iScience, Volume *24*

Supplemental information

Direct synthesis of *p*-methyl benzaldehyde from acetaldehyde via an organic amine-catalyzed dehydrogenation mechanism

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Figure S1. IR Spectra and *in situ* cell, related to Figure 2.

(A and B) CH_3CHO-IR spectra with THP-DPh-OTMS and THP as catalysts (conditions: 45 μmol CH_3CHO, $n_{(CH3CHO)}/n_{(THP\text{-}Ph\text{-}DOTMS)}/n_{(p\text{-}NO2\text{-}Ph\text{-}OH)}$ = 45:0.5:1.2, at 20 °C).

(C) IR difference spectra using THP as catalysts.

(D) Standard IR spectra of reactants, products, and catalysts.

(E) The liquid reaction cell used.

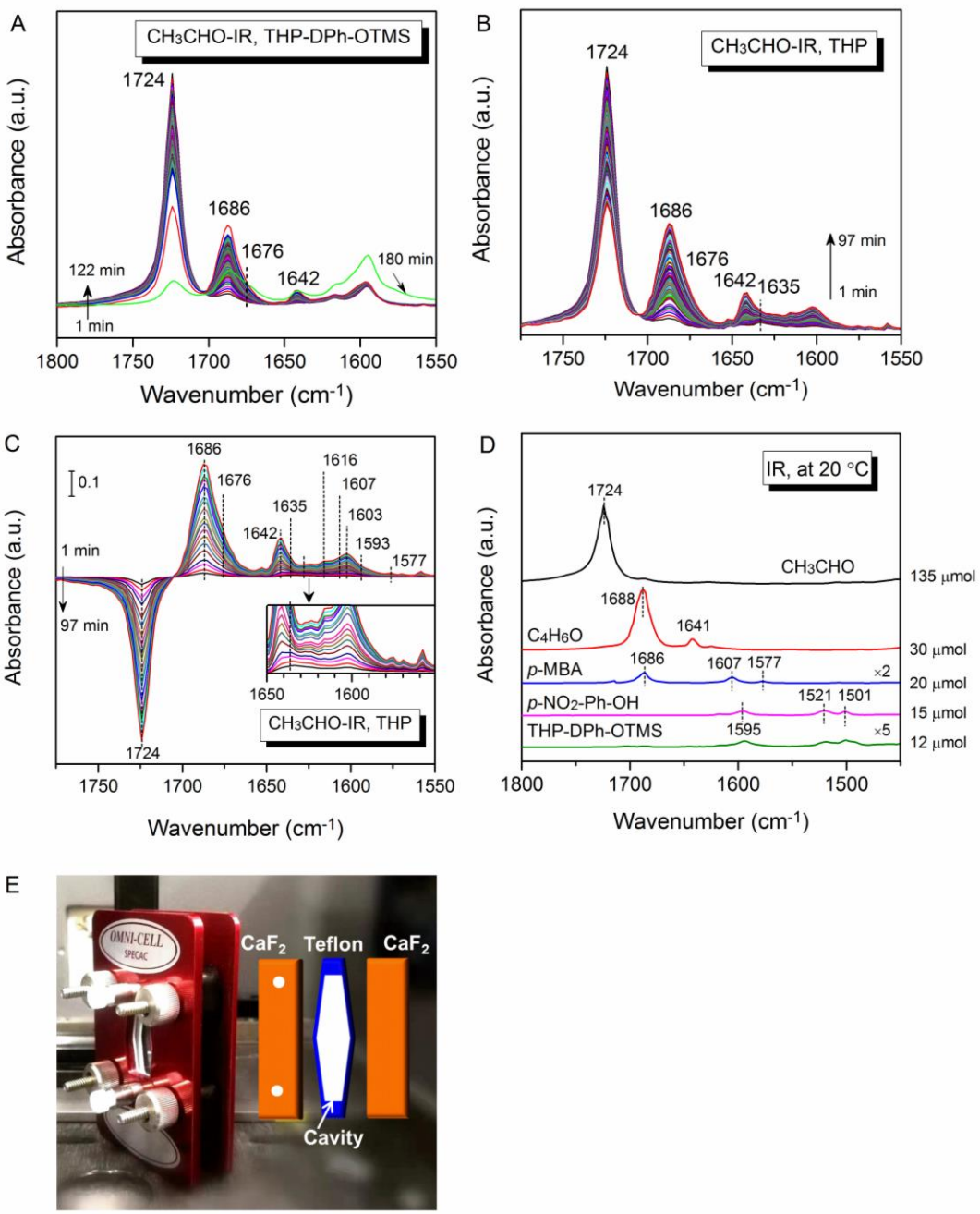

Figure S2. (A) H-NMR and (B) ^{13}C-NMR spectra of *p*-MBA, related to the STAR Methods.

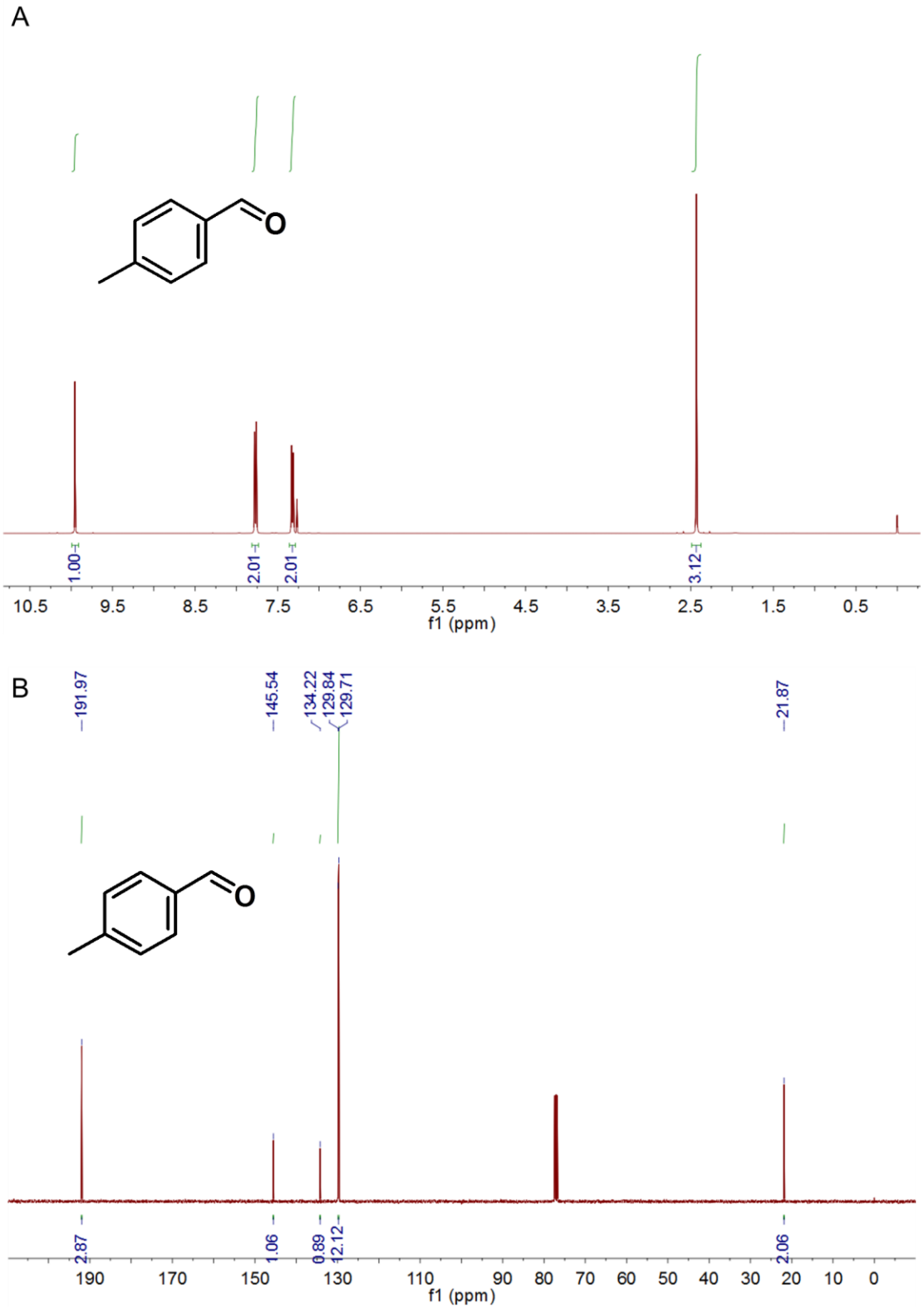

Figure S3. A H-NMR spectrum of THP-DPh-OTMS, related to the STAR Methods.

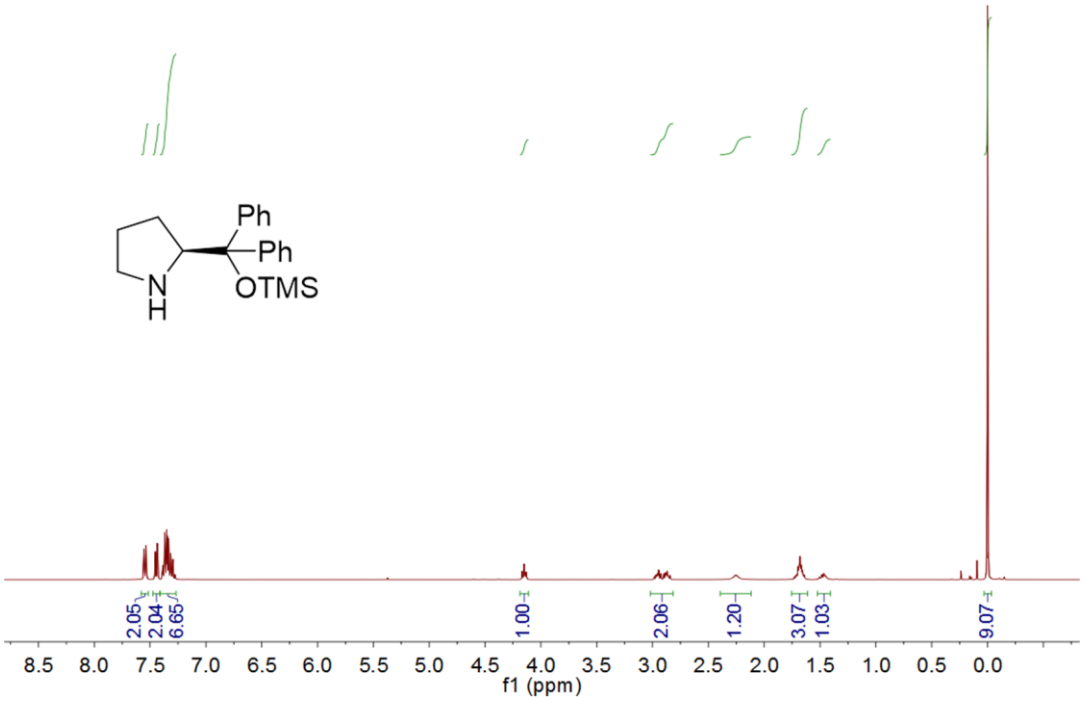

Figure S4. *In situ* H-NMR spectra using CH_3CHO as reactants at 20 °C, related to the STAR Methods (condition: 400 μmol CH_3CHO, 22 μmol THP-DPh-OTMS, and 45 μmol *p*-NO_2-Ph-OH in $CDCl_3$).

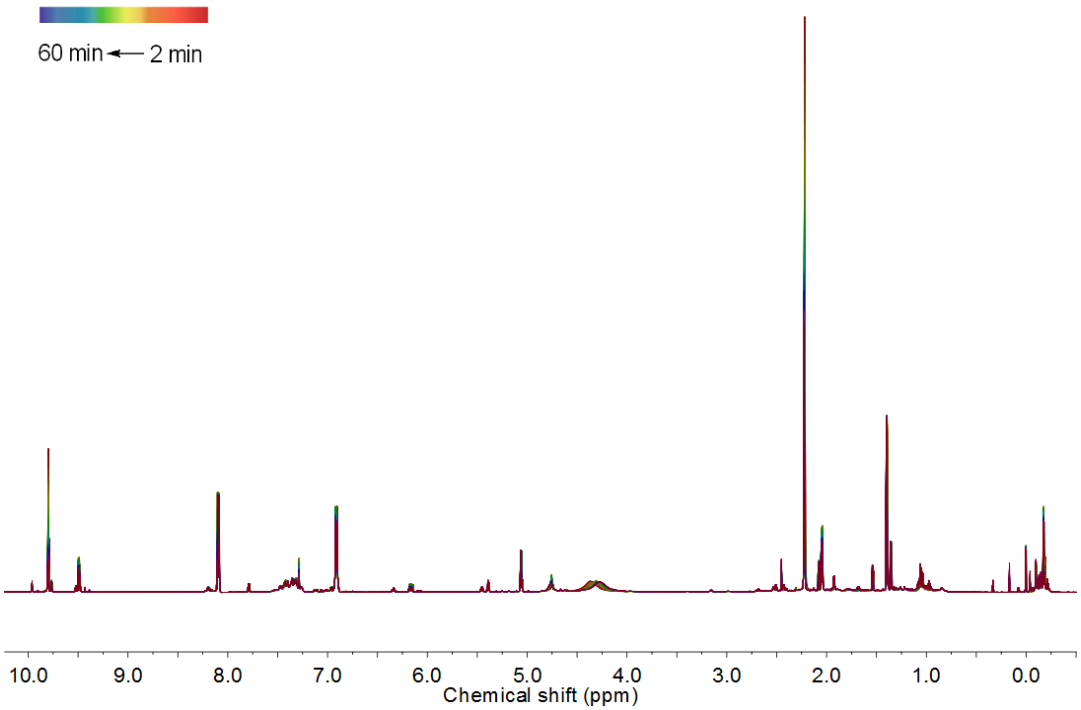

Figure S5. (A and B) Detailed *In situ* H-NMR spectra obtained from Figure S4, related to the STAR Methods. Panels inserted in A and B were the enlarged details.

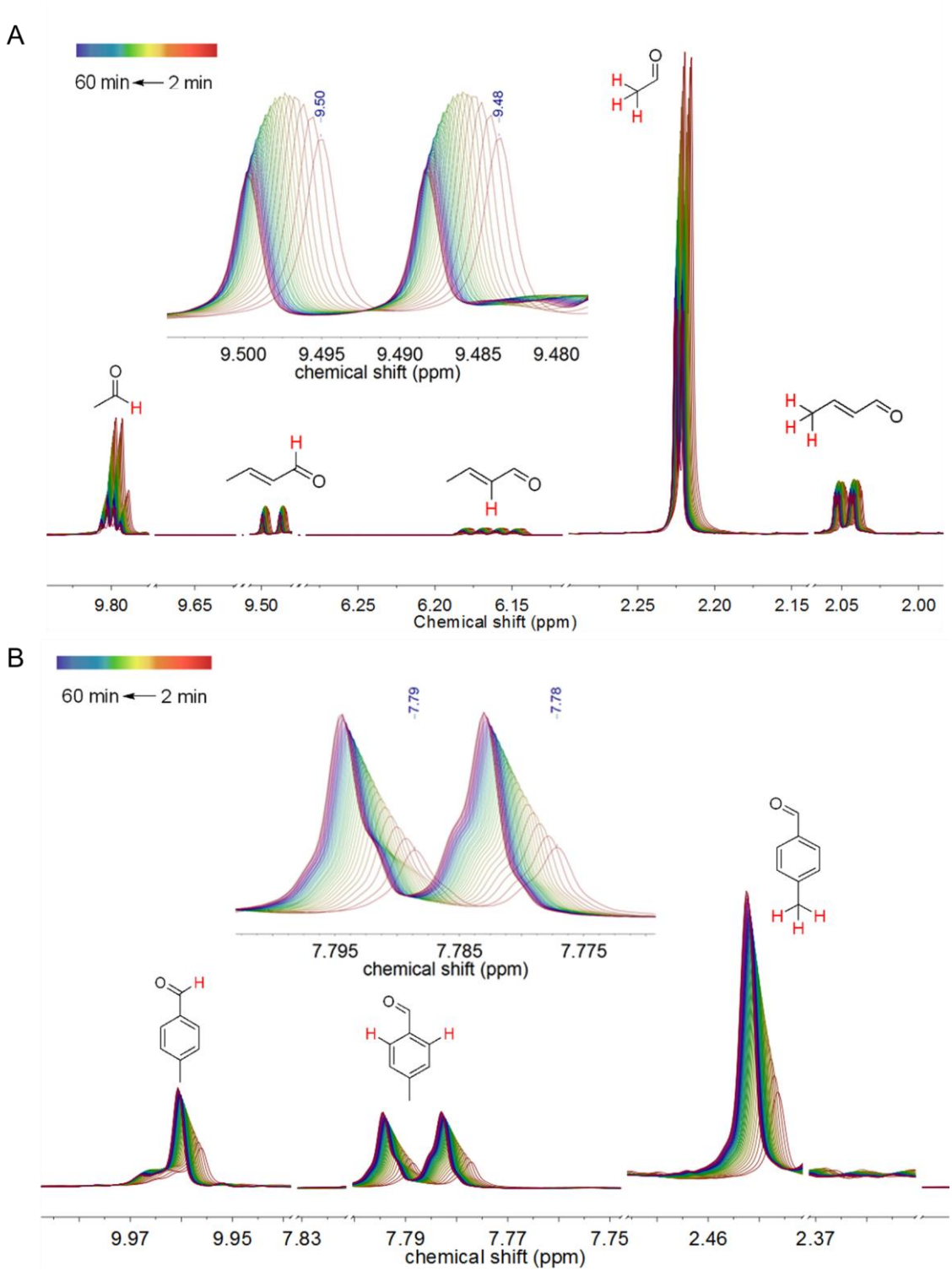

Figure S6. Effect of water amounts on product distributions with THP-DPh-OTMS, related to the STAR Methods (conditions: the amounts of water were varied in the range of 0~4 mmol).

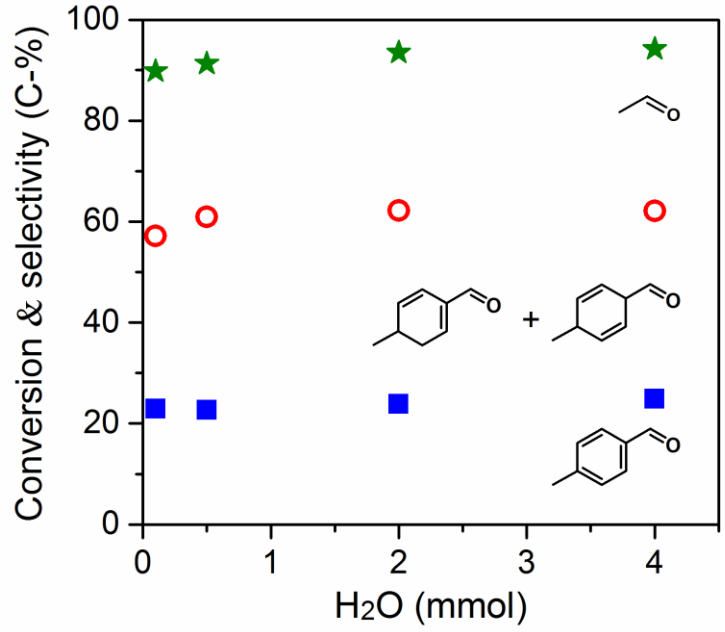

Figure S7. Detected fragment ions of ^{16}O- and ^{18}O-incorporated aldehydes marked in blue and red, respectively, related to the Scheme 2.

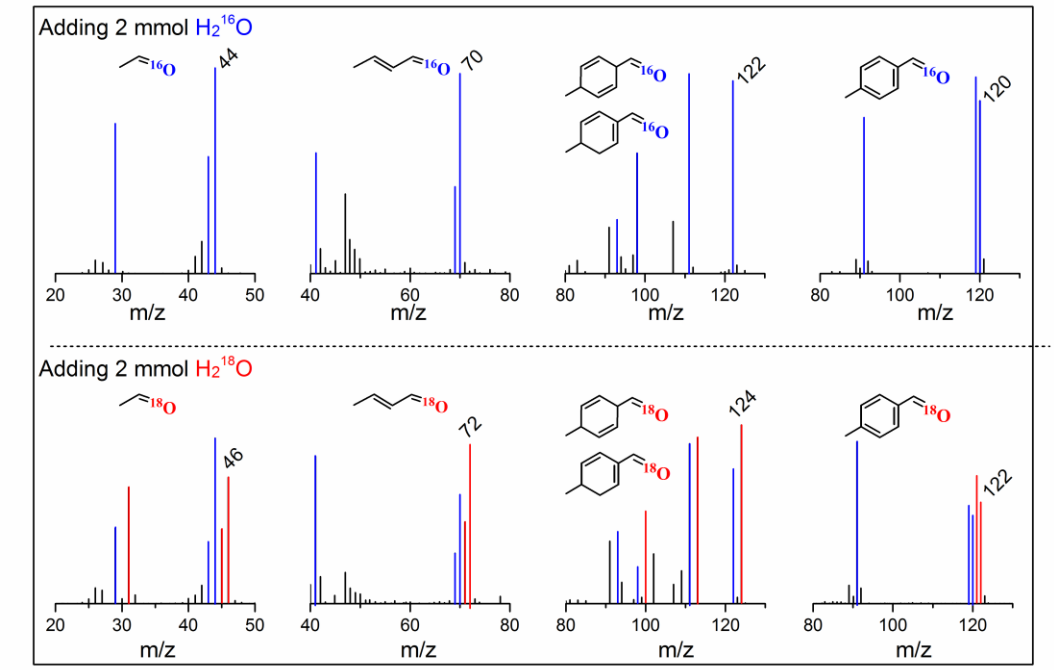

Figure S8. Aldehyde condensation (and aromatization) catalyzed by THP-DPh-OTMS, related to Scheme 3.

(A) *n*-butyraldehyde.

(B) *tran*-2-butenal.

(C) 2-methyl-tran-2-butenal.

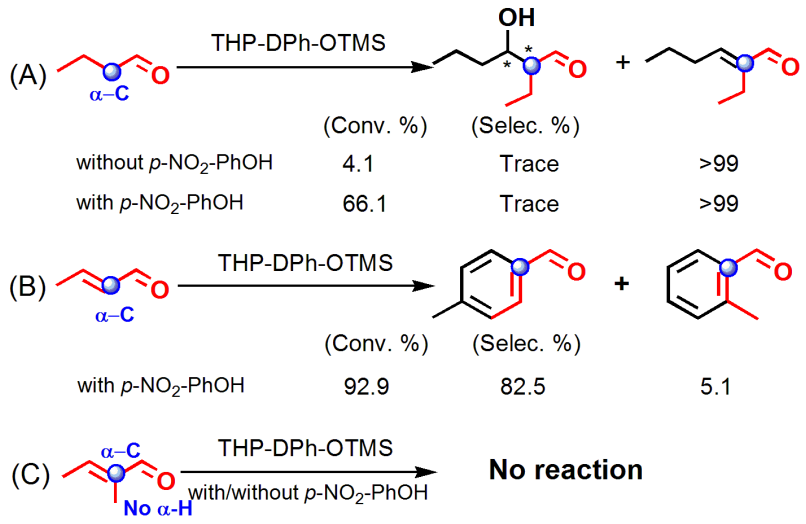

Figure S9. D-substituted experiments using CD_3CDO (chemical purity, Aladdin) as reactant, related to STAR Methods.

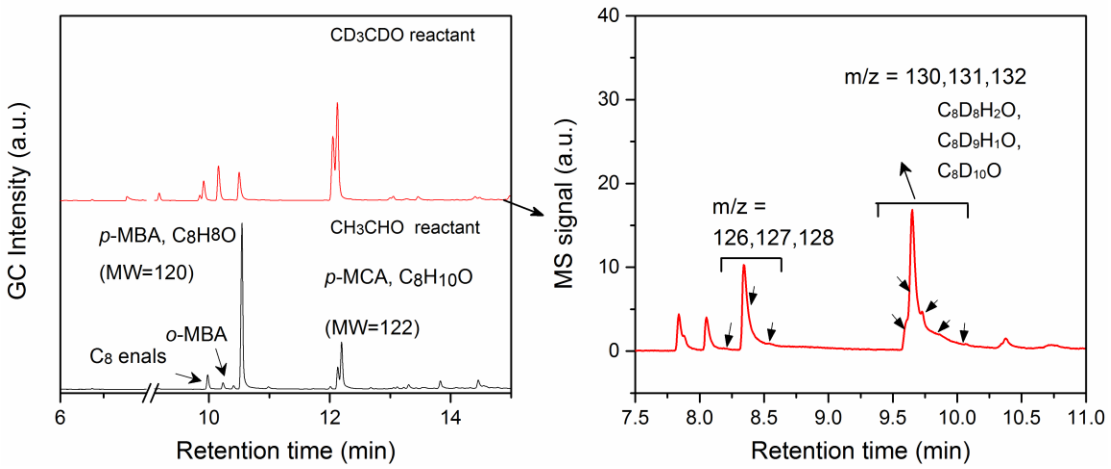

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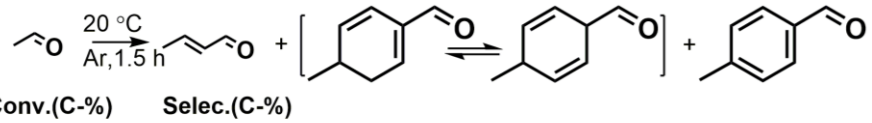
Figure S10. Mechanistic investigation, related to Scheme 5.

Reaction conditions: 1 mmol CH_3CHO, 3 mL $CHCl_3$, 0.1 mmol THP-DPh-OTMS, 0.3 mmol *p*-NO_2-PhOH, 20 °C for 1.5 h, Ar atmosphere. In the controlled experiment, 3 mmol (3 equiv) 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added prior to the reaction.



	Conv.(C-%)	Selec.(C-%)		
	86.5%	**13.9%**	**58.5%**	**19.1%**
With TEMPO 3 equiv	**83.8%**	**12.4%**	**59.6%**	**20.7%**

Figure S11. Scale-up experiments, related to STAR Methods.

(A) Product distributions.

(B) GC profile.

The insert panel in (B) is an optical photograph of the collected product (including 206.5 mg *p*-MBA calculated on basis of the molar percent). $CHCl_3$ shown in (B) was used as solvent to dilute the collected product for injecting into the GC inlet.

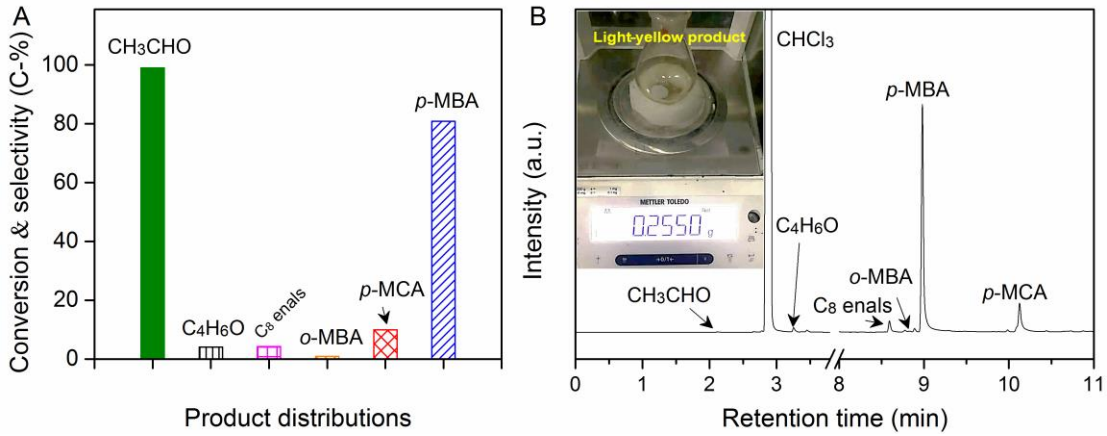


Table S1. Product distributions of acetaldehyde condensation and aromatization,[a] related to Figure 1.

Entry	Catalysts	Organic acid	Solvents	Conversion (C-%)	Selectivity (C-%)						
					p-MBA	*p*-MCA	*o*-MBA	C_8 enals	C_6 enals	C_4 enals	Others
1	THP	*p*-NO_2-PhOH	$CHCl_3$	>99	26.5	24.3	2.9	43.8	Trace	Trace	2.5
2	THP-OH	*p*-NO_2-PhOH	$CHCl_3$	>99	19.8	36.6	7.8	35.5	0.1	0.2	-
3	THP-COOH	*p*-NO_2-PhOH	$CHCl_3$	>99	0.7	7.6	5.7	2.8	Trace	83.0	0.2
4	THP-Ph	p-NO_2-PhOH	$CHCl_3$	>99	13.3	49.3	8.7	28.7	Trace	Trace	-
5	THP-DPh-OTMS	*p*-NO_2-PhOH	$CHCl_3$	88.6	25.3	57.2	5.3	2.6	1.4	8.1	-
6[b]	THP-DPh-OTMS	*p*-NO_2-PhOH	$CHCl_3$	99.8	90.0	4.9	2.4	2.4	Trace	0.3	-
7	THP-DPh-OTMS	*p*-NO_2-PhCOOH	$CHCl_3$	50.5	2.6	1.8	1.0	0.6	7.6	86.4	-
8	THP-DPh-OTMS	PhOH	$CHCl_3$	86.9	4.9	28.8	1.1	4.8	3.1	57.4	-
9	THP-DPh-OTMS	*p*-CH_3-PhOH	$CHCl_3$	77.4	8.5	14.7	0.4	2.7	1.7	72.0	-
10	THP-DPh-OTMS	*p*-COOH-PhOH	$CHCl_3$	82.3	3.2	30.1	2.9	4.1	6.3	53.5	-
11	THP-DPh-OTMS	*p*-NO_2-PhOH	CH_3CN	66.3	8.1	13.4	8.0	8.8	0.9	61.1	-
12	THP-DPh-OTMS	*p*-NO_2-PhOH	C_2H_5OH	27.6	14.1	16.7	7.7	26.8	1.5	33.1	-
13	THP-DPh-OTMS	*p*-NO_2-PhOH	DMF	3.6	Trace	Trace	Trace	42.9	30.4	26.8	-
14	THP-DPh-OTMS	*p*-NO_2-PhOH	DMSO	Trace	-	-	-	-	-	-	-

[a] Reaction conditions: acetaldehyde (1 mmol), solvent (3 mL), catalyst (0.1 mmol), organic acid (0.3 mmol). The reaction mixture was stirred at 20 °C for 2 h under Ar atmosphere in a vial.

[b] Reaction mixture was added 0.1 mmol THP-DPh-OTMS and stirred for another 2 h at 60 °C.

Table S2. Products selectivity under Ar and Air atmosphere,[a] related to STAR Methods.

Reaction atmosphere	Air			Ar			Ar[b]		
Reaction time	Conversion (C-%)	Selectivity (C-%)		Conversion (C-%)	Selectivity (C-%)		Conversion (C-%)	Selectivity (C-%)	
		p-MBA	*p*-MCA		*p*-MBA	*p*-MCA		*p*-MBA	*p*-MCA
1	89.6	21.2	55.3	85.1	20.2	54.0	-	-	-
2	86.5	22.8	56.3	88.6	25.3	57.2	93.0	24.0	58.7
4	91.1	24.7	56.3	90.0	26.0	58.0	-	-	-
10	93.8	32.0	57.4	91.0	31.8	57.2	-	-	-
20	93.5	35.9	55.1	97.5	34.9	58.7	-	-	-
30	94.4	39.0	53.1	93.5	38.9	55.1	-	-	-
40	95.4	42.5	51.5	97.5	41.5	54.5	-	-	-
52	98.2	45.2	47.4	98.3	47.4	45.6	-	-	-
60	98.5	49.5	45.4	-	-	-	-	-	-
72	99.1	51.8	41.9	98.7	49.9	41.9	-	-	-
80	99.5	57.8	35.6	99.3	55.7	39.3	-	-	-

[a] Reaction conditions: CH_3CHO (1 mmol), $CHCl_3$ (3 mL), THP-DPh-OTMS (0.1 mmol), *p*-NO_2-PhOH (0.3 mmol). The reaction mixture was stirred under air or Ar atmosphere at 20 °C. [b] Using further degassed $CHCl_3$ (see Methods Details).

Table S3. Dependence of products selectivity on the type and amounts of samines, [a] related to STAR Methods.

Entry	Adding Amines	Amount (mmol)	T (°C)	*t* (h)	Conversion (C-%)	Selectivity (C-%)		Carbon balance (C-%)
						p-MBA	*p*-MCA	
1	-	-	20	1	87.4	21.7	60.1	~99
2	-	-	40	1	84.1	22.6	55.9	-
3	-	-	60	2	83.4	34.8	45.0	97
4	-	-	60	5	88.1	37.6	43.8	-
5	-	-	60	15	98.4	47.7	41.6	-
6	-	-	60	20	95.3	52.4	35.5	88.8
7	THP-BPh-OTMS	0.1	60	2	99.8	90.0	4.9	88.0
8	$NH(C_2H_5)$	0.3	20	1	99.8	28.0	56.4	-
9	$NH(C_2H_5)$	0.3	40	1	99.8	31.5	49.2	-
10	$NH(C_2H_5)$	0.3	60	1	99.9	59.3	26.4	90
11	$NH(C_2H_5)$	0.15	60	1	99.8	51.1	30.7	-
12	$NH(C_2H_5)$	0.45	60	1	99.8	67.5	17.9	-
13	$NH(C_2H_5)$	0.15	60	2	99.8	80.6	11.4	85.0
14	$N(C_3H_7)$	0.3	60	1	92.5	40.3	48.8	97.5
15	$(NH_2)_2(CH_2)_6$	0.05	60	1	91.1	47.1	37.7	60.3
16	-	-	60	3	91.7[b]	62.1	28.8	58.7

[a] Reaction conditions: CH_3CHO (1 mmol), $CHCl_3$ (3 mL), THP-DPh-OTMS (0.1 mmol), *p*-NO_2-PhOH (0.3 mmol), Ar atmosphere. After reaction for 2 h, organic amines were added and then the mixture was stirred for more time at a certain temperature.

[b] Reaction was directly conducted at 60 °C for 3 h using acetaldehyde as reactant.