Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

A route to sustainable propylene: photocatalytic transfer hydrogenolysis of allyl alcohol with methanol

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\- Table of Contents -

1. Materials and methods

Materials

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. $PdCl_2$ (anhydrous) was obtained from Nacalai. Pd (5 wt %)/C was obtained from Fluka (Sigma-Aldrich). Sodium borohydride ($NaBH_4$) was obtained from Kanto Chemicals. TiO_2 was obtained from Sigma Aldrich [Titanium oxide, mixture of rutile and anatase nanopowder, < 100 nm particle size (BET), 99.5% trace metal basis. Ref. 634662-100G Lot#MKBJ0873V]. Allyl alcohol (> 99.0% by GC-MS) was obtained from Wako Chemicals. The acids and bases were also purchased to Tokyo Chemical Industry (TCI), Wako chemicals, Sigma-Aldrich or Kanto Chemicals. Alcohols used as solvent and hydrogen sources: CH_3OH, dehydrated quality for organic synthesis (Kanto); C_2H_5OH and 2-propanol, HPLC grade (Kanto); 2-methyl-2-propanol, reagent grade (TCI). Standard materials for GC-MS (*n*-octane, *n*-undecane, 1,1,2,2-tetrachloroethane, dimethyl acetal of propionaldehyde (**4**), propanal (**5**), 1-propanol (**6**), and 1,2-dibromopropane (**7**) were obtained from TCI. Standard gases for μGC-TCD: Hydrogen (99.999%) was obtained from Alfa System. Propylene (**1**; 99.5%) and propane (**3**; 99.5%) were obtained from GL Sciences. Standard materials for ICP-OES: Pd $(NO_3)_2$ standard solution (4.95–5.05 mg Pd/mL) and $Y(NO_3)_3$ standard solution (1.00 mg/mL; 1000 ppm) were obtained from Wako Chemicals.

Analytical methods

Gas chromatography/mass spectroscopy (GC-MS). GC-MS analyses were conducted in two different Agilent gas chromatography systems (Agilent 5975) both, equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard) coupled to a mass spectroscopy system (Agilent 6850). Methylal (**8**) and methoxymethanol (**9**) were detected by their mass fragmentation patterns (Section 12 in this ESI). Yield of propanal (**5**) (Table 3, entry 2) was determined using the corresponding calibration line made by an authentic sample.

Micro-gas chromatography/thermal conductivity detector (μGC-TCD). μGC-TCD analyses were conducted in a dual channel micro gas chromatography (μGC) system coupled to a thermal conductivity detector (TCD, Agilent 490). H_2, **1** and **3** were monitored by μGC (Agilent 490) equipped with two different columns: a MS5A 10 m BF column (using Ar as a gas carrier to detect and quantify the hydrogen; isothermal: 80 ºC) and a PoraPLOT Q 10 m column (using He as a gas carrier to detect and quantify the propylene and the propane; isothermal 100 ºC).

Inductively coupled plasma optical emission spectrometry (ICP-OES). ICP-OES analysis was performed in a Varian Vista Pro-X spectrometer using a standard solution of Yttrium as internal standard.

High-resolution transmission electron microscopy (HRTEM). HRTEM observations were performed on a JEM- 2100F (JEOL) high-resolution field-emission gun TEM operated at 80 keV at room temperature and under a pressure of 10^{-6} Pa. Unless otherwise indicated a sample of photocatalyst was dispersed in methanol by ultrasonication for 1 h, and the supernatant was dropped onto a copper grid coated with thin carbon film. The sample was vacuum treated at 473 K for 1 h to remove the methanol before the HRTEM observations were carried out.

X-ray photoelectron spectroscopy (XPS). XPS observations were performed on a Shimadzu ESCA-3400. Unless otherwise indicated, the spectra were normalized to the Ti $2p_{3/2}$ signal (458.5 eV) (Fig. S2A).

Nuclear magnetic resonance (NMR). NMR spectra were recorded on a JEOL JNM-ECA-600 (^{1}H NMR 600 MHz, ^{13}C NMR 150 MHz) spectrometer. Unless otherwise noted spectra was recorded using $CDCl_3$ (0.05% *v*/*v* tetramethylsilane as a standard) as solvent. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethysilane (Me_4Si, δ 0.00 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, dm = doublet of multiplet, t = triplet, q = quartet, m = multiplet, br s = broad signal), coupling constant (Hz), and assignment.

2. Catalyst preparation and characterization

Preparation of Pd (5 wt %)/TiO_2

Pd (5 wt %)/TiO_2 catalyst was prepared in a 200 mL round bottom flask covered with aluminum foil by impregnation of 3.042 g of TiO_2 [Sigma Aldrich mixture of rutile and anatase nanopowder, < 100 nm particle size (BET), 99.5% trace metal basis, Ref. 634662-100G LOT# MKBJ0873V] with a solution of $PdCl_2$ (0.258 g, Nacalai) in a deionized H_2O (45 mL).[1] The slurry was sonicated at 0 ºC for 1 h and then stirred with a magnetic bar for 2 h at room temperature. Then, the slurry was stirred (600 rpm) at 85 ºC until all the liquid was evaporated (overnight). The remaining solid was ground in a mortar and dried at 50 ºC in a vacuum oven for 9 h. The final amount of the solid (pre-catalyst) was 3.165 g. Then, the above-mentioned solid (1.047 g) was re-suspended in 2-propanol (15 mL) in a two-neck round bottom flask (100 mL) equipped with a Dimroth condenser and a three-way glass Teflon stopcock (with a balloon in one of the outlet). After purging with nitrogen, $NaBH_4$ (57.6 mg) in $(CH_3)_2CHOH–H_2O$ (26 mL, 25:1) was added with a syringe (under a stream of nitrogen). After 50 min, the solid was collected by filtration and washed several times with CH_3OH and H_2O (with caution because dry Pd/TiO_2 easy catches fire on a filter paper under air).[2] The final catalyst was dried at 50 ºC in a vacuum oven overnight and finally ground to give Pd (5 wt %)/TiO_2 photocatalyst (930 mg).

Characterization of Pd (5 wt %)/TiO_2:

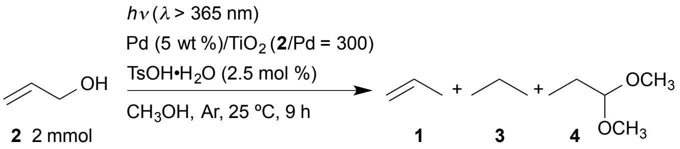
The final palladium content was analysed by ICP-OES after digestion of Pd (5 wt %)/TiO_2 (10.0 mg) by conc. HNO_3 (1 mL) overnight (12 h). The finally found content was 4.78 ± 0.06 wt % of palladium. Energy dispersive X-ray (EDX) spectra show strong peaks arising from Lα and Lβ edges of the Pd atom of a Pd particle in the surface of TiO_2 (Fig. S1A). The Pd particle size in the surface of the TiO_2 is roughly estimated as 4~7 nm on the basis of several low-magnification HRTEM images (Figs. S1A and S1B). XPS analysis of the samples indicates the shift from Pd^{II} species (binding energy of Pd $3d_{5/2}$ = 336.1 eV; PdO -most probable- or $PdCl_2$) to Pd^0 (binding energy of Pd $3d_{5/2}$ = 334.4 eV) by chemical reduction with $NaBH_4$ (Fig. S2B). The Pd/Ti atomic ratios were found 0.099 (before $NaBH_4$ treatment) and 0.055 (after $NaBH_4$ treatment), respectively.

3. Photocatalytic reactions

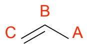
Apparatus

The photocatalytic reactions were carried out in a home-made two-branched cylindrical Pyrex glass reaction vessel of *ca.* 200 mL with a bottom optical window 5 cm in diameter. One branch was connected with a three-way glass Teflon stopcock to a balloon (used to purge the system) and the other branch is capped with a rubber septum (Fig. S3A). The suspension was magnetically stirred (approx. 600 rpm). Near-UV light irradiation was produced by a 300W Xe lamp (Ushio: BA-x300/ES1 Technology; CERMAX PE300PF bulb) equipped with a cold mirror ($\lambda > 365$ nm; total incident radiant flux $(1.53 \pm 0.04) \times 10^{-5}$ lx measured at 550 nm with an illuminance meter T-10 from Konica-Minolta at 13 cm distance from the cold mirror unit).

A typical procedure for the photocatalytic transfer hydrogenolysis (PcTH) of allyl alcohol (2) to propylene (1) (Table 2, entry 1):



A cylindrical Pyrex glass reaction vessel was charged with a magnetic stir bar, Pd (5 wt %)/TiO_2 (15.0 mg), *p*-toluenesulfonic acid monohydrate (9.9 mg, 0.05 mmol), allyl alcohol (**2**, 123.0 mg, 2.12 mmol) and dehydrated CH_3OH (30 mL). After sonication of the mixture (to fully disperse the photocatalyst), the glass reaction vessel was sealed with a rubber septum and the stirred suspension was immediately deaerated with a stream of Ar and irradiated with near-UV light ($\lambda > 365$ nm) for 9 h. By sampling the reaction atmosphere (3.5 mL, gas phase of the reaction vessel), amount of propylene, propane, and H_2 were determined with μGC-TCD using calibration lines. The presence of propylene (**1**, 1.99 mmol, 94% yield), propane (**3**, 0.06 mmol, 3% yield), and H_2 (0.22 mmol) were identified. The conversion of **2** (> 99%) and the amount of dimethyl acetal of propionaldehyde (**4**, 0.04 mmol, 2% yield) were determined by GC-MS analyzes after *n*-octane (30 μL, internal standard) was added to the reaction mixture.

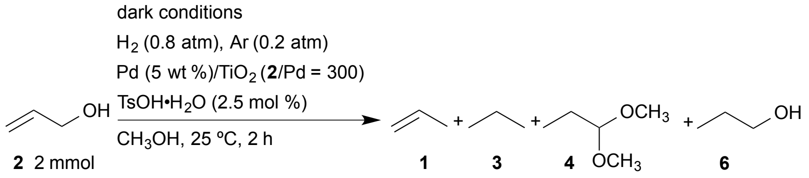


1

^{1}H NMR (600 MHz; $CDCl_3$; Me_4Si) δ 1.72 (3 H, dt, J_{AB} = 6.5 Hz, J_{AC} = 1.5 Hz, H_A), 4.93 (1 H, dm, $J_{BC'}$ = 10.0 Hz, $H_{C'}$), 5.03 (1 H, dm, $J_{BC''}$ = 17.2 Hz, $H_{C''}$) and 5.83 (1 H, m, H_B). **^{13}C NMR** (150 MHz; $CDCl_3$) δ 19.3 (C_A), 115.6 (C_C), and 133.8 (C_B).[3]

4. Reactions with hydrogen gas in the dark

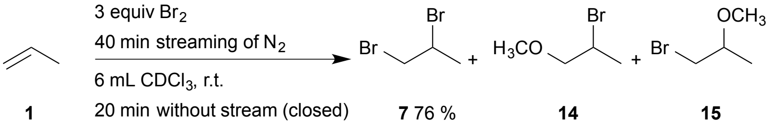
A typical example (Table 3, entry 1)



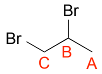
A cylindrical Pyrex glass reaction vessel (covered with an aluminium foil) was charged with a magnetic stir bar, Pd (5 wt %)/TiO_2 (15.0 mg), *p*-toluenesulfonic acid monohydrate (10.0 mg, 0.05 mmol), allyl alcohol (**2**, 136.8 mg, 2.35 mmol) and dehydrated CH_3OH (30 mL). The glass reaction vessel was sealed with a rubber septum, and immediately, the stirred suspension was first deaerated with a stream of Ar and then a 1 L balloon of H_2 gas was attached to one of the reaction vessel branches. After the reaction mixture was stirred for 2 h, the gas and liquid phases were analysed. A trace amount of **1** and **3** (0.68 mmol, 29% yield) were detected in the gas phase (μGC-TCD analyses). After *n*-octane (30 μL) was added to the liquid phase, GC-MS analysis of the liquid phase indicated full conversion of **2** and formation of **4** (1.35 mmol, 58% yield) and *n*-propanol (**6**, 9% yield).

5. Tandem PcTH and bromination reaction

Control experiment[4]



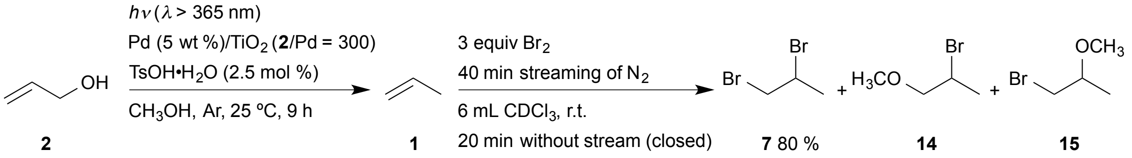
A cylindrical Pyrex glass reaction vessel (*ca.* 200 mL) was charged with a magnetic stir bar, Pd (5 wt %)/TiO_2 (16.5 mg), *p*-toluenesulfonic acid monohydrate (11.0 mg, 0.06 mmol), and dehydrated CH_3OH (30 mL). The reaction vessel was sealed with a rubber septum, the stirred suspension was deaerated with a stream of Ar and propylene (**1**) (48 mL, measured at 25 ºC, 1.96 mmol) was added with a Pressure Lok® precision analytical syringe (12 × 4 mL). The gas phase atmosphere was displaced (through the three-way glass Teflon stopcock, Fig. S3B) to a trap with Br_2 (300 μL, *ca.* 3 equiv) in $CHCl_3$ (*ca.* 6 mL), by bubbling N_2 through the CH_3OH solution for 40 min. Then the trap was closed another 20 min to ensure that the bromination of propylene completes. Analysis of the gas phase of the glass reaction vessel (3.5 mL) by μGC-TCD indicated that propylene (**1**, 0.02 mmol, 1%) remained in the glass reaction vessel. The excess of bromine in the trap was quenched with a saturated aqueous Na_2SO_3 and the aqueous layer was extracted with $CHCl_3$ (2 × 2 mL). *n*-Undecane (50 μL, internal standard) was added in the separatory funnel during the extraction and the organic layer was analyzed by GC-MS: 1,2-dibromopropane (**7**, 1.49 mmol, 76% yield) was present, together with a trace amount of 2-bromo-1-methoxypropane (**14**) and 1-bromo-2-methoxypropane (**15**) as minor products. **14** and **15** was identified by the fragmentation patterns on the GC-MS analyses.[5]



7

^{1}H NMR (600 MHz; $CDCl_3$; Me_4Si) δ 1.83 (3 H, d, J_{AB} = 6.5 Hz, H_A), 3.55 (1 H, t, $J_{BC'}$ = 10.1 Hz, $J_{C'C''}$ = 10.1 Hz, $H_{C'}$), 3.85 (1 H, dd, $J_{BC''}$ = 4.3 Hz, $J_{C'C''}$ = 10.1 Hz, $H_{C''}$) and 4.25 (1 H, m, H_B).[6]

Allyl alcohol (2) to 1,2-dibromopropane (7)



A cylindrical Pyrex glass reaction vessel (*ca.* 200 mL) was charged with a magnetic stirring bar, Pd (5 wt %)/TiO_2 (15.1 mg), *p*-toluenesulfonic acid monohydrate (9.9 mg, 0.05 mmol), allyl alcohol (**2**, 121.4 mg, 2.09 mmol) and dehydrated CH_3OH (30 mL). After sonication of the mixture (to fully disperse the photocatalyst), the glass reaction vessel was sealed with a rubber septum and the stirred suspension was immediately deaerated with a stream of Ar and irradiated with near-UV light (λ > 365 nm) for 9 h. At this point, the gas phase gas was displaced (through the three-way glass Teflon stopcock, Fig. S3B) to a trap with Br_2 (300 μL, *ca.* 3 equiv) in $CDCl_3$ (6 mL), by bubbling N_2 through the CH_3OH solution for 40 min. Then the trap was closed for another 20 min. Analyses of the gas phase of the glass reaction vessel (3.5 mL) by μGC-TCD indicated that **1** (0.08 mmol, 5%) remained in the glass reaction vessel. The excess of bromine in the trap was quenched with saturated aqueous Na_2SO_3. The aqueous layer was extracted with $CDCl_3$ (2 × 2 mL), and the combined organic phase was washed twice with H_2O (2 × 10 mL) and dried over anhydrous Na_2SO_4. 1,1,2,2-

Tetrachloroethane (50 μL, 0.47 mmol, internal standard) was added in the separatory funnel during the extraction and the organic layer was analyzed by GC-MS and ^{1}H NMR: 1,2-dibrompropane (**7**, 1.67 mmol, ^{1}H NMR two-steps-yield: 80%) was detected in the ^{1}H NMR spectrum together with **14** and **15**. **14** and **15** were identified by the fragmentation patterns in the GC-MS analysis (EI)[5] and the peaks of the methyl group in the ^{1}H NMR spectra.[7]

6. Catalyst recycling experiments

First run: according to the typical procedure, the PcTH of **2** was carried out using Pd (5 wt %)/TiO_2 (15.3 mg), *p*-toluenesulfonic acid monohydrate ($TsOH•H_2O$, 10 mg, 0.05 mmol), allyl alcohol (**2**, 124.8 mg, 2.14 mmol), *n*-octane (50 μL) and dehydrated CH_3OH (30 mL). After irradiation with near-UV light (λ > 365 nm) for 4 h, propylene (**1**, 1.24 mmol, 58% yield) and H_2 (0.0039 mmol) were present in the gas phase.
Conversion of **2**: 61%; yield of **4**: not determined.

Between two consecutive runs, the mixture of a previous reaction was transferred to a 45 mL centrifuge tube, the catalyst powder was decantated by centrifugation, and the liquid phase was removed as much as possible by a pipet. The residual powder was washed three times with dehydrated CH_3OH (30 mL) and the final CH_3OH was removed using a pipet. The powder slightly wetted with CH_3OH was transferred into the reaction vessel (photo-flask) used in the previous run, through washing with dehydrated CH_3OH (total volume used for washing: 30 mL). To the Pd/TiO_2 powder suspended in CH_3OH were added **2** (2 mmol), $TsOH•H_2O$ (0.05 mmol) and *n*-octane (50 μL). After purging the vessel with Ar, the PcTH was restarted by irradiating with near-UV light (λ > 365 nm).

Second run: conv. of **2**: 63%. **1**: 63% yield; **3**: not detected; H_2: 0.022 mmol.
Third run: conv. of **2**: 63%. **1**: 62% yield; **3**: not detected; H_2: 0.065 mmol.
Fourth run: conv. of **2**: 59%. **1**: 57% yield; **3**: not detected; H_2: 0.32 mmol.
Fifth run: conv. of **2**: 59%. **1**: 59% yield; **3**: not detected; H_2: 0.65 mmol.

After the fifth run, 13.3 mg of the catalyst was recovered (87%).

7. Catalyst characterization (EDX/HRTEM and XPS)

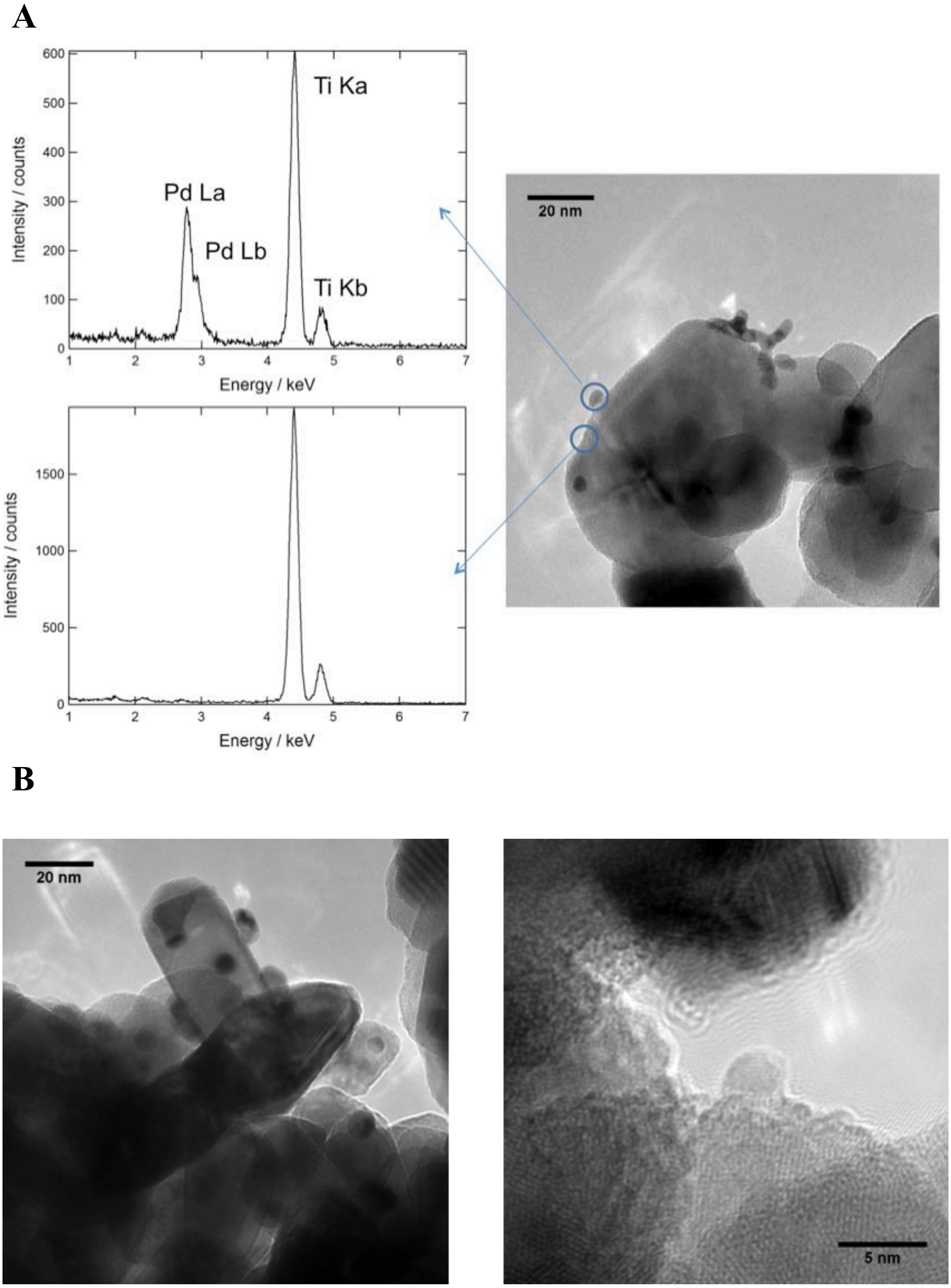


Fig. S1 | A. EDX analyses of the Pd (5 wt %)/TiO_2 observed on TiO_2 surface and on a loaded Pd-particle. **B.** Low-magnification HRTEM images of the Pd (5 wt %)/TiO_2.

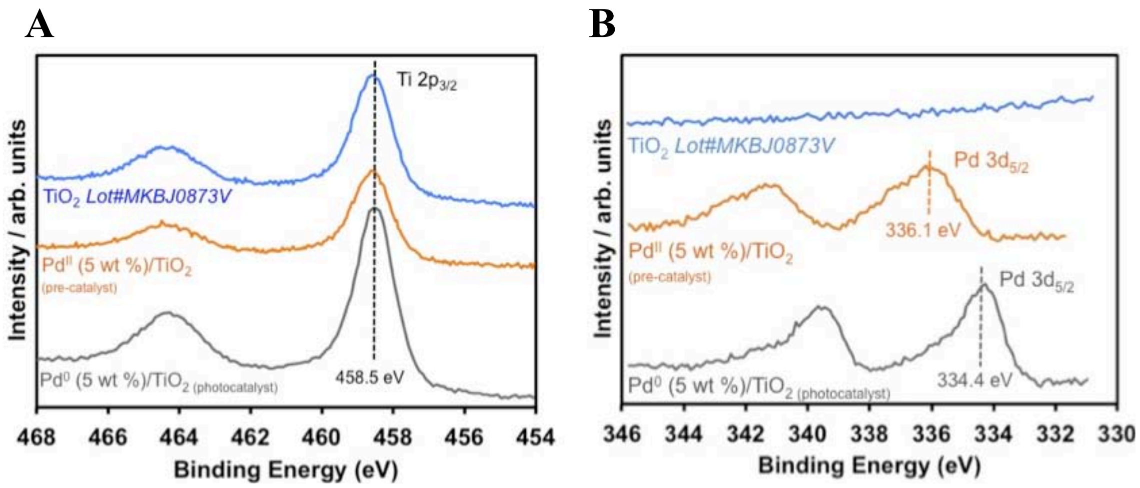
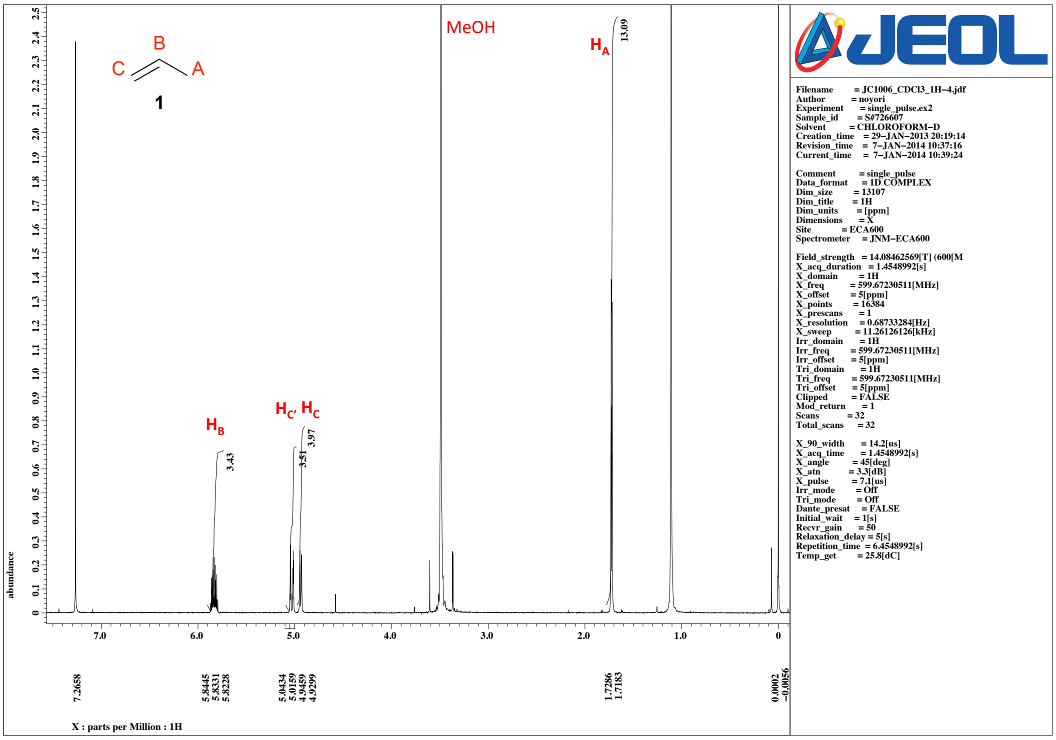


Fig. S2 | XPS spectra for the TiO_2, pre-catalyst and the final photocatalyst. A. High-resolution spectra corresponding to Ti 2p signals. The peak at 458.5 eV ($2p_{3/2}$) corresponds to the titanium (Ti^{4+}) has been used to normalize spectra. **B.** High-resolution spectra corresponding to Pd 3d signals. The peak at 336.1 eV ($3d_{3/2}$) denotes the presence of Pd^{2+} species in the surface (PdO -most probable- or $PdCl_2$) and the peak at 334.4 eV denotes Pd^0 ($3d_{3/2}$) in the surface (Standard binding energies for Pd $3d_{5/2}$ of PdO and $PdCl_2$ and Pd metal are 336.3, 338.0 and 335.1 respectively).

8. NMR analyses of the gas phase after PcTH reaction

Sample preparation: after a typical photocatalytic reaction, approximately a 12 mL of the gas phase was collected with Pressure Lok® precision analytical syringe and injected to a septum-equipped NMR tube (4 × 3 mL).



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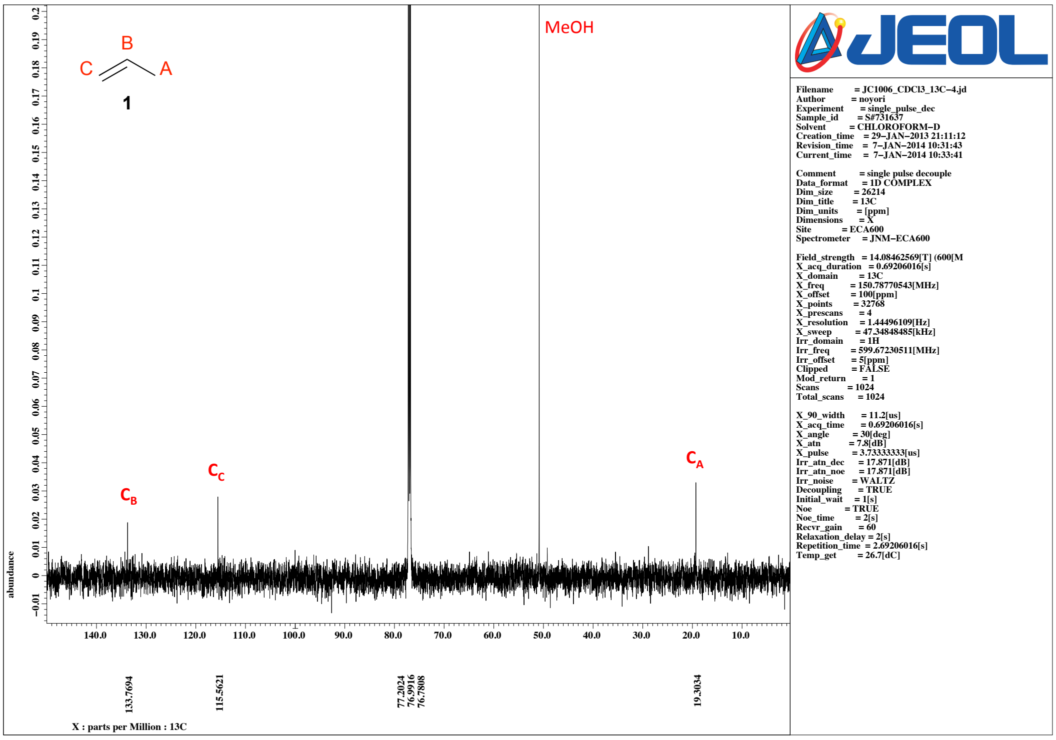
^{1}H NMR (600 MHz) spectrum



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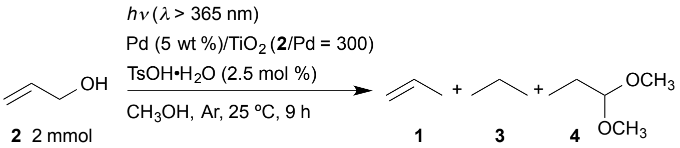
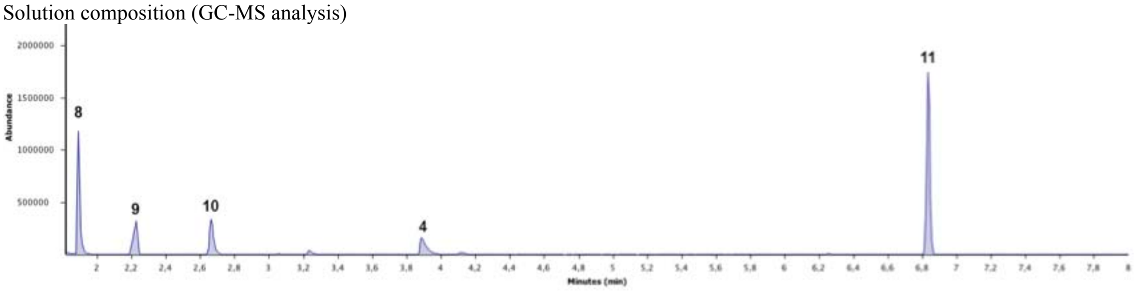
^{13}C NMR (150 MHz) spectrum

9. Typical GC-MS and μGC-TCD analyses after PcTH reaction (Table 2, entry 1):

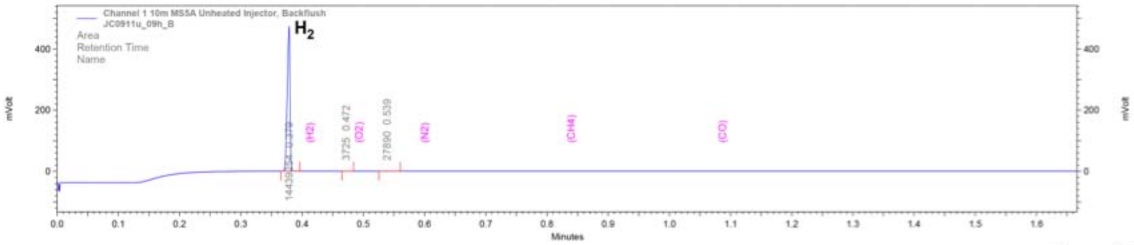


Solution composition (GC-MS analysis)

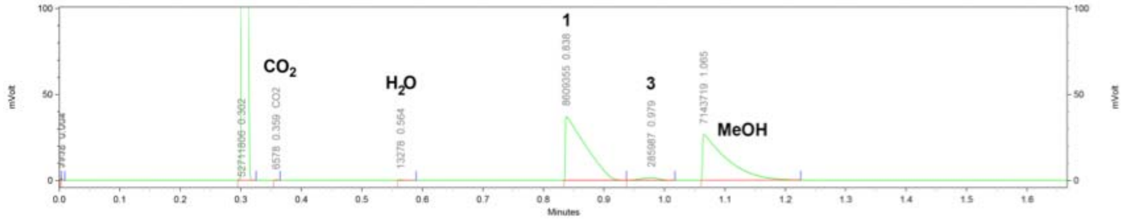


Gas phase composition (μGC-TCD analysis)

Channel 1

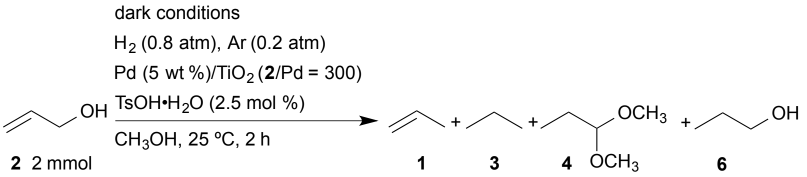


Channel 2

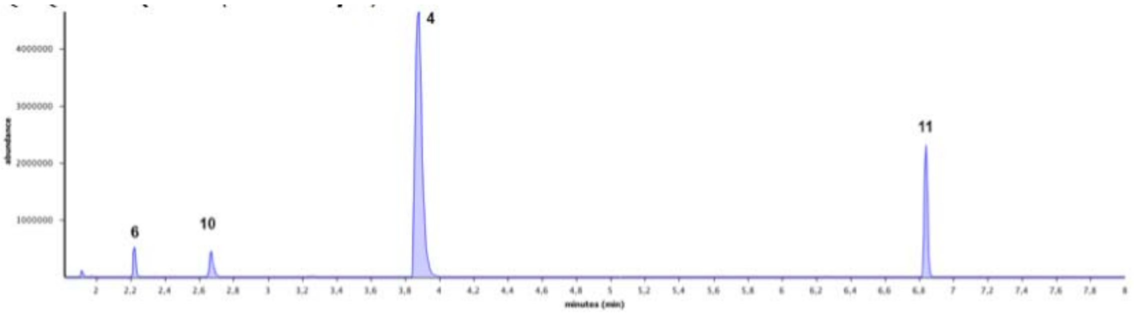


1: propylene. **3:** propane. **4:** dimethyl acetal of propionaldehyde (from isomerization of the double bond of **2**, followed by acetalization of **5**). **8:** methylal (from methanol oxidation). **9:** methoxymethanol (from methanol oxidation). **10:** $CHCl_3$ (from washing). **11:** *n*-octane (internal standard).

10. Typical GC-MS and μGC-TCD analyses under dark conditions (Pd/TiO$_2$ and H$_2$ under acidic conditions) (Table 3, entry 1):

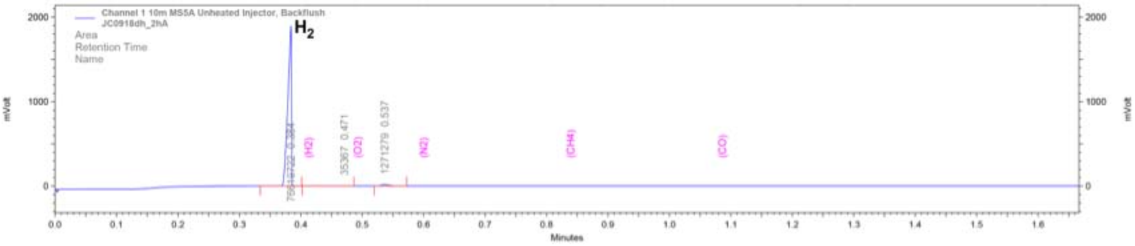


Liquid phase composition (GC-MS analysis)

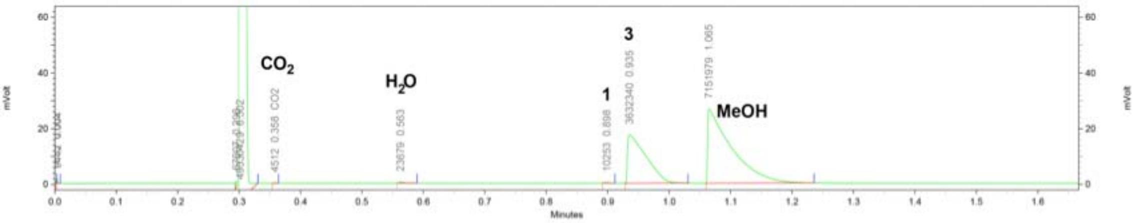


Gas phase composition (μGC-TCD analysis)

Channel 1

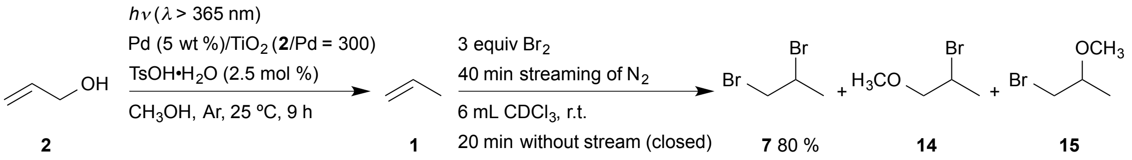


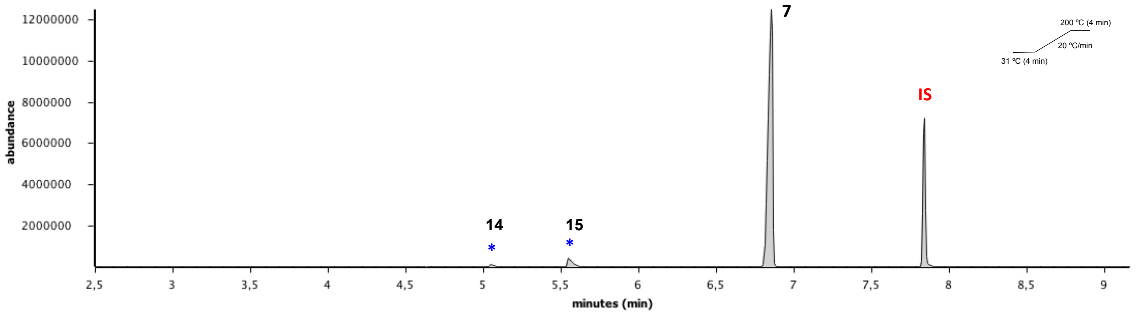
Channel 2



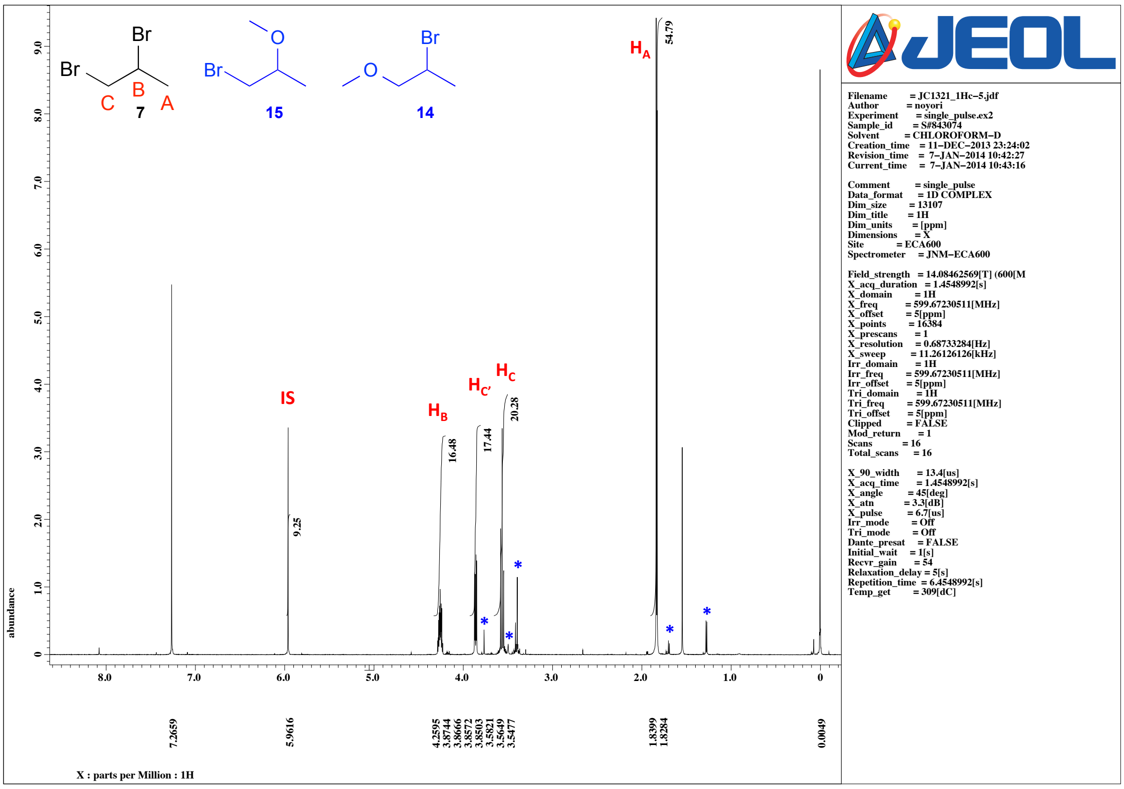
1: propylene. **3:** propane. **4:** dimethyl acetal of propionaldehyde (from isomerization of the double bond of **2**, followed by acetalization of **5**). **6:** *n*-propanol. **10:** CHCl$_3$ (from washing). **11:** *n*-octane (internal standard).

11. GC-MS and ^{1}H-NMR analyses (crude mixture of the tandem reaction after bromination) (Scheme 2):





GC-MS spectrum of the $CDCl_3$ solution. 1,2-Dibromopropane (**7**), 2-bromo-1-methoxypropane (**14**) and 1-bromo-2-methoxypropane (**15**). IS (internal standard): 1,1,2,2-tetrachloroethane.



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Author          = noyori
Experiment      = single_pulse.ex2
Sample_id       = S#843074
Solvent         = CHLOROFORM−D
Creation_time   = 11−DEC−2013 23:24:02
Revision_time   =  7−JAN−2014 10:42:27
Current_time    =  7−JAN−2014 10:43:16

Comment         = single_pulse
Data_format     = 1D COMPLEX
Dim_size        = 13107
Dim_title       = 1H
Dim_units       = [ppm]
Dimensions      = X
Site            = ECA600
Spectrometer    = JNM−ECA600

Field_strength  = 14.08462569[T] (600[M
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X_offset        = 5[ppm]
X_points        = 16384
X_prescans      = 1
X_resolution    = 0.68733284[Hz]
X_sweep         = 11.26126126[kHz]
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Tri_offset      = 5[ppm]
Clipped         = FALSE
Mod_return      = 1
Scans           = 16
Total_scans     = 16

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X_acq_time      = 1.4548992[s]
X_angle         = 45[deg]
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Dante_presat    = FALSE
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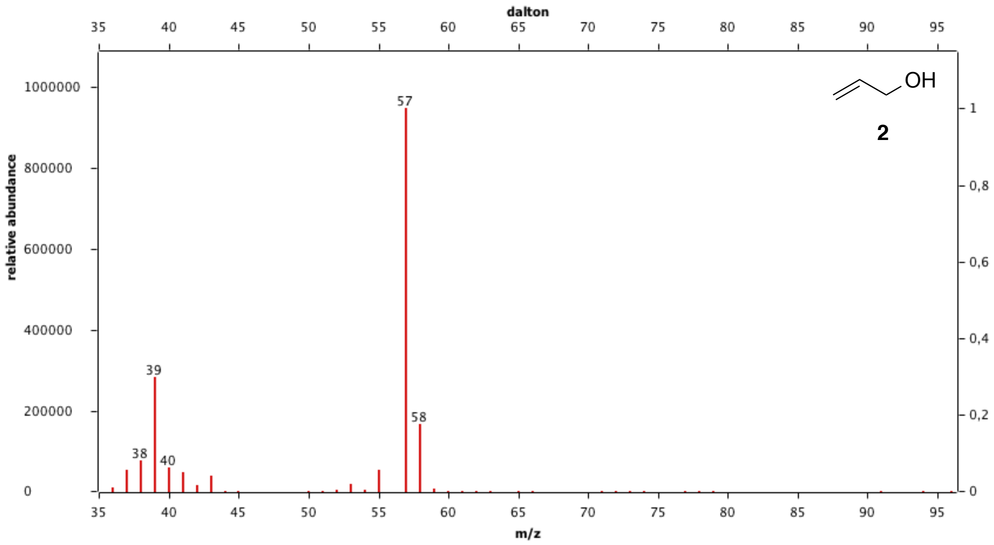
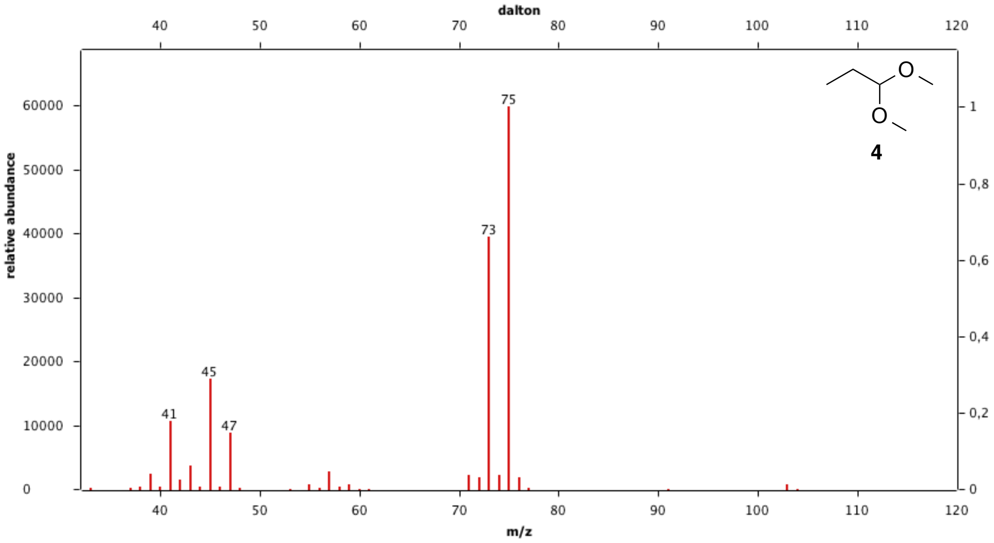
Recvr_gain      = 54
Relaxation_delay = 5[s]
Repetition_time = 6.4548992[s]
Temp_get        = 309[dC]
```

^{1}H NMR spectrum of the crude reaction ($CDCl_3$). IS (internal standard): 1,1,2,2-tetrachloroethane. *Signals from 2-bromo-1-methoxypropane (**14**) and 1-bromo-2-methoxypropane (**15**).

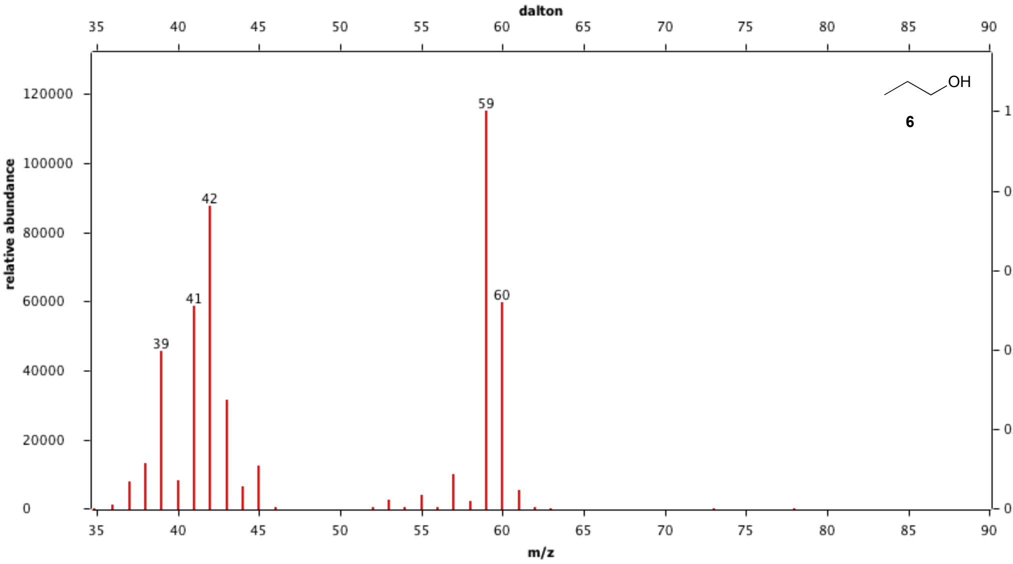
12. Fragmentation patterns in GC-MS (EI)



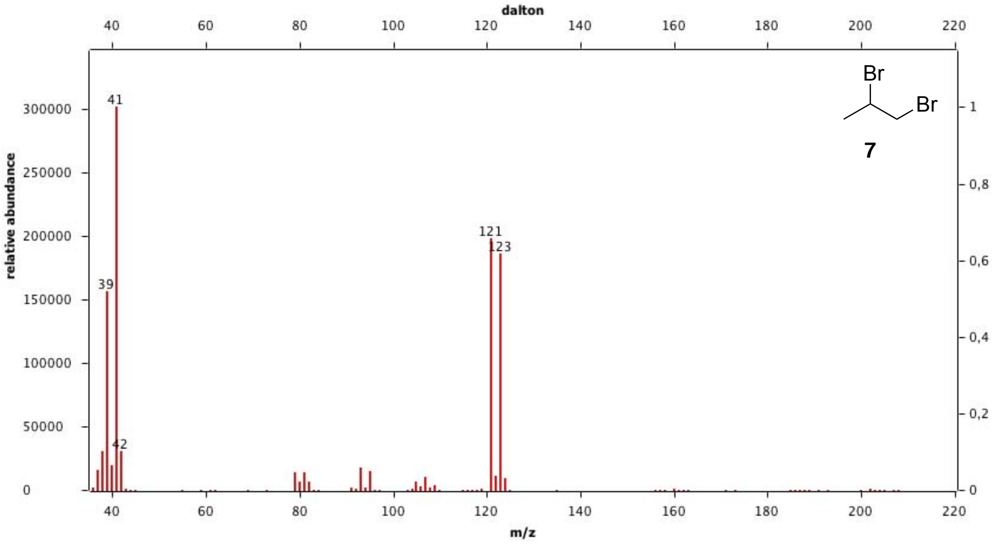
2: allyl alcohol.[8]



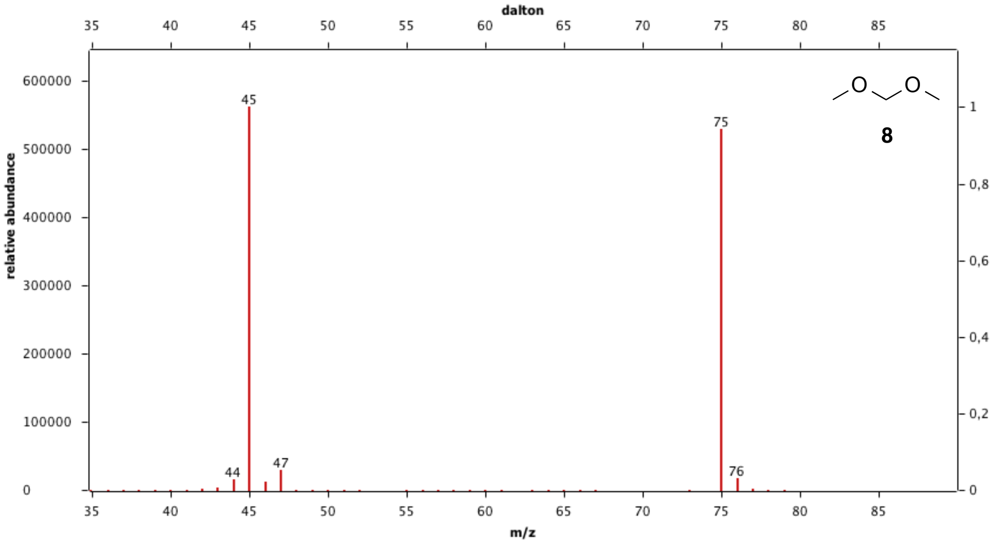
4: dimethyl acetal of propionaldehyde.[9]



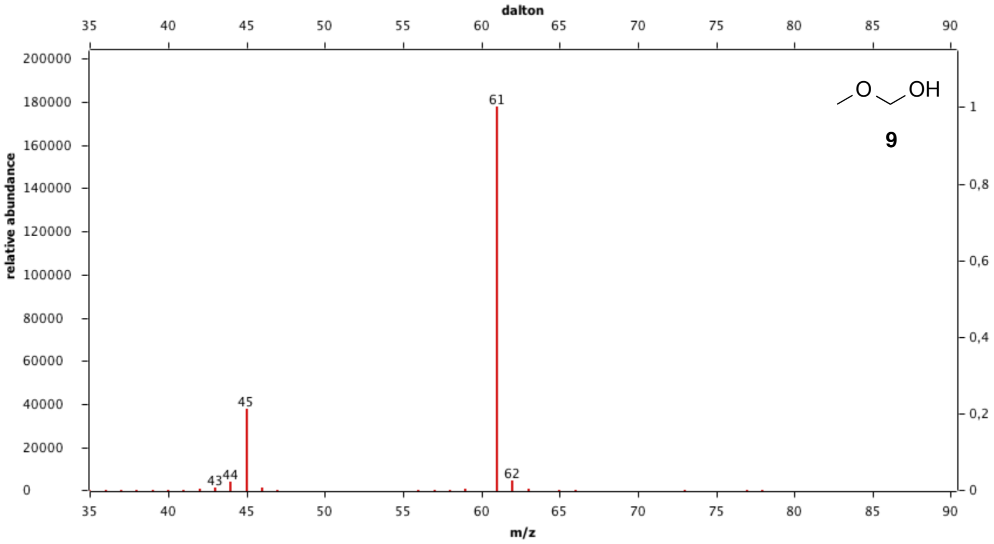
6: *n*-propanol.[10]



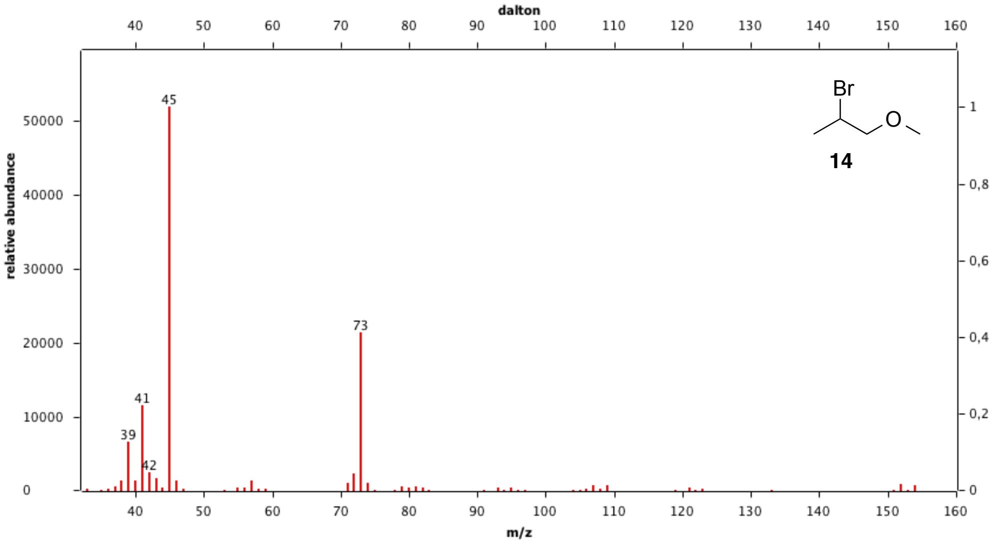
7: 1,2-dibromopropane.[11]



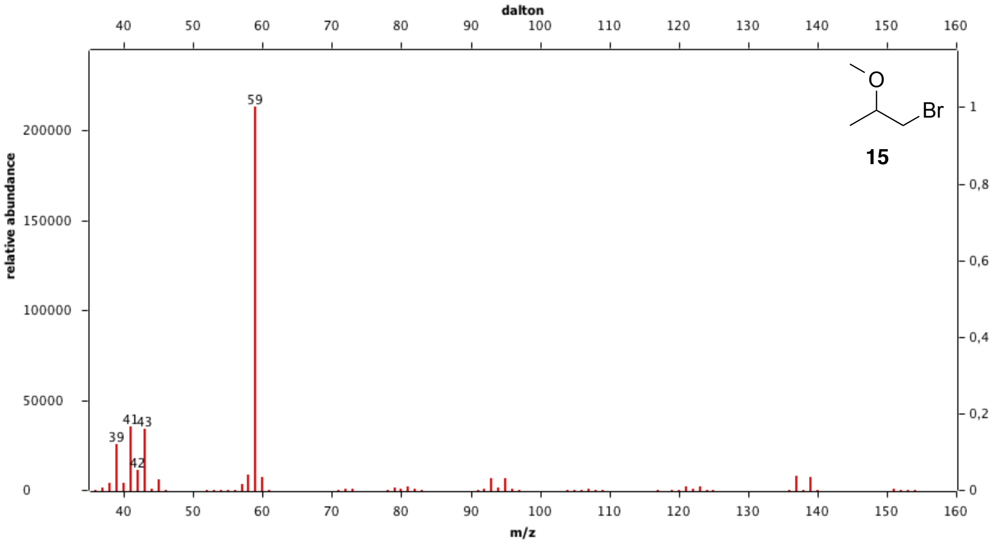
8: methylal.[12]



9: methoxymethanol.[13]



14: 2-bromo-1-methoxypropane.[5]



15: 1-bromo-2-methoxypropane.[5]

13. Photocatalytic system pictures

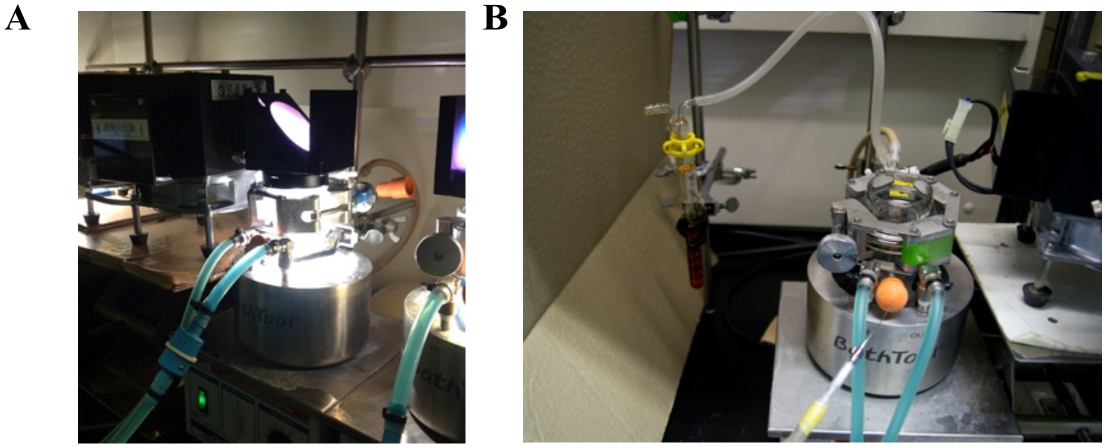


Fig. S3 | Reaction systems. A. Photochemical hydrogenolysis of allyl alcohol (batch mode). **B.** Bromination reaction [streaming of N_2 from a needle (front) through the cylinder-vessel containing propylene (right) to a trap (left) containing $Br_2/CDCl_3$].

14. References

[1] A. Grirrane *et al.*, *Science*, 2008, **322**, 1661.
[2] Ni-Zn/TiO_2 preparation: S. Myagmarjav *et al.*, *Mat. Trans.* 2004, **45**, 2035.
[3] G. R. Fulmer *et al., Organometallics*, 2010, **29**, 2176.
[4] Bromination adapted from: T. J. Barton and N. Tillan, *J. Am. Chem. Soc.* 1987, **109**, 6711.
[5] J. R. Chrétien, J.-D. Courdert and M.-F. Ruasse, *J. Org. Chem.* 1993, **58**, 1917.
[6] http://www.sigmaaldrich.com/spectra/fnmr/FNMR001169.PDF.
[7] J.-E. Dubois and J. R. Chrétien, *J. Am. Chem. Soc.* 1978, **100**, 3506.
[8] CAS: 107-18-6. Spectral data were compared with Wiley Subscription Services, Inc. (US). Mass Spectrum (ID_WID_DLO-067340-5). Nominal Mass: 58.
[9] CAS: 4744-10-9. Spectral data were compared with Wiley Subscription Services, Inc. (US). Mass Spectrum (CAS2009_1_011278). Nominal Mass: 104.
[10] CAS: 71-23-8. Spectral data were compared with Wiley Subscription Services, Inc. (US). Mass Spectrum (ID_WID_DLO-067408-8). Nominal Mass: 60.
[11] CAS: 78-75-1. Spectral data were compared with Wiley Subscription Services, Inc. (US). Mass Spectrum (ID_WID_DLO-067340-5). Nominal Mass: 200.
[12] CAS: 109-87-5. Spectral data were compared with Wiley Subscription Services, Inc. (US). Mass Spectrum (ID_WID_DLO-067799-6). Nominal Mass: 76.
[13] CAS: 4461-52-3.