Supporting Information

Understanding the different oxidative pathways of cyclohexene through modulating reactive oxygen species generated from *tert*-butyl hydroperoxide (TBHP) by various metal salts

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1. Experimetnal section

1.1 General Considerations

Solvents were dried according to the literature procedures and redistilled under an argon atmosphere before use. All air- and moisture-sensitive operations were carried out using standard high vacuum line, Schlenk techniques or in an inert atmosphere glovebox containing an atmosphere of nitrogen.

1.2 Materials

All reagents were purchased from Energy Chemical and Aldrich. Isotopic oxygen ($^{18}O_2$) was purchased from Taiyo Nippon Sanso. The cyclohexene-D_{10} were purchased from C/D/N ISOTopes.

1.3 Instrumentations

GC analyses were performed on a Shimadzu GC-2010 plus equipped with the capillary column (Rtx-5, 30 m × 0.32 mm × 0.25 μm) and the FID detector. The products were identified by comparison of their GC retention times with commercial samples. The CSI-MS spectrometer were obtained on Bruker's timsTOF, and the cold jet is Bruker's CryoSpray. Mass spectra were obtained on a Shimadzu GCMS-2010A. The EPR (Electron Paramagnetic Resonance) spectroscopy measurements were performed on a JESFA-200 (JEOL, Japan) spectrometer using PBN/DMPO as a free-radical spin-trapping agent. EPR analyses were performed at a microwave frequency of 9.20-9.45 GHz at 298K. Instrument conditions for all analyses were as follows: microwave frequency, 9.20-9.45 GHz; modulation amplitude, 0.1 mT; modulation frequency, 100 kHz; power, 2.0 mW; and time constant, 0.03 s.

1.4 Catalytic oxidation of cyclohexene

A 25 mL Schlenck tube was charged with cyclohexene (1.6 mmol), catalyst (4% mol), TBHP (5 equiv.

to substrate), solvent (acetonitrile, 5 mL) through the reaction solution for 4 h at 30 °C. The formation of products was monitored by GC (Shimadzu GC-2010 plus) or GC-MS (Shimadzu GCMS-QP2010).

1.5 Free radical capture experiments

The reaction solution and DMPO or PBN (free-radical spin-trapping agent: DMPO, 5,5-Dimethyl-1-pyrroline N-Oxide; PBN, N-tert-butyl-2-phenylnitrone) are mixed and added to the Wilmad WG-810-A quartz-flat cell. The cell was sealed after filling with the different experimental atmospheres required. EPR analyses were performed under a microwave frequency of 9.26 GHz at 298 K.

2. Results

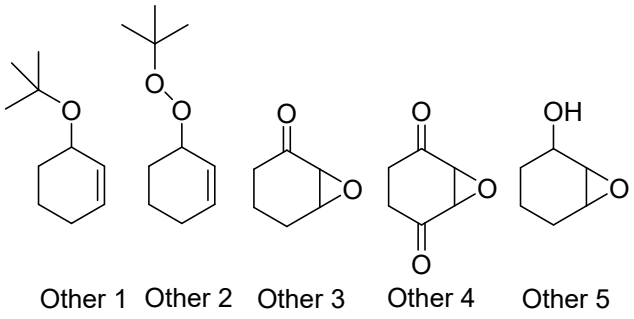


Fig. S1. Other products of cyclohexene oxidation

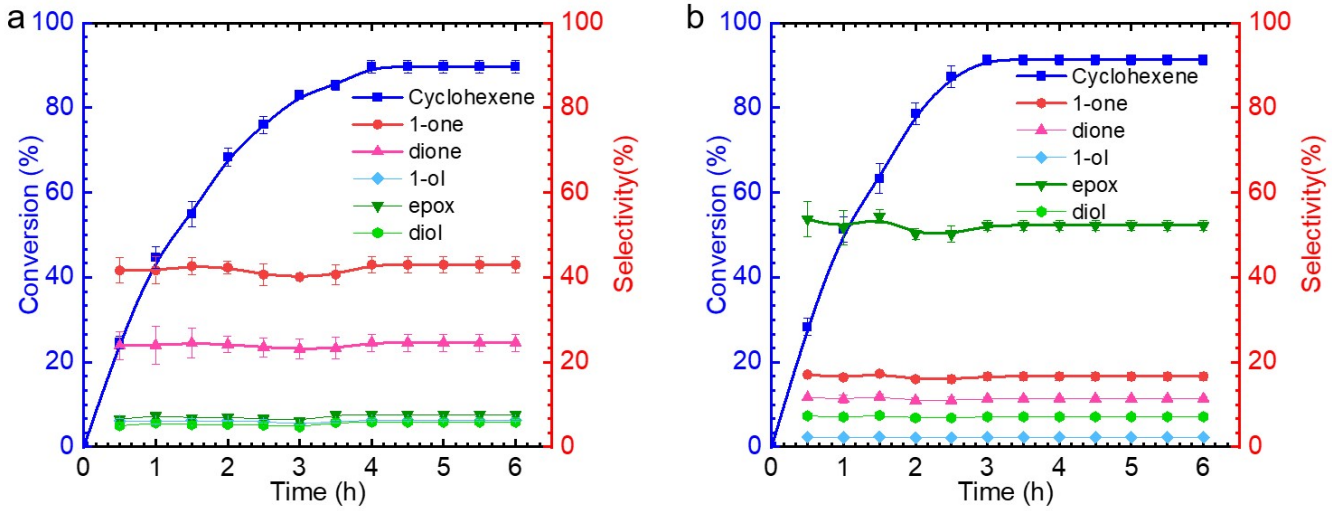


Fig. S2. Time-dependent conversion and product distribution for cyclohexene oxidation in $CuCl_2$(a) and VCl_3(b) system (cyclohexene 1.6 mmol, TBHP 5.0 equiv, 30.0 ℃, 4 mol % catalyst, solvent acetonitrile 5 mL).

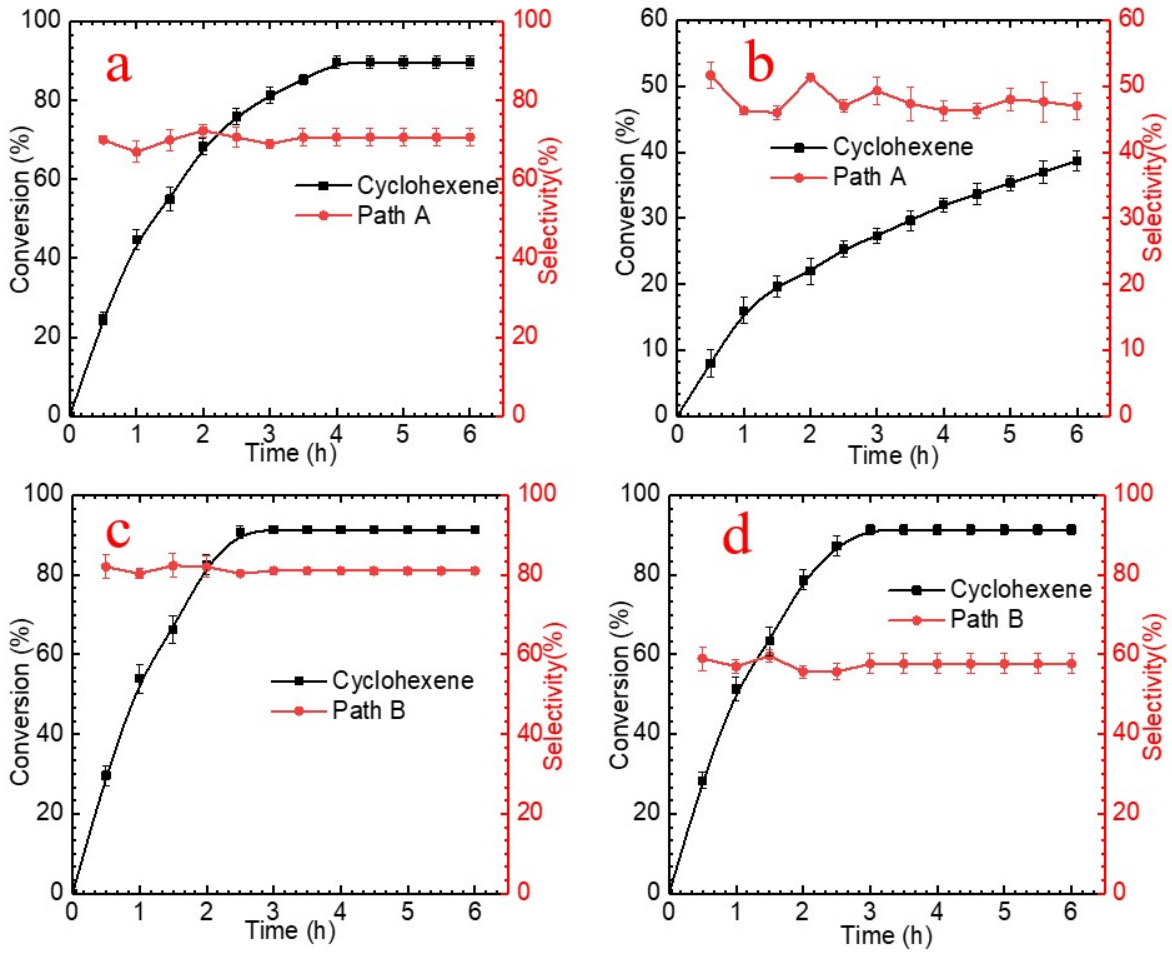


Fig. S3. (a) Effect of reaction time on cyclohexene-H10 epoxidation in the $CuCl_2$ system. (b) Effect of reaction time on cyclohexene-D10 epoxidation in the $CuCl_2$ system. (c) Effect of reaction time on cyclohexene-H10 epoxidation in the VCl_3 system. (d) Effect of reaction time on cyclohexene-D10 epoxidation in the VCl_3 system.

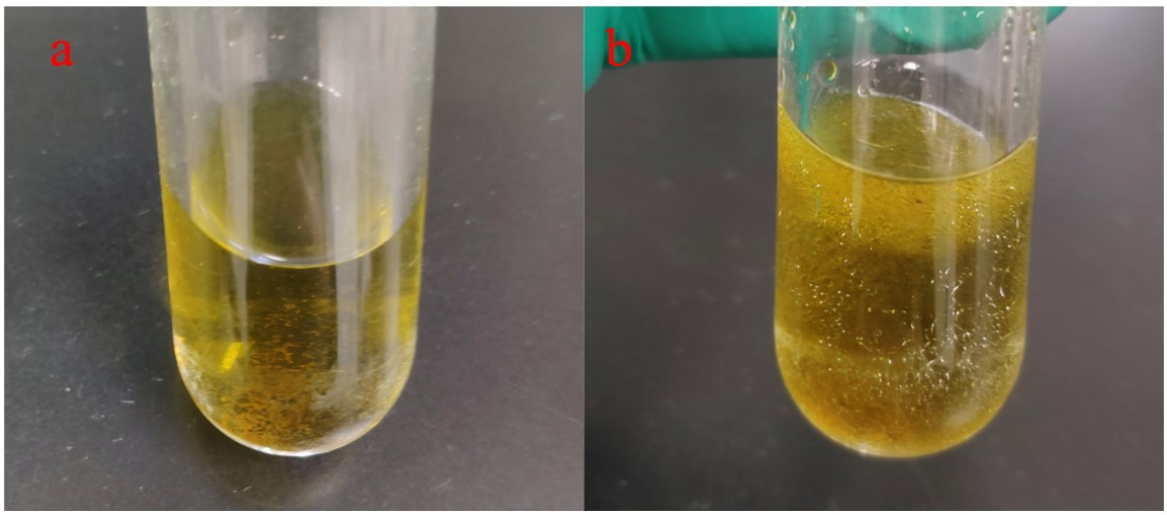


Fig. S4. $CuCl_2$ catalyzed TBHP before (a) and during reaction pictures (b).

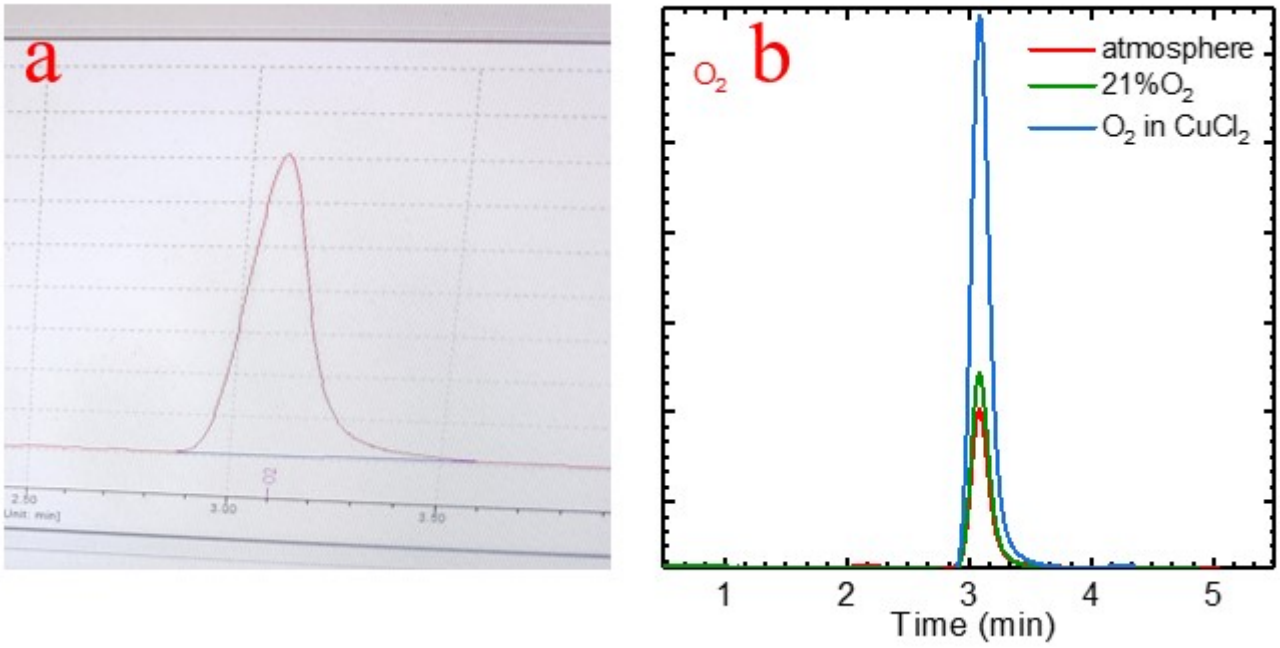


Fig. S5.(a) Gas species produced in $CuCl_2$ systems. (b) O_2 intensity in $CuCl_2$ systems

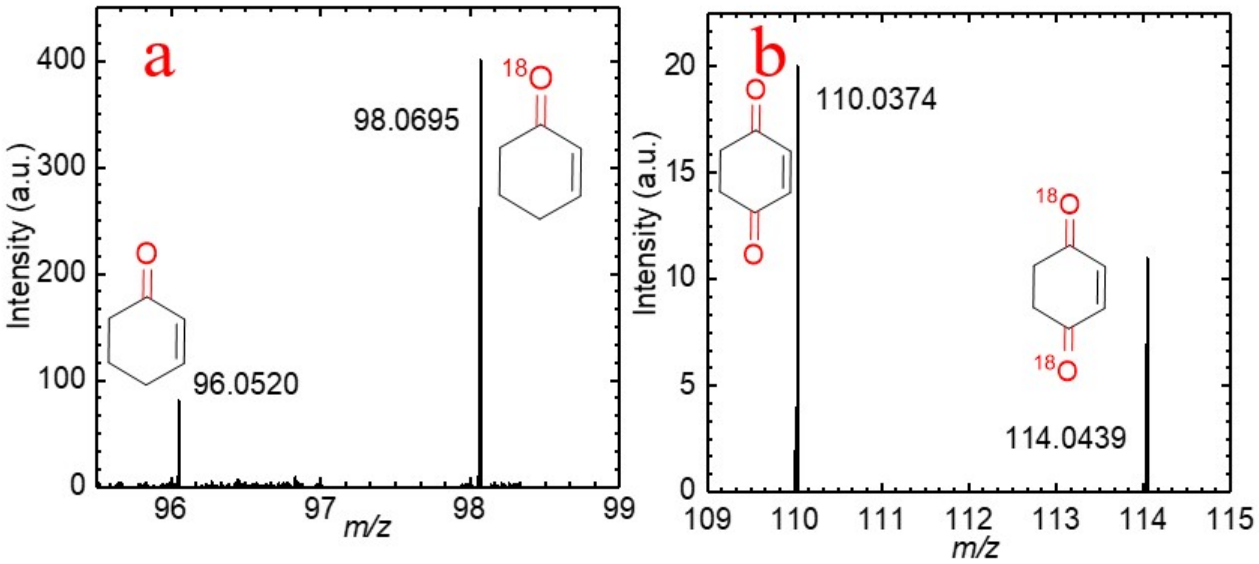


Fig. S6. CSI-MS spectra of $^{18}O_2$ (a) oxygen-labeled cyclohexanone.[$C_6H_8{}^{18}O$]: *m/z* = 98.0695(exp.), *m/z* = 98.0695(cal.); (b) oxygen-labeled 1, 4-cyclohexen-2-one.[$C_6H_6{}^{18}O_2$]: *m/z* = 114.0439(exp.), *m/z* = 114.0453(cal.).

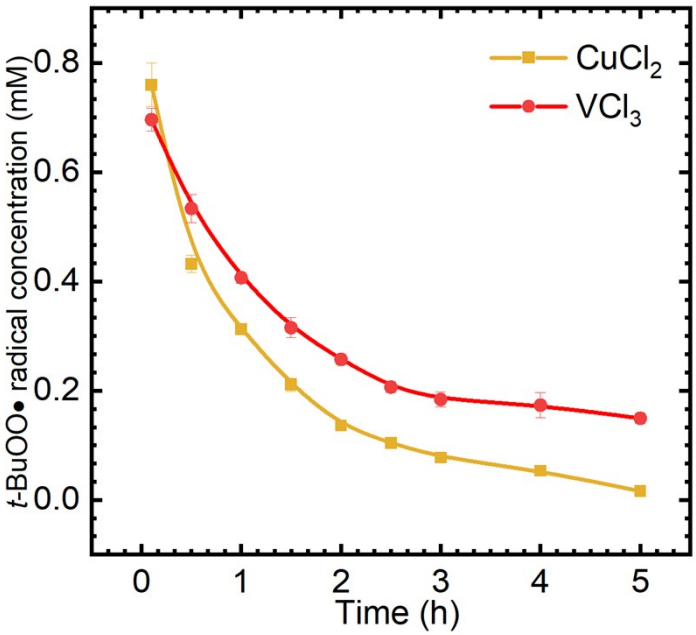


Fig. S7. The consumption of *t*-BuOO• radicals in $CuCl_2$ and VCl_3 system

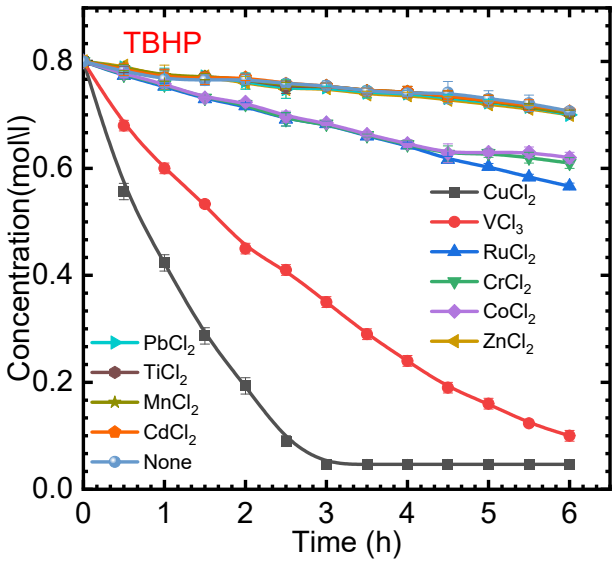


Fig. S8. TBHP consumption rate curves catalyzed by various catalysts

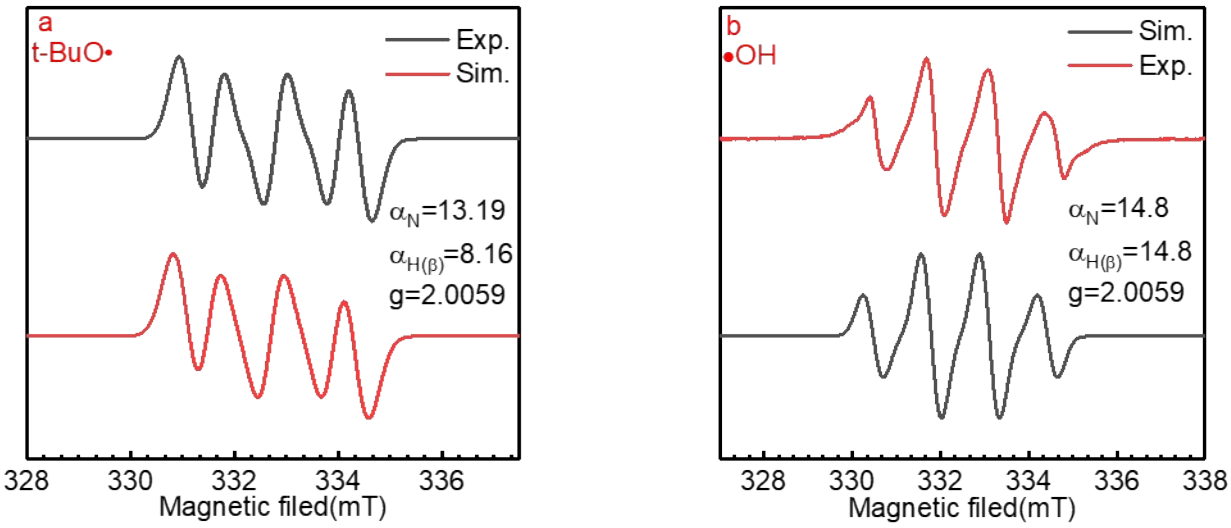


Fig. S9. Experimental (black) and simulated (red) X-band EPR spectra of *t*-BuO• (a) and •OH in the oxidation of cyclohexene (DMPO as a free-radical spin trapping agent).

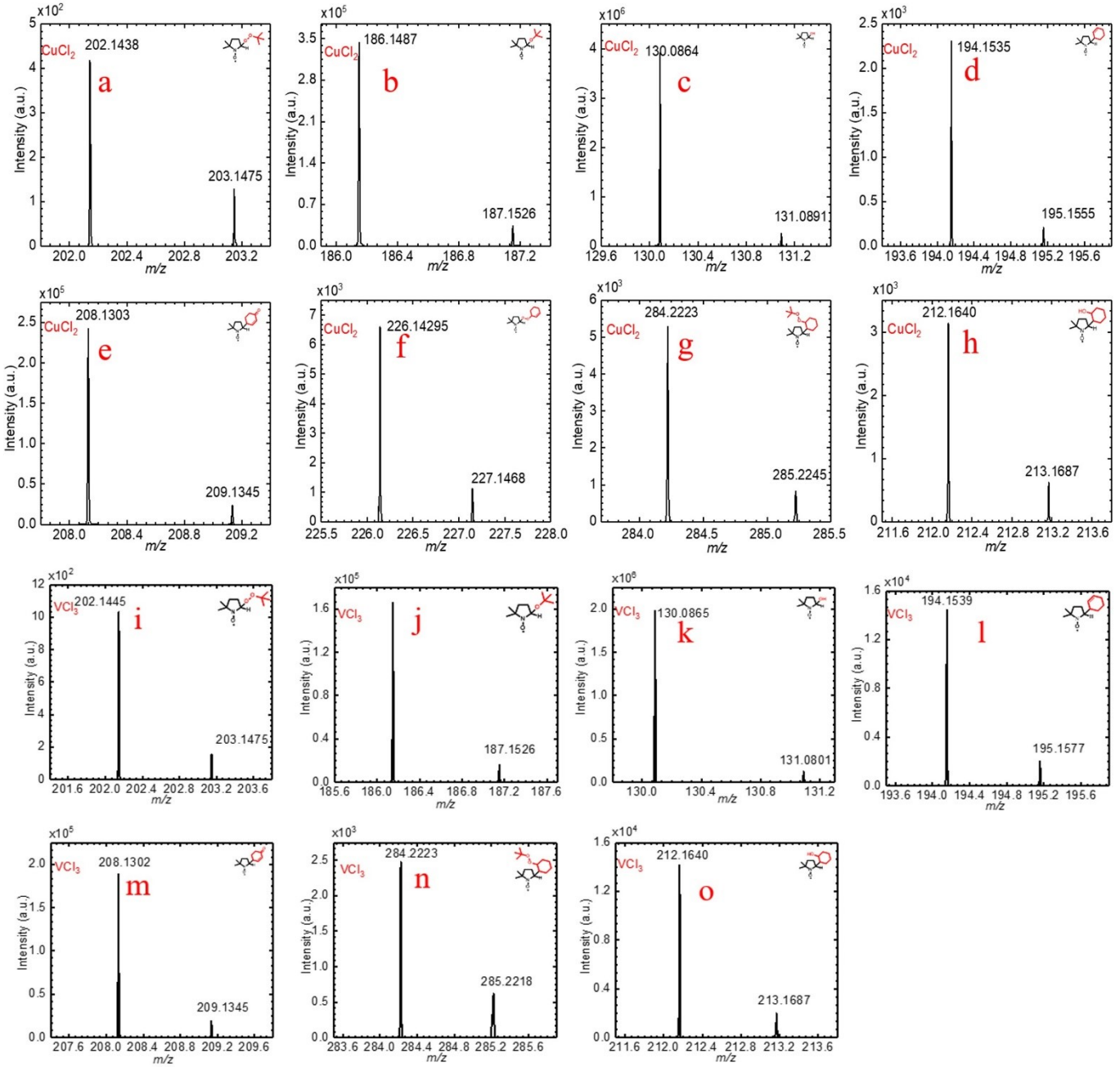


Fig. S10. CSI-MS spectra of DMPO spin adducts of (a) •$O_2C_4H_9$ radical. *m/z* = 202.1438(exp.), *m/z* = 202.1443(cal.), (b) •OC_4H_9 radical. *m/z* = 186.1487(exp.), *m/z* = 186.1494(cal.), (c) •OH radical. *m/z* = 130.0864(exp.), *m/z* = 130.0868(cal.), (d) •C_6H_9 radical. *m/z* = 194.1535(exp.), *m/z*=194.1545(cal.), (e) •OC_6H_7 radical. *m/z* = 208.1303(exp.), *m/z* = 208.1338(cal.), (f) •$O_2C_6H_9$ radical. *m/z* = 226.1430(exp.), *m/z* = 226.1443(cal.), (g) •$O_2C_{10}H_{19}$ radical. *m/z* = 284.2223(exp.), *m/z* = 284.2226(cal.), (h) •OC_6H_{12} radical. *m/z* = 212.1640(exp.), *m/z* = 212.1651(cal.) in $CuCl_2$ catalytic system.

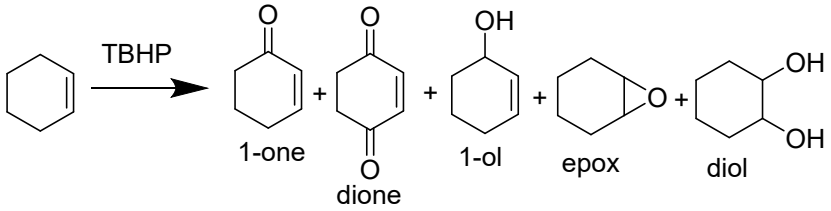
And (i) •$O_2C_4H_9$ radical. *m/z* = 202.1445(exp.), *m/z* = 202.1443(cal.), (j) •OC_4H_9 radical. *m/z* = 186.1489(exp.), *m/z* = 186.1494(cal.), (k) •OH radical. *m/z* = 130.0865(exp.), *m/z* = 130.0868(cal.), (l) •C_6H_9 radical. *m/z* = 194.1539(exp.), *m/z* = 194.1545(cal.), (m) •OC_6H_7 radical. *m/z* = 208.1302(exp.), *m/z* = 208.1338(cal.), (n) •$O_2C_{10}H_{19}$ radical. *m/z* = 284.2223(exp.), *m/z* = 284.2226(cal.), (o) •OC_6H_{12} radical. *m/z* = 228.1600(exp.), *m/z* = 228.1600(cal.) in VCl_3 catalytic system.

Table S1. Catalytic performance of metal salts for cyclohexene selective oxidation [a]

Entry	Catalyst	Conv. (%)	Select. of products (%)		
			Path A	**Path B**	**Others**
1	None	9	33	48	19
2	$CuCl_2$	93	73	13	14
3	VCl_3	90	30	58	12
4	$RuCl_2$	30	32	47	21
5	$CrCl_2$	29	36	42	22
6	$CoCl_2$	25	28	48	24
7	$PbCl_2$	10	32	57	11
8	$TiCl_3$	12	32	43	25

[a] Cyclohexene 1.6 mmol, TBHP 5.0 equiv, 30.0 ℃, 4.0 h, 4 mol % catalyst, MeCN as solvent (5 mL).

Table S2. Effect of catalyst on cyclohexene oxidation [a]



Entry	Catalyst	Conv. (%)	Select. (%)					
			1-one	dione	1-ol	epox	diol	Others
1	None	9	19	8	6	5	43	19
2	VCl_3	90	16	11	3	51	7	12
2	$CuCl_2$	93	43	24	6	7	6	14
3	$RuCl_2$	30	20	9	3	7	40	21
4	$CrCl_2$	29	22	8	6	5	37	22
5	$CoCl_2$	25	15	7	6	5	43	24
6	$ZnCl_2$	7	21	8	4	6	45	16
7	$PbCl_2$	10	18	10	4	6	51	11
8	$TiCl_3$	12	15	12	5	4	39	25
9	$MnCl_2$	8	17	10	5	7	38	23
11	$CdCl_2$	8	18	9	4	6	50	13

[a] Cyclohexene1.6 mmol, TBHP 5.0 equiv, 30.0 ℃, 4.0 h, 4 mol % catalyst, MeCN as solvent (5 mL).

Table S3. Effect of solvent type on cyclohexene oxidation [a]

Entry	Catalyst	Solvent	Conversion (%)	selectivity (%)					
				1-one	dione	1-ol	epox	diol	Others
1	$CuCl_2$	DCM	40	39	11	5	11	8	19
2	$CuCl_2$	DCE	53	40	22	6	7	6	59
3	$CuCl_2$	EA	95	18	10	5	4	4	7
4	$CuCl_2$	THF	10	51	24	3	7	8	14
5	$CuCl_2$	ACN	93	43	24	6	7	6	19
6	VCl_3	DCM	25	15	7	6	5	43	24
7	VCl_3	DCE	30	21	8	4	6	45	16
8	VCl_3	EA	92	18	10	4	6	51	11
9	VCl_3	THF	8	15	12	5	4	39	25
10	VCl_3	ACN	90	16	11	3	51	7	12

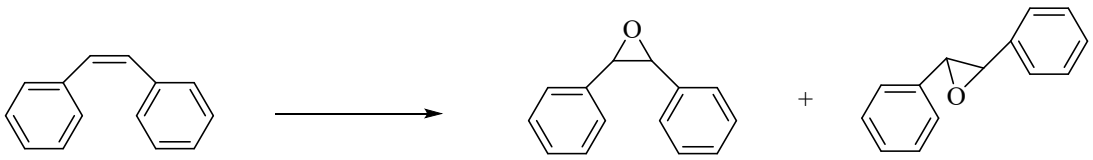
[a] Cyclohexene1.6 mmol, TBHP 5.0 equiv, 30.0 ℃, 4.0 h, 4 mol % catalyst, solvent (5 mL).

Table S4. Effect of temperature type on cyclohexene oxidation [a]

Entry	**Catalyst**	**T (℃)**	**Conv. (%)**	**Select. (%)**					
				1-one	**dione**	**1-ol**	**epox**	**diol**	**Others**
1	$CuCl_2$	30	93	43	24	6	7	6	19
2	$CuCl_2$	40	92	40	21	5	9	5	14
3	$CuCl_2$	50	94	38	19	6	7	6	20
4	$CuCl_2$	60	93	38	19	5	4	5	24
6	VCl_3	30	90	16	11	3	51	7	12
7	VCl_3	40	91	17	10	4	50	8	11
8	VCl_3	50	92	18	13	2	49	6	12
10	VCl_3	60	90	16	14	3	47	7	13

[a] Cyclohexene1.6 mmol, TBHP 5.0 equiv, 4.0 h, 4 mol % catalyst, MeCN as solvent (5 mL).

Table S5. Oxidation of *cis*-stilbene by VCl_3 and $CuCl_2$ [a]

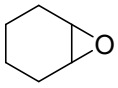
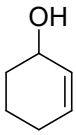
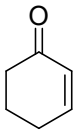


cis-stilbene *cis*-stilbene oxide *trans*-stilbene oxide

Entry	Catalysts	Conv./%	Products/mmol		Ratio of *cis*-/*trans*-oxide
			cis-stilbene oxide	*trans*-stilbene oxide	
1	-	12	0.182	0.009	95/5
2	VCl_3	70	0.123	0.997	11/89
3	$CuCl_2$	23	0.096	0.272	26/74

[a] *cis*-stilbene 1.6 mmol, TBHP 5.0 equiv, MeCN (5 mL), 4.0 h, 4 mol % catalyst.

Table S6. Control experiments with various oxidants [a]

Entry	Substrate	Oxidant	Conversion (%)	Selectivity (%)					
				1-one	dione	1-ol	epox	diol	Others
1		TBHP	0	-	-	-	-	-	-
2		DTBP	0	-	-	-	-	-	-
3		H_2O_2	0	-	-	-	-	-	-
4		TBHP	93	43	24	6	7	6	14
5		DTBP	10	-	-	-	-	-	100
6		H_2O_2	35	38	25	13	--	14	10
7		TBHP	100	67	10	-	-	-	23
8		DTBP	0	-	-	-	-	-	-
9		H_2O_2	68	52	11	-	-	-	37
10		TBHP	10	-	60	-	-	-	40
11		DTBP	0	-	-	-	-	-	-
12		H_2O_2	8	-	76	-	-	-	24

[a] Substrate: 1.6 mmol, oxidant 5.0 equiv, 30.0 °C, 4.0 h, 0.1 MPa, 4 mol % $CuCl_2$, MeCN (5 mL).