Supporting Information

Porous Coordination Polymer-Stabilized Rhodium Single-Atom Catalyst for Regioselective Hydroformylation

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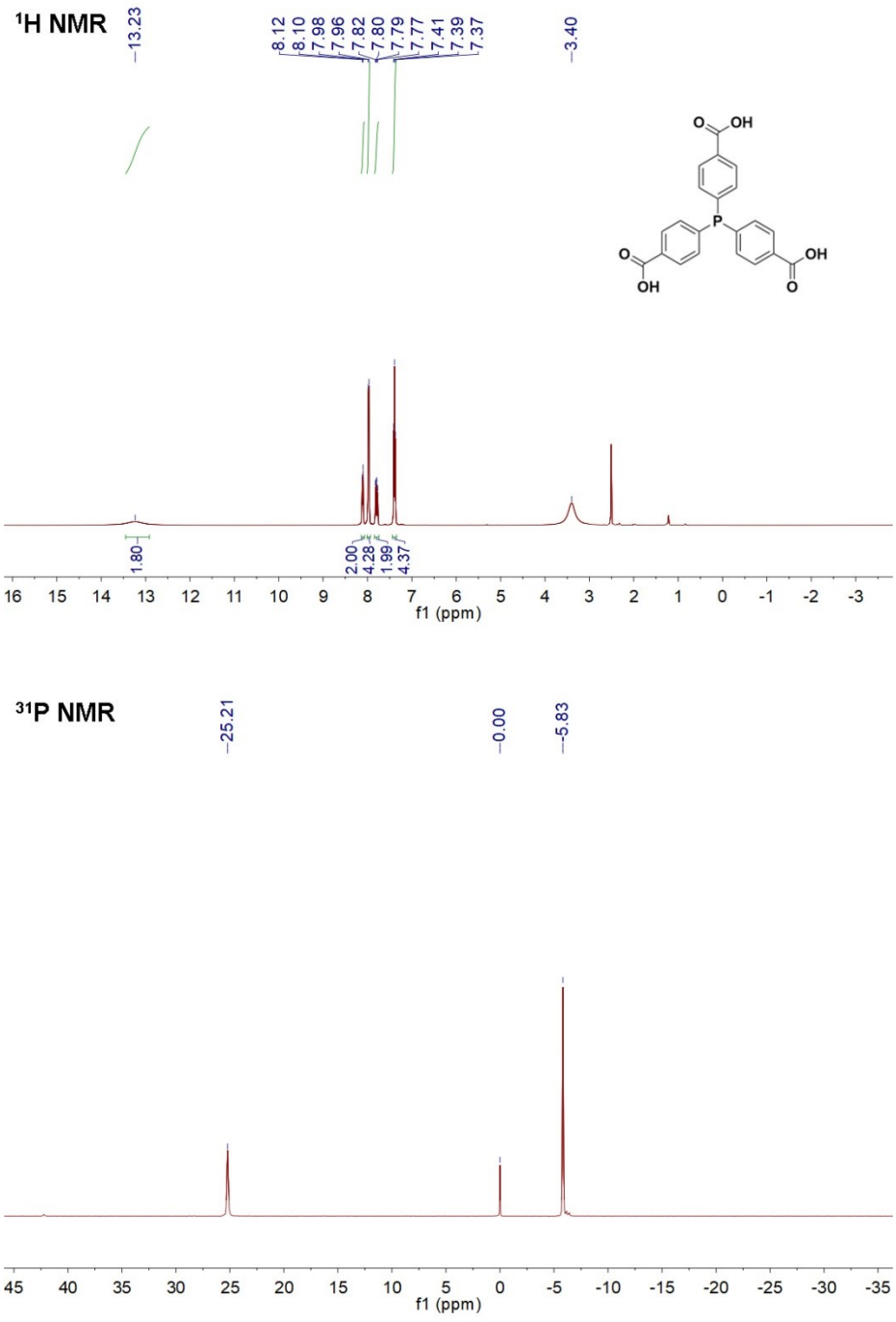


Fig. S1. The ^{1}H NMR and ^{31}P NMR of tri(*p*-tolyl)phosphine. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.23 (s, 2H), 8.14-8.07 (m, 2H, arom), 7.97 (d, 4H, arom., J = 7.1 Hz), 7.83-7.75 (m, 2H, arom.), 7.39 (t, 4H, arom., J = 7.8 Hz). ^{31}P NMR (243 MHz, DMSO-d_6): δ = –5.83 (s, 1P).

Table S1. ICP-OES analysis of the catalysts.

Catalysts	Rh (wt%)
0.08Rh/Zr-HTP	0.08
0.19Rh/Zr-HTP	0.19
0.54Rh/Zr-HTP	0.54
0.92Rh/Zr-HTP	0.92

Table S2. Fitting parameters of solid-state ^{31}P NMR.

Catalysts	P species	Chemical shift (ppm)	Peak area	Percentage (%)
0.19Rh/Zr-HTP	uncoordinated P	-7.4	6.35×10^9	63.9
	P=O	25.2	2.13×10^9	21.5
	P-Rh	33.4	1.45×10^9	14.6
Zr-HTP	uncoordinated P	-7.4	6.27×10^9	71.7
	P=O	25.2	2.48×10^9	28.3

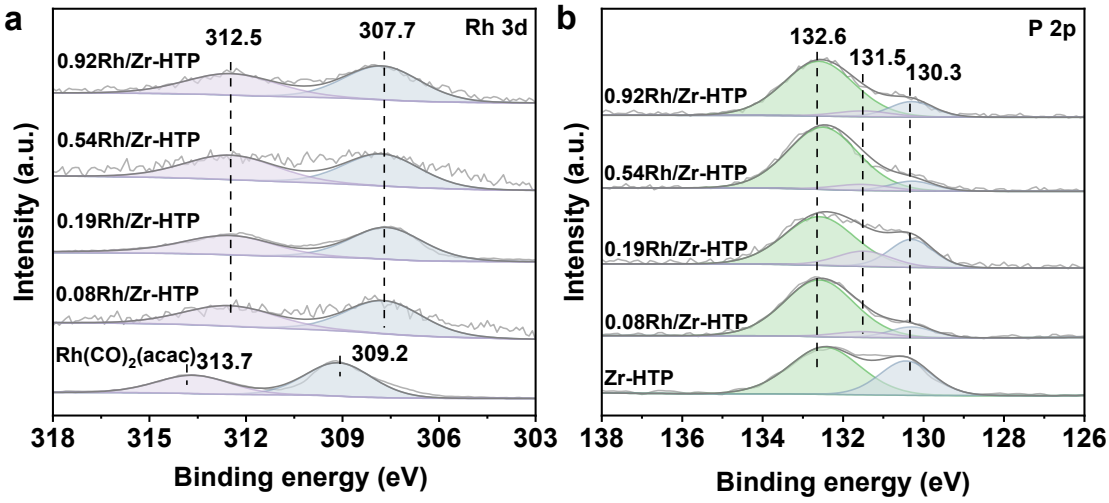


Fig. S2. The XPS spectra of different catalysts.

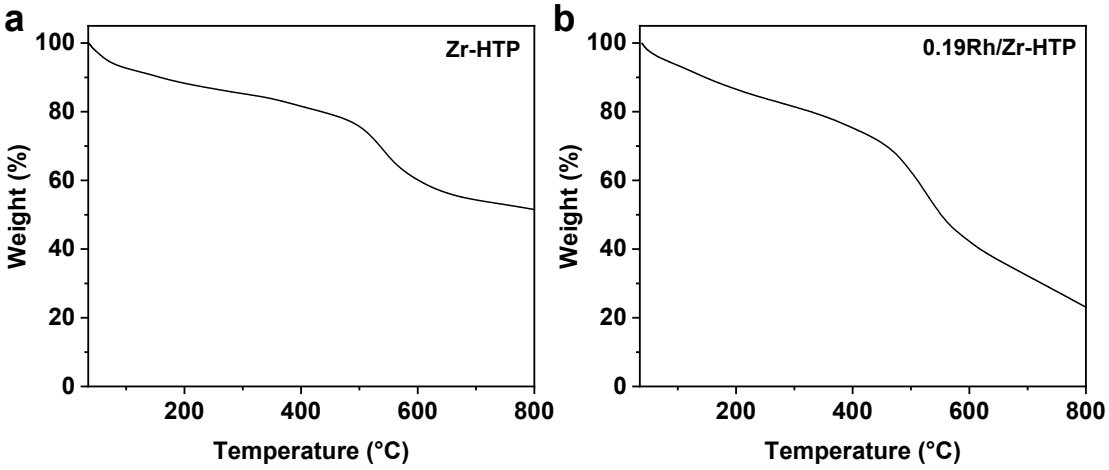


Fig. S3. TGA curves of Zr-HTP and 0.19Rh/Zr-HTP catalysts.

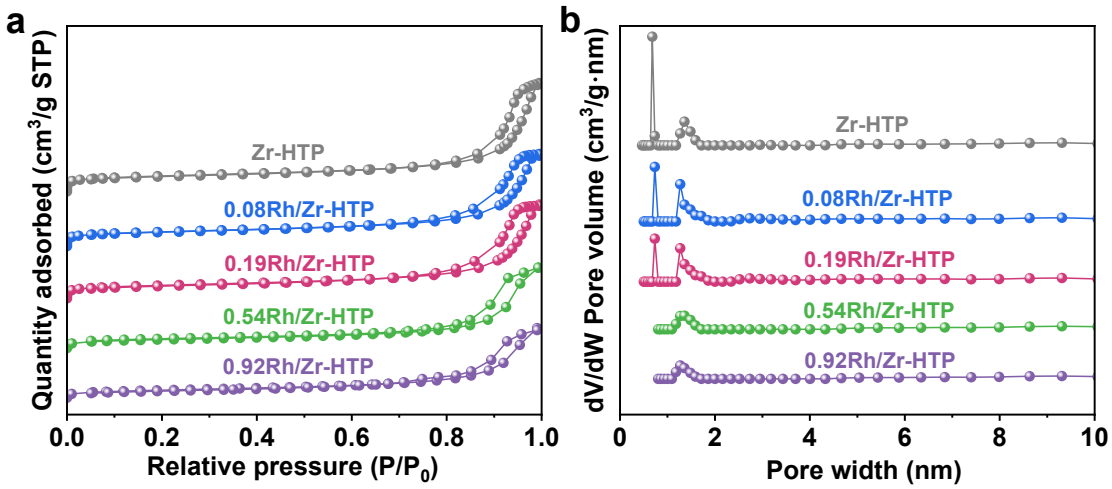


Fig. S4. N_2 sorption isotherms and pore size distributions of different Rh-based catalysts.

Table S3. Physicochemical properties of different Rh-based catalysts.

Samples	BET areas (m^2/g)	Micropore areas (m^2/g)	Pore volumes (cm^3/g)	Micropore volumes (cm^3/g)	Micropore ratio[a] (%)
Zr-HTP	424	173	1.03	0.072	7.0%
0.08Rh/Zr-HTP	395	151	0.87	0.063	7.2%
0.19Rh/Zr-HTP	365	145	0.90	0.059	6.5%
0.54Rh/Zr-HTP	254	33	0.79	0.010	1.3%
0.92Rh/Zr-HTP	233	24	0.70	0.007	1.0%

[a][Micropore ratio] = [Micropore volumes]/[Pore volumes]

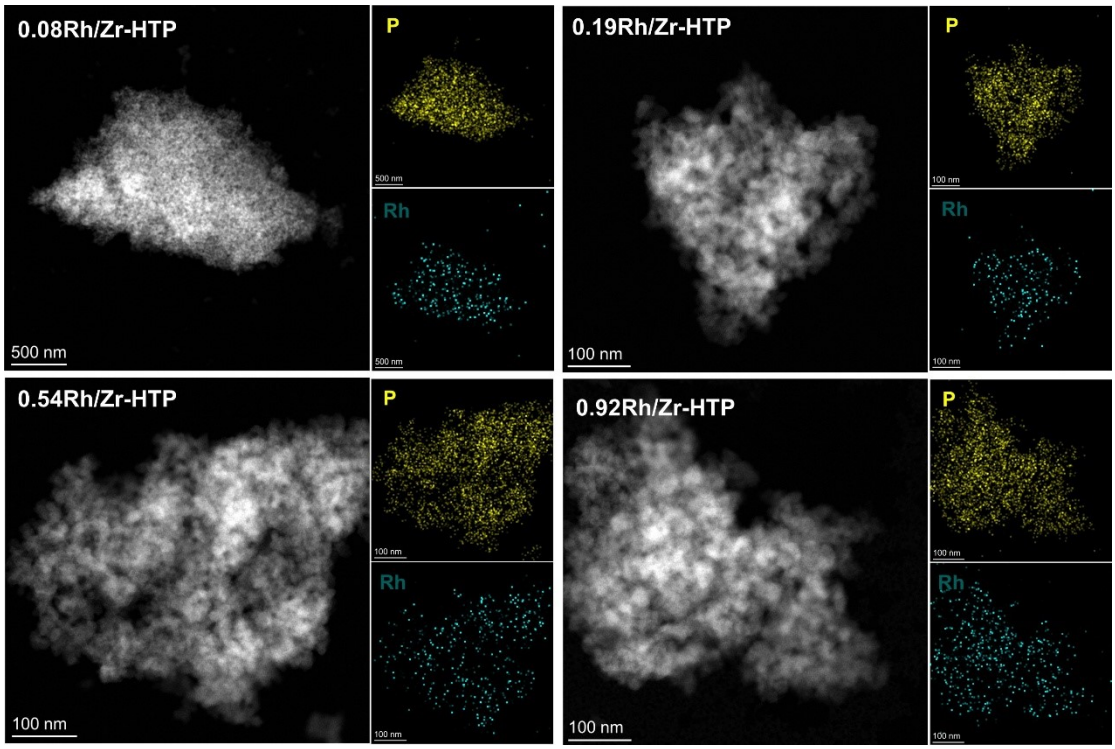


Fig. S5 The HAADF-STEM images of different catalysts and corresponding elemental mappings of Rh and P.

Table S4. Different catalysts for hydroformylation of styrene.[a]

Entry	Catalysts	Con. (%)	Yield (%)		i/n
			iso-aldehyde	n-aldehyde	
1	Zr-HTP[b]	-	-	-	-
2	$Rh(CO)_2(acac)$	99	54.7	44.3	1.2
3	$Rh(PPh_3)_3Cl$	82	42.3	39.7	1.1
4	Rh/C	80	41.1	38.9	1.1
5	0.19Rh/Zr-HTP	96	84.7	11.3	7.5

[a]Reaction conditions: 0.74 μmol Rh-based catalysts, 3.0 mmol styrene, S/C= 4062, 3.0 ml toluene, 90 ℃, 5.0 MPa syngas (CO/H_2= 1:1), 4 h. [b]40 mg Zr-HTP catalyst.

Table S5. ICP-OES analysis of the 0.19Rh/Zr-HTP catalysts.

Catalysts	Rh (wt%)
0.19Rh/Zr-HTP (fresh)	0.19
0.19Rh/Zr-HTP (used seven times)	0.19

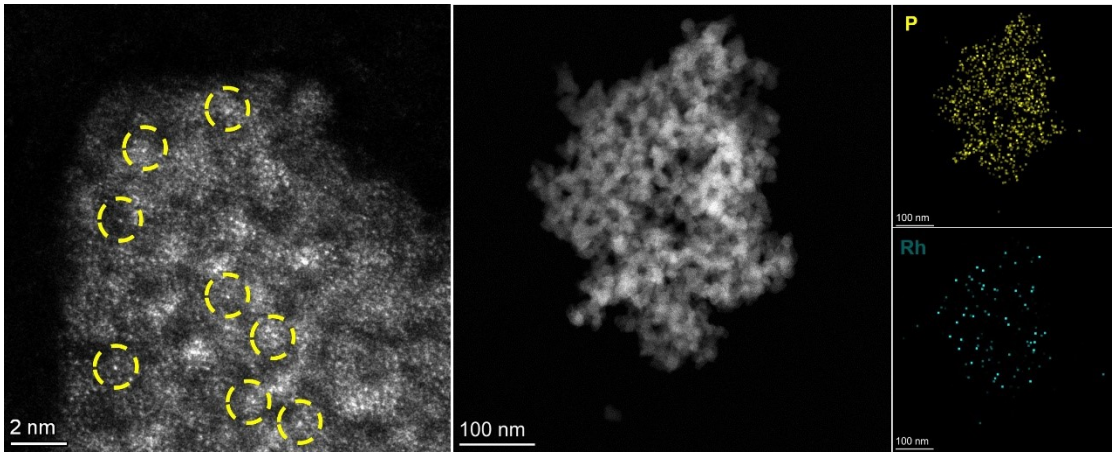


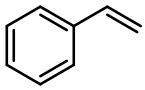
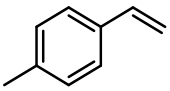
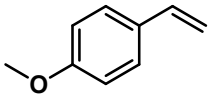
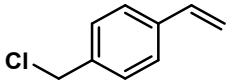
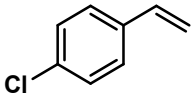
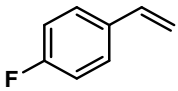
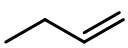
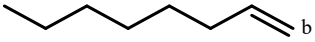
Fig. S6. The HAADF-STEM images of the spent 0.19Rh/Zr-HTP catalyst and corresponding elemental mappings of Rh and P.

Table S6. Comparison of the catalytic performance of the present catalysts with previously reported in the literature.

Catalysts	Substrate	P[a] (MPa)	T (°C)	TOF (h^{-1})	i/n	Ref.
Rh-HCP-PPh_3	styrene	3.0	80	35.7	12.7	1
Rh-PPh_3/SiO_2	styrene	5.0	60	239	5.7	2
2.3%Rh@POP	styrene	3.0	80	679	0.83	3
MOF-808-2.0DPPB-RhH	styrene	2.0	110	239	0.61	4
RhC_x@S-1-400	styrene	4.0	85	737	1.25	5
Rh/MnMOF	styrene	8.0	80	55.6	2.2	6
Rh/3%B-g-C_3N_4	styrene	6.0	100	12000	1.32	7
Rh/ECN(0.1)	styrene	2.0	90	125	1.6	8
Rh@POP-PTBA-HA-50	1-octene	6.0	120	801	0.087	9
Rh/mPPh_3&PPD-POP	1-octene	2.0	110	2000	0.063	10
0.19Rh/Zr-HTP	**styrene**	**5.0**	**90**	**1462**	**7.5**	**This work**

[a]CO/H_2=1:1

Table S7. Hydroformylation of various olefins under biphasic reaction conditions.[a]

Substrate	Con. (%)	Yield (%)		i/n
		iso-aldehyde	n-aldehyde	
	99	87.2	11.7	7.4
	96	83.8	12.2	6.8
	84	72.6	11.4	6.4
	99	93.6	5.4	17.3
	99	86.7	12.3	7.0
	99	86.1	12.9	6.7
	26	-	26	-
	90	-	90	-
	-	46.8	48.1	1.0
	99	47.2	51.8	0.9
 b	99	39.3	57.7	0.7

[a]Reaction conditions: 40 mg 0.19Rh/Zr-HTP, 3.0 mmol olefins, S/C= 4062, 3.0 ml toluene, 90 °C, 5.0 MPa syngas (CO/H_2= 1:1), 6 h. [b]The yield of iso-octene as byproduct was 2%.

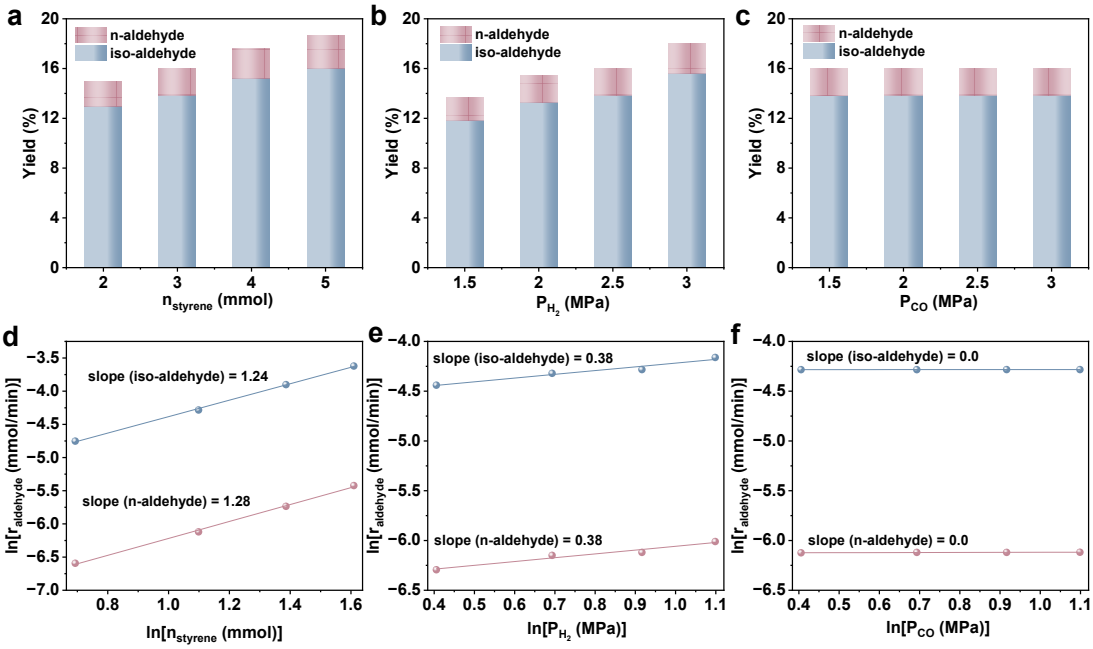


Fig. S7. Initial rate method and reaction order to the hydroformylation reaction of styrene toward (a, d) styrene, (b, e) H_2 and (c, f) CO. Reaction conditions: 40 mg 0.19Rh/Zr-HTP catalyst (0.74 μmol Rh), 3 mL toluene, 90 °C, 30 min. (a, d) 5 MPa syngas, 2/3/4/5 mmol styrene; (b, e) 3 mmol styrene, 2.5 MPa CO, 1.5/2/2.5/3 MPa H_2; (c, f) 3 mmol styrene, 2.5 MPa H_2, 1.5/2/2.5/3 MPa CO.

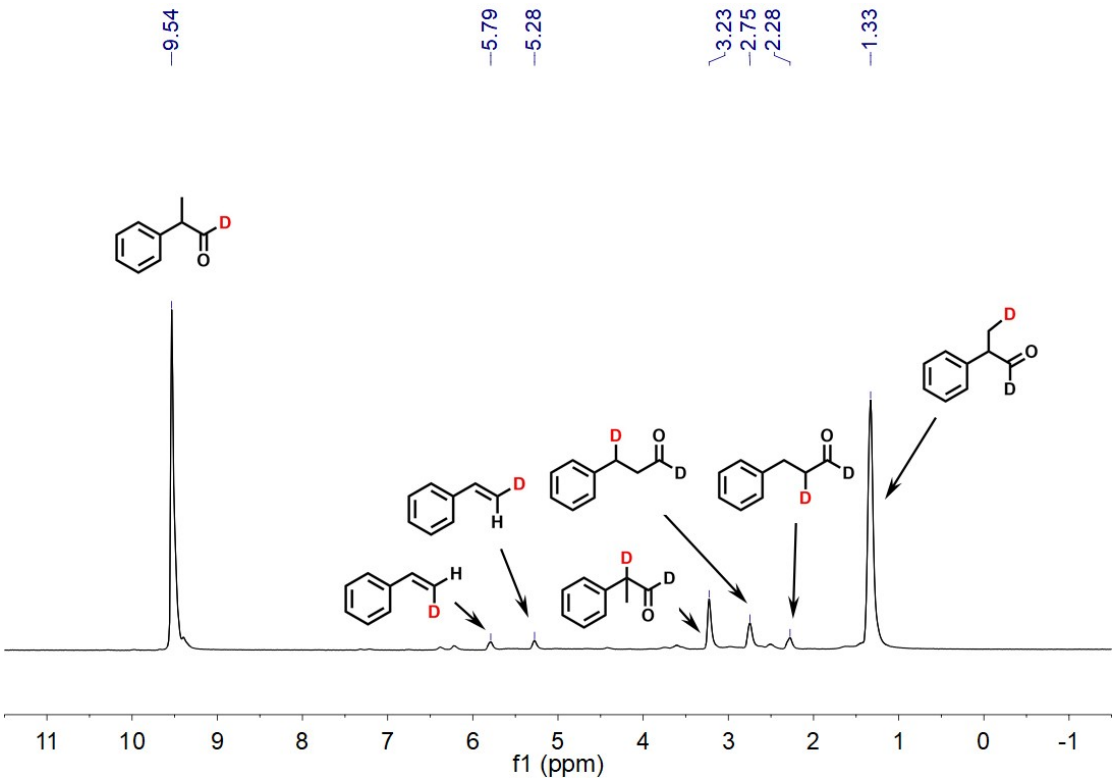


Fig. S8. ^{2}H NMR spectrum (600 MHz) of reaction mixture after deuterioformylation. Reaction conditions: 5.0 mmol styrene, 40 mg 0.19Rh/Zr-HTP (molar ratio of styrene/Rh=1:6770), 4.0 mL toluene, 2.5 MPa CO, 2.5 MPa D_2, 90 °C and 6 h.

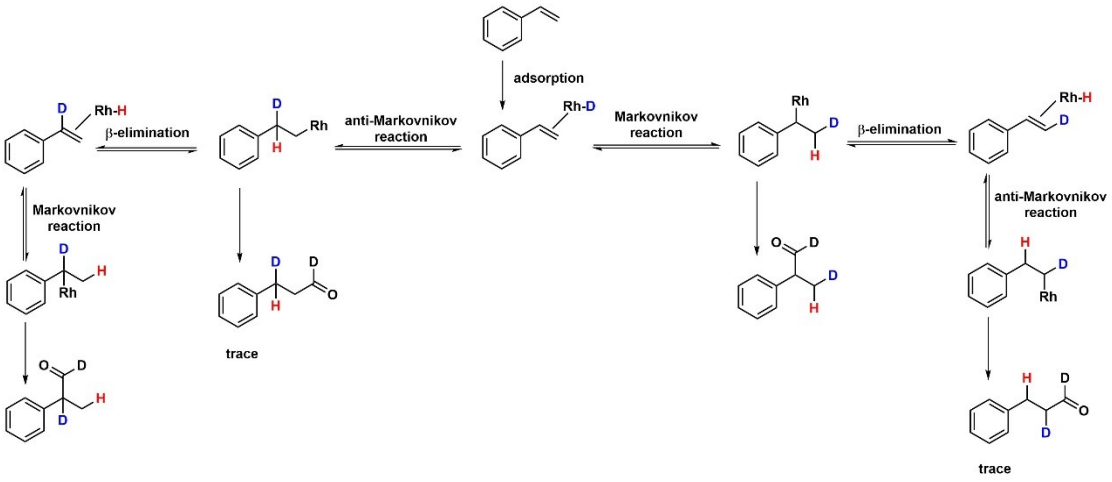


Fig. S9. Graphical representation of product distribution obtained from deuterioformylation of styrene.

Reference

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