

## Supporting Information

### **PdPt/SrTiO<sub>3</sub>:Al-catalyzed redox-selective photoreduction of unsaturated carboxylic acids using minimal electron-donor and water**

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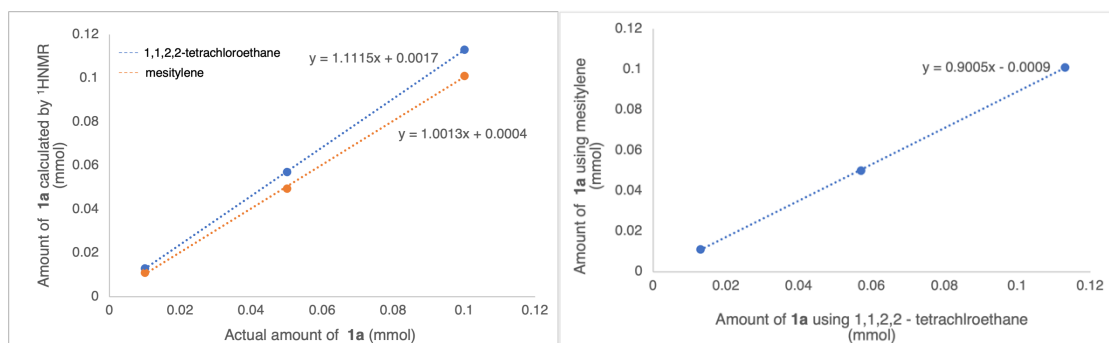
## Table of Contents

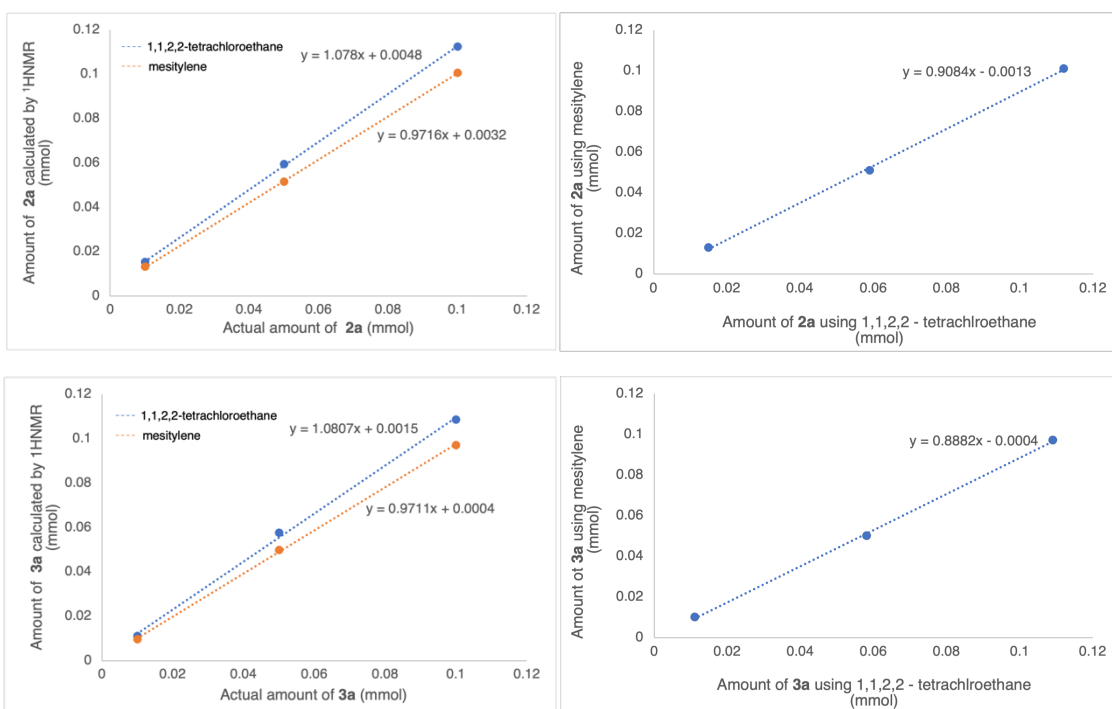
1. **General method**
2. **Materials**
3. **Experimental section**
  - a. **Reaction setups**
  - b. **Recycling experiment**
  - c. **Screening of the reaction conditions**
  - d. **Control experiments: oxidative degradation of benzaldehyde and 2a; interpretation of degradation pathways**
  - e. **Reaction in D<sub>2</sub>O**
  - f. **1 mmol scale reaction**
  - g. **Non-polar substrates**
  - h. **Characterization of the photocatalyst**
  - i. **Isolated yields and characterization of products**
4. **Comparison with previously reported photocatalysts**
5. **Reference**
6. **<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the isolated products**

## 1. General method

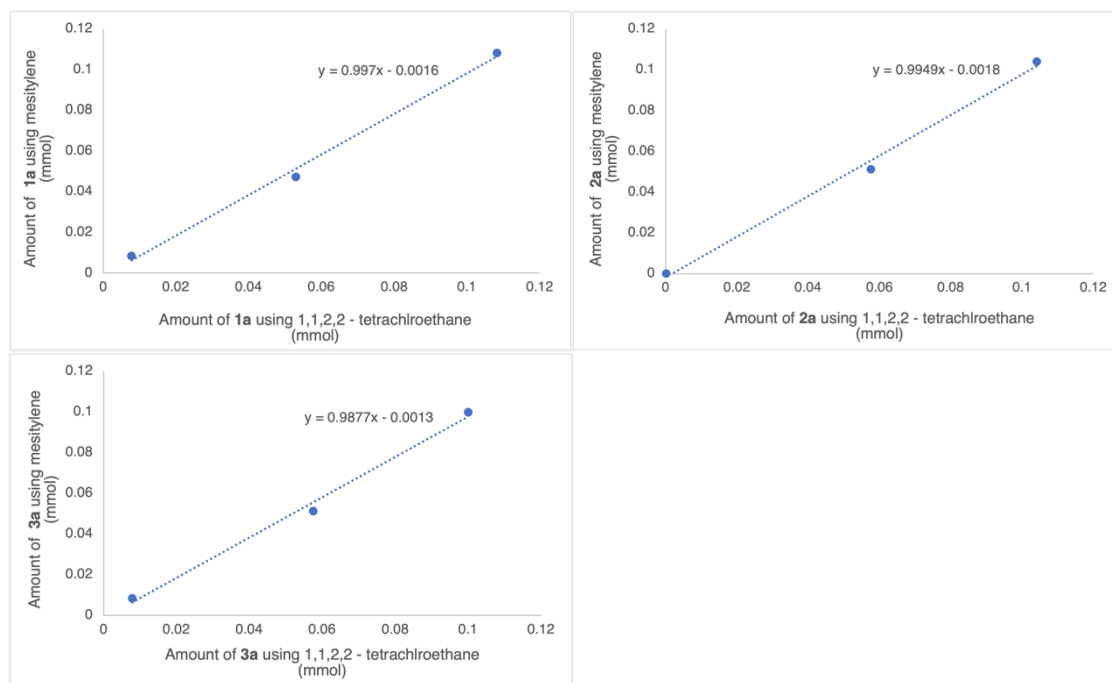
All the reactions were carried out under an N<sub>2</sub> atmosphere using oven-dried glassware and deionized water unless otherwise stated. Photocatalytic reactions were carried out utilizing PER-365 ( $\lambda = 365$  nm, 0.5 W) purchased from Techno Sigma, a solar simulator ( $\lambda = 350$ – $1800$  nm, HAL-320W) with a built-in AM1.5G filter purchased from ASAHI SPECTRA, or PR160L-370 Gen 2 ( $\lambda = 370$  nm, 44 W) purchased from Kessil. <sup>1</sup>H NMR spectra were recorded on JEOL ECA-600 (600 MHz) at room temperature [chemical shift ( $\delta$ ) in ppm relative to tetramethylsilane in CDCl<sub>3</sub> (0.00 ppm) or a solvent peak (D<sub>2</sub>O: 4.79 ppm), coupling constant ( $J$ ) in Hz, and integration]. <sup>13</sup>C NMR spectra were recorded on JEOL ECA-600 (151 MHz) at room temperature [chemical shift ( $\delta$ ) in ppm relative to CDCl<sub>3</sub> (77.2 ppm)]. The following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The diffuse reflectance UV-visible (DR-UV-Vis) spectroscopy was conducted with a UV-2450 spectrometer (SHIMADZU). The XRD patterns were acquired using a MiniFlex 300 powder diffractometer (Rigaku) with Cu K $\alpha$  radiation. The XPS was performed using a PHI Quantera II spectrometer (ULVAC-PHI) with an Al K $\alpha$  radiation source. All binding energies were referenced to the C 1s peak (284.8 eV) arising from adventitious carbon. The images of electron microscopy were obtained by JEM-ARM 200F Cold (JEOL, accelerating voltage of 200 kV). TLC analysis was performed on commercial glass plates bearing a 0.25 mm layer of Merck TLC silica gel 60 GF254.  $\mu$ GC-TCD analyses were conducted in a dual channel micro gas chromatography ( $\mu$ GC) system coupled to a thermal conductivity detector (TCD, Agilent 490). In the optimization study, organic compounds (**1a**, **2a** and **3a**) were quantified by <sup>1</sup>H NMR analysis using internal standards (mesitylene or 1,1,2,2-tetrachloroethane). We found that the amounts of them were accurately quantified with mesitylene, but they were overestimated with 1,1,2,2-tetrachloroethane. Therefore, we made calibration lines, with which we could quantify them accurately using data based on 1,1,2,2-tetrachloroethane.

CDCl<sub>3</sub>:





### DMSO-*d*<sub>6</sub>:



## 2. Materials

### Chemicals

4-Vinylbenzoic acid (stabilized with BHT) (**1e**), (*E*)-4-methoxycinnamic acid (**1b**), phenylpropionic acid (**1f**), 4-chlorocinnamic acid (**1j**), 4-bromocinnamic acid (**1k**), 4-chlorobenzoic acid (**1g**), 4-bromobenzoic acid (**1h**), 4-iodobenzoic acid (**1i**), glycolic acid (GA) and *trans*-stilbene (**4a**) were purchased from Tokyo Chemical Industry. (*E*)-Cinnamic acid (**1a**), oxalic acid dihydrate, hydrochloric acid, sodium hydroxide (granular), potassium carbonate, sodium carbonate, calcium hydroxide, sodium borohydride (granulated), SrCl<sub>2</sub> (anhydrous), 1,1,2,2-tetrachloroethane, DMSO-*d*<sub>6</sub> and mesitylene were received from Kanto Chemical. 3-Methoxycinnamic acid (**1c**) was purchased from Thermo Fisher Scientific. H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and benzaldehyde were provided by FUJIFILM Wako Pure Chemical. Al<sub>2</sub>O<sub>3</sub> (nanopowder), Pd(NO<sub>3</sub>)<sub>2</sub>, glyoxylic acid monohydrate, sodium phosphate, potassium hydroxide and diphenylacetylene (**4b**) were purchased from Sigma-Aldrich. SrTiO<sub>3</sub> (STO) was provided from KOJUNDO Chemical Laboratory. (*E*)- $\alpha$ -Methylcinnamic acid (**1d**) was purchased through ACROS ORGANICS. Calcium carbonate was provided by NACALAI TESQUE, INC. Chloroform-*d* was purchased from Cambridge Isotope Laboratories. These chemicals were used without further purification.

### Photocatalysts

STO:Al was prepared by a reported method.<sup>1</sup>

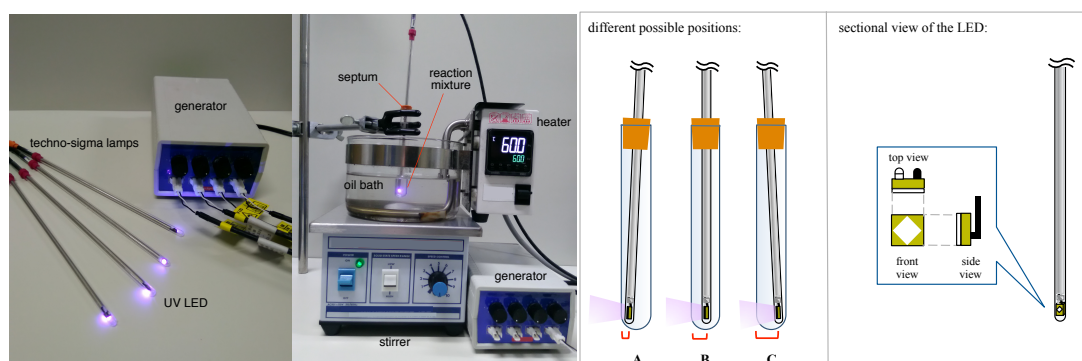
PdPt/STO:Al (1.5 wt% Pd and Pt) was prepared according to a reported procedure.<sup>2</sup> STO:Al (1.0 g), H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (40.1 mg, 0.08 mmol, 15 mg Pt), Pd(NO<sub>3</sub>)<sub>2</sub> (32.3 mg, 0.14 mmol, 15 mg Pd), water (40 mL), and a stirrer bar were placed in a 100 mL round bottom flask with a wide neck and the mixture was subjected to ultrasonic vibration for 10 min. The reaction mixture was stirred vigorously at 80 °C for 16 h (until the solvent was fully evaporated). The obtained powder was grained gently and placed in an alumina crucible. The powder was calcined at 400 °C under air for 2 h (heating program: heating from room temperature to 400 °C for 5.5 h, keeping 400 °C for 2 h). After calcination, the powder was allowed to reach room temperature. Then, the powder was suspended in water (20 mL) in a 50 mL round bottom flask with a stirrer bar and was subjected to ultrasonic vibration for 10 min. NaBH<sub>4</sub> (2 mmol, ca.10 equiv with respect to the metals) in cool water (5 mL, 0 °C) was added dropwise into the flask at room temperature. The suspension was allowed to stir at room temperature for 2 h. The obtained solid was filtered and rinsed with water, and then the residual water was removed under reduced pressure. PdPt/STO:Al indicate PdPt/STO:Al (1.5 wt% Pd and Pt) unless otherwise noted.

### Products

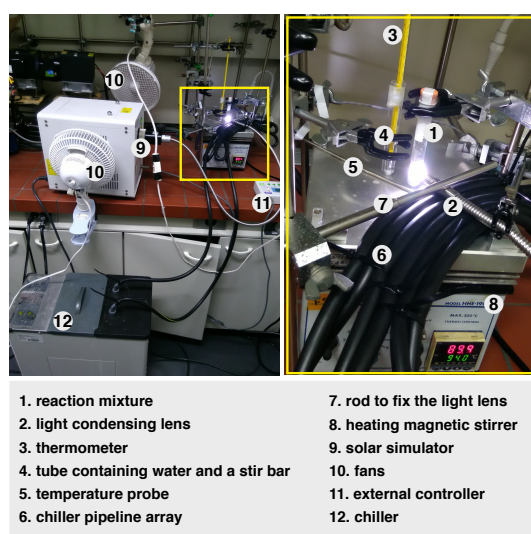
**2a**,<sup>3</sup> **2b**,<sup>3</sup> **2c**,<sup>4</sup> **2d**,<sup>3</sup> **2e**,<sup>5</sup> and **3a**<sup>6</sup> are reported compounds.

### 3. Experimental section

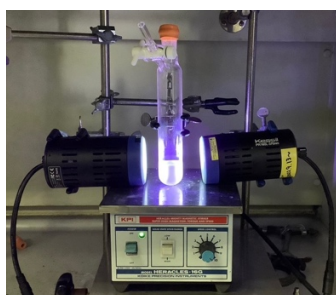
#### a. Reaction setups



**Fig. S1.** Reaction setup using techno-sigma lamp at elevated temperature. Important Note: the techno-sigma LEDs emit UV light in one direction only; therefore, the lamp tube in position C should be adjusted while the LED is facing the entire reaction mixture to ensure reproducibility. The reaction mixture exposed to the light from positions A and B cannot receive the maximum light irradiation.



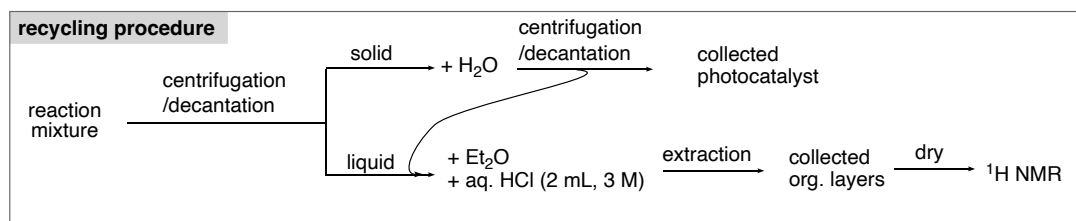
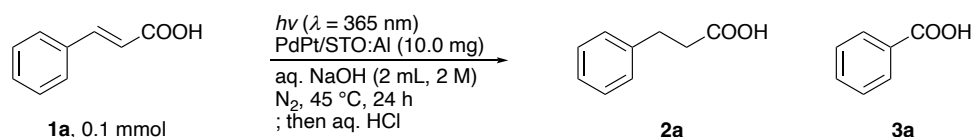
**Fig. S2.** Reaction setup using solar simulator.



**Fig. S3.** Reaction setup using two Kessil lamps (for 1 mmol scale reaction).

## **b. Recycling experiment**

An oven-dried Pyrex glass tube (height = 10.0 cm, diameter = 1.0 cm) was equipped with a Teflon-coated disc-shaped stirrer bar (diameter = 0.9 cm). **1a** (0.1 mmol) and PdPt/STO:Al (10.0 mg) were added to the test tube, and then the tube was sealed with a rubber septum. The reaction atmosphere was replaced with N<sub>2</sub>. Under the flow of N<sub>2</sub>, an aqueous solution of NaOH (2 mL, 2 M) was added to the tube and the rubber septum was replaced with another one to which an NMR tube was inserted. After sonication for 1 min, techno-sigma lamp was inserted into the NMR tube and the reaction mixture was irradiated at 45 °C for 24 h. The reaction mixture was transferred into a 50 mL Falcon tube and was subjected to centrifugation (35,00 rpm, 10 min). The supernatant was decanted. Then, 20 mL of water was added to the solid and the mixture was centrifuged after vigorous shaking. The centrifugation/decantation was repeated three times. The solid residue was dried under reduced pressure, and the obtained powder was used as the photocatalyst in the next reaction run. The combined aqueous liquid was acidified by an aqueous solution of HCl (ca. 2 mL, 3 M) and extracted by diethyl ether three times. Residual water was removed from the combined organic layers using Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the residue was analyzed by <sup>1</sup>H NMR using an internal standard (1,1,2,2-tetrachloroethane).

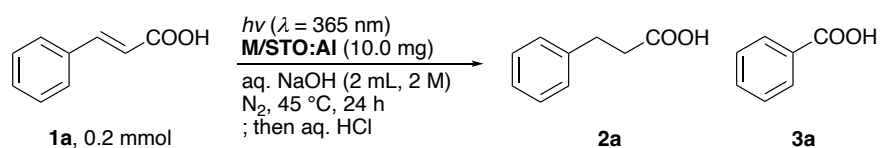


1st run average yield of 2a: 86%				2nd run average yield of 2a: 82%, PDA = 5%				3rd run average yield of 2a: 76%, PDA = 12%			
entry	conversion of 1a (%)	yield of 2a (%)	yield of 3a (%)	entry	conversion of 1a (%)	yield of 2a (%)	yield of 3a (%)	entry	conversion of 1a (%)	yield of 2a (%)	yield of 3a (%)
1	>99	86	4	9	91	85	2	15	92	78	2
2	>99	81	4	10	92	77	2	16	97	70	3
3	99	83	4	11	96	83	<1	17	92	78	2
4	99	89	4	12	96	83	<1	18	92	79	2
5	>99	88	4	13	95	83	1	<b>4th run average yield of 2a: 81%, PDA = 6%</b>			
6	99	89	4	14	94	80	1	entry	conversion of 1a (%)	yield of 2a (%)	yield of 3a (%)
7	99	85	4					19	94	81	4
8	>99	89	4					20	89	80	4

**Fig. S4.** Catalyst recycling experiments. Conversions and yields were determined by  $^1\text{H}$  NMR analysis. PDA: percentage decrease in activity comparing with the 1st run.

### c. Screening of the reaction conditions

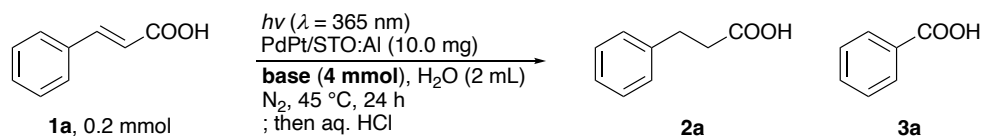
An oven-dried Pyrex glass tube (height = 10.0 cm, diameter = 1.0 cm) was equipped with a Teflon-coated disc-shaped stirrer bar (diameter = 0.9 cm). **1a** and photocatalyst (10.0 mg) were added to the test tube, and then the tube was sealed with a rubber septum. The reaction atmosphere was replaced with  $\text{N}_2$ . Under the flow of  $\text{N}_2$ , an aqueous solution of base (2 mL) was added to the tube and the rubber septum was replaced with another one to which an NMR tube was inserted. After sonication for 1 min, techno-sigma lamp was inserted into the NMR tube and the reaction mixture was irradiated at 45 °C for 24 h. The reaction mixture was transferred to a falcon tube (50 mL) with diethyl ether (ca. 15 mL) and an aqueous solution of HCl (ca. 2 mL, 3 M). The organic layer was separated. The aqueous layer was extracted with diethyl ether (ca. 5 mL) three times. Residual water was removed from the combined organic layers using  $\text{Na}_2\text{SO}_4$ . After filtration and evaporation, the residue was analyzed by  $^1\text{H}$  NMR using an internal standard (mesitylene or 1,1,2,2-tetrachloroethane).

**Table S1.** Optimization of photocatalyst

entry	M/STO:Al	conversion of 1a (%) <sup>a</sup>	yield of 2a (%) <sup>a</sup>	yield of 3a (%) <sup>a</sup>
1	Pd(1.5 wt%)Pt(1.5 wt%)/STO:Al	62	55	4
2	Pd(3 wt%)Pt(3 wt%)/STO:Al	41	39	3
3	Pd(1 wt%)Pt(2 wt%)/STO:Al	49	48	3
4	Pd(2 wt%)Pt(1 wt%)/STO:Al	50	48	3
5	Pd(1.5 wt%)/STO:Al + Pt(1.5 wt%)/STO:Al <sup>b</sup>	62	26	3
6	Pd(1.5 wt%)/STO:Al	24	19	<1
7	Pd(3 wt%)/STO:Al	25	13	<1
8	Pt(1.5 wt%)/STO:Al	23	22	2
9	Pt(3 wt%)/STO:Al	28	16	<1

<sup>a</sup> Determined by <sup>1</sup>H NMR analysis.

<sup>b</sup> Pd(1.5 wt%)/STO:Al (5.0 mg) + Pt(1.5 wt%)/STO:Al (5.0 mg).

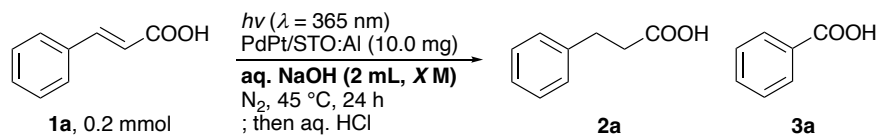
**Table S2.** Optimization of base

entry	base	conversion of 1a (%) <sup>a</sup>	yield of 2a (%) <sup>a</sup>	yield of 3a (%) <sup>a</sup>
1	NaOH	62	55	4
2	KOH	44	32	2
3	Ca(OH) <sub>2</sub>	11	9	<1
4	Na <sub>2</sub> CO <sub>3</sub>	50	38	<1
5	K <sub>2</sub> CO <sub>3</sub>	74	50	2
6	CaCO <sub>3</sub>	33	30	<1
7	Na <sub>3</sub> PO <sub>4</sub>	22	5	<1

<sup>a</sup> Determined by <sup>1</sup>H NMR analysis.

**Table S3.** Optimization of NaOH concentration

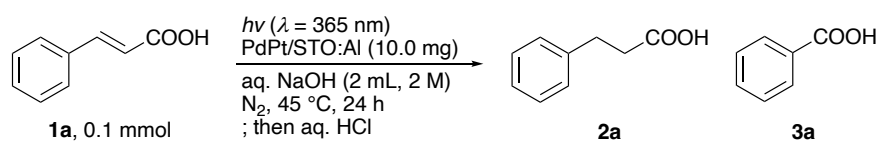




entry	NaOH (X M)	dispersion of photocatalyst	conversion of <b>1a</b> (%) <sup>a</sup>	yield of <b>2a</b> (%) <sup>a</sup>	yield of <b>3a</b> (%) <sup>a</sup>
1	0	not dispersed	37	29	<1
2	1.0	partially dispersed	50	48	2
3	2.0	well-dispersed	62	55	4

<sup>a</sup> Determined by <sup>1</sup>H NMR analysis.

**Table S4.** Control experiments.



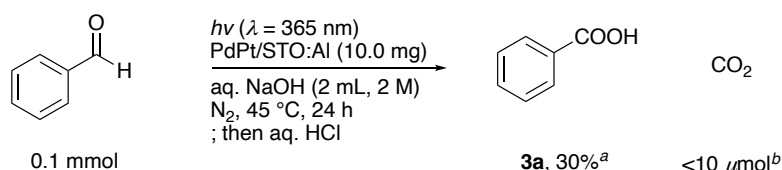
entry	difference	conversion of <b>1a</b> (%) <sup>a</sup>	yield of <b>2a</b> (%) <sup>a</sup>	yield of <b>3a</b> (%) <sup>a</sup>
1	none	>99	86	5
2	with glycolic acid (0.034 mmol)	>99	>99	<1
3	0.2 mmol of <b>1a</b>	62	55	4
4	without irradiation	11	<1	<1
5	without photocatalyst	10	<1	<1
6	without irradiation and photocatalyst	10	<1	<1
7	with tap water	>99	84	4
8	under air	96	82	7
9 <sup>b</sup>	with solar simulator	43	31	1
10 <sup>b</sup>	with solar simulator, 96 h	>99	86	4

<sup>a</sup> Determined by <sup>1</sup>H NMR analysis.

<sup>b</sup> See **Fig. S2** for the reaction setup.

#### d. Control experiments: oxidative degradation of benzaldehyde and 2a; interpretation of degradation pathways

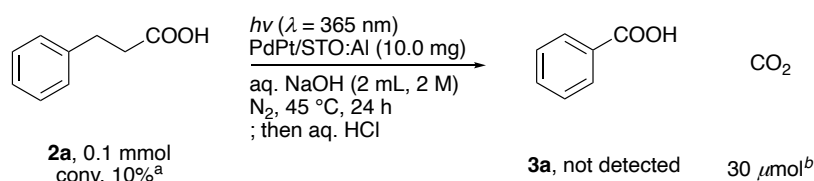
**2a** or benzaldehyde was used as follows. An oven-dried Pyrex glass tube (height = 10.0 cm, diameter = 1.0 cm) was equipped with a Teflon-coated disc-shaped stirrer bar (diameter = 0.9 cm). **2a** (0.1 mmol) and PdPt/STO:Al (10.0 mg) were added to the test tube, and then the tube was sealed with a rubber septum. The reaction atmosphere was replaced with N<sub>2</sub>. Under the flow of N<sub>2</sub>, benzaldehyde (0.1 mmol) and an aqueous solution of NaOH (2 mL, 2 M) were added to the tube and the rubber septum was replaced with another one to which an NMR tube was inserted. After sonication for 1 min, techno-sigma lamp was inserted into the NMR tube and the reaction mixture was irradiated at 45 °C for 24 h. After an aqueous solution of HCl (ca. 2 mL, 3M) were injected into the reaction tube, gas-phase analysis of the headspace was carried out with  $\mu$ GC-TCD. Then, the reaction mixture was transferred to a falcon tube (50 mL) with diethyl ether (ca. 15 mL). The organic layer was separated. The aqueous layer was extracted with diethyl ether (ca. 5 mL) three times. Residual water was removed from the combined organic layers using Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the residue was analyzed by <sup>1</sup>H NMR using an internal standard (mesitylene).



<sup>a</sup> Determined by <sup>1</sup>H NMR analysis.

<sup>b</sup> Determined by  $\mu$ GC-TCD analysis.

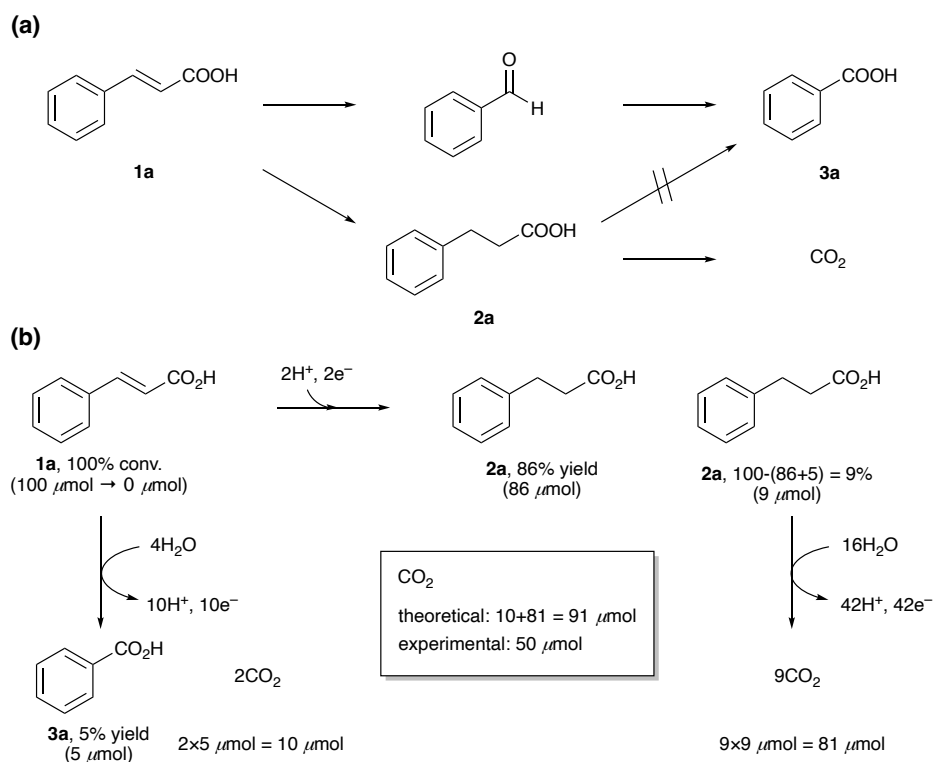
**Scheme S1.** Reaction of benzaldehyde.



<sup>a</sup> Determined by <sup>1</sup>H NMR analysis.

<sup>b</sup> Determined by  $\mu$ GC-TCD analysis.

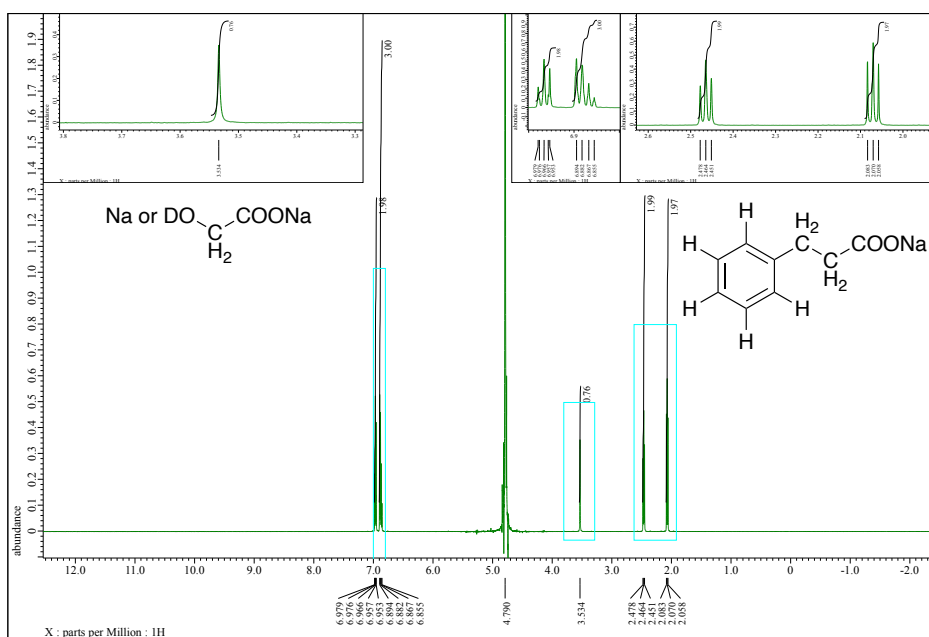
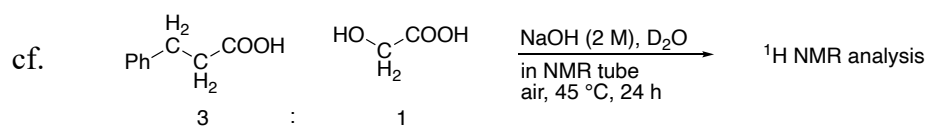
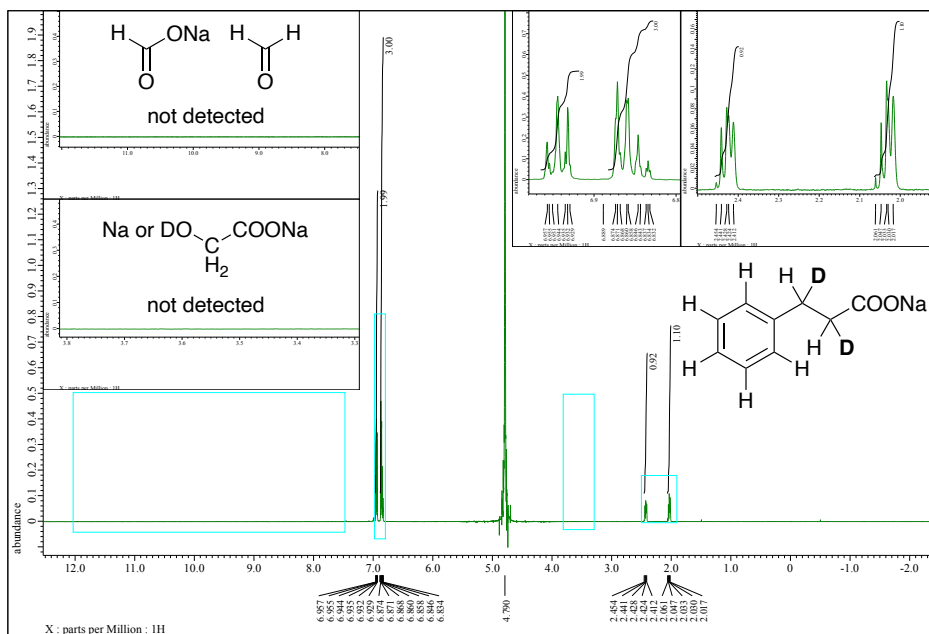
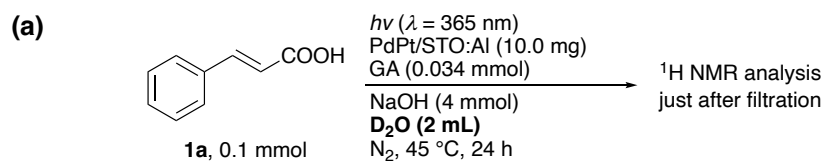
**Scheme S2.** Reaction of **2a**.

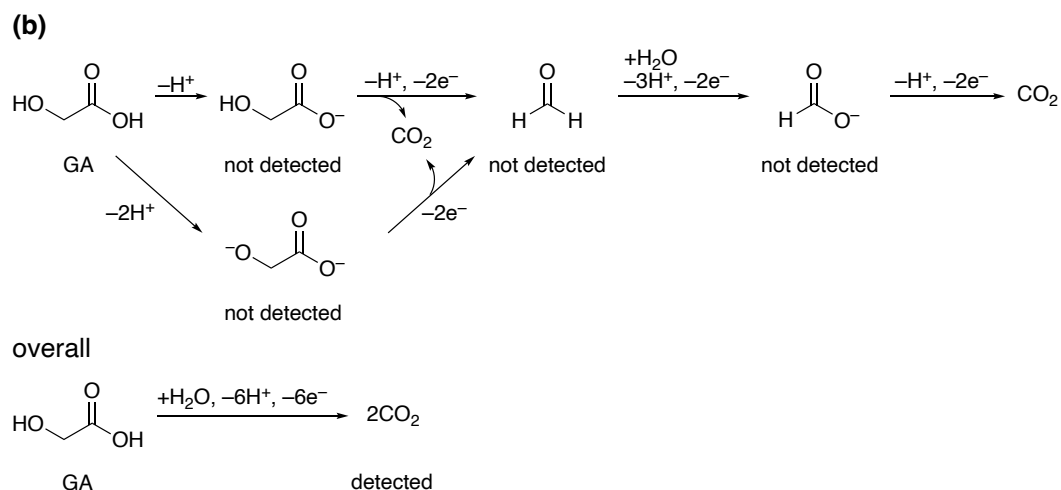


**Scheme S3.** (a) Possible pathways of oxidative degradation of **1a** and **2a** in the absence of GA. (b) Elucidation of the carbon-balance of the reaction without GA (Table 1, entry 7). **1a** (100  $\mu\text{mol}$ ) was fully consumed, and **2a** (86  $\mu\text{mol}$ ) was observed. Additionally, **3a** (5  $\mu\text{mol}$ ) was formed, which should be accompanied with CO<sub>2</sub> (10  $\mu\text{mol}$ ). Given that the missing **1a** (9  $\mu\text{mol}$ ) was converted into CO<sub>2</sub> via **2a** with its 9 carbon atoms per 1 molecule, 81  $\mu\text{mol}$  of CO<sub>2</sub> should be generated. Thus, the expected amount of CO<sub>2</sub> generated in total is calculated to be 91  $\mu\text{mol}$ . In the gas-phase analysis after acidifying the reaction mixture with aq. HCl, 50  $\mu\text{mol}$  of CO<sub>2</sub> was observed, which suggest that oxidative degradation of **1a** and **2a** occurred. The discrepancy between theoretical and experimental amounts of CO<sub>2</sub> (91  $\mu\text{mol}$  vs. 50  $\mu\text{mol}$ ) can be attributable to the following two reasons:

- High water solubility of CO<sub>2</sub>: Considering CO<sub>2</sub> is very soluble in water (ca. 40  $\mu\text{mol}$  in 1 mL water, 1 atm, 25  $^{\circ}\text{C}$ ), a portion of the generated CO<sub>2</sub> was dissolved in the aqueous media even after acidification, and was not detected in the gas-phase analysis.
- Quantification error: It should be noted that **1a**, **2a**, and **3a** were quantified by <sup>1</sup>H NMR analysis, which was not entirely accurate. In practice, the yields of **2a** were slightly varied among the eight reaction runs under the completely identical conditions (86 $\pm$ 3%; Table 1, entry 7; Fig. S4, 1st run). The trivial difference in the yield of **2a** ( $\pm$ 3  $\mu\text{mol}$ ) leads to a huge difference of the theoretically expected amount of CO<sub>2</sub> generated during the oxidative degradation of **2a** with 9 carbons (9 $\times$ ( $\pm$ 3) =  $\pm$ 27  $\mu\text{mol}$ ).

e. Reaction in D<sub>2</sub>O

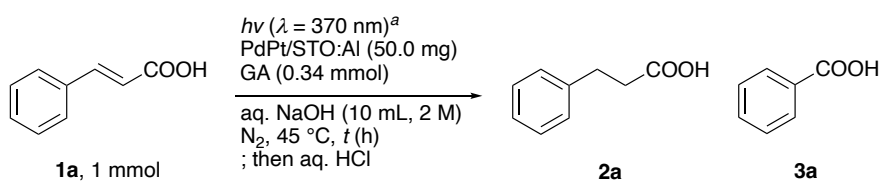




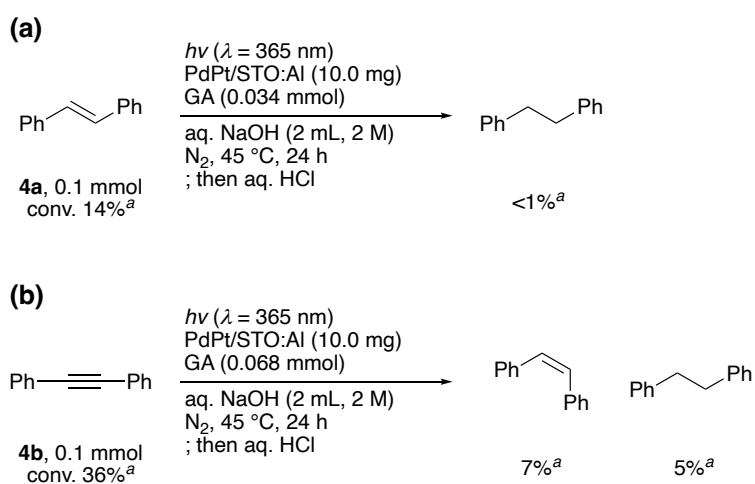
**Fig. S5.** (a)  $^1\text{H}$  NMR analysis for the reaction in  $\text{D}_2\text{O}$ . (b) Plausible oxidative pathway of GA

#### f. 1 mmol scale reaction

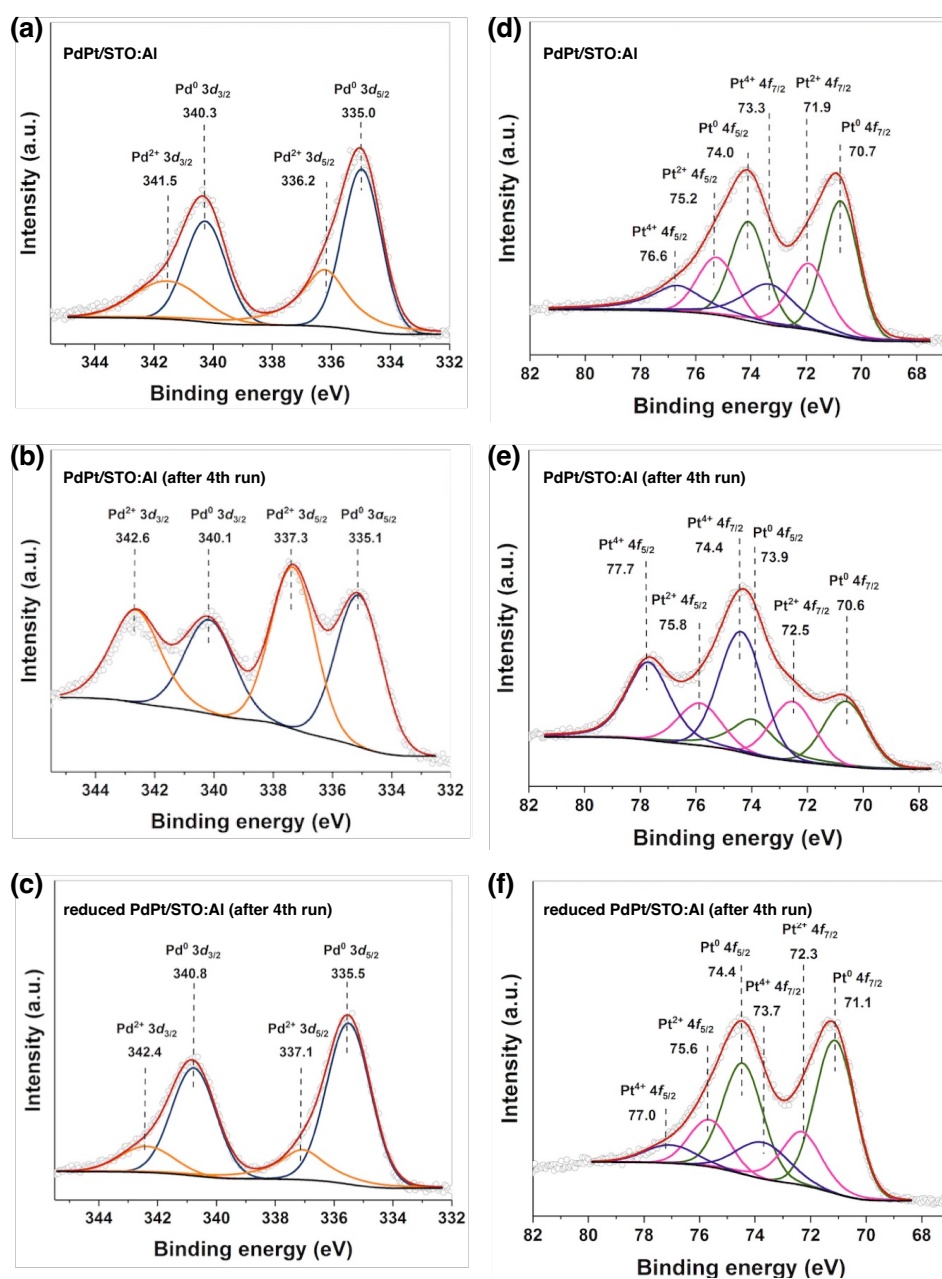
In the reaction using **1a** (1 mmol), minimal GA (0.34 mmol) under light irradiation of 24 h from stronger Kessil lamps, **1a** was completely consumed, and **2a** was obtained in moderate yield (77%) with negligible **3a** (1%) (Table S5, entry 1). Given that **1a** was oxidized to **3a** in the absence of GA (Scheme S3a), GA would work as the dominant e-donor for the hydrogenation of **1a**, preventing the oxidative degradation of **1a** to **3a**. On the other hand, some unidentified side products were also observed by  $^1\text{H}$  NMR analysis in the 24 h reaction. We conducted an additional experiment using a 1 mmol of **1a** with a shortened reaction time of 8 h, where **2a** was almost exclusively obtained (86%), while **3a** (1%) and unidentified side products were hardly detected (Table S5, entry 2). These results suggest that the minimal amount of GA (0.34 mmol) efficiently functioned as the 6e-donor for the hydrogenation of **1a** (2e-acceptor, 1 mmol). It should also be noted that hydrogenated product **2a** was decomposed to unidentified side products under strong light irradiation, and this was not completely deterred even by shortening reaction time. That is one reason why the yield of **2a** in the 1 mmol-scale reaction (86%) was not as high as that in the 0.1 mmol-scale reaction (>99%, Table 1, entry 12).

**Table S5.** 1 mmol-scale reaction.

entry	<i>t</i> (h)	conversion of <b>1a</b> (%) <sup>b</sup>	yield of <b>2a</b> (%) <sup>b</sup>	yield of <b>3a</b> (%) <sup>b</sup>
1	24	>99	77	1
2	8	>99	86	1

<sup>a</sup> See **Fig. S3** for the reaction setup.<sup>b</sup> Determined by <sup>1</sup>H NMR analysis.**g. Non-polar substrates**<sup>a</sup> Determined by <sup>1</sup>H NMR analysis.**Scheme S4.** Reactivity of non-polar organic compounds.

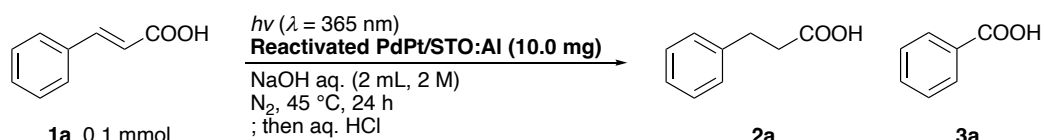
## h. Characterization of the photocatalyst



**Fig. S6.** XPS spectra of (a) PdPt/STO:Al, (b) PdPt/STO:Al after the 4th run, and (c) reduced PdPt/STO:Al after the 4th run for Pd 3d, and (d–f) those for Pt 4f. (a) The binding energy of the  $\text{Pd}^0 3d_{5/2}$  peak of PdPt/STO:Al was lower than the standard value of bulk  $\text{Pd}^0$  (experimental: 335.0 eV; literature: 335.2 eV).<sup>7</sup> (d) The same tendency was observed with the  $\text{Pt}^0 4f_{7/2}$  peak (experimental: 70.7 eV; literature: 71.2 eV).<sup>7</sup> These XPS results suggest electronic interaction of both Pd and Pt with STO:Al. (c, f) Reduction of the PdPt/STO:Al recovered after the 4th run was conducted by the following procedure: The recovered PdPt/STO:Al (38 mg) after the 4th run in the recycling experiments was placed in an oven-dried 100 mL round-bottom flask with a stirrer bar. Water (40 mL) was added, and the

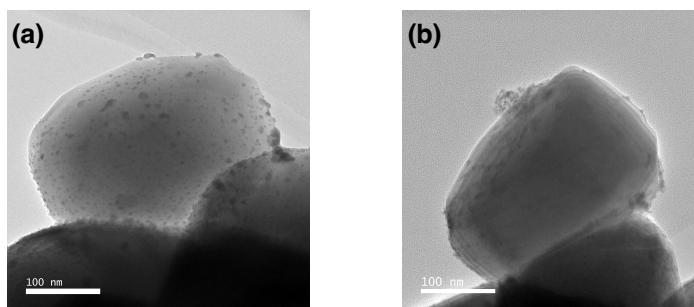
mixture was subjected to ultrasonic vibration for 10 min. NaBH<sub>4</sub> (0.08 mmol, ca. 10 equiv with respect to the metals) in cool water (5 mL, 0 °C) was added dropwise into the flask at room temperature. The suspension was allowed to stir at room temperature for 2 h. The obtained solid was filtered and rinsed with water, and then the residual water was removed under reduced pressure.

**Table S6.** Reactions using the reactivated PdPt/STO:Al.



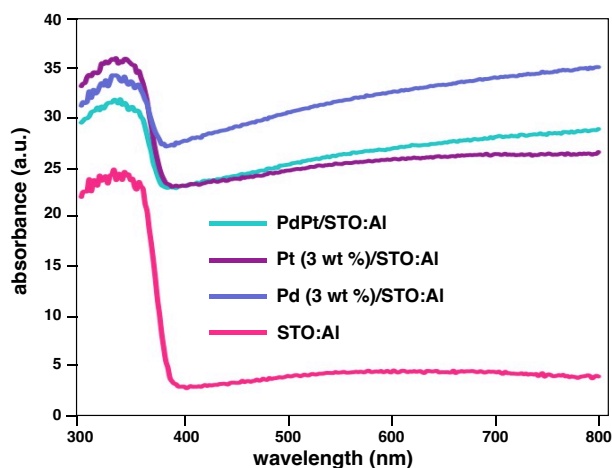
entry	conversion of <b>1a</b> (%) <sup>a</sup>	yield of <b>2a</b> (%) <sup>a</sup>	yield of <b>3a</b> (%) <sup>a</sup>
1	69	58	3
2	65	53	3

<sup>a</sup> Determined by <sup>1</sup>H NMR analysis.

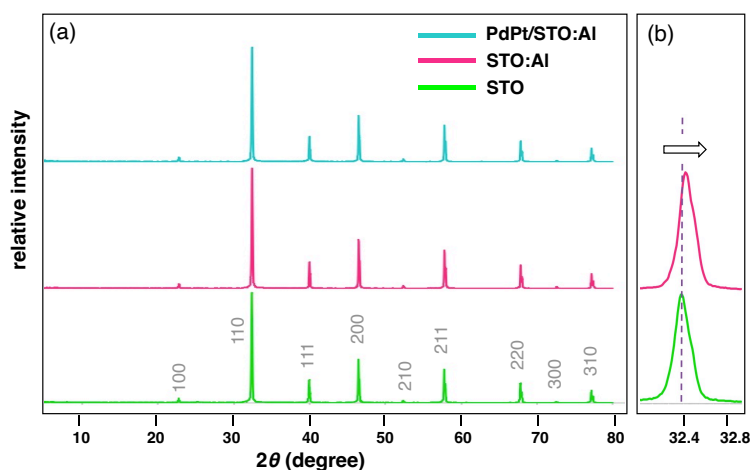


**Fig. S7.** TEM images of PdPt/STO:Al (a) before the reaction and (b) after the 4th run.





**Fig. S8.** DR-UV-Vis spectra of PdPt/STO:Al, Pt (3 wt%)/STO:Al, Pd (3 wt%)/STO:Al, and STO:Al. The maximum absorption centers were located at 300–380 nm irrespective of the different metallic loading.

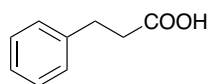


**Fig. S9.** (a) XRD patterns of PdPt/STO:Al, STO:Al, and STO (Miller indices are written above peaks in grey). (b) XRD peak shifting of STO and STO:Al. The diffraction peaks were assigned to the pure phase of STO with a Pm-3m space group (ICSD 23076). Although no observable peaks corresponding to Al, Pd and Pt species were detected, the dispersion of Al within the STO lattice could be realized based on the slight XRD peak shifts to the higher angles.

## i. Isolated yields and characterization of products

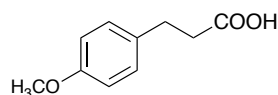
### General procedure

An oven-dried Pyrex glass tube (height = 10.0 cm, diameter = 1.0 cm) was equipped with a Teflon-coated disc-shaped stirrer bar (diameter = 0.9 cm). Unsaturated carboxylic acid or halogenated benzoic acid (**1**), GA and PdPt/STO:Al (10.0 mg) were added to the test tube, and then the tube was sealed with a rubber septum. The reaction atmosphere was replaced with N<sub>2</sub>. Under the flow of N<sub>2</sub>, an aqueous solution of NaOH (2 mL, 2 M) was added to the tube and the rubber septum was replaced with another one to which an NMR tube was inserted. After sonication for 1 min, techno-sigma lamp was inserted into the NMR tube and the reaction mixture was irradiated at 45 °C for 24 h. The reaction mixture was transferred to a falcon tube (50 mL) with diethyl ether (ca. 15 mL) and an aqueous solution of HCl (ca. 2 mL, 3 M). The organic layer was separated. The aqueous layer was extracted with diethyl ether (ca. 5 mL) three times. Residual water was removed from the combined organic layers using Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the residue was analyzed by <sup>1</sup>H NMR using an internal standard (mesitylene). When the reaction was completed cleanly, the crude product was dried under reduced pressure to remove the internal standard and solvents, and the isolated yield was determined based on the weight of the residue.



### 3-Phenylpropanoic acid (**2a**)<sup>3</sup>

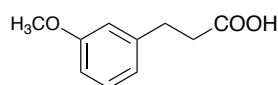
According to the general procedure, (*E*)-cinnamic acid (**1a**, 14.8 mg, 0.10 mmol) and GA (2.6 mg, 0.034 mmol) were used. The desirable product (**2a**, 13.4 mg, 0.089 mmol, 89%) was obtained as a white solid: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 7.30 (t, *J* = 7.8 Hz, 2H), 7.23–7.21 (m, 3H), 2.97 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): 178.4, 140.3, 128.8, 128.5, 126.6, 35.6, 30.8; ESI-MS: *m/z* calcd. for C<sub>9</sub>H<sub>9</sub>O<sub>2</sub> ([M-H]<sup>-</sup>) 149.0608, found 149.0607.



### 3-(4-Methoxyphenyl)propionic acid (**2b**)<sup>3</sup>

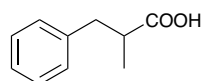
According to the general procedure, (*E*)-4-methoxycinnamic acid (**1b**, 17.6 mg, 0.10 mmol) and GA (2.7 mg, 0.035 mmol) were used. The desirable product (**2b**, 16.2 mg, 0.090 mmol, 90%) was obtained as a yellow solid: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 7.12 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.65

(t,  $J = 7.8$  Hz, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 178.7, 158.3, 132.4, 129.4, 114.1, 55.4, 36.0, 29.9; ESI-MS:  $m/z$  calcd. for  $\text{C}_{10}\text{H}_{11}\text{O}_3$  ( $[\text{M}-\text{H}]^-$ ) 179.0714, found 179.0708.



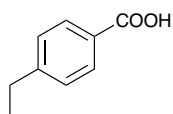
### 3-(3-Methoxyphenyl)propionic acid (**2c**)<sup>4</sup>

According to the general procedure, 3-methoxycinnamic acid (**1c**, 18.0 mg, 0.10 mmol) and GA (2.9 mg, 0.038 mmol) were used. The desirable product (**2c**, 17.1 mg, 0.094 mmol, 94%) was obtained as a yellow solid:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 7.23–7.20 (m, 1H), 6.81–6.76 (m, 3H), 3.80 (s, 3H), 2.94 (t,  $J = 7.8$  Hz, 2H), 2.68 (t,  $J = 7.8$  Hz, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 178.7, 159.9, 141.9, 129.8, 120.8, 114.3, 111.9, 55.4, 35.6, 30.8; ESI-MS:  $m/z$  calcd. for  $\text{C}_{10}\text{H}_{11}\text{O}_3$  ( $[\text{M}-\text{H}]^-$ ) 179.0714, found 179.0720.



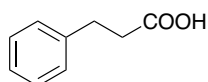
### 2-Methyl-3-phenylpropanoic acid (**2d**)<sup>3</sup>

According to the general procedure, (*E*)- $\alpha$ -methylcinnamic acid (**1d**, 16.2 mg, 0.10 mmol) and GA (2.8 mg, 0.036 mmol) were used. The desirable product (**2d**, 14.9 mg, 0.091 mmol, 91%) was obtained as a white solid:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 7.29 (t,  $J = 7.2$  Hz, 2H), 7.23–7.18 (m, 3H), 3.08 (dd,  $J = 13.8, 6.6$  Hz, 1H), 2.80–2.74 (m, 1H), 2.68 (dd,  $J = 13.8, 8.4$  Hz, 1H), 1.19 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 181.7, 139.2, 129.2, 128.6, 126.6, 41.3, 39.5, 16.7; ESI-MS:  $m/z$  calcd. for  $\text{C}_{10}\text{H}_{11}\text{O}_2$  ( $[\text{M}-\text{H}]^-$ ) 163.0765, found 163.0758.



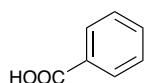
### 4-Ethylbenzoic acid (**2e**)<sup>5</sup>

According to the general procedure, 4-vinylbenzoic acid (**1e**, 15.2 mg, 0.10 mmol) and GA (2.7 mg, 0.035) were used. The desirable product (**2e**, 11.0 mg, 0.073 mmol, 71%) was obtained as a white solid:  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 8.03 (d,  $J = 8.4$  Hz, 2H), 7.30 (d,  $J = 7.8$  Hz, 2H), 2.73 (q,  $J = 7.8$  Hz, 2H), 1.27 (t,  $J = 7.8$  Hz, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ): 172.3, 151.0, 130.6, 128.2, 126.9, 29.2, 15.4; ESI-MS:  $m/z$  calcd. for  $\text{C}_9\text{H}_9\text{O}_2$  ( $[\text{M}-\text{H}]^-$ ) 149.0608, found 149.0606.



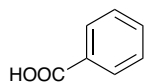
### 3-Phenylpropanoic acid (2a)<sup>3</sup>

According to the general procedure, phenylpropionic acid (**1f**, 14.6 mg, 0.10 mmol) and GA (5.6 mg, 0.073 mmol) were used. The desirable product (**2a**, 14.2 mg, 0.095 mmol, 95%) was obtained as a white solid: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 7.30 (t, *J* = 7.8 Hz, 2H), 7.23–7.21 (m, 3H), 2.96 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): 178.9, 140.3, 128.8, 128.4, 126.6, 35.7, 30.8; ESI-MS: *m/z* calcd. for C<sub>9</sub>H<sub>9</sub>O<sub>2</sub> ([M-H]<sup>-</sup>) 149.0608, found 149.0608.



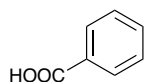
### Benzoic acid (3a)<sup>6</sup>

According to the general procedure, 4-chlorobenzoic acid (**1g**, 15.5 mg, 0.10 mmol) and GA (2.8 mg, 0.036 mmol) were used. The desirable product (**3a**, 11.6 mg, 0.095 mmol, 95%) was obtained as a white solid: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 8.13–8.12 (m, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): 172.0, 134.0, 130.4, 129.4, 128.7; ESI-MS: *m/z* calcd. for C<sub>7</sub>H<sub>5</sub>O<sub>2</sub> ([M-H]<sup>-</sup>) 121.0295, found 121.0292.



### Benzoic acid (3a)<sup>6</sup>

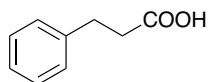
According to the general procedure, 4-bromobenzoic acid (**1h**, 20.6 mg, 0.10 mmol) and GA (2.8 mg, 0.036 mmol) were used. The desirable product (**3a**, 10.1 mg, 0.083 mmol, 81%) was obtained as a white solid: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 8.14–8.12 (m, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): 172.1, 134.0, 130.4, 129.5, 128.7; ESI-MS: *m/z* calcd. for C<sub>7</sub>H<sub>5</sub>O<sub>2</sub> ([M-H]<sup>-</sup>) 121.0295, found 121.0294.



### Benzoic acid (3a)<sup>6</sup>

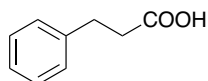
According to the general procedure, 4-iodobenzoic acid (**1i**, 24.8 mg, 0.10 mmol) and GA (2.8 mg, 0.036 mmol) were used. The desirable product (**3a**, 11.0 mg, 0.090 mmol, 90%) was obtained as a white solid: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): 8.13–8.12 (m, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): 171.7,

134.0, 130.4, 129.4, 128.7; ESI-MS:  $m/z$  calcd. for  $C_7H_5O_2$  ( $[M-H]^-$ ) 121.0295, found 121.0295.



### 3-Phenylpropanoic acid (2a)<sup>3</sup>

According to the general procedure, 4-chlorocinnamic acid (**1j**, 18.2 mg, 0.10 mmol) and GA (5.2 mg, 0.068 mmol) were used. The desirable product (**2a**, 11.2 mg, 0.075 mmol, 75% ) was obtained as a white solid:  $^1H$  NMR (600 MHz,  $CDCl_3$ ): 7.30 (t,  $J = 7.8$  Hz, 2H), 7.23–7.21 (m, 3H), 2.97 (t,  $J = 7.2$  Hz, 2H), 2.69 (t,  $J = 7.2$  Hz, 2H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ ): 177.4, 140.3, 128.8, 128.5, 126.6, 35.5, 30.8; ESI-MS:  $m/z$  calcd. for  $C_9H_9O_2$  ( $[M-H]^-$ ) 149.0608, found 149.0610.



### 3-Phenylpropanoic acid (2a)<sup>3</sup>

According to the general procedure, 4-bromocinnamic acid (**1k**, 22.9 mg, 0.10 mmol) and GA (5.1 mg, 0.067 mmol) were used. The desirable product (**2a**, 11.9 mg, 0.079 mmol, 79%) was obtained as a white solid:  $^1H$  NMR (600 MHz,  $CDCl_3$ ): 7.30 (t,  $J = 7.8$  Hz, 2H), 7.23–7.21 (m, 3H), 2.97 (t,  $J = 7.8$  Hz, 2H), 2.69 (t,  $J = 7.8$  Hz, 2H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ ): 178.5, 140.3, 128.8, 128.5, 126.6, 35.6, 30.8; ESI-MS:  $m/z$  calcd. for  $C_9H_9O_2$  ( $[M-H]^-$ ) 149.0608, found 149.0601.

## 4. Comparison with previously reported photocatalysts

**Table S7.** Comparison of photocatalysts for reduction of organic compounds using water as proton donor<sup>a</sup>

Photo-catalyst <sup>b</sup>	Main substrate (Sub) and product (Pro) studied	Typical reaction conditions <sup>c</sup>	Efficiency	Selectivity for Pro	Reusability (PDA) <sup>d</sup>	Ref
Pd/TiO <sub>2</sub> (25 mg)	Sub = 4-nitroacetophenone (0.1 mmol), Pro = 4-aminoacetophenone	$h\nu$ ( $\lambda = 350$ nm), <b>glucose (0.5 mmol)</b> , H <sub>2</sub> O (1 mL), 25 °C, 12 h	Conv. > 99% Yield > 99%	99%	ca. 10% in the 4th run	8
PdPt/TiO <sub>2</sub> (10 mg)	Sub = 2-methyl-3-buten-2-ol (0.5 mmol), Pro = 2-methyl-3-buten-2-ol	$h\nu$ ( $\lambda < 400$ nm), <b>CH<sub>3</sub>OH (2.5 mL)</b> , H <sub>2</sub> O (7.5 mL), 3 h	Conv. > 99% Yield = 94%	94%	N.D.	9
porous CdSe (5 mg)	Sub = 4-iodoanisole (0.1 mmol), Pro = anisole	$h\nu$ ( $\lambda > 280$ nm), <b>Na<sub>2</sub>SO<sub>3</sub> (1.25 mmol)</b> , CH <sub>3</sub> CN (2.5 mL), H <sub>2</sub> O (2.5 mL), r.t., 2 h	Conv. > 99% Yield > 99%	> 99%	ca. 10% in the 3rd run; ca. 30% in the 4th run	10
Pd/KPCN (10 mg)	Sub = $\beta$ -methylstyrene (0.1 mmol), Pro = Ph(CHD) <sub>2</sub> CH <sub>3</sub>	$h\nu$ ( $\lambda = 420$ nm), <b>CD<sub>3</sub>OD (1.5 mL)</b> , D <sub>2</sub> O (1.5 mL), ethyl acetate (2 mL), AlCl <sub>3</sub> (0.1 mmol), r.t., 4 h	Conv. N.D. Yield = 96%	$\geq 96\%$	N.D.	11
Pd/g-C <sub>3</sub> N <sub>4</sub> (30 mg)	Sub = styrene (10 mmol), Pro = ethylbenzene	$h\nu$ (visible light), <b>Mg powder (15 mmol)</b> , H <sub>2</sub> O (10 mL), NiCl <sub>2</sub> (1 mmol), r.t., 12 h	Conv. > 99% Yield > 99%	> 99%	ca. 20% in the 6th run	12
Au/CdS (5 mg)	Sub = 4-iodoanisole (0.1 mmol), Pro = anisole	$h\nu$ ( $\lambda > 400$ nm), <b>Na<sub>2</sub>SO<sub>3</sub> (1 mmol)</b> , CH <sub>3</sub> CN (2.5 mL), H <sub>2</sub> O (2.5 mL), r.t., 30 min	Conv. > 99% Yield > 99%	> 99%	ca. 5% in the 4th run	13
Pt/CNB (15 mg)	Sub = styrene (0.15 mmol), Pro = ethylbenzene	$h\nu$ ( $\lambda = 420$ nm), <b>triethanolamine (0.5 mL)</b> , 1,4-dioxane (3 mL), H <sub>2</sub> O (2 mL), 35 °C, 5 h	Conv. = N.D. Yield = 99%	$\geq 99\%$	< 10% in the 5th run	14
Pd NSs/CPCN (40 mg)	Sub = 2-chlorobenzonitrile (0.2 mmol), Pro = benzonitrile	$h\nu$ ( $\lambda = 427$ nm), <b>triethanolamine (0.9 mL)</b> , C <sub>2</sub> H <sub>5</sub> OH (1 mL), H <sub>2</sub> O (8.1 mL), 24 h	Conv. = N.D. Yield > 98%	> 98%	ca. 40% in the 4th run	15
TiO <sub>2</sub> /Ce <sub>2</sub> S <sub>3</sub> nano-hybrid (15 mg)	Sub = nitrobenzene (0.066 mmol), Pro = aniline	$h\nu$ ( $\lambda = 365$ nm), <b>triethanolamine (0.5 mL)</b> , 1,4-dioxane (4 mL), H <sub>2</sub> O (1 mL), 30 °C, 90 min	Conv. = N.D. Yield = 99%	$\geq 99\%$	ca. 10% in the 5th run	16
D-ZIS (5 mg)	Sub = benzophenone (0.1 mmol), Pro = Ph <sub>2</sub> CHOH	$h\nu$ ( $\lambda > 420$ nm), <b>Na<sub>2</sub>SO<sub>3</sub> (2 mmol)</b> , CH <sub>3</sub> CN (0.2 mL), H <sub>2</sub> O (1.8 mL), 24 h	Conv. = N.D. Yield = 92%	$\geq 92\%$	ca. 20% in the 5th run	17
CdSe QDs (40 nmol)	Sub = benzophenone (0.2 mmol), Pro = Ph <sub>2</sub> CDOH (after work-up with H <sub>2</sub> O)	$h\nu$ ( $\lambda = 450$ nm), <b>triethylamine (0.4 mmol)</b> , CH <sub>3</sub> CN (2 mL), D <sub>2</sub> O (5 mmol), r.t., 12 h	Conv. = N.D. Yield = 97%	$\geq 97\%$	ca. 15% in the 5th run	18
Pd <sub>1</sub> /mpg-C <sub>3</sub> N <sub>4</sub> (10 mg)	Sub = styrene (0.1 mmol), Pro = ethylbenzene	$h\nu$ ( $\lambda = 427$ nm), <b>triethanolamine (0.5 mL)</b> , 1,4-dioxane (3 mL), H <sub>2</sub> O (2 mL), 35 °C, 10 h	Conv. = N.D. Yield = 98%	$\geq 98\%$	ca. 20% in the 5th run	19

Pt/LCN (20 mg)	Sub = 4-nitrophenol (0.01 mmol), Pro = 4-aminophenol	$h\nu$ ( $\lambda > 420$ nm), <b>triethanolamine (10 mL)</b> , H <sub>2</sub> O (90 mL), 20 °C 100 min	Conv. = 96.5% Yield = 95.4%	98.9%	N.D.	20
Pd/g-C <sub>3</sub> N <sub>4</sub> (15 mg)	Sub = 3,4-dimethoxy bromobenzene (0.5 mmol), Pro = 1,2- dimethoxybenzene	$h\nu$ ( $\lambda = 365$ nm), <b>1,4-dioxane (3 mL)</b> , <b>H<sub>2</sub>O (5 mL)</b> , FeCl <sub>3</sub> ·6H <sub>2</sub> O (0.15 mmol), 25 °C, 20 h	Conv. > 99% Yield = 85%	85%	ca. 5% in the 5th run; ca. 20% in the 7th run	21
Ni-N/CN (20 mg)	Sub = 2- ethylnaphthalene (0.1 mmol), Pro = 2- vinylnaphthalene	$h\nu$ ( $\lambda = 420$ nm), <b>triethylamine (0.5 mmol)</b> , CH <sub>3</sub> CN (7 mL), H <sub>2</sub> O (3 mL), 25 °C, 3 h	Conv. = 100% Yield = 92%	92%	ca. 10% in the 6th run	22
PdPt/STO: Al (10 mg)	Sub = <i>trans</i> -cinnamic acids (0.1 mmol), Pro = 3-phenylpropanoic acid (after work-up with aq. HCl)	$h\nu$ ( $\lambda = 365$ nm), <b>glycolic acid (0.034 mmol)</b> , NaOH (4 mmol), H <sub>2</sub> O (2 mL), 45 °C, 24 h	Conv. > 99% Yield > 99%	> 99%	6% in the 4th run	This work

<sup>a</sup> Collected are papers in which D<sub>2</sub>O was used to elucidate the proton donor. N.D. = no data. <sup>b</sup> KPCN = K cations intercalated polymeric carbon nitride; g-C<sub>3</sub>N<sub>4</sub> = graphitic carbon nitride; CNB = barbituric acid doped carbon nitride; NSs = nanosheets; CPCN = crystallined polymeric carbon nitriles; D-ZIS = defective two-dimensional ZnIn<sub>2</sub>S<sub>4</sub>; QDs = quantum dots; Pd<sub>1</sub>/mpg-C<sub>3</sub>N<sub>4</sub>: palladium single-atom catalysts supported on mesoporous carbon nitride; LCN = 3D hierarchical porous loofah-like carbon nitride sponge; Ni-N/CN = tri-*s*-triazine nitrogen-ligated mononuclear Ni on carbon nitride nanosheets. <sup>c</sup> Plausible electron donors are indicated in bold font. <sup>d</sup> PDA: percentage decrease in activity comparing with the 1st run.

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## 6. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of the isolated products

