Supporting Information for

Asymmetric Electrocarboxylation of 4'-methylacetophenone over PrCoO₃ Perovskites

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1. Supplementary Methods

The product obtained by asymmetric electrocarboxylation of 4'-methylacetophenone is 2-hydroxy-2-(4-methylphenyl)propanoic acid. The ee value and yield are both detected by HPLC. The specific detection method is as follows: chiral chromatographic column: AD-H, the mobile phase ratio: n-hexane: isopropanol: trifluoroacetic acid = 80:20:1, the UV detection wavelength: 235 nm, the mobile phase flow rate: 0.50 mL/min, the injection volume: 20 μL. Peaks of both R and S configurations of 2-hydroxy-2-(4-methylphenyl)propanoic acid (**Fig. S1**) can be detected by HPLC.

The ee value of the product is determined by the peak integral area corresponding to the two configurations of R and S in **Fig. S2**, using the following formula:

$$ee = |([R]-[S])/([R]+[S])| \times 100\%$$

Where [R] and [S] are corresponded to the peak integrated areas of the R and S configuration products from the HPLC chart, respectively.

The yield of the product was calculated from the sum of the areas of the two peaks, ie, [R]+[S], according to the calibration curve.
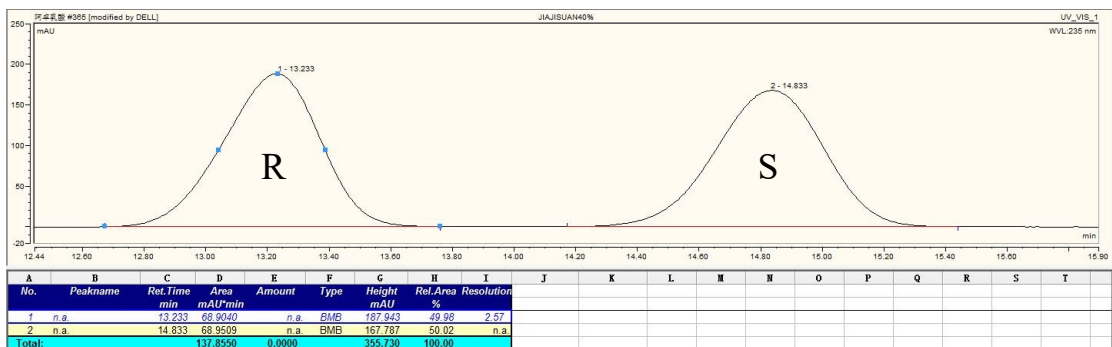
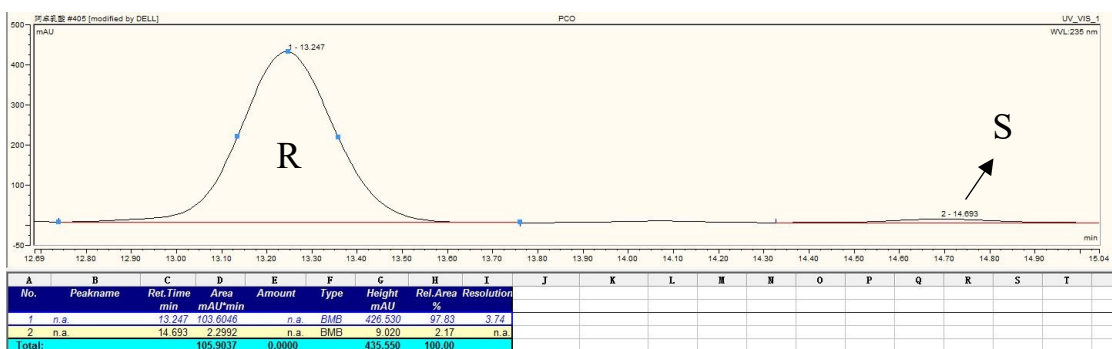**Fig. S1** HPLC chromatogram of standard product.

Fig. S2 HPLC chromatogram of post-electrolysis solution obtained on PrCoO$_3$ cathode.
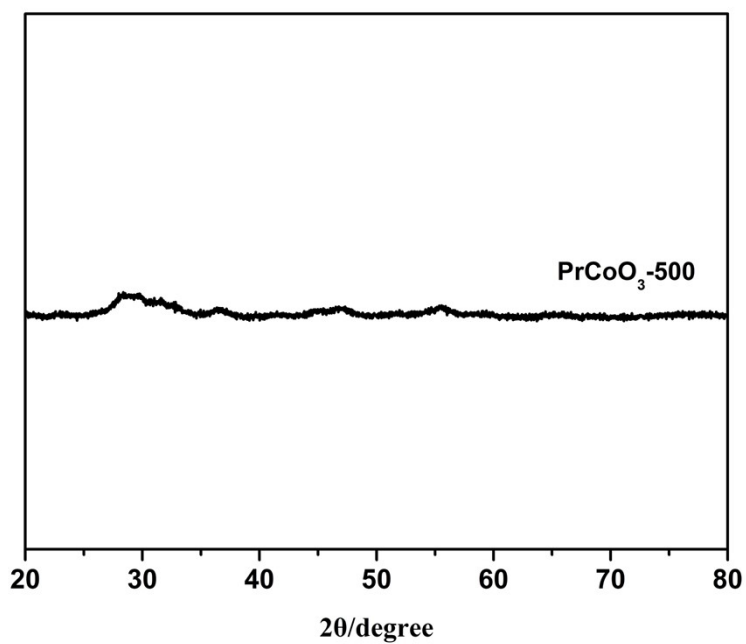
2. Supplementary Figures
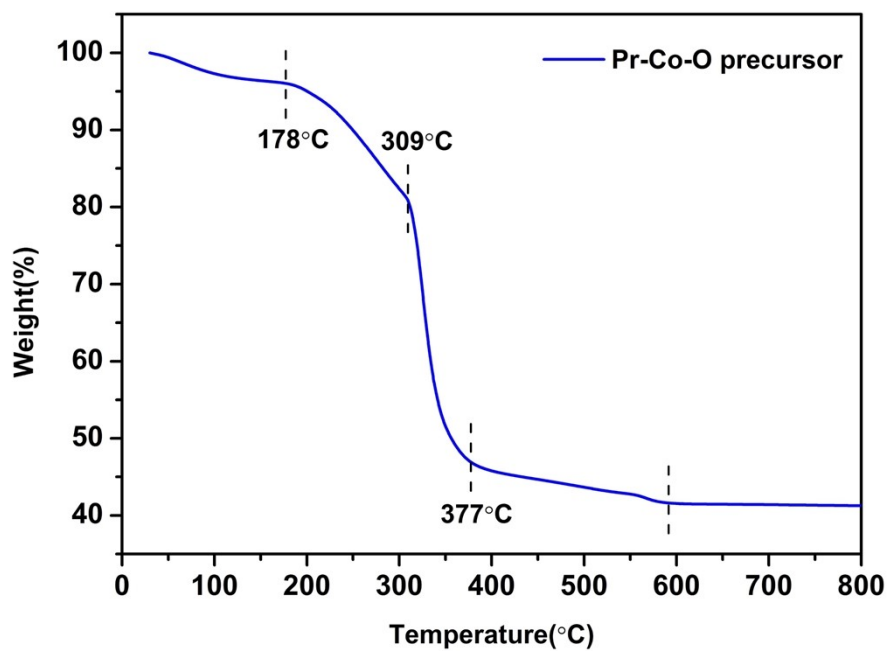

Fig. S3 XRD pattern of $PrCoO_3$-500.

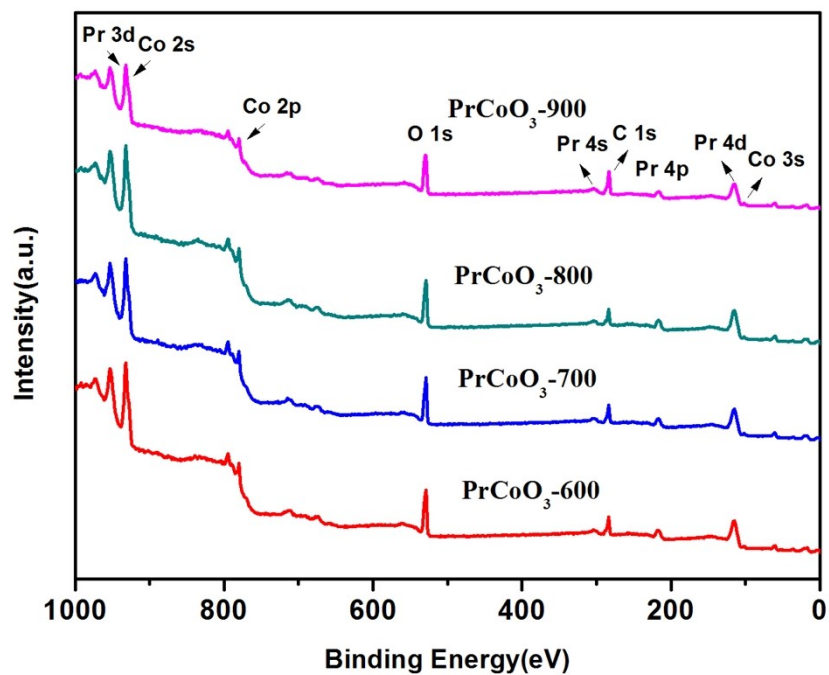**Fig. S4** TGA curve of Pr-Co-O precursor.
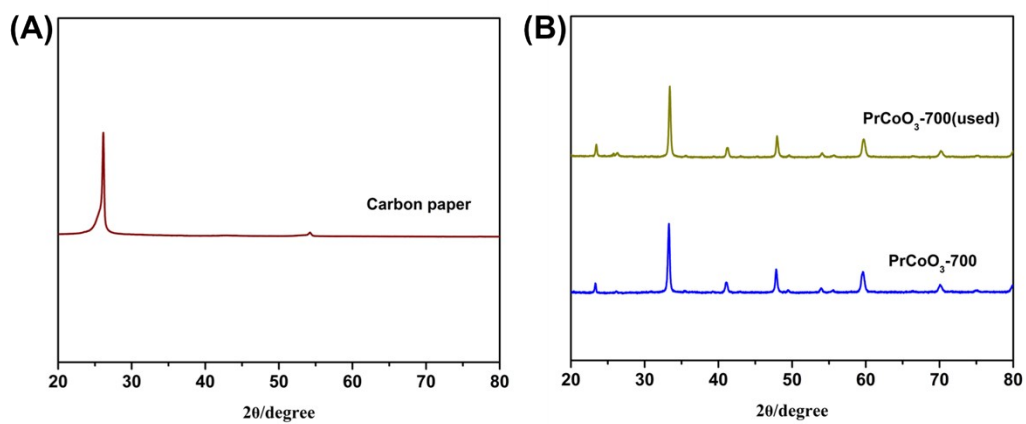
Fig. S5 XPS spectra of PrCoO$_3$-T.

Fig. S6 XRD patterns of (A) PrCoO$_3$-700 before and after use and (B) CP.
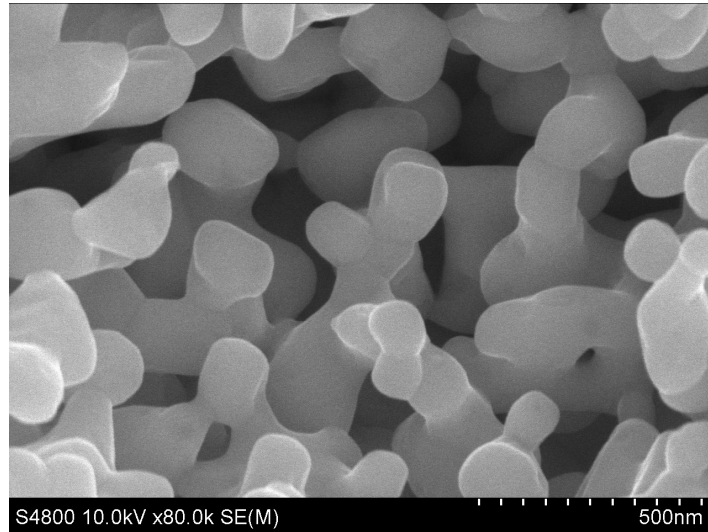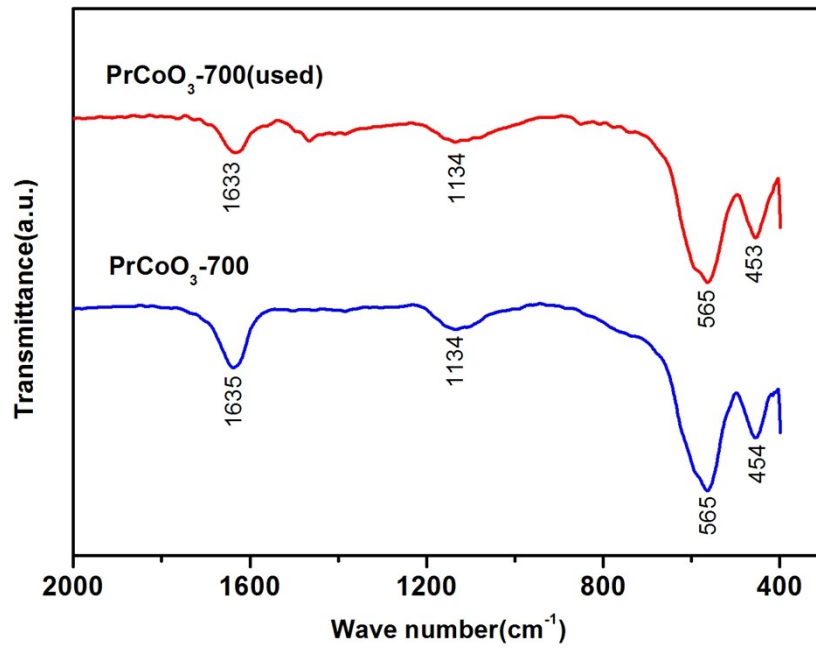
Fig. S7 SEM image of used PrCoO$_3$-700.

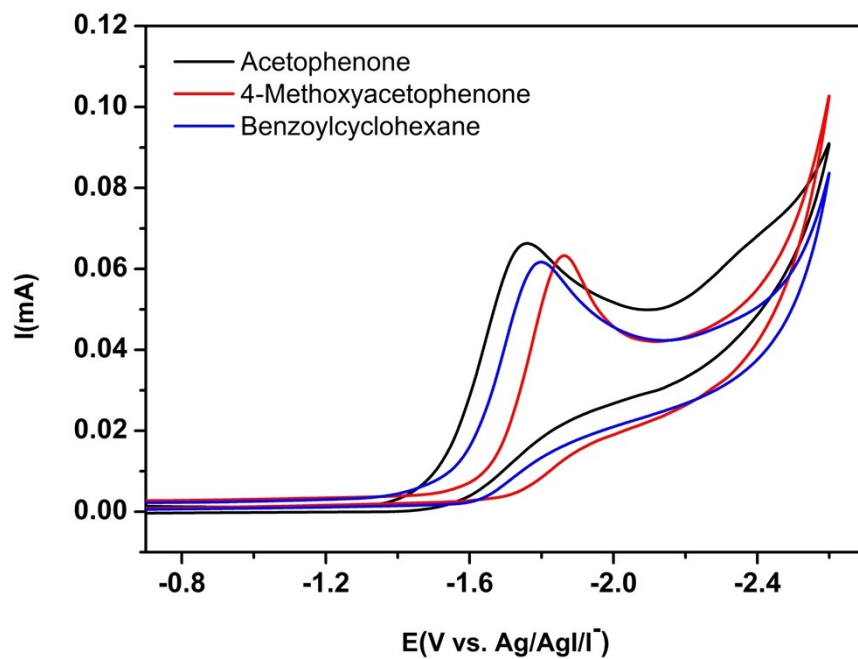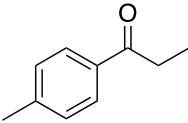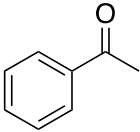**Fig. S8** FT-IR spectra of PrCoO$_3$-700 before and after use.

Fig. S9 Cyclic voltammograms of 10 mM different aromatic ketones in DMF-0.1 M TEAI with the scan rate of 0.1 V s^{-1} under CO_2 atmosphere on $PrCoO_3$-700.

3. Supplementary Tables

Table S1 O 1s and Co $2p_{3/2}$ XPS analyses of $PrCoO_3$-T

Material	$O_A:O_L$	Co^{3+}/Co^2
$PrCoO_3$-600	1.02	2.69
$PrCoO_3$-700	1.65	2.78
$PrCoO_3$-800	1.07	2.48
$PrCoO_3$-900	1.01	2.34

Table S2 Compared of $PrCoO_3$ for asymmetric electrocarboxylation of aromatic ketones with other published methods

Substrate	Electrode	Inducer	Yield (%)[b]	ee (%)[c]	Ref.
	Ss	CN	37.4	S-32.8	[1]
	Ss	CD	24.5	R-29.8	[2]
	$LaFeO_3$	t-Bu(R,R)salen(Co(II))	50	R-82	[3]
	$La_7Sr_3Fe_8Ni_2O_3$	t-Bu(R,R)salen(Co(II))	79	R-94	[4]
	$PrCoO_3$	t-Bu(R,R)salen(Co(II))	54	R-95	This work

[a] Solvent: DMF. Anode: Pt Mesh. Supporting electrolyte: 0.1 M TEAI. Substrate concentration: 50 mM. Inducer concentration: 2.5 mM. $P(CO_2)$: 1×10^5 Pa. Temperature: 20°C.
[b] The yield was based on the substrate.
[c] The ee was determined by HPLC analysis. R- (S-): Rectus (Sinister) configuration dominated.

4. References

[1]   S.-F. Zhao, M.-X. Zhu, K. Zhang, H. Wang and J.-X. Lu, *Tetrahedron Letters*, 2011, **52**, 2702-2705.

[2]   K. Zhang, H. Wang, S.-F. Zhao, D.-F. Niu and J.-X. Lu, *Journal of Electroanalytical Chemistry*, 2009, **630**, 35-41.

[3]   L.-R. Yang, J.-J. Zhang, Y.-J. Zhao, Z.-L. Wang, H. Wang and J.-X. Lu, *Electrochimica Acta*, 2021, **398**, 139308-139316.

[4]   L.-R. Yang, Y.-J. Zhao, C.-J. Jiang, R. Xiong, H. Wang and J.-X. Lu, *Journal of Catalysis*, 2021, **401**, 224-233.