# Supporting information

# Photocatalytic Oxidation-Hydrogenolysis of Lignin β-O-4 Models via Dual Light Wavelength Switching Strategy

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# 1. Catalyst Characterization

Powder X-ray diffraction patterns were conducted with a PANalytical X-Pert PRO diffractometer, using Cu-Kα radiation at 40 kV and 20 mA. Continuous scans were collected in the 2θ ranges 10-80°. Transmission electron microscopy (TEM, JEOL JEM-2000EX) was used to observe the sample morphology. UV-Vis diffuse reflectance spectra was recorded on JASCO V-650 UV-Vis spectrophotometer. Electron paramagnetic resonance (EPR) tests were performed on a Bruker spectrometer in the X-band at 77 K with a field modulation of 100 kHz. The microwave frequency was maintained at 9.401 GHz.

# 2. Additional Experimental Results



**Figure S1.** Optimization of reaction conditions for photocatalytic C–O bond cleavage via hydrogenolysis. (a) and (b) Screen of different week bases and their amounts. (c) Influence of solvents. Only protic solvents except 'BuOH promote the C–O bond cleavage of **1b**. CH<sub>3</sub>CN and 1,2-DCE (1,2-dichloroethane) show near no activities in the hydrogenolysis of **1b**. (d) Time curve of the C–O bond cleavage of **1b**. **1b** was totally cleaved in 4 h, but the yields of **1c** and **1d** reach their maximum at 5 h. After 5 h of reaction, the yield of **1d** decreases slowly with reaction time.



Figure S2. TEM of TiO<sub>2</sub>. (a) and (b) TEM of TiO<sub>2</sub> (anatase, hydrophilic, 40 nm). (c) HR-TEM of

 $TiO_2$  (anatase, hydrophilic, 40 nm). (d) Size distribution of  $TiO_2$  (anatase, hydrophilic, 40 nm).



Figure S3. TEM of  $TiO_2$  with different mainly exposed crystal facets. (a) (101) crystal facet. (b)

(111) crystal facet. (c) (001) crystal facet.



**Figure S4.** TEM of Pd/ZnIn<sub>2</sub>S<sub>4</sub>. (a) TEM of Pd/ZnIn<sub>2</sub>S<sub>4</sub>, and the ZnIn<sub>2</sub>S<sub>4</sub> is nanosheets. (b) HR-TEM of Pd/ZnIn<sub>2</sub>S<sub>4</sub>. 0.322 nm is the interplanar distance of (102) crystal facet. (c) HR-TEM of Pd/ZnIn<sub>2</sub>S<sub>4</sub>. 0.419 nm is the interplanar distance of (006) crystal facet. (d) EDX of Pd/ZnIn<sub>2</sub>S<sub>4</sub> indicates the existence of Pd.



Figure S5. (a) X-Ray diffraction patterns of  $TiO_2$  with different mainly exposed crystal facets. (b) X-Ray diffraction patterns of Pd/ZnIn<sub>2</sub>S<sub>4</sub>.

X-Ray diffraction patterns of the as-prepared  $TiO_2$  are in accord with anatase  $TiO_2$ . While the broad peak of Pd/ZnIn<sub>2</sub>S<sub>4</sub> suggests the nanosheet feature of Pd/ZnIn<sub>2</sub>S<sub>4</sub> and is well accord with the XRD pattern in literature.<sup>1</sup> Besides, the presence of (006) diffraction peak is observed and confirms the (006) crystal facet in Figure S4(c).



**Figure S6.** (a) The UV-visible diffuse reflectance spectra and (b) curves of the Kubelka–Munk function plotted against the photon energy of  $TiO_2$  with different mainly exposed crystal facets. (c) The UV-visible diffuse reflectance spectra of Pd/ZnIn<sub>2</sub>S<sub>4</sub>.

The UV-visible diffuse reflectance shows that the as-prepared  $TiO_2$  with varied exposed crystal facets adsorb light above 400 nm. However, the Kubelka-Munk function plotted aganst the photon energy indicates nearly no decrease of bandgap of different  $TiO_2$ . Therefore, the reaction results of the C–O bond hydrogenolysis cleavage of **1b** can exclude the influence of the light absorption of  $TiO_2$  with varied exposed crystal facets.

The UV-visible diffuse reflectance spectra of  $Pd/ZnIn_2S_4$  indicates the light harvesting beyond 800 nm. The absorption at 455 nm is intensively enough to drive photocatalytic oxidation of **1a** in O<sub>2</sub> atmosphere.

		Catalyst, NaOAc	OH +	<	
	1b		1c 1d		
Entry	Catalytst <sup>b</sup>	Conv. (%)	Yield (%)		
			1c	1d	
1	_	> 99	93	90	
2	Pd/TiO <sub>2</sub>	70	41	38	
3	Rh/TiO <sub>2</sub>	64	39	38	
4	Pt/TiO <sub>2</sub>	48	24	25	
5	Ru/TiO <sub>2</sub>	38	18	21	
6	Au/TiO <sub>2</sub>	57	46	44	

Table S1. Influence of Metal loadings on the C–O bond hydrogenolysis cleavage of 1b.<sup>a</sup>

<sup>*a*</sup> Reaction conditions: 0.1 mmol **1b**, 5 mg Catalyst, 0.75 mL EtOH, N<sub>2</sub> atmosphere, 5 h, 5.6 W LED (365 nm). <sup>*b*</sup> The loadings of metal is 2 wt%, and is reduced with 30 mL/min H<sub>2</sub> at 400 °C for 4 h.

		Pd/Zn 455 nm, O	lln₂S₄ P₂, solvent		+ )	OH +	+ Others	
		Reaction				Sel. (%)		
Entry	Solvent	nt time (h)	hv	Conv. (%) —	1b	1c	1d	
1	MeCN	24	+	>99	97	< 1	< 1	
2	EtOH	24	+	70	48	< 1	3	
3 <sup><i>b</i></sup>	EtOH	22	_	4	< 1	< 1	< 1	

 Table S2. Screening of reaction conditions for photocatalytic oxidation of 1a over Pd/ZnIn<sub>2</sub>S<sub>4</sub>.<sup>a</sup>

<sup>a</sup> Reaction conditions: 0.1 mmol 1a, 10 mg Pd/ZnIn<sub>2</sub>S<sub>4</sub>, 0.75 mL Solvent, O<sub>2</sub> atmosphere, 5.6 W

LED (455 nm).<sup>b</sup> Reacted at 65 °C in the dark.



Table S3. Scope of  $\beta$ -O-4 alcohols for photocatalytic oxidation of 1a over Pd/ZnIn<sub>2</sub>S<sub>4</sub>.<sup>*a*</sup>

<sup>a</sup> Reaction conditions: 0.1 mmol 1a, 10 mg Pd/ZnIn<sub>2</sub>S<sub>4</sub>, 0.75 mL CH<sub>3</sub>CN, O<sub>2</sub> atmosphere, 5.6 W

LED (455 nm).

#### 3. Synthesis of Model Compounds

#### Preparation of 2-phenoxy-1-phenylethanone (1b)

2-Phenoxy-1-phenylethanone was prepared by reference.<sup>2,3</sup> To a solution of phenol (6.9 g, 73 mmol) and K<sub>2</sub>CO<sub>3</sub> (10.4 g, 75 mmol) in acetone (150 mL) was added 2-bromoacetophenone (14.0 g, 70 mmol) with Ar atmosphere protection and was stirred at RT for 16 h. After reaction, the suspension was filtered and concentrated *in vacuo*. The solid was dissolved in ethyl acetate and washed with NaOH aqueous (5%, 30mL) and water (30mL) successively. The organic phase was then dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was recrystallized from ethanol to give 2-phenoxy-1-phenylethanone as a white solid in 87% yield. The spectral data were in accordance with those previously reported.

For the other methoxy substituted 2-phenoxy-1-phenylethanone, the procedures are the same as described above, except that different stating materials was used.



#### Procedure for preparation of 2-phenoxy-1-phenylethanol

2-Phenoxy-1-phenylethanol was prepared referred to literature. To THF/water mixed solvent (50 mL, 4:1 v/v) was added 2-phenoxy-1-phenylethanone (2.12 g, 10 mmol). Afterwards, NaBH<sub>4</sub> (0.76 g, 20 mmol) was added in one portion and stirred at r.t. for 1 h followed by the addition of excess amount of saturated NH<sub>4</sub>Cl aqueous solution (30 mL). Then the crude product was

extracted with 20 mL of ethyl acetate for three times. The combined organic extracts were washed with brine (100 mL) and dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic solvent was distilled under vacuum to give 2-phenoxy-1-phenylethanol as a white solid. Spectral data were in accordance with those previously reported.

For the other methoxyl substituted 2-phenoxy-1-phenylethanol, the preparation procedure is the same as described above, except that using different stating materials.





1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one



1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one was prepared by the literature procedures. To a stirring suspension of  $K_2CO_3$  (0.6 g, 4.3 mmol) and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone (1.2 g, 4 mmol) in a mixed solution of ethanol and acetone (v/v=1:1, 20ml) at r.t was added formaldehyde aqueous solution (36.5-38%) (0.6 mL, 7.3 mmol). After 4 h of reaction, the reaction mixture was concentrated in *vacuo* to give a solid product. The obtained solid was purified by column chromatography (pentane/ethyl acetate, 1:1) to yield 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one as a little yellow solid (1.19 g, 3.6 mmol) in 90% yield.

#### 2-phenoxy-1-phenylethanone



Prepared from 2-bromoacetophenone and phenol in 87% yield. White solid. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 8.08 – 8.00 (m, 2H), 7.73 – 7.64 (m, 1H), 7.56 (dd, *J*=10.6 Hz, 4.8, 2H), 7.39 – 7.29 (m, 2H), 7.08 – 6.94 (m, 3H), 5.35 (s, 2H). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 194.29, 158.12, 134.68, 133.80, 129.54, 128.83, 127.94, 121.47, 114.64, 70.61.

#### 2-(2-methoxyphenoxy)-1-phenylethanone



Prepared from 2-bromoacetophenone and guaiacol in 71% yield. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.06 – 7.97 (m, 2H), 7.60 (t, *J*=7.4 Hz, 1H), 7.48 (t, *J*=7.7 Hz, 2H), 7.02 – 6.82 (m, 4H), 5.34 (s, 2H), 3.88 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 194.59, 149.86, 147.57, 134.69, 133.74, 128.79, 128.12, 122.52, 120.81, 115.02, 112.27, 72.19, 55.93.

#### 1-(4-methoxyphenyl)-2-phenoxyethanone



Prepared from 2-bromo-1-(4-methoxyphenyl)ethanone and phenol in 83% yield. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.00 (d, *J*=8.8 Hz, 2H), 7.27 (dd, *J*=13.0 Hz, 4.4, 2H), 7.02 – 6.90 (m, 5H), 5.20 (s, 2H), 3.87 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 193.13, 164.06, 158.13, 130.58, 129.56, 127.70, 121.57, 114.82, 114.02, 70.76, 55.53.

#### $\label{eq:2-2-methoxyphenoxy} 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanone$



Prepared from 2-bromo-1-(4-methoxyphenyl)ethanone and guaiacol in 88% yield. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.08 – 7.96 (m, 2H), 7.00 – 6.81 (m, 6H), 5.27 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 193.15, 163.97, 149.78, 147.67, 130.52, 127.75, 122.34,

 $120.81,\,114.79,\,113.96,\,112.22,\,72.02,\,55.93,\,55.51.$ 

#### 1-(3, 4-dimethoxy phenyl)-2-(2-methoxy phenoxy) ethanone



Prepared from 2-bromo-1-(3,4-dimethoxyphenyl)ethanone and guaiacol in 92% yield. Little yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.68 (dd, *J*=8.4 Hz, 1.9, 1H), 7.60 (d, *J*=1.8 Hz, 1H), 7.02 – 6.82 (m, 5H), 5.29 (s, 2H), 3.98 – 3.86 (m, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 193.30, 149.76, 149.23, 147.63, 127.89, 122.80, 122.37, 120.83, 114.76, 112.20, 110.50, 110.16, 72.08, 56.11, 56.01, 55.92.

#### 2-phenoxy-1-phenylethanol



Prepared from 2-phenoxy-1-phenylethanone and NaBH<sub>4</sub> in 98% yield. White solid. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ = 7.46 (d, *J*=7.3 Hz, 2H), 7.42 – 7.21 (m, 5H), 6.98 – 6.89 (m, 3H), 5.00 (dt, *J*=7.8 Hz, 4.0, 1H), 4.05 (ddd, *J*=17.5, 9.9, 5.8 Hz, 2H), 3.68 (d, *J*=4.0 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN) δ = 159.36, 142.10, 130.09, 128.84, 128.22, 126.98, 121.42, 117.88, 115.17, 73.62, 72.36.

#### 2-(2-methoxyphenoxy)-1-phenylethanol



Prepared from 2-(2-methoxyphenoxy)-1-phenylethanone and NaBH<sub>4</sub> in 94% yield. White solid. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ = 7.48 – 7.41 (m, 2H), 7.41 – 7.25 (m, 3H), 6.90 (dddd, *J*=9.6, 7.8, 5.5, 2.4 Hz, 4H), 4.99 (dt, *J*=7.8, 3.8 Hz, 1H), 4.05 (ddd, *J*=18.0, 10.1, 5.9 Hz, 2H), 3.80 (s, 3H), 3.69 (d, *J*=3.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN) δ = 150.46, 148.93, 142.06, 128.83, 128.21, 127.00, 122.36, 121.51, 117.88, 115.39, 113.08, 75.26, 72.47, 56.07.

#### 1-(4-methoxyphenyl)-2-phenoxyethanol



Prepared from 1-(4-methoxyphenyl)-2-phenoxyethanone and NaBH<sub>4</sub> in 90% yield. White solid. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  = 7.44 – 7.31 (m, 2H), 7.31 – 7.23 (m, 2H), 6.98 – 6.88 (m, 5H), 4.94 (dt, *J*=7.3, 3.5 Hz, 1H), 4.02 (qd, *J*=9.8, 5.9 Hz, 2H), 3.77 (s, 3H), 3.59 (d, *J*=3.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN)  $\delta$  = 159.85, 159.39, 134.10, 130.09, 128.24, 121.38, 117.88, 115.17, 114.19, 73.60, 71.95, 55.48.

#### 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol



Prepared from 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone and NaBH<sub>4</sub> in 87% yield. White solid. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  = 7.35 (t, *J*=5.7 Hz, 2H), 7.01 – 6.82 (m, 6H), 4.93 (dd, *J*=7.7, 3.7 Hz, 1H), 4.01 (ddd, *J*=18.0, 10.0, 6.0 Hz, 2H), 3.76 (t, *J*=15.3 Hz, 6H), 3.72 (s, 1H). <sup>13</sup>C NMR (101

MHz, CD<sub>3</sub>CN) δ = 159.85, 150.36, 148.93, 134.04, 128.27, 122.26, 121.52, 117.91, 115.18, 114.19,

113.02, 75.18, 72.03, 56.06, 55.48.

1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one



<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ = 7.75 (dd, *J*=8.5, 2.0 Hz, 1H), 7.56 (d, *J*=2.0 Hz, 1H), 7.04 – 6.89 (m, 3H), 6.89 – 6.73 (m, 2H), 5.56 (dd, *J*=5.5, 4.3 Hz, 1H), 3.99 (td, *J* = 6.0, 3.3 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 3.72 (q, *J* = 5.9 Hz, 1H), 3.23 (dd, *J*=7.9, 4.5 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN) δ = 195.86, 154.61, 150.46, 149.73, 147.68, 128.88, 123.96, 122.89, 121.30, 117.90, 116.26,

113.28, 111.50, 111.31, 82.55, 63.63, 56.22, 56.01, 55.98.

2-phenoxy-1-phenylethanone



# $\label{eq:constraint} \textbf{2-} (\textbf{1-methoxyphoxy}) \textbf{-} \textbf{1-phenylethanone}$



# 1-(4-methoxyphenyl)-2-phenoxyethanone



2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanone



# 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone



# 2-phenoxy-1-phenylethanol

7.45 7.37 7.37 7.32 7.32 7.32 7.32 7.32 7.29 7.29 7.29 7.29 7.29 7.25 7.25 7.25	6.96 6.93 6.93 6.91 6.91	5.02 5.01 5.01 4.99 4.09 4.07 3.99	3.68 3.67
			$\square$



# $\label{eq:2-2-2} 2-(2-methoxy phenoxy)-1-phenylethanol$



# 1- (4-methoxy phenyl)-2-phenoxy ethanol



# $\label{eq:2-2-methoxyphenoxy} \textbf{2-} (2-methoxyphenoxy) \textbf{-} \textbf{1-} (4-methoxyphenoyl) ethanol$



# **References:**

- (1) Chen, Z.; Xu, J.; Ren, Z.; He, Y.; Xiao, G. J. Solid State Chem. 2013, 205, 134-141.
- (2) Picart, P.; Muller, C.; Mottweiler, J.; Wiermans, L.; Bolm, C.; Dominguez de Maria, P.; Schallmey,
- A. ChemSusChem 2014, 7, 3164-3171.
- (3) Dawange, M.; Galkin, M. V.; Samec, J. S. M. ChemCatChem 2015, 7, 401-404.