cm quartz cuvette containing the solution sample. An R2949 photomultiplier tube (Hamamatsu) coupled to an f/4 mm monochromator (Acton, Princeton Instrument) was served to achieve signal detection (390 nm−650 nm). Pre-amplified S3399 silicon photodiode (Hamamatsu) was served to achieve signal detection (660 nm−950 nm). Transient absorption kinetic data at each wavelength were acquired on a computer interfaced digital oscilloscope (LeCroy 4024, 12 bit, 200 MHz) with typical 50 laser pulse averages. The two-color two-pulse laser flash photolysis experiment was realized by synchronizing the two lasers. A second Q-switched frequency-doubled pulsed Nd:YAG laser (Quantel Q-Smart 450, 10 Hz) was used as the excitation source to output a 532 nm pulsed laser (5−8 nm full width at half-maximum). The excitation light intensity of both lasers was rationally adjusted by varying the Q-switch delays and measured using a power meter. The second laser beam (532 nm laser, beam diameter about 1.2 cm) in front of a 1 cm quartz cuvette completely covered the first laser beam (355 nm laser, beam diameter about 0.8 cm) through the beam expander. Before starting the measurement, carefully adjust the laser and probe beam directions so that the two laser and probe beams must overlap the maximum area. Safety goggles must be worn throughout the experiment to avoid eye damage.

Nanosecond Transient Absorption Full Spectrum

2 mL of PTH (1 mM) + 1a (100 mM) aerated CH_3CN solution was added to a 1 cm quartz cuvette. Transient absorption spectral signals in the range of 390 nm−950 nm were collected after 355 nm pulsed laser excitation (20 mJ/cm^2 per pulse).

Two-Color Two-Pulse Laser Flash Photolysis Experiment

The transient kinetic of PTH^+ at 510 nm was monitored in 2 mL PTH (1 mM) CH_3CN solution after two-color two-pulse laser excitation. The second laser pulse (λ_{ex} = 532 nm, 140 mJ/cm^2 per pulse) was delayed by 500 ns compared with the first laser pulse (λ_{ex} = 355 nm, 40 mJ/cm^2 per pulse). The TA kinetics PTH^+ at 510 nm of 1 mM PTH + 1a (200, 400, 600, 800 and 1000 mM) were also monitored with the same two-color two-pulse laser photolysis procedure as above. In the presence of 1000 mM 1a, the same method was also used to detect the absorption difference spectra of PTH recorded from 390 nm–950 nm in oxygen-saturated CH_3CN after two pulsed-laser excitations.

During the photolysis experiment, two additional 532 nm notch filters were added to avoid the influence of the 532 nm laser.

Photocatalytic Cleavage of Lignin Model Substrates

0.1 mmol 1a and 15 mol% PTH were dissolved in a glass tube containing 2 mL CH_3CN. The reaction system was not completely sealed to ensure air circulation. The reaction solution was carried out at room temperature for 48 h under the 390 nm LED (multi-channel photoreactor system) excitation, and the whole reaction process was cooled by a fan. Meanwhile, the solution was kept stirring with a magnetic stirrer all the time during the reaction. After the reaction was completed, the reaction system was adjusted to a constant volume, and the product was quantified by high performance liquid chromatography (HPLC). The same photocatalytic cleavage method described above was used for other model substrates. The two-photon excitation steady-state photolysis experiment was performed by irradiating the reaction solution with 390 nm (Kessil) and white light from both sides of the quartz cuvette for 4, 8, 14, 24, 36 and 48 h, respectively. Similarly, control experiment was performed only under 390 nm (Kessil) irradiation.

HPLC

An Agilent 1260 Infinity II was used to test the HPLC with an autosampler, UV-vis detector and C18 column (4.6 × 150 mm, 5 μm). The mobile phase consisted of A (pure water containing 1‰ trifluoroacetic acid) and B (CH_3CN). The mobile phase elution program was set to 0 min (90% A, 10% B), 10 min (50% A, 50% B), 14 min (50% A, 50% B), 19 min (10% A, 90% B), 24.1 min (90% A, 10% B), the test was stopped at 25 min, and the flow rate was 1 mL min^{-1}.

Figure S1-S13

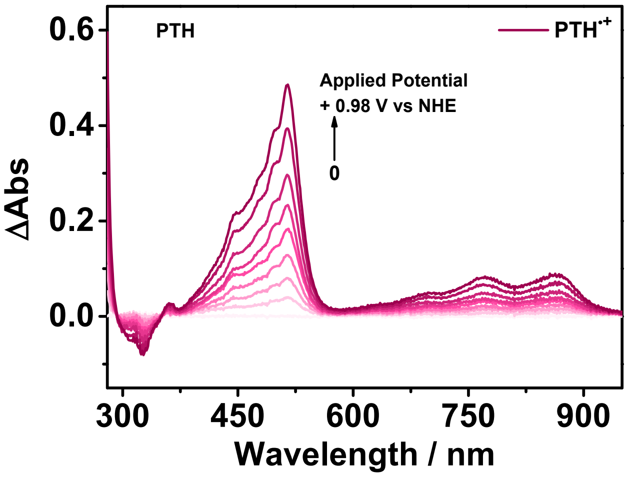


Figure S1. The UV−vis−NIR absorption change of PTH with increasing applied potential from 0 to 0.98 V vs NHE in 100 mM TBAClO$_4$ CH$_3$CN solution.

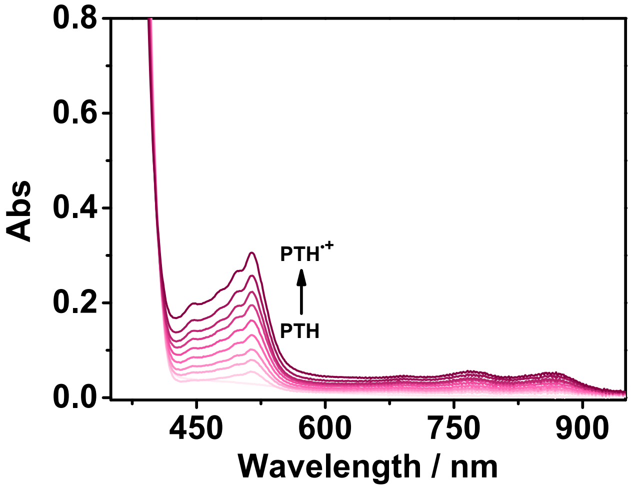


Figure S2. The UV−vis−NIR absorption change of PTH under 390 nm light excitation in CH_3CN in ambient air condition.

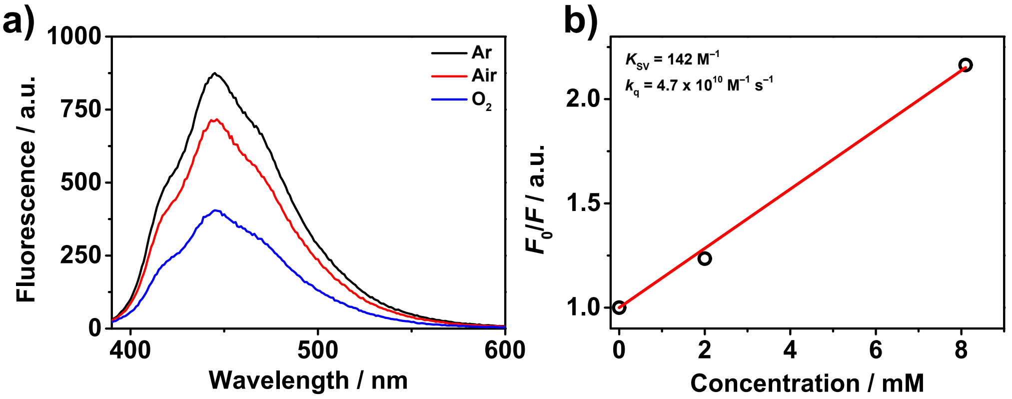


Figure S3. a) Fluorescence spectra of PTH (λ_{ex} = 355 nm) in argon-purged, aerated, and oxygen-purged CH_3CN respectively. b) The corresponding Stern−Volmer plot for fluorescence intensity quenching. The ambient dissolved oxygen[1] and saturated oxygen[2] concentrations in CH_3CN solution were approximately 2 mM and 8.1 mM, respectively. The dynamic quenching constant (K_{SV}) obtained by the slope of the Stern-Volmer plot was around 142 M^{-1}. The fluorescence lifetime (τ_0) of PTH in CH_3CN was 3 ns.[3] $k_q = K_{SV} / \tau_0 = 4.7 \times 10^{10}\ M^{-1}\ s^{-1}$.

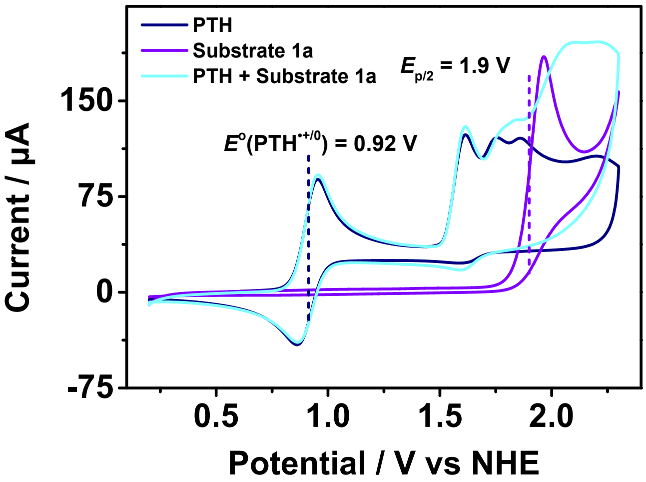


Figure S4. Cyclic voltammograms of 5 mM PTH (navy), 5 mM 1a (violet), and 5 mM PTH + 5 mM 1a (cyan) in 100 mM TBAClO$_4$ CH$_3$CN solution at the scan rate of 50 mV s^{-1}.

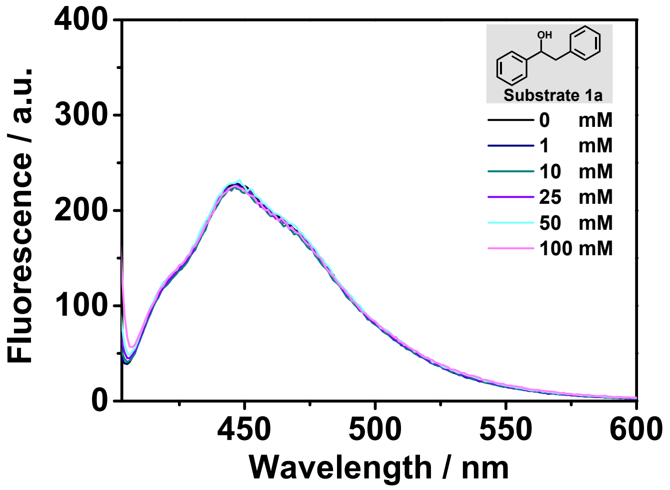


Figure S5. Fluorescence spectra of PTH in CH_3CN upon titration with different concentrations of 1a (λ_{ex} = 395 nm).

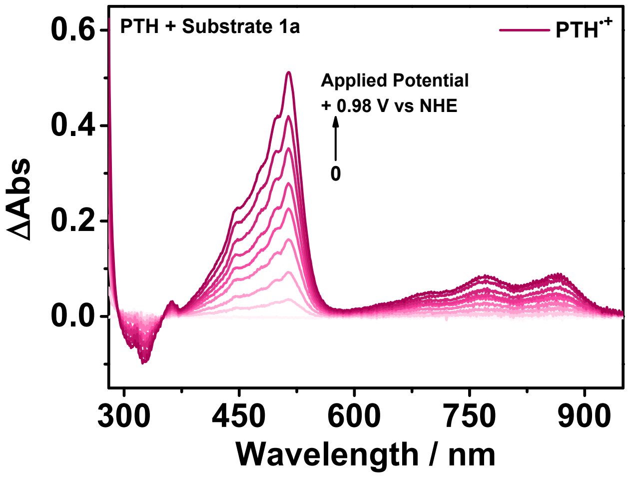


Figure S6. The UV−vis−NIR absorption change of PTH (300 μM) + 1a (20 mM) measured with the increasing applied potential from 0 to 0.98 V vs NHE in 100 mM TBAClO$_4$ CH$_3$CN solution.

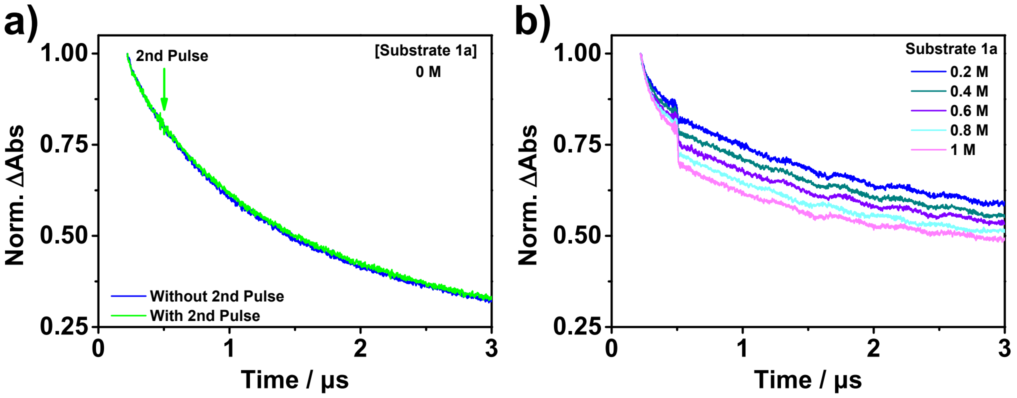


Figure S7. a) Kinetic data for $PTH^{\bullet+}$ at 510 nm in a representative two-pulse TA experiment with the second laser pulse excitation (green) or only first laser pulse (blue). b) Kinetic data for $PTH^{\bullet+}$ at 510 nm in variable concentrations of 1a (0, 200, 400, 600, 800 and 1000 mM) after excitation with two laser pulses. All two-pulse TA experiments were performed with a second laser pulse delayed by 500 ns after the first laser pulse.

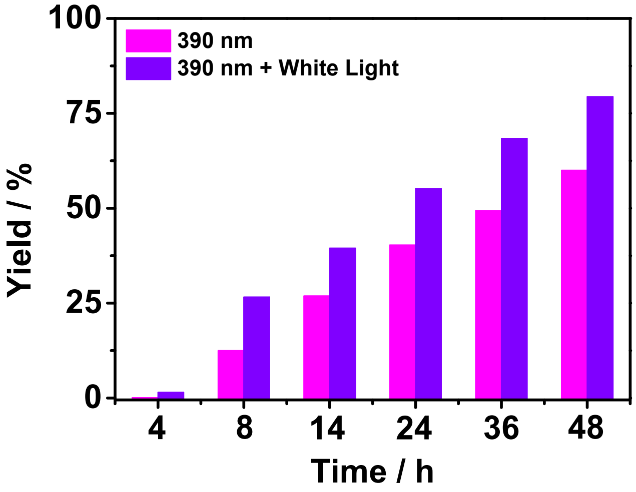
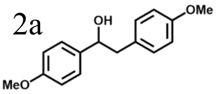
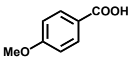
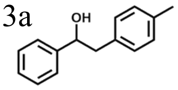
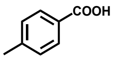
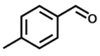
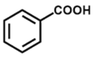
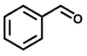
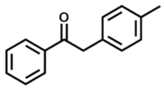
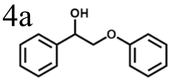
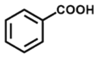
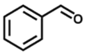
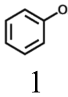
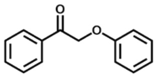
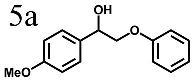
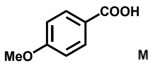
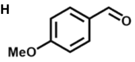
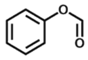
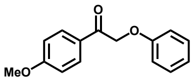
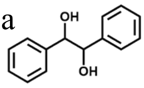
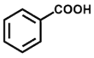
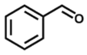


Figure S8. Steady-state photolysis of 1a under 390 nm or 390 nm + white light irradiation. (Magenta: combined yield of benzoic acid and benzaldehyde under 390 nm irradiation. Violet: combined yield of benzoic acid and benzaldehyde under 390 nm + white light irradiation.)

Table S1

Table S1. Oxidative cleavage of other lignin model substrates by PTH

Entry	Substrate	Con. (%)	Main Products (Yield, %)
2	2a 	>99	 81
3	3a 	>99	 41  4  66  3  5
4	4a 	>99	 51  3  1  7
5	5a 	>99	 47  2  20  2
6	6a 	>99	 77  17

Standard reaction conditions: 0.1 mmol substrate, 15 mol% PTH, 2 mL CH_3CN, 390 nm LED (15 mW·cm^{-2}), air, 48 h, room temperature. All yield determined by HPLC analysis.

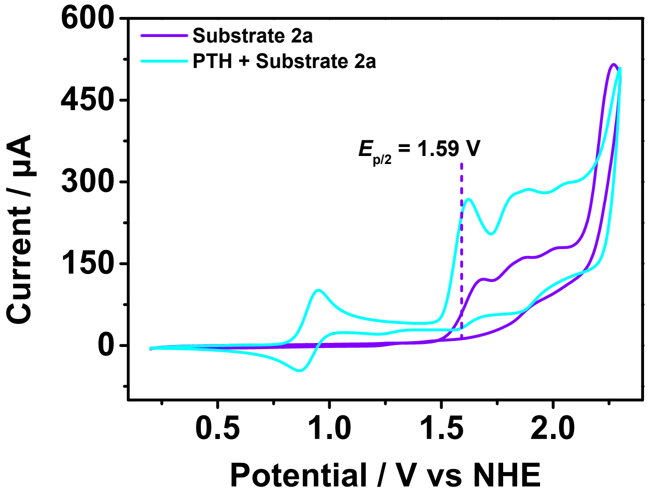


Figure S9. Cyclic voltammograms of 5 mM 2a (violet) and 5 mM PTH + 5 mM 2a (cyan) in 100 mM $TBAClO_4$ CH_3CN solution at the scan rate of 50 mV s^{-1}.

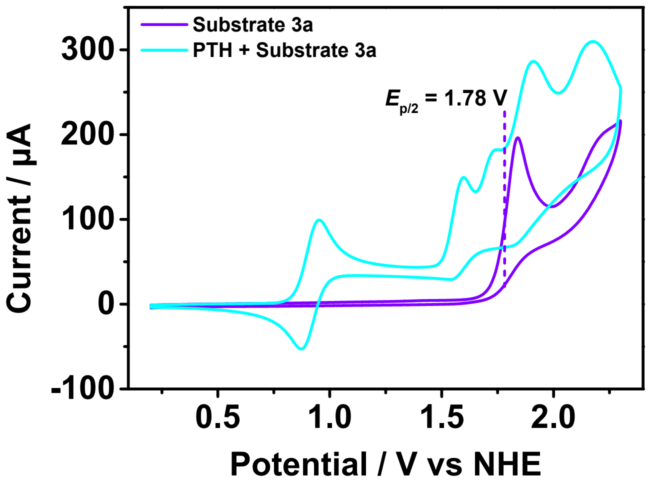


Figure S10. Cyclic voltammograms of 5 mM 3a (violet) and 5 mM PTH + 5 mM 3a (cyan) in 100 mM TBAClO$_4$ CH$_3$CN solution at the scan rate of 50 mV s^{-1}.

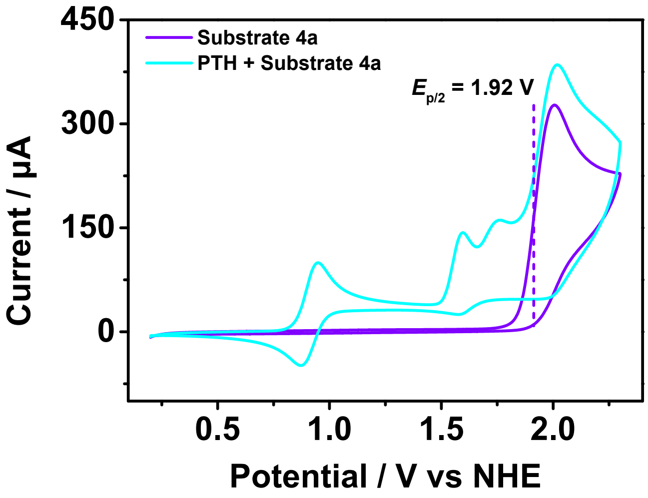


Figure S11. Cyclic voltammograms of 5 mM 4a (violet) and 5 mM PTH + 5 mM 4a (cyan) in 100 mM TBAClO$_4$ CH$_3$CN solution at the scan rate of 50 mV s^{-1}.

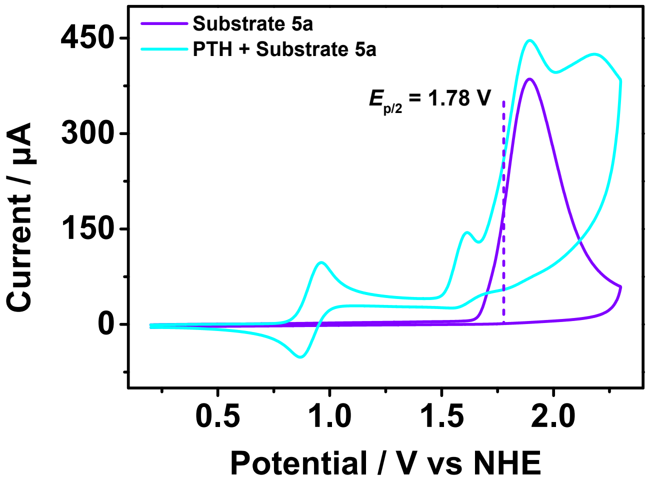


Figure S12. Cyclic voltammograms of 5 mM 5a (violet) and 5 mM PTH + 5 mM 5a (cyan) in 100 mM TBAClO$_4$ CH$_3$CN solution at the scan rate of 50 mV s^{-1}.

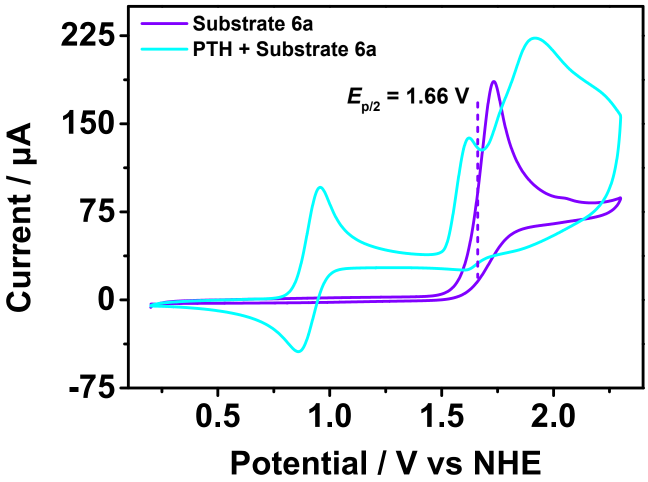


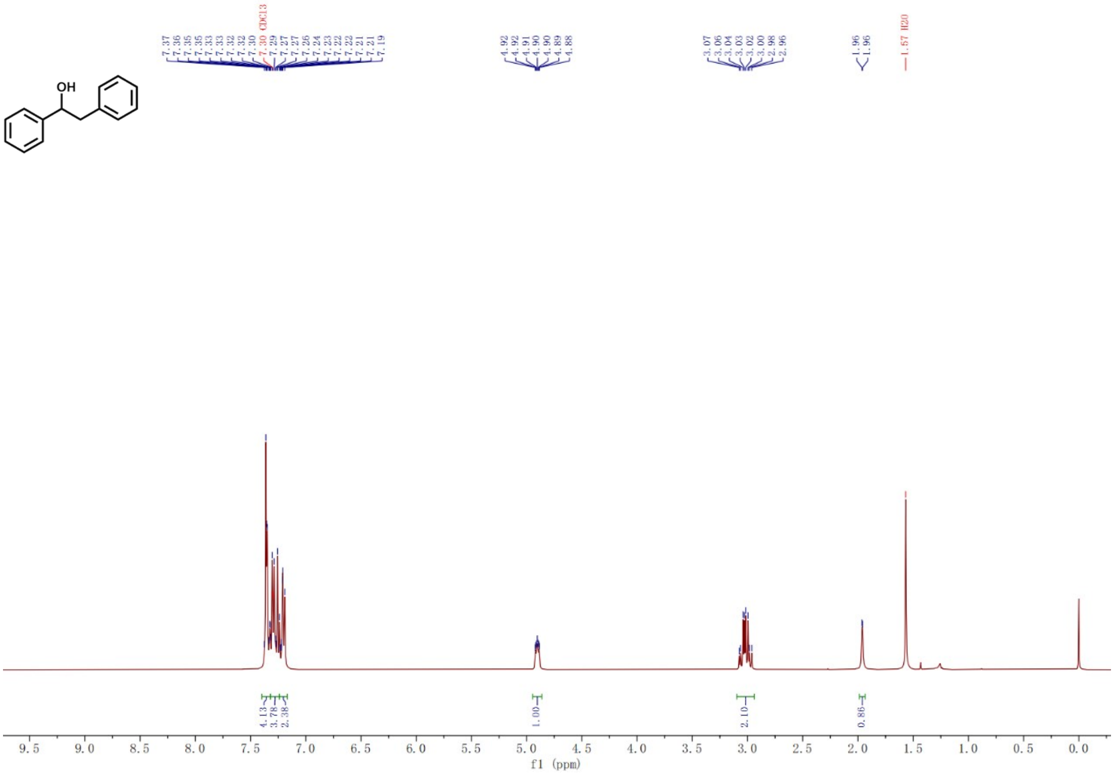
Figure S13. Cyclic voltammograms of 5 mM 6a (violet) and 5 mM PTH + 5 mM 6a (cyan) in 100 mM TBAClO_4 CH_3CN solution at the scan rate of 50 mV s^{-1}.

Synthesis and Characterization of Lignin Model Substrates

Lignin Model Substrate 1a: 1,2-Diphenylethanol

1,2-Diphenylethanol was synthesized according to the procedures reported in the previous literature.[4] THF/H_2O (25 mL, v/v = 4/1) was added to a 100 mL round bottom flask, followed by addition of 2-phenylacetophenone (0.98 g, 5 mmol) while stirring with a magnetic stirrer. $NaBH_4$ (0.76 g, 20 mmol) was added and the reaction was stirred at room temperature for 12 h. Then, the reaction was quenched by the addition of excess saturated NH_4Cl aqueous solution (30 mL). The crude product was extracted with dichloromethane (3 x 30 mL), and further dried with a large amount of anhydrous Na_2SO_4. The organic solvent was filtered and concentrated under vacuum. Finally, the product was further purified by flash silica column chromatography using hexane/ethyl acetate (3:1) as eluent.

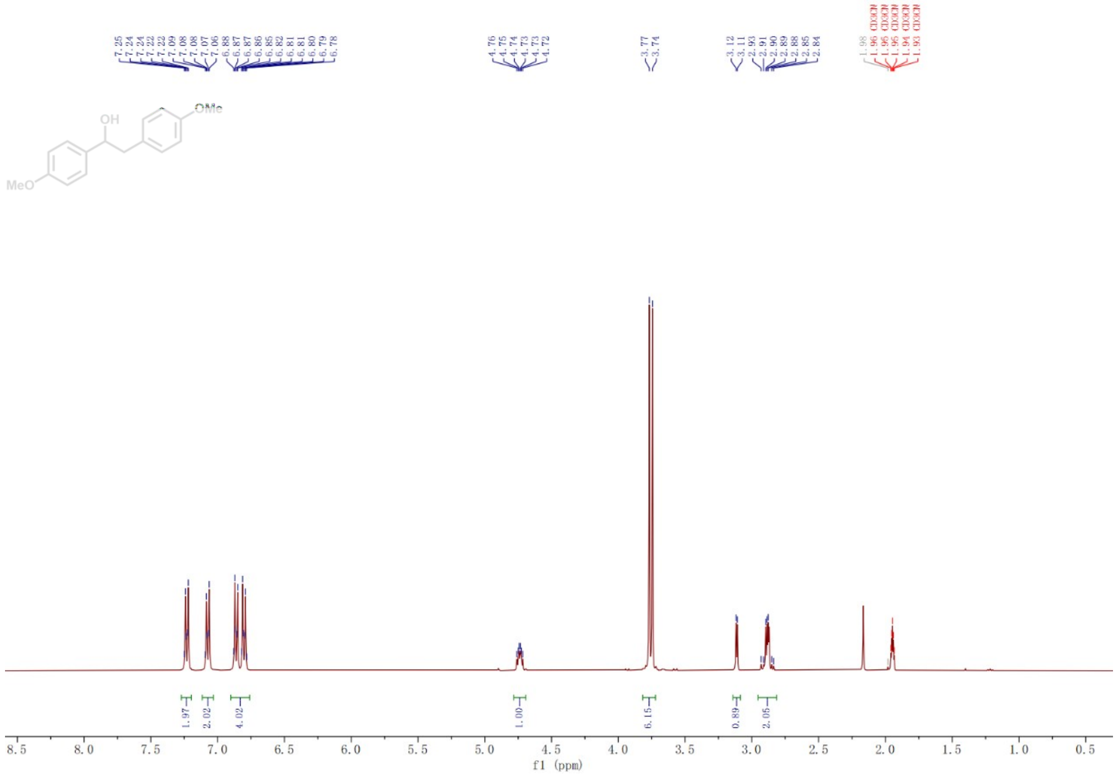
Substrate 1a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 7.32 – 7.24 (m, 4H), 7.24 – 7.17 (m, 2H), 4.90 (ddd, J = 7.7, 5.0, 1.9 Hz, 1H), 3.02 (qd, J = 13.6, 6.7 Hz, 2H), 1.96 (d, J = 2.7 Hz, 1H).



Lignin Model Substrate 2a: 1,2-Bis(4-methoxyphenyl)ethanol

Substrate 2a was synthesized in the same manner as described above for substrate 1a, except that the 2-phenylacetophenone was adjusted to 1,4-di(4-methoxyphenyl)ethanone (1.28 g, 5 mmol).

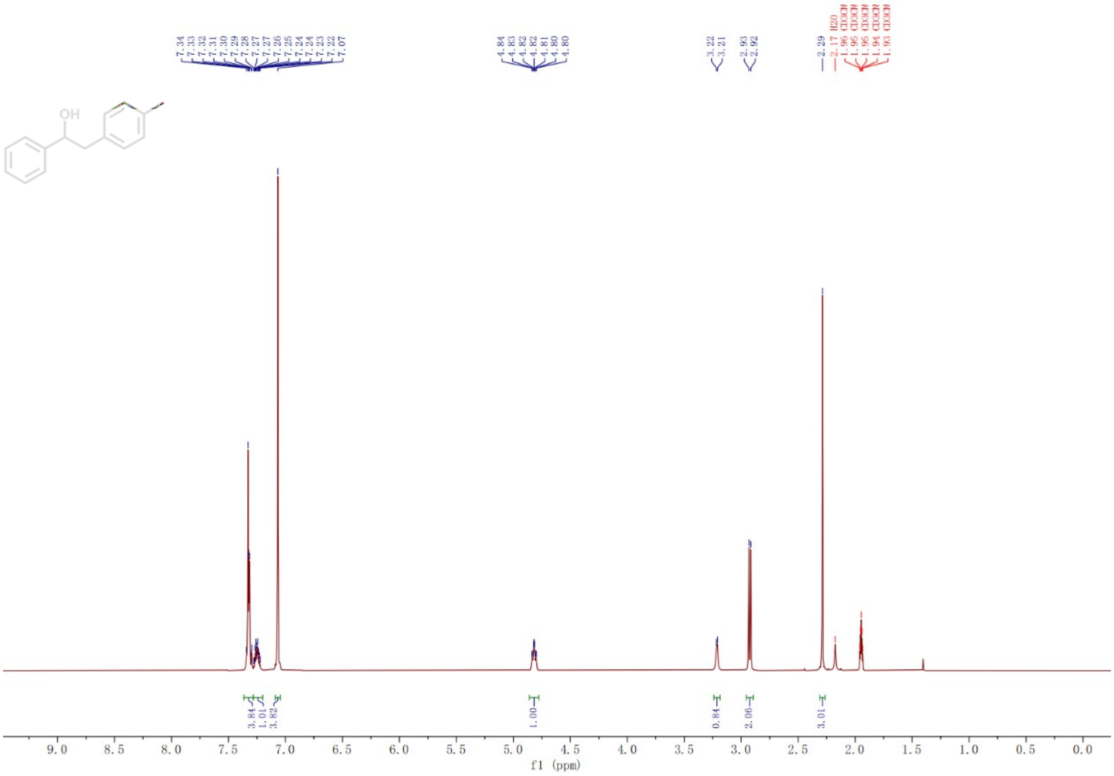
Substrate 2a: ^{1}H NMR (400 MHz, CD_3CN) δ 7.27 – 7.20 (m, 2H), 7.11 – 7.03 (m, 2H), 6.90 – 6.76 (m, 4H), 4.74 (td, J = 6.9, 4.4 Hz, 1H), 3.76 (d, J = 9.4 Hz, 6H), 3.11 (d, J = 4.2 Hz, 1H), 2.95 – 2.81 (m, 2H).



Lignin Model Substrate 3a: 4-Methylbenzylphenyl alcohol

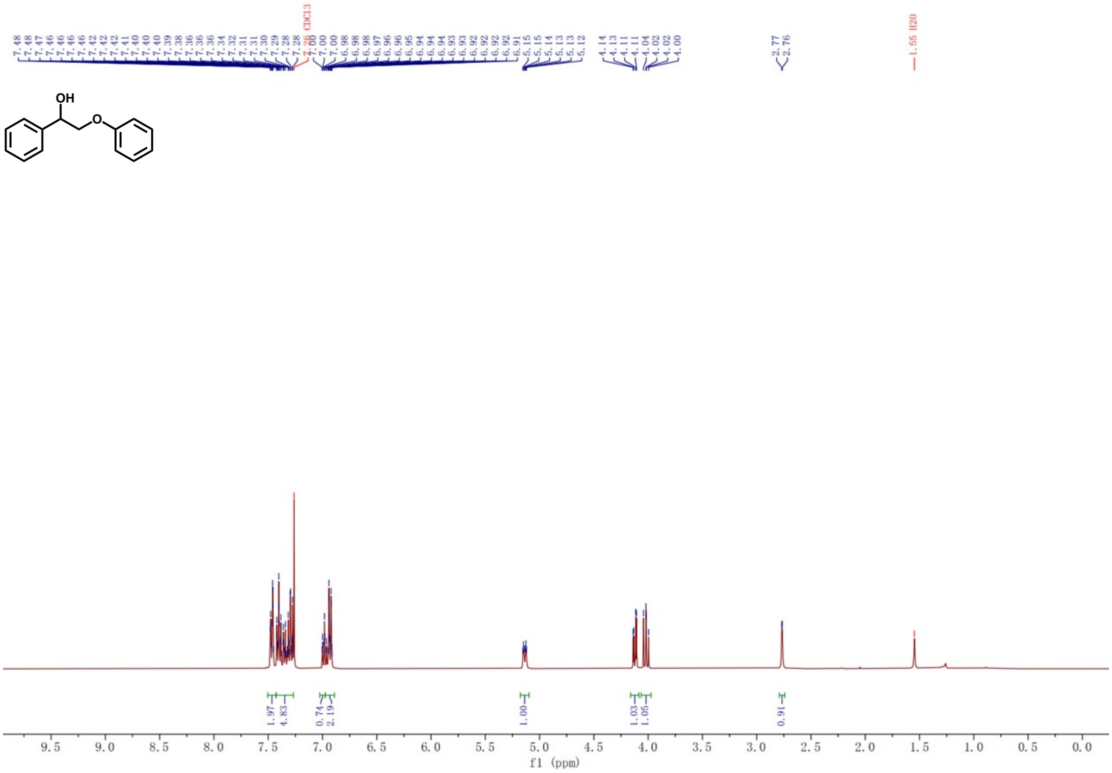
Substrate 3a was synthesized in the same manner as described above for substrate 1a, except that the 2-phenylacetophenone was adjusted to 4-methylbenzyl phenyl ketone (1.05 g, 5 mmol).

Substrate 3a: ^{1}H NMR (400 MHz, CD_3CN) δ 7.36 – 7.28 (m, 4H), 7.25 (qt, J = 5.4, 2.7 Hz, 1H), 7.07 (s, 4H), 4.82 (ddd, J = 8.3, 6.5, 2.4 Hz, 1H), 3.21 (d, J = 3.6 Hz, 1H), 2.92 (d, J = 6.8 Hz, 2H), 2.29 (s, 3H).



Lignin Model Substrate 4a: 2-Phenoxy-1-phenylethanol, commercially available

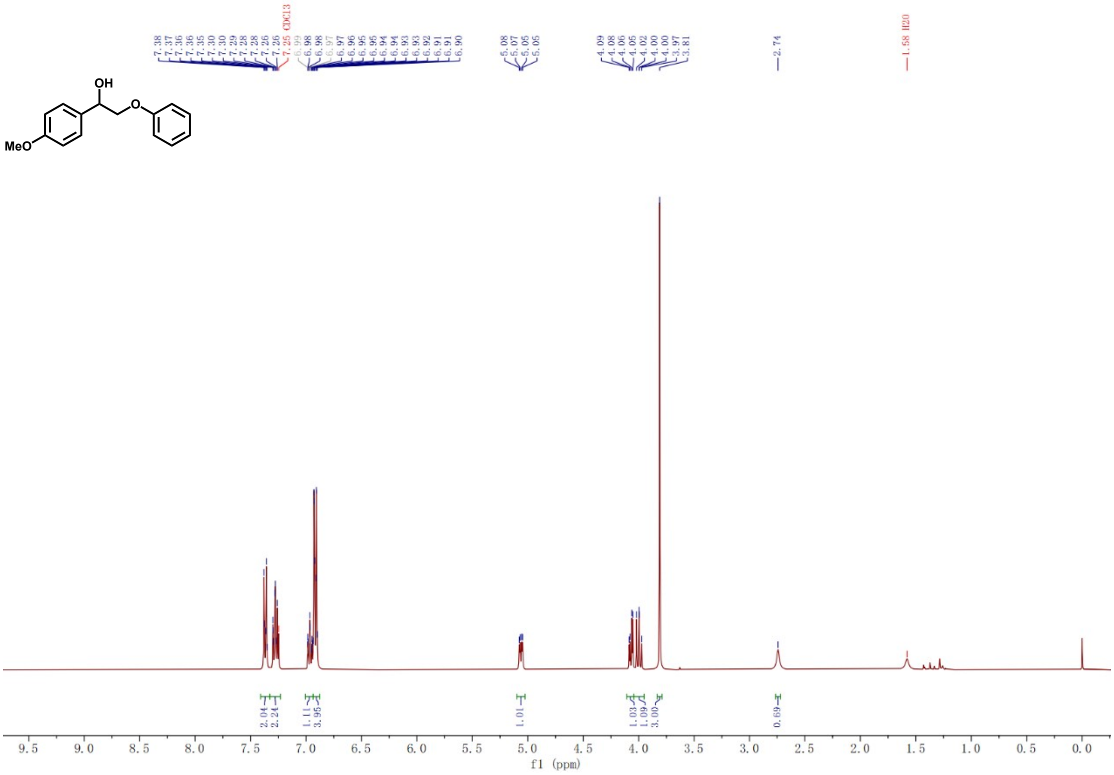
Substrate 4a: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.43 (m, 2H), 7.43 – 7.27 (m, 5H), 6.99 (dt, J = 7.4, 1.1 Hz, 1H), 6.97 – 6.89 (m, 2H), 5.14 (dt, J = 9.0, 2.5 Hz, 1H), 4.12 (dd, J = 9.6, 3.2 Hz, 1H), 4.02 (dd, J = 9.6, 8.8 Hz, 1H), 2.77 (d, J = 2.3 Hz, 1H).



Lignin Model Substrate 5a: 1-(4-methoxyphenyl)-2-phenoxyethanol

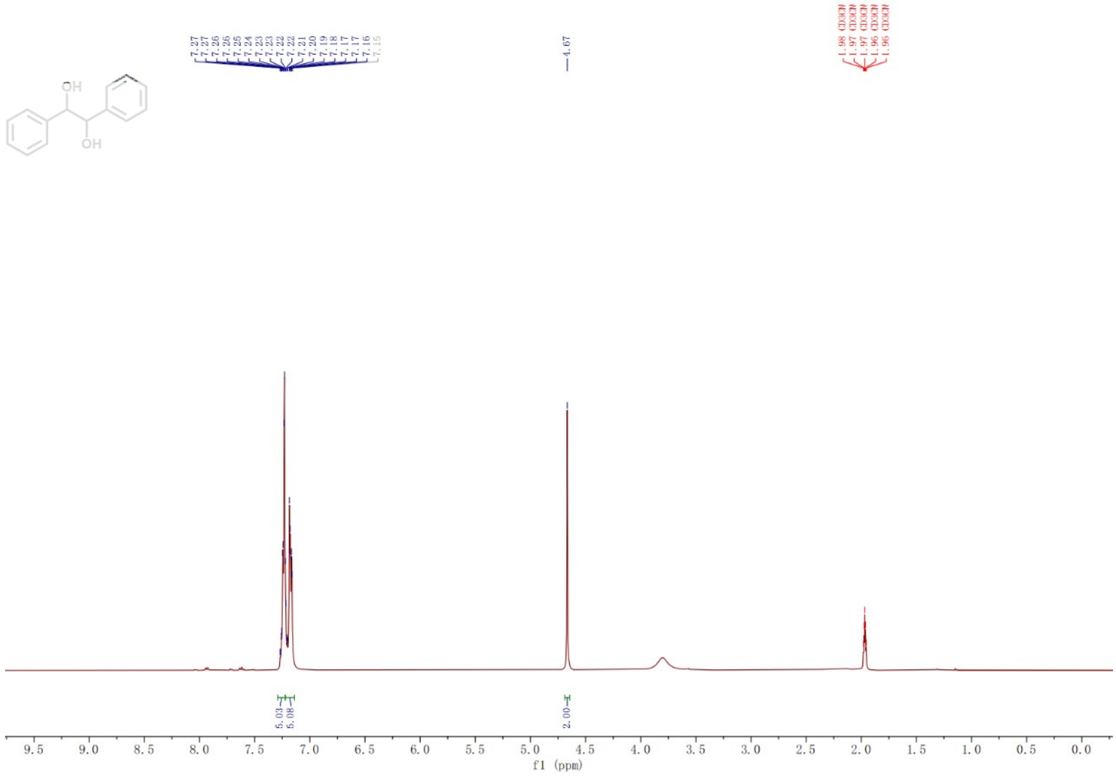
1-(4-Methoxyphenyl)-2-phenoxyethanol was synthesized according to a two-step procedure reported in the previous literature.[5] **Step 1:** Acetone (50 mL) was added to a 250 mL round bottom flask, followed by addition of K_2CO_3 (1.037 g, 7.5 mmol) and phenol (0.589 g, 6.25 mmol) while stirring with a magnetic stirrer. 2-Bromo-4'-methoxyacetophenone (1.145 g, 5 mmol) was added and the reaction was stirred at room temperature for 12 h. The reaction mixture was filtered and washed with acetone and concentrated under vacuum. Finally, the product was further purified by flash silica column chromatography using petroleum ether/ethyl acetate (6:1) as eluent. **Step 2:** The above product was added to a 100 mL round bottom flask containing THF/H_2O (25 mL, v/v = 4/1), then $NaBH_4$ (4 eq.) was added while stirring with a magnetic stirrer and reacted at room temperature for 12 h. Next, the reaction was quenched by addition of excess saturated NH_4Cl aqueous solution (30 mL), then extracted with dichloromethane (3 x 30 mL) and dried over copious amounts of anhydrous Na_2SO_4. The reaction mixture was filtered and concentrated under vacuum. Finally, the product was further purified by flash silica column chromatography using hexane/ethyl acetate (3:1) as eluent.

Substrate 5a: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 – 7.33 (m, 2H), 7.33 – 7.23 (m, 2H), 6.96 (td, J = 7.4, 1.1 Hz, 1H), 6.94 – 6.88 (m, 4H), 5.06 (dd, J = 8.7, 3.3 Hz, 1H), 4.07 (dd, J = 9.6, 3.4 Hz, 1H), 4.00 (dd, J = 9.6, 8.7 Hz, 1H), 3.81 (s, 3H), 2.74 (s, 1H).



Lignin Model Substrate 6a: 1,2-Diphenyl-1,2-etanediol, commercially available

Substrate 6a: ^{1}H NMR (400 MHz, CD_3CN) δ 7.24 (dd, J = 5.3, 2.0 Hz, 5H), 7.22 – 7.14 (m, 5H), 4.67 (s, 2H).



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