Supplementary Information

Construction of a P/S dual-atom coordinated Co heterogeneous mononuclear complex catalyst for hydroformylation

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Supplementary Figures

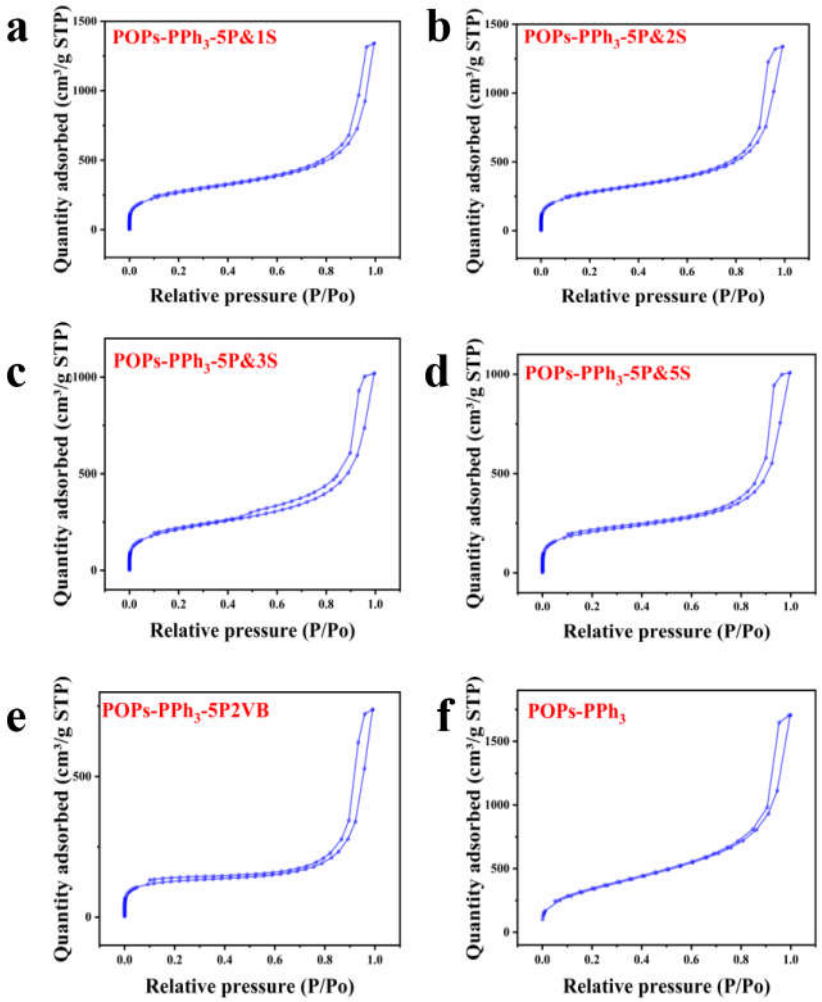


Figure S1. The nitrogen physical adsorption curves of POPs-PPh_3-P&S：（a）POPs-PPh_3-5P&1S;（b）POPs-PPh_3-5P&2S;（c）POPs-PPh_3-5P&3S;（d）POPs-PPh_3-5P&5S;（e）POPs-PPh_3-5P&2VB;　(f) POPs-PPh_3

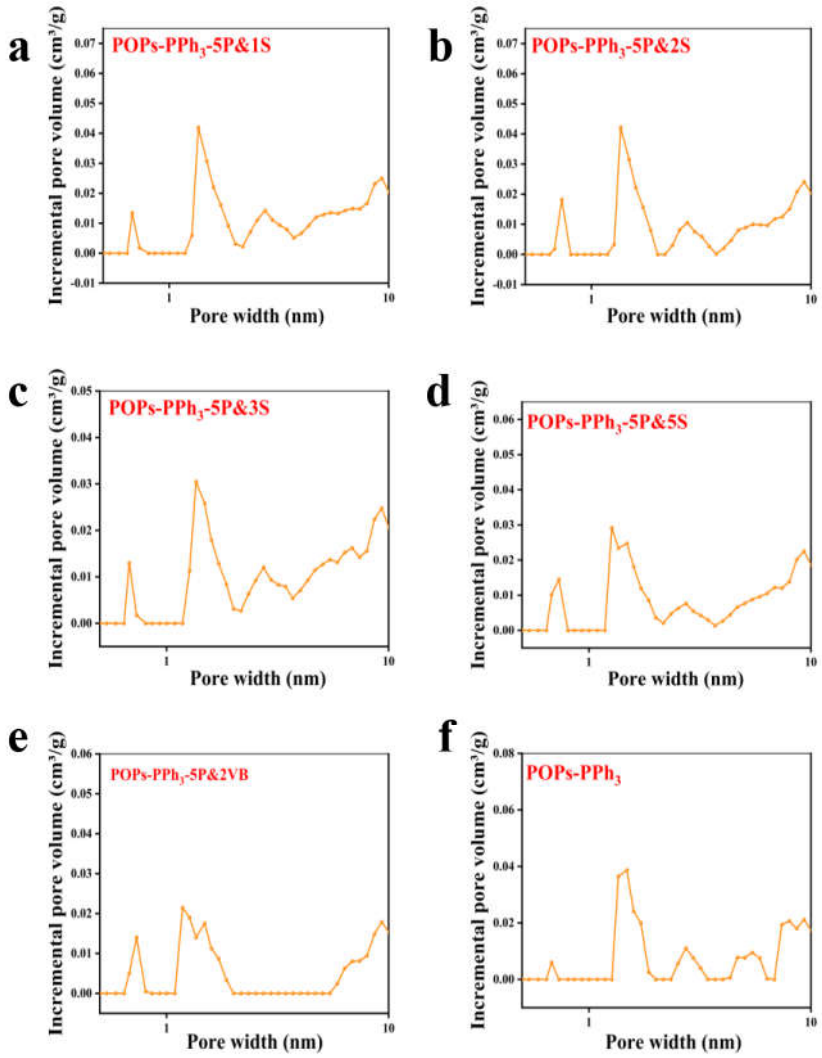


Figure S2. The pore distribution curves of POPs-PPh_3- P&S ：（a）POPs-PPh_3-5P&1S;（b）POPs-PPh_3-5P&2S;（c）POPs-PPh_3-5P&3S;（d）POPs-PPh_3-5P&5S;（e）POPs-PPh_3-5P&2VB; (f) POPs-PPh_3

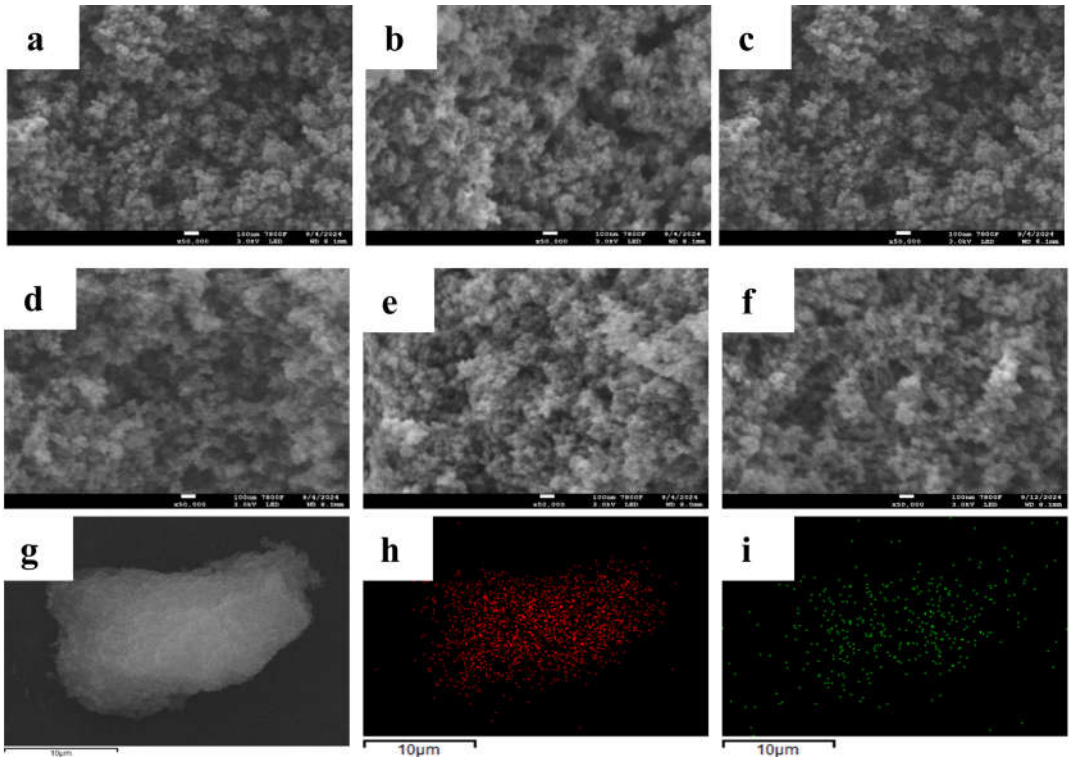


Figure S3. The SEM images of POPs-PPh_3- P&S: (a) POPs-PPh_3 (b) POPs-PPh_3-5P&1S (c) POPs-PPh_3-5P&2S (d) POPs-PPh_3-5P&3S (e) POPs-PPh_3-5P&5S (f) POPs-PPh_3-5P&2VB (g-i) EDS of the POPs-PPh_3-5P&2S, the red color was P and the green color was S.

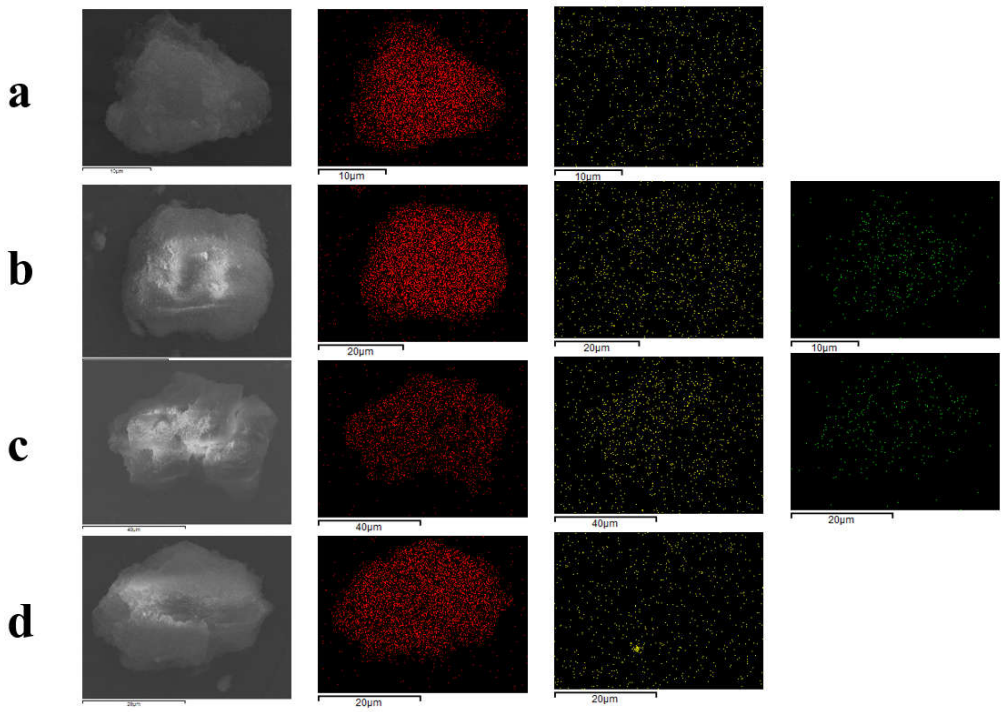


Figure S4. The EDS mapping of Co_1/POPs-PPh_3-P&S (a) Co_1/POPs-PPh_3 (b) Co_1/POPs-PPh_3-5P&1S (c) Co_1/POPs-PPh_3-5P&2S (d) Co_1/POPs-PPh_3-5P&2VB. The red color was P, the yellow color was Co, the green color was S.

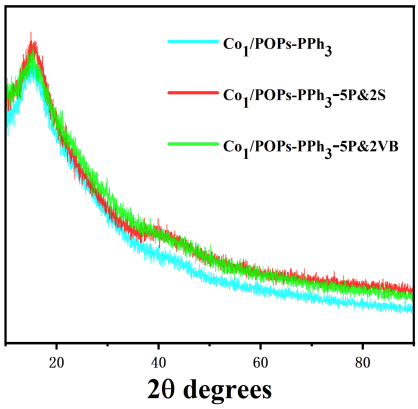


Figure S5. XRD comparison of Co_1/POPs-PPh_3, Co_1/POPs-PPh_3-5P&2S, and Co_1/POPs-PPh_3-5P&2VB

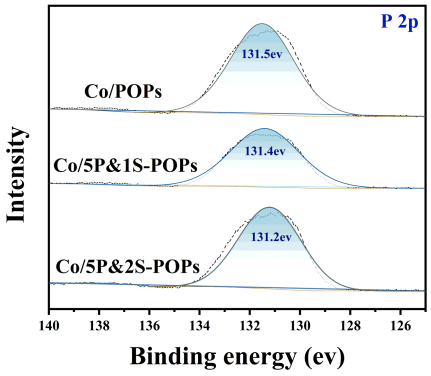


Figure S6. XPS Characterizatio of P 2p

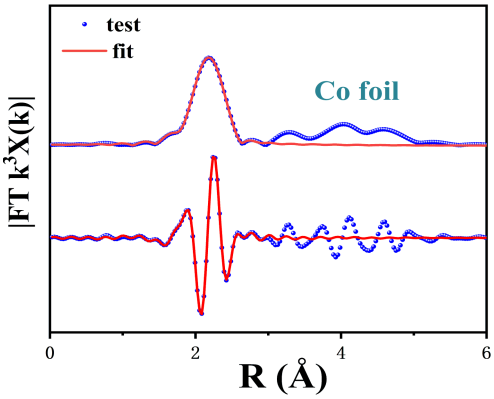


Figure S7. Co K-edge WT-EXAFS contour plots of Co foil

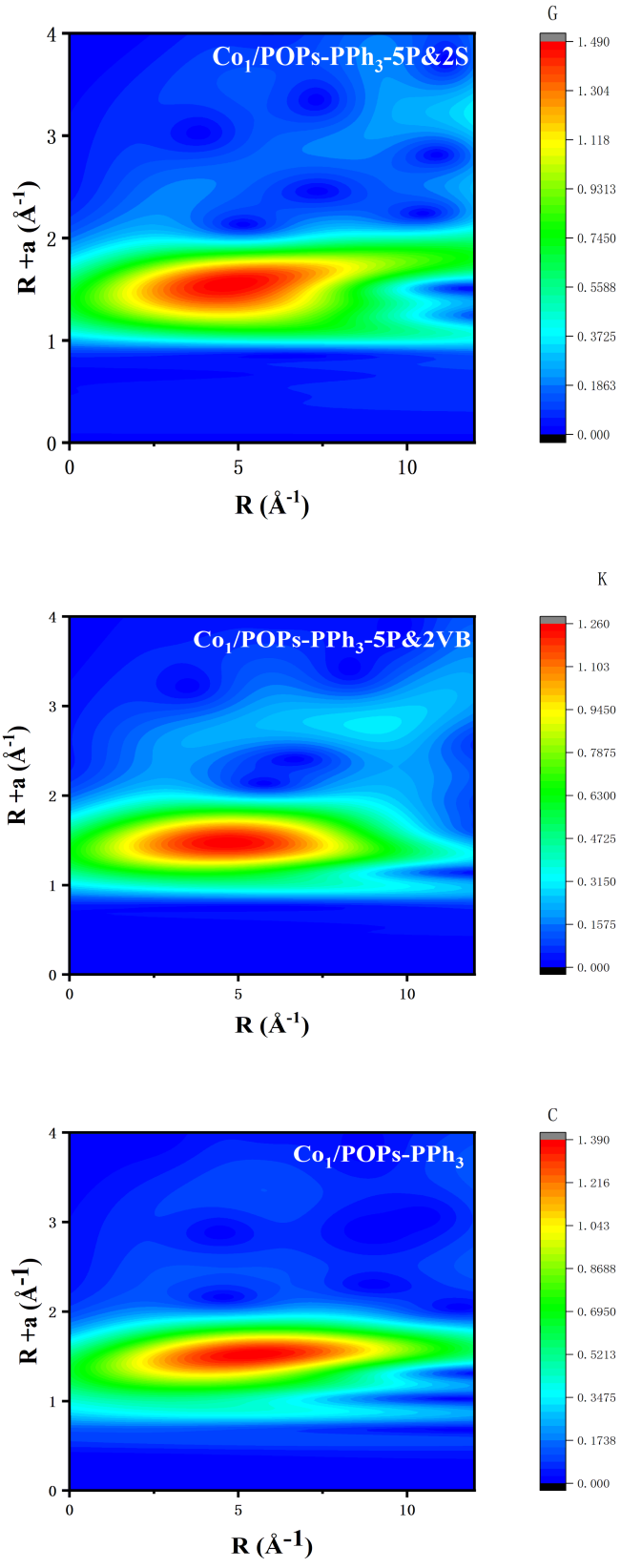


Figure S8. Wavelet transform analysis of Co_1/POPs- PPh_3-P&S

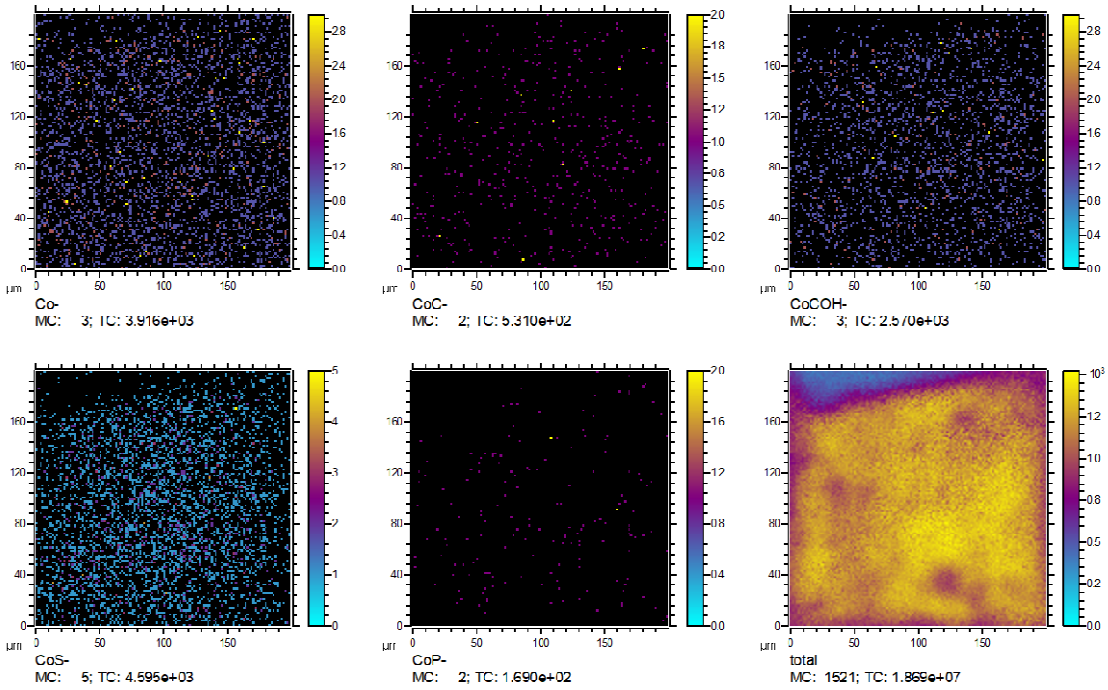


Figure S9. TOF-SIMS analysis of Co_1/POPs- PPh_3-P&S

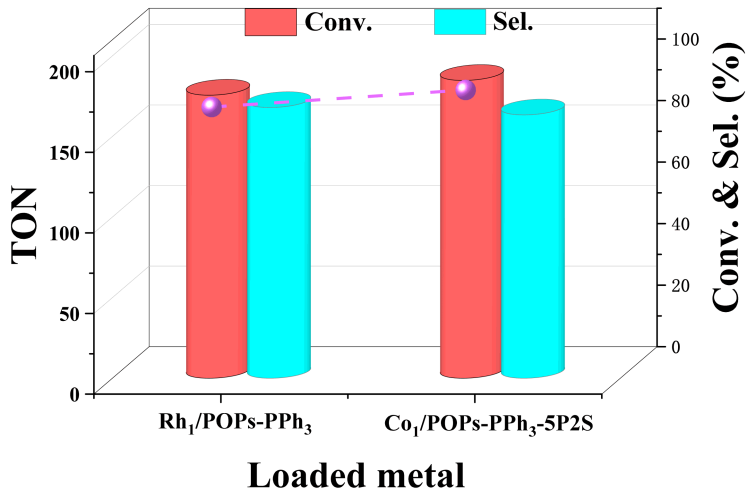


Figure S10. Comparison of catalytic performance over different catalysts (S/C=200, 8 MPa, 160 °C, 30 h)

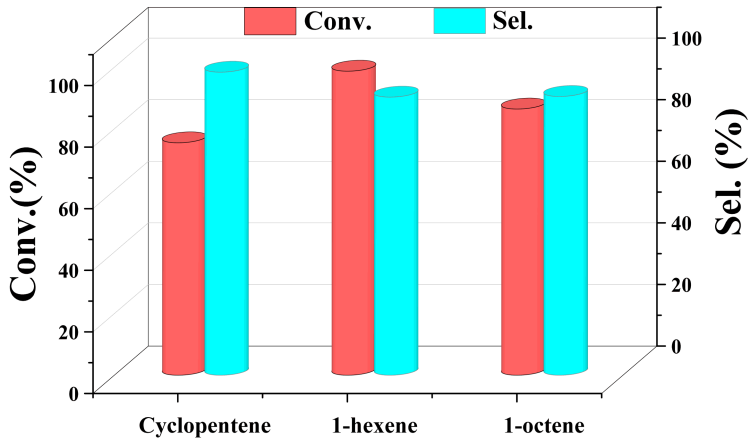


Figure S11. Catalytic performance of Co_1/POPs-PPh_3-5P&2S catalyst over different substrates（Reaction conditions: 5 mmol olefin, 20 mg catalyst, at 120 °C under 2 MPa for 6 h）.

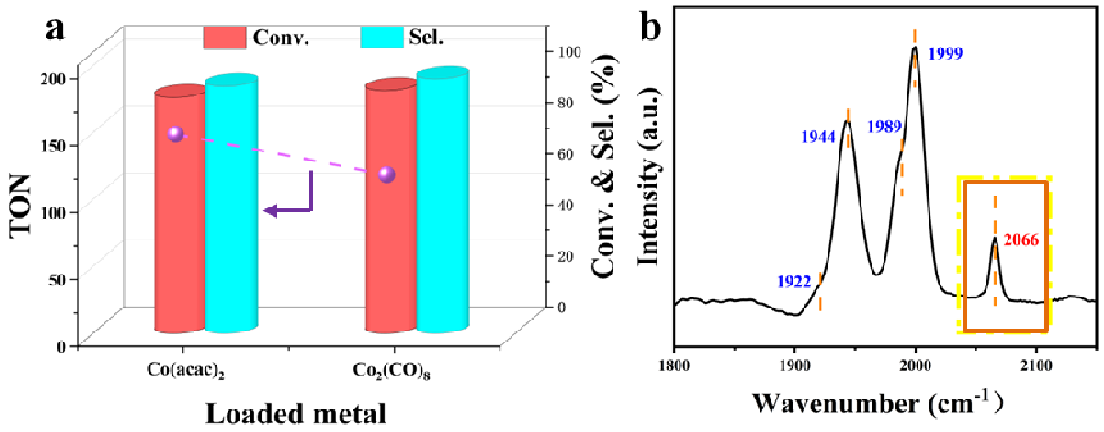


Figure S12. (a) Comparison of catalytic data over different supported metals (S/C = 200, 2 MPa, 120 °C, 30 h); (b) In-situ FTIR spectrum of $Co(acac)_2$-loaded Co_1/POPs-PPh_3-5P2S at 2 MPa.

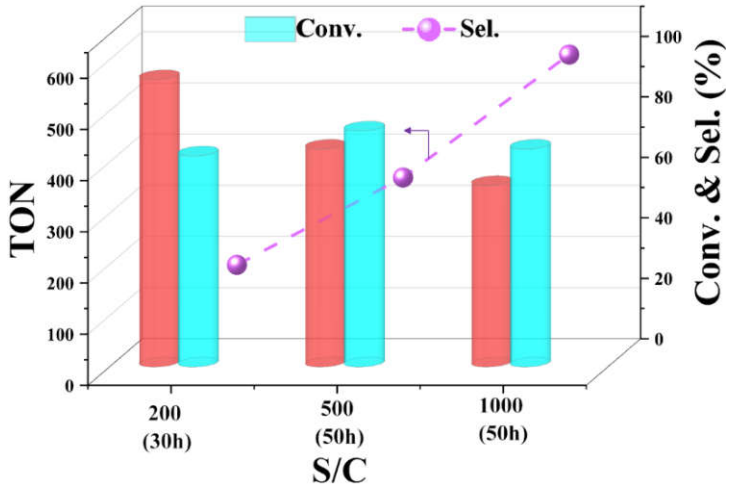


Figure S13. Catalytic performance of the Co_1/POPs-PPh_3-5P&2S catalyst under different reaction conditions. From left to right:(1) S/C = 200, 6 MPa, 120 °C, 30 h; (2) S/C = 500, 6 MPa, 120 °C, 50 h; (3) S/C = 1000, 6 MPa, 120 °C, 50 h.

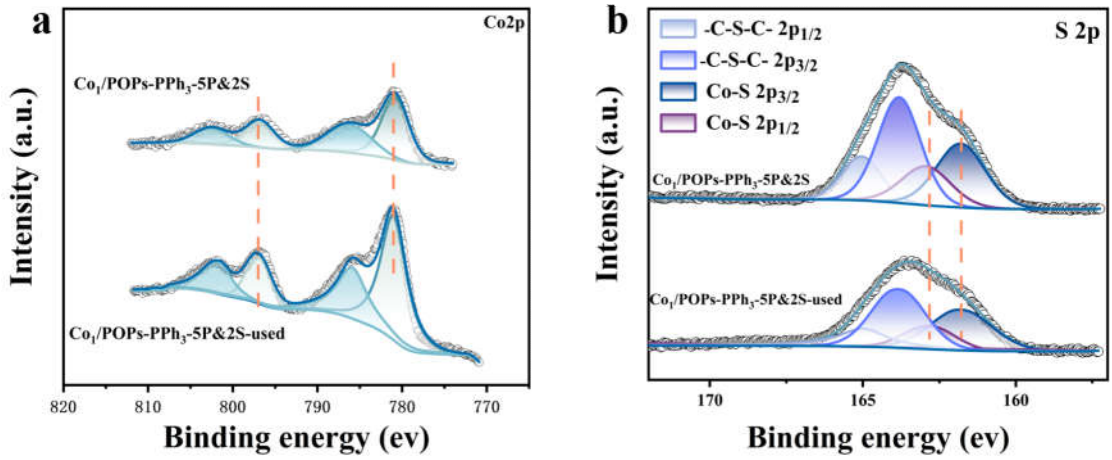


Figure S14. XPS spectra of Co 2p and P 2p for Co_1/POPs-PPh_3-5P&2S before and after reaction.

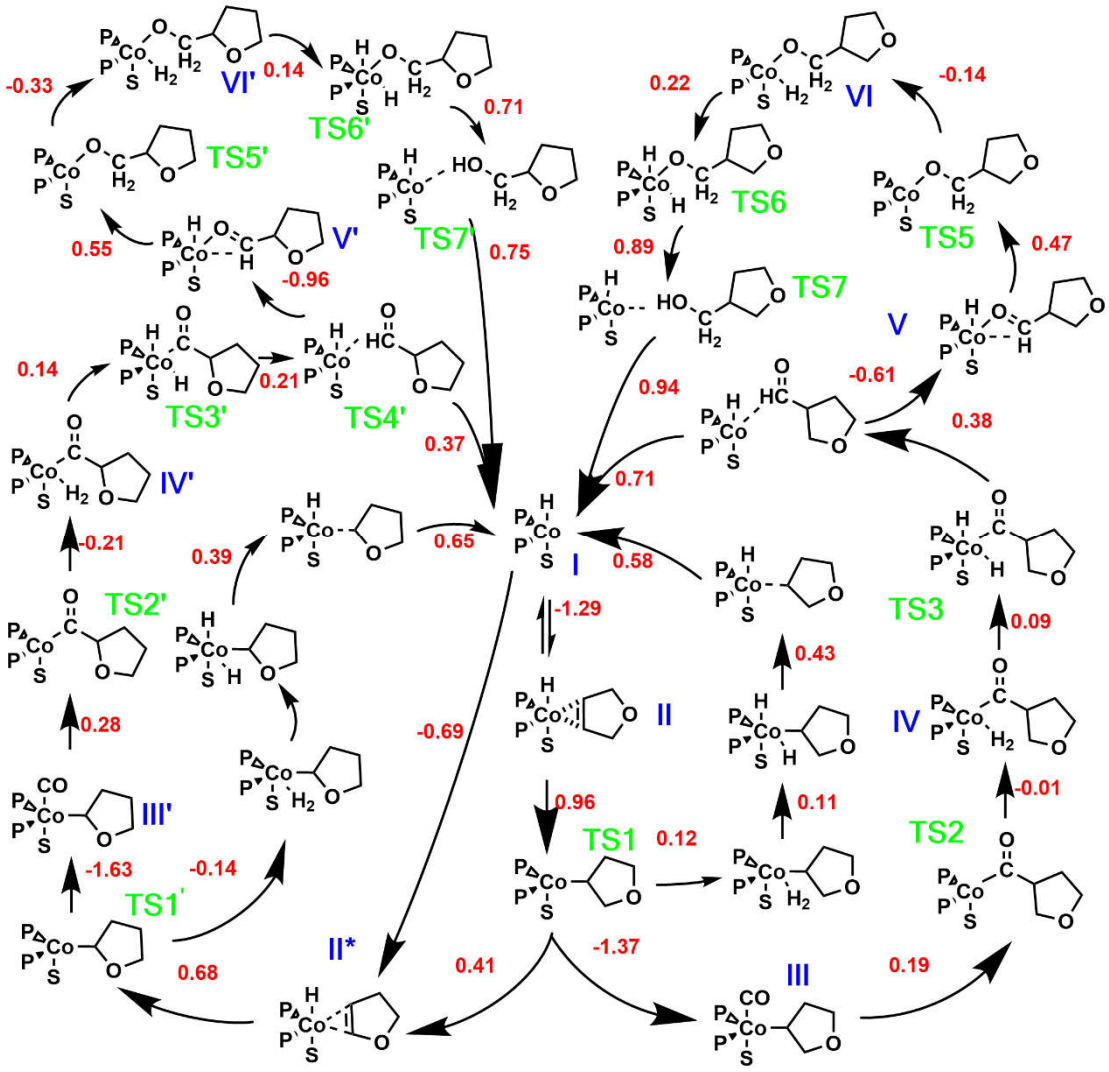


Figure S15. Complete reaction process of Co_1/POPs-PPh_3-5P&2S

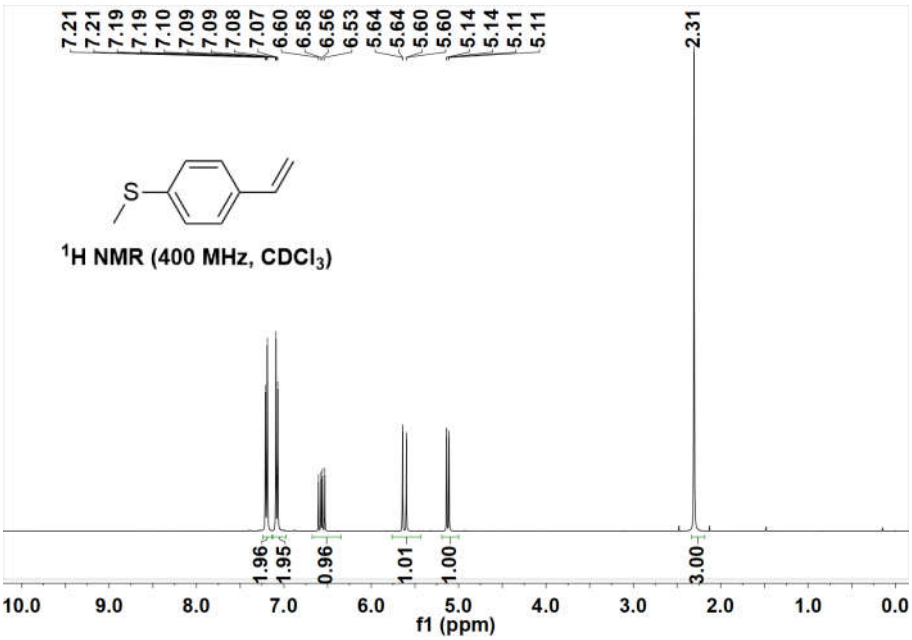


Figure S16. The ^{1}H NMR (400 MHz, CDCl3) of the vinyl anisole monomers (4-Vinylphenyl Methyl Sulfide)

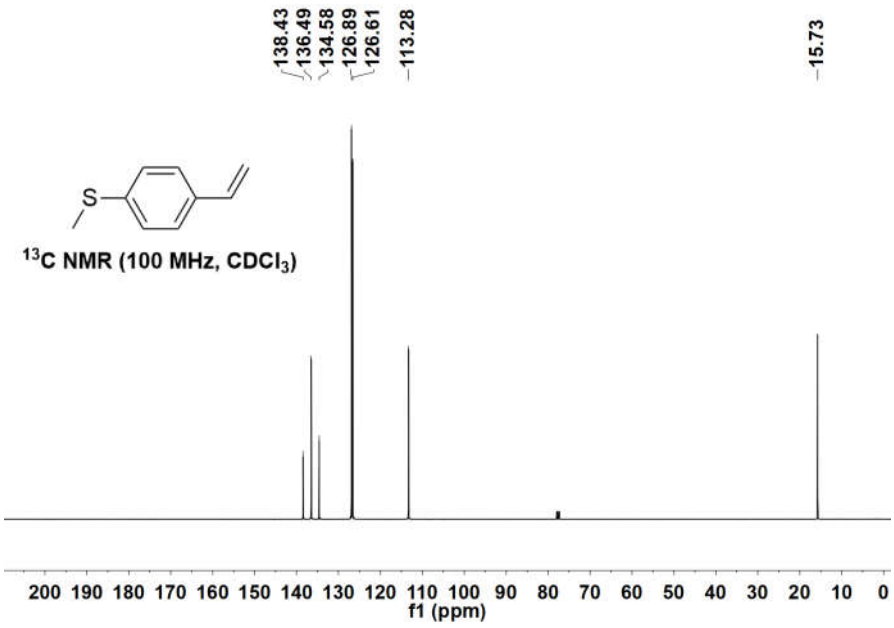


Figure S17. The ^{13}C NMR (100 MHz, $CDCl_3$) of of the vinyl anisole monomers (Vinylphenyl Methyl Sulfide).

Table S1. Textural parameters of Co_1/POPs-PPh_3-P&S

Catalyst	Pore Volume (nm)	BET (cm^3/g)
Co_1/POPs-PPh_3	2.77	1103.0
Co_1/POPs-PPh_3-5P&1S	2.08	913.9
Co_1/POPs-PPh_3-5P&2S	2.06	924.1
Co_1/POPs-PPh_3-5P&3S	1.58	731.5
Co_1/POPs-PPh_3-5P&5S	1.52	694.9
Co_1/POPs-PPh_3-5P&2VB	1.13	392.8
POPs-PPh_3	3.68	1426.6
POPs-PPh_3-5P&1S	2.43	945.2
POPs-PPh_3-5P&2S	2.07	934.9
POPs-PPh_3-5P&3S	2.07	894.9
POPs-PPh_3-5P&5S	1.56	689.5
POPs-PPh_3-5P&2VB	1.14	402.6

Table S2. The curve-fitting analysis of the EXAFS traces.

Sample	Shell	CN	R (Å)	σ^2 (10^{-2} Å^2)	ΔE$_0$ (eV)	r-factor (%)
Co foil	Co-Co	12*	2.49	0.006	8.2	0.03
Co$_1$/POPs-PPh$_3$	Co-C	2.1	2.21	0.004	8.0	0.012
	Co-P	2.2	2.45	0.0141	-7.5	
Co$_1$/POPs-PPh$_3$-5P&2S	Co-C	1	1.99	0.003	-5	0.23
	Co-P	2	2.35	0.006	-10	
	Co-S	1	2.36	0.003	-10	
Co$_1$/POPs-PPh$_3$-5P&2VB	Co-C	2.8	2.26	0.007	5.0	0.0046
	Co-P	1.5	2.43	0.009	-5.1	

Table S3. Test of different catalysts in hydroformylation of 2,5-DHF.

Samples	Conv. (%)	Selec. (%)		
		3-FT	THFA	THF
homo Co/PPh_3[a]	22.8	45.5	31.4	23.1
homo Rh/PPh_3[b]	90	87	/	2
Co_1/POPs-PPh_3[c]	80.5	14.2	63.1	22.7
Co_1/POPs-PPh_3-5P&2S[c]	95.0	69.8	16.7	13.5
Co_1/POPs-PPh_3-5P&2S[d]	96.8	85.6	0	14.6

[a] S/C=200, PPh_3 0.1g, $Co_2(CO)_8$ 7.2mg, toluene 5g, 2.5-DHF 0.59 g, 30h, 120 ℃, 6MPa, syngas: $CO:H_2$ = 1:1;

[b] 2,5-DHF (1 mmol, 70.09 mg), $[Rh(cod)Cl]_2$ 0.01 mmol (1% mmol), S/Rh = 50, $[Rh(cod)Cl]_2/PPh_3$ mole ratio =1/20, $[Rh(cod)Cl]_2$/diphosphine ligand mole ratio =1/10, CO/H_2 = 1/1, 3.0 MPa; Solvent 1.0 ml; temp. 80 ◦C, reaction time 8 h;[1]

[c] S/C=200, 0.1 g catalyst (Co loading at 2.5 %), toluene 5g, 2.5-DHF 0.59g, 30h, 120℃, 6MPa, Syngas: $CO:H_2$ = 1:1;

[d] S/C=200, 0.1 g catalyst (Co loading at 2.5 %), toluene 5g, 2.5-DHF 0.59g, 30h, 160℃, 8MPa, Syngas: $CO:H_2$ = 1:1

Table S4. Change temperature response data (Pressure of 6 MPa, the rest of the reaction conditions are referred to Figure 5e.)

Temperature/℃	Conv.%	3-FA	THFA	THF
70	/	/	/	/
90	12.5	54.9	29.6	15.5
120	95	69.8	16.7	13.5
140	100	72	9	19

Table S5. Change pressure response data (temperature of 120 ℃, the rest of the reaction conditions are referred to Figure 5d.)

Pressure/MPa	Conv.%	3-FA	THFA	THF
1	/	/	/	/
3	36.5	25.8	56.5	17.7
5	54.4	71.8	21.3	6.9.
6	95	69.8	16.7	13.5

Table S6. Co concentration of fresh and used catalysts

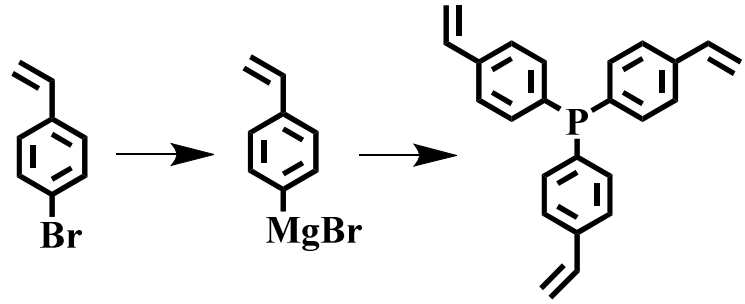
Sample	**Co concentration (%)**
Co_1/POPs-PPh_3-5P&2S (fresh sample)	2.328
Co_1/POPs-PPh_3-5P&2S (spent sample)	2.316
Co_1/POPs-PPh_3-5P&2S (Reaction liquid)	$1.4*10^{-6}$

Supplementary Methods

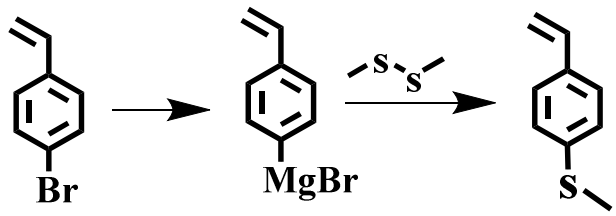
Chemicals

Solvents were purified according to standard laboratory methods. Other commercially available reagents were purchased in high purity and used without further purification.

Material synthesis



tris-(4-vinylphenyl)-phosphine (1): First, 1.2g magnesium chips, 3 grains of iodine and 20 mL anhydrous THF were mixed in a flask. The flask was kept 323K by oil bath and protected by Ar atmosphere. The flask was kept at 328 K by oil bath and protected by Ar atmosphere. Next, 4-bromostyrene (9.15g, 50 mmol) were dissolved in 100 mL anhydrous THF and added dropwise to the flask in 1 h, then reacted for 3 h. Then the solution was transferred to a cold bath and kept at 263 K. Next, PCl_3 (2.25 g in 30 mL THF) was added to the solution over 1h at 0 °C, followed by stirring at room temperature for 1 h. Finally, 50 mL saturated NH_4Cl solution were added dropwise to the solution. The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether) to give 1 as a white solid. The product weighed 9.52g, with a yield of 58%. ^1H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ 7.37 (d, 6H), 7.22-7.31 (t, 6H), 6.64-6.75 (t, 3H), 5.75(d, 3H), 5.27 (d, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.7, 126.28, 126.35, 133.78, 133.97, 136.35, 136.53, 136.63, 138.00 ppm. ^{31}P NMR (162 MHz): δ -6.72 ppm.[2]



4-Vinylphenyl Methyl Sulfide: The preparation method of the format reagent was the same as above. A solution of dimethyl disulfide (13.5 g, 144 mmol) in 50 ml of anhydrous tetrahydrofuran was added dropwise to a Grignard reagent prepared from 4-chlorostyrene (15.1 g, 108 mmol) and Mg (3.46 g, 142 mmol) in anhydrous THF (100 mL) at 263 K. The mixture was stirred at room temperature for 1 hour. After conventional work-up, the remaining oil was fractionated at 65-66 °C (0.30 mmHg) to give a colorless liquid. The product was obtained in 6.90 g with a yield of 43%. ^{1}H NMR ($CDCl_3$) δ 2.31 (3H), 5.11-5.14 (2H), 5.60-5.64 (2H), 6.53-6.60 (2H), 7.07-7.1 (2H), 7.19-7.21 (2H); ^{13}C NMR ($CDCl_3$) δ 15.73, 113.28, 126.61, 126.85, 134.58, 136.49, 138.43. [3]

References

[1] P. Wang, H. Shi, B. Feng, D. Zhao, D. Yang, *Mol. Catal.,* **2023**, 548, 113459.

[2] M. Jiang, L. Yan, Y. Ding, Q. Sun, J. Liu, H. Zhu, R. Lin, F. Xiao, Z. Jiang, J. Liu, *J. Mol. Catal. A: Chem.,* **2015**, 404, 211–217.

[3] A. Hirao, H. Shione, T. Ishizone, S. Nakahama, *Macromolecules,* **1997**, 30, 3728–3731.