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Metal–organic framework ZIF-8 loaded with rhodium nanoparticles as a catalyst for hydroformylation

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Synthesis. All synthetic manipulations were carried out on air. Solvents were purchased from commercial sources and purified by distilling from conventional drying agents under an argon atmosphere prior to use.

ZIF-8: A solution of $Zn(NO_3)_2$ $6H_2O$ (2.93 g, 9.87 mmol) in 200 ml of methanol was quickly added to a solution of 2-methylimidazole (6.489 g, 79.04 mmol) in 200 ml of methanol. The reaction mixture was stirred at room temperature for 1.5 h. The resulting suspension was centrifuged at 60000 rpm for 3 min to produce a precipitate that was washed with DMF and then 3 times with methanol to exclude any residues of 2-methylimidazole. The resulting product was dried under vacuum. Yield: 0.4352 g (19.37%). Calculated for $C_{48}H_{60}N_{24}Zn_6$ (%): C, 42.22; H, 4.43; N, 24.62. Found (%): C, 42.29; H, 4.46; N, 24.67.

Catalytic activity of Rh@ZIF-8. A 5 ml autoclave was charged with 20 mg of 1-decene or 15 mg of styrene and 2 mg of Rh@ZIF-8 (10 mol% for rhodium) in 2.5 ml of toluene. The autoclave was sealed, and syngas was introduced until the pressure of 5 MPa was reached. The reaction mixture was heated while stirring at 100°C for 12 h. After the reaction was complete, the autoclave was cooled to room temperature and the pressure was released.

Catalytic activity of $RhCl_3$@ZIF-8. A 5 ml autoclave was charged with 15 mg of styrene and 2 mg of $RhCl_3$@ZIF-8 (10 mol% in rhodium) in 2.5 ml of toluene. The autoclave was sealed, and syngas was introduced until the pressure of 5 MPa was reached. The reaction mixture was heated while stirring at 100°C for 12 h. After the reaction was complete, the autoclave was cooled to room temperature and the pressure was released.

Powder X-ray diffraction. The measurements of the powdered samples of **ZIF-8**, **Rh@ZIF-8** and **$RhCl_3$@ZIF-8** were carried out using a Bruker D8 Advance diffractometer (λ[CuKα] = 1.5418 Å, Ni filter, Bragg–Brentano geometry, 1D-detector LynxEye) in a $\Theta/2\Theta$ scanning mode from 4° to 60° with a step size of 0.02°. The data were processed by EVA[S1] and TOPAS 4.2[S2] program packages.

Gas chromatography-mass spectrometry (GC-MS). Analytical gas chromatography of the reaction mixtures was carried out using a Shimadzu GCMS-QP2020 gas chromatography-mass spectrometer with an electron ionization source, equipped with a library of mass spectra of organic compounds NIST17. The following parameters were used: column: Shimadzu SH-Rtx-5MS (30 m × 0.25 mm × 0.25 µm); oven temperature: 50°C, hold for 3 min, ramp to 200°C at 30°C/min, hold for 11 min; injection temperature: 250°C; splitting ratio: split 1:10; MS ion source temperature: 200°C; interface temperature: 250°C; total run time: 20 min.

NMR spectroscopy. ^1H NMR spectra were recorded in chloroform-d1 with a Varian Inova 400 spectrometer (400 MHz ^1H frequency). The measurements were done using the residual signals of this solvent as a reference (^1H -7.26 ppm).

Scanning Electron Microscopy (SEM). SEM images for powdered samples placed on a 25 mm aluminum stage and fixed with a conductive carbon tape were obtained in the secondary electron mode at an accelerating voltage of 5 kV and low vacuum mode with a Hitachi TM4000Plus benchtop electron microscope equipped with an energy dispersive X-ray detector.

Supplementary References:

S1. *DIFFRAC.EVA*, Bruker AXS GmbH.: Karlsruhe, Germany, 2011.

S2. A. Coelho, *TOPAS 4.2*, Bruker AXS GmbH: Karlsruhe, Germany, 2009.

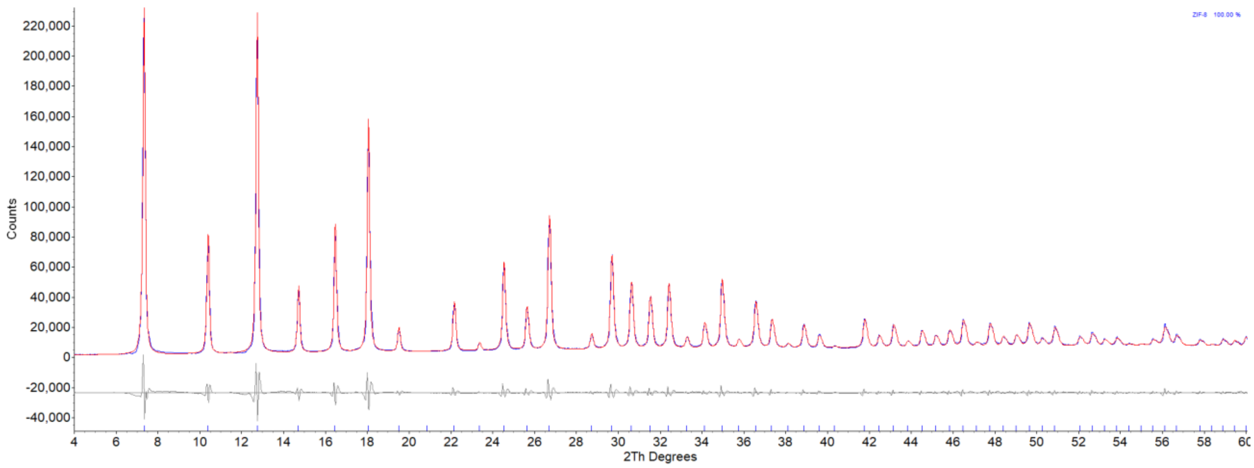


Figure S1. X-ray diffractograms collected from a powdered sample of ZIF-8 (blue line) and calculated for ZIF-8 (red line) and their difference (black line).

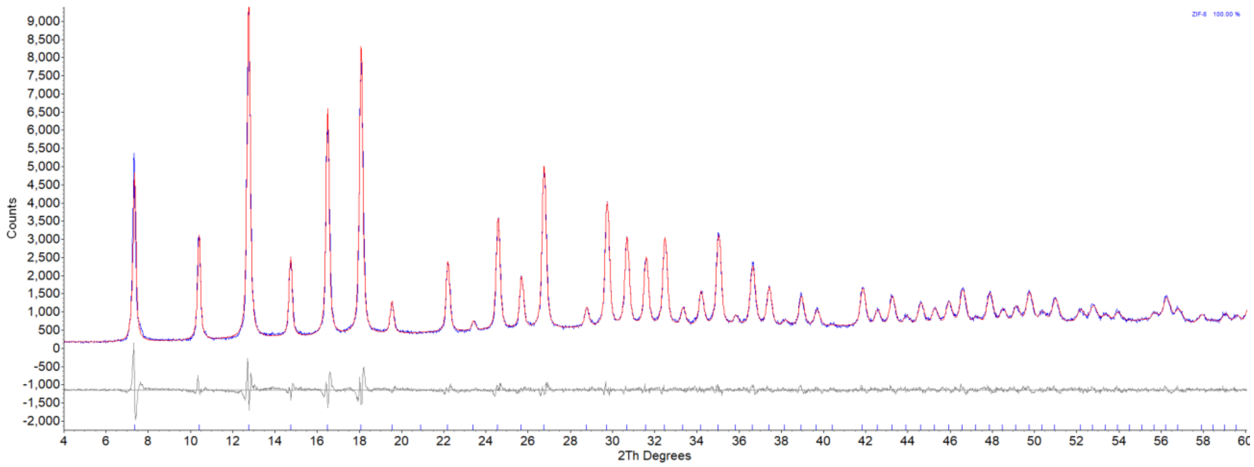
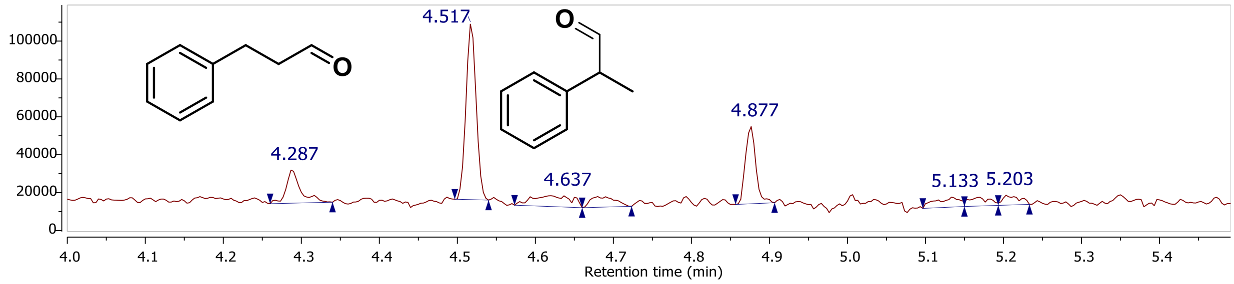


Figure S2. X-ray diffractograms collected from a powdered sample of $RhCl_3$@ZIF-8 (blue line) and calculated for ZIF-8 (red line) and their difference (black line).



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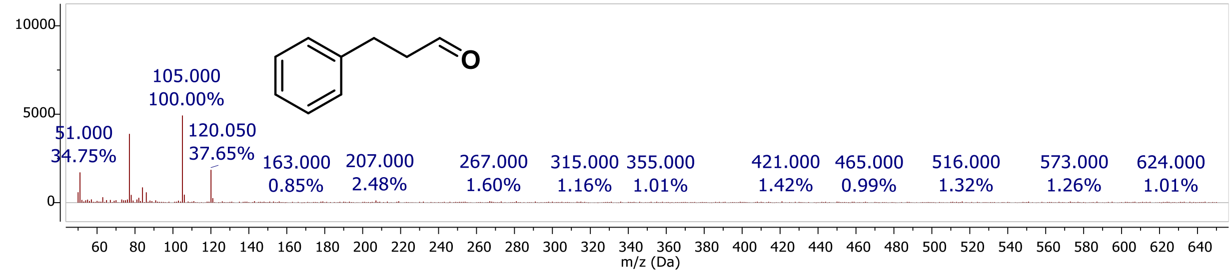

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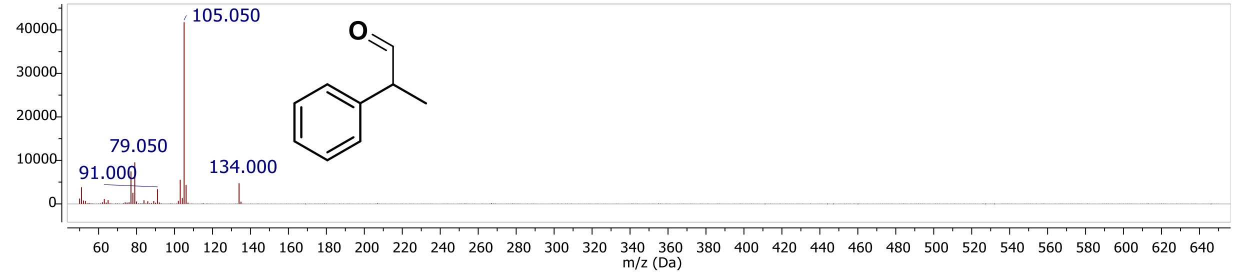


Figure S3. GC-MS analysis of products resulted from the styrene hydroformylation reaction catalyzed by Rh@ZIF-8.

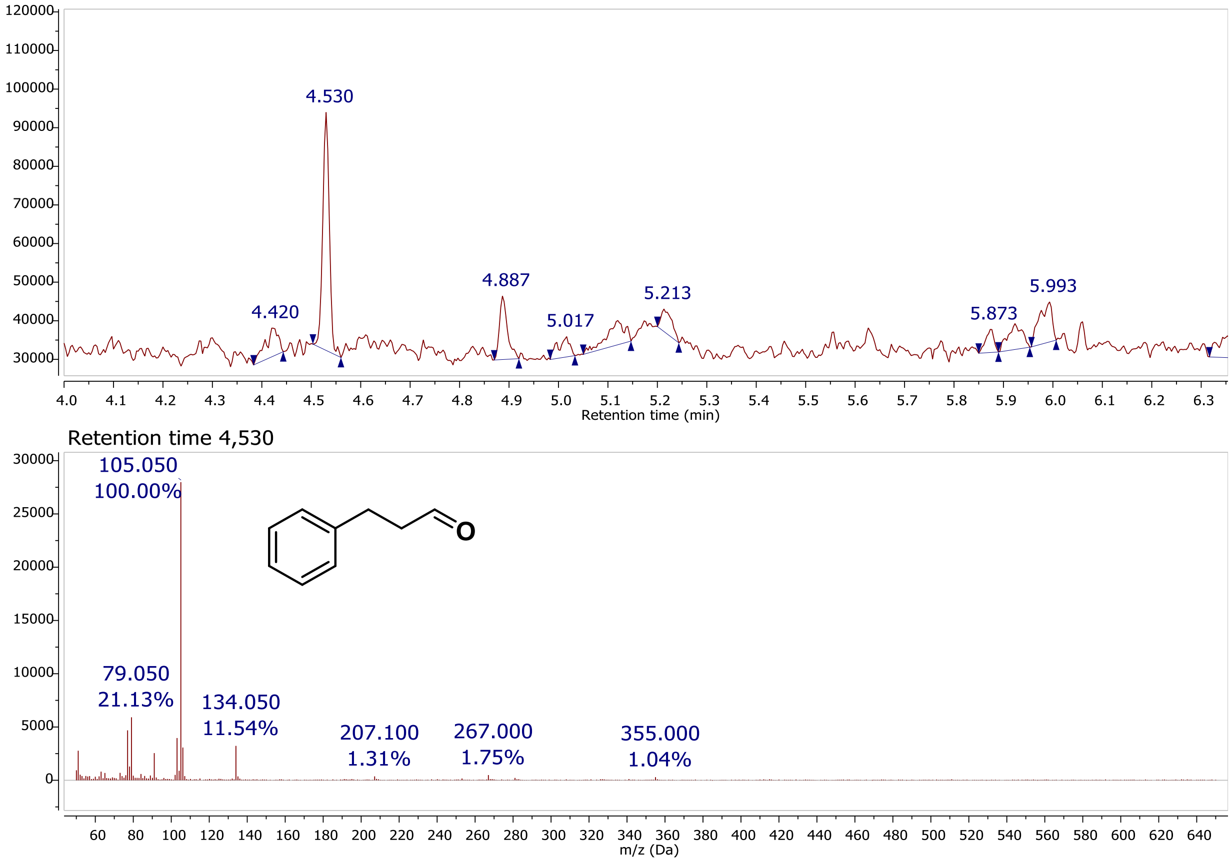


Figure S4. GC-MS analysis of products resulted from the styrene hydroformylation reaction catalyzed by $RhCl_3$@ZIF-8.

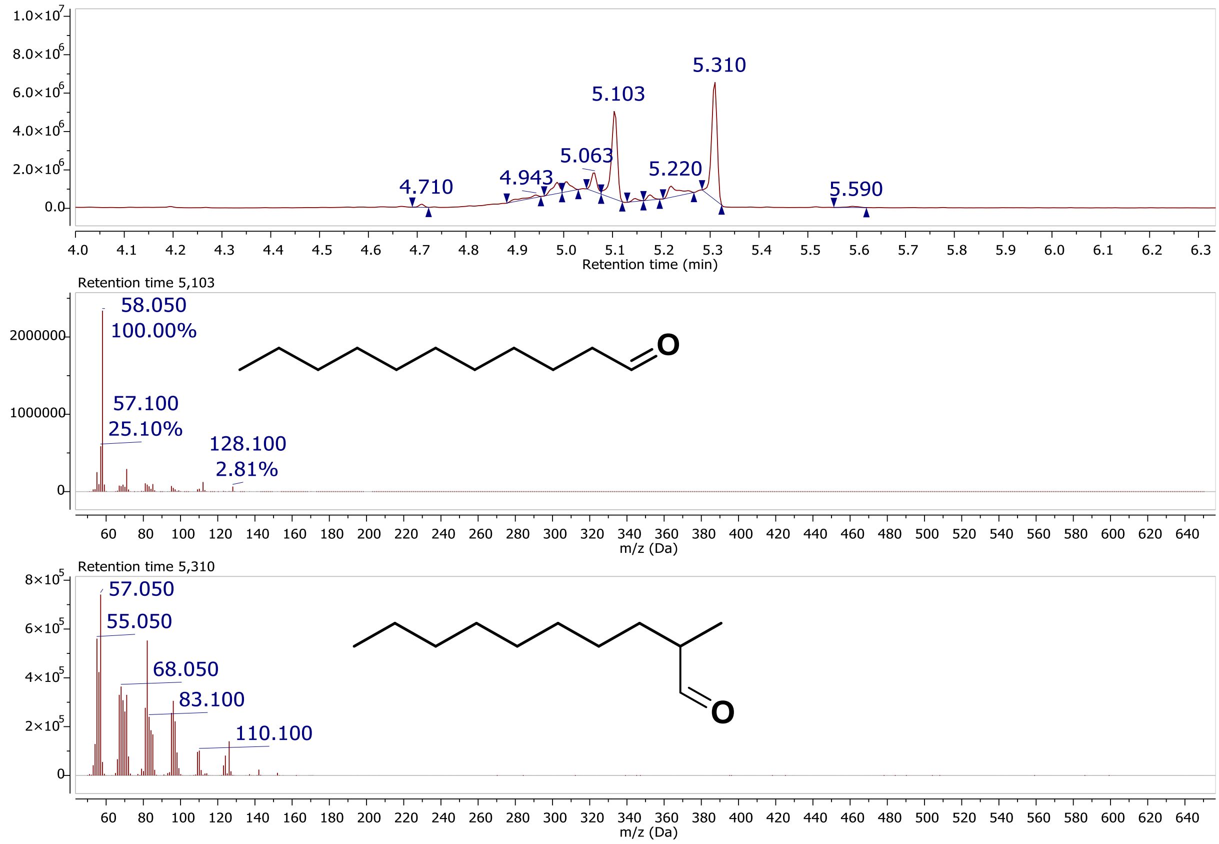
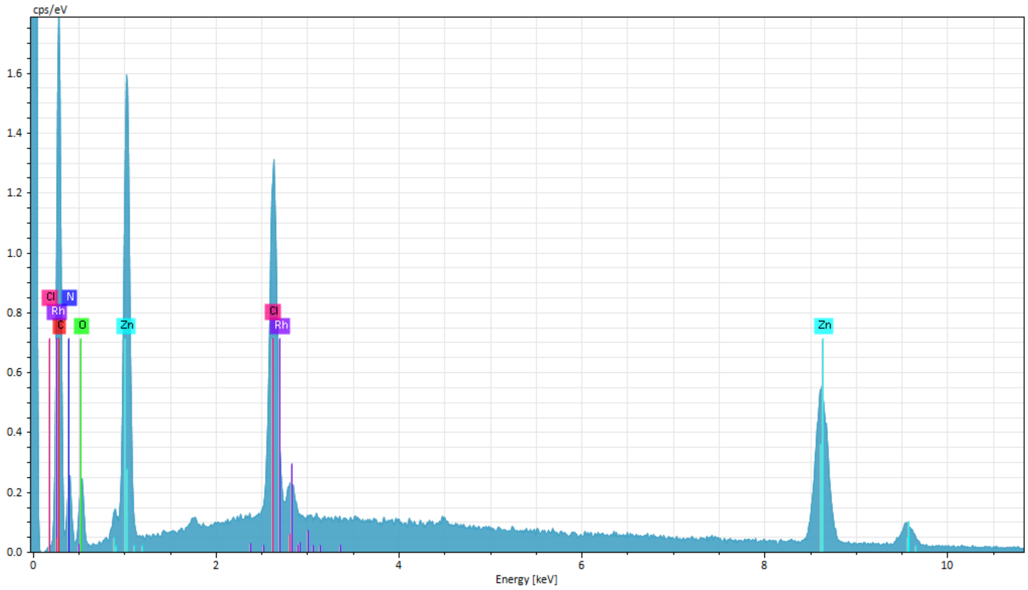


Figure S5. GC-MS analysis of products resulted from the 1-decene hydroformylation reaction catalyzed by Rh@ZIF-8.



Spectrum	C	N	O	Cl	Zn	Rh	Sum
Sample 1 259	26.99	6.39	2.56	5.91	30.77	0.27	72.90

Figure S6. Elemental composition of a powdered sample of Rh@ZIF-8 identified by energy dispersive X-ray spectroscopy.

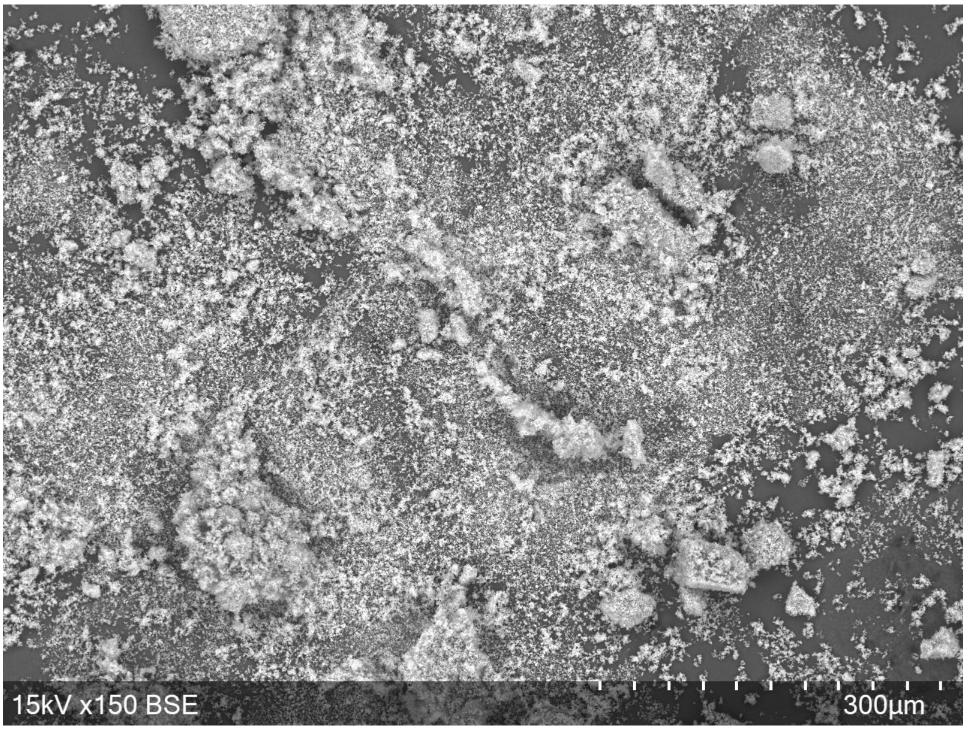


Figure S7. SEM view of a powdered sample of Rh@ZIF-8.

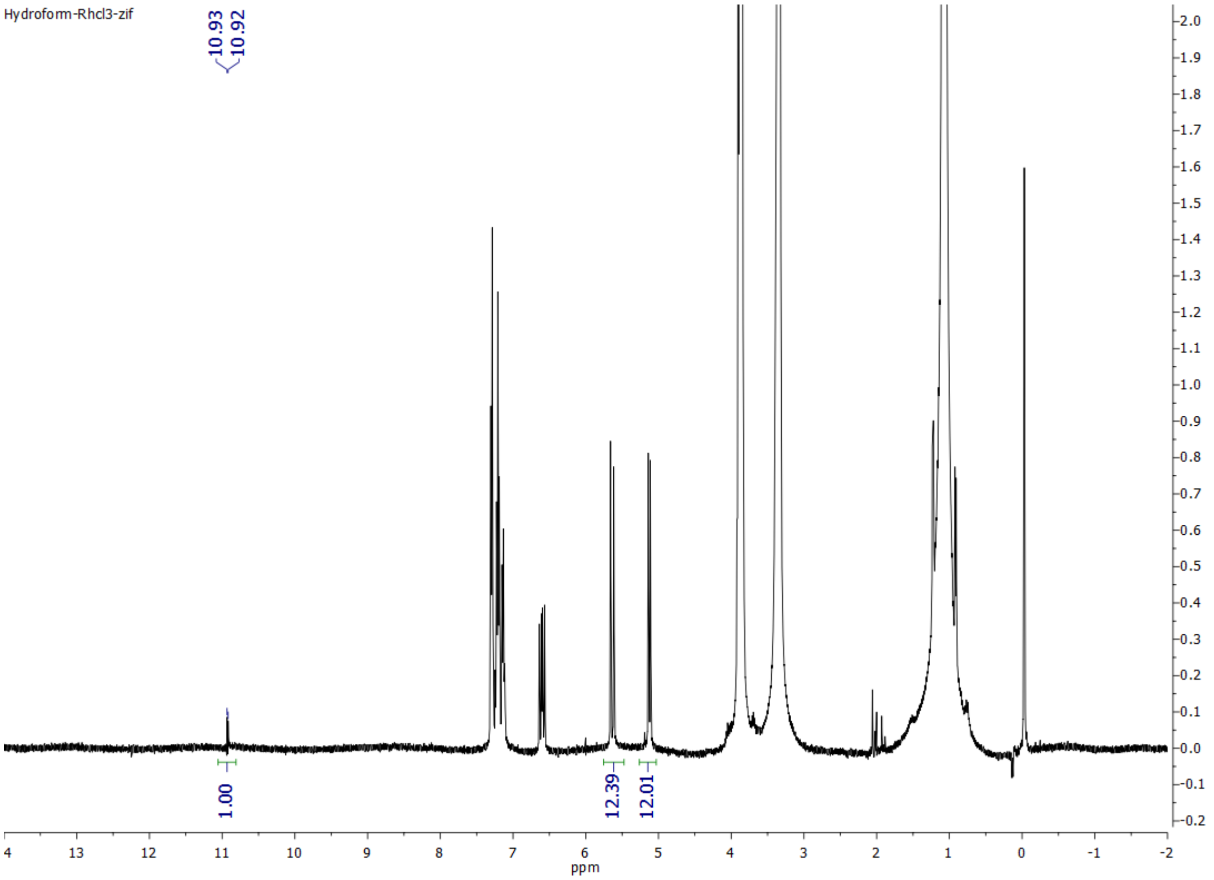


Figure S8. ^{1}H NMR spectra of styrene hydroformylation reaction mixture catalyzed by Rh@ZIF-8.

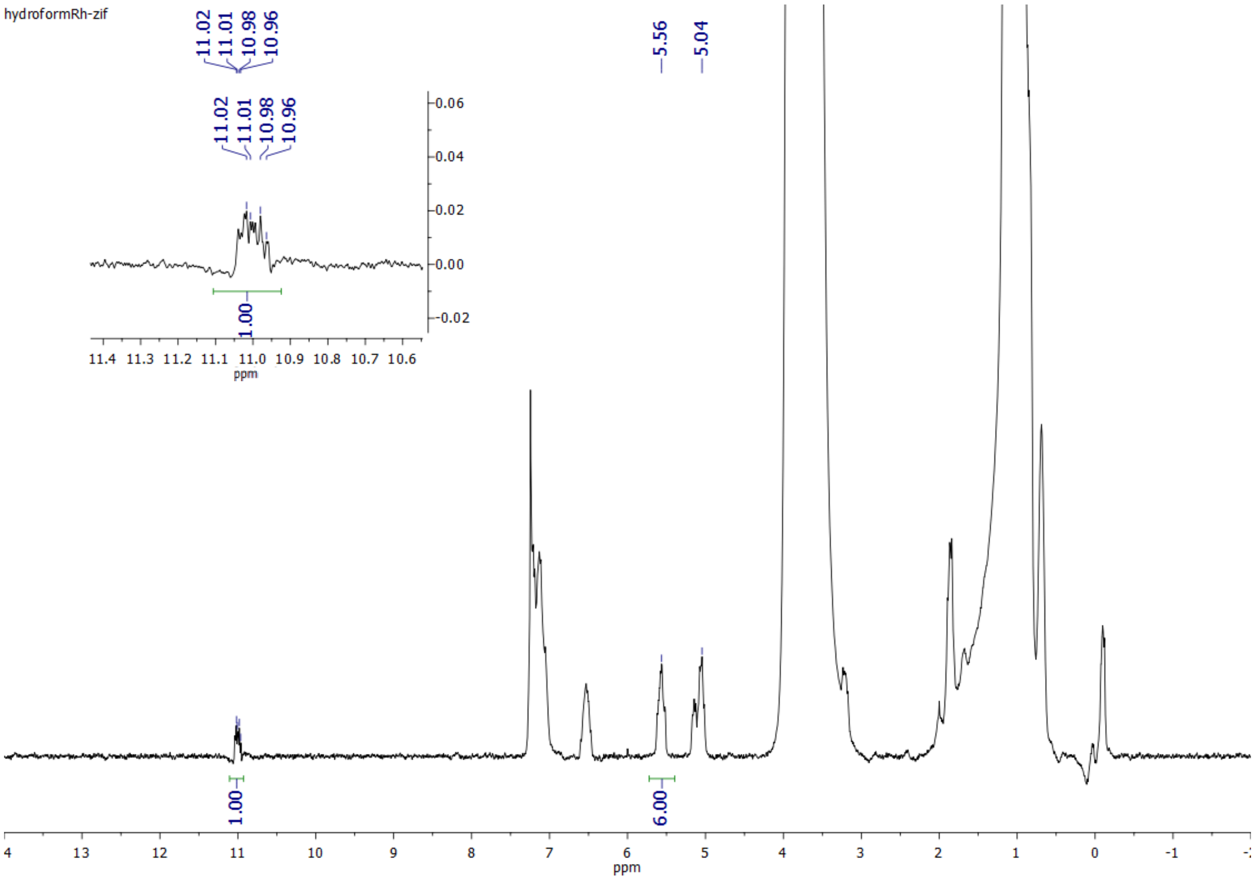


Figure S9. ^{1}H NMR spectra of styrene hydroformylation reaction mixture catalyzed by Rh@ZIF-8.

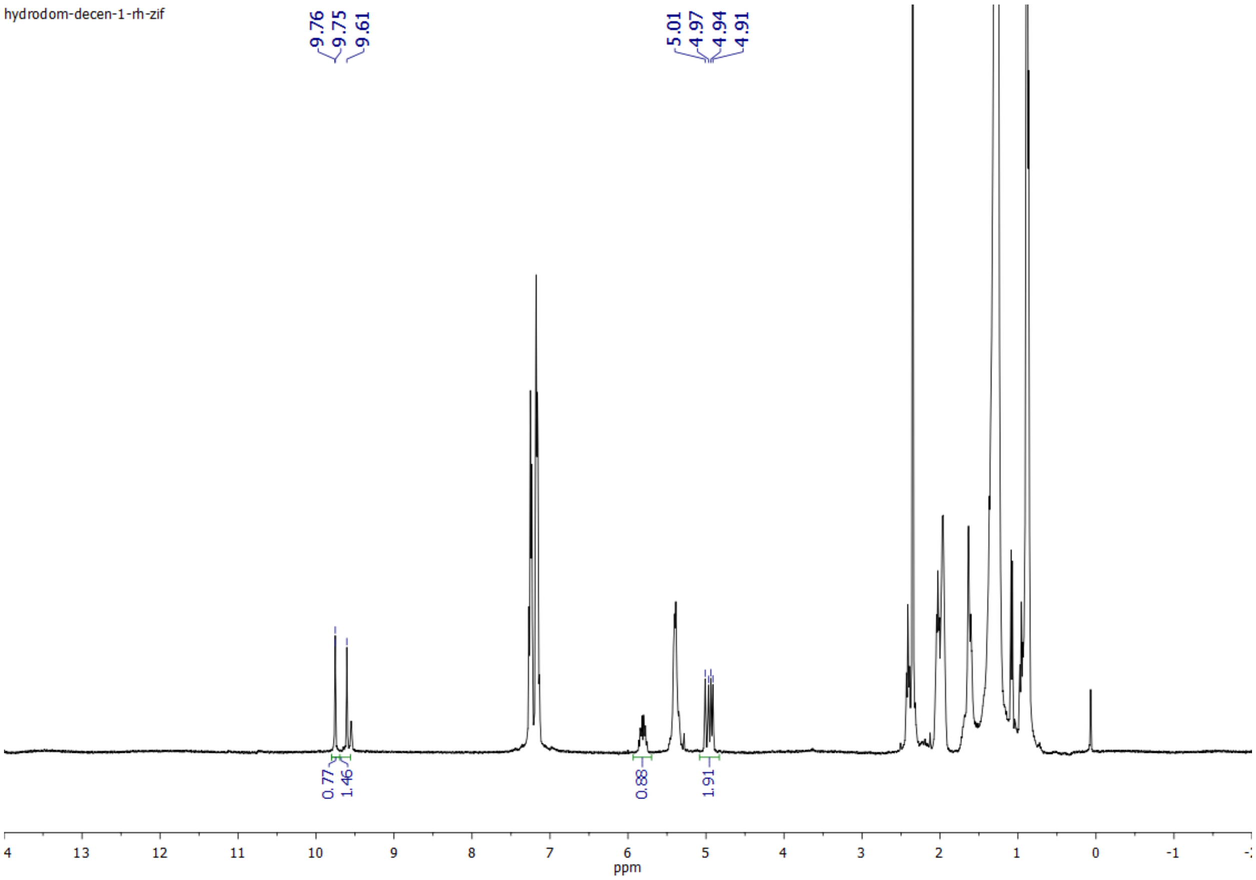


Figure S10. ^{1}H NMR spectra of 1-decene hydroformylation reaction mixture catalyzed by Rh@ZIF-8.

Supplementary References:

S1. *DIFFRAC.EVA*, Bruker AXS GmbH.: Karlsruhe, Germany, 2011.

S2. A. Coelho, *TOPAS 4.2*, Bruker AXS GmbH: Karlsruhe, Germany, 2009.