Supporting Information

Visible-light-mediated metal-free regioselective oxidative C-C bond cleavage of lignin dimers to aromatic acids

Ye Meng, Jie Li, Huan Liu, Honguo Wu*, Hu Li*

National Key Laboratory of Green Pesticide, Key Laboratory of Green Pesticide & Agricultural Bioengineering, Ministry of Education, State-Local Joint Laboratory for Comprehensive Utilization of Biomass, College of Pharmacy & Center for R&D of Fine Chemicals, Guizhou University, Guiyang, Guizhou 550025, China.

* Corresponding authors.

1. Experimental section

1.1. Chemicals and Reagents

2,4,6-Triphenylpyrylium tetrafluoroborate (TPP, 98%), acetonitrile (CH_3CN, >99%), ethanol (C_2H_5OH, >99.7%), methanol (CH_3OH, 99.5%), and dichloromethane (CH_2Cl_2, 99.5%) were purchased from Shanghai Aladdin Reagent Co., Ltd. All lignin model substrates and other reagents were bought from Shanghai Bide Medical Technology Co., Ltd.

1.2 Photocatalytic reactions

For the photocatalytic reaction, in general, a mixture of 2.5 mol% of photocatalyst (TPP), 0.1 mmol of the substrate, and 3 mL of the solvent was placed into a 10 mL quartz reaction tube. The resulting mixture was stirred in the dark for 0.5 h to obtain adsorption equilibrium under an air atmosphere. The reaction mixture was stirred under visible light irradiation using a 300 W Xe lamp (Perfectlight Co., PLE-SXE300, $\lambda > 400$ nm) at 25 °C controlled by cooling water. Products were confirmed by gas chromatography-mass spectrometry (GC-MS, Agilent 6890N GC/5973 MS, Santa Clara, CA) spectra, ^1H and ^{13}C NMR spectra (JEOL-ECX500 500Mz spectrometer), and compared with standard samples. The conversion of the substrate and the yield of the product were determined by high-performance liquid chromatography (HPLC, Agilent Technologies 1260 Infinity II), using the below analysis conditions: Injection, 10 μL; mobile phase, CH_3CN/H_2O (6/4, 5 mM CH_3COONH_4 aqueous solution); flow rate, 0.6 mL/min; TCC temperature, 35 °C; detector, UV 250 nm.

1.3. UV-Vis determination

The acetonitrile solution of **TPP** (1.0×10^{-4} mol L^{-1}) and **1a** or **1d** (1.0×10^{-2} mol L^{-1}) were prepared as stock solutions. In detail, 3 mL of **TPP** stock solution was added to the quartz cuvette, followed by adding the corresponding **1a** or **1d** stock solution and maintaining the molar ratio of 0, 1/3, 2/3, 1.0, 4/3, 5/3, 2.0, 7/3, 8/3, and

3.0. The measurements were performed at room temperature with a TU-1901 external spectrometer.

1.4. NMR titration experiments

The **1a**, **1d**, and **TPP** were each dissolved in acetonitrile-D_3, respectively. The **1a** or **1d** solution concentration was fixed at 0.1 mM in all analyses. The TPP (catalytic amount) solution was added to the **1a** or **1d** solution, and the ^{1}H NMR spectra were recorded at appropriate intervals using a JEOL-ECX500 500Mz spectrometer at 25 °C.

2. Computational methods

The M06-2X density functional method was employed in this work to carry out all the computations.[S1] The 6-31G(d) basis set was used for the atoms in geometry optimizations using the PCM model with acetonitrile as the solvent.[S2,S3] Vibrational frequency analyses at the same level of theory were performed on all optimized structures to characterize stationary points as local minima or transition states. Furthermore, intrinsic reaction coordinate (IRC) computations were carried out to confirm that transition states connect to the appropriate reactants and products. The single-point energy calculations were carried out using the def2-TZVP basis set to provide better energy correction.[S4] All DFT theoretical calculations were performed using the Gaussian 16 software program package.[S5]

3. Supplementary Tables and Figures

As shown in Fig. S1A and S1B, various scavengers were added to the system to further identify the active substances and reaction pathways of photocatalytic selective oxidative cleavage of the C-C bond. The conversion of **1a** and **1d** was significantly suppressed by the addition of NaN_3 ($^1O_2$ scavenger), benzoquinone (BQ, $\cdot O_2^-$ scavenger), or silver nitrate ($AgNO_3$, e^- scavenger), but scarcely affected by isopropyl alcohol (IPA, ·OH scavenger) and ethylenediaminetetraacetic acid (EDTA, TPP* scavenger), revealing that $^1O_2$ and $\cdot O_2^-$ were the main reactive oxygen species and played an important role in the conversion of **1a** and **1d**. Additionally, the addition of $AgNO_3$ also had an obvious inhibitory effect on the reaction, mainly indicating that electron transfer was also the main process of the reaction. The above results confirmed that the catalytic process belonged to a visible-light-mediated free radical reaction system.

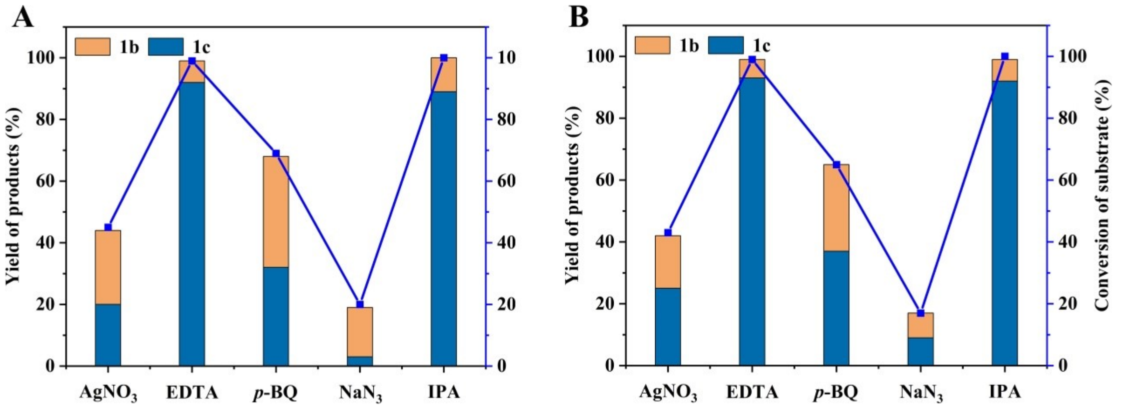


Fig. S1 The oxidative C-C bond cleavage of **1a** (A) and **1d** (B) in the presence of different scavengers. Reaction conditions: 0.1 mmol **1a** or **1d**, 2 mol % TPP, 1 equiv. quencher, 3 mL CH_3CH, $\lambda > 400$ nm irradiation for 6 h at 25 °C under air atmosphere.

As shown in Fig. S2A and S2B, the absorbance of the system increased after gradually adding solution **1a** or **1d** to the TPP solution, indicating the existence of weak interactions between the catalyst and the substrate.

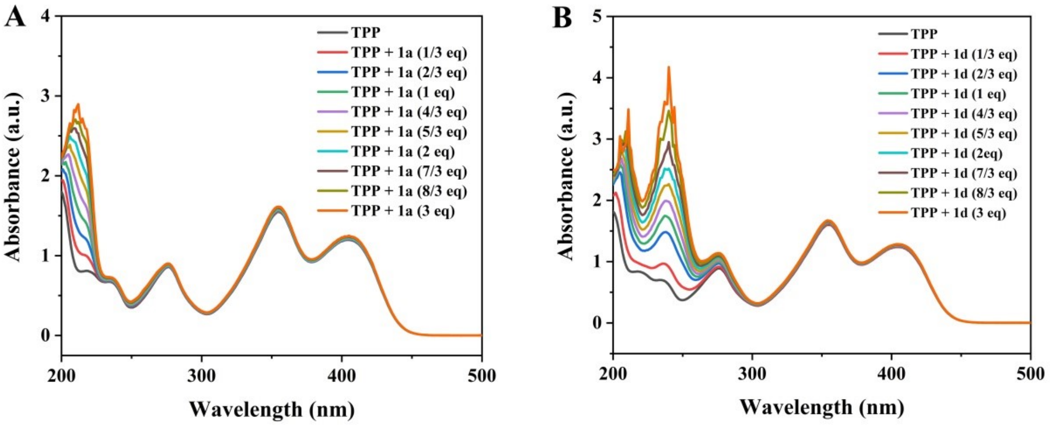


Fig. S2 The UV-Vis spectra of (A) **TPP-1a**, and (B) **TPP-1d** in different molar ratios.

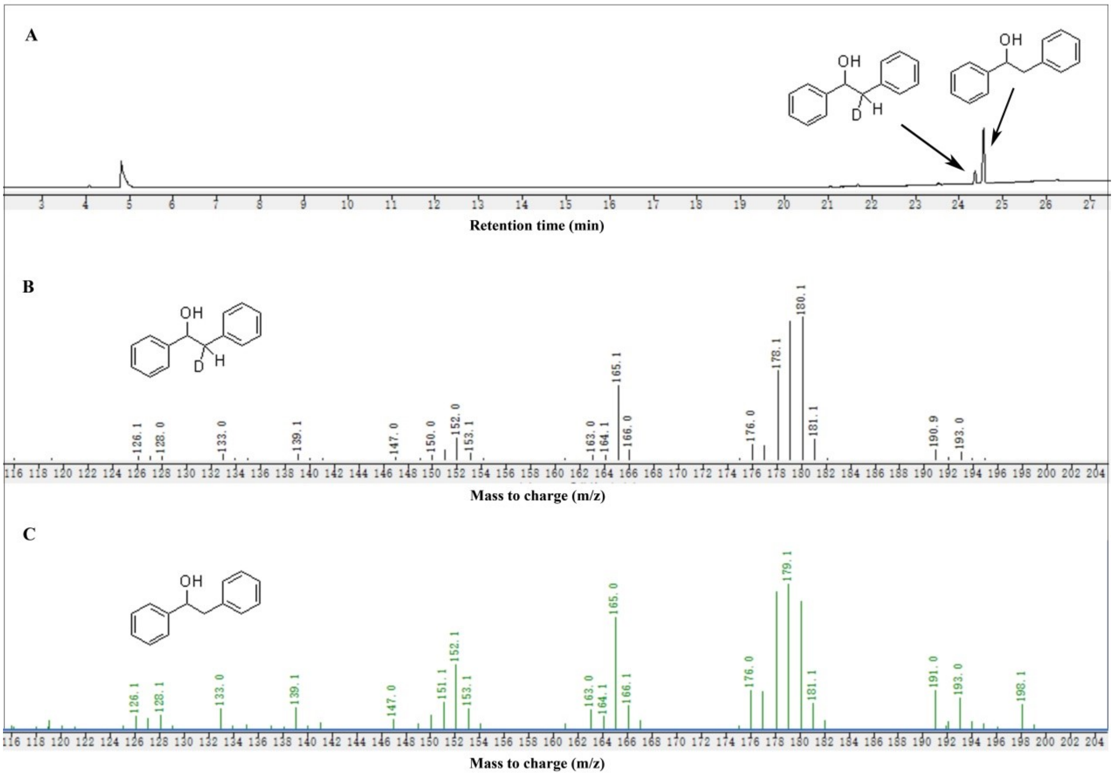


Fig. S3 The GC-MS spectra of 1,2-diphenylethan-1-ol (**1a**) in CD_3CN.

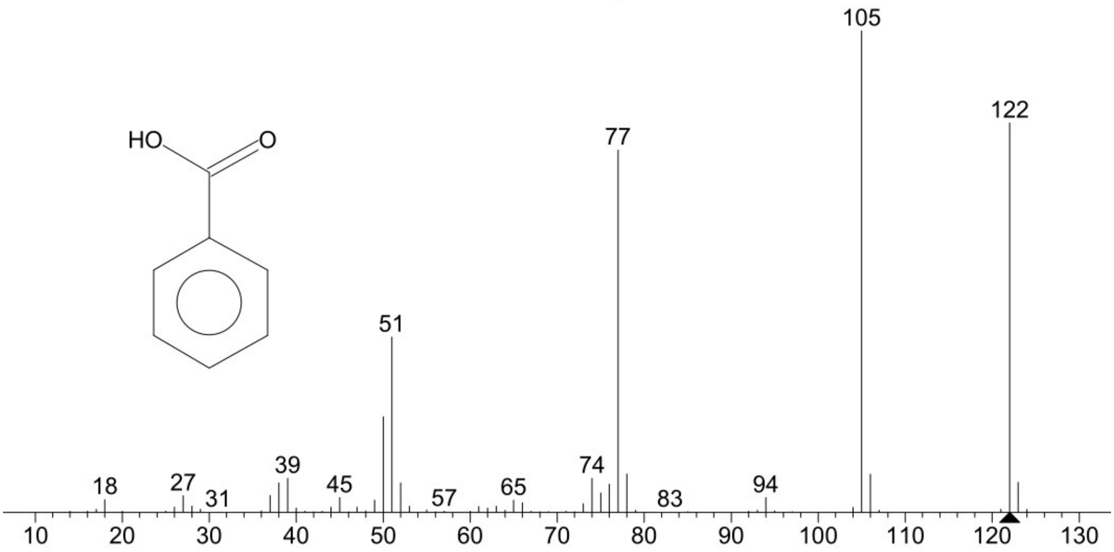


Fig. S4 The mass spectrum of benzoic acid.

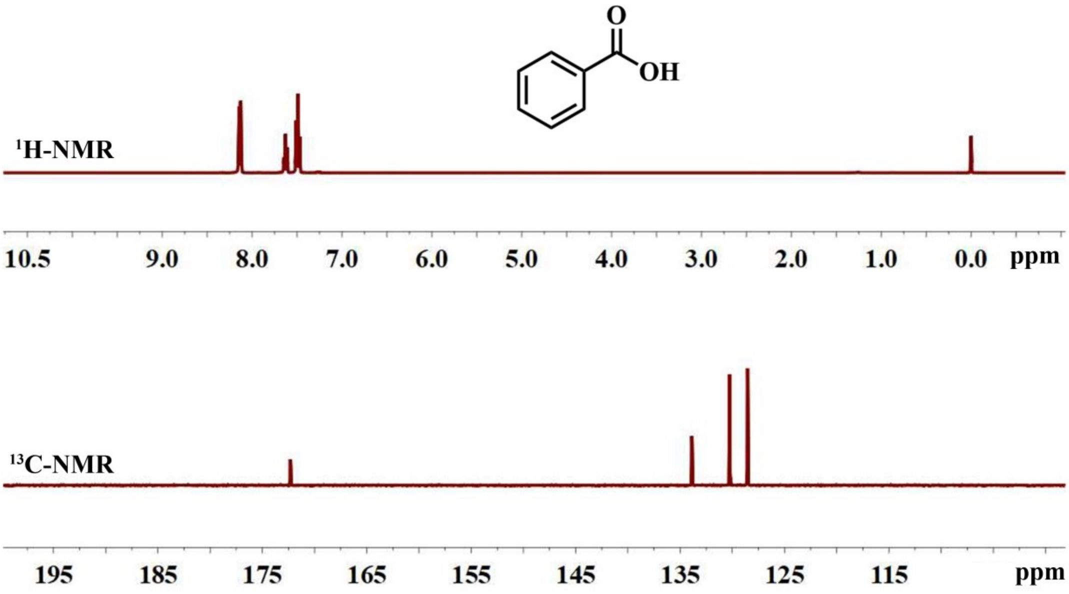


Fig. S5 The ^{1}H and ^{13}C NMR spectra of benzoic acid.

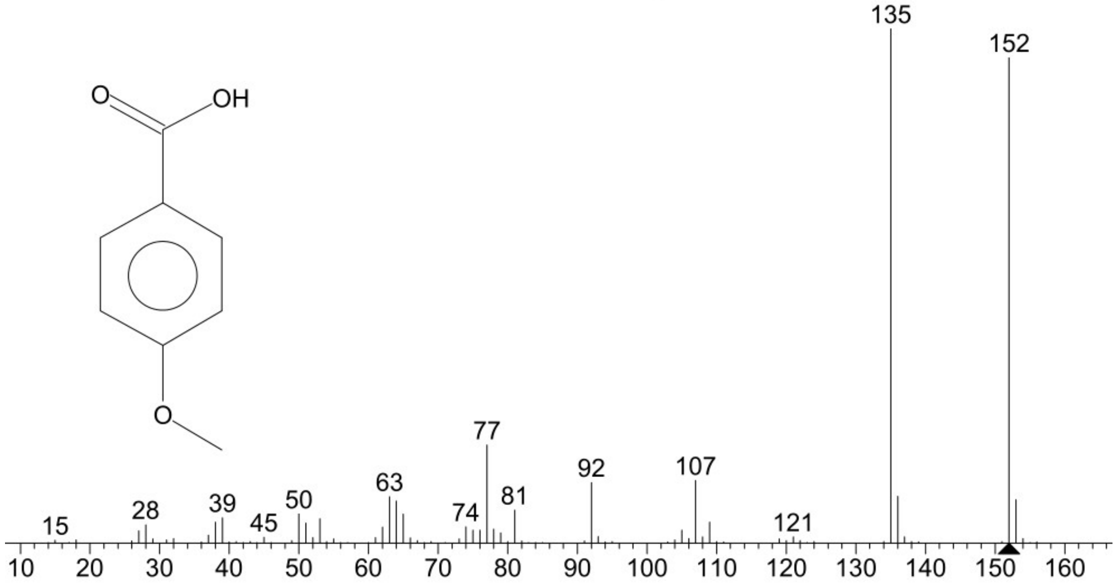


Fig. S6 The mass spectrum of 4-methoxybenzoic acid.

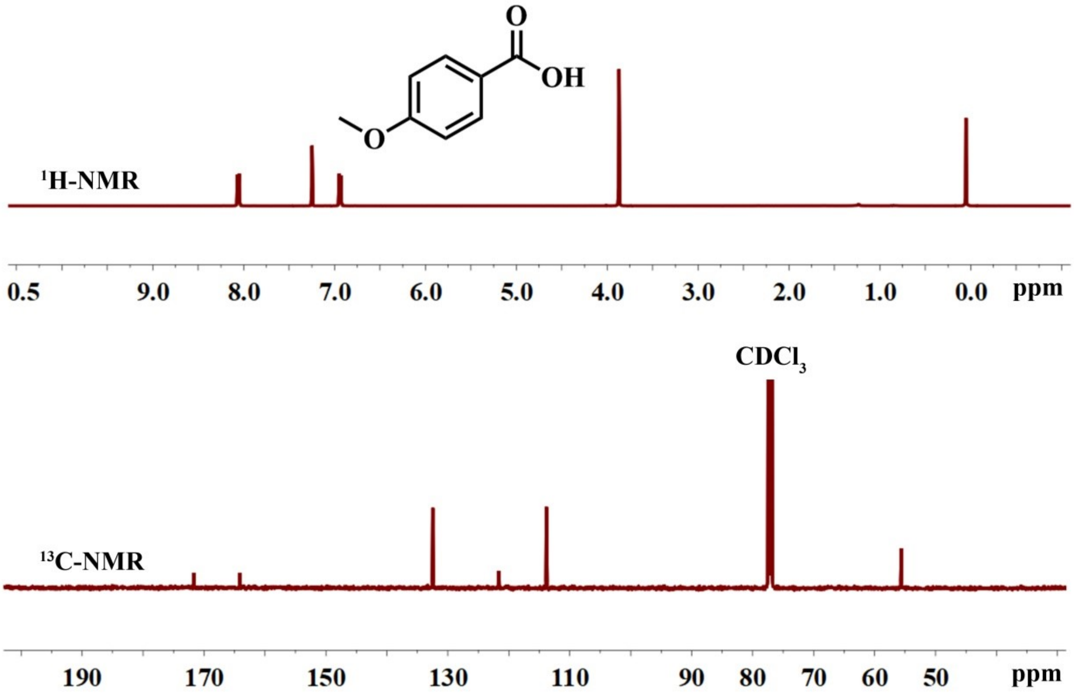


Fig. S7 The ^{1}H and ^{13}C NMR spectra of 4-methoxybenzoic acid.

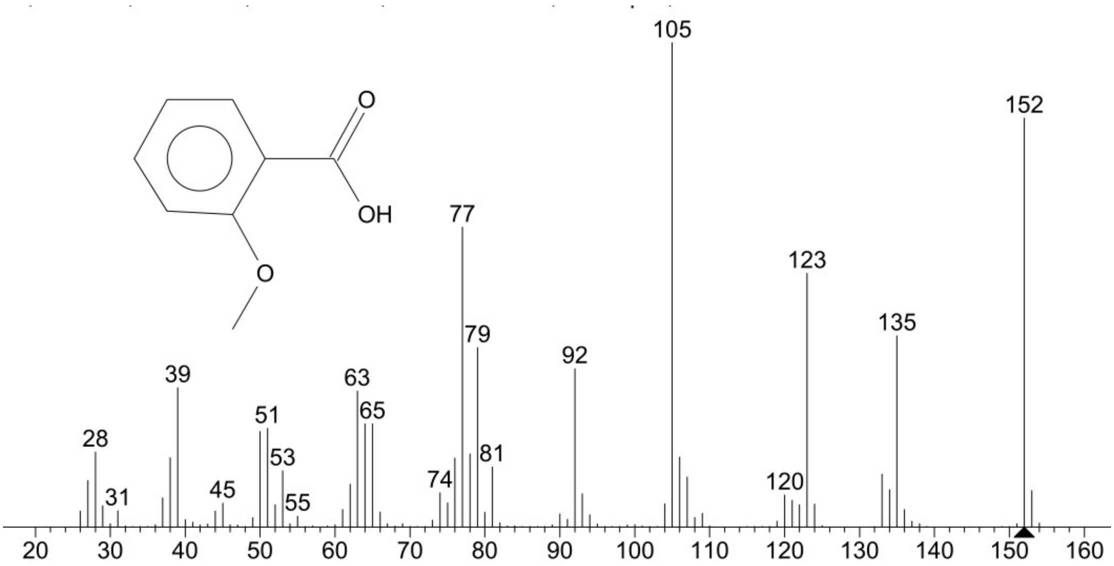


Fig. S8 The mass spectrum of 2-methoxybenzoic acid.

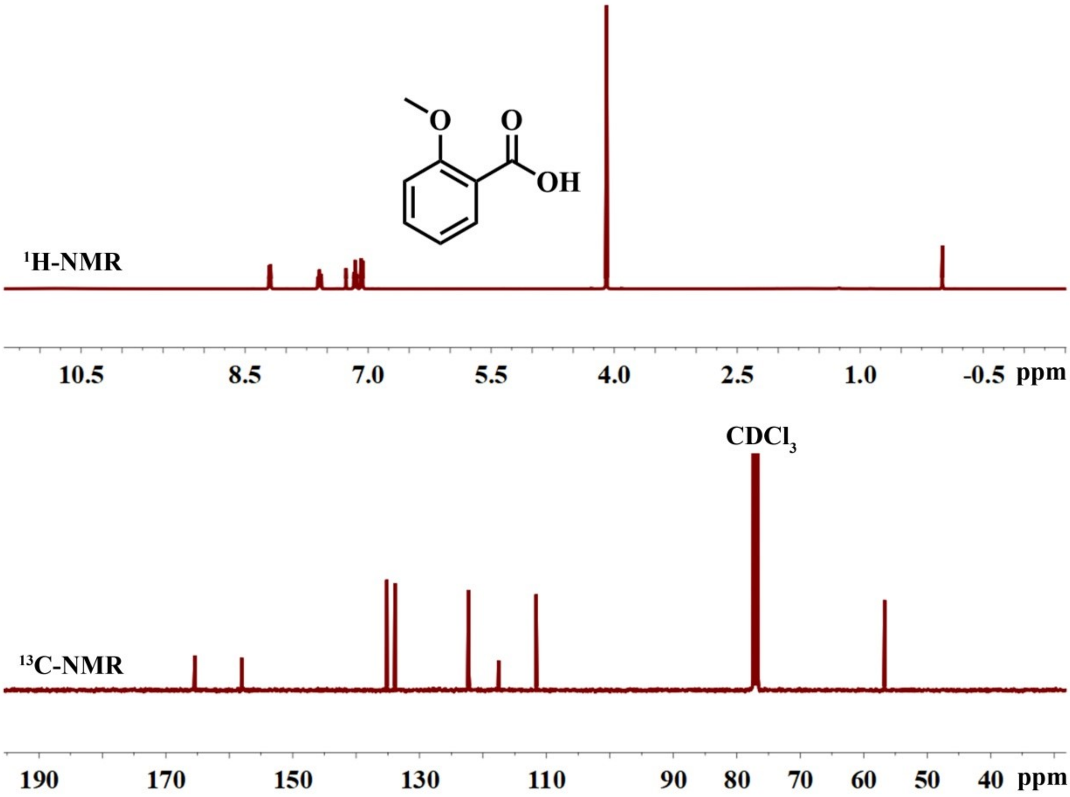


Fig. S9 The ^{1}H and ^{13}C NMR spectra of 2-methoxybenzoic acid

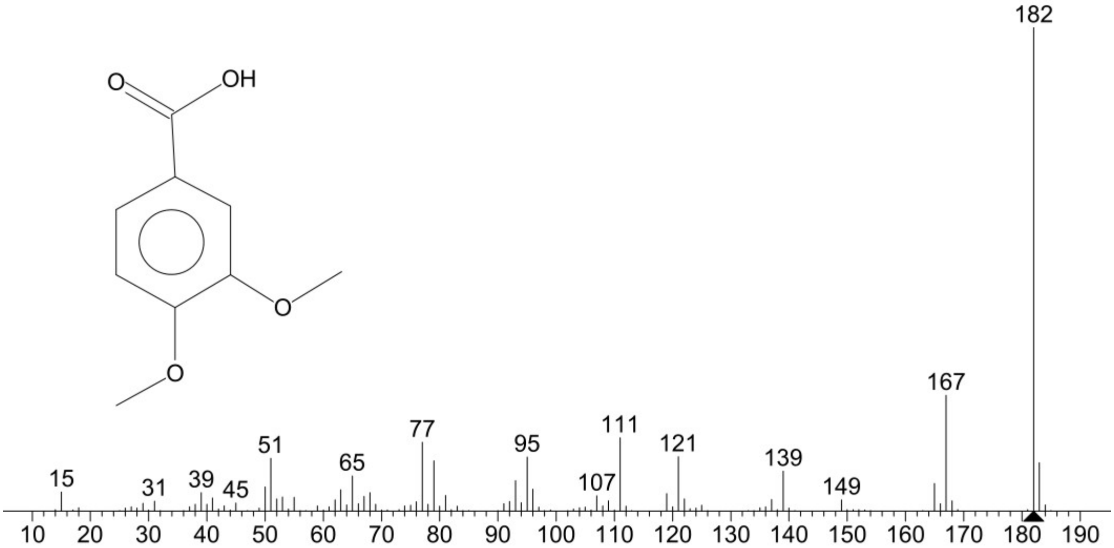


Fig. S10 The mass spectrum of 3,4-dimethoxybenzoic acid.

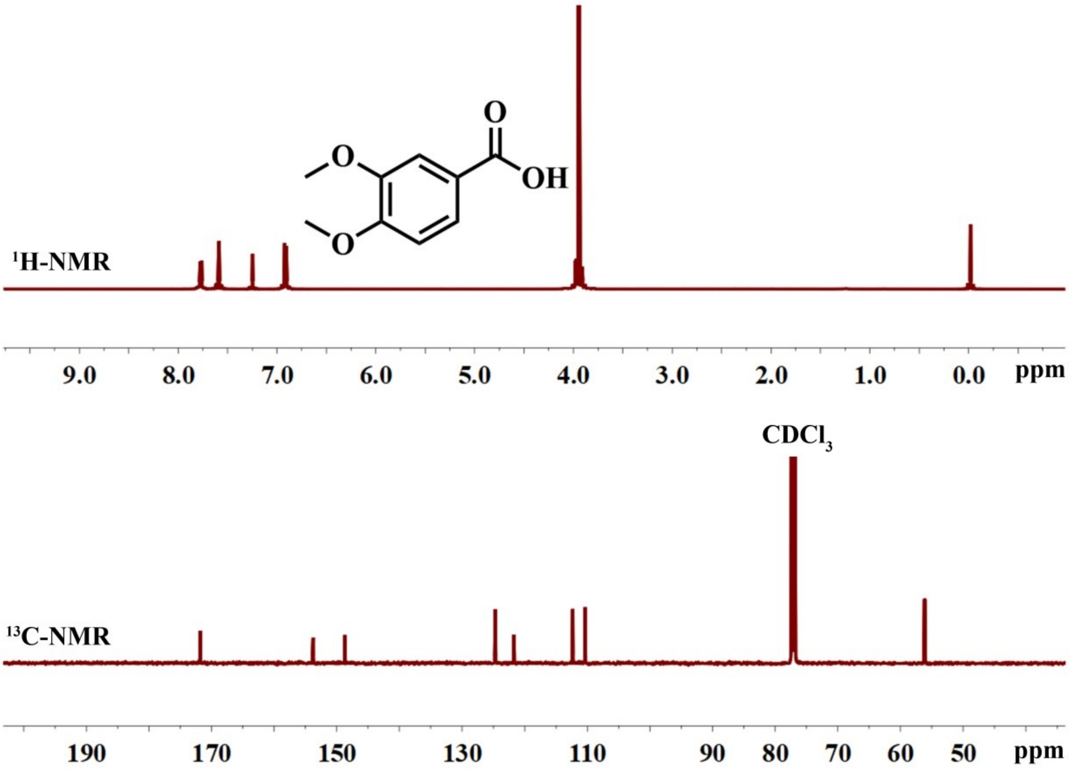
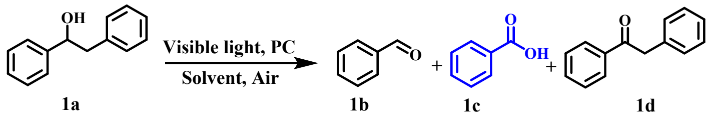


Fig. S11 The ^{1}H and ^{13}C NMR spectra of 3,4-dimethoxybenzoic acid.

Table S1 Results of the TPP-catalyzed oxidative C-C bond cleavage of **1a**.



Entry	PC dosage	Solvent	Conv. (%)	Yield (%)		
				1b	**1c**	**1d**
1	None	CH_3CN	2%	/	/	/
2	1 mol% TPP	CH_3CN	78%	28%	50%	
3	2 mol% TPP	CH_3CN	＞99%	2%	97%	/
4	2.5 mol% TPP	CH_3CN	＞99%	1%	98%	/
5[b]	2 mol% TPP	CH_3CN	2%	/	/	2%
6[c]	2 mol% TPP	CH_3CN	0	/	/	/
7	2 mol% TPP	CH_3OH	28%	19%	6%	3%
8	2 mol% TPP	CH_3CH_2OH	57%	3%	49%	4%
9	2 mol% TPP	CH_2Cl_2	10%	6%	/	4%

[a] Reaction conditions: 0.1 mmol substrate, 0-2.5 mol% photocatalyst (PC), 3 mL solvent, $\lambda >$ 400 nm, air atmosphere, 25 °C, and 8 h. [b] N_2 atmosphere. [c] Without light irradiation.

Initially, our investigations were commenced with the selective cleavage of the C-C bond in the lignin *β*-1 model compound 1,2-diphenylethan-1-ol (**1a**) under various reaction conditions (Table S1). It was found that the amount of used PC was positively correlated with the conversion of **1a** (Entries 1-4). The conversion of **1a** was only 2% after 8 h of visible-light irradiation without PC, and no product was detected (Entry 1). When PC was used in a dosage of 2 mol%, the conversion of **1a** was more than 99%, and benzoic acid (**1c**) was formed in an almost quantitative yield (up to 97%) with benzaldehyde (**1b**) in a yield of only 2% (Entry 3). These results indicated that PC played a key role in the photocatalytic oxidation system for selective C-C bond scission. In an N_2 atmosphere, only 2% of **1a** was converted to 2-phenylacetophenone (**1d**), indicating that molecular oxygen could be the source of the active species in the reaction (Entry 5). The substrate did not transform under the dark condition, suggesting that it is a light-excited reaction process (Entry 6). In addition, the effects of different solvents were evaluated, and the results showed that none of them had good catalytic activity and selectivity (Entries 7-9), except CH_3CN (Entry 3) under identical reaction conditions. Overall, it can be speculated that the whole reaction process is the participation of oxygen-active species in the photocatalytic transformation system.

Table S2 The DFT calculation data

Entry	G	G correction	delta G(kcal/mol)	E（big）	G(big)	delta G(kcal/mol)	
TPP	-960.963752	0.280117		-961.58937	-961.309253		
1a	-616.673156	0.204428		-617.11544	-616.911012		
i	-1577.633228	0.510332	2.3092368	-1578.723535	-1578.213203	4.43147562	4.4
ii	-1577.596305	0.507293	23.16955173	-1578.679985	-1578.172692	25.42105761	29.85253323
iii	-1577.625349	0.509236	-18.22540044	-1578.712584	-1578.203348	-19.23694656	10.61558667
1d	-615.503293	0.181088		-615.915199	-615.734111		
I	-1576.461251	0.489045	3.63579294	-1577.521297	-1577.032252	6.97289112	6.9
II	-1576.431026	0.485215	18.96648975	-1577.485538	-1577.000323	20.03576679	27.00865791
III	-1576.461815	0.48898	-19.32040539	-1577.520866	-1577.031886	-19.80609813	7.20255978

Table S3 Photocatalytic results in oxidative C-C bond cleavage of lignin *β*-O-4 models

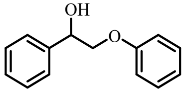
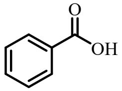
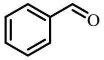
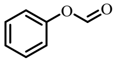
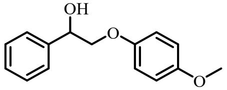
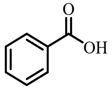
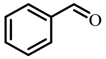
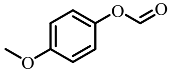
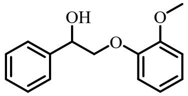
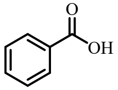
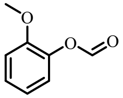
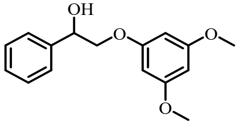
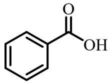
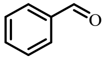
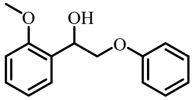
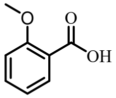
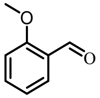
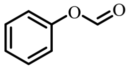
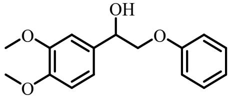
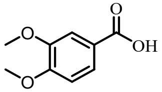
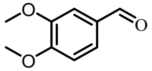
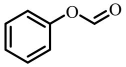
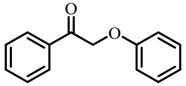
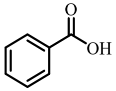
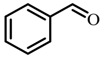
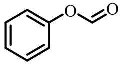
Entry	Substrate	Time (h)	Yield of products (%)		
			Aromatic acid	Aromatic aldehyde	Aromatic methyl esters
1		8	 **95%**	 **4%**	 **16%**
2		8	 **93%**	 **6%**	 **8%**
3		8	 **99%**	/	 **2%**
4		8	 **96%**	 **3%**	/
5		8	 **93%**	 **7%**	 **11%**
6		8	 **92%**	 **6%**	 **5%**
7		8	 **98%**	 **1%**	 **20%**

Table S4 Performance comparison of the developed system with previously reported photocatalytic systems for oxidative C-C bond cleavage of lignin models

Entry	Catalyst	Model compound	Reaction condition	Conversion (%)	Selectivity of C-C bond (%)	Reference
1	Vanadium-complex 1, 10 mol %	Alcohol β-O-4, $sp^3(C_\alpha$-$C_\beta)$	30 °C, reflux, >420 nm, 24 h	100	67.9	*Chem, Sci.* 2015, **6**, 7130-7142
2	Vanadium-complex 2, 10 mol%		Room temp., white LED, 24 h	76	79.9	*ACS Catal.* 2017, **7**, 4682-4691
3	Mpg-C_3N_4, 10 mg		Room temp., 455 nm LED, 10 h	96	74.3	*ACS Catal.* 2017, **7**, 3850-3857
4	Mo_{132}, 1 mol% + $K_2S_2O_8$, 1 equiv.		10 °C, reflux, 300 W Xe, 6 h	91.6	85.4	*ACS Sustainable Chem. Eng.* 2023, **11**, 7624-7632
5	Vanadium-complex 3, 10 mol %	Alcohol β-1, $sp^3(C_\alpha$-$C_\beta)$	25-40 °C, 455 nm LED, 6 h	99	52	*ACS Catal.* 2020, **10**, 632-643
6	CuOx/ceria/anatase nanotube, 10 mg		Room temp., 455 nm LED, 5 h	72	98	*ACS Catal.* 2018, **8**, 4761-4771
7	TPP，2.5 mol%	Alcohol and ketone β-O-4, $sp^3(C_\alpha$-$C_\beta)$	25 °C, >400 nm Xe, 4-8 h	100	>99	This work
8	TPP，2.5 mol%	Alcohol and ketone β-1, $sp^3(C_\alpha$-$C_\beta)$	25 °C, >400 nm Xe, 8-10 h	100	>99	This work

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