Supporting Information for

Oxygen Vacancies Regulated Selective Hydrogenation of *α,β*-unsaturated Aldehydes over LDH Surface Group Coordinated Transition Metal Photocatalysts

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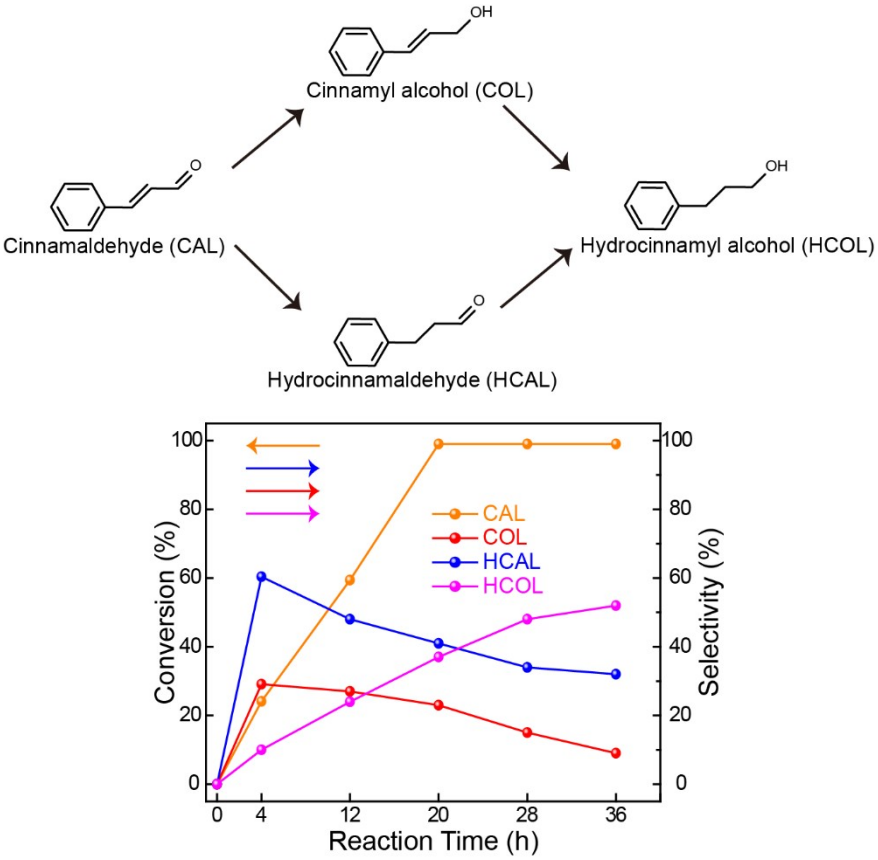


Fig. S1 Time−conversion plots for cinnamaldehyde reduction under visible light irradiation catalyzed by Ru/LDH catalyst.

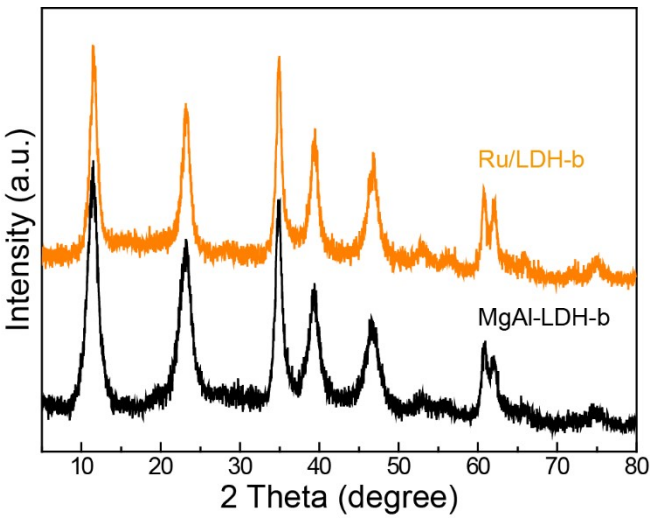


Fig. S2 XRD patterns of LDH-b and Ru/LDH-b.

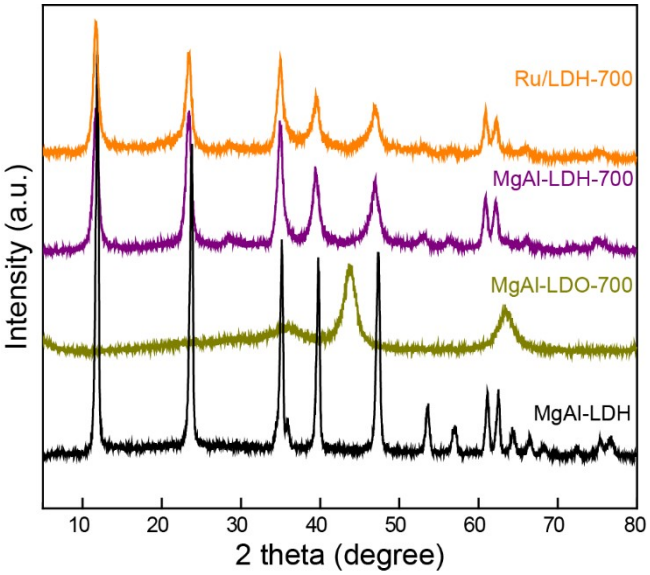


Fig. S3 The XRD patterns of various samples.

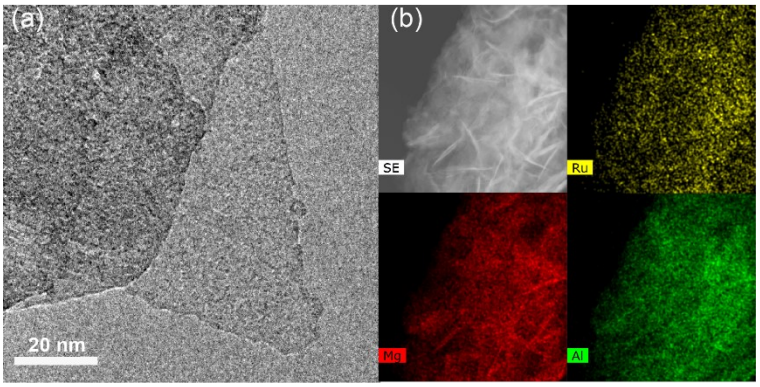


Fig. S4 (a) TEM image and (b) EDX mappings of Ru/LDH-700 catalyst.

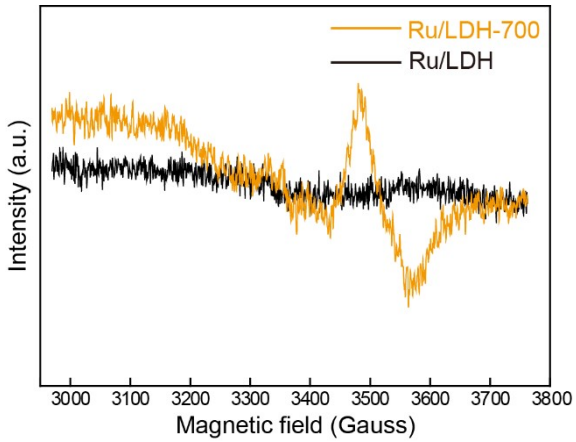


Fig. S5 EPR patterns of Ru/LDH and Ru/LDH-700 catalysts.

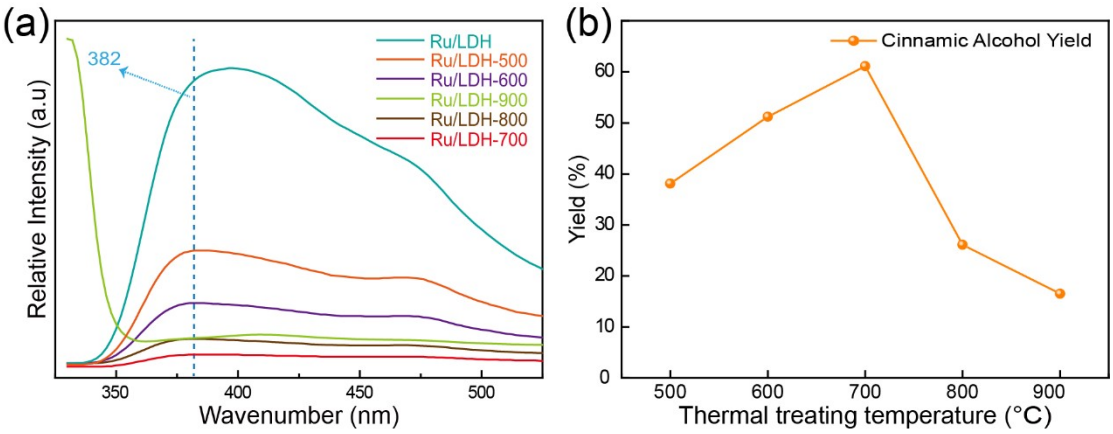


Fig. S6 (a) The PL spectra and (b) Effect of calcination temperatures on the yield of cinnamyl alcohol.

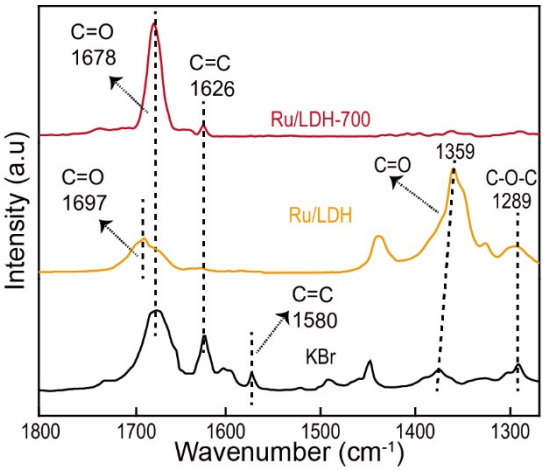


Fig. S7 DRIFTS of cinnamaldehyde adsorbed on KBr, Ru/LDH and Ru/LDH-700.

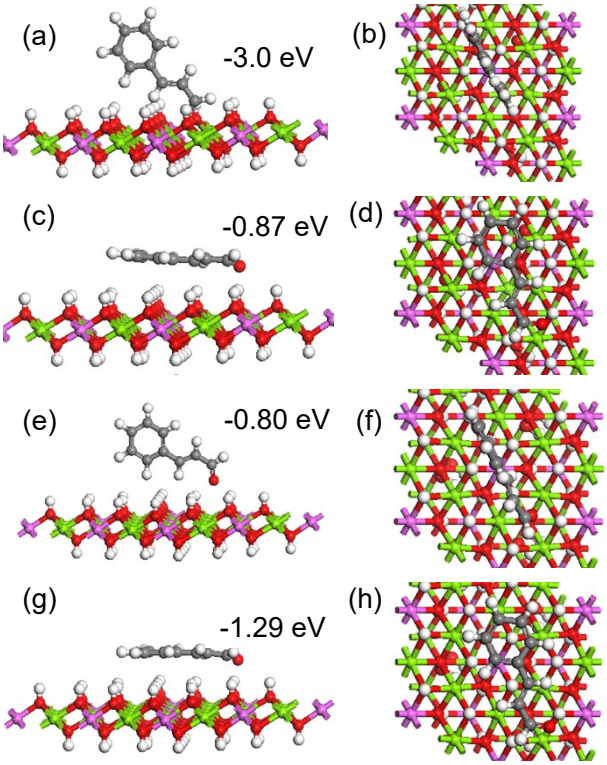


Fig. S8 The optimized structure for adsorption of cinnamaldehyde molecule using –C=O (a, b) or –C=C group (c, d) on MgAl-LDH-700. The optimized structure for adsorption of cinnamaldehyde molecule using –C=O (e, f) or –C=C group (g, h) on MgAl-LDH catalyst. Atom coloring: Mg, purple; Al, green; O, red; H, white; C, black.

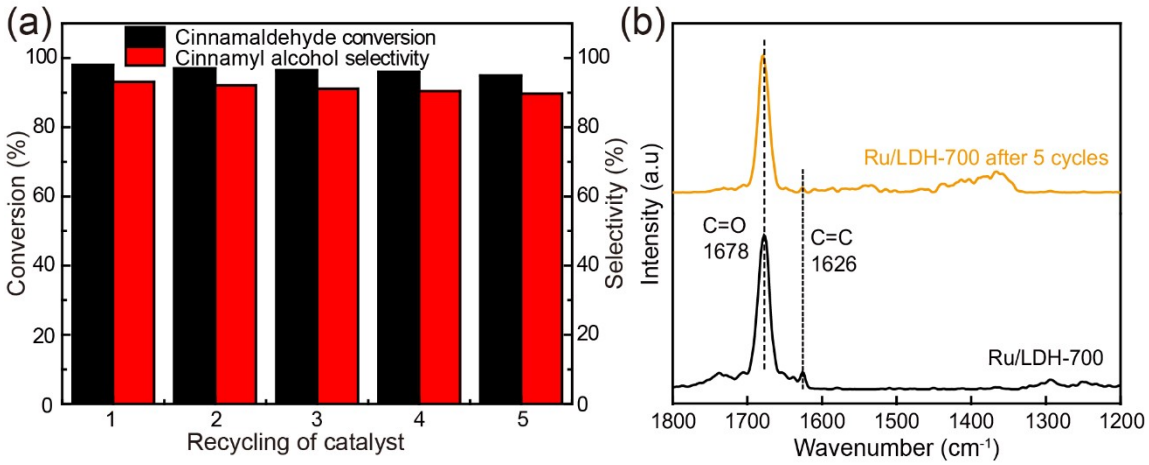


Fig. S9 (a) Recyclability in selective hydrogenation of cinnamaldehyde over Ru/LDH-700 catalyst and (b) DRIFTS of cinnamaldehyde adsorbed on fresh and used Ru/LDH-700 photocatalyst.

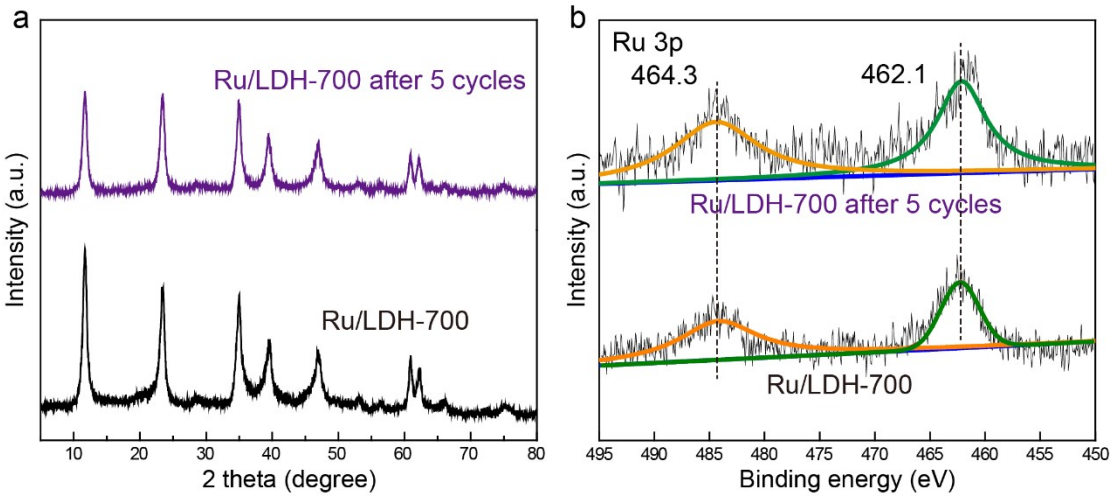


Fig. S10 (a) XRD patterns and (b) XPS spectra of the fresh and used Ru/LDH-700 photocatalyst.

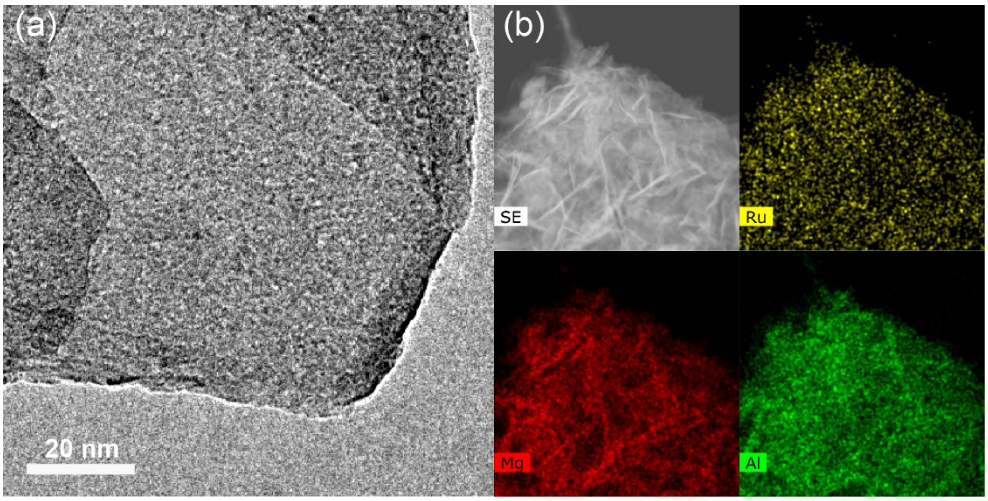


Fig. S11 TEM image (a) and EDX mappings (b) of Ru/LDH-700 photocatalyst used for five cycles.

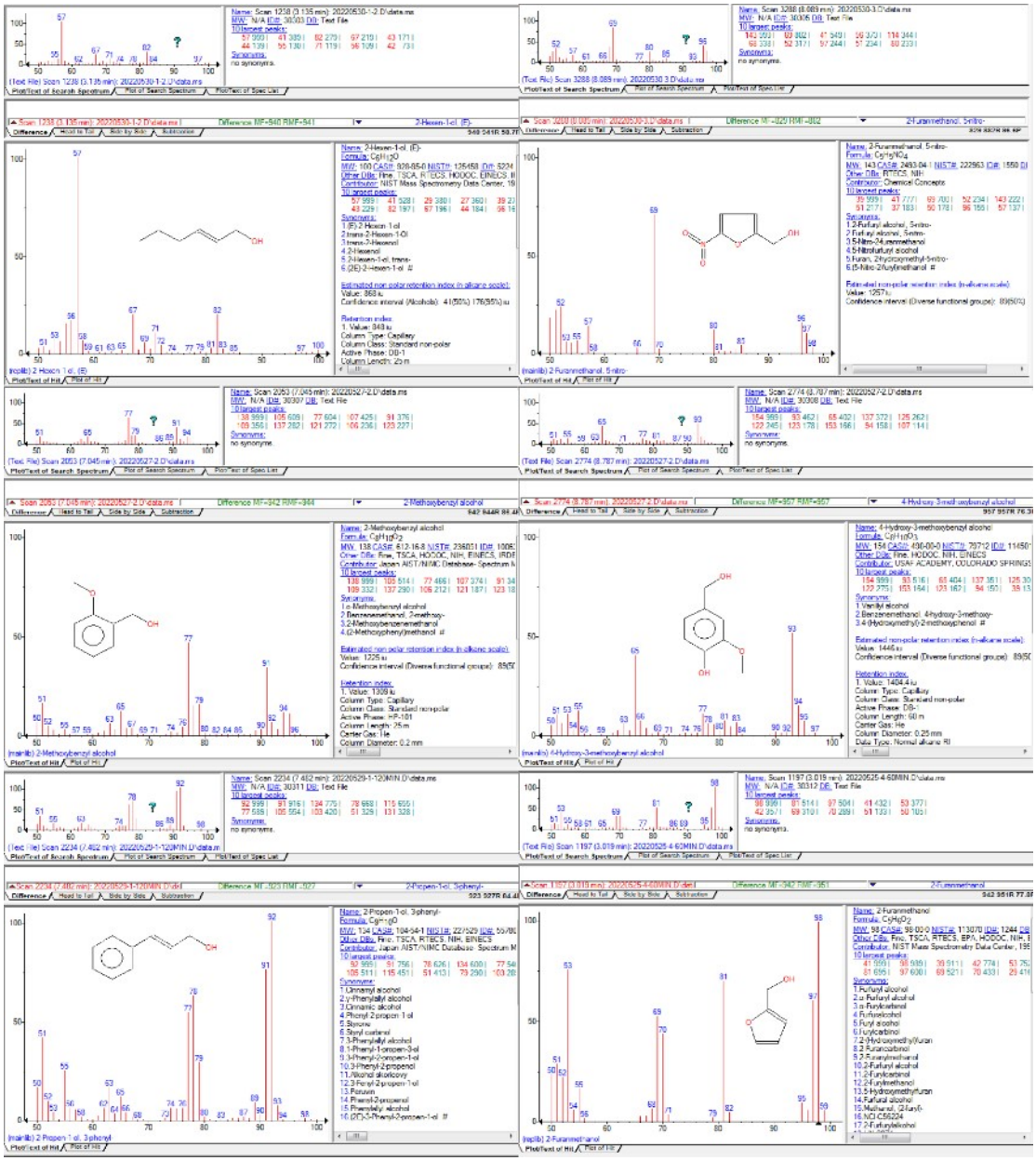


Fig. S12 Mass spectrometry data of various reaction products.

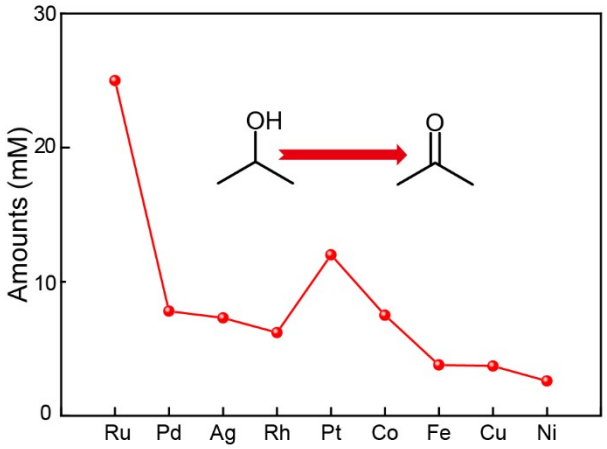


Fig. S13 Comparison of isopropanol activation ability of various catalysts.

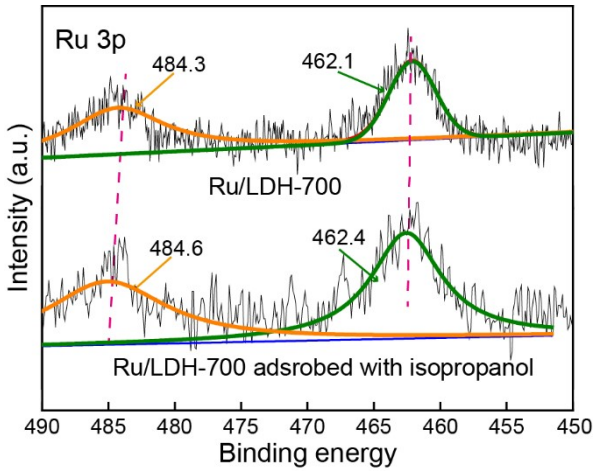


Fig. S14 Ru 3*p* XPS spectra of Ru/LDH-700 and Ru/LDH-700 after isopropyl alcohol adsorption.

Table S1 Effect of Ru loadings on the cinnamaldehyde hydrogenation[a]

Entry	Sample	Ru loading (wt%)[b]	Incident light	Conv. (%)	Sel. (%)
1	LDH-700	0	Visible	2.4	91.6
2	LDH-700	0	Dark	1.2	92.8
3	1.9 wt% Ru/LDH-700	1.9	Visible	4.7	91.4
4	1.9 wt% Ru/LDH-700	1.9	Dark	1.6	92.1
5	3.2 wt% Ru/LDH-700	3.2	Visible	43.7	91.9
6	3.2 wt% Ru/LDH-700	3.2	Dark	17.6	92.7
7	4.3 wt% Ru/LDH-700	4.3	Visible	67.1	91.6
8	4.3 wt% Ru/LDH-700	4.3	Dark	24.3	93.4
9	6.2 wt% Ru/LDH-700	6.2	Visible	71.5	90.7
10	6.2 wt% Ru/LDH-700	6.2	Dark	36.4	92.1

[a] Reaction conditions: 0.1 mmol reactant, 2 mL isopropyl alcohol, 80 °C, 20 mg catalyst, 4 h, Xe lamp irradiation (420–800 nm, 500 mW cm^{-2}), 1 atm Ar.

[b] Determined by inductively coupled plasma (ICP) analysis.

Table S2 Effect of catalyst usage on the cinnamaldehyde hydrogenation

Entry	catalyst amount (mg)	Incident light	Conversion (%)	Selectivity (%)
1	10	Visible	4.5	91.5
2	10	Dark	1.3	92.4
3	15	Visible	39.7	93.4
4	15	Dark	12.6	92.7
5	20	Visible	67.1	91.6
6	20	Dark	24.3	93.4
7	30	Visible	88.4	91.4
8	30	Dark	42.7	93.1

Reaction conditions: catalyst 4.3 wt% Ru/LDH-700, cinnamaldehyde 0.1 mmol, isopropyl alcohol 2 mL, 80 °C, 4 h, Xe lamp irradiation (420–800 nm, 500 mW cm^{-2}), 1 atm Ar.

Table S3 Effect of cinnamaldehyde concentration

Entry	Cinnamaldehyde concentration (mol L^{-1})	Incident light	Conversion (%)	Selectivity (%)
1	0.025	Visible	99.9	93.1
2	0.025	Dark	66.1	93.9
3	0.05	Visible	67.1	91.6
4	0.05	Dark	24.3	93.4
5	0.75	Visible	52.5	91.1
6	0.75	Dark	20.8	92.5
7	0.1	Visible	39.1	90.7
8	0.1	Dark	17.4	91.4

Reaction conditions: 20 mg 4.3 wt% Ru/LDH-700, 2 mL isopropyl alcohol, 80 °C, 4 h, Xe lamp irradiation (420–800 nm, 500 mW cm^{-2}), 1 atm Ar.

Table S4 Influence of reaction temperature

Entry	T (°C)	Incident light	Conv. (%)	Sel. (%)
1	60	Visible	7.2	94.2
2	60	Dark	1.8	93.5
3	80	Visible	38.4	91.9
4	80	Dark	13.1	93.6
5	100	Visible	97.5	91.1
6	100	Dark	51.8	92.5

Reaction conditions: 0.1 mmol reactant, 2 mL isopropyl alcohol, 20 mg 4.3 wt% Ru/LDH-700, 2 h, Xe lamp irradiation (420–800 nm, 500 mW cm^{-2}), 1 atm Ar.

Table S5 Textural properties of various samples.

Entry	Catalyst	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore size (nm)
1	MgAl-LDH	23.86	0.071	12.56
2	Ru/LDH	21.37	0.073	10.67
3	MgAl-LDH-700	91.51	0.50	20.77
4	Ru/LDH-700	84.77	0.43	19.17
5	MgAl-LDH-b	106.31	0.58	25.34
6	Ru/LDH-b	97.46	0.51	23.97

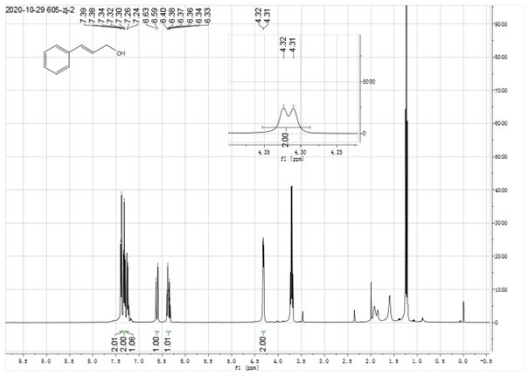
Table S6 Catalytic performance of Ru/LDH-b for cinnamaldehyde reduction

Entry	Catalyst	Incident light	Conv. (%)	Sel. (%)
1	4.3 wt% Ru/LDH-b	Visible	17.2	28.7
2	4.0 wt% Ru/LDH-b	Dark	8.1	31.4

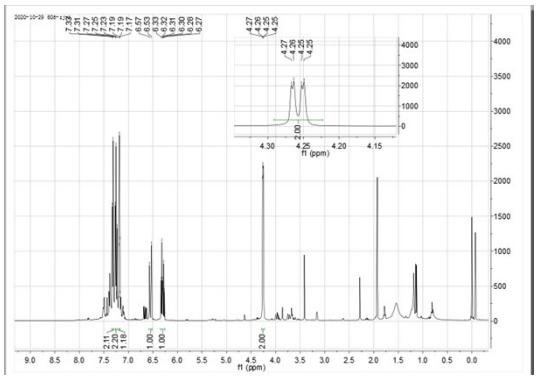
Reaction conditions: 0.1 mmol reactant, 2 mL isopropyl alcohol, 80 °C, 20 mg catalyst, 4 h, Xe lamp irradiation (420–800 nm, 500 mW cm^{-2}), 1 atm Ar.

Isotope labeling experiments

Reaction conditions: cinnamaldehyde 0.1 mmol, Ru/LDH-700 20 mg, 2-propanol–OD 2 mL, Ar 1 atm, 80 °C, 6 h, Xe lamp irradiation (420–800 nm, 500 mW cm^{-2}). The product was determined by 1H NMR and 13C NMR. The position of deuterium was confirmed by comparing the 1H NMR, and 13C NMR of cinnamic alcohol standard sample and the product.



Product of isotope labeling experiments:1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.38 (d, J = 4.0 Hz, 2H), 7.32 (t, J = 16.0 Hz, 2H), 7.25 (d, J = 24.0 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.36 (dt, J = 16.0 & 8 Hz, 1H), 4.31 (d, J = 4.0 Hz, 2H).



Cinnamic alcohol standard sample: 1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.32 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H), 6.36 (dt, J = 16.0 & 4 Hz, 1H), 4.26 (dd, J = 8.0 & 4.0 Hz, 2H).