A sustainable and product-controllable aerobic oxidative cleavage of vicinal diols using vanadium-based photocatalyst

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Supporting Information

1. The characterization of catalysts

1.1 Photoelectrochemical detection of different catalysts

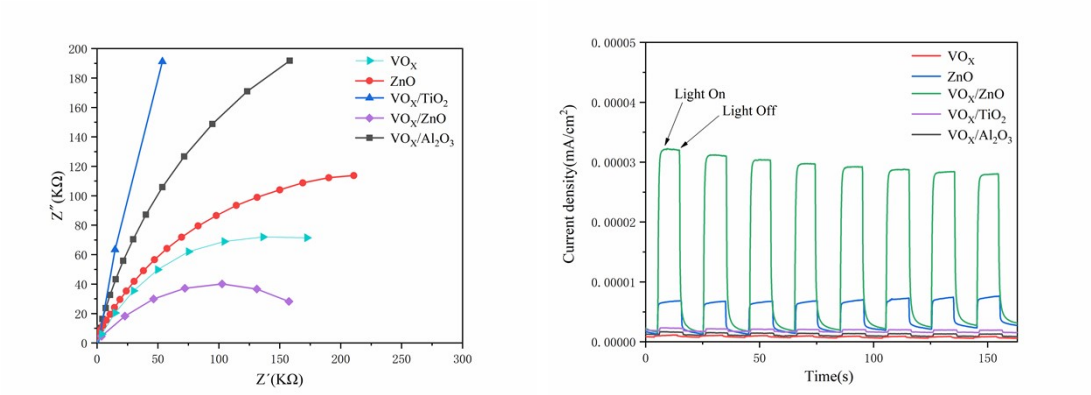


Figure S1. The photocurrent density spectra (left) and EIS Nyquist plots (right) of different samples

1.2 SEM image

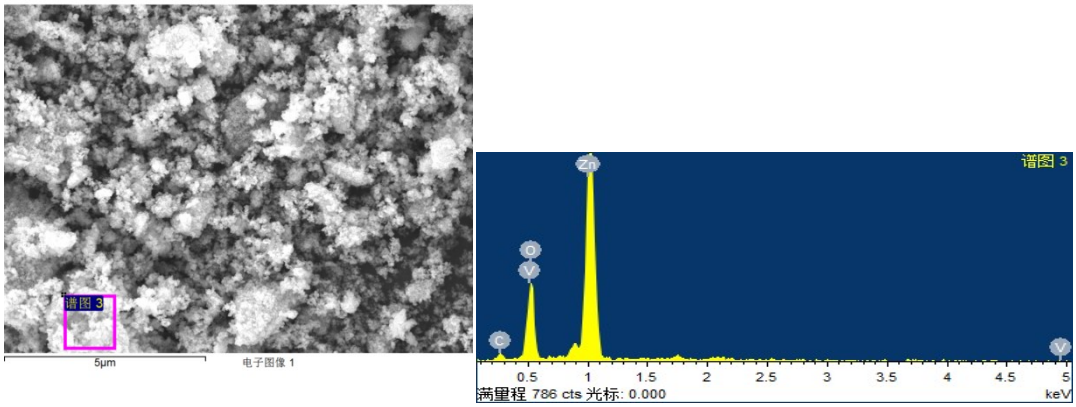


Figure S2. The SEM image of VO_x/ZnO sample

1.3 XPS spectrum of VO_x/ZnO photocatalyst

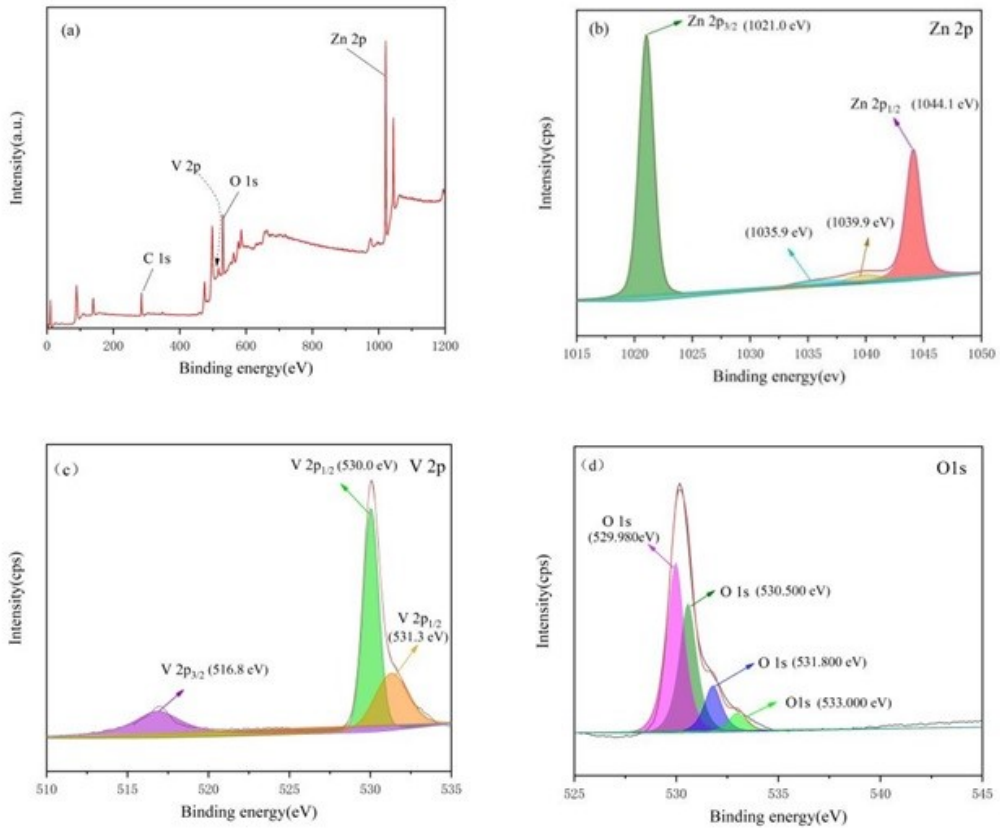


Figure S3. The XPS spectrum of VO_x/ZnO sample (a) and the results of Zn2p core (b), V2p core (c), O1s core (d)

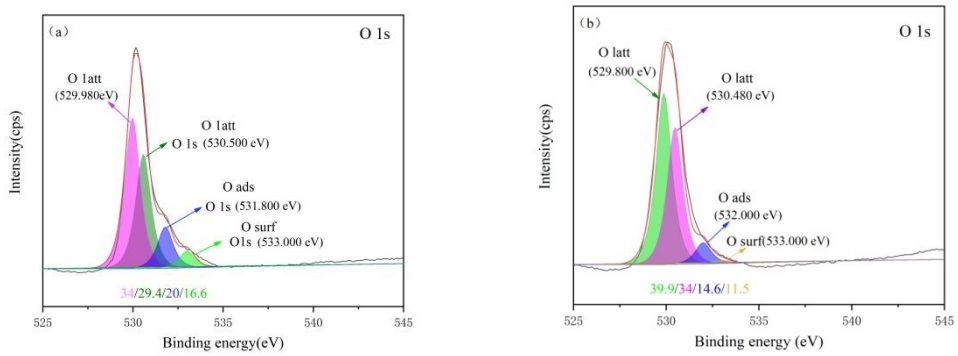


Figure S4. The comparison of XPS result of O1s core for the VO_x/ZnO and VO_x/ZrO_2 catalysts

1.4 The UV-vis spectra and NH_3-TPD data of different catalysts

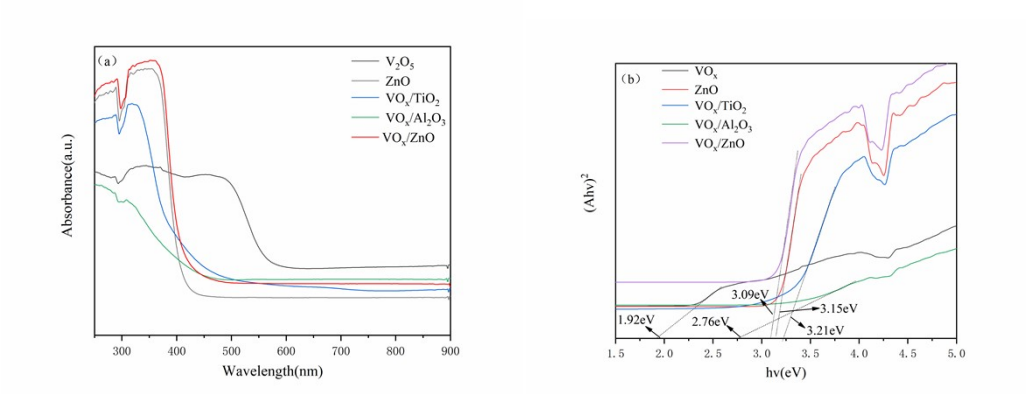


Figure S5. The UV-vis spectra (a) and the band gap energy (b) of differet photocatalysts

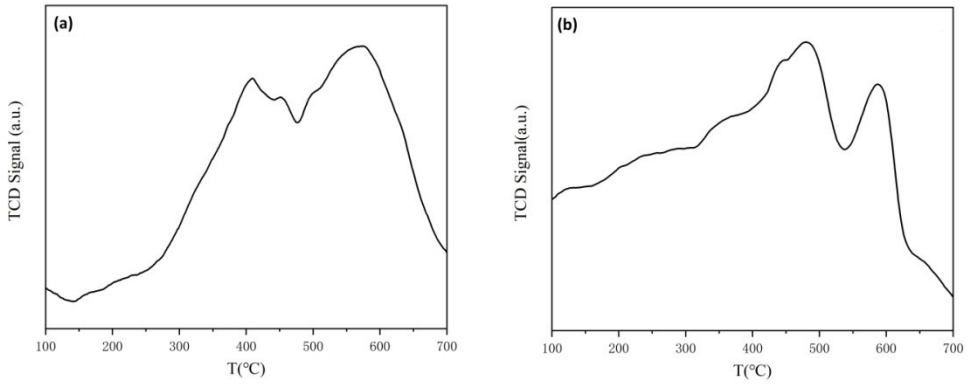


Figure S6. The NH_3-TPD result of ZnO sample (a) and VO_x/ZnO photocatlyst (b)

1.5 BET detection

Table S1. The N_2 physisorption results of different catalysts

Catalyst	Surface area (m^2/g)	Pore Volume (m^3/g)	Pore Size (Å)
ZnO	19.5776	0.000831	71.0930
VO_x/ZnO	18.1030	0.00120	51.210
VO_x	2.5210	0.000613	48.266

2. The influence of oxygen pressure on the oxidative cleavage process of vicinal diols

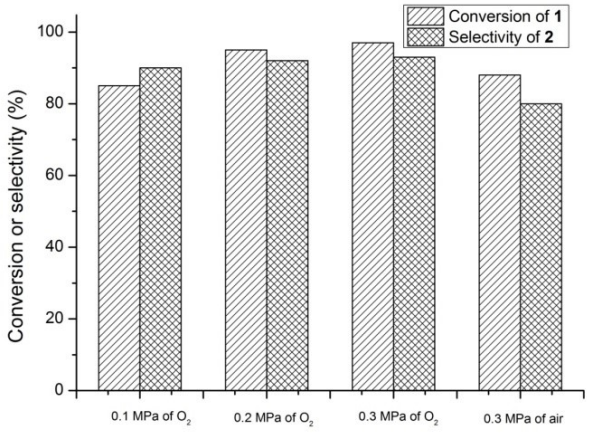


Figure S7. The influence of oxygen pressure (reaction conditions: 0.1 g of **1**, 50 mg of VO_x/ZnO catalyst, in 10 mL methanol solvent, Xe lamp with a light intensity of 220 mW /cm^2, for 8 h)

3. Results of control experiments for oxidative cleavage reaction of 1 with VO_x in methanol

Table S2. The results of control experiments to study the mechanism [a]

Entry	Additive	Conv.(%)[b]	Product distribution [b]	
			2	**3+5+others**
1	Silver nitrate	52	15	85
2	Ammonium oxalate	26	32	68
3	*p*-benzoquinone	60	5	95
4	*β*-carotene	70	-	>99
5	Diphenylamine	24	10	90
6	TEMPO	32	<1	>99
7	TEMPO+ *p*-benzoquinone	<3	-	>98

[a] Reaction conditions: 0.1 g of compound 1, 50 mg of VO_x, in 10 mL CH_3OH, under 0.2 MPa of O_2, Xe lamp with a light intensity of 200 mW, 5 h; [b] The results are obtained by GC with internal standard technique.

4. The possible reaction mechanism for the oxidative cleavage process with the VO_x/ZnO photocatalyst

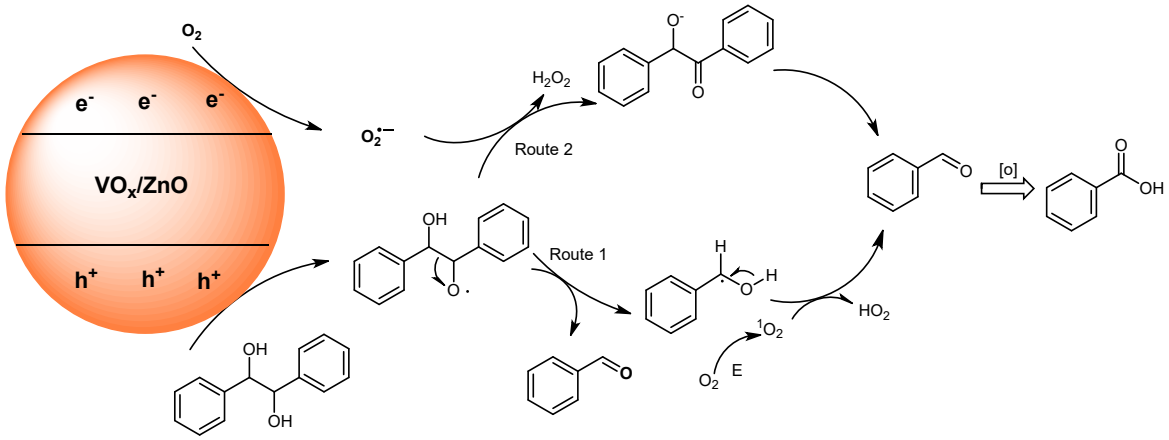


Figure S8. Proposed reaction mechanism for oxidative cleavage process of **1** under the oxygen atmosphere

5. **The results of oxidative cleavage process compared with the previous works**

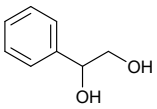
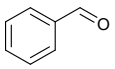
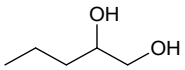
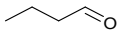
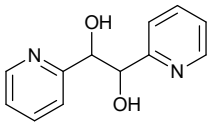
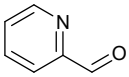
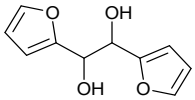
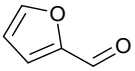
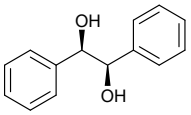
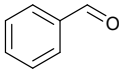
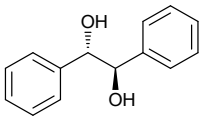
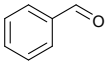
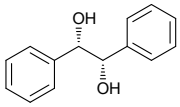
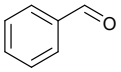
Table S3. The compared results for the oxidative cleavage process of hydrobenzoin

Reaction conditions	Conv.(%)[b]	Product Distribution(%)[b]		Ref.
		Benzaldehyde	**Benzoic acid**	
AgOTf, NaOMe (3 equv.）37 °C, 12 h	>99	96	-	Angew. Chem. Int. Ed., 2018, 57, 2616
Vanadium complex, in toluene solvent, 0.7 h, 100 °C,	99	99	-	Adv. Synth. Catal. 2018, 360, 3286
$CeCl_3 \cdot 7 H_2O$, TBACl (50mol%), in CH_3CN solvent, LED 455 nm, 18 h	>99	85	-	Chem. Commun., 2019, 55, 486
Na-Mn-LMO (1%Mn) ,O_2 1-butanol 100 °C，1 h	99	>99	-	Angew. Chem. Inter. Ed., 2017, 56, 9561
EcoMnOx (10%Mn) O_2 1-butanol 100 °C, 1 h	98	99	-	ACS Sustainable Chem. Eng., 2017, 5, 3214
CN 620, visible light 2wt%CTAB/H_2O O_2 (1atm)	>99	75	-	Green Chem., 2020, 22, 5042
VO_x/ZnO, visible light O_2 ,CH_3OH 10 h	100	91	-	This work
VO_x, visible light O_2 , CH_2Cl_2 5 h	99	-	100	This work

As shown in Table S3, the previous researches provide the technology for either the production of aldehyde or as the generation of ester (or acid) from vinical diols with the suitable catalysts; however, the regulation and controlling of product selectivity is not enough to carry out and understand the oxidative cleavage of 1, 2-diols from the catalytic method. This work presents a novel, mild and adjustable oxidative cleavage process of C-C bond using the vanadium oxide-based photocatalysts. In case of the oxidative transformation of hydrobenzoin, a complete conversion with 91% selectivity of benzaldehyde was obtained in methanol using the VO_x/ZnO as catalyst, and 99% conversion in 100% selectivity of benzoic acid was attained with the VO_x as the catalyst in dichloromethane solvent.

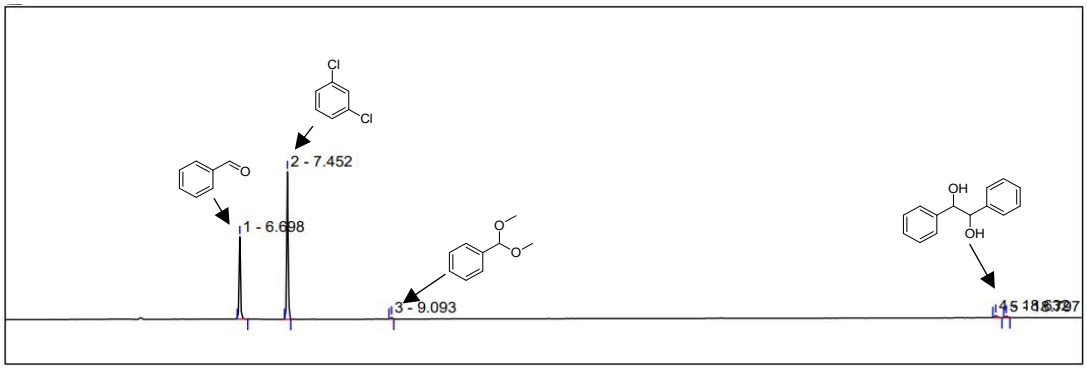
6. **The photocatalytic oxidative cleavage reactions of different vicinal diols**

Table S4. The oxidative transformations of different 1, 2-diols with VO_x/ZnO as catalyst [a]

Entry	The substrate	product	Conversion (%)[b]	Select. (%) [b]
1			15.0	97
2			5.8	90
3			85	93
4			90	91
5[c]			62	92
6[c]			26	90
7[c]			55	91

[a]Reaction conditions: 0.1 g substrate, 50 mg of VO_x/ZnO photocatalyst, in 10 mL methanol, under 0.2 MPa of O_2, Xe lamp with a light intensity of 220 mW /cm^2, for 8 h. [b]The results are obtained by GC with internal standard technique. [c]Reaction was performed at the conditions of Xe lamp with a light intensity of 220 mW/cm^2 under 0.2 MPa of O_2 for 3 h.

7. The GC and GC-MS spectra of reaction products



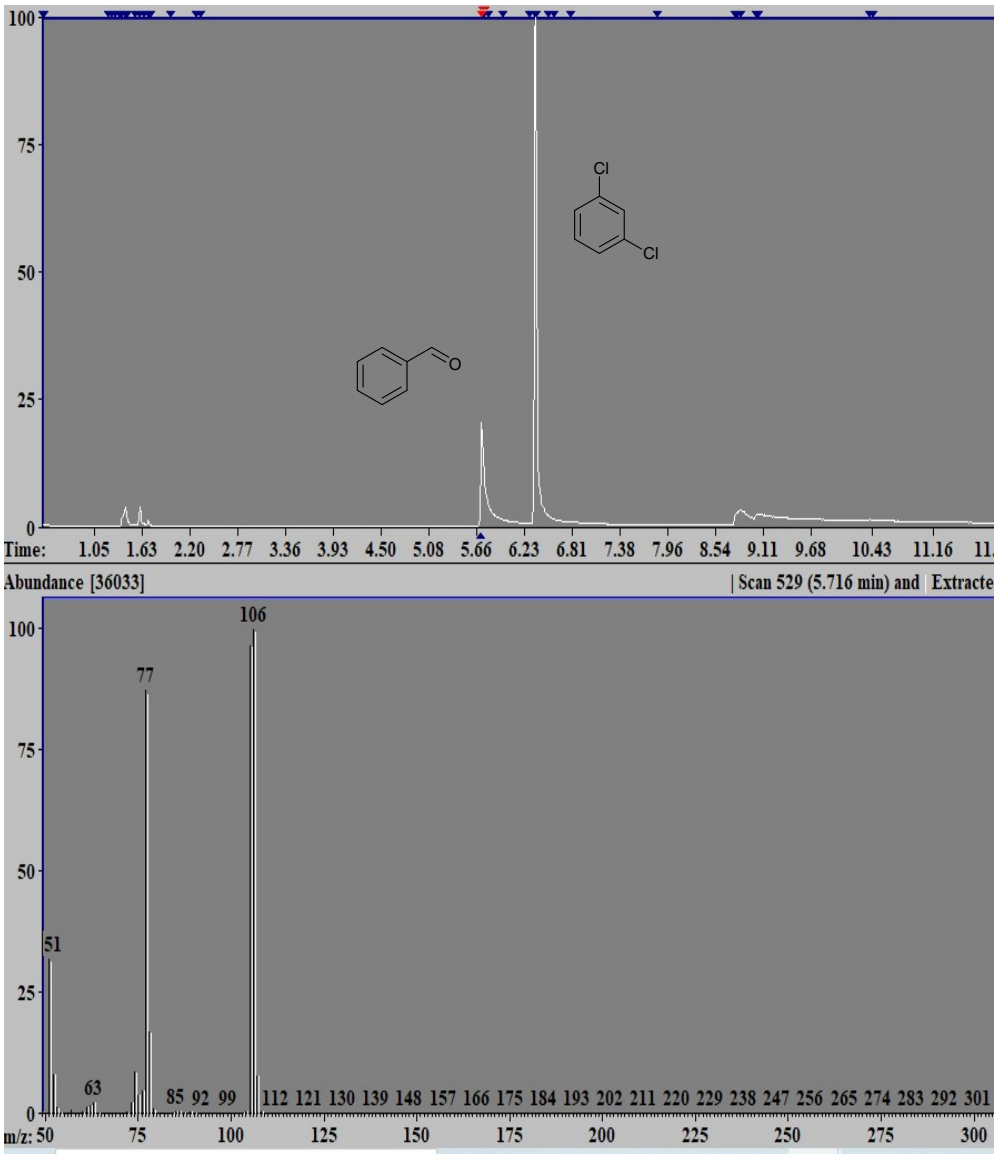


Figure S9. The GC and GC-MS spectra for oxidative cleavage of hydrobenzoin with VO_x/ZnO

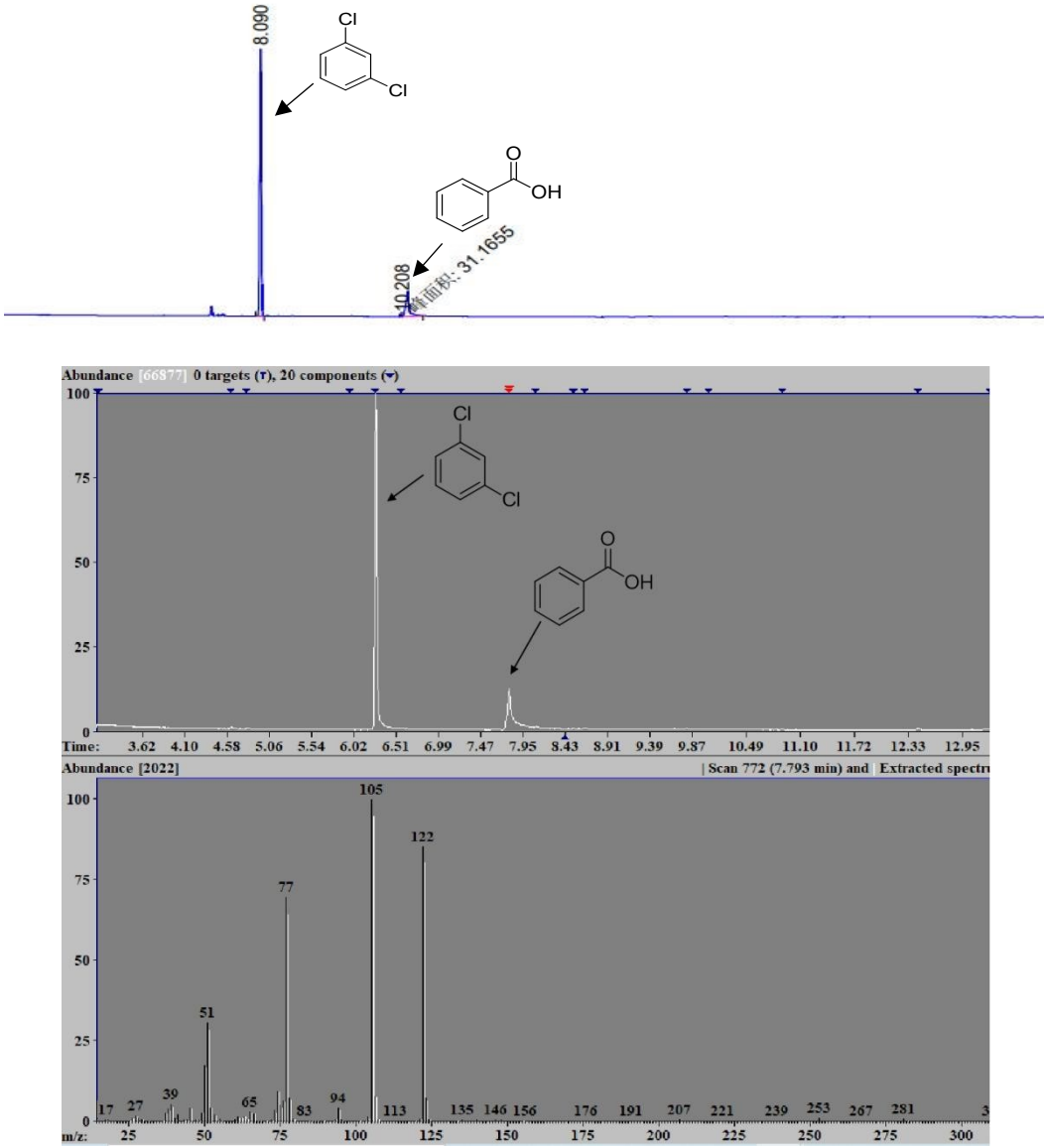


Figure S10. The GC and GC-MS spectrs for oxidative cleavage of hydrobenzoin with VO_x catalyst