

## Electronic Supplementary Information

### Chiral $\alpha$ -Hydroxy Acid-Coadsorbed TiO<sub>2</sub> Photocatalysts for Asymmetric Induction in Hydrogenation of Aromatic Ketones

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## 1. Experimental Details

### 1.1 Materials

Polycrystalline TiO<sub>2</sub> powder (Degussa P25, specific surface area: ca. 50 m<sup>2</sup>g<sup>-1</sup>) was purchased from Japan Aerosil and used as received. Rutile TiO<sub>2</sub> powder (Kanto Chemical, > 99.9%) was commercially obtained and used as received. Anatase TiO<sub>2</sub> powders, TIO-7 and TIO-13, were supplied as reference photocatalysts from the Catalysis Society of Japan. Transmission electron microscopy (TEM) images and X-ray diffraction (XRD) patterns of these TiO<sub>2</sub> powders were obtained using a JEOL JEM-1400Plus (80 kV) and a Rigaku, Ultima IV equipped with Cu *K* $\alpha$  radiation source ( $\lambda = 0.15418$  nm), respectively. A ratio of anatase/rutile in the P25 TiO<sub>2</sub> powder was roughly estimated to be 8/2 by the XRD measurement.

The following reagents were used for substrates, chiral reagents, and quantification of products as received: acetophenone (AP, Nacalai Tesque, 98.5%), 2'-acetonaphthone (2-NP, TCI, >98.0%), (*R*)-(+)-1-phenylethyl alcohol ((*R*)-APOH, TCI, >98.0%), (*S*)-(–)-1-phenylethyl alcohol ((*S*)-APOH, TCI, >98.0%), (*R*)-(+)-1-(2-naphthyl)ethanol ((*R*)-NPOH, Aldrich, 98%), 1-(2-naphthyl)ethanol (NPOH, racemic mixture, TCI, 98%), D-(–)-mandelic acid ((*R*)-MA, TCI, >99.0%), L-(+)-mandelic acid ((*S*)-MA, TCI, >99.0%), ethyl D-(–)-mandelate (TCI, >98.0%), ethyl L-(+)-mandelate (TCI, >98.0%), (*R*)-(–)-1-phenylethan-1,2-diol ((*R*)-1P1,2D, TCI, >98%), (*S*)-(+)-1-phenylethan-1,2-diol ((*S*)-1P1,2D, TCI, >98%), (*R*)-(–)-2-phenylpropionic acid ((*R*)-2PA, Combi-Blocks, 97%), (*S*)-(+)-2-phenylpropionic acid ((*S*)-2PA, Combi-Blocks, 98%), D-(–)-lactic acid ((*R*)-LA, Sigma-Aldrich, >98%), L-(+)-lactic acid ((*S*)-LA, Sigma-Aldrich, >98%), 1,2-diphenylethanone (TCI, 98.0%). Specially reagent grade of ethanol and methanol were purchased from Nacalai Tesque and used for a solvent in photocatalytic reactions and eluent on a high performance liquid chromatography (HPLC) without further purification.

### 1.2 Irradiation experiment

All irradiation experiments were carried out for a mixture of aromatic ketones (0.13 mmol) and TiO<sub>2</sub> (0.10 g) in deaerated ethanol solution (25 mL) in the presence or absence of chiral reagents (0.25 mmol) under the irradiation with UV light (> 350 nm) at 32 °C. The solutions were placed in a cylindrical glass cell (40 mm × 45 mm i.d.) and sealed with a rubber septum. Argon gas (99.99%) was passed into the solutions through the rubber septum for 30 min and then the degassed solutions were stirred in a water bath for 30 min to attain thermal equilibrium at 32 °C in the dark. The suspended solutions were irradiated with UV light (wavelength > 350 nm) from a 300 W xenon arc

lamp (ILC Technology, CERMAX LX300) through a dichroic mirror and a cut-off filter (Toshiba UV-35). Light intensity was measured to be  $720 \text{ mW cm}^{-2}$  by the use of thermopile sensor (Coherent 210).

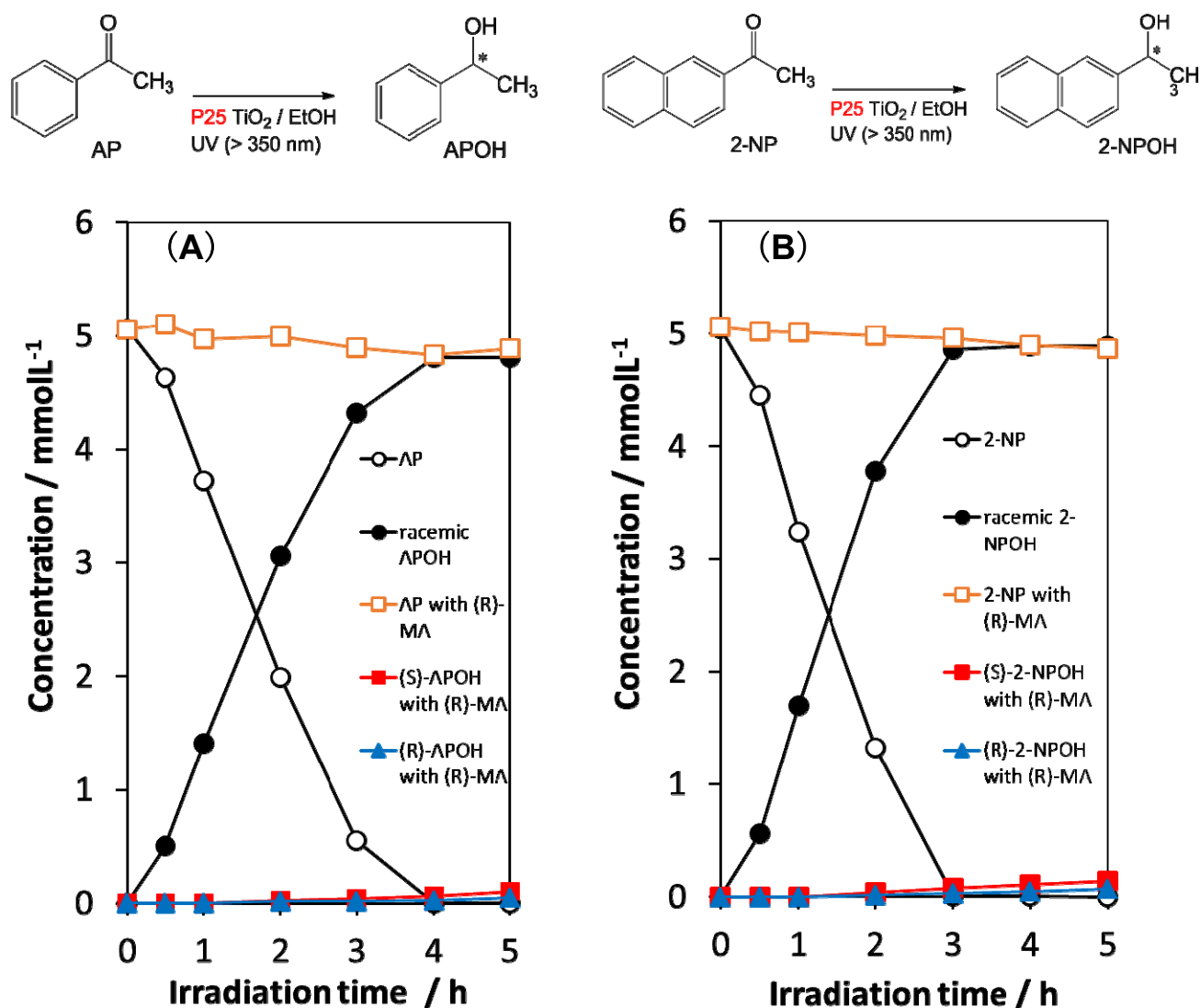
### 1.3 Product analysis

After appropriate irradiation times, 0.2 mL of sample solution was withdrawn and centrifuged to remove the photocatalyst powders. Concentrations of the substrates and products in supernatants were determined using a JASCO UV-detected HPLC system (PU-2080 pump, DG-2080-35 degasser, CO-2065 column oven, UV-2075 UV/vis photodetector). A normal-phase system with a chiral column (Daicel Chiralpak IB, 250 mm  $\times$  4.6 mm i.d.) was adopted to analyze AP and APOH. A mobile phase was hexane/ethanol (9/1) with a flow rate of 0.7 mL/min. Chromatograms were monitored at 215 nm. On the other hand, a reverse-phase system with a chiral column (Daicel Chiralcel OD-RH, 150 mm  $\times$  4.6 mm i.d.) was used to analyze 2-NP and 2-NPOH. A mobile phase was methanol/water (3/1) with a flow rate of 0.7 mL/min. Chromatograms were monitored at 286 nm.

1,2-Diphenylethanone, produced as a side product, was assigned as follows: After 1 hour UV irradiation ( $> 350 \text{ nm}$ ) to a mixture of 2-NP (0.13 mmol),  $\text{TiO}_2$  (TIO-13, 0.10 g), and (*S*)-MA (0.25 mmol) in deaerated ethanol suspension (25 mL), the suspension was filtered and evaporated under reduced pressure. The obtained residue was re-dissolved in ca. 1 mL of ethanol, and each 10 micro-litter of the solution repeatedly injected to the reverse-phase HPLC system as described above. The fraction appeared at around 4.4 min retention time was repeatedly collected and evaporated under the reduced pressure. The obtained residue was re-dissolved in 0.5 mL of ethanol. One micro-litter of the solution was analyzed on a gas chromatography-mass spectroscopy (GC-MS) instrument (Agilent 6890/5973) equipped with a capillary column (HP-5MS, 30 m  $\times$  0.25 mm i.d., film thickness 0.25  $\mu\text{m}$ ). Helium carrier gas was used with linear velocity of 36.8 cm/s. A sample solution (1  $\mu\text{l}$ ) was injected with split ratio of 100/1. The injector temperature was 250  $^\circ\text{C}$ , and the column temperature was kept at 70  $^\circ\text{C}$  for the first 2 min and then increased at the rate of 10  $^\circ\text{C}/\text{min}$  to 250  $^\circ\text{C}$ . The mass spectrometer was set to scan mass units 35-500 for electron impact ionization with a source temperature of 230  $^\circ\text{C}$ . A considerable amount of the side product with a molecular ion ( $\text{M}^+$ ) of  $m/z = 196$  and fragment ions of  $m/z = 77$  and 105 was detected on a chromatogram at 15.04 min retention time. This peak was confirmed by the comparison with the authentic sample of 1,2-diphenylethanone.

## 2. Results

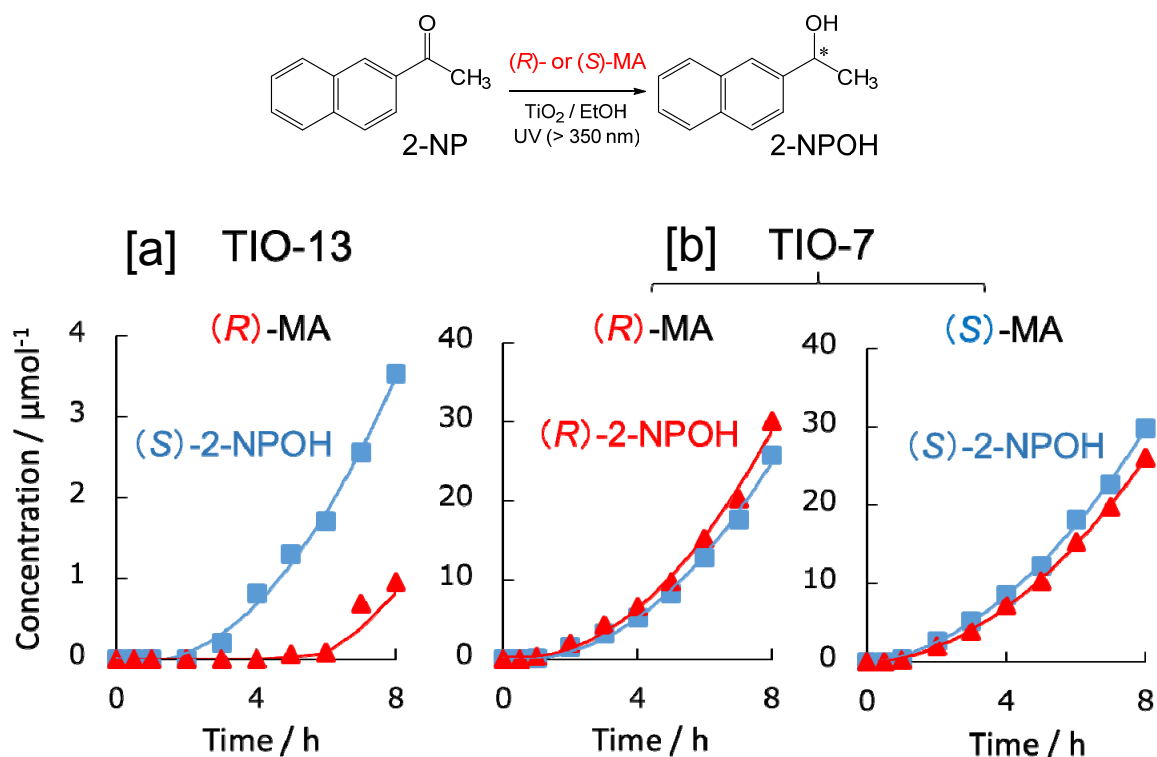
Fig. 1S (A) and (B) indicate that degradation of aromatic ketones and productions of secondary alcohols on UV-irradiated P25 TiO<sub>2</sub> completed within 4 h in the absence of (*R*)-MA, while the reaction rates became much slower to ca. 1/100 in the presence of (*R*)-MA. Fig. S1 (A) and (B) also show the preferential productions of *S*-enantiomers of APOH and 2-NPOH in the presence of (*R*)-MA.



**Fig. S1** Time courses of (A) AP degradation and APOH production and (B) 2-NP degradation and 2-NPOH production on P25 TiO<sub>2</sub> (anatase/rutile = ca. 8/2) in deaerated ethanol (25 mL) under UV irradiation (> 350 nm) at 32 °C. The black open (○) and close (●) circles show degradation of substrates and production of racemic secondary alcohols in the absence of (*R*)-MA, respectively. The orange open squares (□) indicate degradation of substrates in the presence of 0.25 mmol (*R*)-MA. The red squares (■) and blue triangles (▲) indicate productions of (*S*)- and (*R*)-enantiomers of the chiral secondary alcohols, respectively.

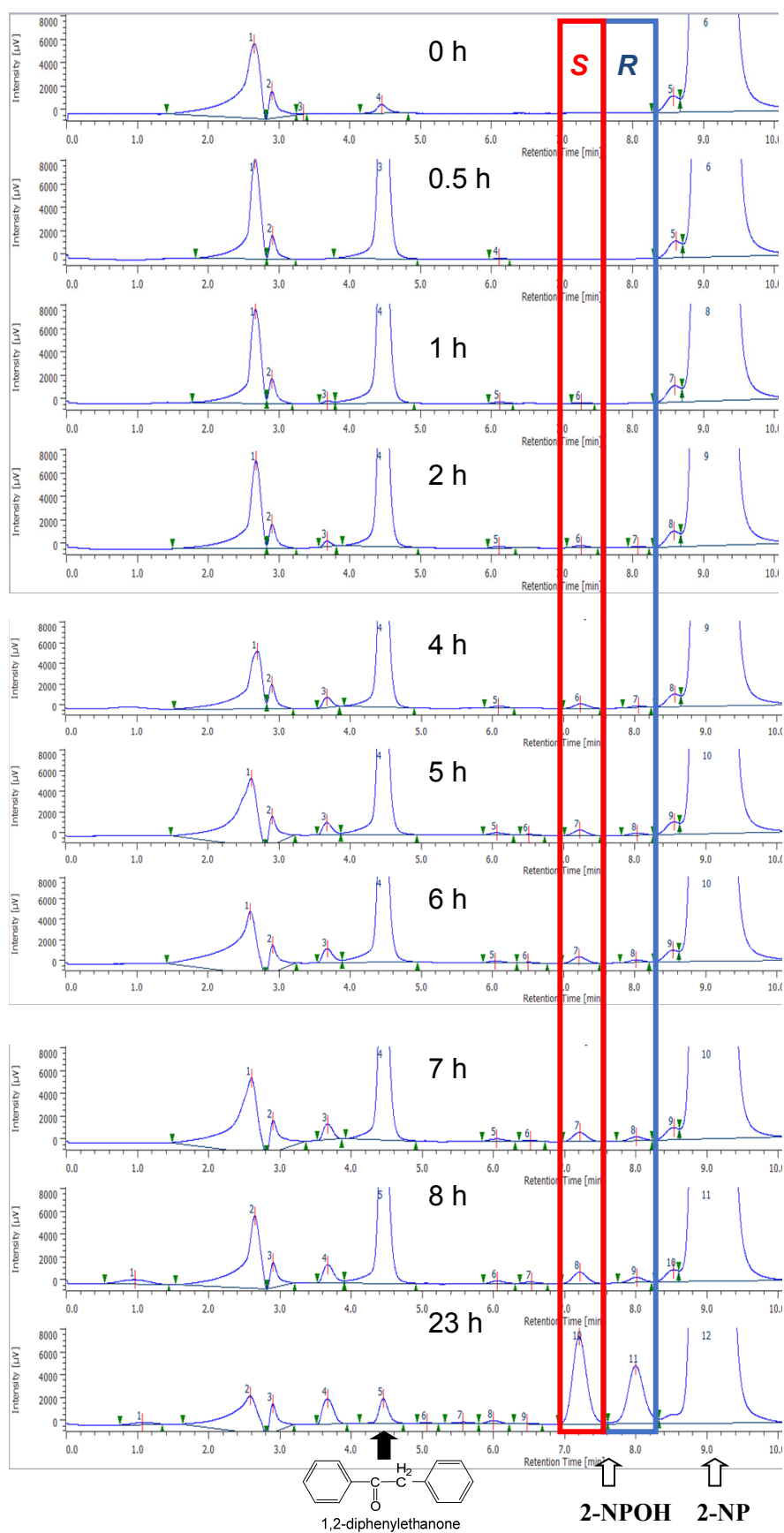
Fig. S2 [a] shows that *S*-enantiomer of 2-NPOH was predominantly obtained by using (*R*)-MA on TIO-13 (anatase). On the other hand, Fig. S2 [b] indicates that the inversion of absolute stereochemistry was observed in the hydrogenation of 2-NP on TIO-7 (anatase); *R*-enantiomer of 2-NPOH was obtained by using (*R*)-MA and vice versa.

The appearance of induction period (ca. 2-4 h for TIO-13 and ca. 1 h for TIO-7) in each sample may be caused by the electron accumulation at defective Ti states on TiO<sub>2</sub>.<sup>1</sup> These Ti states are widely distributed within the bandgap of TiO<sub>2</sub> powders. Among the defective Ti states, deep trap states are not responsible for the hydrogenation reaction, whereas shallow trap states can take part in the reaction at TiO<sub>2</sub>/solution interface. The electrons accumulated in these shallow states are highly reactive at the interface enough to react with aromatic ketones adsorbed on TiO<sub>2</sub>. However, the reductive reaction should occur after saturation of the intra-bandgap deep Ti states during UV irradiation. See the reference 1 in details.



**Fig. S2** Time evolutions of 2-NPOH enantiomers on [a] TIO-13 (Tayca AMT-600) and [b] TIO-7 (Sakai Chemical SSP-24) in deaerated ethanol containing each MA enantiomer (0.25 mmol) under UV irradiation (> 350 nm) at 32 °C. Red and blue lines indicate *R*- and *S*-enantiomers of 2-NPOH, respectively.

Fig. S3 depicts changes in HPLC chromatograms with irradiation time for 2-NPOH production from 2-NP on P25 TiO<sub>2</sub> in deaerated ethanol containing (*R*)-MA enantiomer. A considerable amount of the side product of 1,2-ethanedione, a small amount of the products (*S*)-2-NPOH and (*R*)-2-NPOH, and the substrate of 2-NP were detected on the chromatograms at 4.4, 7.1, 8.0, and 9.0 min retention time, respectively.



**Fig. S3** Changes in HPLC chromatograms with irradiation time for 2-NPOH production on P25 TiO<sub>2</sub> in deaerated ethanol containing (*R*)-MA enantiomer (0.25 mmol) under UV irradiation (> 350 nm) at 32 °C.

### 3. Reference

1. S. Kohtani, A. Kawashima and H. Miyabe, *Catalysts*, 2017, **7**, 303.