Supplementary Information (SI) for Sustainable Energy & Fuels.

Hydrogen Gas Production and Storage Cycle with Benzyl Alcohol/Benzaldehyde

Tomoyuki Ito,† [a] Takumi Ichimura,† [a] Hitoshi Kasai,[a] Kouki Oka*[, a, b, c]

[a]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan.*
E–mail: oka@tohoku.ac.jp
[b]*Carbon Recycling Energy Research Center Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan*
[c]*Deuterium Science Research Unit, Center for the Promotion of Interdisciplinary Education and Research Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan*
†These authors contributed equally
*Corresponding author

1. Experimental

1.1. Materials

Benzyl alcohol, benzaldehyde, and toluene were purchased from FUJIFILM Wako Pure Chemical Corporation. Baker's yeast (Nisshin Super Camellia dry yeast) was purchased from Nisshin Seifun Welna Inc. Aqua(2,2′-bipyridine-6,6′-dionato)(penta-methylcyclopentadienyl)iridium(III) (**Ir cat.**) was purchased from Kanto Chemical Co., Inc. *p*-Xylene was purchased from Tokyo Chemical Industry Co., Ltd. Pinane was purchased from Sigma-Aldrich Co. LCC.

1.2. Characterization

^{1}H NMR spectra were recorded on a Bruker AVANCE III 400 (400 MHz) spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Gas chromatography (**GC**) analyses of the evolved H_2 were performed on a Shimadzu GC–2014 gas chromatograph using a packed column (Molecular Sieve 5A).

1.3. Supplementary Method

1.3.1. Dehydrogenation of benzyl alcohol to benzaldehyde with Ir cat.

Benzyl alcohol (1 mmol) and Ir cat. (0.5–1.5 mol% vs. benzyl alcohol) were dissolved in p-xylene or pinane (5.0 mL) under air, and benzyl alcohol was dehydrogenated under reflux conditions (the aluminum bath temperature was set at 180 or 220°C).

1.3.2. Analysis of H_2 evolved via the dehydrogenation of benzyl alcohol shown in Fig. S3.

Benzyl alcohol (0.4 mmol), **Ir cat.** (0.5 mol% vs. benzyl alcohol), and *p*-xylene (3 mL) were added to a test tube, and the mixture was stirred and refluxed for 5 min in an aluminum bath, whose temperature was set at 180°C). The conversion of benzyl alcohol to benzaldehyde was determined by ^{1}H NMR. The volume of evolved H_2 was estimated by **GC** analysis.

1.3.3. Kinetic analysis of dehydrogenation of benzyl alcohol with Ir cat. shown in Fig. 2.

Benzyl alcohol (1 mmol) and **Ir cat.** (0.5 mol% vs. benzyl alcohol) were dissolved in *p*-xylene (5.0 mL) under air, and the reaction mixture was stirred at different temperatures (the aluminum bath temperature was set at 100–130°C). The conversions were

determined to estimate the rate constants.

1.3.4. Hydrogenation of benzaldehyde to benzyl alcohol with Ir cat. and H_2.

Benzaldehyde (1 mmol) and **Ir cat.** (0.5 mol% vs. benzyl alcohol) were dissolved in *p*-xylene or pinane (5.0 mL) under air. The mixture was added in flask and a balloon filled with H_2 was connected to the flask. The hydrogenation of benzaldehyde was carried out under H_2 atmosphere (1 atm) with stirring (the aluminum bath temperature was set at 60°C).

1.3.5. Hydrogenation of benzaldehyde to benzyl alcohol with baker's yeast.

A suspension of baker's yeast (1 g) in water (10 mL) was stirred for 1 h at 25°C. Subsequently, benzaldehyde (1 mmol) was added to the suspension. The reaction mixture was stirred for 6 h at 25°C. After the reaction, the mixture was extracted with ethyl acetate, which was then evaporated to obtain benzyl alcohol.

2. Supplementary Figures

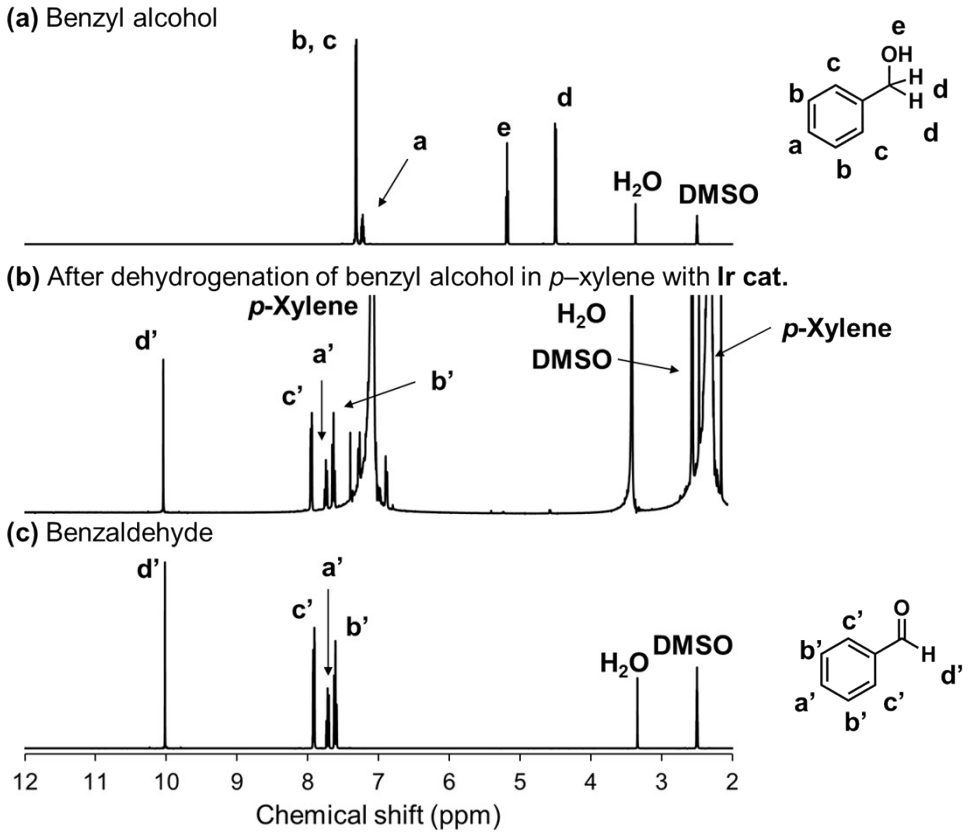

Fig. S1. 400 MHz ^{1}H NMR spectra of (a) benzyl alcohol, (b) after dehydrogenation of benzyl alcohol in *p*-xylene with **Ir cat.** (0.5 mol% vs. benzyl alcohol), and (c) benzaldehyde in DMSO-d_6.

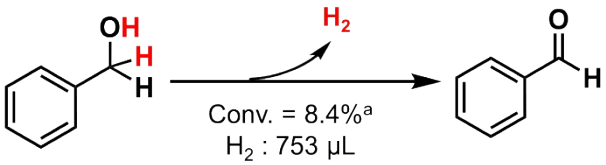

Fig. S2. Dehydrogenation of benzyl alcohol in *p*-xylene in the presence of **Ir cat.** (benzyl alcohol: 0.4 mmol; *p*-xylene: 3 mL; **Ir cat.**: 0.5 mol% (vs. benzyl alcohol); temperature: 180°C; reaction time: 5 min). [a] Determined by ^{1}H NMR.

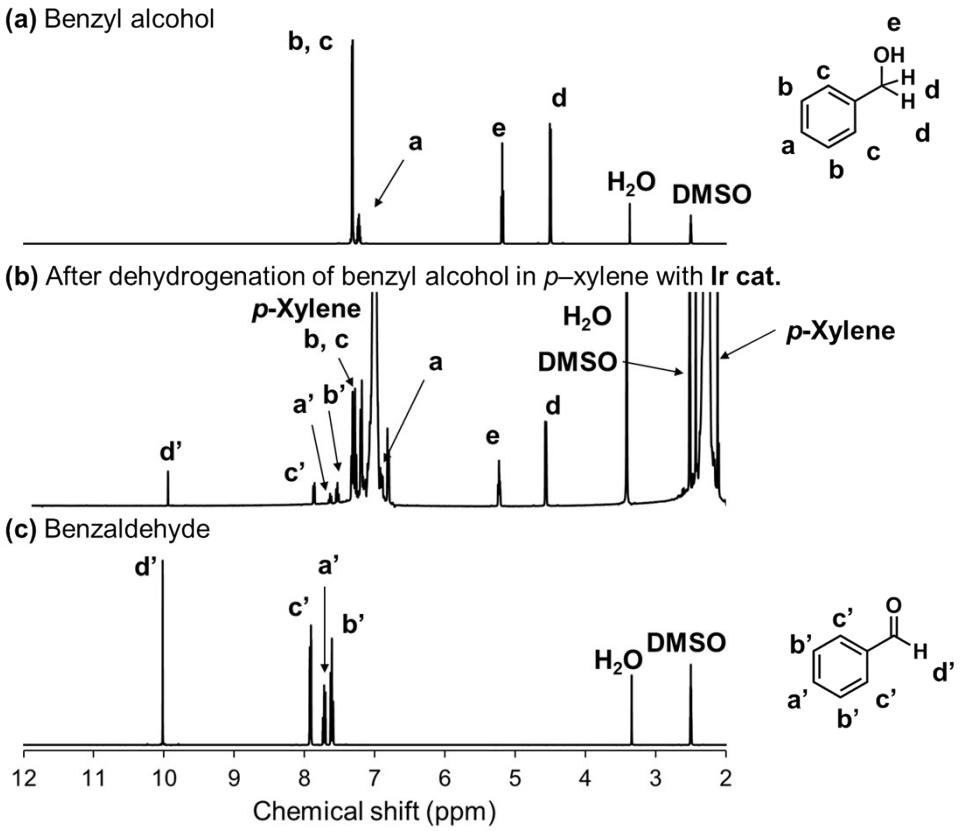

Fig. S3. 400 MHz ^{1}H NMR spectra of (a) benzyl alcohol, (b) after dehydrogenation of benzyl alcohol in *p*-xylene with **Ir cat.** (0.5 mol% vs. benzyl alcohol) under equilibrium conditions, and (c) benzaldehyde in DMSO-d_6.

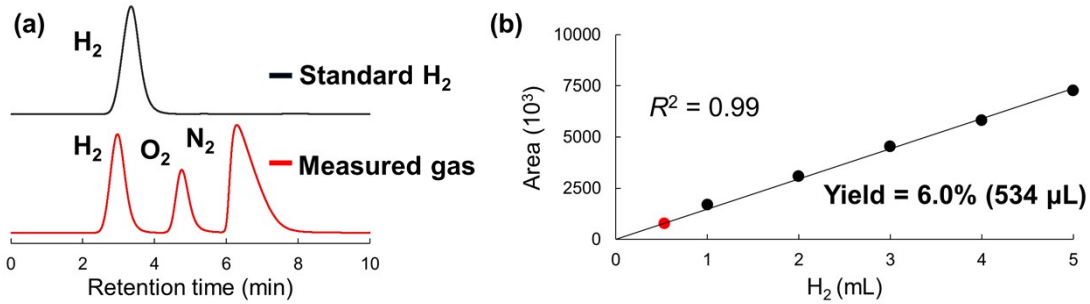

Fig. S4. (a) Gas chromatograms standard H_2 (black line) and measured gas (red line). (b) Calibration curve of H_2 volume prepared by gas chromatography results, and a red circle denotes the evolved gas.

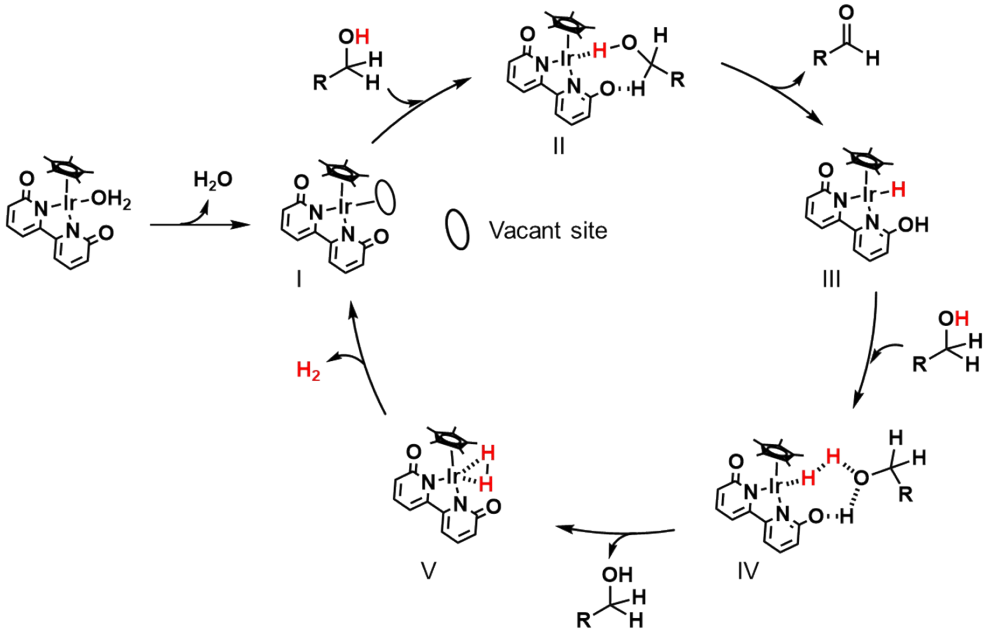

Fig. S5. Previously reported mechanism for the dehydrogenation of primary alcohols in the presence of **Ir cat.**[1]

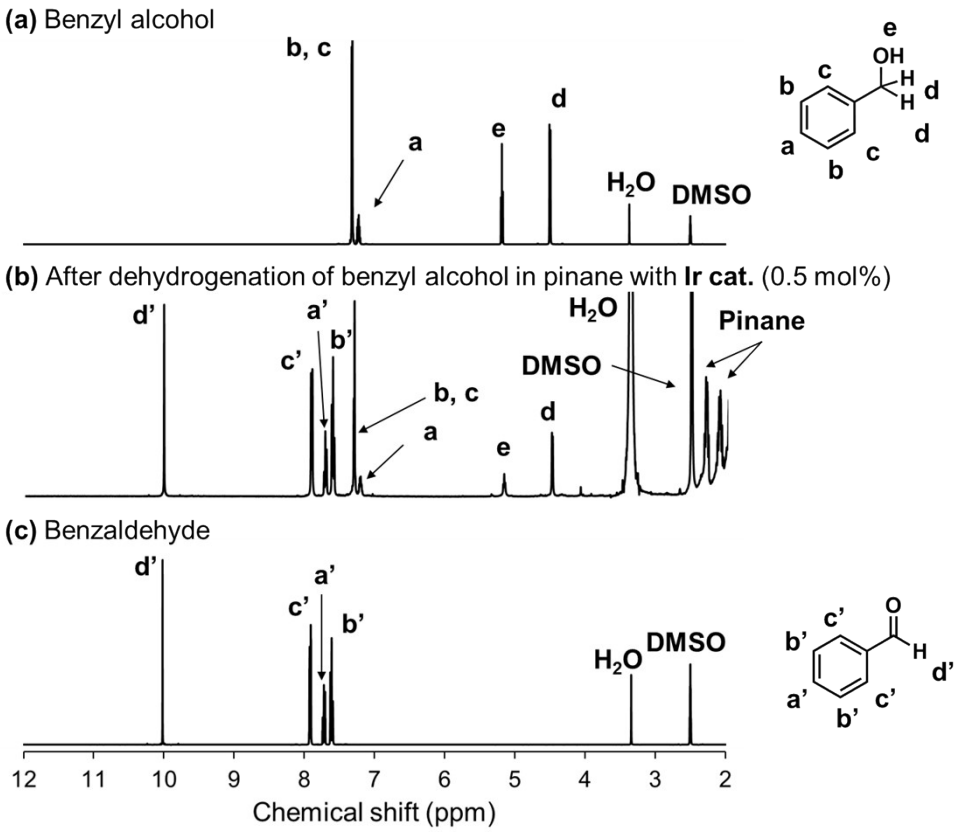

Fig. S6. 400 MHz ^{1}H NMR spectra of (a) benzyl alcohol, (b) after dehydrogenation of benzyl alcohol in pinane with **Ir cat.** (0.5 mol% vs. benzyl alcohol), and (c) benzaldehyde in DMSO-d_6.

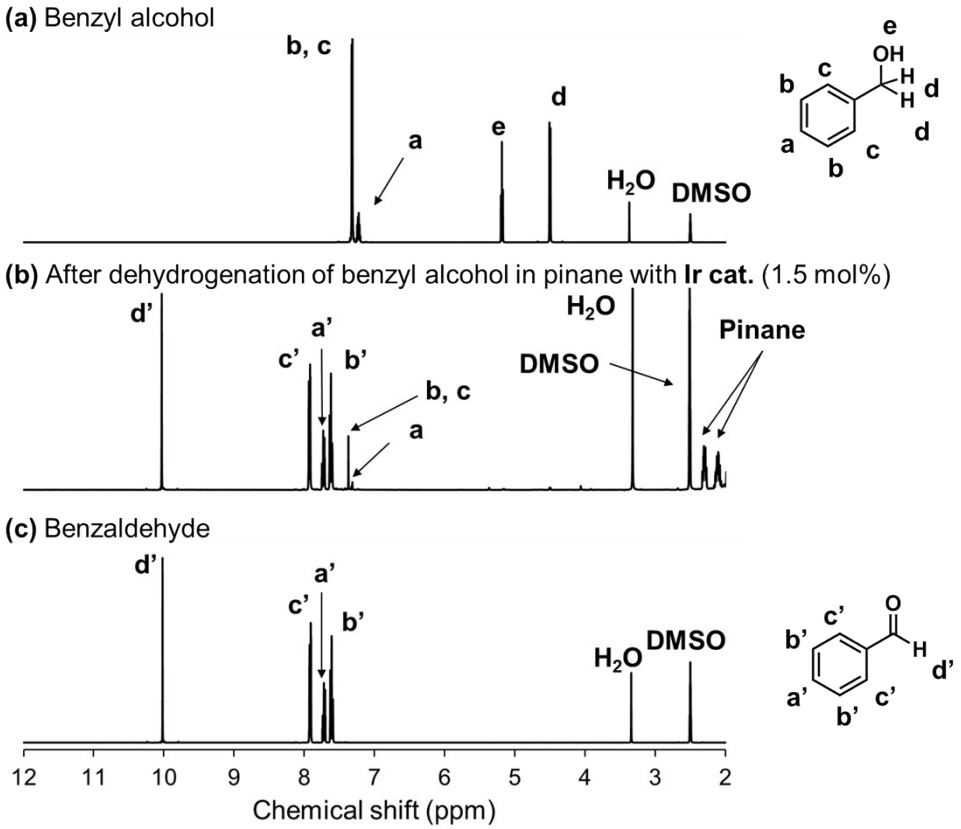

Fig. S7. 400 MHz ^{1}H NMR spectra of (a) benzyl alcohol, (b) after dehydrogenation of benzyl alcohol in pinane with **Ir cat.** (1.5 mol% vs. benzyl alcohol), and (c) benzaldehyde in DMSO-d_6.

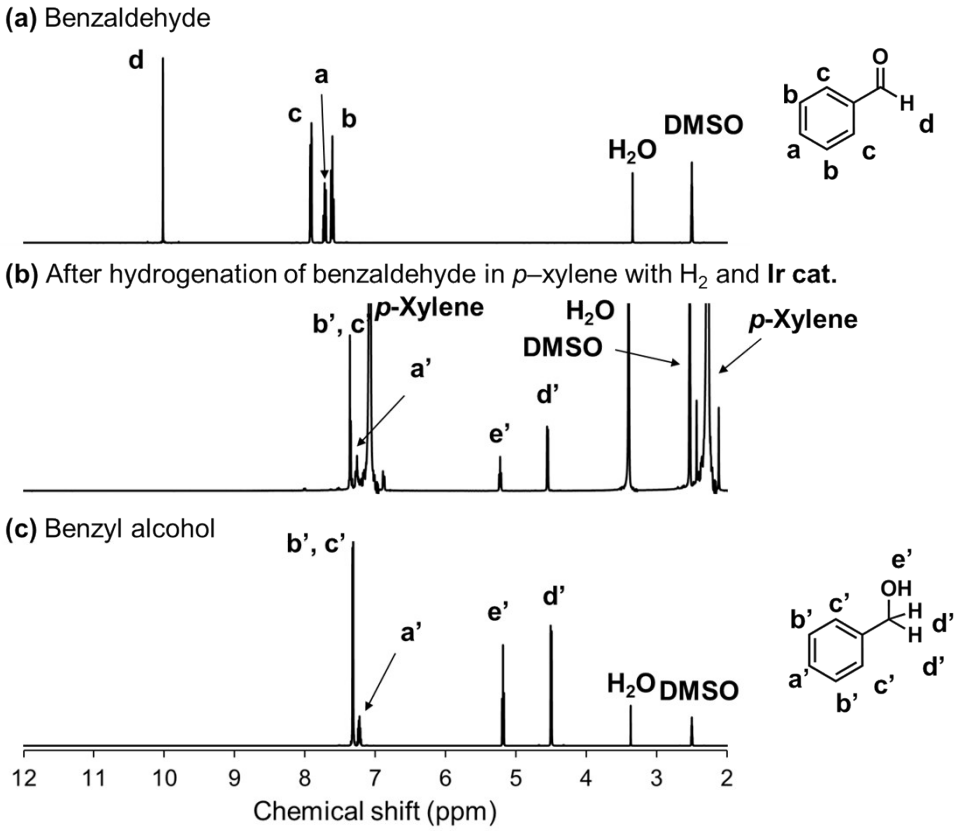

Fig. S8. 400 MHz ^{1}H NMR spectra of (a) benzaldehyde, (b) after hydrogenation of benzaldehyde in *p*-xylene with H_2 and **Ir cat.** (0.5 mol% vs. benzyl alcohol), and (c) benzyl alcohol in DMSO-d_6.

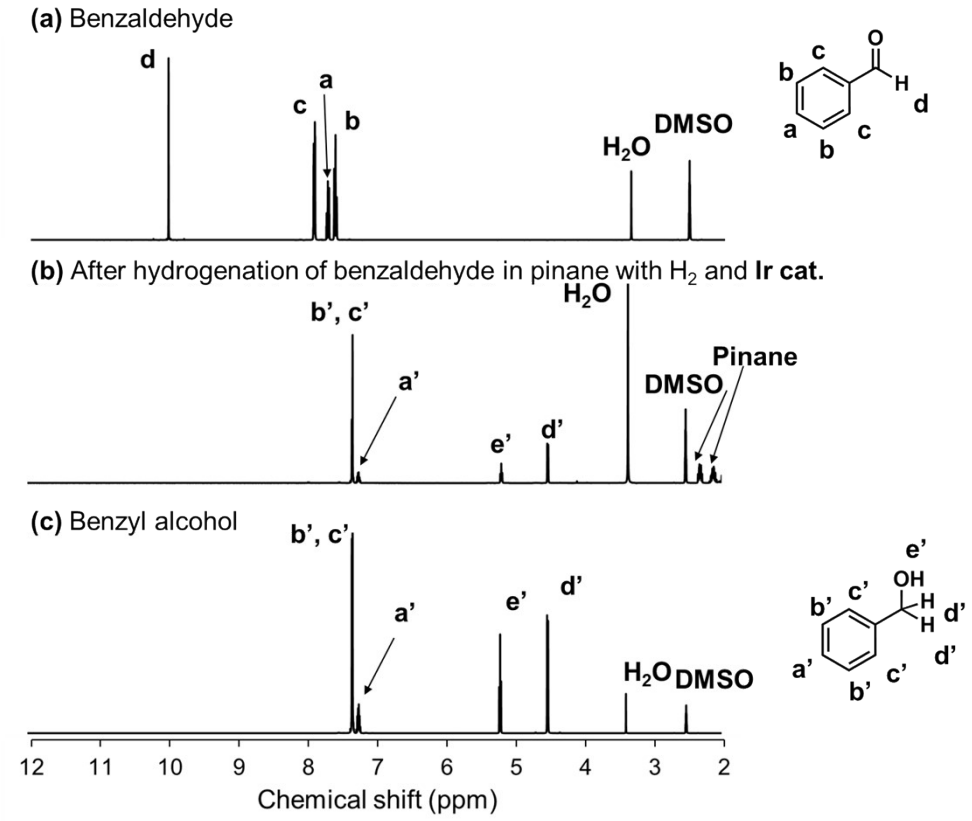

Fig. S9. 400 MHz ^{1}H NMR spectra of (a) benzaldehyde, (b) after hydrogenation of benzaldehyde in pinane with H_2 and **Ir cat.** (0.5 mol% vs. benzyl alcohol), and (c) benzyl alcohol in DMSO-d_6.

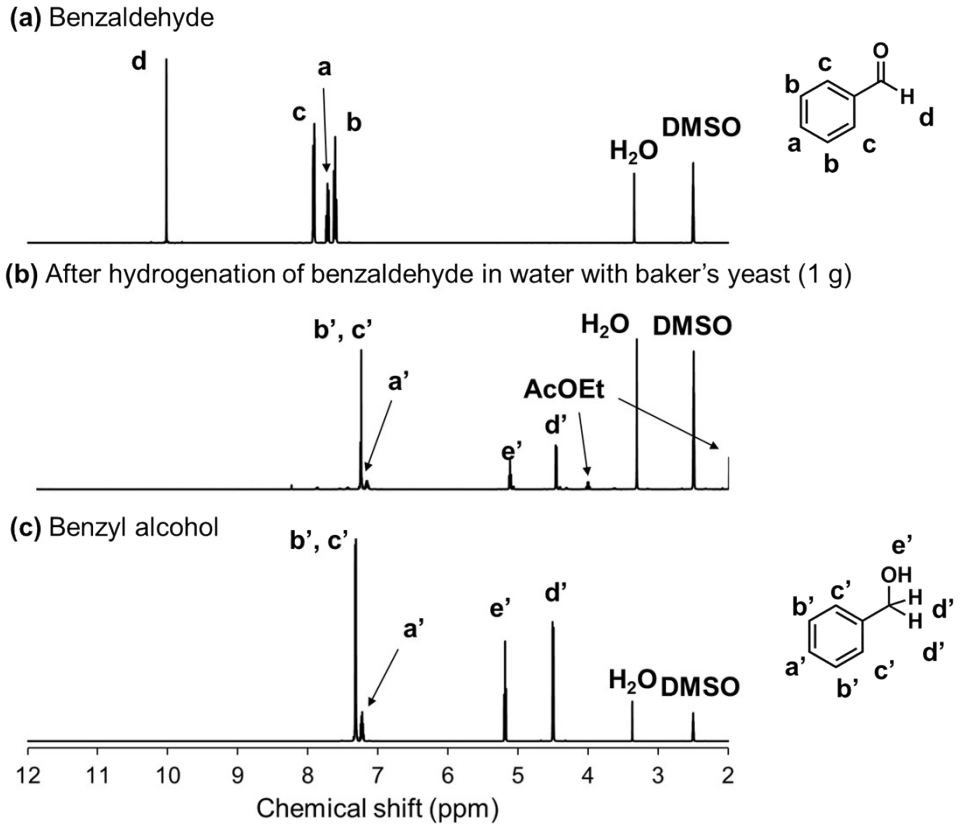

Fig. S10. 400 MHz ^{1}H NMR spectra of (a) benzaldehyde, (b) after hydrogenation of benzaldehyde in water with baker's yeast (1 g), and (c) benzyl alcohol in DMSO-d_6.

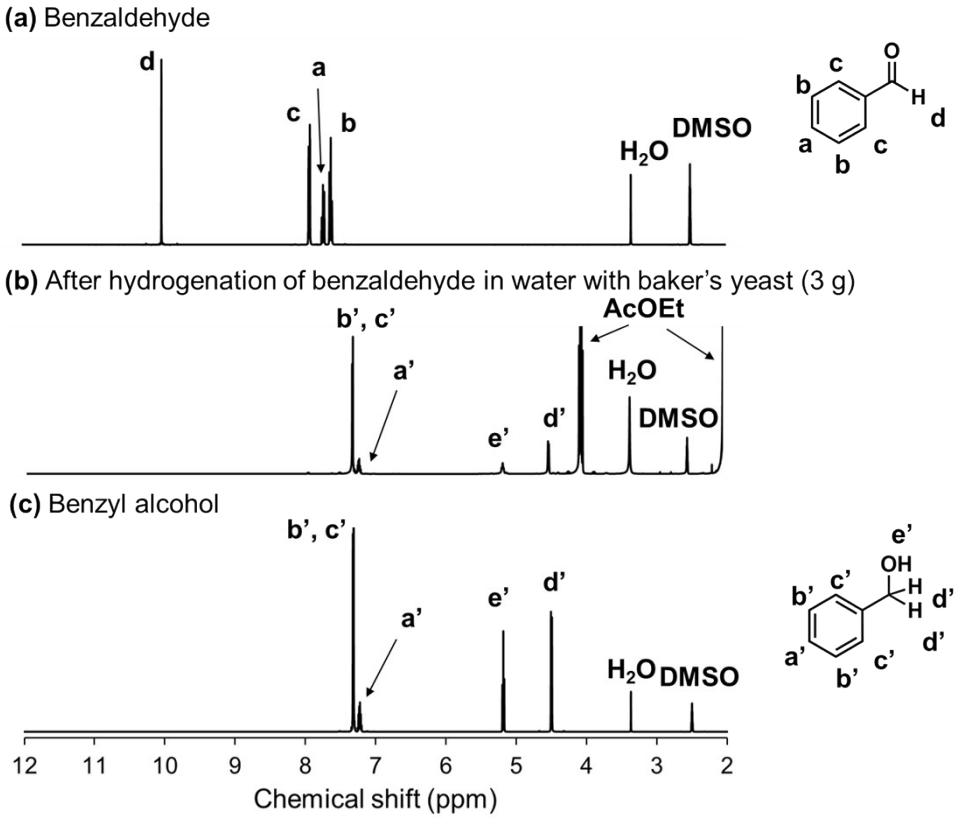

Fig. S11. 400 MHz ^{1}H NMR spectra of (a) benzaldehyde, (b) after hydrogenation of benzaldehyde in water with baker's yeast (3 g), and (c) benzyl alcohol in DMSO-d_6.

3. Supplementary Tables

Table S1. Dehydrogenation of benzyl alcohol with **Ir cat.** at different temperatures. Dehydrogenation of benzyl alcohol with **Ir cat.** is a second-order reaction described by $v = k$[benzyl alcohol][**Ir cat.**], where v and k denote the rate and rate constant of the reaction, respectively.[2] Given that **Ir cat.** remains constant during the reaction, dehydrogenation becomes a pseudo-first-order reaction represented by $v' = k'$[benzyl alcohol], where $k' = k$[**Ir cat.**].

Entry	Temperature (°C)	Conversion (%)[a]				Reaction rate constant
		20 s	40 s	60 s	80 s	k ($\times 10^{-3} \cdot M^{-1} \cdot s^{-1}$)
1	100	4.11	5.11	5.48	6.14	0.9
2	110	8.51	10.8	11.5	12.3	1.9
3	120	9.41	11.9	13.1	14.9	2.3
4	130	11.3	15.0	18.5	20.4	3.2

Benzyl alcohol: 1.0 mmol, **Ir cat.**: 0.5 mol% (vs. benzyl alcohol), solvent: *p*-xylene. [a] Determined by ^{1}H NMR.

Table S2. Dehydrogenation of benzyl alcohol with the same amount of **Ir cat.** in *p*-xylene or pinane.

Entry	Solvent	Temperature (°C)	Reaction time (h)	Conversion (%)[a]
1	*p*-Xylene	180 (reflux)	10	100
2	Pinane	220 (reflux)	24	83

Benzyl alcohol: 1 mmol, **Ir cat.**: 0.5 mol% (vs. benzyl alcohol). [a] Determined by ^{1}H NMR.

References

1. G. Zeng, S. Sakaki, K.-i. Fujita, H. Sano and R. Yamaguchi, *ACS Catal.*, 2014, **4**, 1010-1020.
2. K. Oka, M. Kataoka, Y. Kaiwa and K. Oyaizu, *Bull. Chem. Soc. Jpn.*, 2021, **94**, 2770-2773.