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Supporting Information for

Probing the correlations between the defects in metal-organic frameworks and their catalytic activity by an epoxide ring-opening reaction

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Table of Contents

Section S1. Instrumentation

NMR spectra were collected on a Bruker Avance III 500 MHz system equipped with DCH CryoProbe at IMSERC (Integrated Molecular Structure Education and Research Center) at Northwestern University. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Smartlab instrument. Samples were scanned at 45 kV and 160 mA, a step size of $2\theta = 0.02°$ (1.28 s per step) over a 2θ range of 2 to 30°. Nitrogen adsorption isotherm measurements were carried out on a Micromeritics Tristar II 3020 at 77 K. Samples were heated at elevated tempeature under vacuum for 12 h prior to measuring the isotherms. GC-MS analysis was performed on a time-of-flight GC mass spectrometer from Waters Micromass GCT Premier. GC-FID analysis were carried out on an Agilent Technologies 7820A GC system equipped with an Agilent J&W GC HP-5 capillary column (30 m × 320 μm × 0.25 μm film thickness).

Section S2. Materials Syntheses and Charaterizations

Zr-UiO-66[1], Zr-UiO-67 (HCl)[1], Zr-PCN-57[2], Hf-UiO-66[3], Zr-NU-1000[4], Hf-NU-1000[5] and Zr-MOF-808[6] were synthesized according to methods reported in the literature.

Synthesis of Zr-UiO-67 (BA). $ZrCl_4$ (120 mg, 0.515 mmol), biphenyl-4,4′-dicarboxylic acid (BPDC) (100mg, 0.413 mmol), benzoic acid (1.5 g, 12.3 mmol), and *N,N'*-dimethylformamide (DMF) (18 mL) were added to an 8-dram vial. The mixture was sonicated for 30 min, then incubated in an oven at 100 °C for 48 h. The resulting white solid was washed with fresh DMF (3 × 20 mL) and then with acetone (3 × 20 mL). After drying the sample in a vacuum oven, the sample was activated on a SmartVacPrep port by heating at 120 °C under vacuum for 12 h. Yield: 27% white microcrystalline powder.

Synthesis of Hf-UiO-67. Same procedure as ZrUiO-67 (BA), except $HfCl_4$ (120 mg, 0.374 mmol) was used instead of $ZrCl_4$. Yield: 65% white microcrystalline powder.

Synthesis of Hf-PCN-57. $HfOCl_2{\cdot}8H_2O$ (120 mg, 0.293 mmol), 2′,3′,5′,6′-tetramethyl-terphenyl-4,4″-dicarboxylic acid (TPDC-4CH_3) (100 mg, 0.267 mmol), benzoic acid (1.0 g, 8 mmol), and DMF (20 mL) were added to an 8-dram vial. The mixture was sonicated for 30 min, then incubated in an oven at 100 °C for 24 h. The sample was washed and activated using the same procedure as that of Zr-UiO-67 (BA). Yield: 72% white microcrystalline powder.

Synthesis of Hf-MOF-808: $HfOCl_2{\cdot}8H_2O$ (205 mg, 0.50 mmol), 1,3,5-benzenetricarboxylic acid (H_3BTC) (110 mg, 0.50 mmol), DMF/formic acid (20 mL/20 mL) were added to a 100 mL VWR vial.

The mixture was sonicated for 30 min, then incubated in an oven at 100 °C for 72 h. The resulting white solid was washed with fresh DMF (3 × 20 mL) and then with acetone (3 × 20 mL). After drying the sample in a vacuum oven, the sample was activated on a SmartVacPrep port by heating at 150 °C under vacuum for 12 h. Yield: 68% white microcrystalline powder.

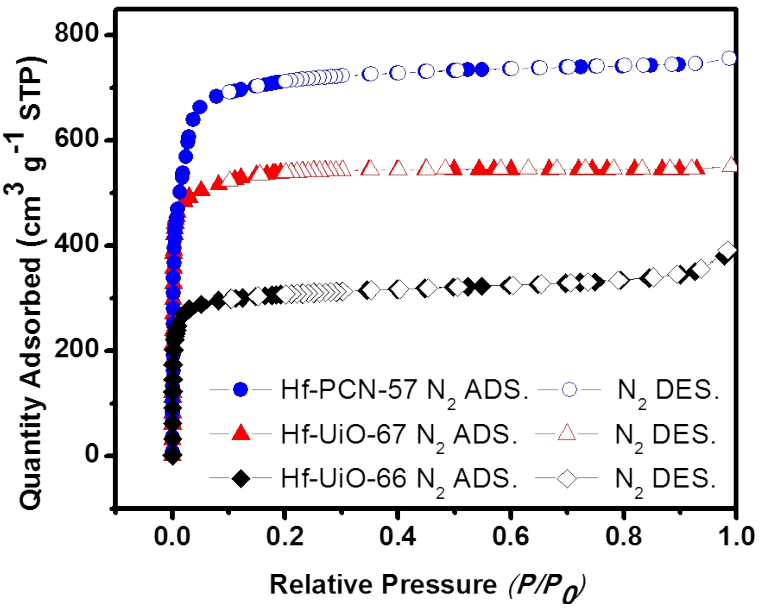

Fig. S1 N_2 isotherms of Hf-UiO-66, 67 and Hf-PCN-57 at 77K.

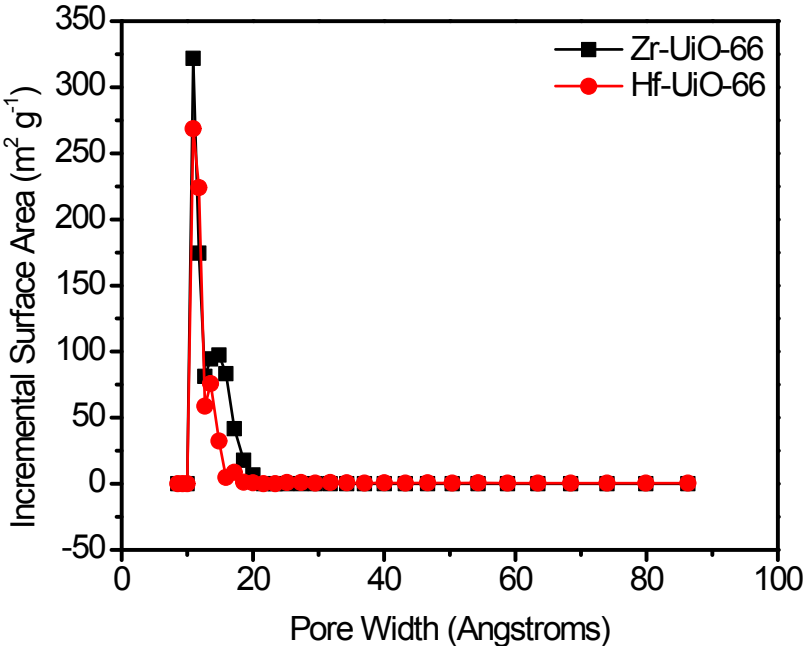

Fig. S2 Pore size distribution (PSD) of Zr- and Hf-UiO-66 calculated by DFT.

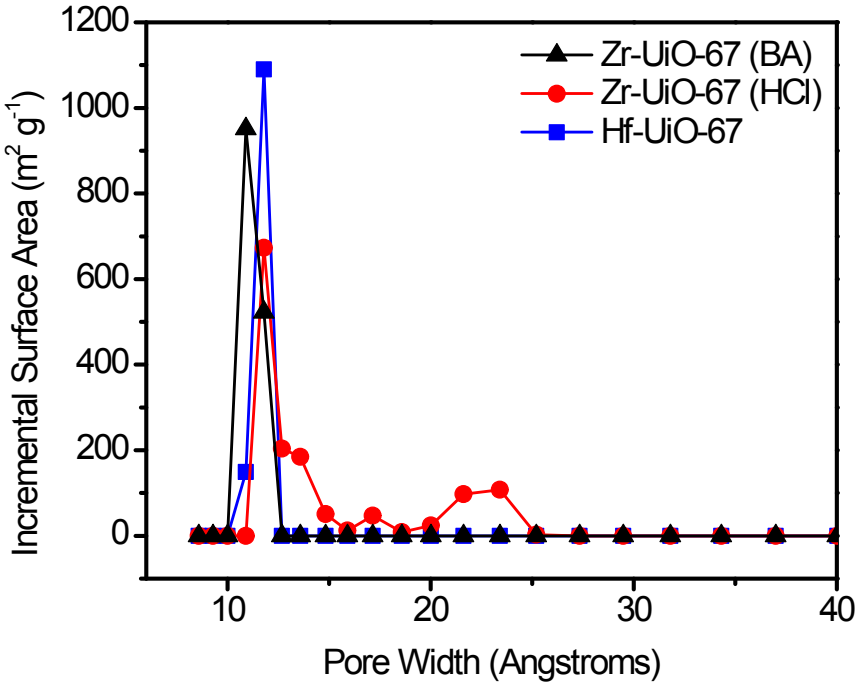

Fig. S3 Pore size distribution (PSD) of Zr-UiO-67 (BA), Zr-UiO-67 (HCl) and Hf-UiO-67 calculated by DFT. Mesopores (20-500 Å) were observed in Zr-UiO-67 (HCl).

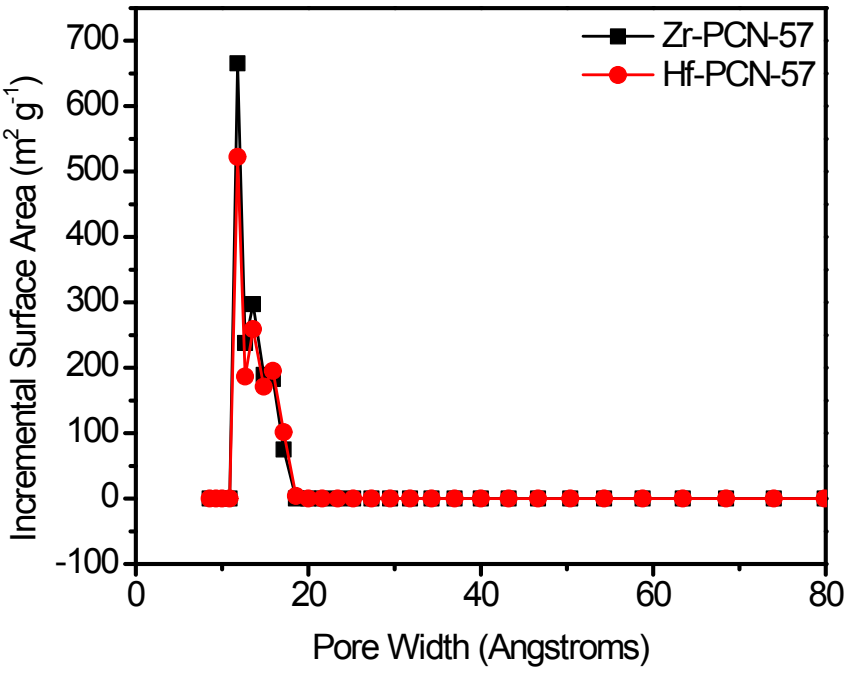

Fig. S4 Pore size distribution (PSD) of Zr- and Hf-PCN-57 calculated by DFT.

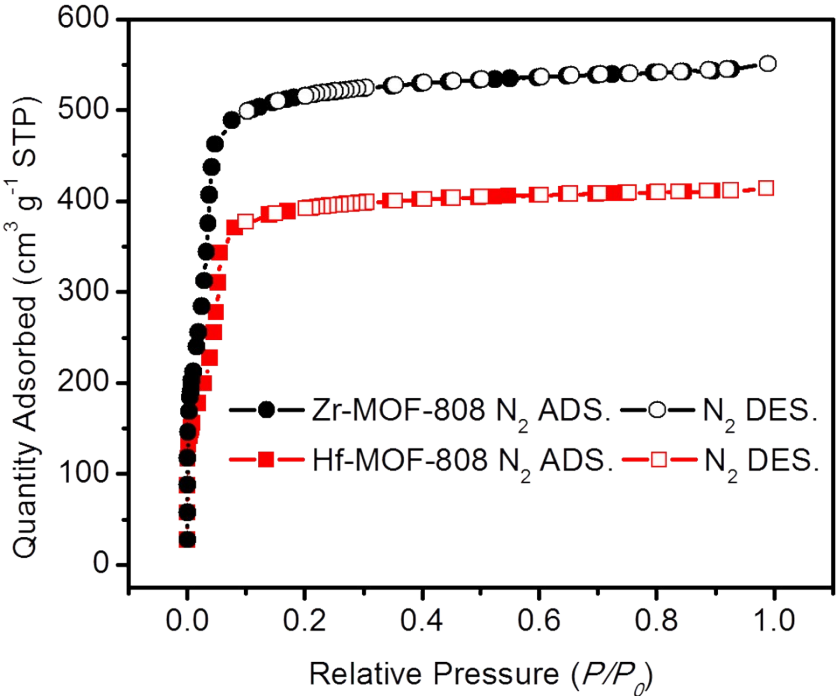

Fig. S5 N_2 isotherms of Zr- and Hf-MOF-808 at 77 K.

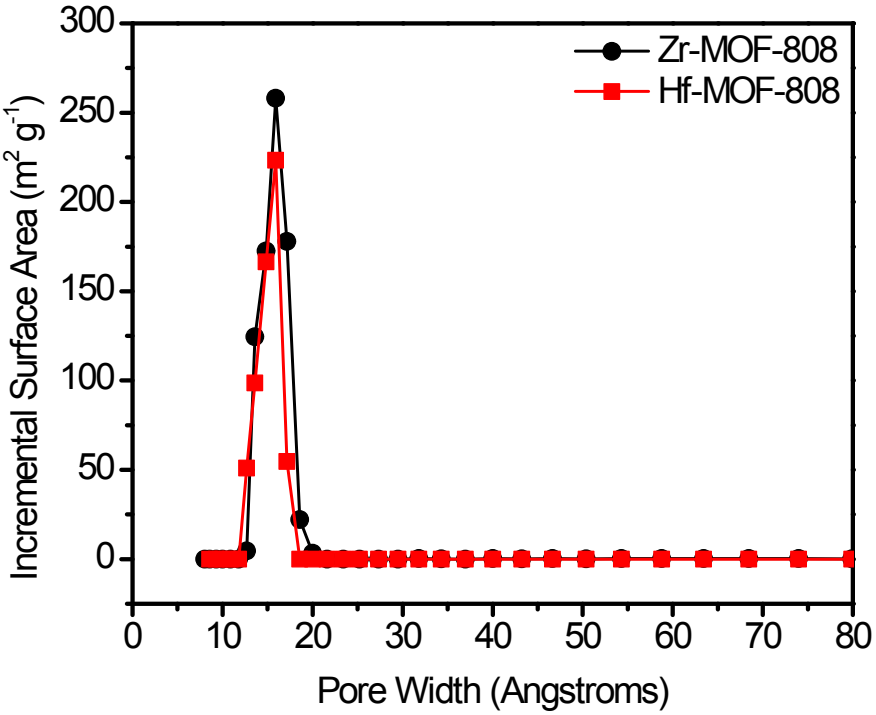

Fig. S6 Pore size distribution (PSD) of Zr- and Hf-MOF-808 calculated by DFT.

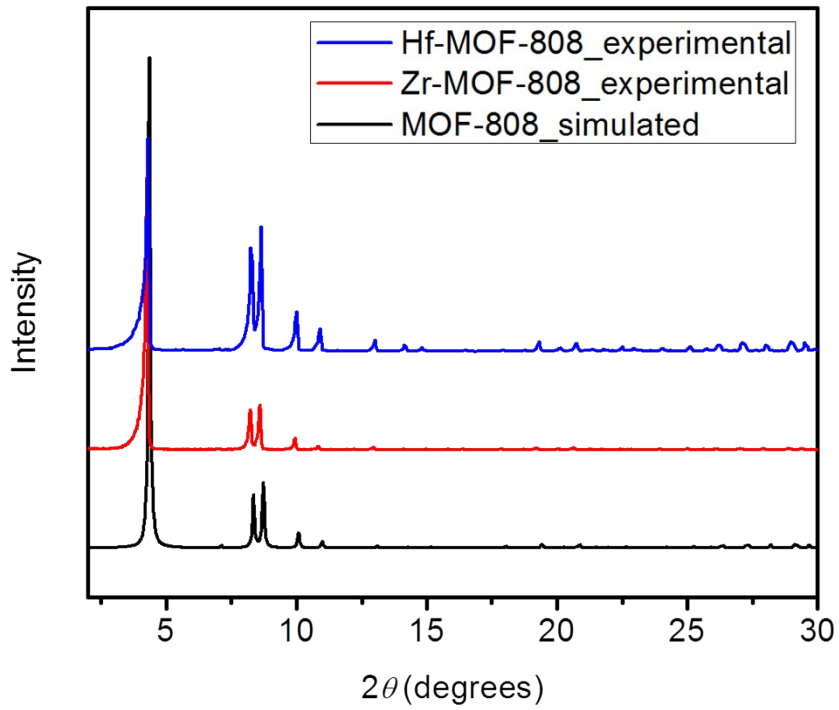

Fig. S7 PXRD of Zr- and Hf-MOF-808, simulanted and experimental

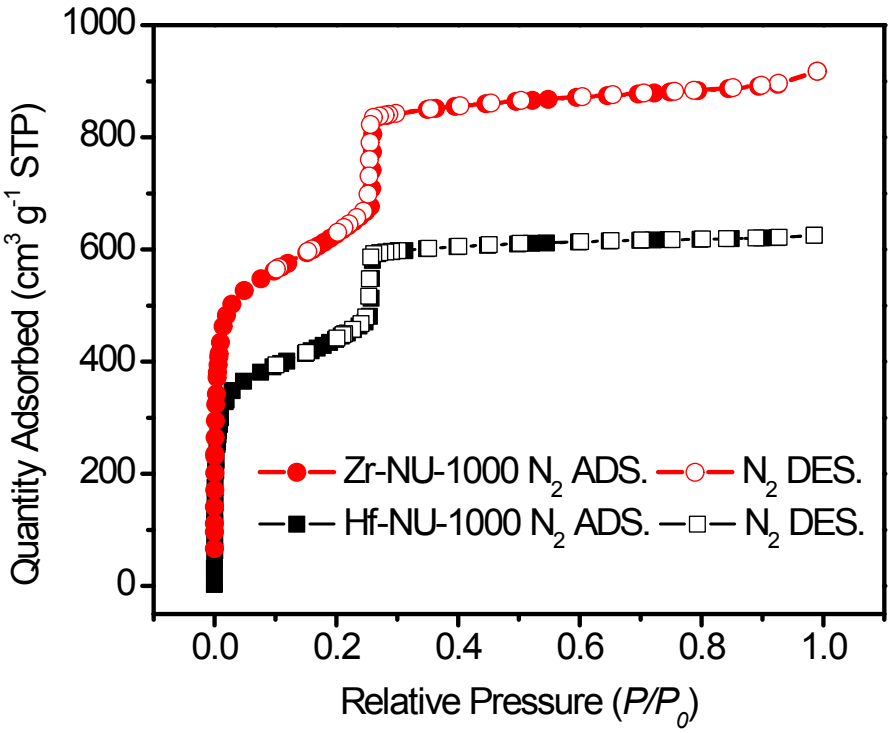

Fig. S8 N_2 isotherms of Zr- and Hf-NU-1000 at 77 K.

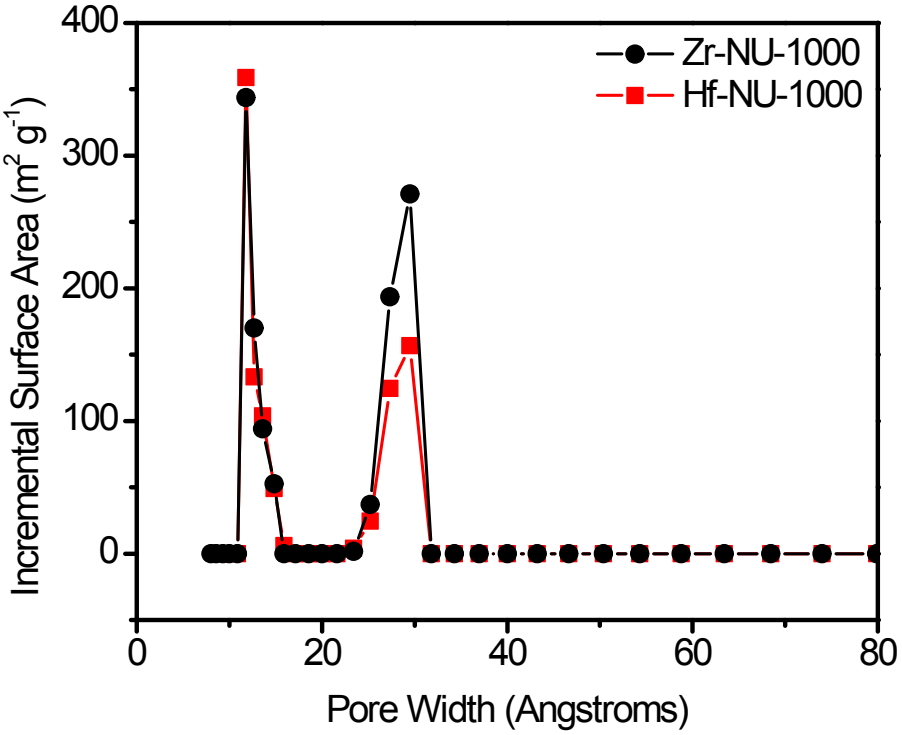

Fig. S9 Pore size distribution (PSD) of Zr- and Hf-NU-1000 calculated by DFT.

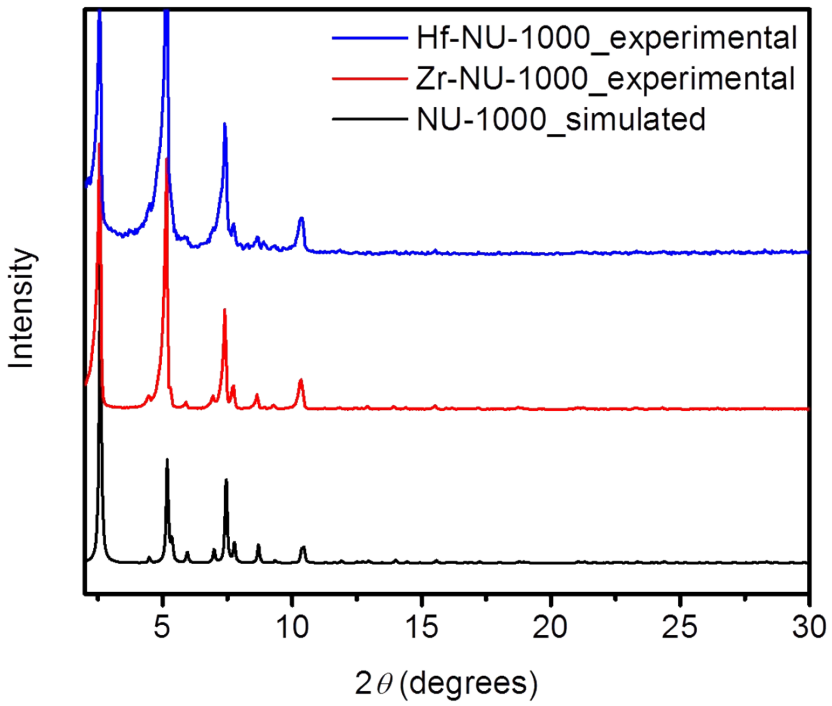

Fig. S10 PXRD of Zr- and Hf-NU-1000, simulanted and experimental

Section S3. Catalytic Studies

The styrene oxide ring-opening reaction was carried out in a boil-proof micro-centrifuge tube (1.5 mL). Into the micro-centrifuge tube, styrene oxide (23 μL, 0.2 mmol), anhydrous isopropanol (500 μL, 6.5 mmol) and 1-bromo-3,5-difluorobenzene (10 μL, 0.09 mmol) were added and mixed by swirling for 5s. After adding catalyst (1 mol%, calculated based on the Zr_6 cluster) into the mixture, the micro-centrifuge tube was then sealed and put onto a heater/shaker reaction station (temperature: 55 ℃, agitation speed: 550 rpm). Aliquots were prepared by withdrawing 3μL liquid from the reaction and diluted with 0.9 mL dichloromethane.

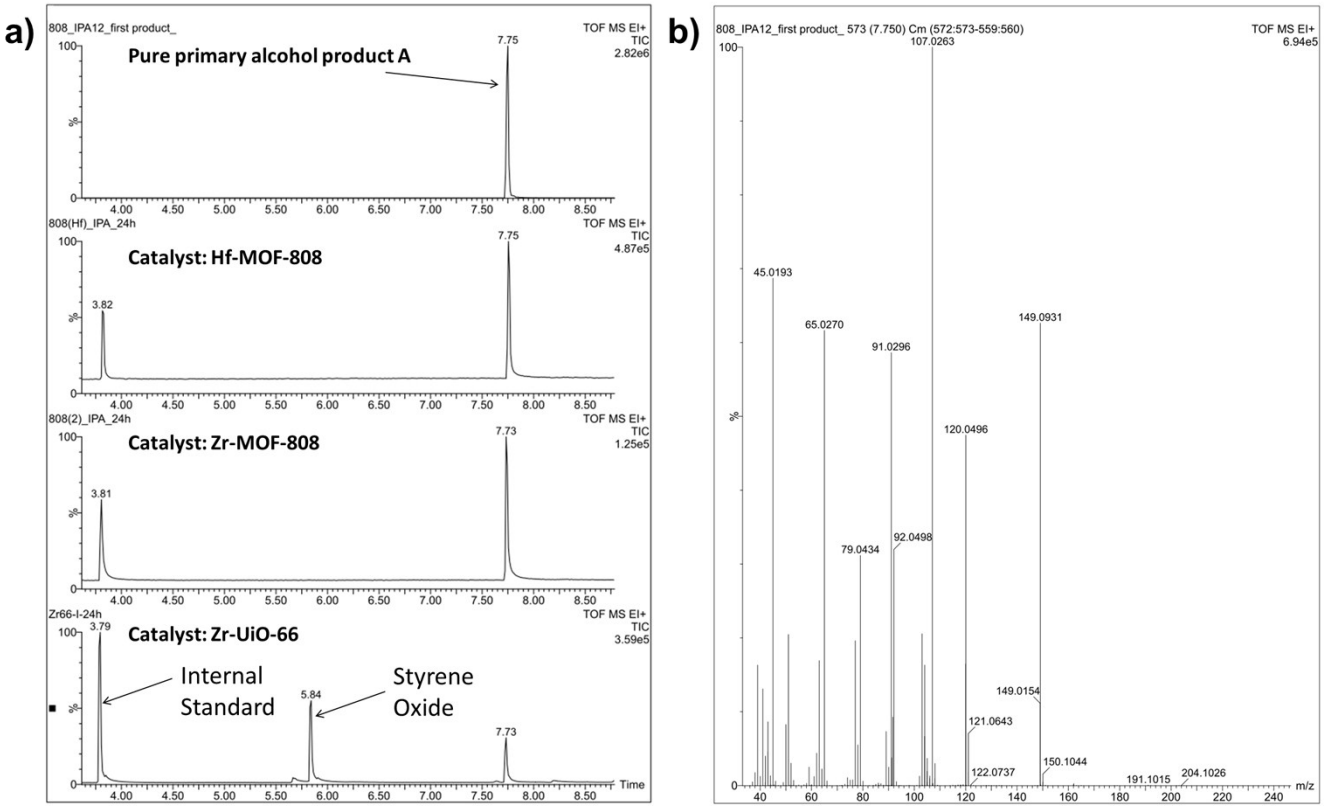

Fig. S11 a) Gas chromatography (GC) signals indicating the MOF catalysts (MOF-808 and UiO-type MOFs) are regio-selective, as only primary alcohol product was observed. b) Mass spectrometry of the primary alcohol product of styrene oxide ring-opening reaction with isopropanol. The observed regioselectivity with UiOs and MOF-808 can be attributed to a π-stacking interaction between the aromatic ring in styrene oxide and the aromatic ring in the MOF ligands. This interaction has been previously shown to alter the activation free energies of the two pathways, ultimately favoring substitution at the benzylic position, based on computational modeling.

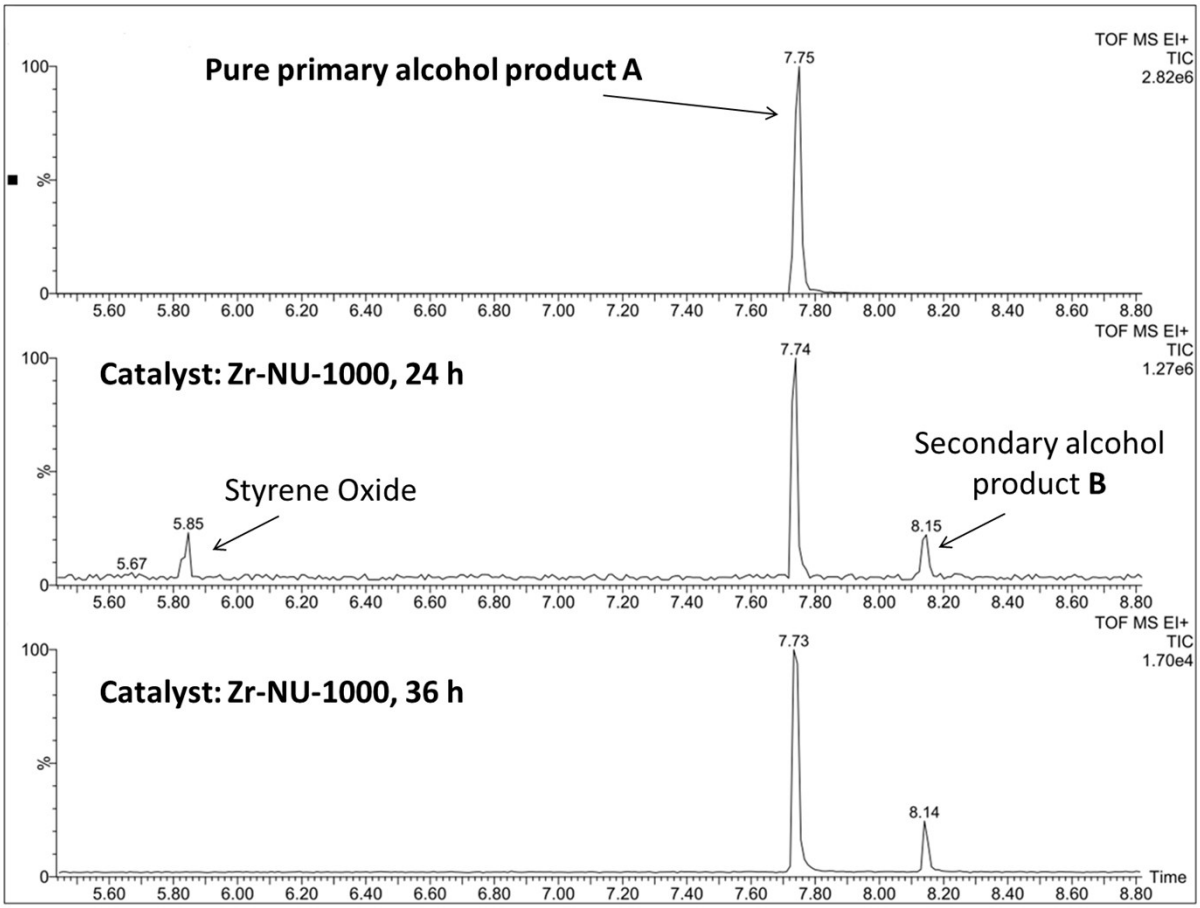

Fig. S12 a) Gas chromatography (GC) signals of the styrene oxide ring-opening reaction with isopropanol when using NU-1000 as the catalyst, both primary and secondary alcohol products (**A** and **B**) were obtained, with the selectivity of A : B = 4.5 : 1. Since NU-1000 has larger pores than UiOs and MOF-808, the lower selectivity of NU-1000 (compared to UiOs and MOF-808) is probably due to a weaker π-stacking interaction between styrene oxide and the MOF.

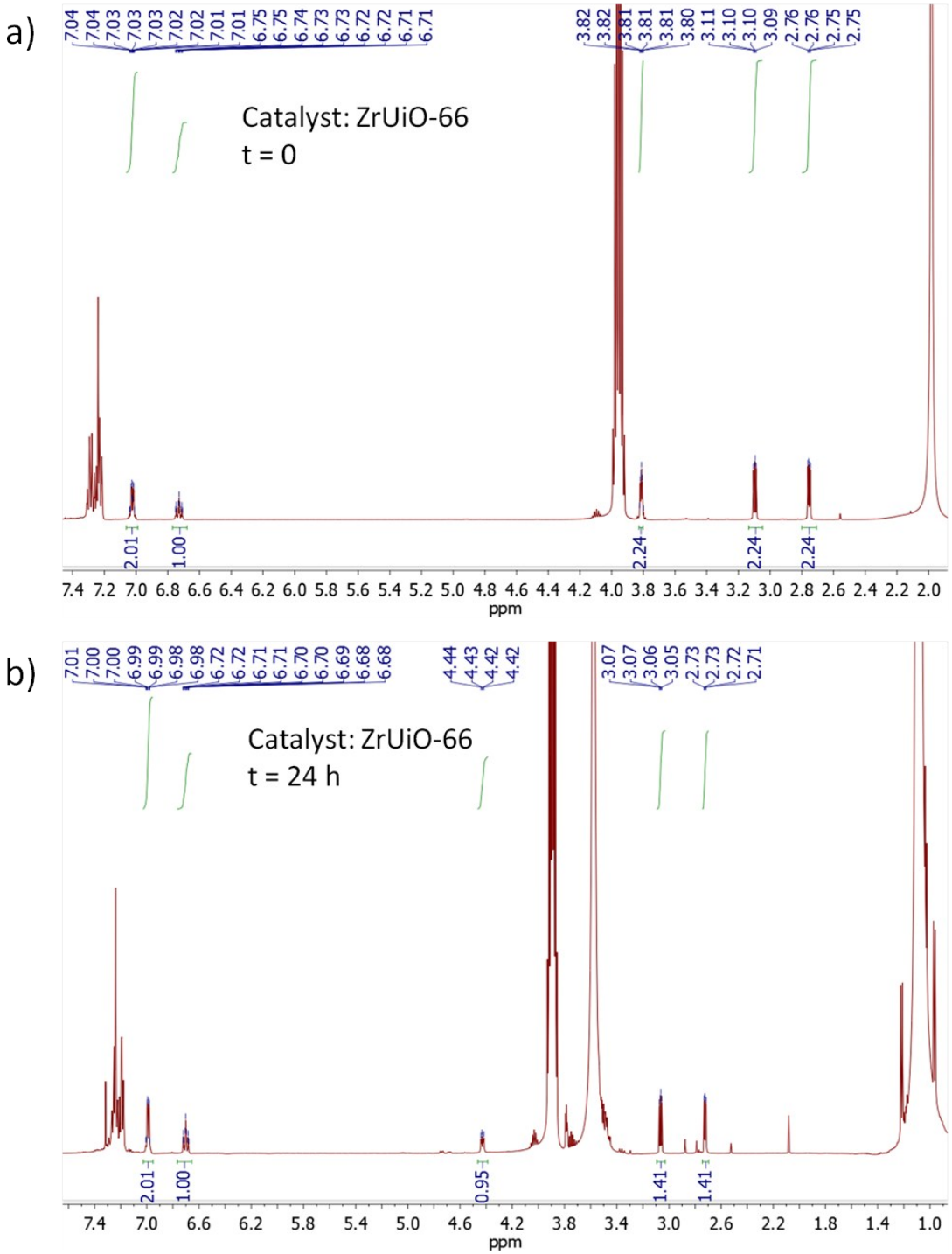

Fig. S13 ^{1}H NMR spectra of the styrene oxide ring-opening reaction with isopronol in the presence of 3.4 mg Zr-UiO-66. The reaction is performed at 55 °C. NMR samples were collected at 0 (a) and 24 h (b) of the reaction, dissolved in $CDCl_3$.

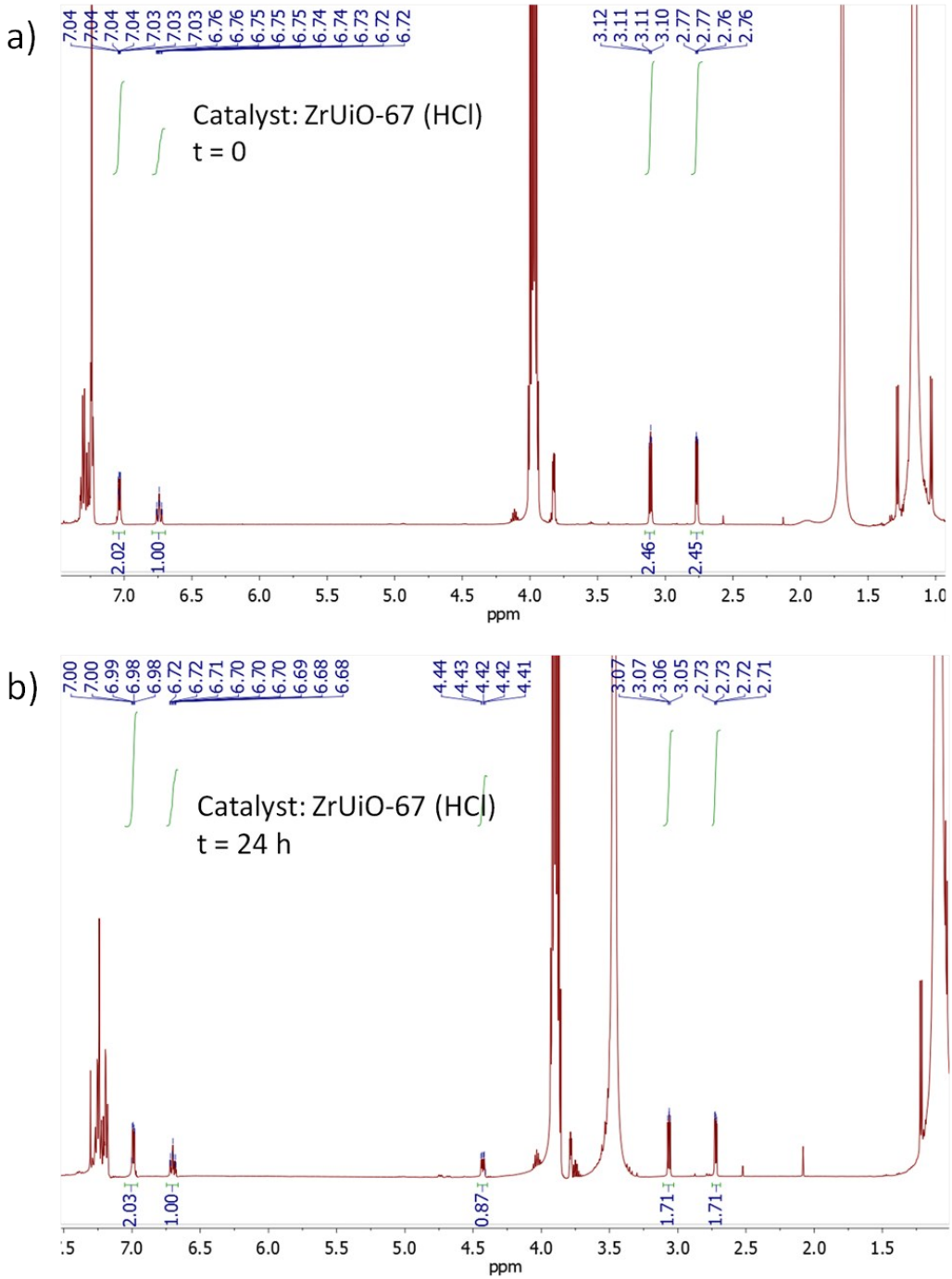

Fig. S14 ^{1}H NMR spectra of the styrene oxide ring-opening reaction with isopronol in the presence of 4.3 mg Zr-UiO-67 (HCl). The reaction is performed at 55 °C. NMR samples were collected at 0 (a) and 24 h (b) of the reaction, dissolved in $CDCl_3$.

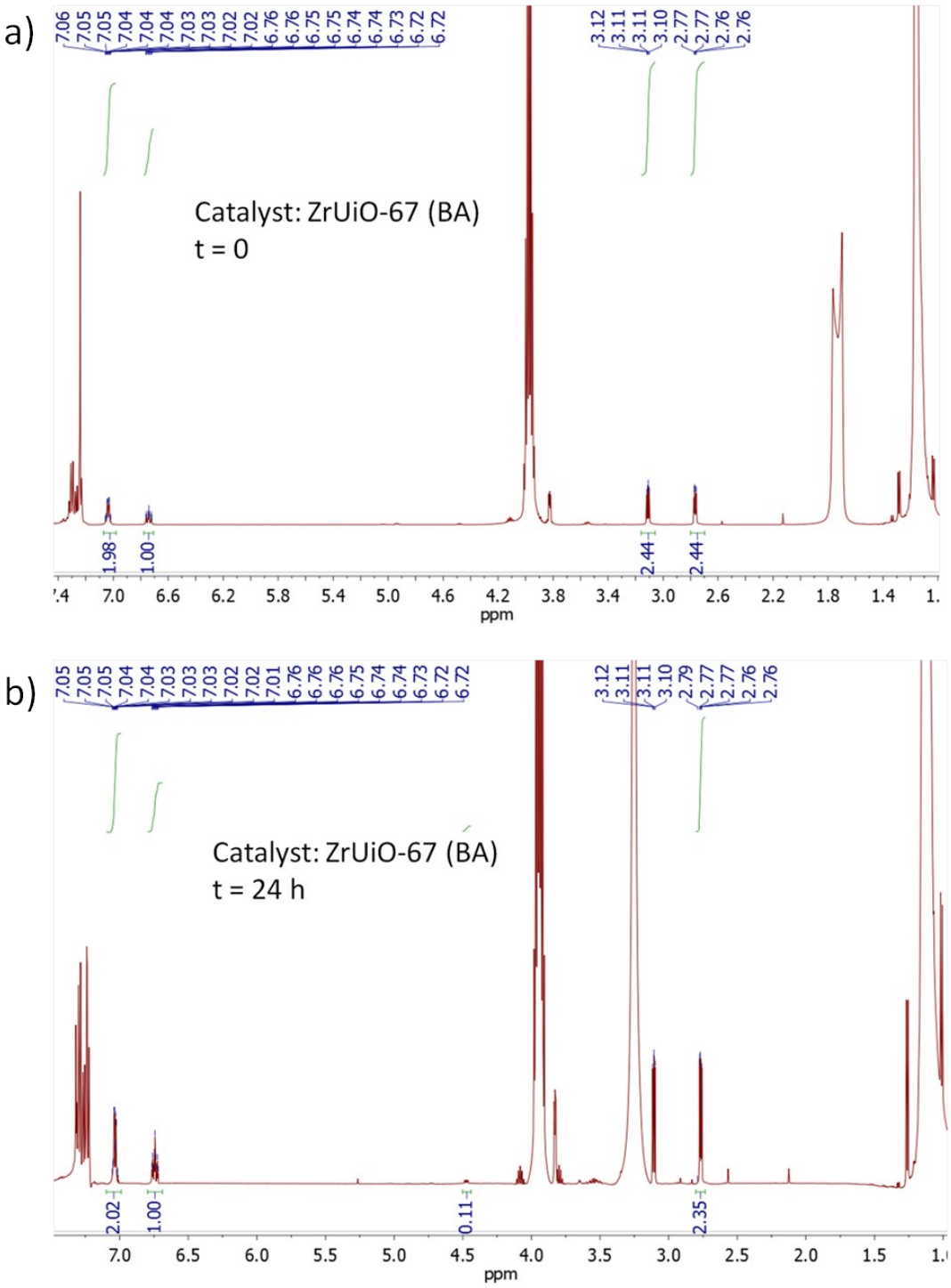

Fig. S15 ^{1}H NMR spectra of the styrene oxide ring-opening reaction with isopronol in the presence of 4.3 mg Zr-UiO-67 (BA). The reaction is performed at 55 °C. NMR samples were collected at 0 (a) and 24 h (b) of the reaction, dissolved in $CDCl_3$.

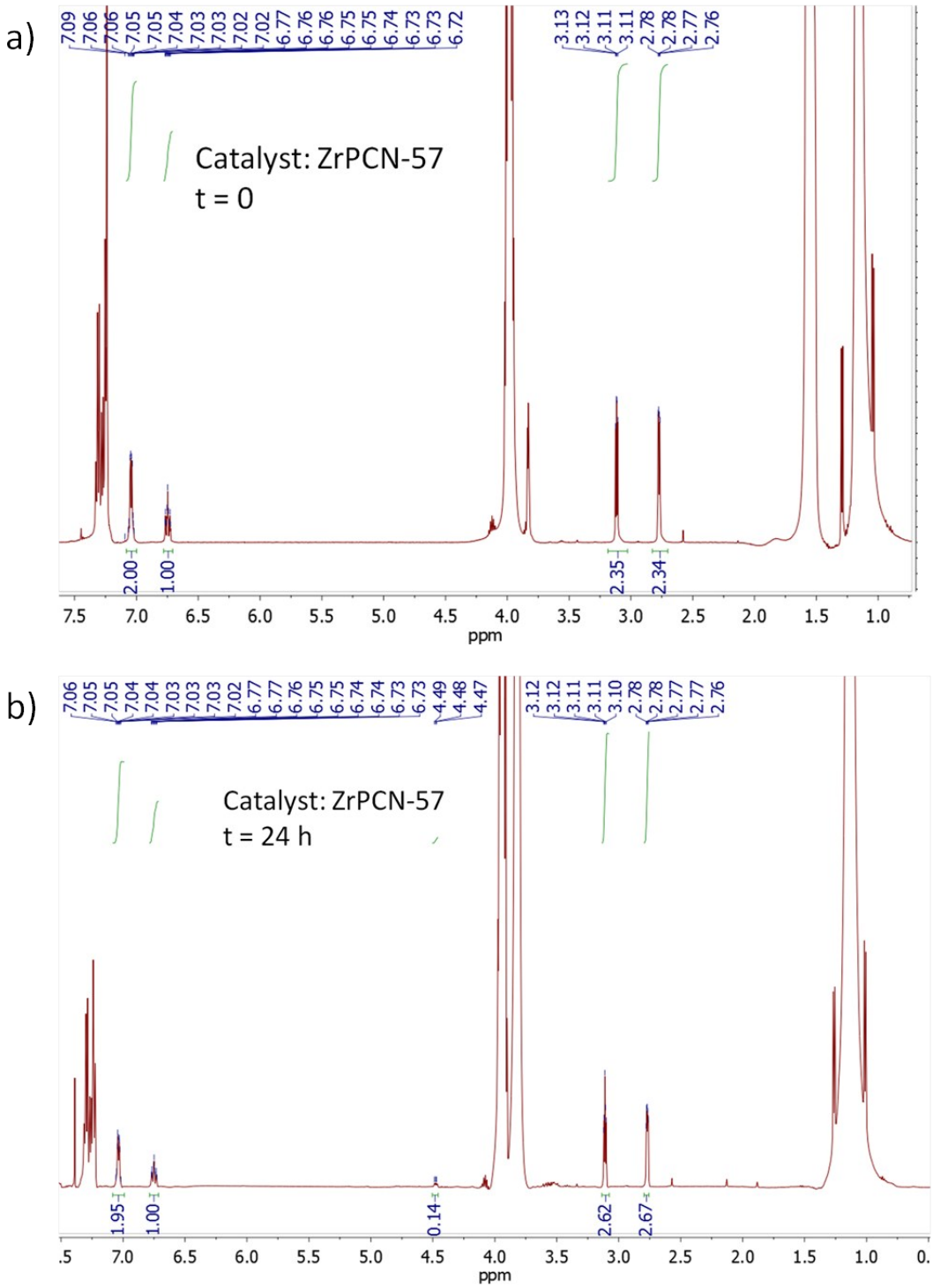

Fig. S16 ^{1}H NMR spectra of the styrene oxide ring-opening reaction with isopronol in the presence of 5.9 mg Zr-PCN-57. The reaction is performed at 55 °C. NMR samples were collected at 0 (a) and 24 h (b) of the reaction, dissolved in $CDCl_3$.

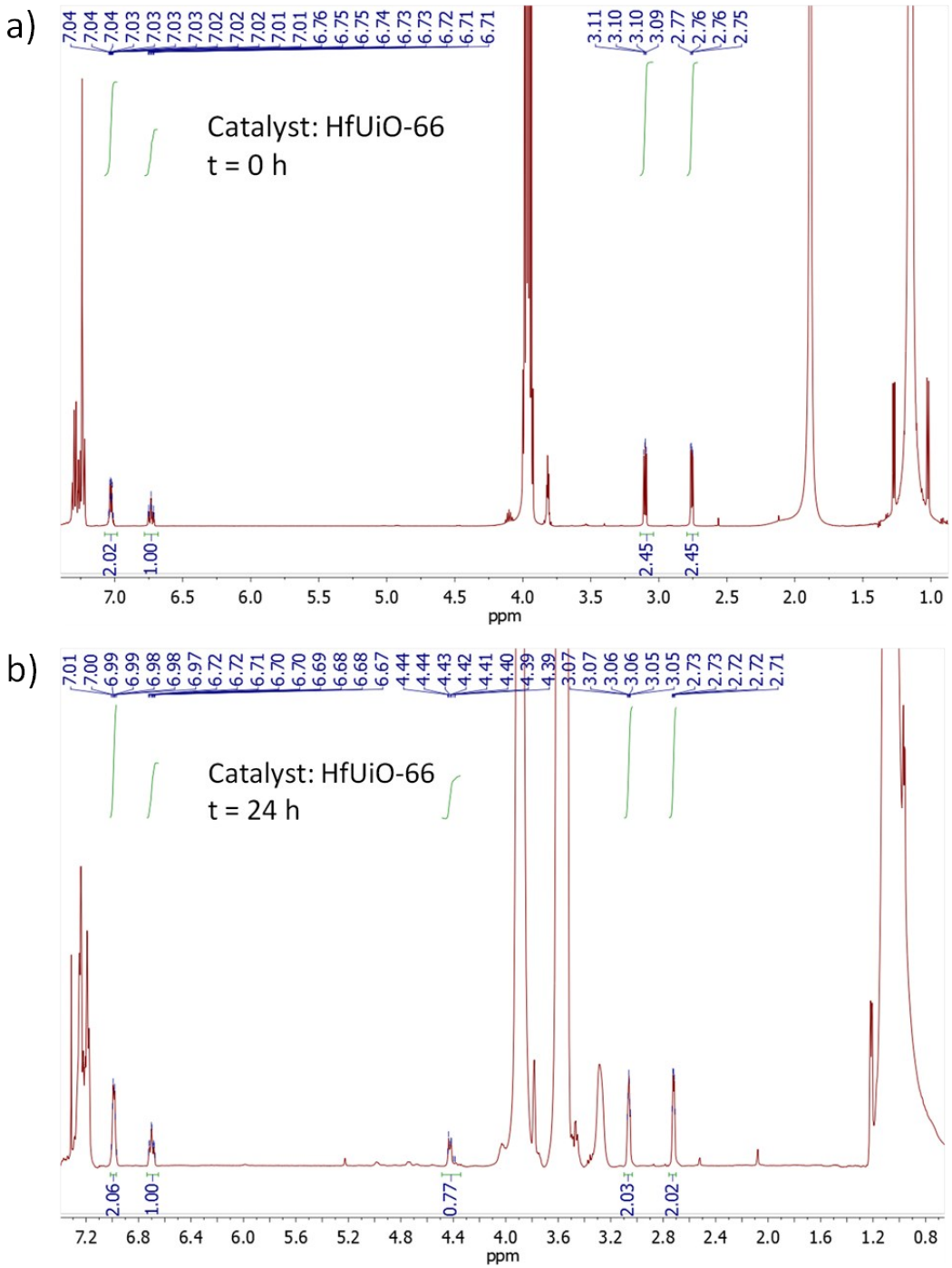

Fig. S17 ^{1}H NMR spectra of the styrene oxide ring-opening reaction with isopronol in the presence of 4.4 mg Hf-UiO-66. The reaction is performed at 55 °C. NMR samples were collected at 0 (a) and 24 h (b) of the reaction, dissolved in $CDCl_3$.

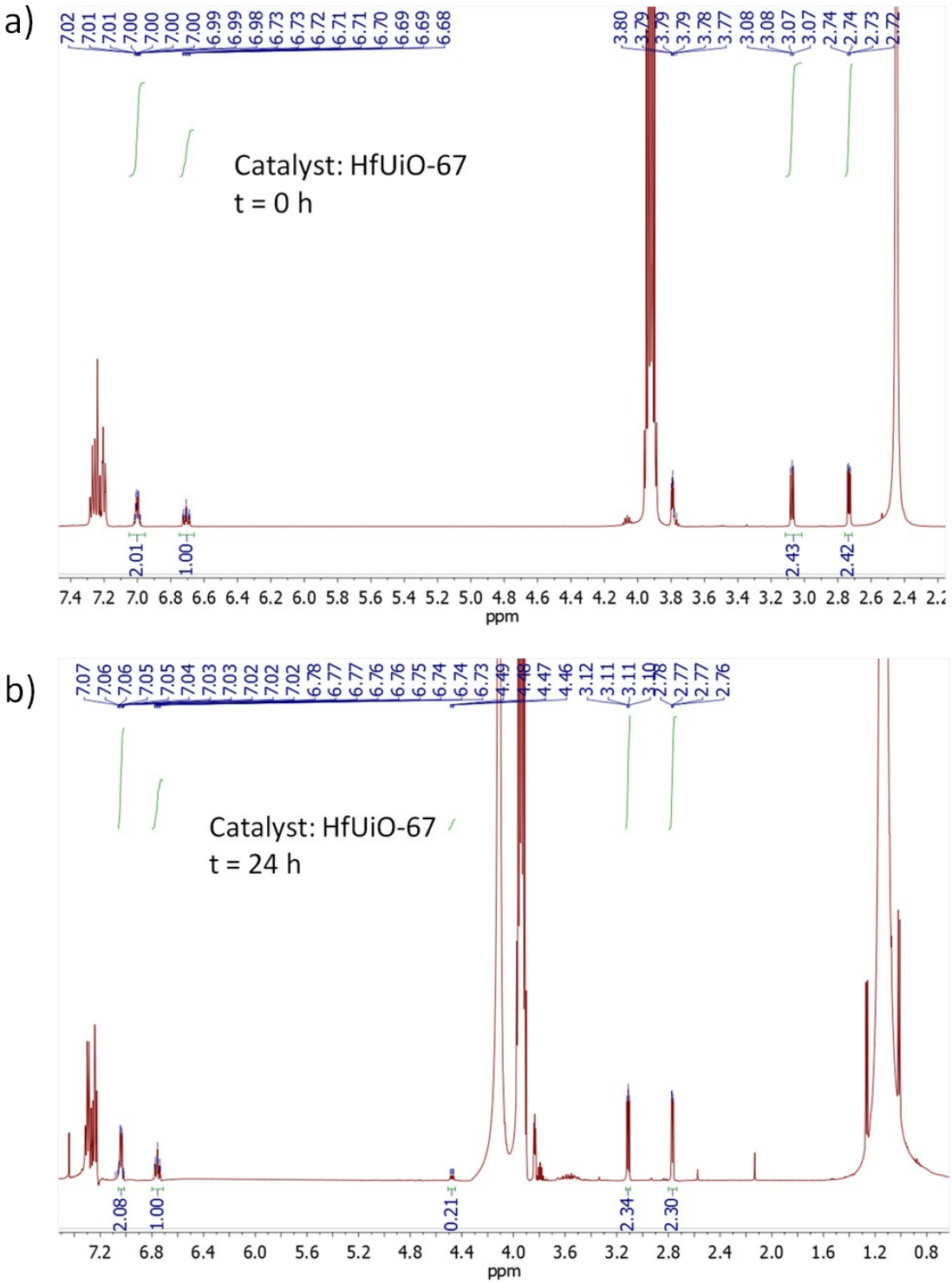

Fig. S18 ^{1}H NMR spectra of the styrene oxide ring-opening reaction with isopronol in the presence of 5.3 mg Hf-UiO-67. The reaction is performed at 55 °C. NMR samples were collected at 0 (a) and 24 h (b) of the reaction, dissolved in $CDCl_3$.

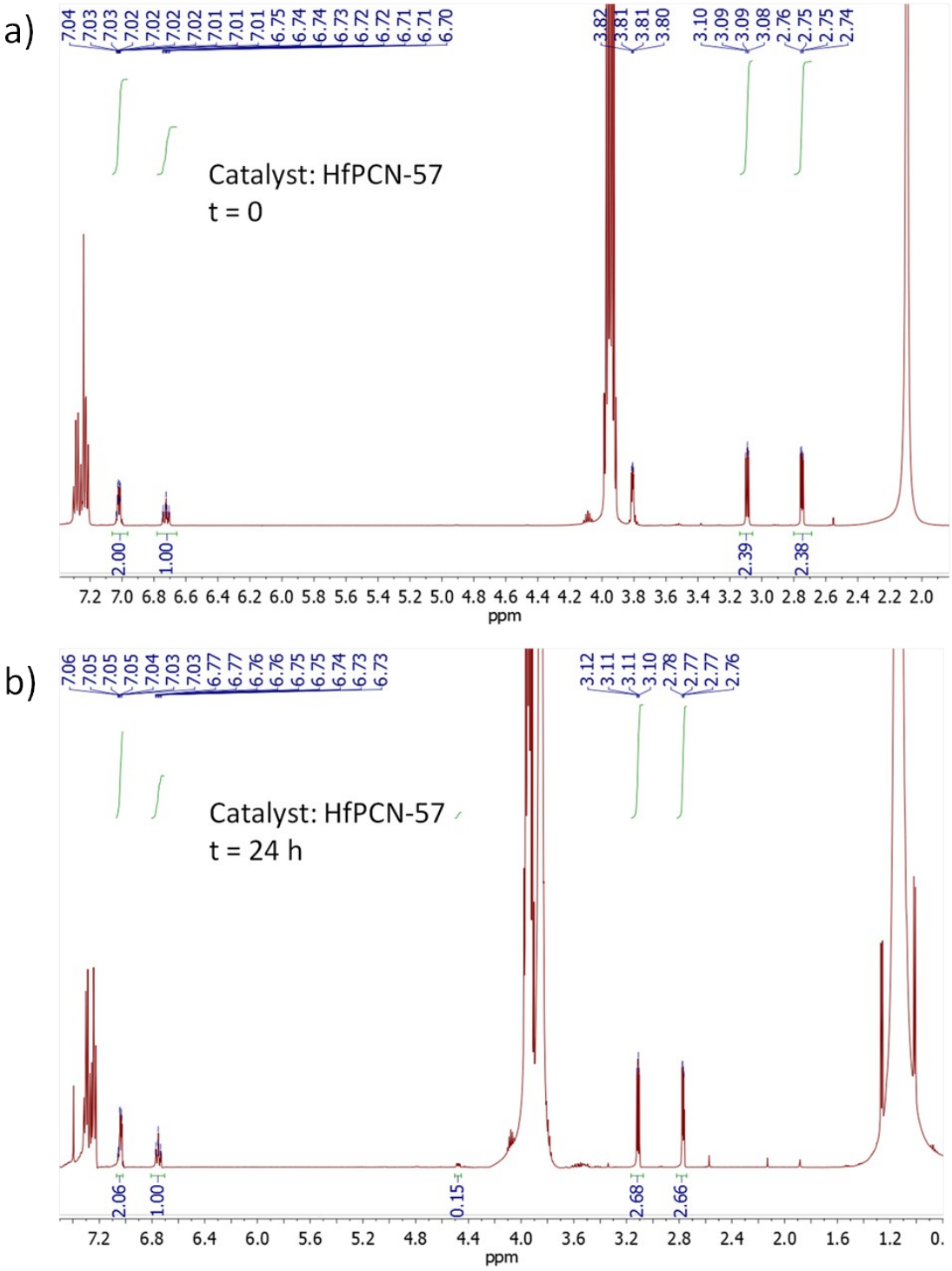

Fig. S19 ^{1}H NMR spectra of the styrene oxide ring-opening reaction with isopronol in the presence of 6.9 mg Hf-PCN-57. The reaction is performed at 55 °C. NMR samples were collected at 0 (a) and 24 h (b) of the reaction, dissolved in $CDCl_3$.

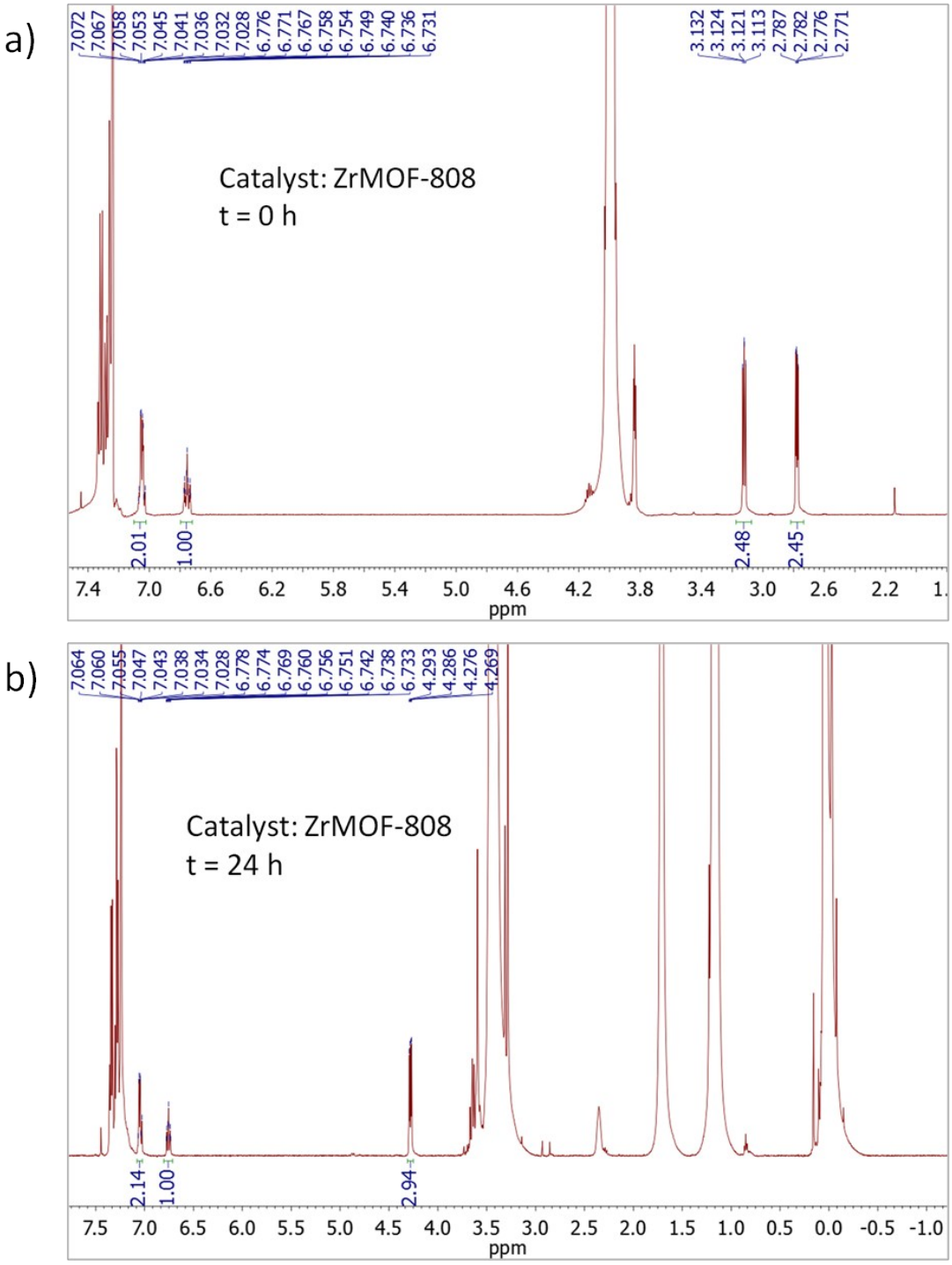

Fig. S20 ^{1}H NMR spectra of the styrene oxide ring-opening reaction with isopronol in the presence of 3.1 mg Zr-MOF-808. The reaction is performed at 55 °C. NMR samples were collected at 0 (a) and 24 h (b) of the reaction, dissolved in $CDCl_3$.

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