Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for

Photocatalytic transfer hydrogenolysis of aromatic ketones using alcohols

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1. IR spectra of catalysts

During photo-deposition, some species may be absorbed on the surface of photocatalyst, and these adsorbates could participate in the following reaction. Herein the IR spectra of prepared catalysts were collected and compared with that of TiO_2. No difference was observed between Pd/TiO_2 catalysts and TiO_2 support suggesting no or trace mount of adsorbates on the prepared catalysts.

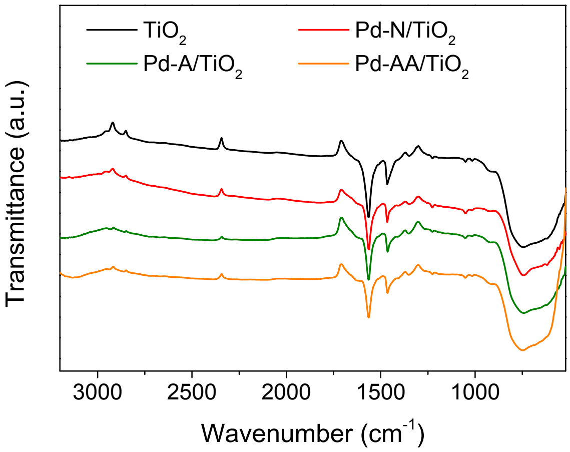


Figure S1 IR spectra of TiO_2, $Pd\text{-}N/TiO_2$, $Pd\text{-}A/TiO_2$ and $Pd\text{-}AA/TiO_2$.

2. Analysis of nitrogen-contained gas products during Pd-N/TiO_2 preparation and catalyzed reaction

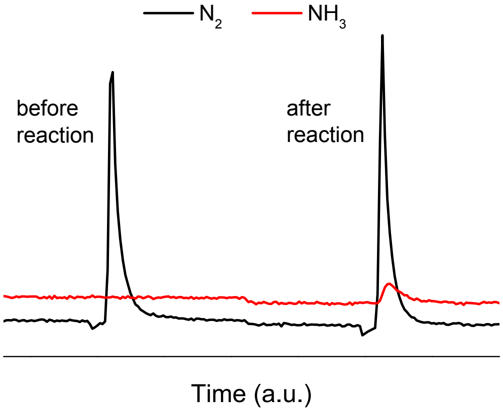


Figure S2 Analysis of nitrogen-contained gas products by mass spectrometer after Pd-N/TiO_2 catalyzed transfer hydrogenolysis in methanol.

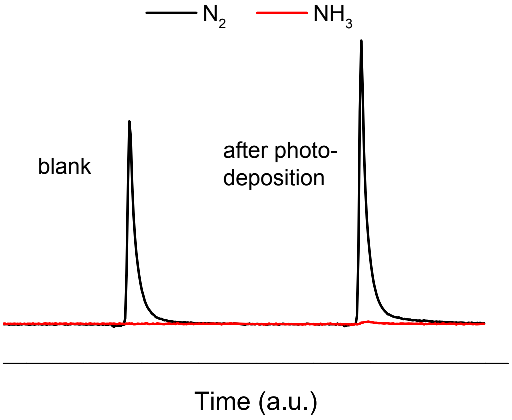


Figure S3 Analysis of nitrogen-contained gas products by mass spectrometer after photodeposition of $Pd(NO_3)_2$ on TiO_2.

Trace amount of ammonia was generated during Pd-N/TiO_2 catalyzed transfer hydrogenolysis. However, the main reason for lower conversion of AP could be the state of Pd particle rather the reduction of nitrate ion. Obvious nitrogen gas generation was observed during photodeposition, thus the nitrate ion was mainly consumed by photo-generated electron on TiO_2, which competed with the hydrogenation of Pd^{2+}. After photodeposition, the amount of nitrate ion should be much lower than initial value (3.5 wt% based on support). In the following reaction, such little amount of retained nitrate ion on catalyst could hardly affect the photoreduction of substrate.

3. The catalytic tests in water-contained ethanol

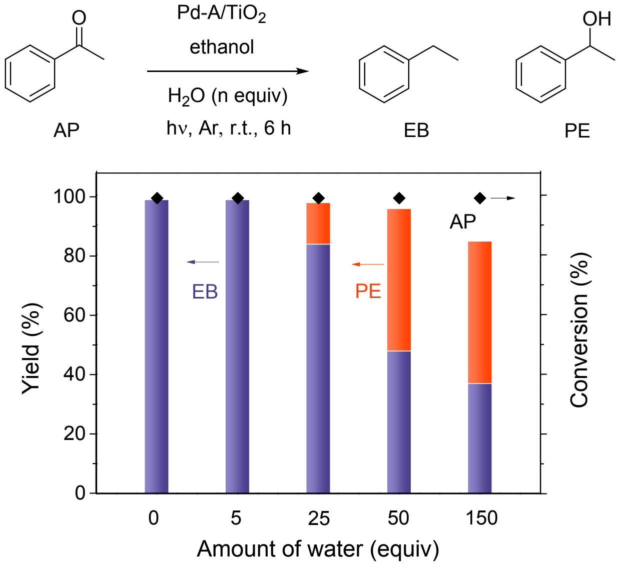


Figure S4 The effect of water on the transfer hydrogenolysis. Conditions: AP (0.2 mmol), Pd-A/TiO_2 (Pd 3 wt%, 10 mg), ethanol (1 mL), 365 nm LEDs.

4. Apparent quantum yield measurements

The AQY of photocatalytic transfer hydrogenolysis of AP were measured over Pd-A/TiO_2 catalyst with LEDs lamp (365 ± 5 nm) by top irradiation. The number of photons reaching the top of the reaction solution was measured by a calibrated Si photodiode (LS-100, EKO Instruments Co., Ltd.). The apparent quantum yield (η) for the transfer hydrogenolysis of AP was calculated by the following equation:

$$\eta = \frac{(4n_{EB} + 2n_{PE})(mol) \times N_A\ (mol^{-1})}{I\ (cm^{-2} \cdot s^{-1}) \times t\ (s) \times S\ (cm^2)} \times 100\%$$

Where n_{EB}, n_{PE}, N_A, I, t and S represent the amount of produced EB, the amount of produced PE, Avogadro's constant, light intensity, reaction time and irradiation area, respectively.

Conditions: AP (0.8 mmol), Pd-A/TiO_2 (Pd 3 wt%, 40 mg), ethanol (28 mL), 365 nm LEDs (33.6 V * 1.49 A), reactor (r, 30 cm), argon, room temperature, 1 h.

The obtained apparent quantum yield was 150%. Further exploration is needed to explain the reason for such a high AQY.

5. Recycle experiments of Pd-A/TiO_2

Recycle experiments were used to test the stability of photocatalyst. After each photocatalytic experiment, the catalyst was separated from centrifugation and washed with excess ethanol. The solution was analyzed by GC.

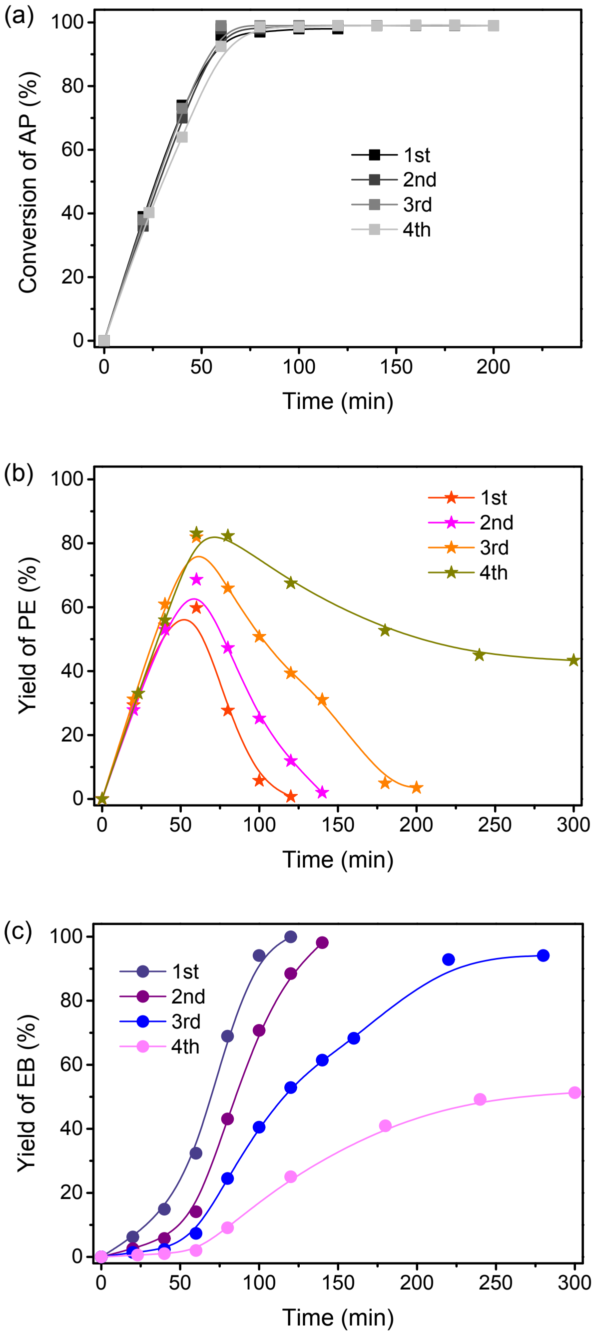
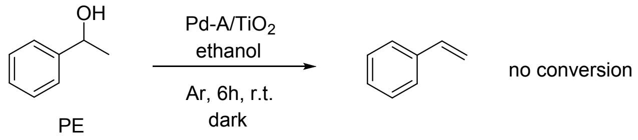


Figure S5 Recycle experiments of Pd-A/TiO_2. Conditions: AP (0.8 mmol), Pd-A/ TiO_2 (40 mg, Pd 3 wt% based on TiO_2), EtOH (1 mL), Ar, 365 nm (35V*3A), room temperature. The conversion and yields were determined by GC with mesitylene as internal standard.

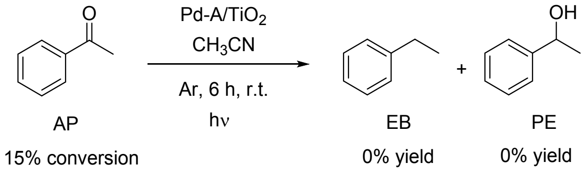
6. Conversion of 1-phenylethanol on Pd-A/TiO_2 under dark conditions



eq S1

Conditions: PE (0.2 mmol), Pd-A/TiO_2 (10 mg, Pd 3 wt% based on TiO_2), EtOH (1 mL), Ar, room temperature, 6 h. The solution was analyzed by GC-MS and no styrene was detected.

7. Usage of protonic acid as a hydrogen donor



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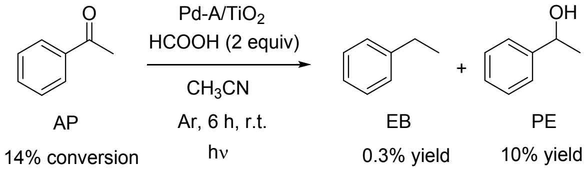

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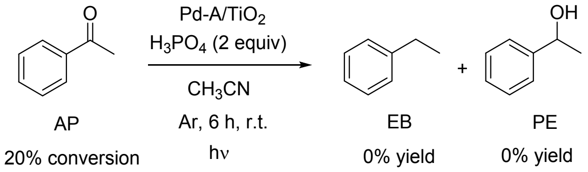


eq S4

Conditions: AP (0.2 mmol), Pd-A/TiO_2 (10 mg, Pd 3 wt% based on TiO_2), CH_3CN (1 mL). The conversion and yields were quantified by GC using mesitylene as internal standard.

8. NMR analysis of isotopic labelling experiments

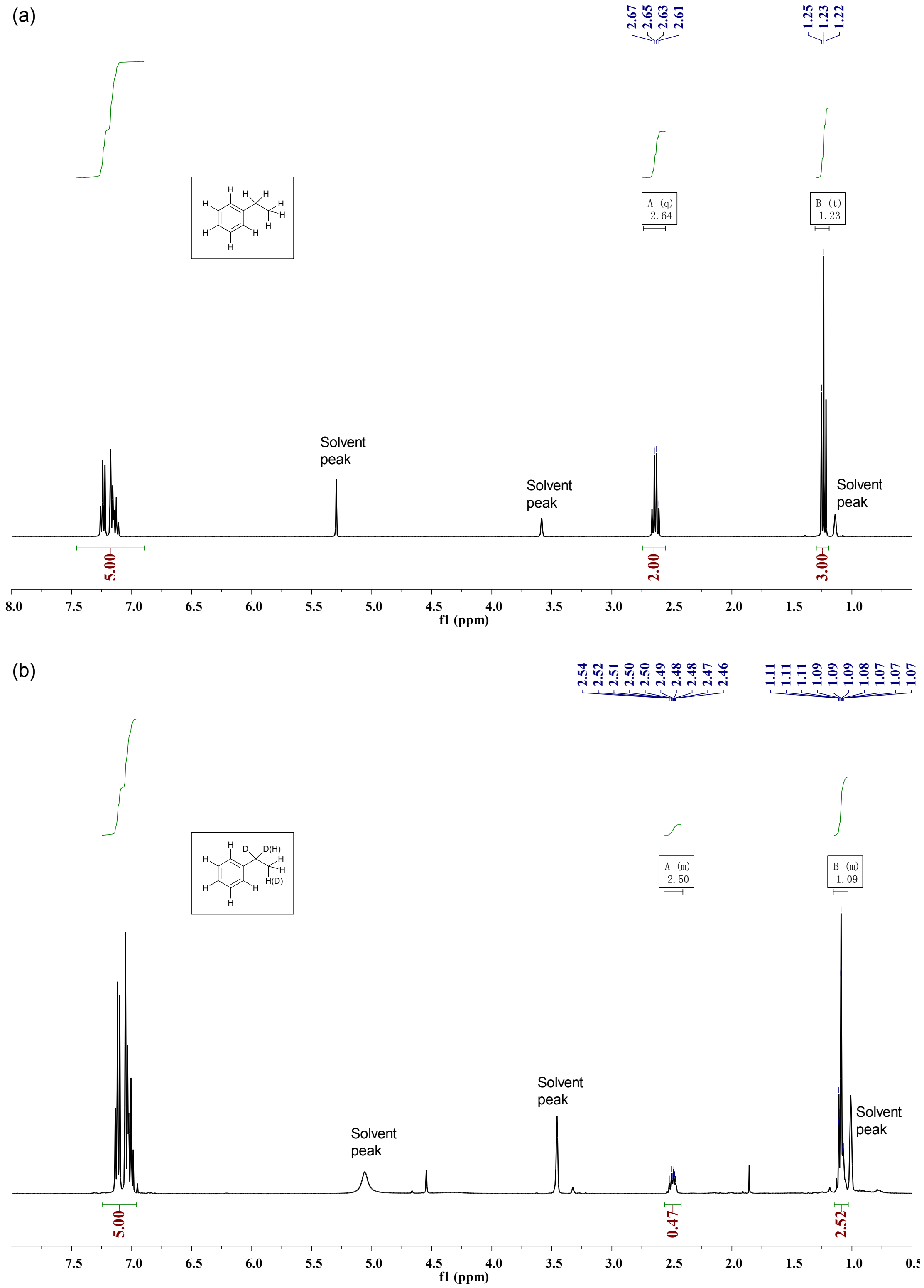
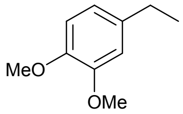


Figure S6 ^{1}H NMR analysis of (a) pure ethylbenzene and (b) the obtained product from isotopic labelling experiment of AP in ethanol-D$_6$.

9. NMR data and spectra of isolated product

4-ethyl-1,2-dimethoxybenzene



^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.87 – 6.63 (3 H, m), 3.85 (6 H, d, *J* = 9.7), 2.59 (2 H, q, *J* = 7.6), 1.22 (3 H, t, *J* = 7.6).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.83, 147.05, 136.97, 119.49, 111.33, 55.93, 28.48, 15.85.