Electronic Supplementary Material (ESI) for Green Chemistry.

Rhombohedral ZnIn2S4-Catalysed Anodic Direct Electrochemical Oxidative Cleavage of C-O Bond in α-O-4 Linkages in Ambient Conditions

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1. Supplementary experimental results

Figure S1. Field emission scanning electron microscopy (FESEM) images of pure carbon cloth.

Figure S2. Field emission scanning electron microscopy (FESEM) images of (a,b) H-ZIS, (d,e) ZIS-400 and (g,h) ZIS-600. Corresponding EDS patterns of (c) H-ZIS, (f) ZIS-400 and (i) ZIS-600 electrodes.

Figure S3. Field emission scanning electron microscopy (FESEM) images of cross section of the damaged electrode.

Figure S4. (a) Normalised Zn K-edge and (b) In K-edge XANES spectra of H-ZIS and R-ZIS electrodes. (c) Fourier transform of Zn K-edge EXAFS spectra in the R-space and (d-g) wavelet transform contour plot of H-ZIS and R-ZIS electrodes. (h) Fitting results of H-ZIS and R-ZIS at In K-edge and Zn K-edge.

Figure S5. LSV plots of the H-ZIS, ZIS-400, ZIS-600, and R-ZIS electrodes, obtained using the prepared pH 9 borate buffer electrolyte with and without a BPE substrate. The scan rate was 50 mV/s.

Figure S6. XRD patterns of R-ZIS electrode before and after four cycling reactions. (b, c) FESEM images of the used R-ZIS electrode.

Figure S7. Product distributions in the control experiment with the addition of phenol and benzyl alcohol intermediates on the (a) H-ZIS and (b) R-ZIS electrodes.

Figure S8. Product distributions in the control experiment with the addition of phenol and benzyl alcohol intermediates in BPE on the (a,c) H-ZIS and (b,d) R-ZIS electrodes.

Figure S9. Catalysis of BPE using the R-ZIS electrode in pH 9 buffer solutions without applied voltage in flowing O_2 conditions.

Figure S10. Mass spectra (selected ion monitoring mode) of benzyl alcohol (m/z = 108,110), benzaldehyde (m/z = 106,108), benzoic acid (m/z = 122, 126), phenol (m/z = 94, 96), hydroquinone (m/z = 110, 112), and para-benzoquinone (m/z = 108, 110) derived from BPE in isotope-labelled electrolyte.

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2.3 NMR spectra

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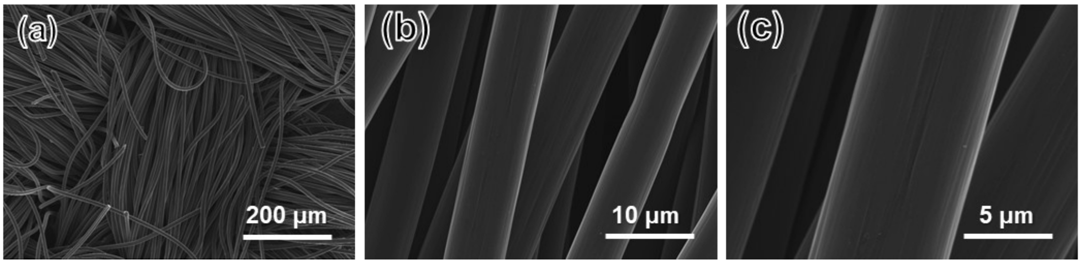

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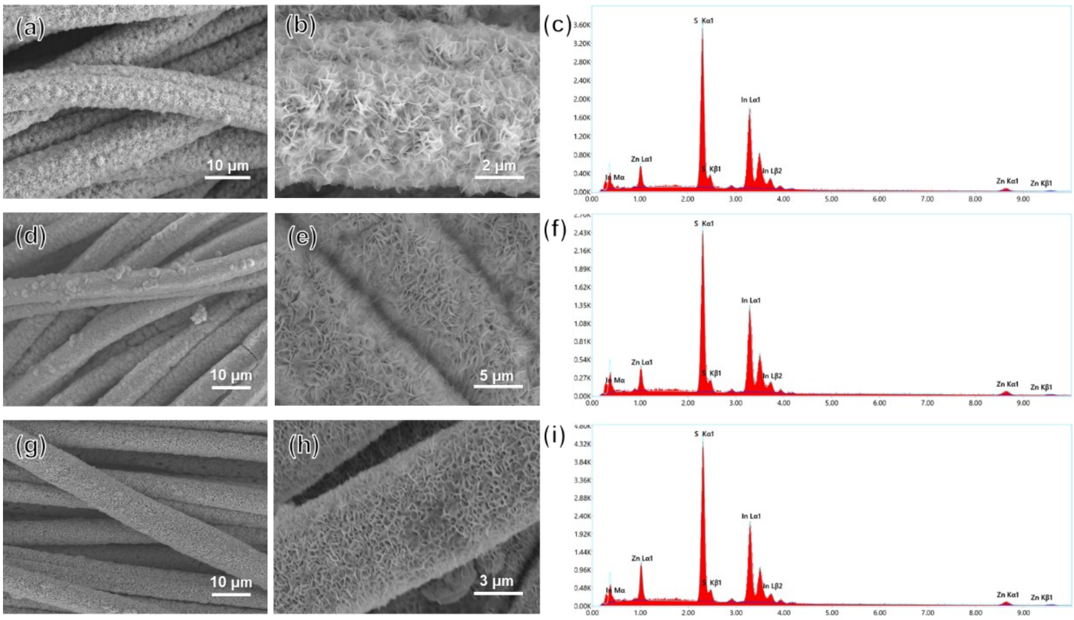

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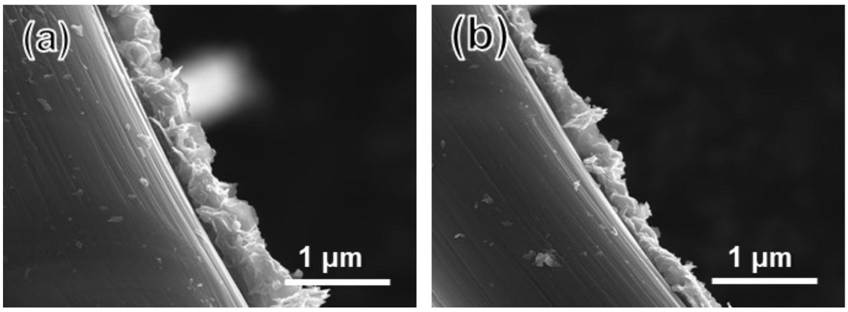
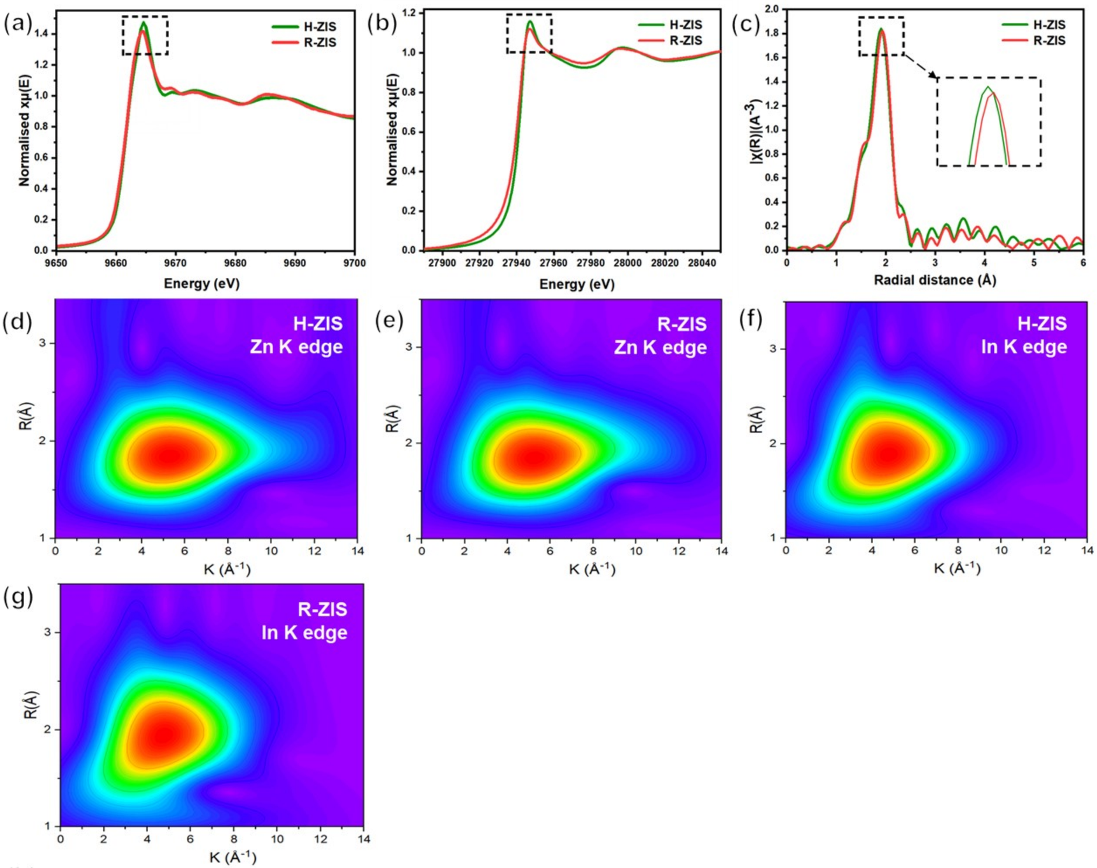


Figure S3. Field emission scanning electron microscopy (FESEM) images of the cross section of electrode after deliberately scratched off.



(h)

In K edge (H-ZIS)	In-S Coordination number	6.27±0.53	In K edge (R-ZIS)	In-S Coordination number	5.22±0.56
	In-S Bond Length	2.52±0.01		In-S Bond Length	2.56±0.01
	In-S Debye-Waller factor	0.0156		In-S Debye-Waller factor	0.0167
	R factor of total fitting	0.015		R factor of total fitting	0.013
Zn K edge (H-ZIS)	Zn-S Coordination number	4.16±0.39	Zn K edge (R-ZIS)	Zn-S Coordination number	3.49±0.68
	Zn-S Bond length	2.34±0.01		Zn-S Bond length	2.35±0.01
	Zn-S Debye-Waller factor	0.0056		Zn-S Debye-Waller factor	0.0054
	R factor of total fitting	0.015		R factor of total fitting	0.013

Figure S4. (a) Normalised Zn K-edge and (b) In K-edge XANES spectra of H-ZIS and R-ZIS electrodes. (c) Fourier transform of Zn K-edge EXAFS spectra in the *R*-space and (d-g) wavelet transform contour plots of H-ZIS and R-ZIS electrodes. (h) Fitting results of H-ZIS and R-ZIS at In K-edge and Zn K-edge.

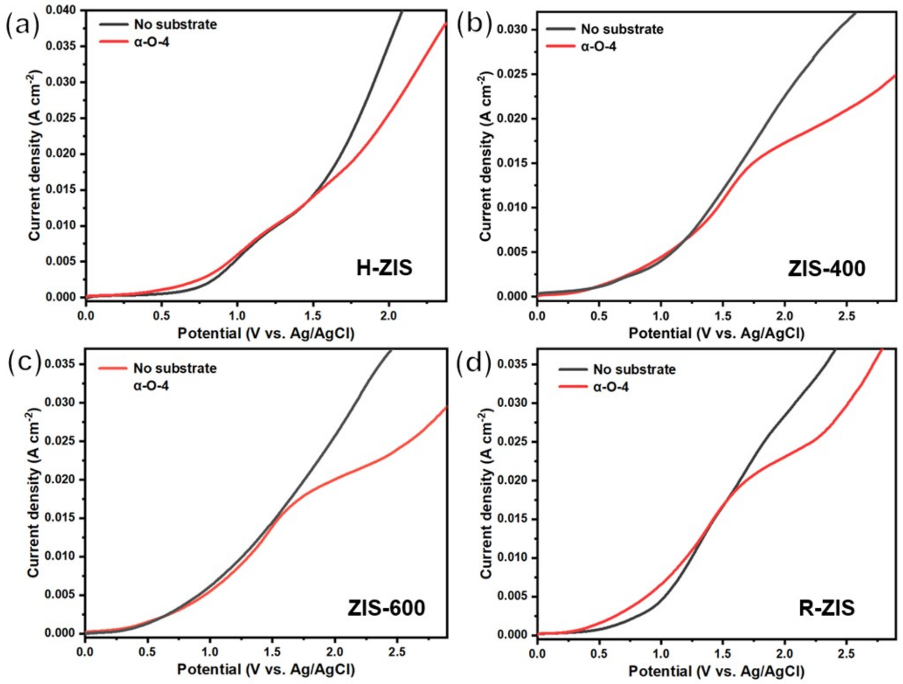


Figure S5. LSV plots of the H-ZIS, ZIS-400, ZIS-600, and R-ZIS electrodes, obtained using the prepared pH 9 borate buffer electrolyte with and without a BPE substrate. The scan rate was 50 mV/s.

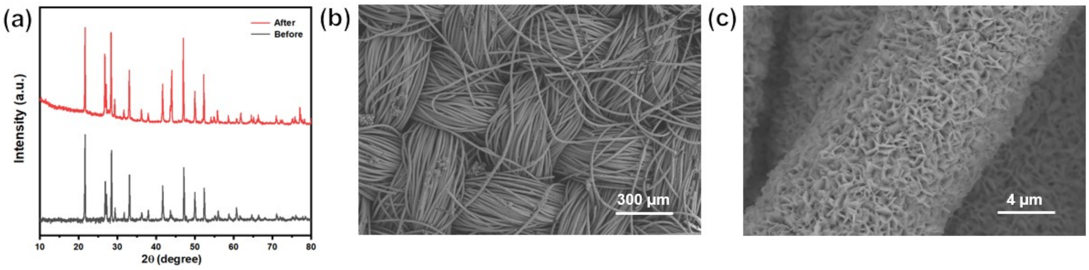


Figure S6. XRD patterns of R-ZIS electrode before and after four cycling reactions. (b, c) FESEM images of the used R-ZIS electrode.

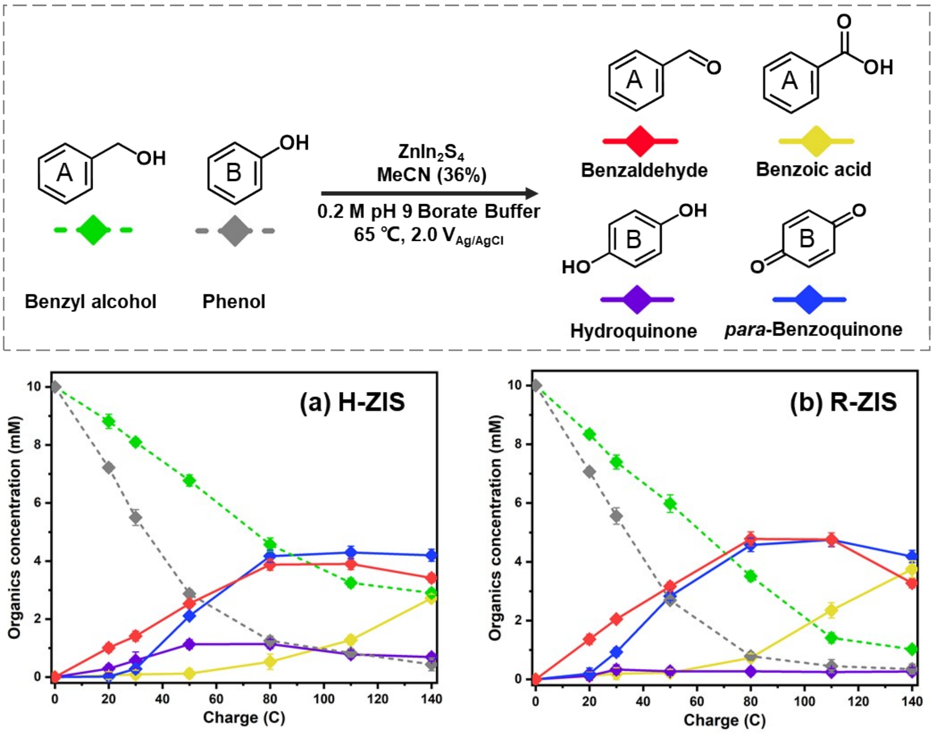


Figure S7. Product distributions in the control experiment with the addition of phenol and benzyl alcohol intermediates on the (a) H-ZIS and (b) R-ZIS electrodes.

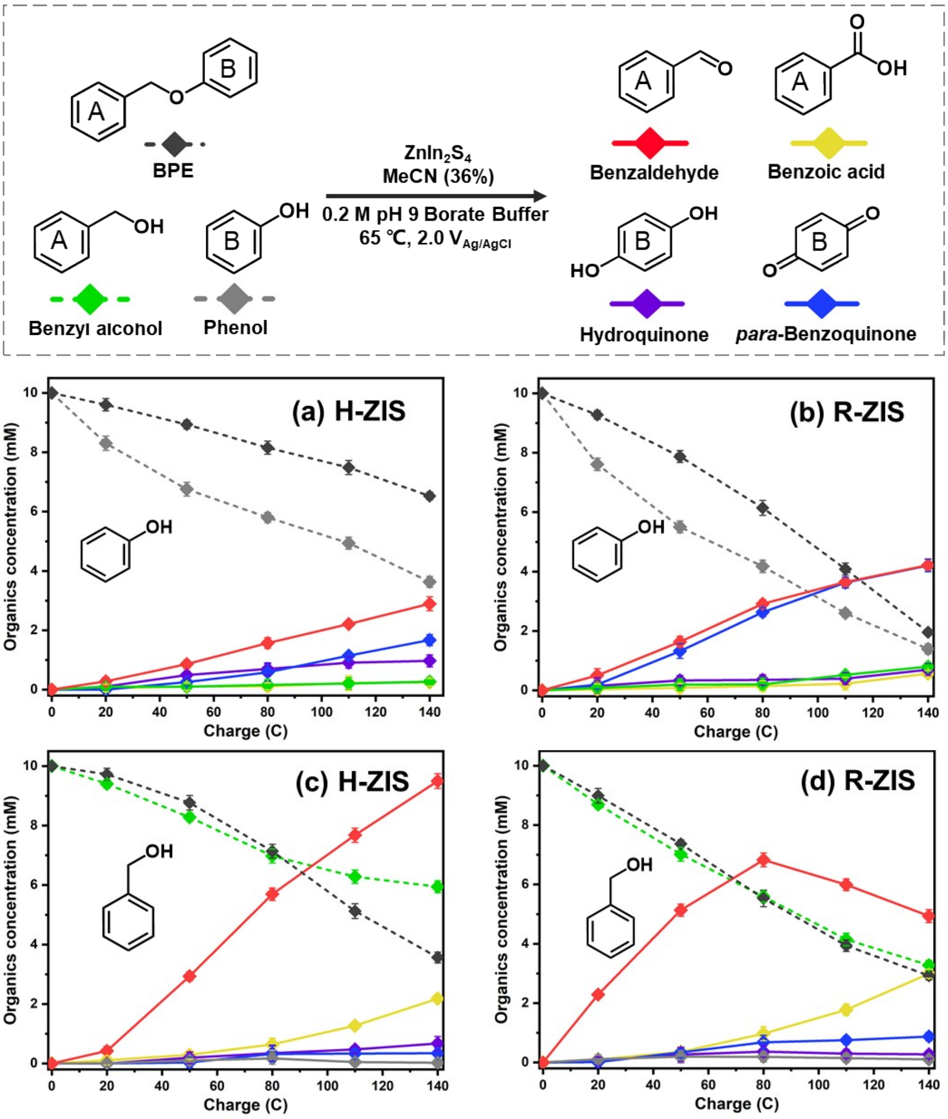


Figure S8. Product distributions in the control experiment with the addition of phenol and benzyl alcohol intermediates in BPE on the (a,c) H-ZIS and (b,d) R-ZIS electrodes.

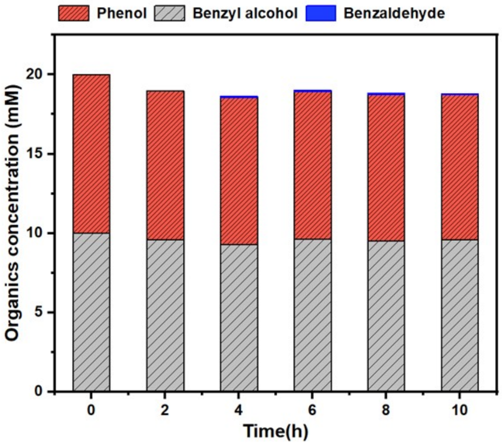


Figure S9. Catalysis of BPE using the R-ZIS electrode in pH 9 buffer solutions without applied voltage in flowing O_2 conditions.

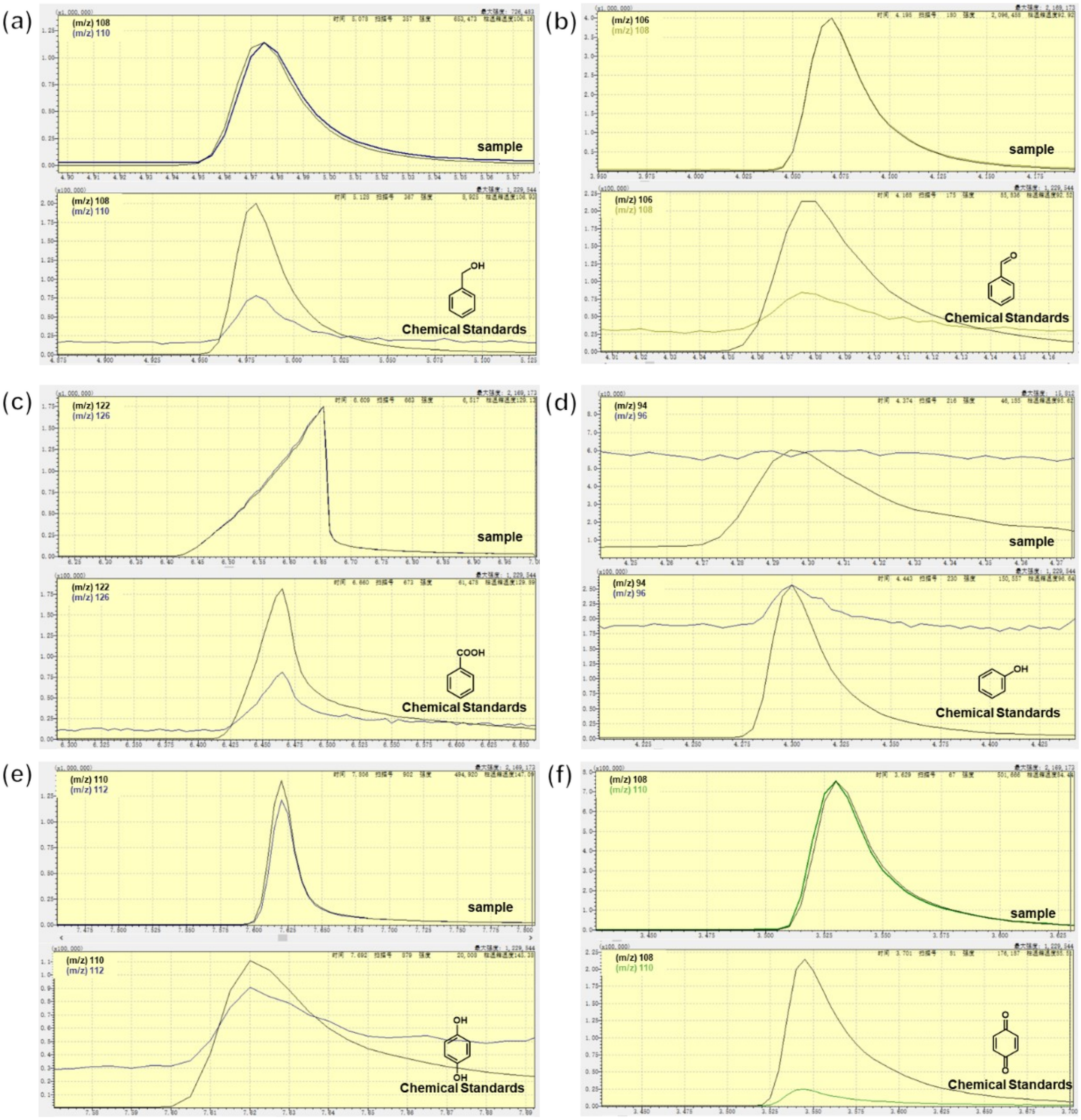


Figure S10. Mass spectra (selected ion monitoring mode) of benzyl alcohol (*m*/*z* = 108,110), benzaldehyde (*m*/*z* = 106,108), benzoic acid (*m*/*z* = 122, 126), phenol (*m*/*z* = 94, 96), hydroquinone (*m*/*z* = 110, 112), and para-benzoquinone (*m*/*z* = 108, 110) derived from BPE in isotope-labelled electrolyte.

Table S1 Previously reported electrocatalytic oxidative systems for α-O-4/β-O-4 dimers.

Electrochemical Oxidation of α-O-4 Dimers							
Substrate	**Working Electrode**	**Conversion**	**Faradaic Efficiency**	**Carbon Balance**	**Electrolyte**	**Additional Oxidant**	**Ref**
Benzyl-O-phenolic/ benzyl-O-phenyl	RuO_2–IrO_2/Ti mesh C-PTFE	65.1%/ 1.87%	5.4%	None	1 M NaOH (20-80 ℃)	O_2	1
Benzyl-O-phenolic	RuO_2–IrO_2/Ti mesh C-PTFE	92.5%	7.3%	None	[BMIM]BF_4	O_2	2
Benzyl-O-phenolic	RuO_2–IrO_2/Ti mesh Graphite felt	96.2%	14.7-29.5%	None	[$HNEt_3$][HSO_4] and CH_3CN (1:6) (20-80 ℃)	O_2	3
Electrochemical Oxidation of β-O-4 dimers							
2-phenoxy-1-phenylethanol and its derivatives	Pt foil	>99%	FE=12% in water (70% aq soln)	None	CH_3CN/THF, tert-butyl hydroperoxide	^{t}BuOOH (mediator)	4
2-phenoxy-1-phenylethanol and its derivatives	Pt$_1$/N-CNTs	99%	FE=5.6% for benzaldehyde	None	CH_3CN, tert-butyl hydroperoxide	^{t}BuOOH (mediator)	5
2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethenone and its derivatives	Graphite plate	None	None	None	CH_3OH	NaI (mediator)	6
2-(2-Methoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propanediol and its derivatives	RVC foam	None	None	None	CH_3CN and H_2O (70:30)	TEMPO/ ACT (mediators)	7
2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol and its derivatives	Carbon	None	None	None	TEATS, CH_3OH, CH_3CN	None	8
2-(2-methoxyphenoxy)-1-phenylethanone	Pt sheet electrode	94.55-100%	None	None	0.01 M $LiClO_4$/CH_3CN	None	9
2-phenoxy-1-phenylethanol and its derivatives	Pt micro-disc	39.6-43.5%	None	None	0.1 M $LiClO_4$/CH_3CN	None	10
1G, 1S, 1P	2,6-Lutidine/ Pyridine/ 2,4,6-Collidine	None	43-94%	None	0.1 M $LiClO_4$/CH_3CN	None	11
1-(4-hydroxy-3-methoxyphenyl)-1-[(2-methoxyphenyl)oxy]ethane-1,2-diol and its derivatives	DS-CoS	96%/ 98%	83.6%/ 87.2%	None	1 M KOH (PH=13.6)	None	12

TEMPO: 2,2,6,6-Tetramethylpiperidine 1-Oxyl

ACT: 4-acetamido-TEMPO

TEATS: Tetraethylammonium p-toluenesulfonate

Table S2. Contents of Zn and In metals in the R-ZIS electrode sample before and after use.

Sample	**Weight (mg)/ Area (cm^2)**	**Element**	**Content (mg cm^{-2})**	**Mole (μmol cm^{-2})**	**Standard deviation**
R-ZIS	25/0.5	Zn	0.36	5.51	0.004
		In	1.27	11.06	0.046
R-ZIS (used)	22/0.5	Zn	0.31	4.74	0.001
		In	1.10	9.58	0.031

2. Synthesis of Model Compounds

2.1 Synthesis of α-O-4 dimeric model compounds

The benzyl phenyl ether (BPE) derivative model compounds (Table 1, compound b to d) were synthesized using the Williamson ether synthesis according to literature.[13] To a solution of substituted benzylbromide (2 mmol) and phenol (3 mmol) in Acetone (9 mL) was added K_2CO_3 (4 mmol) and the reaction was refluxed for 12 h. After cooling to room temperature, the reaction was filtered, and the solvent was removed under reduced pressure. Silica gel column chromatography afforded the desired product (elute: n-hexane/ethyl acetate). ^1H NMR spectra were recorded at 400 MHz in $CDCl_3$ (Bruker Advance-III).

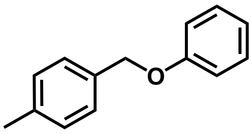
2.2 Synthesis of β-O-4 dimeric model compounds

Substituted 2-Phenoxy-1-phenylethanone (Table 1, compound i to j) was prepared by the literature procedures.[14] A 50 mL of pressure bottle was charged with phenol (7.3 mmol,) and K_2CO_3 (7.5 mmol,) in acetone (15 mL) under an Ar atmosphere and stirred at room temperature (r.t.) for 30 min. To this solution, substituted 2-bromoacetophenone (7 mmol) was added, and the resulting suspension was stirred at r.t. for 16 h, after which the suspension was filtered and concentrated in vacuo. The solid was dissolved in ethyl acetate and washed with aqueous NaOH (5%, 10 mL) and deionized water (10 mL). The organic phase was dried over anhydrous Na_2SO_4. The crude product was recrystallized from ethanol to give substituted 2-phenoxy-1-phenylethanone as a white solid.

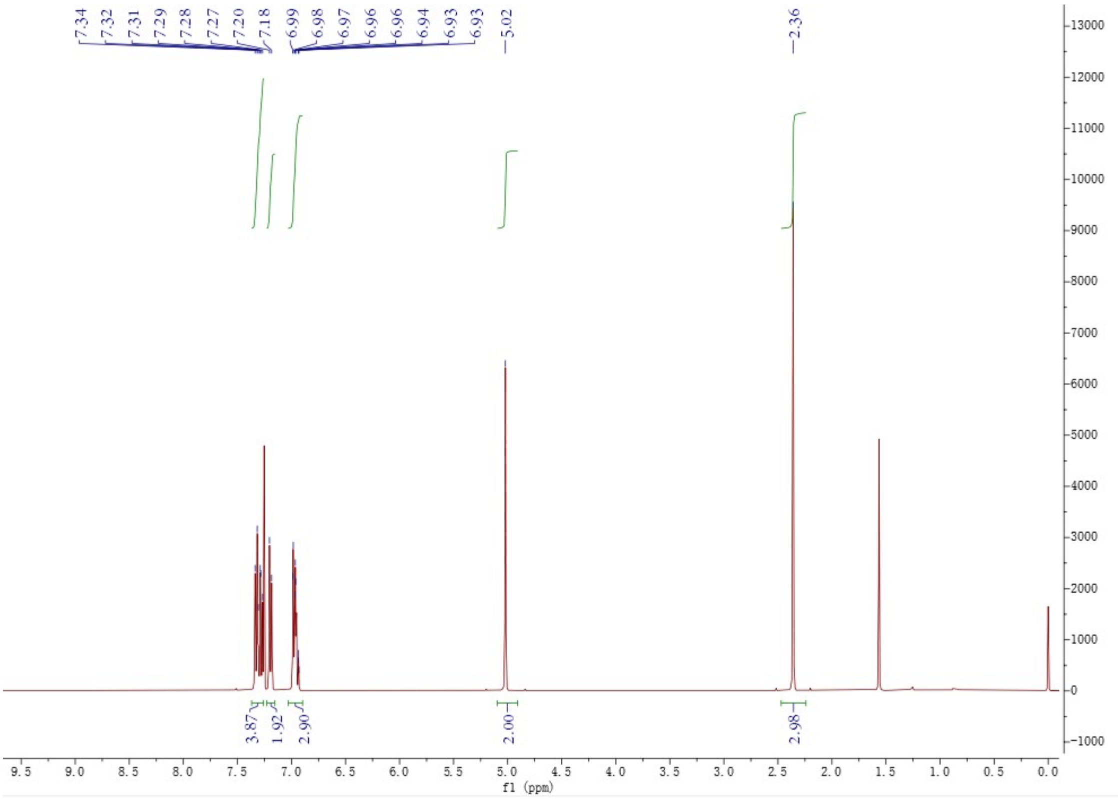
For substituted 2-Phenoxy-1-phenylethanol, a pressure bottle of 100 mL was charged with substituted 2-phenoxy-1-phenylethanone (10 mmol) and THF/water solvent (50 mL, v/v = 4/1) was added. $NaBH_4$ (12 mmol) was added in one portion and stirred at r.t. for 1.5 h. Then, an excess of saturated NH_4Cl aqueous solution (30 mL) was added. The crude product was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. The organic solvent was concentrated in vacuo and the obtained solid was dried at 45 °C for 8 h. Spectral data were in accordance with those previously reported. Silica gel column chromatography afforded the desired product (elute: n-hexane/ethyl acetate). ^1H NMR spectra were recorded at 400 MHz in $CDCl_3$ (Bruker Advance-III). Other dimeric model compounds were purchased from Aladdin Bio-Chem Technology Co., Ltd.

2.3 NMR spectra

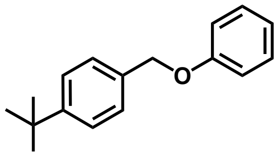
1-methyl-4-(phenoxymethyl)benzene



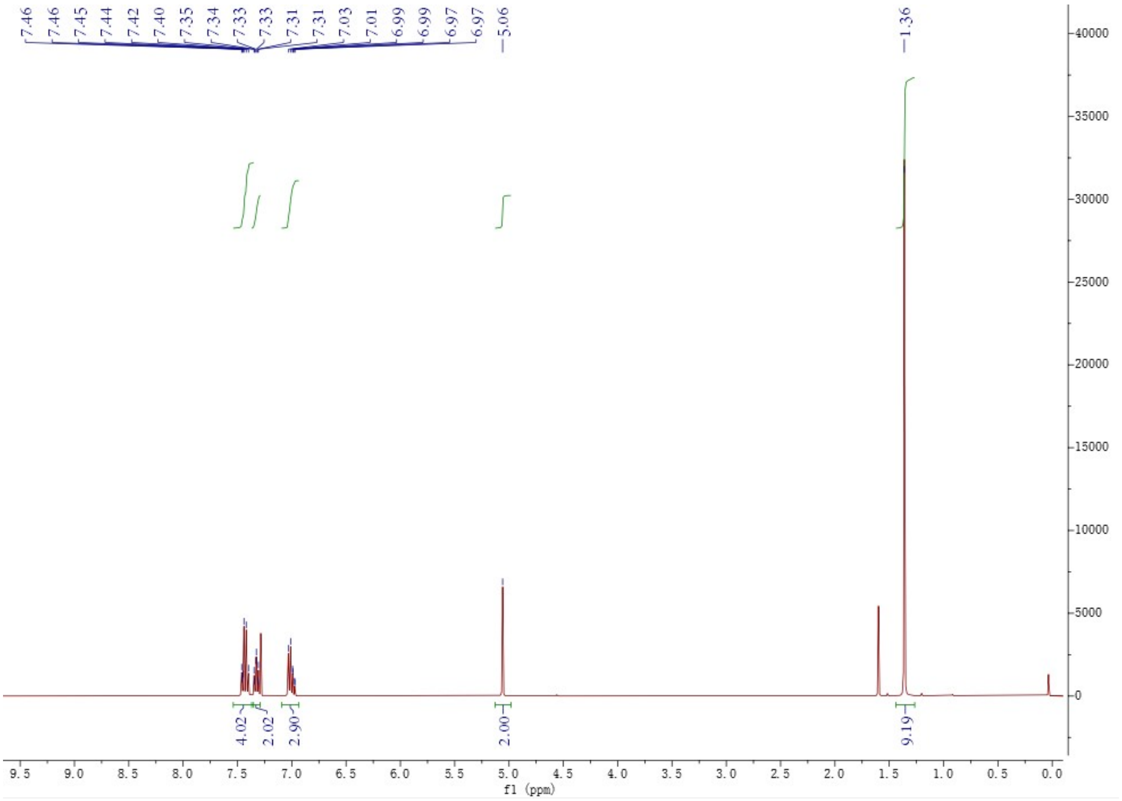
Prepared from 4-methylbenzyl bromide and phenol in 67% yield. Crystalline solid.



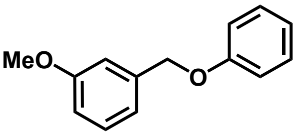
1-(*tert*-Butyl)-4-(phenoxymethyl)benzene



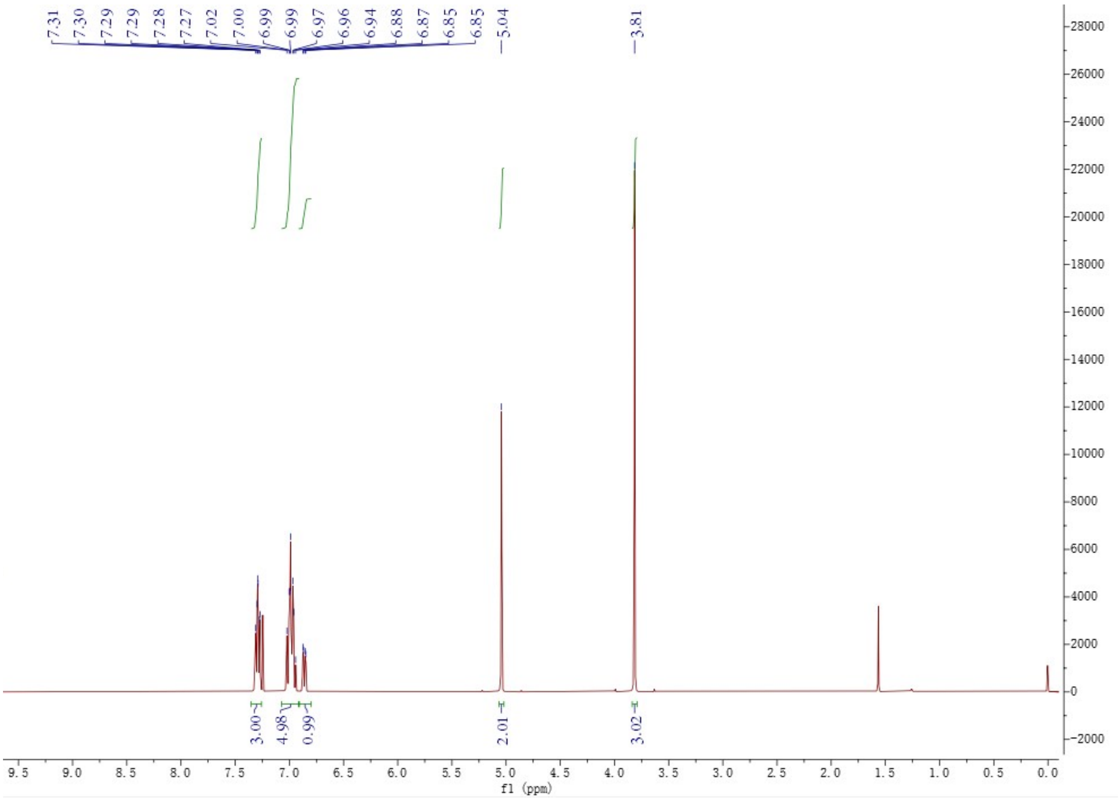
Prepared from 1-(bromomethyl)-4-(tert-butyl)benzene and phenol in 45% yield. Crystalline solid.



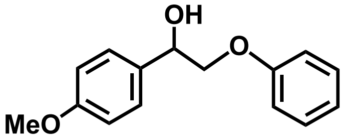
1-methoxy-3-(phenoxymethyl)benzene



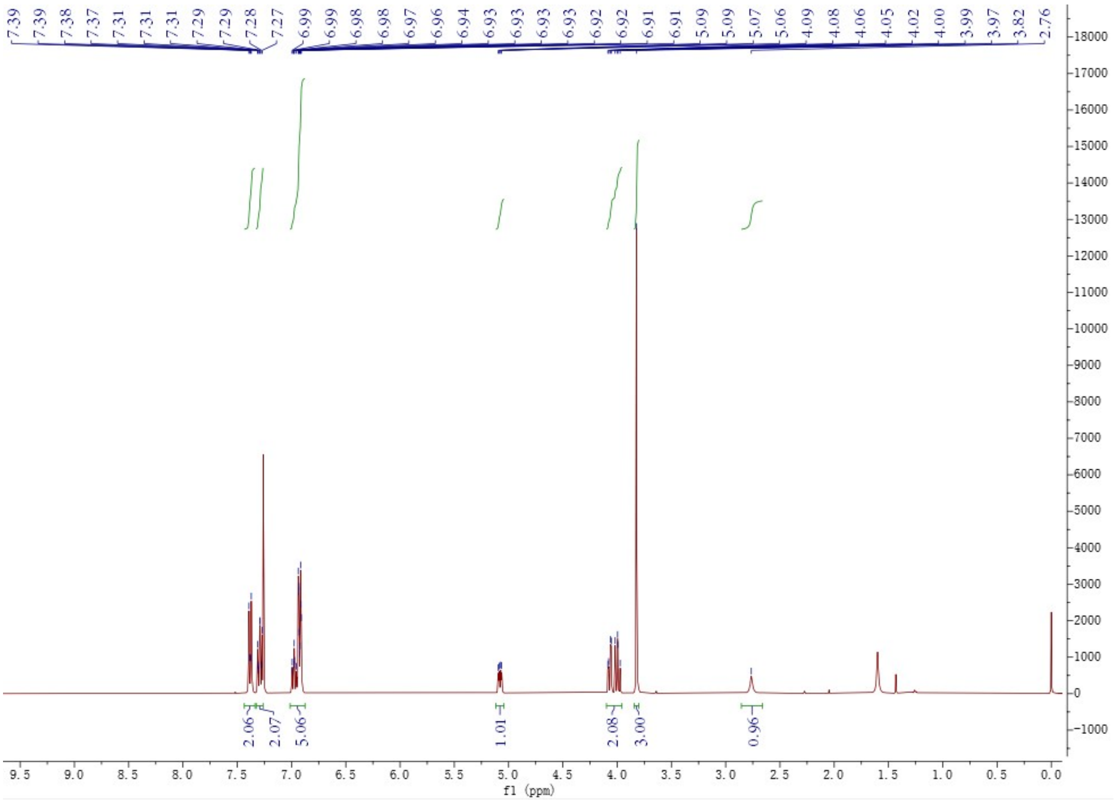
Prepared from 3-methoxybenzyl bromide and phenol in 70% yield. Crystalline solid.



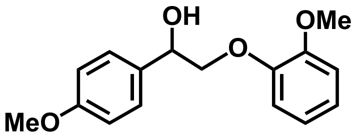
1-(4-methoxyphenyl)-2-phenoxyethanol



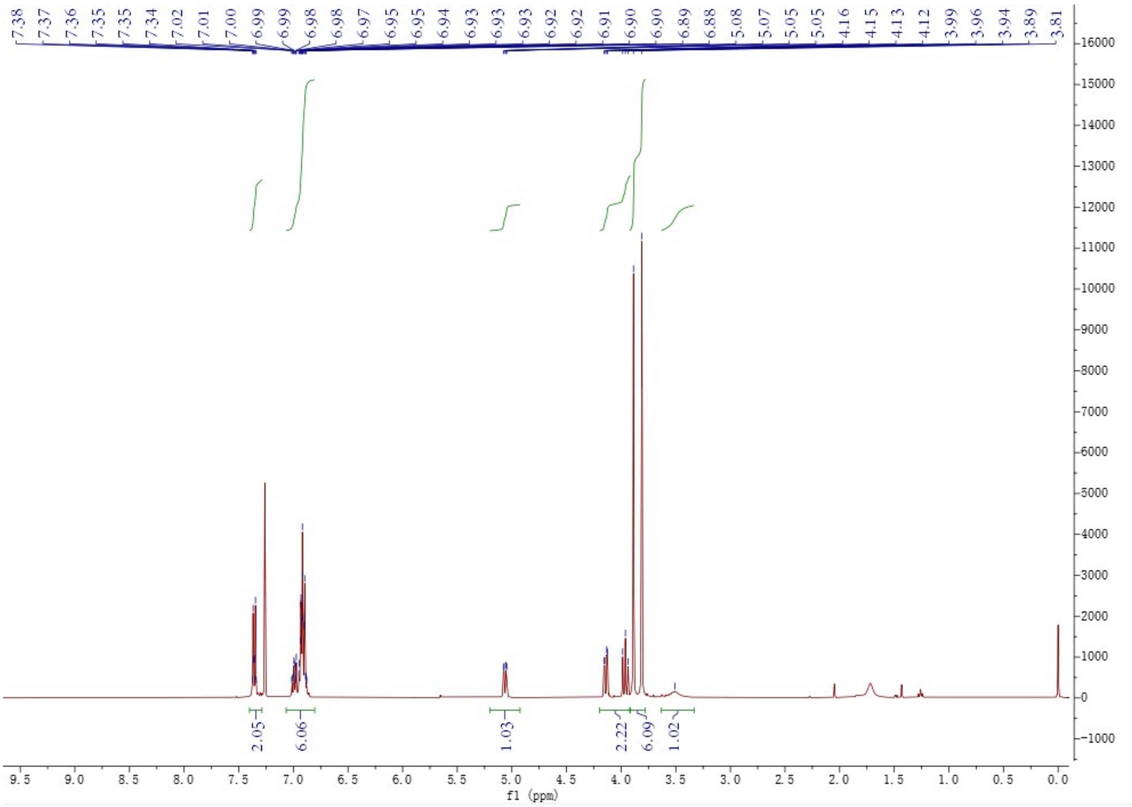
Prepared from 2-bromo-1-(4-methoxyphenyl)ethanone and phenol in 90% yield. White solid.



2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol



Prepared from 2-bromo-1-(4-methoxyphenyl)ethanone and guaiacol in 87% yield. White solid.



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