Electronic supplementary information (ESI) for

"Release and catch" catalysis by tungstate species for the oxidative cleavage of olefins

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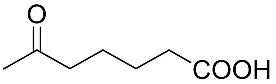
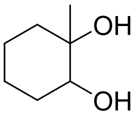
Data of oxidized products

6-Oxo-heptanoic acid (2a) (CAS No. 3128-07-2)[S1,S2]



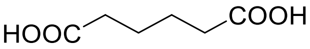
GC (InertCap FFAP capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (250 °C, 6 min), progress rate (10 °C·min^{-1}), injection temperature (250 °C), detection temperature (250 °C), retention time (18.6 min). MS (EI): *m/z* (%): 144 (1) [M^+], 126 (35), 111 (10), 101 (32), 98 (26), 84 (25), 83 (25), 73 (30), 71 (16), 69 (14), 59 (21), 58 (97), 57 (10), 56 (25), 55 (100). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.58-1.68 (m, 4H), 2.16 (s, 3H), 2.33-2.42 (m, 2H), 2.43-2.54 (m, 2H), 7.35-9.38 (brs, 1H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, TMS): δ 23.1, 24.1, 30.0, 33.8, 43.3, 179.2, 209.3.

1-Methyl-1,2-cyclohexanediol (4a) (CAS No. 6296-84-0)[S1,S3]



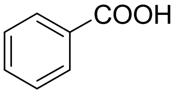
GC (InertCap FFAP capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (250 °C, 6 min), progress rate (10 °C·min^{-1}), injection temperature (250 °C), detection temperature (250 °C), retention time (12.7 min). MS (EI): *m/z* (%): 130 (7) [M^+], 112 (22), 97 (26), 84 (16), 83 (12), 71 (100), 70 (47), 69 (23), 68 (10), 58 (43), 57 (26), 56 (12), 55 (24).

Adipic acid (2b) (CAS No. 124-04-9)[S1,S4]



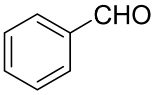
GC (InertCap FFAP capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (40 °C, 3 min), final column temp. (250 °C, 20 min), progress rate (10 °C·min^{-1}), injection temperature (250 °C), detection temperature (250 °C), retention time (34.2 min). MS (EI): *m*/*z* (%): 128 (5), 100 (100), 87 (30), 82 (13), 73 (25), 69 (34), 60 (39), 58 (11), 56 (11), 55 (56), 54 (14).

Benzoic acid (2c) (CAS No. 65-85-0)[S1,S4,S5]



GC (InertCap FFAP capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (250 °C, 6 min), progress rate (10 °C·min^{-1}), injection temperature (250 °C), detection temperature (250 °C), retention time (17.7 min). MS (EI): *m*/*z* (%): 122 (84) [M^+], 105 (100), 77 (76), 51 (34), 50 (20).

Benzaldehyde (CAS No. 100-52-7)[S1,S4,S6]



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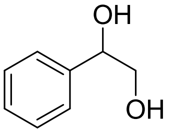
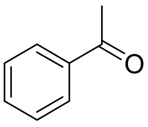
1-Phenylethane-1,2-diol (CAS No. 93-56-1)[S1,S4,S6]



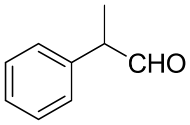
GC (InertCap FFAP capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (250 °C, 6 min), progress rate (10 °C·min^{-1}), injection temperature (250 °C), detection temperature (250 °C), retention time (18.7 min). MS (EI): *m*/*z* (%): 138 (2) [M^+], 120 (21), 107 (37), 106 (30), 105 (35), 104 (12), 92 (26), 91 (100), 79 (32), 78 (16), 77 (60), 65 (25), 63 (12), 51 (34), 50 (18).

Acetophenone (2d) (CAS No. 98-86-2)[S1,S4,S7]



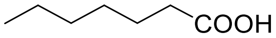
GC (InertCap 5 capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (280 °C, 8 min), progress rate (10 °C·min^{-1}), injection temperature (280 °C), detection temperature (280 °C), retention time (5.6 min). MS (EI): *m*/*z* (%): 120 (34) [M^+], 105 (100), 77 (79), 51 (28), 50 (11).

2-Phenylpropionaldehyde (CAS No. 93-53-8)[S1,S4,S8]



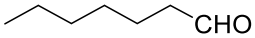
GC (InertCap 5 capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (280 °C, 8 min), progress rate (10 °C·min^{-1}), injection temperature (280 °C), detection temperature (280 °C), retention time (6.1 min). MS (EI): *m*/*z* (%): 134 (12) [M^+], 106 (11), 105 (100), 103 (15), 79 (23), 77 (21), 51 (10).

Heptanoic acid (2e) (CAS No. 111-14-8)[S1,S4,S9]



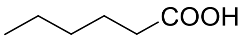
GC (InertCap FFAP capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (250 °C, 6 min), progress rate (10 °C·min^{-1}), injection temperature (250 °C), detection temperature (250 °C), retention time (12.9 min). MS (EI): *m*/*z* (%): 130 (0.2) [M^+], 101 (7), 87 (24), 73 (50), 71 (33), 70 (17), 61 (12), 60 (100), 55 (29).

Heptanal (CAS No. 111-71-7)[S1,S4,S10]



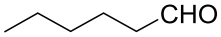
GC (InertCap FFAP capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (250 °C, 6 min), progress rate (10 °C·min^{-1}), injection temperature (250 °C), detection temperature (250 °C), retention time (3.8 min). MS (EI): *m*/*z* (%): 114 (1) [M^+], 96 (14), 86 (18), 81 (28), 72 (12), 71 (30), 70 (100), 68 (19), 67 (11), 57 (55), 55 (64).

Hexanoic acid (2f) (CAS No. 142-62-1)[S1,S4,S11]



GC (InertCap FFAP capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (250 °C, 6 min), progress rate (10 °C·min^{-1}), injection temperature (250 °C), detection temperature (250 °C), retention time (11.8 min). MS (EI): *m*/*z* (%): 87 (15), 73 (49), 61 (10), 60 (100), 57 (10), 56 (11), 55 (15).

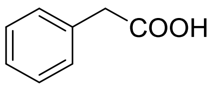
Hexanal (CAS No. 66-25-1)[S1,S4,S12]



GC (InertCap FFAP capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (250 °C, 6 min), progress rate (10 °C·min^{-1}), injection temperature (250 °C), detection temperature

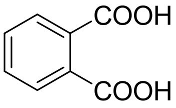
(250 °C), retention time (2.9 min). MS (EI): *m*/*z* (%): 100 (0.5) [M^+], 82 (21), 72 (27), 71 (11), 67 (15), 58 (12), 57 (66), 56 (100), 55 (22).

Phenylacetic acid (CAS No. 103-82-2)[S1,S13]



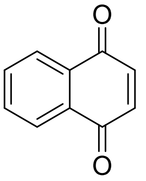
GC (InertCap FFAP capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (250 °C, 6 min), progress rate (10 °C·min^{-1}), injection temperature (250 °C), detection temperature (250 °C), retention time (18.7 min). MS (EI): *m*/*z* (%): 136 (35) [M^+], 92 (21), 91 (100), 65 (18).

Phthalic acid (2h) (CAS No. 88-99-3)



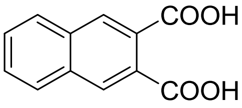
HPLC (Inertsil ODS-3 column, 4.6 mm × 250 mm, GL Science Inc.): eluent (CH_3OH/H_2O, 9/1 v/v, 0.4 mL·min^{-1}), oven temp. (40 °C), retention time (7.7 min).

1,4-Naphthoquinone (CAS No. 130-15-4)



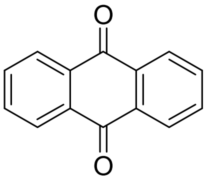
HPLC (Inertsil ODS-3 column, 4.6 mm × 250 mm, GL Science Inc.): eluent (CH_3OH/H_2O, 9/1 v/v, 0.4 mL·min^{-1}), oven temp. (40 °C), retention time (9.3 min).

2,3-Naphthalenedicarboxylic acid (2i) (CAS No. 2169-87-1)



HPLC (Inertsil ODS-3 column, 4.6 mm × 250 mm, GL Science Inc.): eluent (CH_3OH/H_2O, 9/1 v/v, 0.4 mL·min^{-1}), oven temp. (40 °C), retention time (25.6 min).

Anthraquinone (CAS No. 84-65-1)[S1,S4,S14]



GC (InertCap 5 capillary column, 0.25 mm × 30 m, GL Science Inc.): initial column temp. (80 °C, 2 min), final column temp. (280 °C, 8 min), progress rate (10 °C·min^{-1}), injection temperature (280 °C), detection temperature (280 °C), retention time (20.1 min). MS (EI): *m*/*z* (%): 209 (17), 208 (96) [M^+], 207 (13), 181 (13), 180 (90), 153 (12), 152 (100), 151 (47), 150 (24), 126 (14), 77 (11), 76 (52), 75 (22), 74 (18), 63 (13), 50 (33).

Additional references

S1 Spectral data were obtained from Wiley Subscription Services, Inc. (US).

S2 F. Foubelo, F. Lloret and M. Yus, *Tetrahedron*, 1992, **48**, 9531.

S3 C. Döbler, G. M. Mehltretter, U. Sundermeier and M. Beller, *J. Am. Chem. Soc.*, 2000, **122**, 10289.

S4 SDBSWeb, http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, accessed January 2017).

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S9 S. Bernhardt, A. Metzger and P. Knochel, *Synthesis*, 2010, 3802.

S10 M. E. González-Núñez, R. Mello, A. Olmos, R. Acerete and G. Asensio, *J. Org. Chem.*, 2006, **71**, 1039.

S11 A. Botezatu, B. S. Kemp and G. J. Pickering, *Molecules*, 2016, **21**, 1238.

S12 J. K. Patra, G. Das and K.-H. Baek, *Molecules*, 2015, **20**, 12093.

S13 M. S. Gachet, O. Kunert, M. Kaiser, R. Brun, R. A. Muñoz, R. Bauer and W. Schühly, *J. Nat. Prod.*, 2010, **73**, 553.

S14 K. S. Jang, H. Y. Shin and D. Y. Chi, *Tetrahedron*, 2008, **64**, 5666.

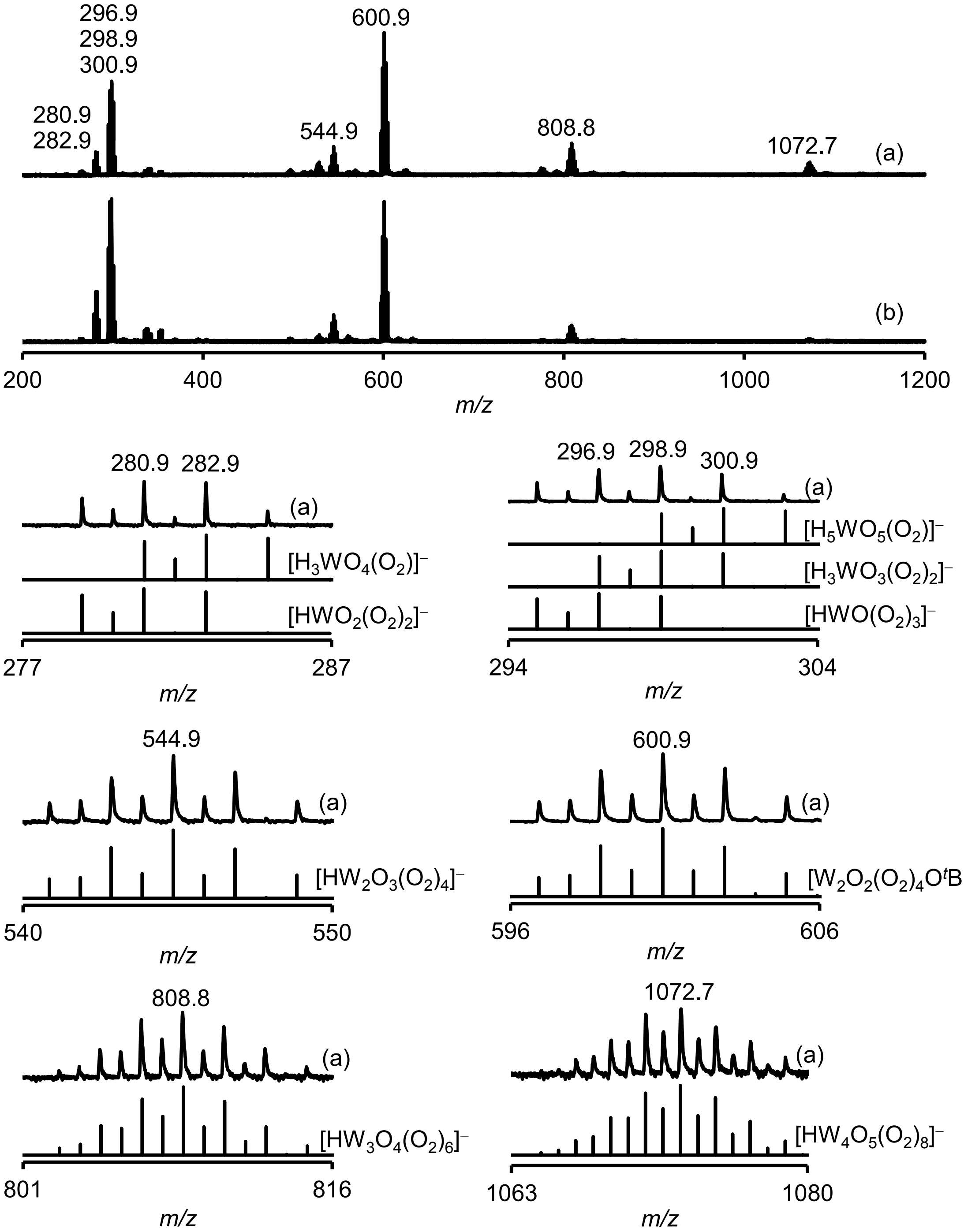


Fig. S1 CSI-mass spectra (negative-ion mode) of the reaction filtrates and their assignments. Reaction conditions: ^{t}BuOH (1.5 mL), 30% aqueous H_2O_2 (2.5 mmol), 80 °C, 1 h, (a) WO_3 (50 μmol), and (b) W/Zn–SnO_2 (100 mg). The signal sets at *m/z* 280.9, 282.9, 296.9, 298.9, 300.9, 544.9, 600.9, 808.8, and 1072.7 were assignable to $[HWO_2(O_2)_2]^-$, $[H_3WO_4(O_2)]^-$, $[HWO(O_2)_3]^-$, $[H_3WO_3(O_2)_2]^-$, $[H_5WO_5(O_2)]^-$, $[HW_2O_3(O_2)_4]^-$, $[W_2O_2(O_2)_4O^tBu]^-$, $[HW_3O_4(O_2)_6]^-$, and $[HW_4O_5(O_2)_8]^-$, respectively.

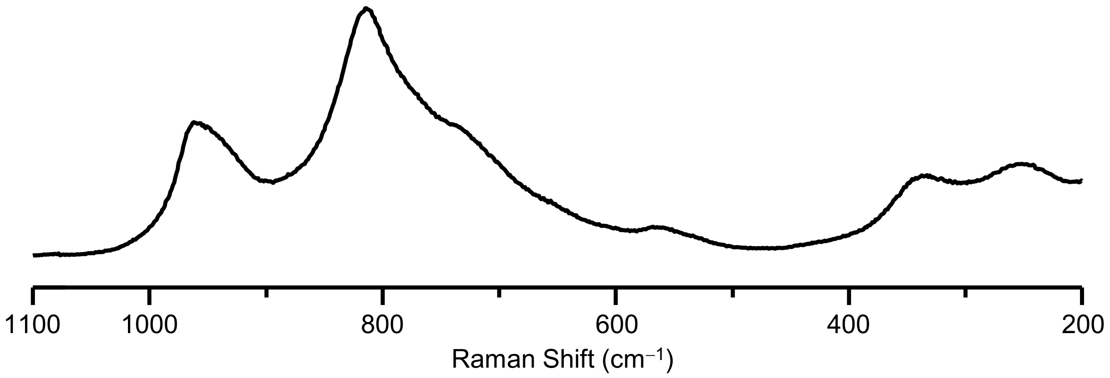


Fig. S2 Raman spectrum of the precipitate obtained after the reaction in Fig. 1 (see Fig. 1c).

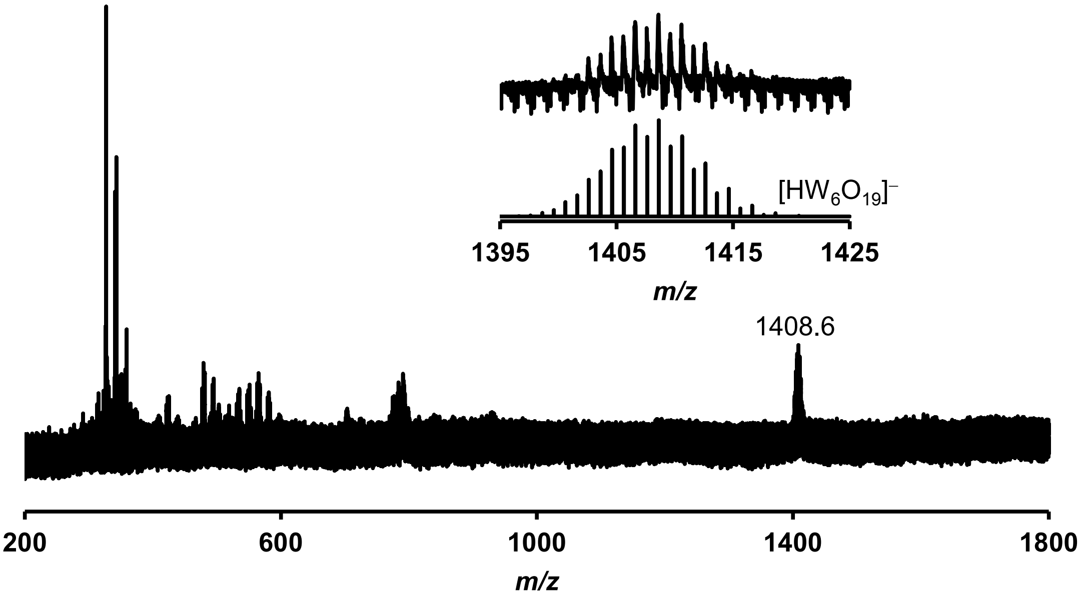


Fig. S3 CSI-mass spectrum (negative-ion mode) of the filtrate of the solution after the reaction for entry 2, Table 1. The signal set at *m/z* 1408.6 was assignable to $[HW_6O_{19}]^-$.

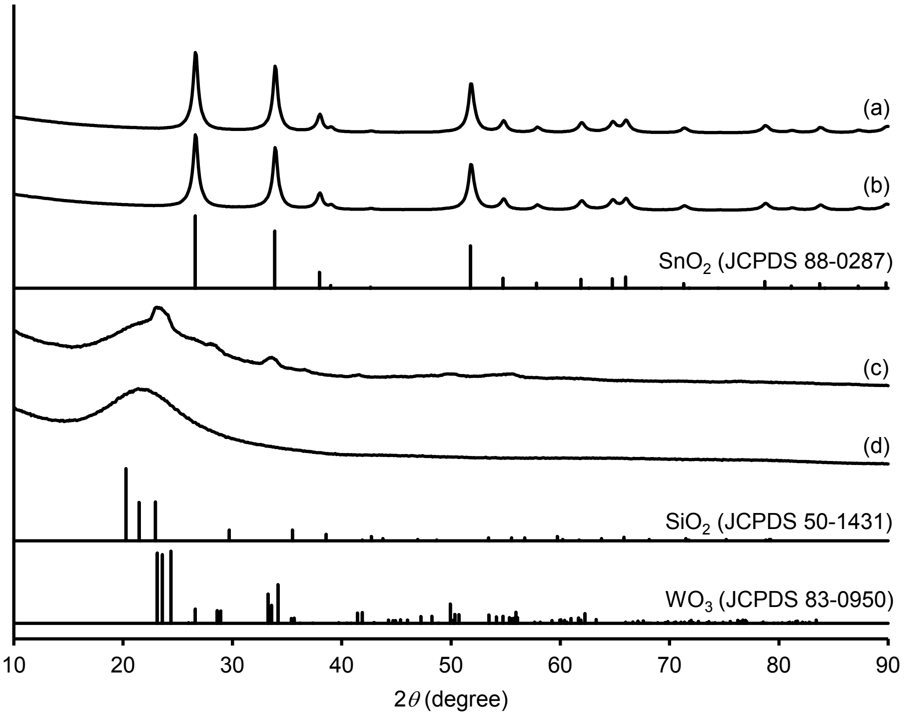


Fig. S4 XRD patterns of (a) W/SnO$_2$, (b) SnO$_2$, and (c) W/SiO$_2$ and (d) SiO$_2$.

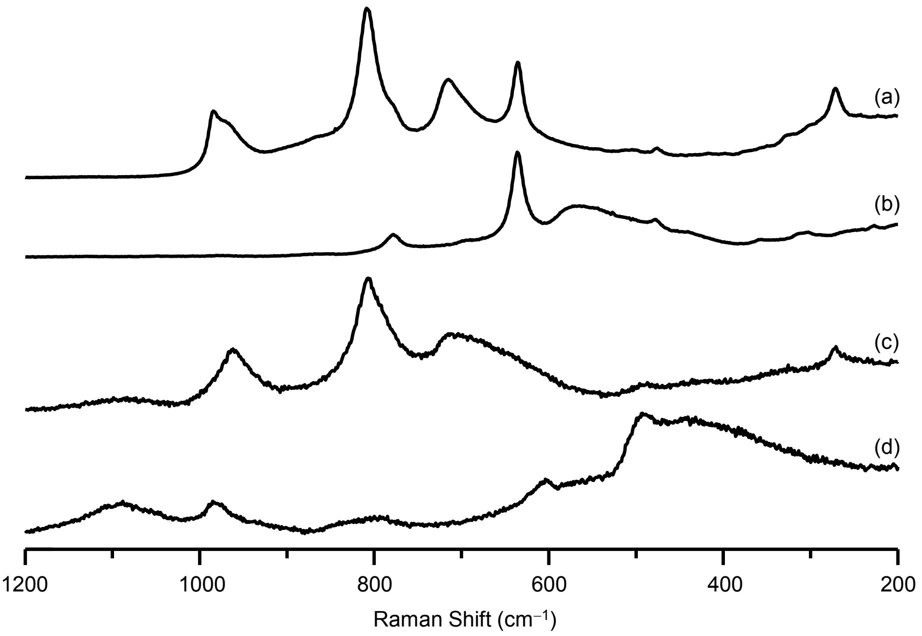


Fig. S5 Raman spectra of (a) W/SnO$_2$, (b) SnO$_2$, and (c) W/SiO$_2$ and (d) SiO$_2$.

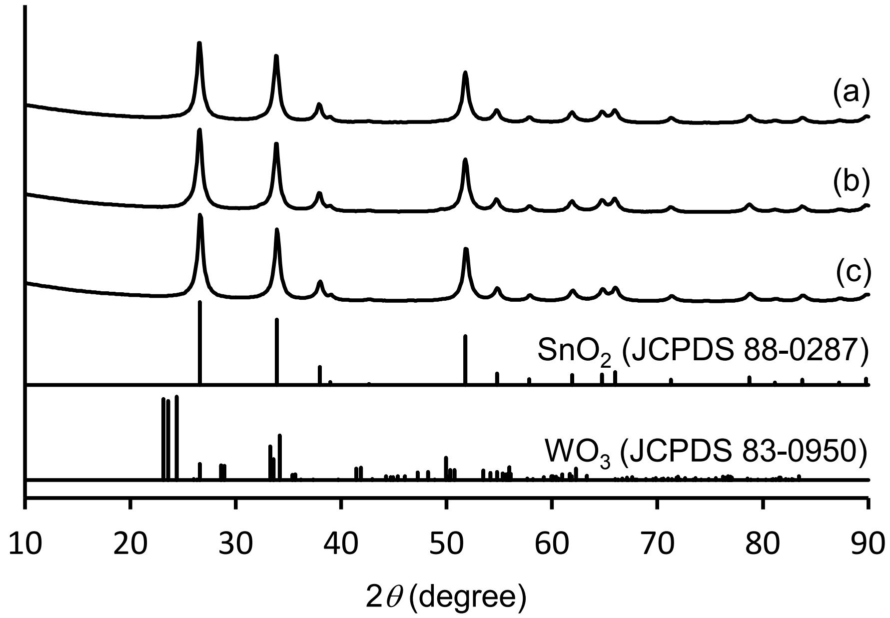


Fig. S6 XRD patterns of (a) W/Zn–SnO_2, (b) Zn–SnO_2, and (c) SnO_2.

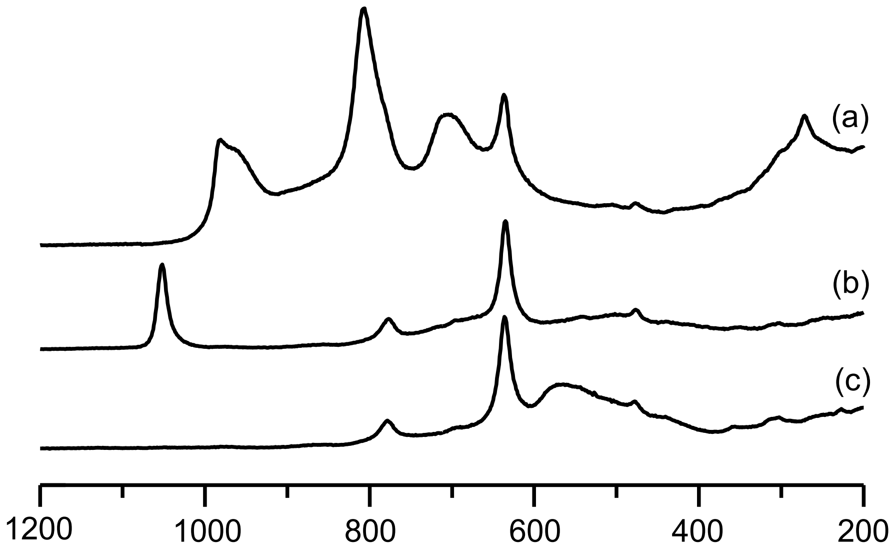


Fig. S7 Raman spectra of (a) W/Zn–SnO_2, (b) Zn–SnO_2, and (c) SnO_2. The spectrum of Zn–SnO_2 has a signal at 1050 cm^{-1} which is assignable to the $\nu(NO_3^-)$ vibration derived from $Zn(NO_3)\cdot 6H_2O$.

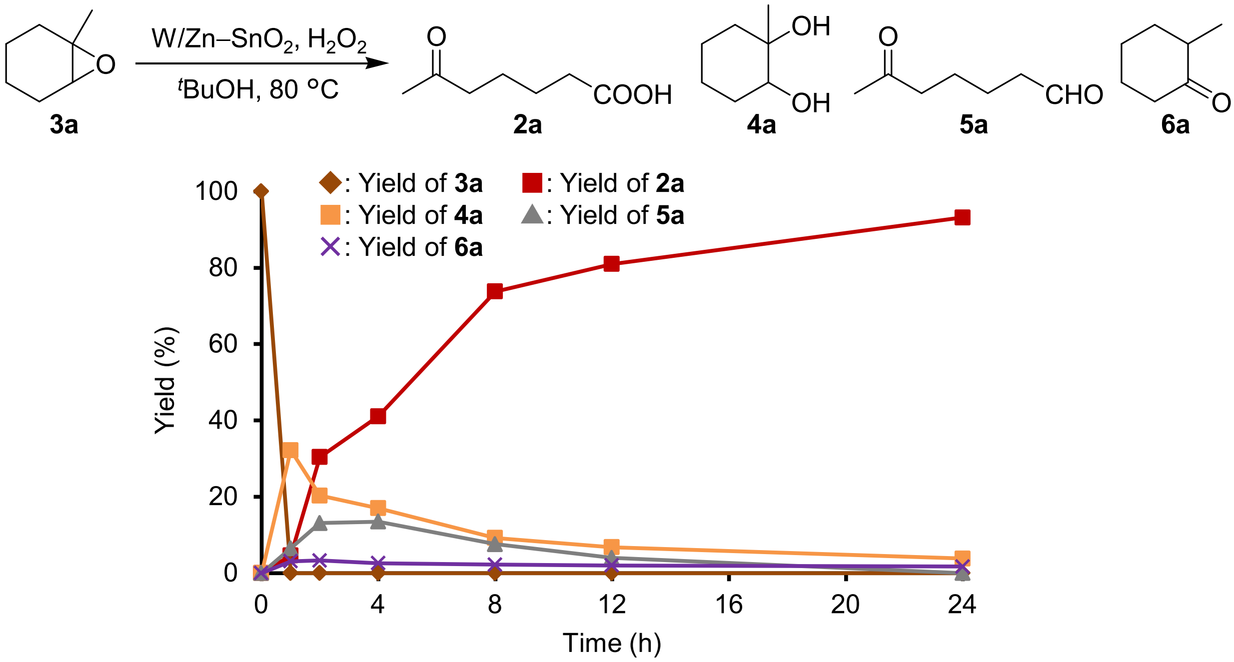


Fig. S8 Reaction profile for the W/Zn–SnO$_2$-catalyzed oxidative cleavage of **3a** into **2a** using H_2O_2 as the oxidant. Reaction conditions: **3a** (0.5 mmol), W/Zn–SnO$_2$ (100 mg, W: 10 mol% with respect to **3a**), 30% aqueous H_2O_2 (2.0 mmol), ^{t}BuOH (1.5 mL), H_2O (2.2 mmol), and 80 °C. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard.

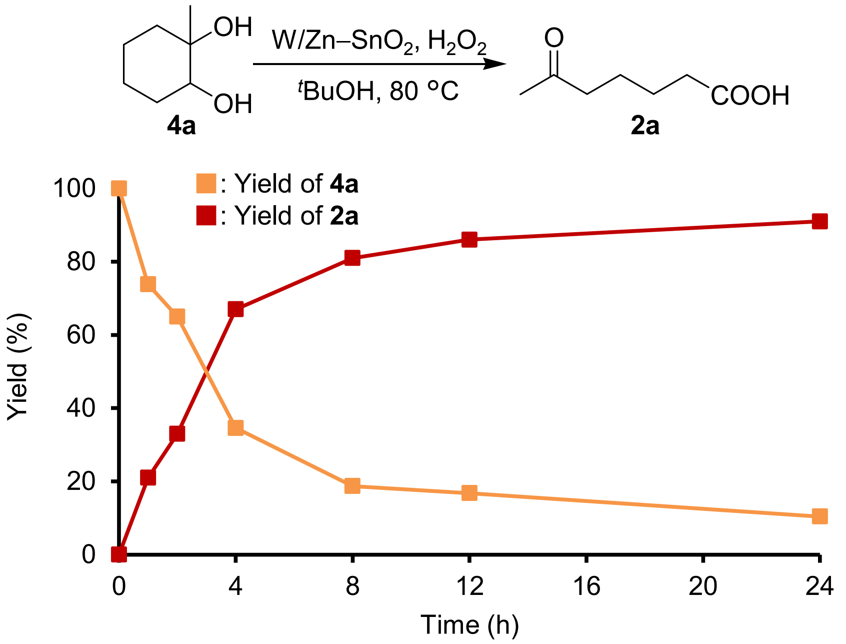


Fig. S9 Reaction profile for the W/Zn–SnO$_2$-catalyzed oxidative cleavage of **4a** into **2a** using H_2O_2 as the oxidant. Reaction conditions: **4a** (0.5 mmol), W/Zn–SnO$_2$ (100 mg, W: 10 mol% with respect to **3a**), 30% aqueous H_2O_2 (2.0 mmol), ^{t}BuOH (1.5 mL), H_2O (2.2 mmol), and 80 °C. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard.

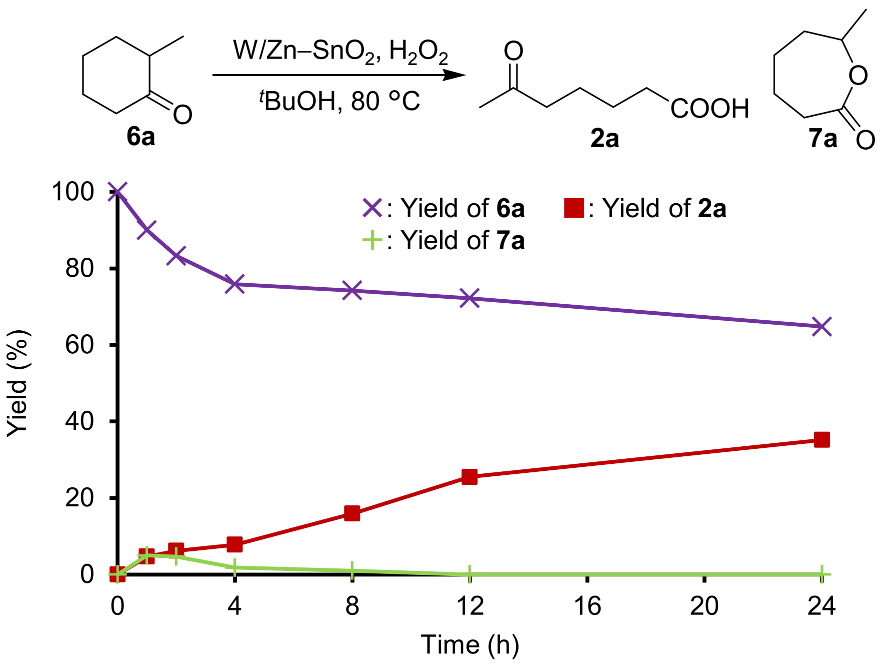


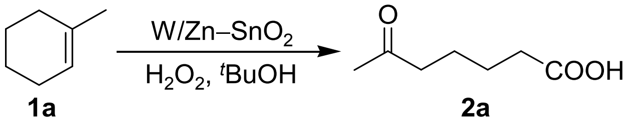
Fig. S10 Reaction profile for the W/Zn–SnO$_2$-catalyzed oxidative cleavage of **6a** into **2a** using H_2O_2 as the oxidant. Reaction conditions: **2a** (0.5 mmol), W/Zn–SnO$_2$ (100 mg, W: 10 mol% with respect to **3a**), 30% aqueous H_2O_2 (2.0 mmol), ^{t}BuOH (1.5 mL), H_2O (2.2 mmol), and 80 °C. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard.

Table S1 Decomposition of H_2O_2 in the presence of various supports[a]

Entry	Support	Decomposition of H_2O_2 (%)
1	SnO_2	4
2	SiO_2	3
3	Al_2O_3	60
4	ZrO_2	>99
5	TiO_2	>99
6	ZnO	>99
7	MgO	>99

[a] Reaction conditions: Support (100 mg), 30% aqueous H_2O_2 (2.5 mmol), *t*BuOH (1.5 mL), 80 °C, 1 h. The amounts of remaining H_2O_2 were determined by $Ce^{3+/4+}$ titration.

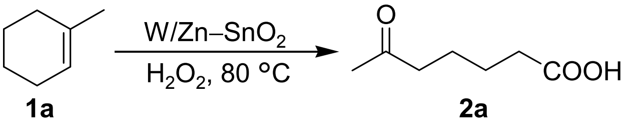
Table S2 Effect of reaction temperatures on the W/Zn–SnO_2-catalyzed oxidative cleavage of **1a** with H_2O_2[a]



Entry	Temperature (°C)	Yield (%)	Tungsten leaching (%)
1	60	34	8
2	70	65	3
3	80	83	<1
4	90	75	<1

[a] Reaction conditions: **1a** (0.5 mmol), W/Zn–SnO_2 (W: 9.1 wt%, Zn: 0.7 wt%, 125 mg), 30% aqueous H_2O_2 (2.5 mmol), *t*BuOH (1.5 mL), 24 h. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard. Tungsten leaching was determined by ICP-AES analysis.

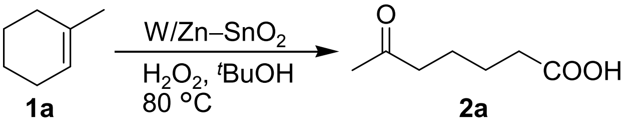
Table S3 Effect of solvents on the W/Zn–SnO_2-catalyzed oxidative cleavage of **1a** with H_2O_2[a]



Entry	Solvent	Yield (%)	Tungsten leaching (%)
1	^{t}BuOH	83	<1
2	CH_3CN	85	2
3	EtOAc	47	<1
4	DMC	35	<1
5	H_2O	30	6

[a] Reaction conditions: **1a** (0.5 mmol), W/Zn–SnO_2 (W: 9.1 wt%, Zn: 0.7 wt%, 125 mg), 30% aqueous H_2O_2 (2.5 mmol), solvent (1.5 mL), 80 °C, 24 h. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard. Tungsten leaching was determined by ICP-AES analysis.

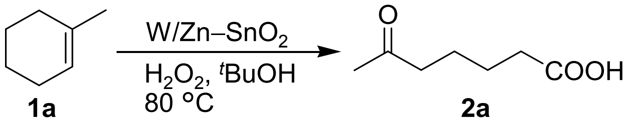
Table S4 Effect of the amounts of supported zinc species on the W/Zn–SnO_2-catalyzed oxidative cleavage of **1a** with H_2O_2[a]



Entry	Zn loading (wt%)	Yield (%)	Tungsten leaching (%)
1	0	62	<1
2	0.4	65	<1
3	0.7	83	<1
4	0.9	87	<1
5	1.1	83	<1
6	1.5	30	<1

[a] Reaction conditions: **1a** (0.5 mmol), W/Zn–SnO_2 (W: 9.1 wt%, 125 mg), 30% aqueous H_2O_2 (2.5 mmol), ^{t}BuOH (1.5 mL), 80 °C, 24 h. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard. Tungsten leaching was determined by ICP-AES analysis.

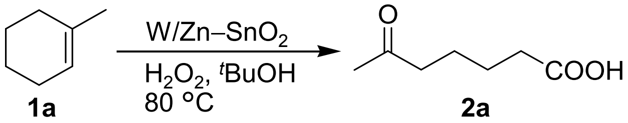
Table S5 Effect of the amounts of supported tungsten species on the W/Zn–SnO_2-catalyzed oxidative cleavage of **1a** with H_2O_2[a]



Entry	W loading (wt%)	Yield (%)	Tungsten leaching (%)
1	0	<1	–
2	3.3	58	<1
3	6.3	61	<1
4	7.7	70	<1
5	9.1	87	<1
6	10.4	81	1
7	11.7	81	1

[a] Reaction conditions: **1a** (0.5 mmol), W/Zn–SnO_2 (Zn: 0.9 wt%, 125 mg), 30% aqueous H_2O_2 (2.5 mmol), ^{t}BuOH (1.5 mL), 80 °C, 24 h. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard. Tungsten leaching was determined by ICP-AES analysis.

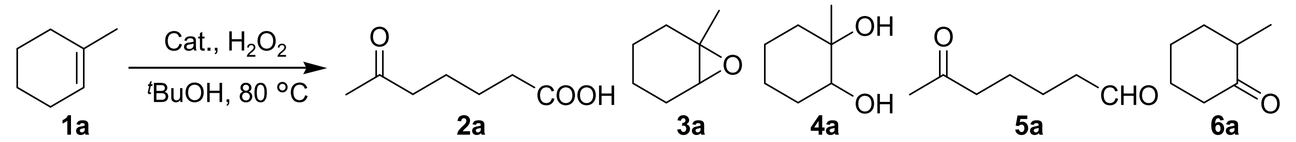
Table S6 Effect of the amounts of W/Zn–SnO_2 on the oxidative cleavage of **1a** with H_2O_2[a]



Entry	Amount of the catalyst (mg)	Yield (%)	Tungsten leaching (%)
1	0	<1	–
2	50	95	5
3	75	89	1
4	100	92	<1
5	125	87	<1
6	150	83	<1

[a] Reaction conditions: **1a** (0.5 mmol), W/Zn–SnO_2 (W: 9.1 wt%, Zn: 0.9 wt%), 30% aqueous H_2O_2 (2.5 mmol), ^{t}BuOH (1.5 mL), 80 °C, 24 h. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard. Tungsten leaching was determined by ICP-AES analysis.

Table S7 Detailed comparison of W/SnO_2 and W/Zn–SnO_2 for the oxidative cleavage reaction of **1a** into **2a**[a]



Entry	Cat.	Time (h)	Conv. (%)	Yield (%) 2a	3a	4a	5a	6a	TBHP (mmol)
1		0.5	88	4	2	20	5	8	0.11
2	W/SnO_2	4	>99	36	<1	15	10	10	0.38
3		24	>99	64	<1	10	<1	7	0.58
4		0.5	76	3	1	25	8	3	0.03
5	W/Zn–SnO_2	4	>99	44	<1	18	21	2	0.07
6		24	>99	92	<1	3	<1	<1	0.14

[a] Reaction conditions: **1a** (0.5 mmol), Catalyst (100 mg, W: 10 mol% with respect to **1a**), 30% aqueous H_2O_2 (2.5 mmol), ^{t}BuOH (1.5 mL), 80 °C. Yields were determined by GC analysis using *o*-dichlorobenzene as an internal standard.