Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

1. Analytical methods, calculations, and characterization techniques

Materials

Methanol (HPLC grade), chloroform (HPLC grade), ethyl acetate (HPLC grade), tetrahydrofuran (THF, HPLC grade), *N,N*-dimethylformamide (DMF, HPLC grade), dichloromethane (DCM, HPLC grade), Celite® S, $ZrOCl_2 \cdot 8\ H_2O$, pyrrole, propionic acid, 4-tert-butylbenzoic acid, 3,3-dimethylbutanoic acid, formic acid, ethyl diazo acetate (10wt% in DCM), mesitylene and potassium hydroxide were purchased from Sigma Aldrich. Methyl-p-formylbenzoate was purchased from ChemPUR. Diethylformamide was purchased from TCI Chemicals. $RhCl_3 \cdot x\ H_2O$ was purchased from Carbolution. 8-dram vials for MOF synthesis (TraceClean®) were purchased from VWR. All purchased chemicals were used without further purification. All synthesis and catalysis runs were carried out under air, if not stated other.

Adsorption measurements

Adsorption measurements with N_2 (99.999 vol%) at 77 K were carried out on a 3Flex Physisorption from *Micromeritics Instrument Corp.*, which uses a volumetric method to determine the amount adsorbed under an equilibrated gas pressure. Adsorption data were processed using the 3Flex Software Version 5.01 by *Micromeritics Instrument Corp.* and plotted in OriginPro 2019b by *OriginLab Corp.* Samples were transferred into pre-weighed sample tubes and capped with *Micromeritics* CheckSeals. Samples were subsequently activated at 393 K for 12 hours under a dynamic vacuum of approx. 10^{-3} mbar using a SmartVac Prep by *Micromeritics Instrument Corp.* to ensure absence of unwanted adsorbates and identical pre-measurement states of all samples. In particular, this unusually low activation temperature and time was chosen for all samples to ensure structural integrity of the immobilized molecular complexes which are known to sublime and decompose comparatively readily. The mass of the adsorbents was then recorded, generally in the range of 25 – 40 mg. The free space of the sample tube was determined prior to measuring each adsorption isotherm using Helium (99.999 vol%). A liquid nitrogen bath was used for measurements at 77 K.

The apparent surface area was derived using the Brunauer-Emmett-Teller (BET) model, is hence given as the 'BET area' and based on N_2 isotherms measured at 77 K. To determine this value for microporous materials, care was taken to adhere to the Rouquerol criteria.[1]

The pore size distribution (PSD) was derived by fitting N_2 isotherms measured at 77 K with sets of theoretical isotherms (kernel) derived from two-dimensional non-local-density functional theory (2D-NLDFT) based methods for specific pore sizes and geometry. As an approximation, cylindrical pores on an oxide surface were assumed for all materials to allow comparability within this series. Fitting was done using the respective kernel available via the 3Flex Software Version 5.01 by *Micromeritics Instrument Corp.*

Attenuated total reflectance infrared spectroscopy (ATR-IR)

ATR-IR measurements were carried out on a *PerkinElmer* Frontier FT-IR spectrometer featuring an ATR plate with a diamond crystal with a 2 cm^{-1} resolution and 16 accumulated scans.

Inductively coupled plasma mass spectrometry (ICP-MS)

To obtain an accurate quantification of the Zr and Rh amount immobilized in MOF samples, ICP-MS for zirconium and rhodium, respectively, was conducted on a *Perkin Elmer* NexIon

350D ICP-MS instrument. The respective samples were immersed in concentrated 7.5 mL nitric acid and 2.5 mL H_2O_2 30 % (v/v) and treated in the microwave at 150 °C for 10 min. Subsequently, the microwave-digested samples were diluted 1/100 with Millipore Milli-Q® water. Each solvent was extra pure and checked for possible analyte contaminations before measurement. ^{103}Rh and ^{94}Zr were used as target masses for the analytes and ^{115}In as an internal standard. Analyte quantification was carried out in standard mode with correction equation to avoid polyatomic interferences. Detection limit for Zr was 0.13 µg L^{-1} and 0.29 µg L^{-1} for Rh. External Calibration was performed in the range of 0 µg L^{-1} to 100 µg L^{-1}. Each sample was measured with five measurement replicates, a dwell time per 50 ms and an integration time of 750 ms. The Zr and Rh concentrations were blank corrected via measurement of blank samples.

Gas chromatography (GC)

GC is performed with an *Agilent Technologies* 7890B GC with a flame ionization detector (FID). The substance separation occurs via a capillary column HP-5 (length 30 m, inside diameter 0.32 mm, film 0.25 µm, stationary phase (5%-phenyl)-methylpolysiloxane)). Sample preparation is performed by retrieving 50 µL aliquot from the reaction supsension, adding 1.5 mL of the respective solvent and removing the MOF by a syringe filter (13 mm PTFE membrane with 0.2 µm pore size).

Nuclear magnetic resonance (NMR)

Liquid state NMR spectra were recorded by a *Bruker* AVIII 400 US (^1H: 400.13 MHz) at ambient temperature (298 K). The ^1H NMR spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane. ^1H NMR spectra are calibrated against the residual proton and natural abundance carbon resonances of the respective deuterated solvent as an internal standard ($CDCl_3$: δ (^1H) = 7.26 ppm, DMSO-d_6: δ (^1H) = 2.50 ppm). The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet.

Powder x-ray diffraction (PXRD)

PXRD measurements were performed on a silicon single-crystal wafer using *Bragg-Brentano* geometry in a *Rigaku* MiniFlex 600-C diffractometer. X-ray Cu K_α radiation (λ_1 - 1.5406 Å, λ_2 - 1.5444 Å, I_2/I_1 - 0.5) was used, and K_β radiation was removed by a Ni-filter. The measurement range, unless stated otherwise, was from 2.0° to 50.0° (2θ) with a step size of 0.010 degrees and a scan rate of 5 degrees per minute.

Pawley profile fit analysis was carried out for the pattern of PCN-222 and PCN-222(Rh) by using TOPAS v6. Standard deviations of all parameters were calculated and "randomize_on_errors" was used to achieve the minimum of refinement.

Solid-state UV-Vis spectroscopy

Solid-state UV-Vis spectra were recorded on a *Shimadzu* UV-3600 Plus UV-Vis-NIR spectrophotometer. Powder samples were fixed between two quartz glass slides for measurement. Measurement parameters: Medium Scan Speed, slit width (20) with External(3Detector) unit, enabled stair correction, baseline correction ($BaSO_4$ background), S/R exchange normal, slit and detector lock normal.

UV-Vis spectroscopy

UV-Vis spectra were recorded on an *Agilent Technologies* Cary 60 with a scan rate of 600 nm/min. Baseline correction was performed with the respective pure solvent. Each sample was measured in a QS Suprasil 10.00 mm quartz glass cuvette from *Heraeus Quarzglas GmbH.*

DFT

Geometries of the model complexes were performed using the ORCA5.0[2]software package with the 3-parameter hybrid functional B3LYP[3]. Grimme's Dispersion correction including Becke-Johnson damping (D3BJ)[4] was used. The structure optimization and analytical calculations of the Hessian were performed using Ahlrich's def2-SVP basis set.[5]

2. Synthetical procedures

5,10,15,20-tetrakis(4-carboxylphenyl)-porphyrin ($TCPPH_2$)

The synthesis was adapted from a literature known procedure.[6] The first step was the synthesis of *tetrakis*(4-methoxycarbonylphenyl)-porphyrin (TPPCOOMe) by adding pyrrole (3.09 mL, 44.9 mmol, 1.1 equiv.) and methyl-p-formylbenzoate (6.93 g, 42.3 mmol, 1.0 equiv.) to refluxing propionic acid (100 mL). After refluxing for 22 h under continuous stirring, the precipitate was filtrated and washed with methanol (MeOH, 30 mL), ethyl acetate (EtOAc, 10 mL) and tetrahydrofuran (THF, 10 mL) to yield the purple-colored product (5.45 g, 6.44 mmol, 15% yield). Analytics matched literature reports.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.82 (s, 8H, *β*-pyrrole), 8.45 (d, ^3J = 8.1 Hz, 8H, phenyl), 8.38 (d, ^3J = 8.2 Hz, 8H, phenyl), 4.12 (s, 12H, COOMe), -2.81 (s, 2H, N*H*).

Anal. calcd. (%) for TPPCOOMe: C, 73.75; H, 4.52; N, 6.62. Found (%): C, 72.80; H, 4.66; N, 6.30.

In the second step, TPPCOOMe (1.00 g, 1.19 mmol, 1.0 equiv.) was dissolved in a 1:1 mixture of THF/MeOH (70 mL). A solution of KOH (3.5 g, 62.4 mmol, 52 equiv.) in H_2O (30 mL) was added. The resulting mixture was refluxed for 15 h. After removing the organic solvents in vacuo, the solid was redissolved in H_2O (150 mL) at 90 °C for 15 min. The solution was filtered and acidified with 1 M HCl (100 mL). The resulting green precipitate was filtered and dried to obtain the product, (864 mg, 1.09 mmol, 92% yield). Analytics matched literature reports.

^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 13.29 (s, 4H, COO*H*), 8.87 (s, 8H, *β*-pyrrole), 8.40 (d, ^3J = 8.3 Hz, 8H, phenyl), 8.36 (d,^3J = 8.4 Hz, 8H, phenyl), -2.94 (s, 2H, N*H*).

Anal. calcd. (%) for **TCPP**: C, 72.91; H, 3.82; N, 7.09. Found (%): C, 67.85; H, 3.89; N, 6.37. Crystal water: 3 H_2O.

5,10,15,20-tetrakis(4-carboxylphenyl)-porphyrinato-Rhodium(III) Chloride (Rh-TCPP)

The synthesis was adapted from a literature known procedure.[7] TPPCOOMe (168.2 mg, 0.2 mmol, 1.0 equiv.) and $RhCl_3 \cdot x\ H_2O$ (104.2 mg, 0.8 mmol (calculated without xH_2O, 4 equiv.) were refluxed in benzonitrile (5 mL) for 2 h. After the mixture was cooled to room temperature, the solvent was removed under vacuo. The dark purple precipitate purified by column chromatography over silica with EtOAc/DCM (1/1). Solvent removal yielded Rh(TPPCOOMe)Cl (118 mg, 0.12 mmol, 60% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 8.88 (s, 8H, *β* -pyrrole), 8.41 (m, 16H, phenyl), 4.06 (s, 12H, COO*Me*).

For saponification, different batches of Rh-TPPCOOMe were combined. Rh-TPPCOOMe (350 mg, 356 µmol, 1.0 equiv.) was dissolved in THF/MeOH 1:1 (40 mL). KOH (300 mg, 5.35 mmol, 15 equiv.) was dissolved in H_2O (20 mL) and added to the prior solution. The reaction mixture

was refluxed for 13 h under continuous stirring. After the mixture was cooled to room temperature, the organic solvents were removed by rotary evaporation. The crude product was dissolved in H_2O (35 mL) and heated at 90 °C for 10 min. After cooling to room temperature, the aqueous mixture was acidified with 1 M HCl solution (25 mL). The resulting violet precipitate was isolated by centrifugation and washed with H_2O (8 × 30 mL). The violet product was dried *in vacuo* overnight (295 mg, 318 µmol, 89% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 13.41 (s, 4H, COO*H*), 8.95 (m, 8H, *β*-pyrrole),

8.38 (m, 16H, phenyl), -2.93 (s, 0.33H, N*H*). Rh-metalation of 84%.

Anal. calcd. (%) for **Rh-TCPP**: C, 62.18; H, 3.04; N, 6.04. Found (%): C, 62.60; H, 3.84; N, 6.32.

PCN-222

The synthesis was adapted from a literature known procedure.[8,9] In a 20 mL screw cap vial, $TCPPH_2$ (12.5 mg, 0.016 mmol, 1.00 equiv.) and $ZrOCl_2{\cdot}8\,H_2O$ (23.5 mg, 0.073 mmol, 4.56 equiv.) were dissolved in N,N-diethylformamide (DEF, 3 mL). After addition of 4-*tert*-butylbenzoic acid (1350 mg, 7.57 mmol, 473 equiv.), the mixture was ultrasonicated for 10 min. To increase the yield, seeds of PCN-222 are added. The mixture was heated at 120 °C for 12 h in an oven. The solid was separated by centrifugation and soaked with DMF (3 × 6 mL) and dried *in vacuo*. The solid (12.2 mg) was dispersed in DMF (8.1 mL) and acidified with 8 M HCl (0.3 mL). The mixture was heated in an oven at 120 °C for 12 h. The purple solid was collected by centrifugation and soaked in DMF (3 × 6 mL) and acetone (3 × 6 mL) and dried *in vacuo* to yield the product. For dehydration (=activation) the product is heated at 120 °C *in vacuo* (10^{-3} mbar) overnight. Analytics matched literature reports.

PCN-224

The synthesis was adapted from a literature known procedure.[8,9] In a 20 mL screw cap vial, $TCPPH_2$ (16.0 mg, 0.020 mmol, 1.00 equiv.) and $ZrOCl_2{\cdot}8\,H_2O$ (30.0 mg, 0.093 mmol, 4.65 equiv.) were dissolved in N,N-dimethylformamide (DMF, 4 mL). After addition of formic acid (0.69 mL, 17.2 mmol, 860 equiv.) and 3,3-dimethylbutanoic acid (0.81 mL, 6.36 mmol, 318 equiv.), the mixture was ultrasonicated for 10 min. To increase the yield, seeds of PCN-224 are added. The mixture was heated at 120 °C for 12 h in an oven. The solid was separated by centrifugation and soaked with DMF (3 × 6 mL) and dried *in vacuo*. The solid (31.1mg) was dispersed in DMF (21 mL) and acidified with 8 M HCl (1.6 mL). The mixture was heated in an oven at 120 °C for 12 h. The purple solid was collected by centrifugation and soaked in DMF (3 × 10 mL) and acetone (3 × 10 mL) and dried *in vacuo* to yield the product which was activated at 120 °C *in vacuo* (10^{-3} mbar) for 16 h. Analytics matched literature reports.

MOF-525

The synthesis was performed according to a literature known procedure.[10] In a 100 mL laboratory bottle, $ZrOCl_2{\cdot}8\,H_2O$ (125 mg, 0.39 mmol, 11.8 equiv.) was suspended in DMF (60 mL) and ultrasonicated for 30 min. $TCPPH_2$ (26 mg, 0.033 mmol, 1.0 equiv.) was added to the solution and the mixture was ultrasonicated for 10 min. Afterwards, acetic acid (10 mL) was added and the resulting solution was heated at 80 °C for three days. The precipitate was filtered and soaked with DMF (3 × 40 mL) and acetone (3 × 40 mL) over one day. The solid was dried in vacuo and activated at 120 °C *in vacuo* (10^{-3} mbar) for 16 h to yield the product. Analytics matched literature reports.

Metalation of PCN-222, PCN-224 and MOF-525 with Rh

$RhCl_3 \cdot xH_2O$ (38.4 mg for PCN-222 and 30.6 mg for PCN-224 and 41.5 mg for MOF-525) and the MOF powder (20 mg) were suspended in DMF (4 mL). The suspension was heated in a heating block at 120°C for 24 °C while stirring at 300 rpm. The product was isolated by centrifugation and washed with DMF (3 × 6 mL) and acetone (3 × 6 mL). Drying *in vacuo* yielded the product. The different synthesis batches were combined to perform all catalytic experiments and characterizations with the same batch of material. For dehydration the product is heated at 120 °C *in vacuo* overnight.

3. Material Characterization

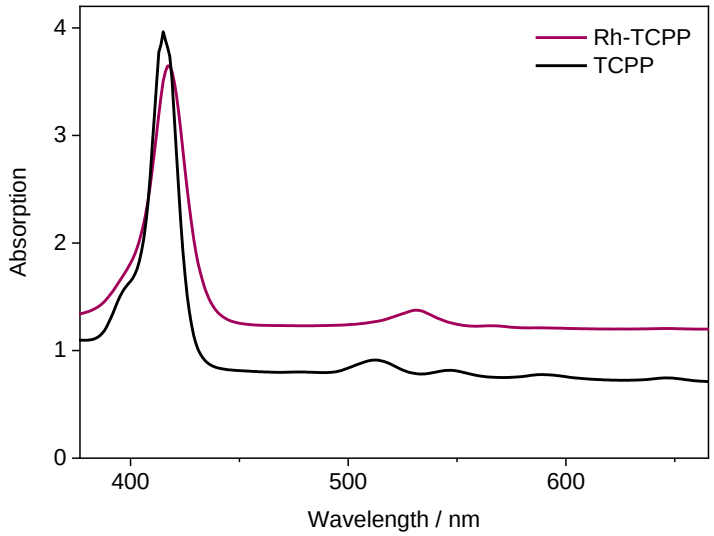


Figure S1: UV-vis spectra of TCPP and Rh-TCPP in Ethanol.

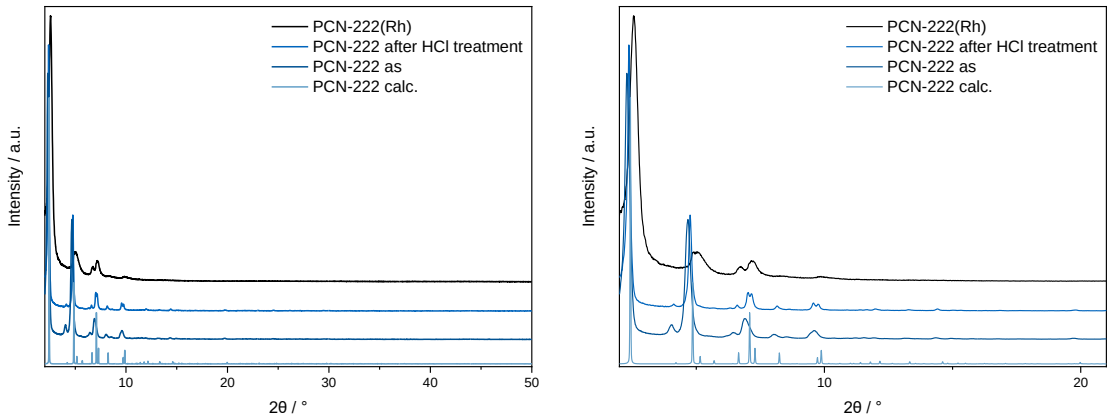


Figure S2: PXRD pattern for PCN-222 of as-synthesized (as) material, after HCl treatment and after metalation with Rhodium.

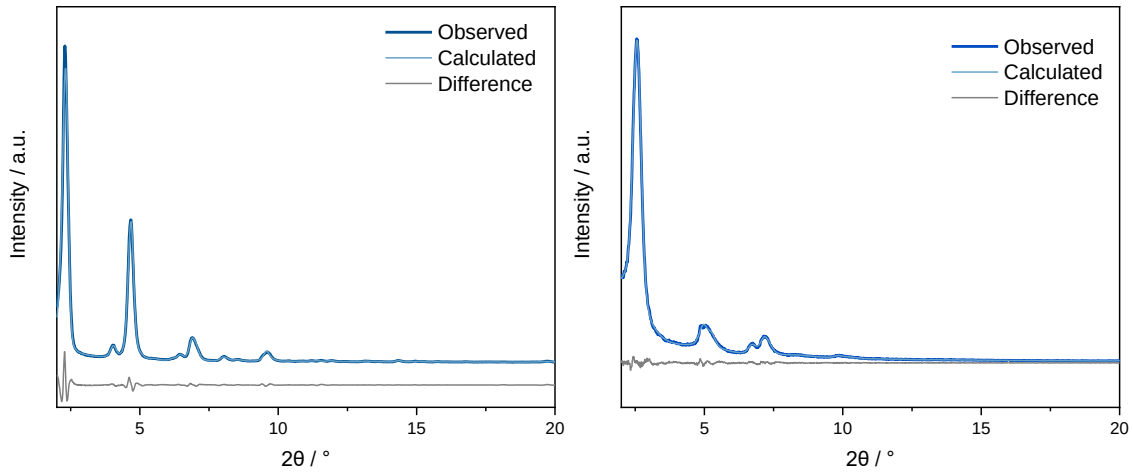


Figure S3: PXRD pattern of PCN-222 (left) and PCN-222(Rh) (right) shown in blue, the calculated data from Pawley profile fit analysis in light blue and the difference curve of the Pawley profile fit shown in grey.

Table S1: Comparison of the crystallographic data of the MOFs PCN-222 and PCN-222(Rh), extracted from the measured PXRD data of the respective materials.

	PCN-222	**PCN-222(Rh)**
a (Å)	43.34(1)	42.82(1)
b (Å)	43.34(1)	42.82(1)
c (Å)	17.49(1)	17.44(1)
α = β (°)	90	90
γ (°)	120	120
Cellvolume V (Å^3)	28455.24(20)	27704.26(101)
Space group	P6/mmm	P6/mmm
r_wp	6.47	3.15
r_exp	0.47	0.73
GOF	13.30	4.35

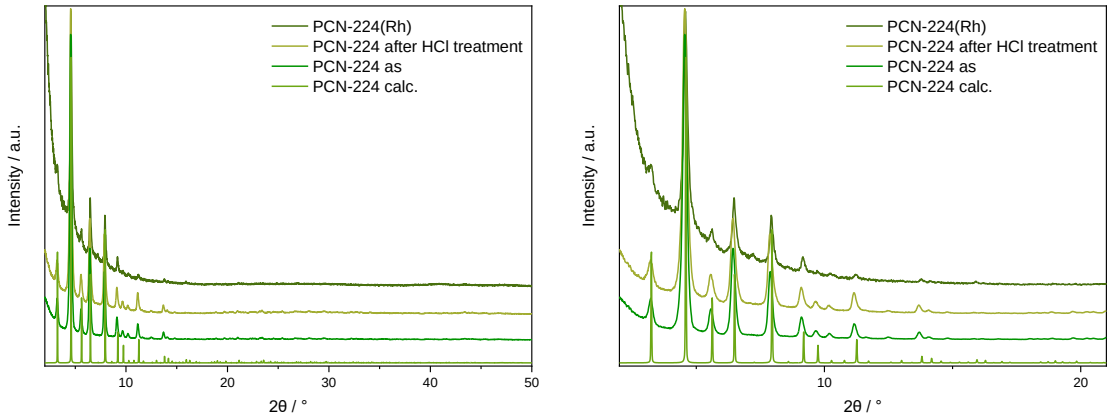


Figure S4: PXRD pattern for PCN-224 of as-synthesized (as) material, after HCl treatment and after metalation with Rhodium.

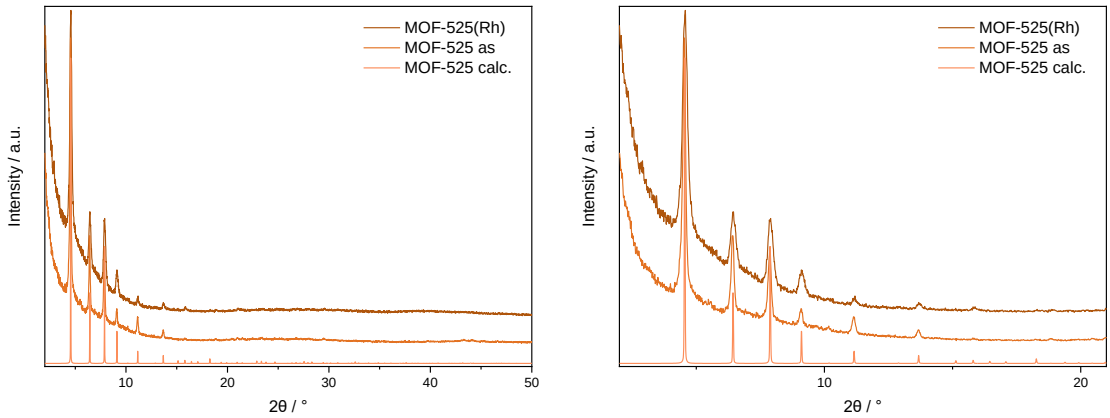


Figure S5: PXRD pattern for MOF-525 of as-synthesized (as) material and after metalation with Rhodium.

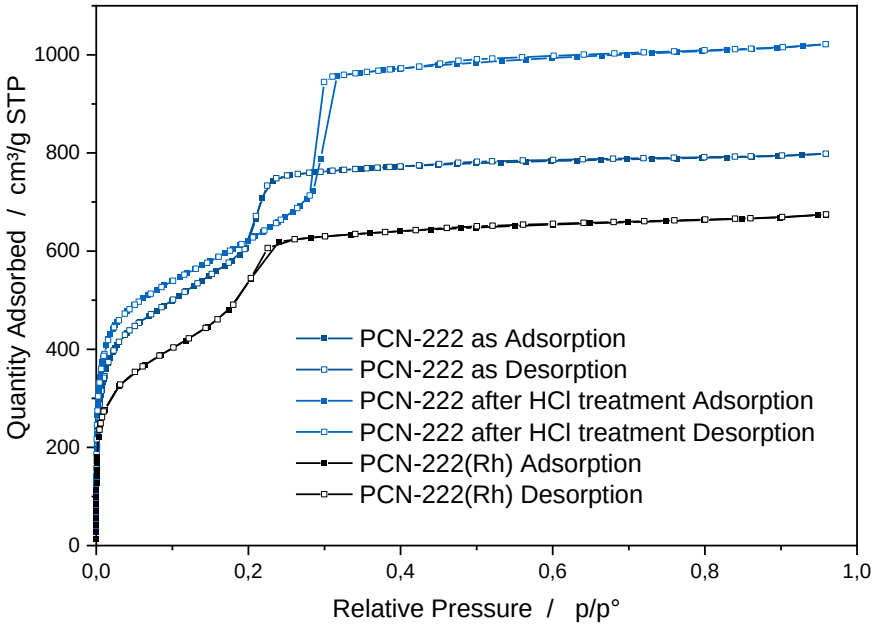


Figure S6: N_2 adsorption isotherms at 77 K for as-synthesized PCN-222, PCN-222 after HCl treatment and PCN-222(Rh) after activation at 120 °C in vacuo for 12 hours. The BET surface areas are calculated as 1989 ± 7.7 $m^2 \cdot g^{-1}$ (PCN-222), 2154 ± 5.7 $m^2 \cdot g^{-1}$ (PCN-222 after HCl treatment), 1692 ± 29 $m^2 \cdot g^{-1}$ (PCN-222(Rh)).

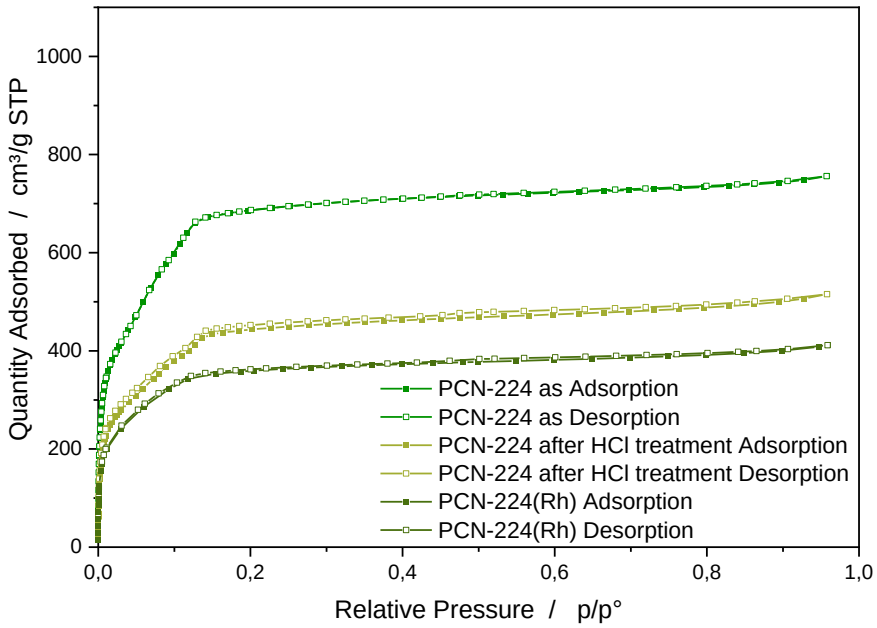


Figure S7: N_2 adsorption isotherms at 77 K for as-synthesized PCN-224, PCN-224 after HCl treatment and PCN-224(Rh) after activation at 120 °C in vacuo for 12 hours. The BET surface areas are calculated as 1978 ± 26 $m^2 \cdot g^{-1}$ (PCN-224), 1572 ± 26 $m^2 \cdot g^{-1}$ (PCN-224 after HCl treatment), 1314 ± 19 $m^2 \cdot g^{-1}$ (PCN-224(Rh)).

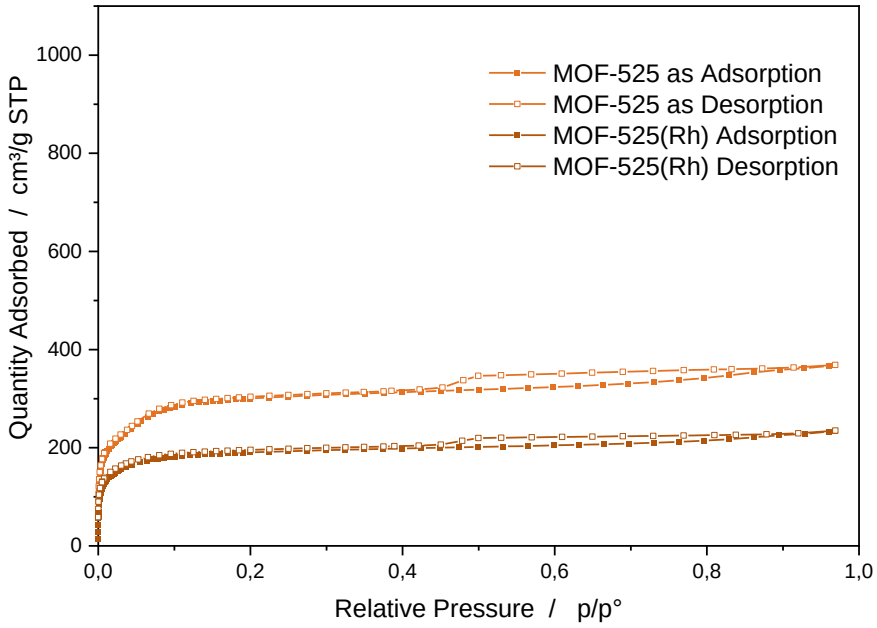


Figure S8: N_2 adsorption isotherms at 77 K for as-synthesized MOF-525 and MOF-525(Rh) after activation at 120 °C in vacuo for 12 hours. The BET surface areas are calculated as 1014 ± 9.5 $m^2 \cdot g^{-1}$ (MOF-525), 743 ± 3.2 $m^2 \cdot g^{-1}$ (MOF-525(Rh)).

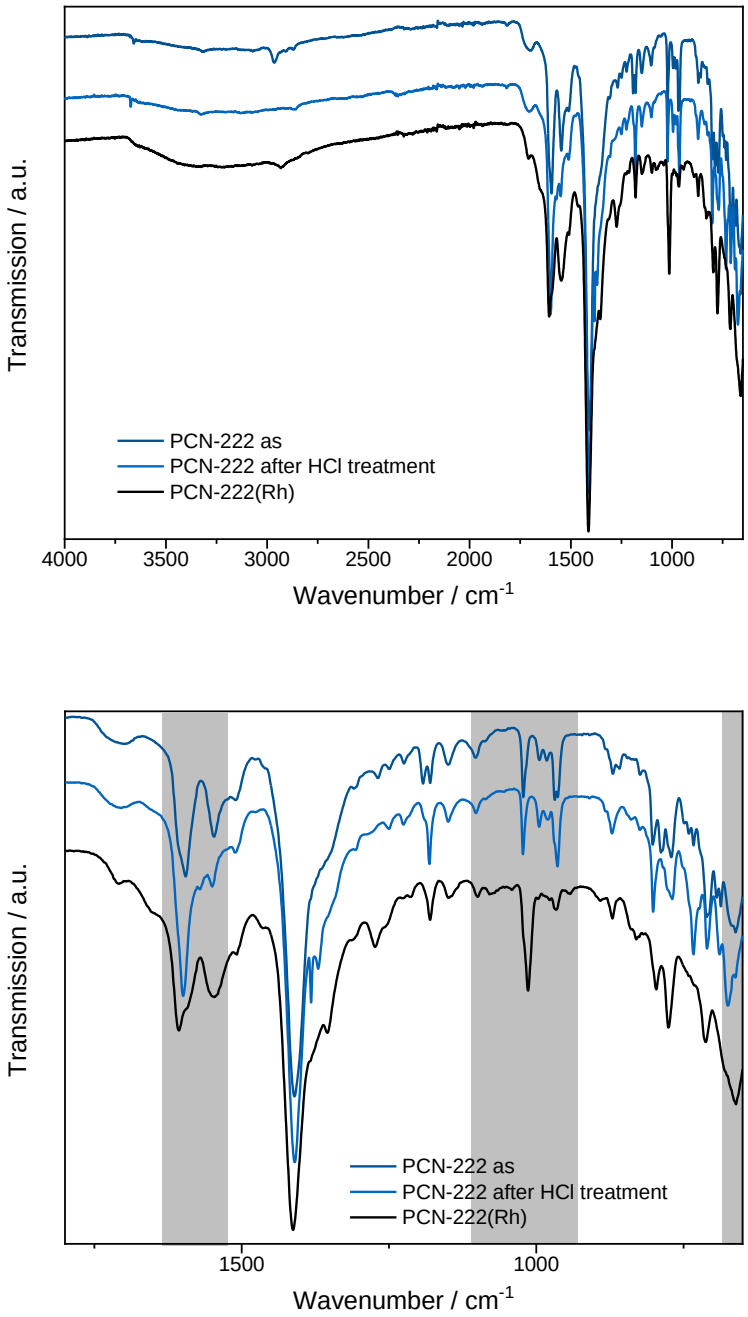


Figure S9: Normalized IR spectra of PCN-222 as, after HCl treatment and PCN-222(Rh). Grey area represents changing wavenumber region upon Rh-metalation. A peak at 662 cm^{-1} appears upon Rh-metalation characteristic for the Rh-N bond. In the regions around 990 cm^{-1} and 1600 cm^{-1} N-H plane modes of the porphyrin's pyrrole unit are located which change upon metalation.[11]

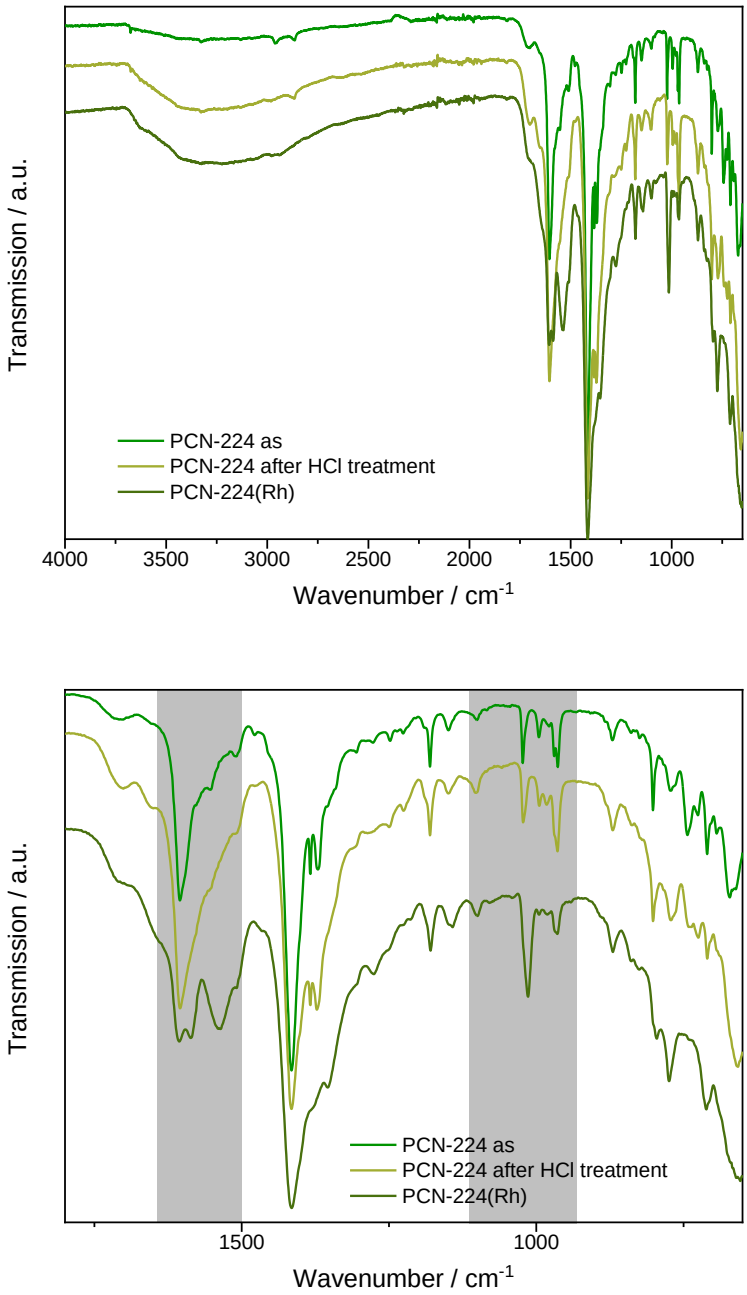


Figure S10: Normalized IR spectra of PCN-224 as, after HCl treatment and PCN-224(Rh). Grey area represents changing wavenumber region upon Rh-metalation. In the regions around 990 cm^{-1} and 1600 cm^{-1} N-H plane modes of the porphyrin's pyrrole unit are located which change upon metalation.[11]

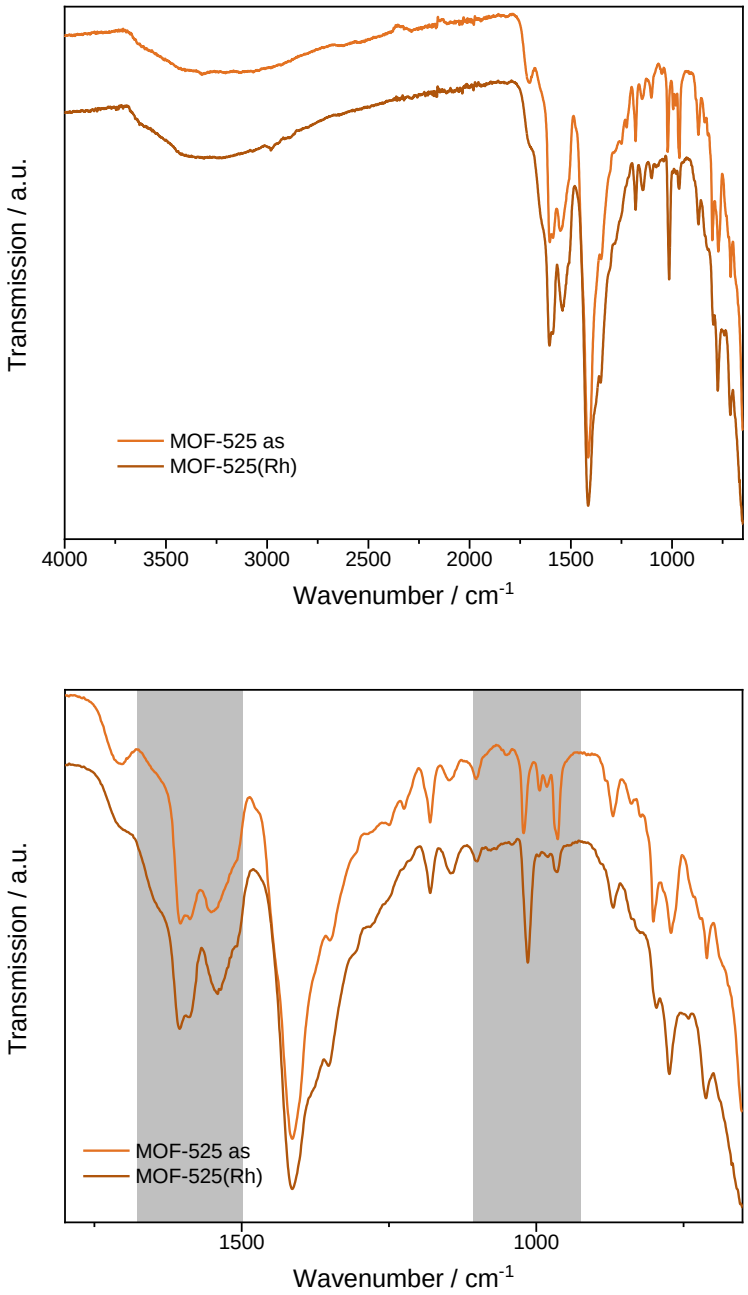


Figure S11: Normalized IR spectra of MOF-525 as and MOF-525(Rh). Grey area represents changing wavenumber region upon Rh-metalation. In the regions around 990 cm^{-1} and 1600 cm^{-1} N-H plane modes of the porphyrin's pyrrole unit are located which change upon metalation.[11]

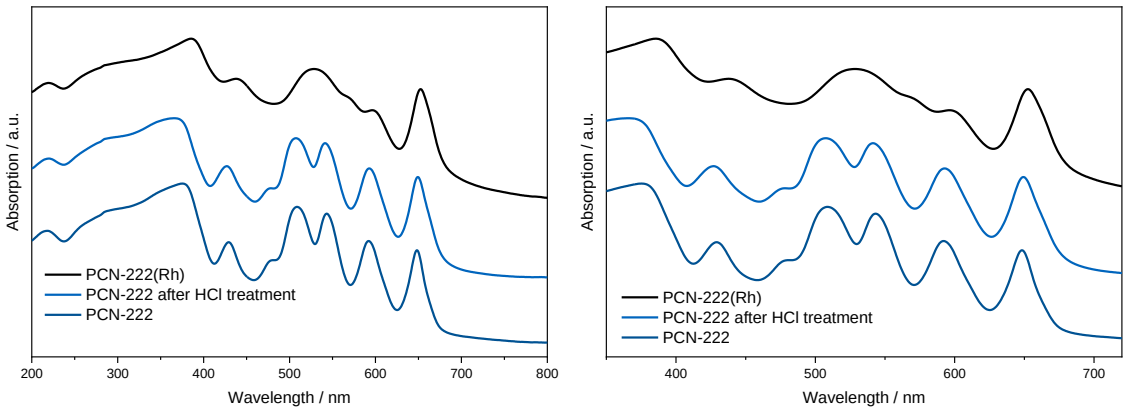


Figure S12: Normalized solid-state UV-vis spectra of PCN-222 as-synthesized, after HCl treatment and PCN-222(Rh).

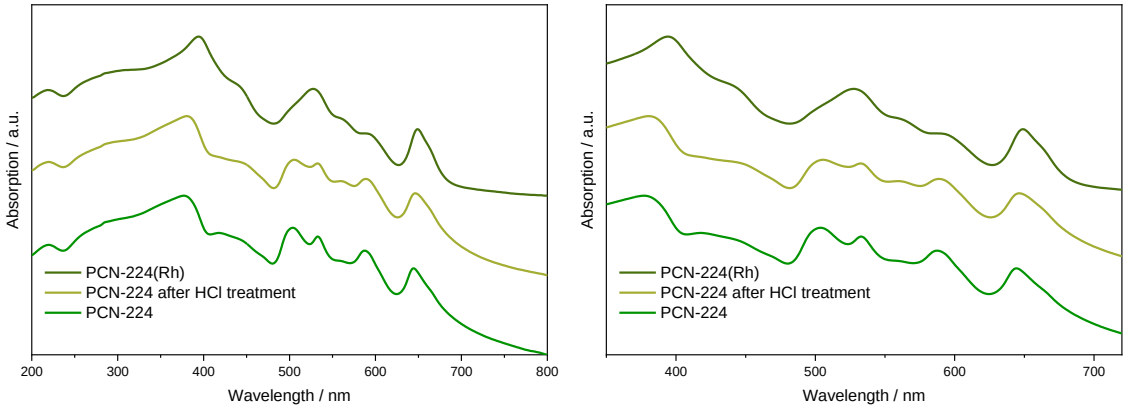


Figure S13: Normalized solid-state UV-vis spectra of PCN-224 as-synthesized, after HCl treatment and PCN-224(Rh).

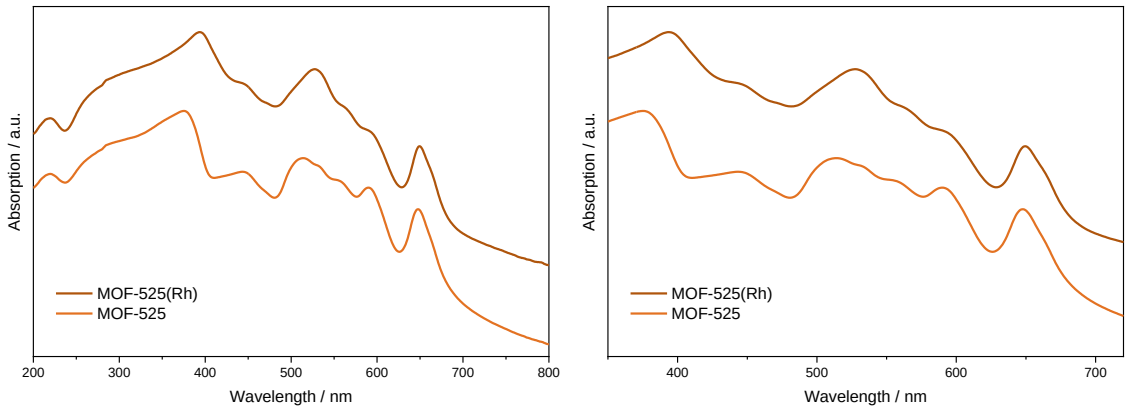


Figure S14: Normalized solid-state UV-vis spectra of MOF-525 as-synthesized and MOF-525(Rh).

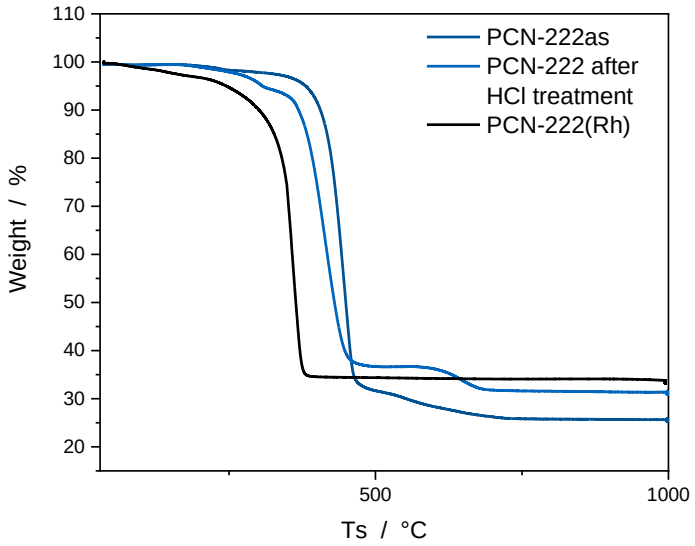


Figure S15: TGA curve of PCN-222 as synthesized, PCN-222 after HCl treatment and PCN-222(Rh).

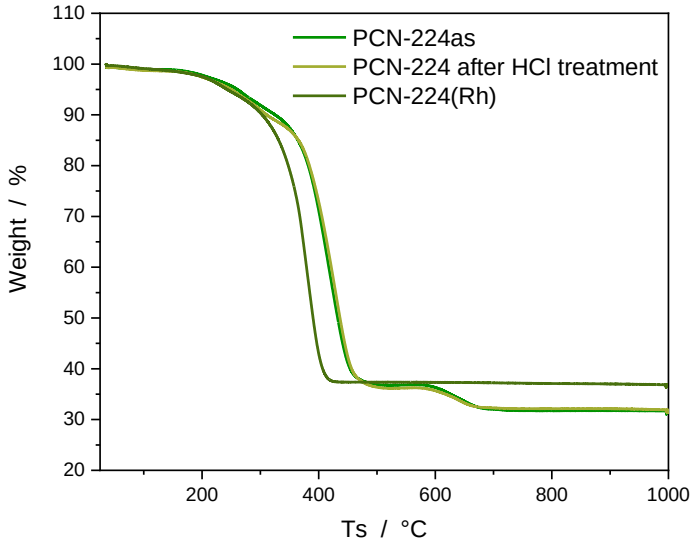


Figure S16: TGA curve of PCN-224 as synthesized, PCN-224 after HCl treatment and PCN-224(Rh).

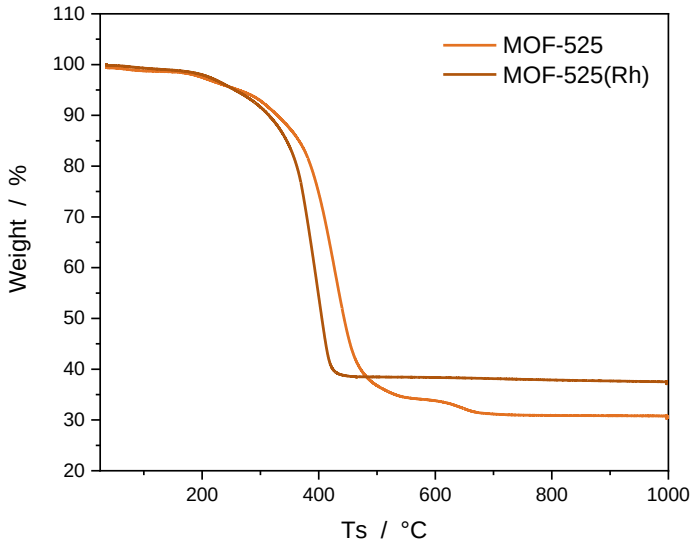


Figure S17: TGA curve of MOF-525 as synthesized and MOF-525(Rh).

Table S2: Linker defects of different MOFs calculated from TGA curves according to [12].

	ideal sum formula	#$TCPPH_2$ $linkers_{ideal}$	#$TCPPH_2$ $linkers_{real}$
PCN-222 as	$Zr_6(OH)_{16}(TCPP\text{-}H_2)_2$ [a]	2	2.49
PCN-222 after HCl	$Zr_6(OH)_{16}(TCPP\text{-}H_2)_2$ [a]	2	1.77
PCN-224 as	$Zr_6O_4(OH)_{10}(H_2O)_6(TCPP\text{-}H_2)_{1.5}$ [b]	1.5	1.52
PCN-224 after HCl	$Zr_6O_4(OH)_{10}(H_2O)_6(TCPP\text{-}H_2)_{1.5}$ [b]	1.5	1.44
MOF-525 as	$Zr_6O_4(OH)_4(TCPP\text{-}H_2)_3$ [c]	3	2.13

[a] taken from [6,13].
[b] taken from [13,14]
[c] taken from [15].

Table S3: wt% of Rh, approximated percentage of Linker metalation (calculated from ideal sum formula of the respective MOF and therefore only for estimation) and Zr:Rh ratios for PCN-222(Rh), PCN-224(Rh) and MOF-525(Rh) determined by ICP-MS analysis.

	wt% Rh	Approx. % of Linker metalated	Zr:Rh	$Zr:Rh_{theo}$
PCN-222(Rh)	8.25	58.55	2.46	3
PCN-224(Rh)	6.51	53.57	3.41	4
MOF-525(Rh)	9.37	70.41	2.83	2

4. Catalytic Performance Tests

Catalytic Setup and reaction conditions

Styrene

Standard cyclopropanation catalysis runs with styrene as substrate were performed in 5 mL capped vials with an 8 mm PTFE stirring bar. The MOF (2.00 mg for PCN-22(Rh), 2.53 mg for PCN-224(Rh) and 1.76 mg for MOF-525(Rh)), 0.73 mL (6.38 mmol, 25 000 equiv.) styrene and 56.4 µL mesitylene as internal standard were stirred at 350 min^{-1} at room temperature. A solution of 49.0 µL ($0.25 \cdot 10^{-3}$ mmol, 1.0 equiv.) ethyl diazoacetate (EDA, 10wt% in DCM) in 1.10 mL DCM was added dropwise via a motorized syringe pump with a rate of 0.5 mL/h. The evolving N_2 was released via a separate needle.

4-Aminostyrene

For 4-Aminostyrene as substrate, the MOF (1.38 mg for PCN-22(Rh), 1.75 mg for PCN-224(Rh) and 1.21 mg for MOF-525(Rh)), 382 mg (3.21 mmol, 18 900 equiv.) 4-Aminostyrene, 38.8 µL mesitylene as internal standard and 1.50 mL DCM were suspended in a 5 mL capped vial with an 8 mm PTFE stirring bar. The mixture was stirred at 350 min^{-1} at room temperature. A solution of 33.8 µL ($0.17 \cdot 10^{-3}$ mmol, 1.0 equiv.) EDA (10wt% in DCM) in 0.75 mL DCM was added dropwise via a motorized syringe pump with a rate of 0.5 mL/h. The evolving N_2 was released via a separate needle.

For the investigation of the influence of EDA/substrate ratio, the amount of substrate was reduced accordingly.

4-Chlorostyrene

For 4-Chlorostyrene as substrate, 2.00 mg for PCN-22(Rh), 0.80 mL (6.6 mmol, 25 000 equiv.) 4-Chlorostyrene and 56.4 µL mesitylene as internal standard were suspended in a 5 mL capped vial with an 8 mm PTFE stirring bar. The mixture was stirred at 350 min^{-1} at room temperature. A solution of 49.0 µL ($0.25 \cdot 10^{-3}$ mmol, 1.0 equiv.) EDA (10wt% in DCM) in 1.10 mL DCM was added dropwise via a motorized syringe pump with a rate of 0.5 mL/h. The evolving N_2 was released via a separate needle.

Additive Approach

For catalytic experiments with additives (pyridine, aniline, phenol) the catalysis was performed in the same way as without additive. For the addition of the respective additives, stock solutions with particular mol% of additives (regarding Rh) were prepared and directly added to the suspension of MOF, internal standard and 4-Aminostyrene in DCM.

Recycling

For recycling experiments the cyclopropanation is performed with standard conditions for the substrate styrene with PCN-222(Rh) (2.00 mg) as catalyst. After 6 h after complete EDA addition, a sample of the reaction suspension is taken and analyzed by GC for determination of conversion and selectivity. The MOF is separated from the reaction mixture via centrifugation (10 min, 7830 rpm), and washed with DCM (3×4 mL). After drying, the MOF is reused for a further catalysis cycle.

Sample preparation

After the addition of EDA to the suspension of MOF, substrate and internal standard, a 30 µL sample was taken via a piston pipette and diluted in 1.5 mL DCM (the end of EDA addition is defined as starting point, 0h). The suspension was filtered via a 13 mm PTFE membrane syringe filter with a pore size of 0.22 µm into a GC vial. Further samples were taken after every hour until 6 h of reaction time and a further sample after 24 h.

Calculation of Conversion, Yield and Selectivity

For the calculation of conversion, yield and selectivity a standard mixture (EDA and mesitylene) is prepared which serves as reference for each kinetic measurement. The conversion of the reaction is calculated as follows from the areas (A) of the respective signals in the gas chromatogram:

$$C(t) = \frac{\frac{A_{EDA,0}}{A_{Mes,0}} - \frac{A_{EDA,t}}{A_{Mes,t}}}{\frac{A_{EDA,0}}{A_{Mes,0}}}$$

The selectivity towards the cis- and trans-product is calculated by dividing the area of the respective product by the sum of all areas of all products and side products. The yield is calculated by multiplying conversion and selectivity (divided by 100).

Cyclopropanation of Styrene

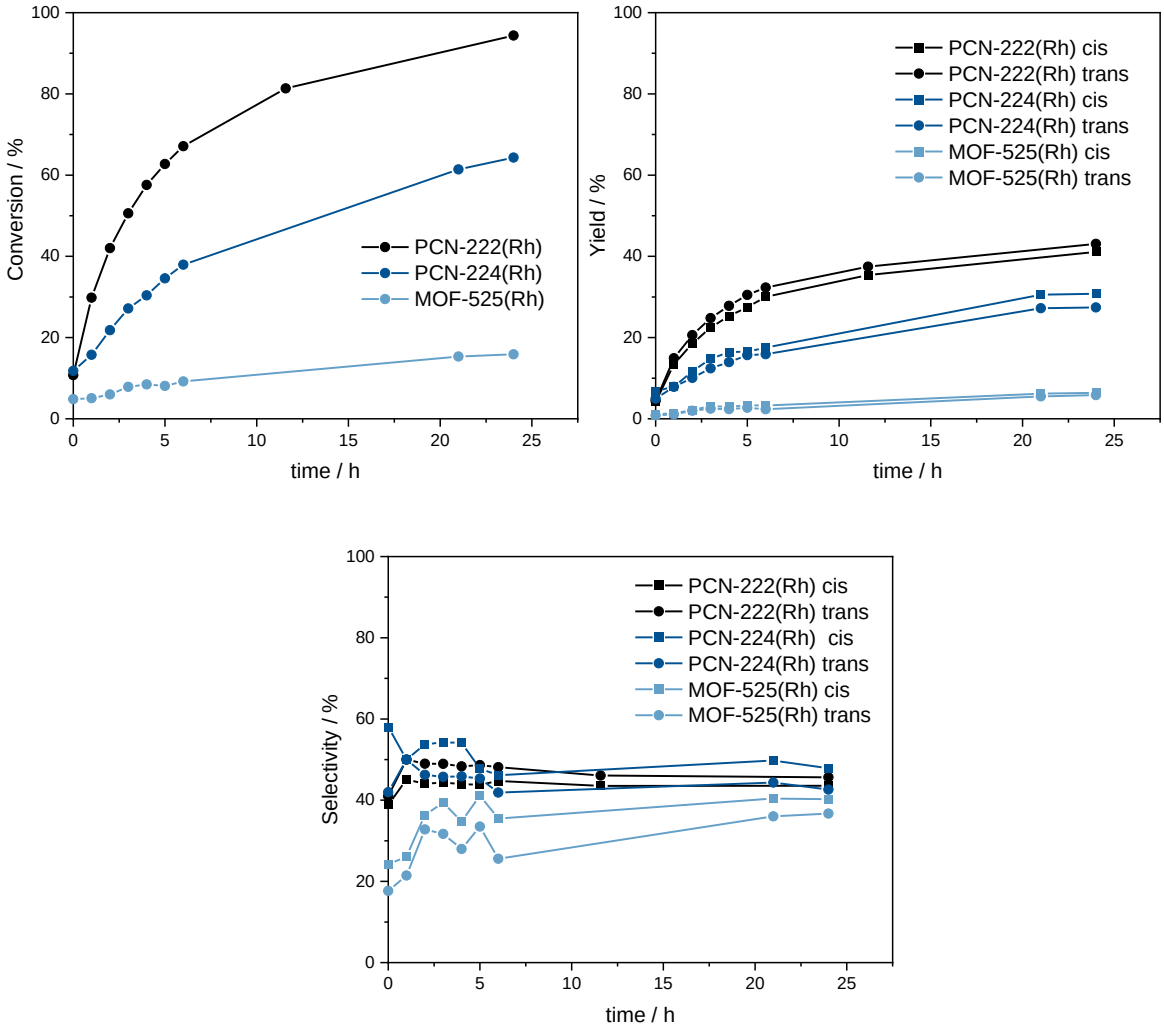


Figure S18: Catalytic performance texts of styrene cyclopropanation with EDA under standard reaction conditions. Conversion, Yield and Selectivity as a function of reaction time for PCN-222(Rh), PCN-224(Rh) and MOF-525(Rh).

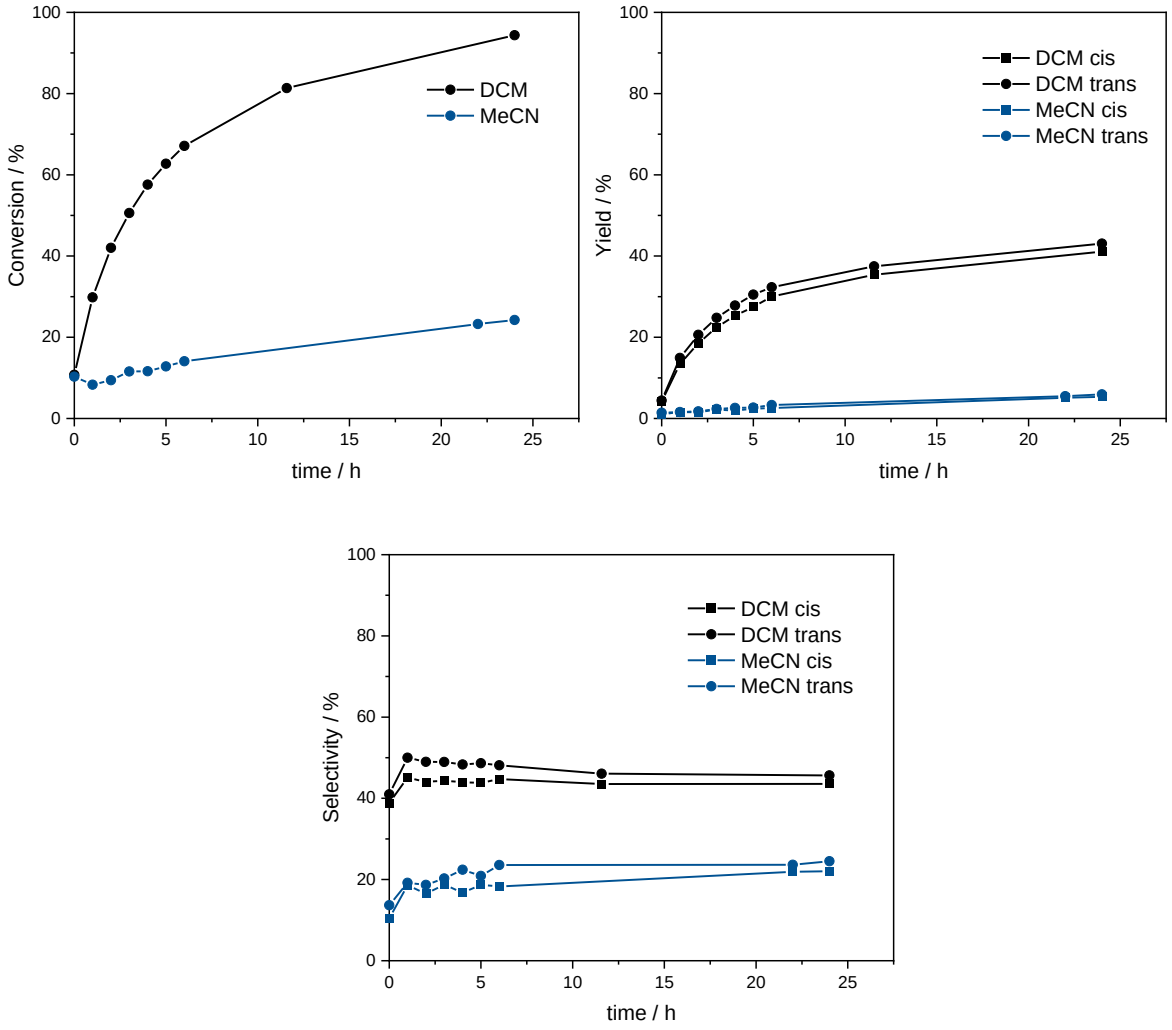


Figure S19: Catalytic performance texts of styrene cyclopropanation with EDA varying the solvent from DCM to MeCN. Conversion, Yield and Selectivity as a function of reaction time for PCN-222(Rh).

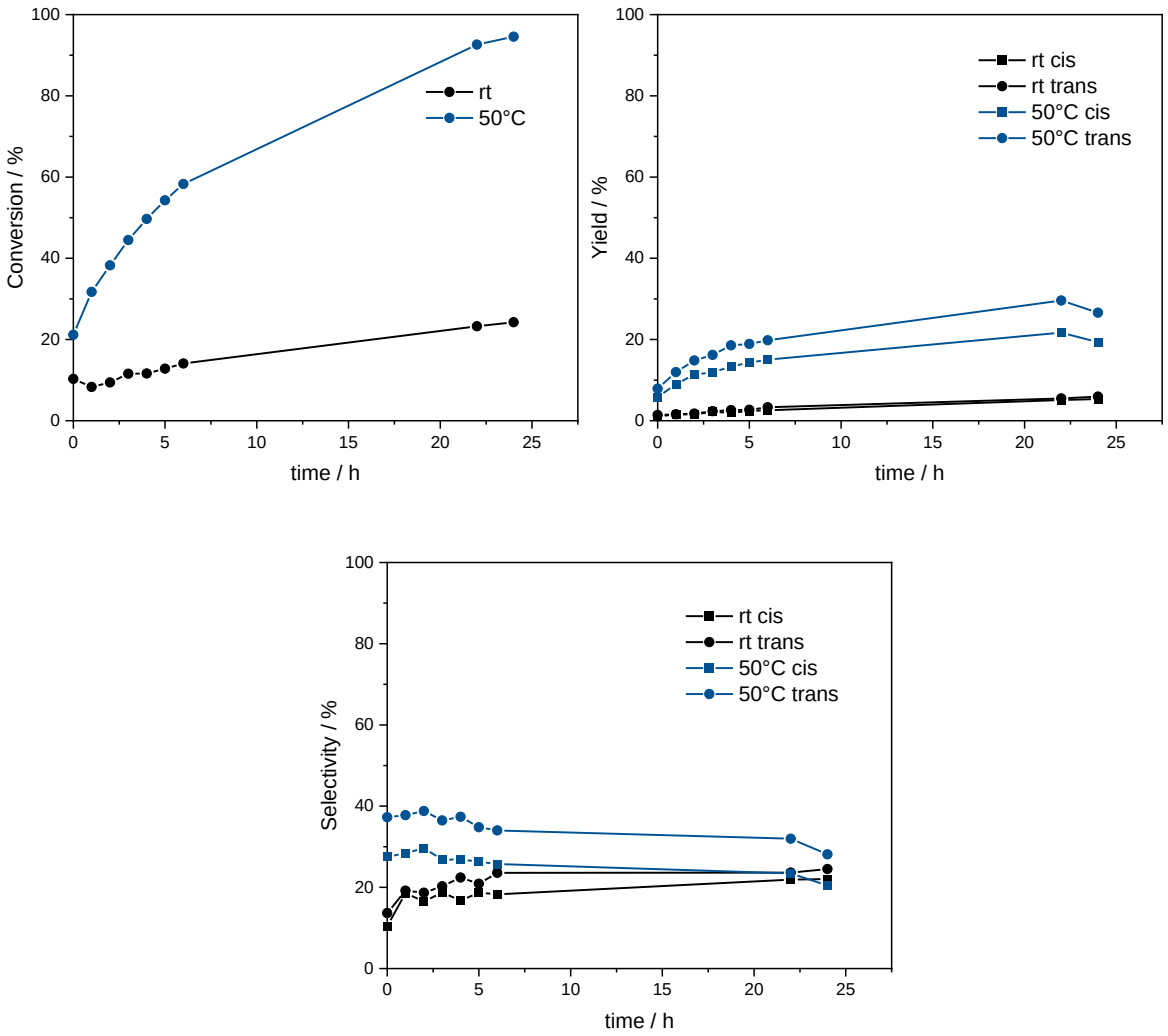


Figure S20: Catalytic performance texts of styrene cyclopropanation with EDA varying the reaction temperature (rt versus 50 °C). Conversion, Yield and Selectivity as a function of reaction time for PCN-222(Rh).

Blank Experiments

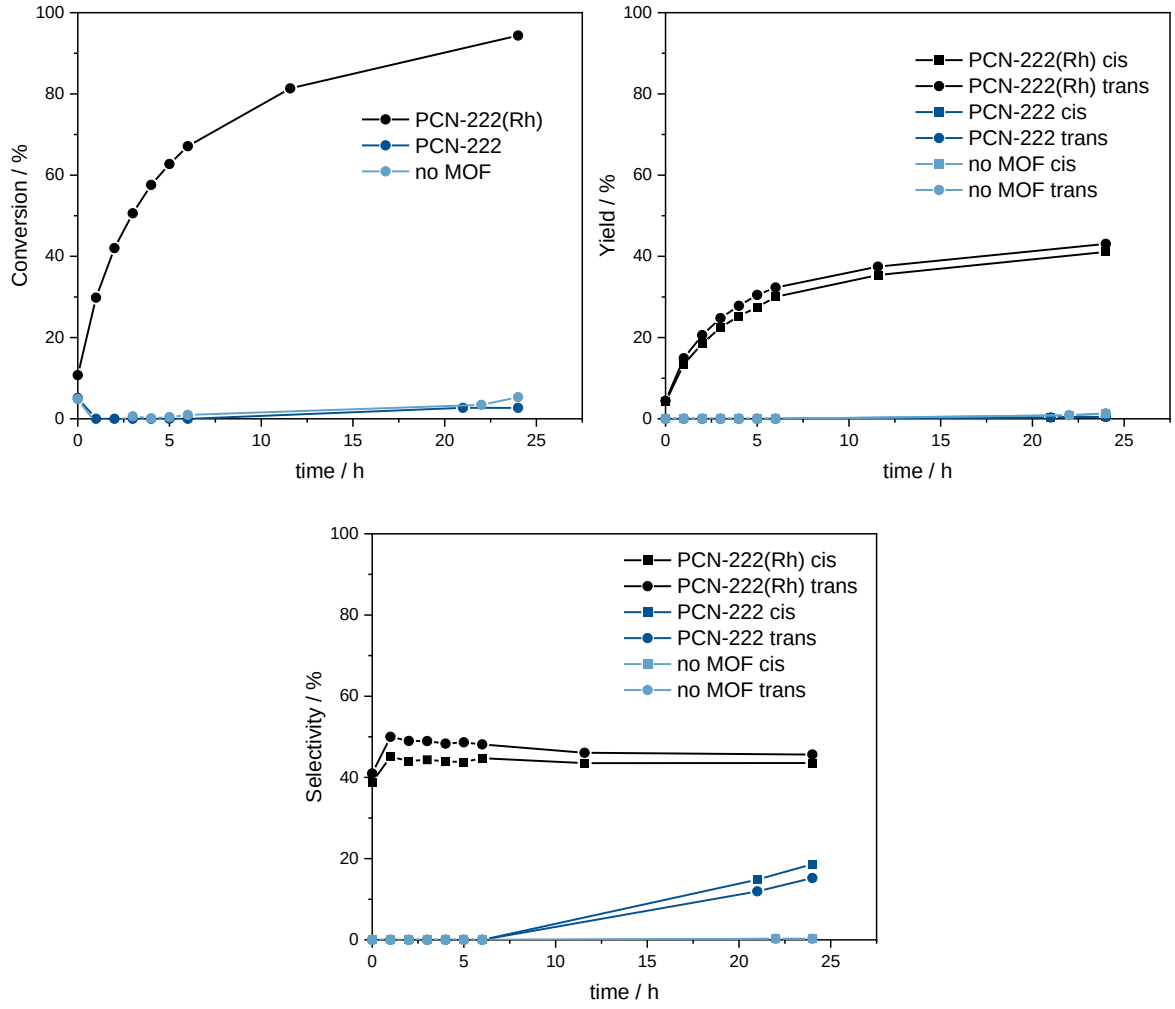


Figure S21: Control experiments of catalytic styrene cyclopropanation performance under standard reaction conditions. Conversion, Yield and Selectivity as a function of reaction time for PCN-222(Rh), PCN-222 and the reaction without MOF.

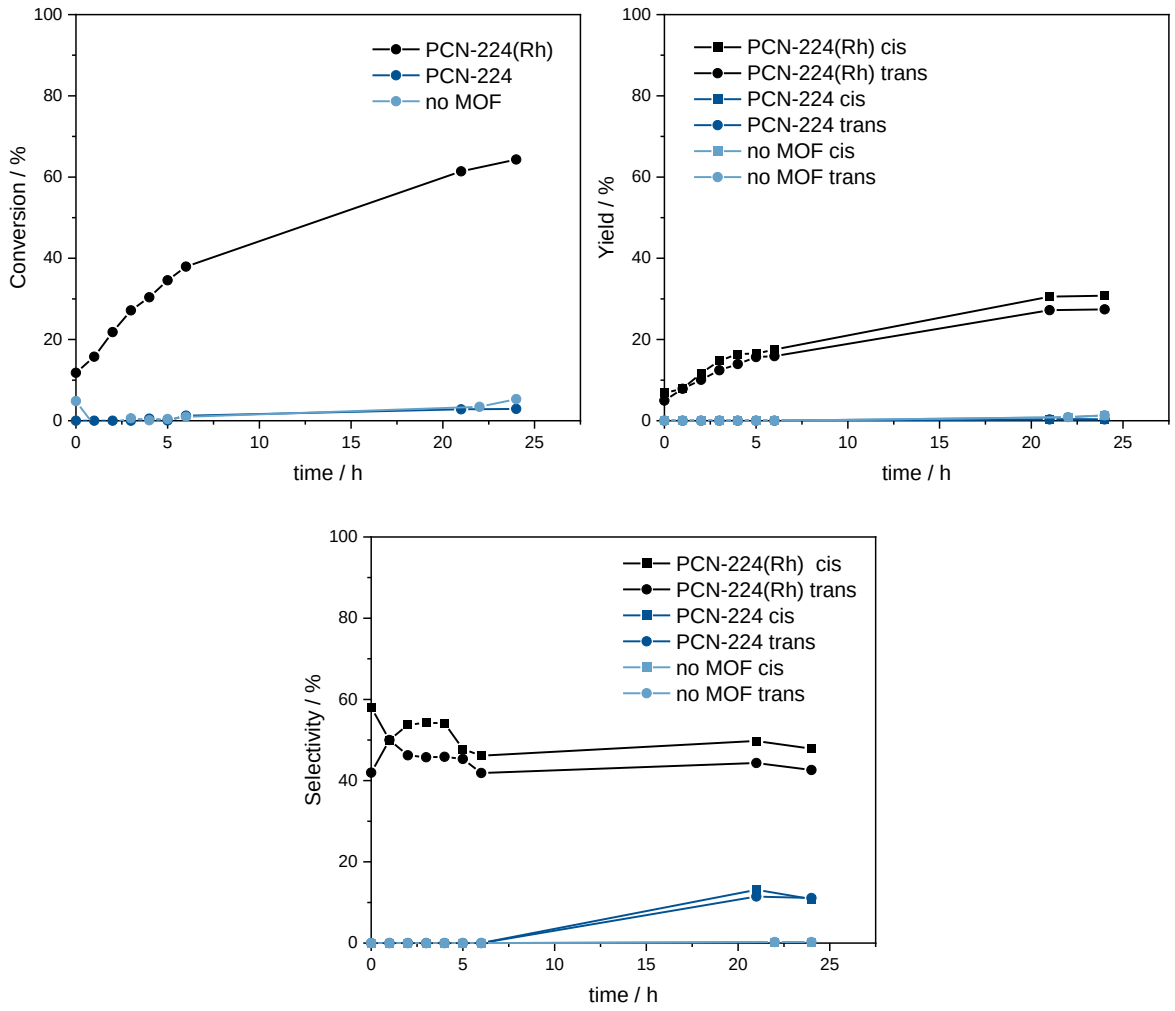


Figure S22: Control experiments of catalytic styrene cyclopropanation performance under standard reaction conditions. Conversion, Yield and Selectivity as a function of reaction time for PCN-224(Rh), PCN-224 and the reaction without MOF.

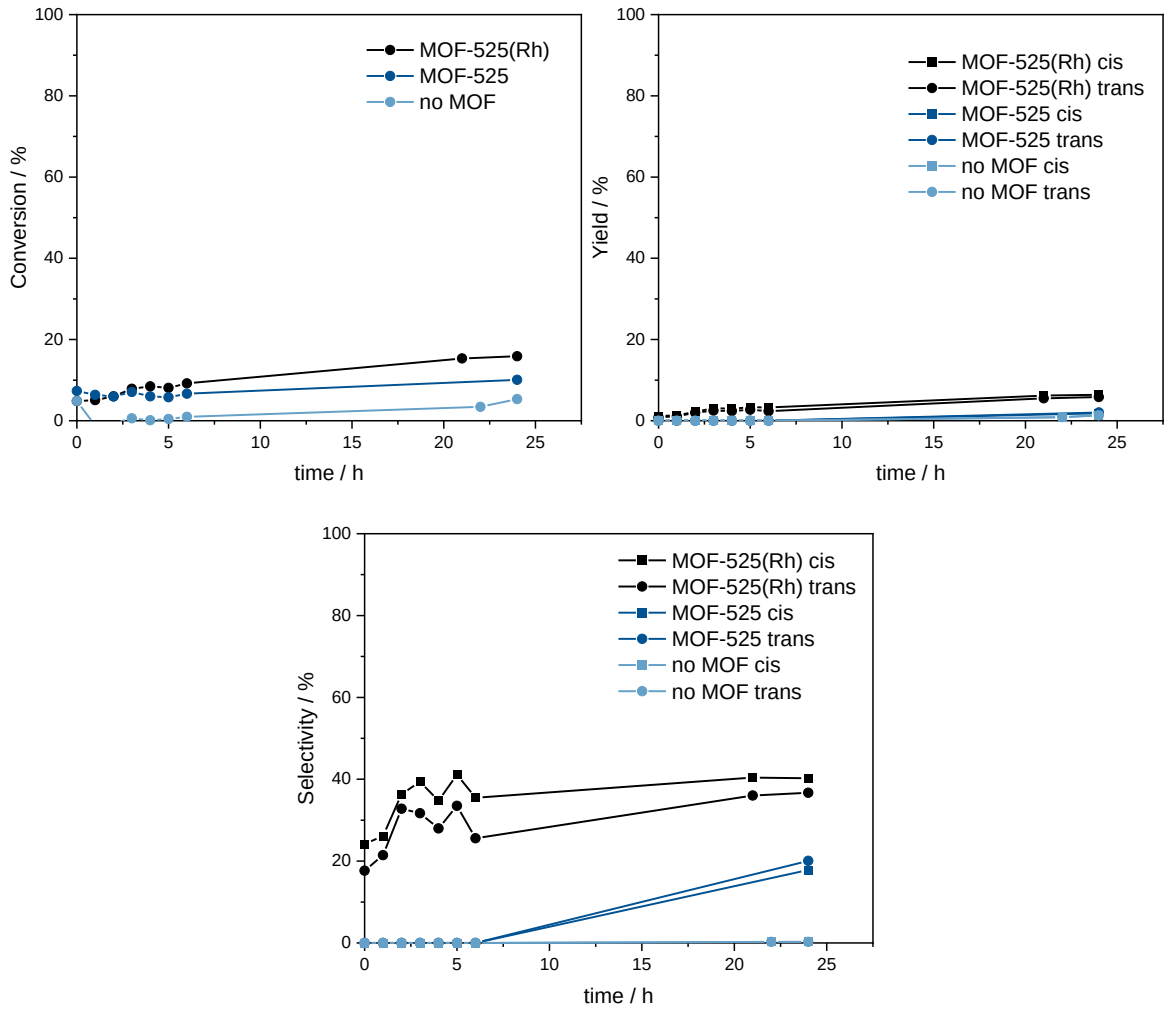


Figure S23: Control experiments of catalytic styrene cyclopropanation performance under standard reaction conditions. Conversion, Yield and Selectivity as a function of reaction time for MOF-525(Rh), MOF-525 and the reaction without MOF.

Recycling Studies

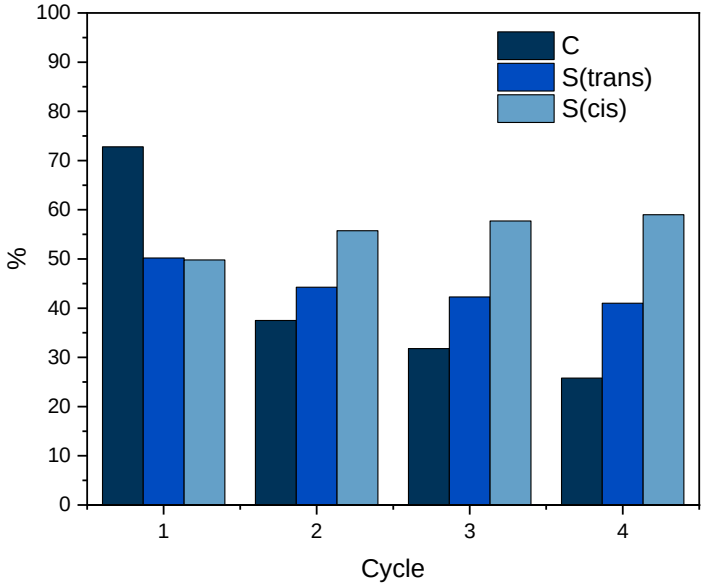


Figure S24: Recycling experiments for the cyclopropanation catalysis of styrene with EDA and PCN-222(Rh) as catalyst after 6h after complete EDA addition via a motorized syringe pump (0.5 mL/h). Reaction conditions: catalyst loading: 0.04 mol% Rh, room temperature, DCM, mesitylene as internal standard, stirring 350 min^{-1}. After the reaction, the catalyst is separated via centrifugation and washed with dichloromethane (3×4 mL).

For catalyst recycling the first cycle is performed according to the standard procedure for styrene as substrate with PCN-222(Rh) as catalyst. After 6 h after complete EDA addition, the MOF is separated from the mixture and washed with DCM. This step causes a loss of a certain amount of solid MOF. Due to the in general small quantities of materials used and the challenges of material synthesis/availability and upscaling this decrease in catalyst amount has to be considered. Simultaneously, a precise adjustment of reactants (to keep the catalyst loading constant) is challenging, since the exact quantity of Rh in the MOF and potential additional molecules in the MOF pores cannot be determined after each cycle. Therefore, an error in the calculated performance values is expected.

MOF stability characterization

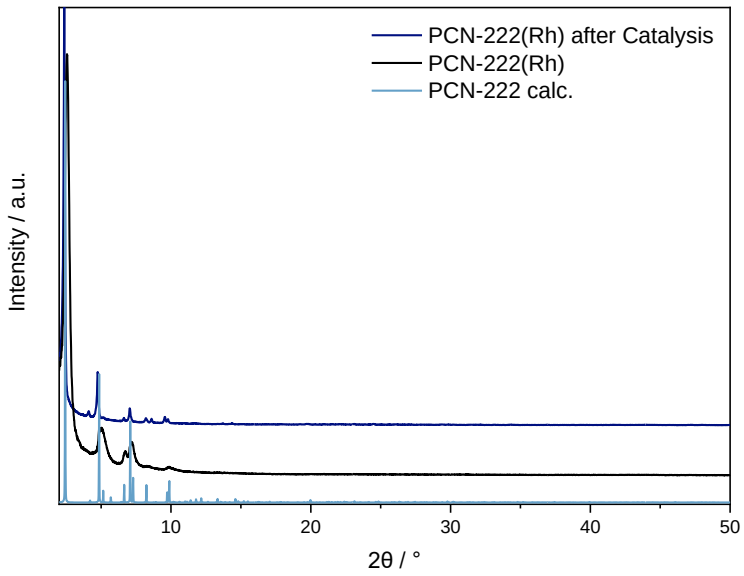


Figure S25: Powder X-Ray diffraction pattern of PCN-222(Rh) catalysts after 24h of reaction in comparison to PCN-222(Rh) before catalysis and its calculated pattern. The MOF is separated from the reaction suspension via centrifugation, washed with DCM (1× 8 mL) and dried under air.

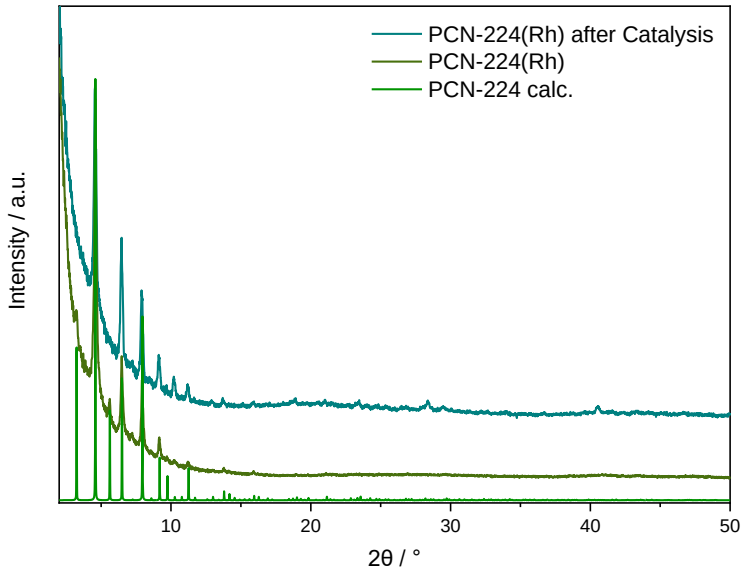


Figure S26: Powder X-Ray diffraction pattern of PCN-224(Rh) catalysts after 24h of reaction in comparison to PCN-224(Rh) before catalysis and its calculated pattern. The MOF is separated from the reaction suspension via centrifugation, washed with DCM (1× 8 mL) and dried under air.

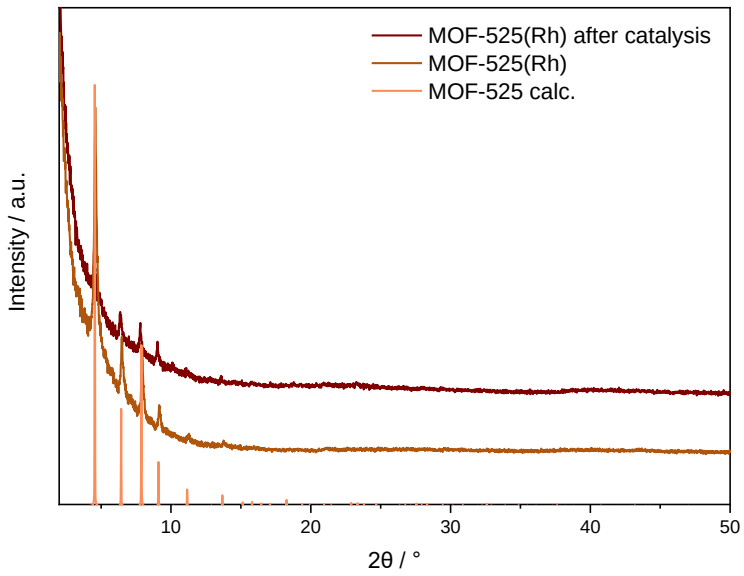


Figure S27: Powder X-Ray diffraction pattern of MOF-525(Rh) catalysts after 24h of reaction in comparison to MOF-525(Rh) before catalysis and its calculated pattern. The MOF is separated from the reaction suspension via centrifugation, washed with DCM (1× 8 mL) and dried under air.

Substrate Variation

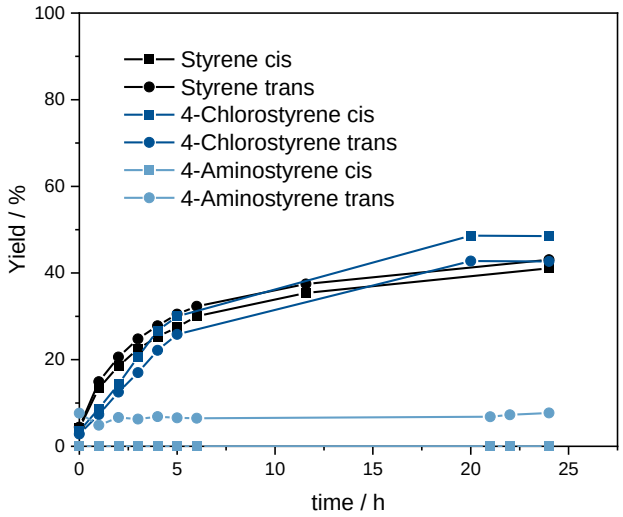


Figure S28: Catalytic performance texts of the cyclopropanation with EDA varying the substrates (styrene, 4-chlorostyrene, 4-aminostyrene). The Yield is given as a function of reaction time for PCN-222(Rh).

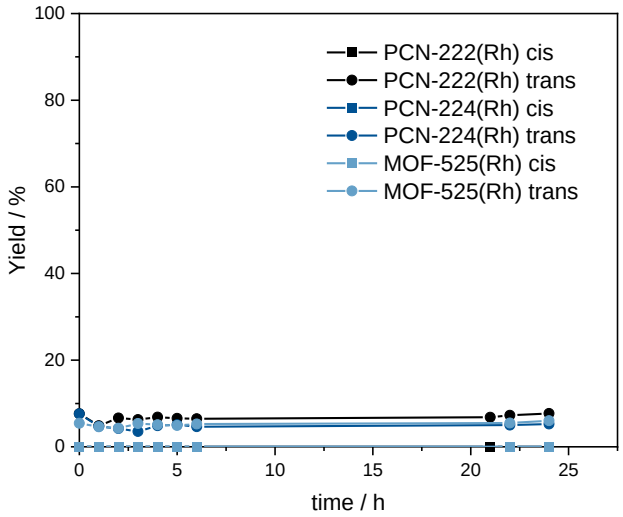


Figure S29: Catalytic performance texts of the cyclopropanation of 4-aminostyrene with EDA varying the catalyst (PCN-222(Rh), PCN-224(Rh), MOF-525(Rh)). The Yield is given as a function of reaction time.

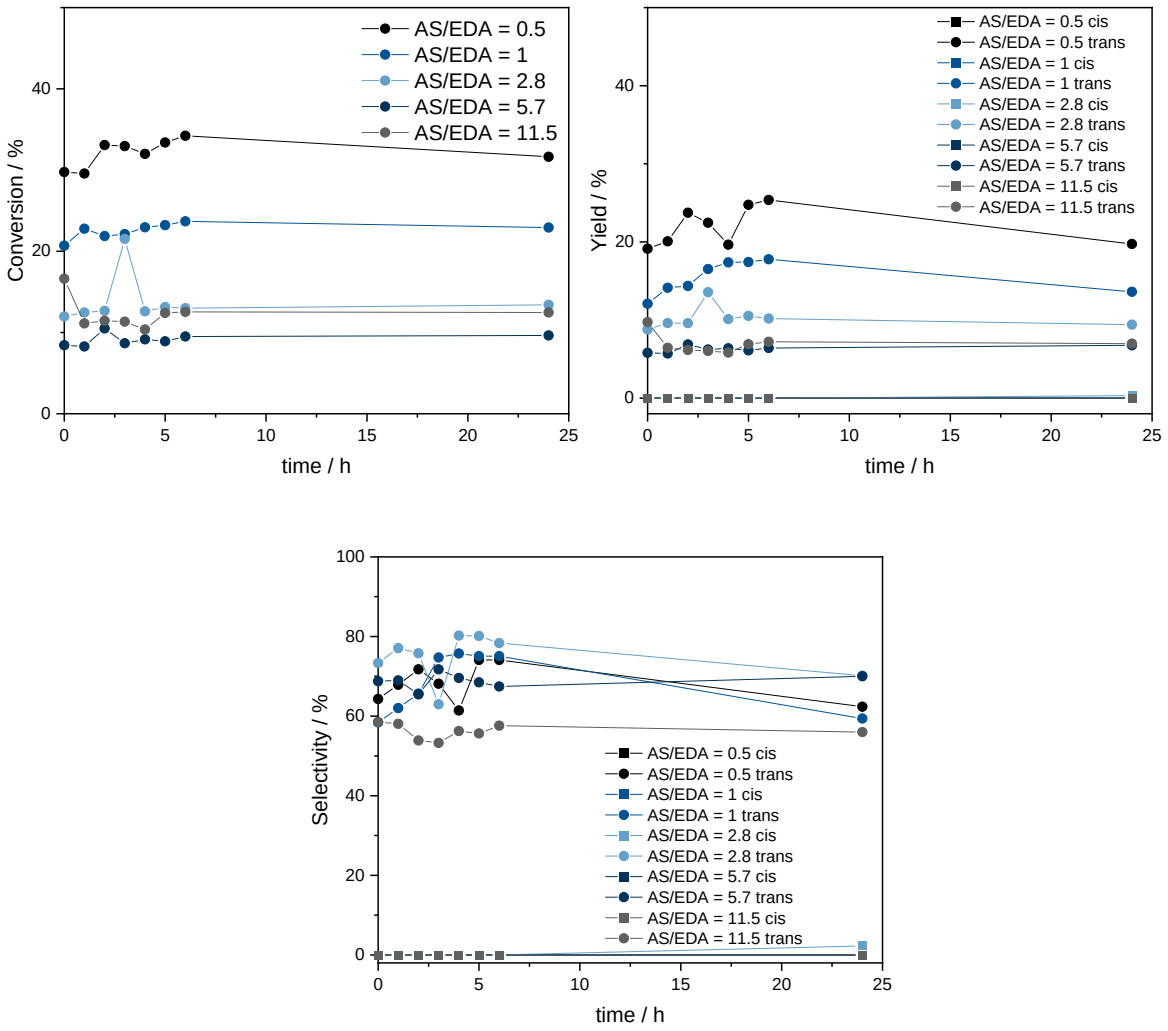


Figure S30: Catalytic performance texts of the cyclopropanation of 4-aminostyrene with EDA varying AS/EDA ratio. Conversion, Yield and Selectivity as a function of reaction time for PCN-222(Rh).

Additives

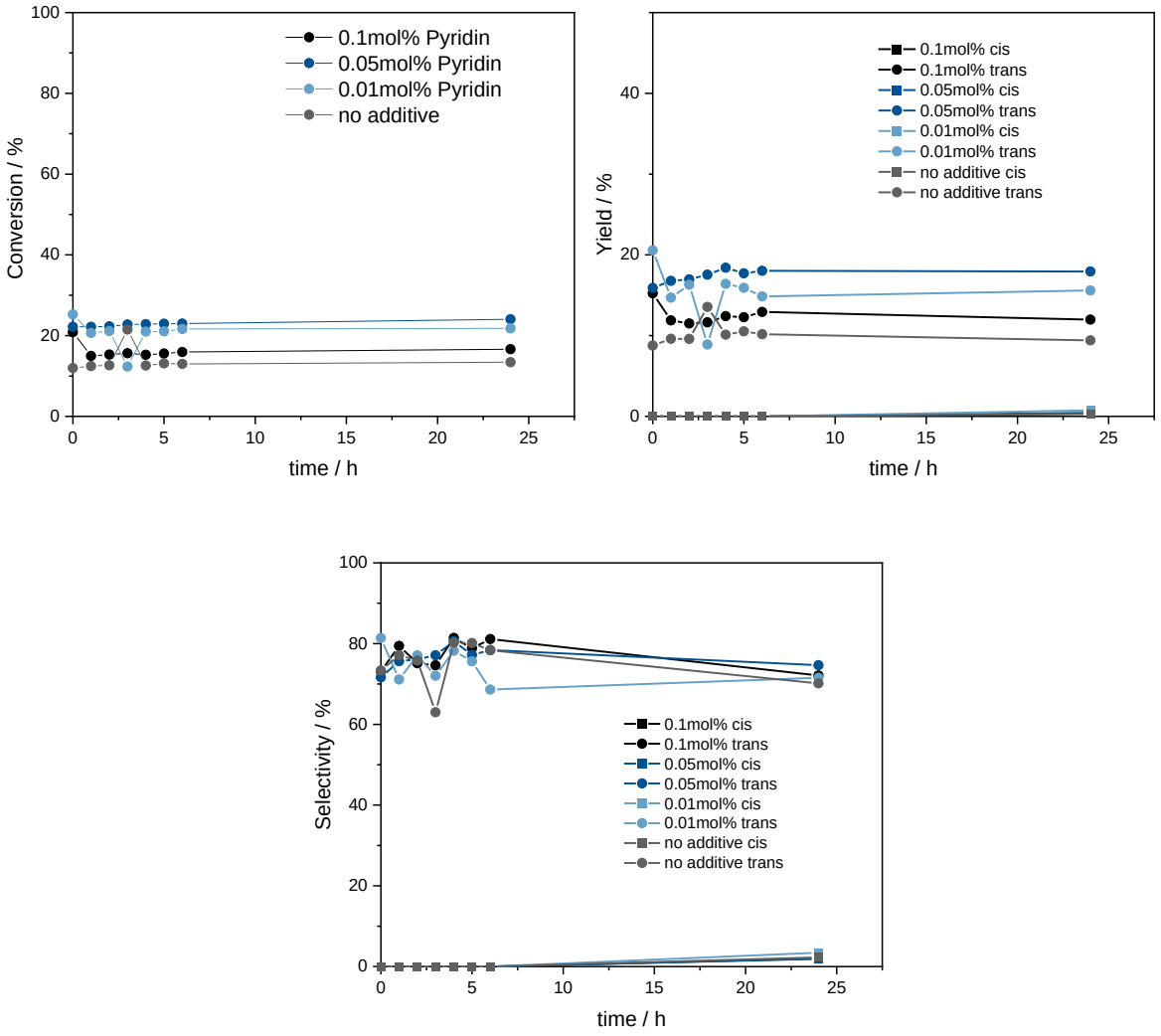


Figure S31: Catalytic performance texts of the cyclopropanation of 4-aminostyrene with EDA adding different concentrations (regarding Rh) of pyridine. Conversion, Yield and Selectivity as a function of reaction time for PCN-222(Rh).

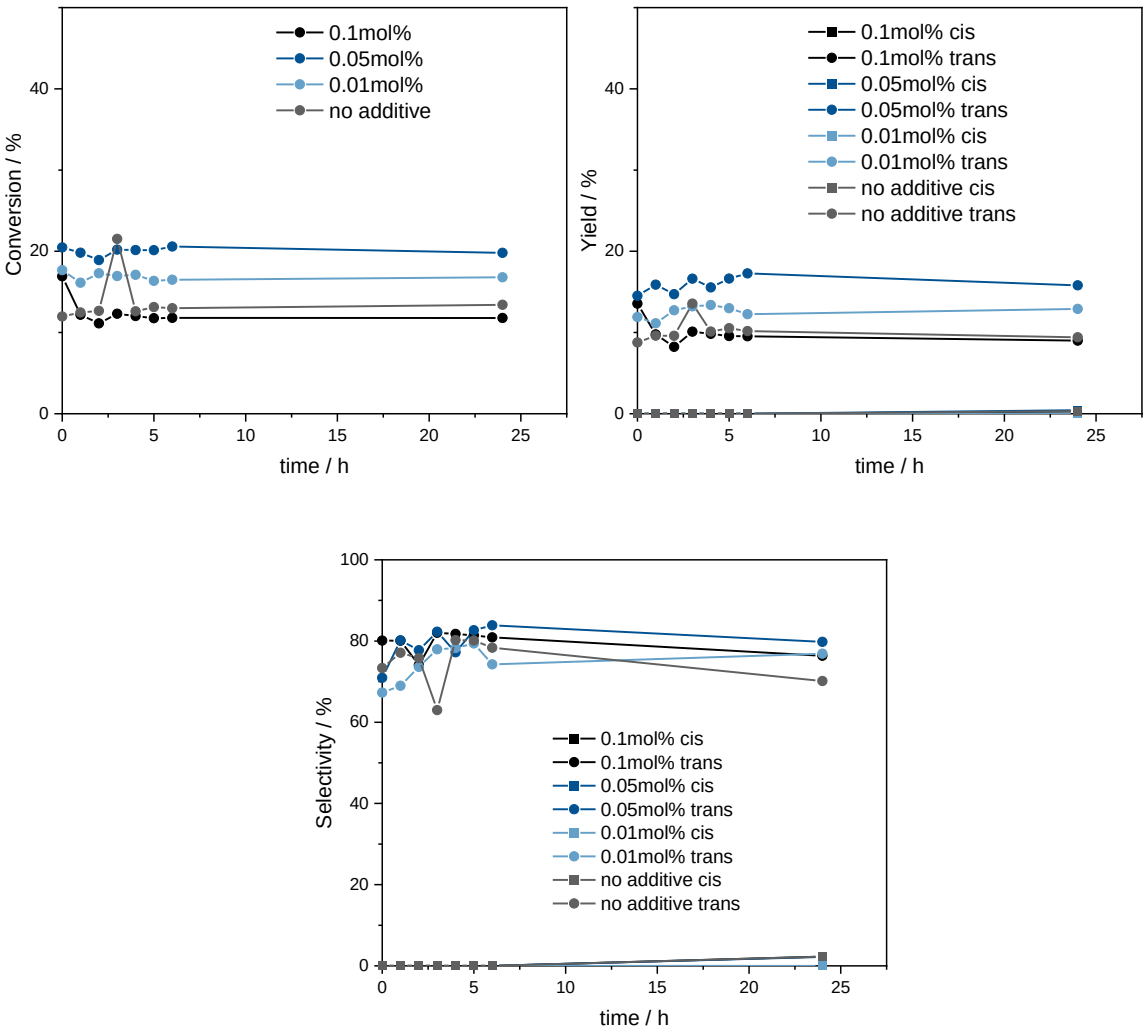


Figure S32: Catalytic performance texts of the cyclopropanation of 4-aminostyrene with EDA adding different concentrations (regarding Rh) of aniline. Conversion, Yield and Selectivity as a function of reaction time for PCN-222(Rh).

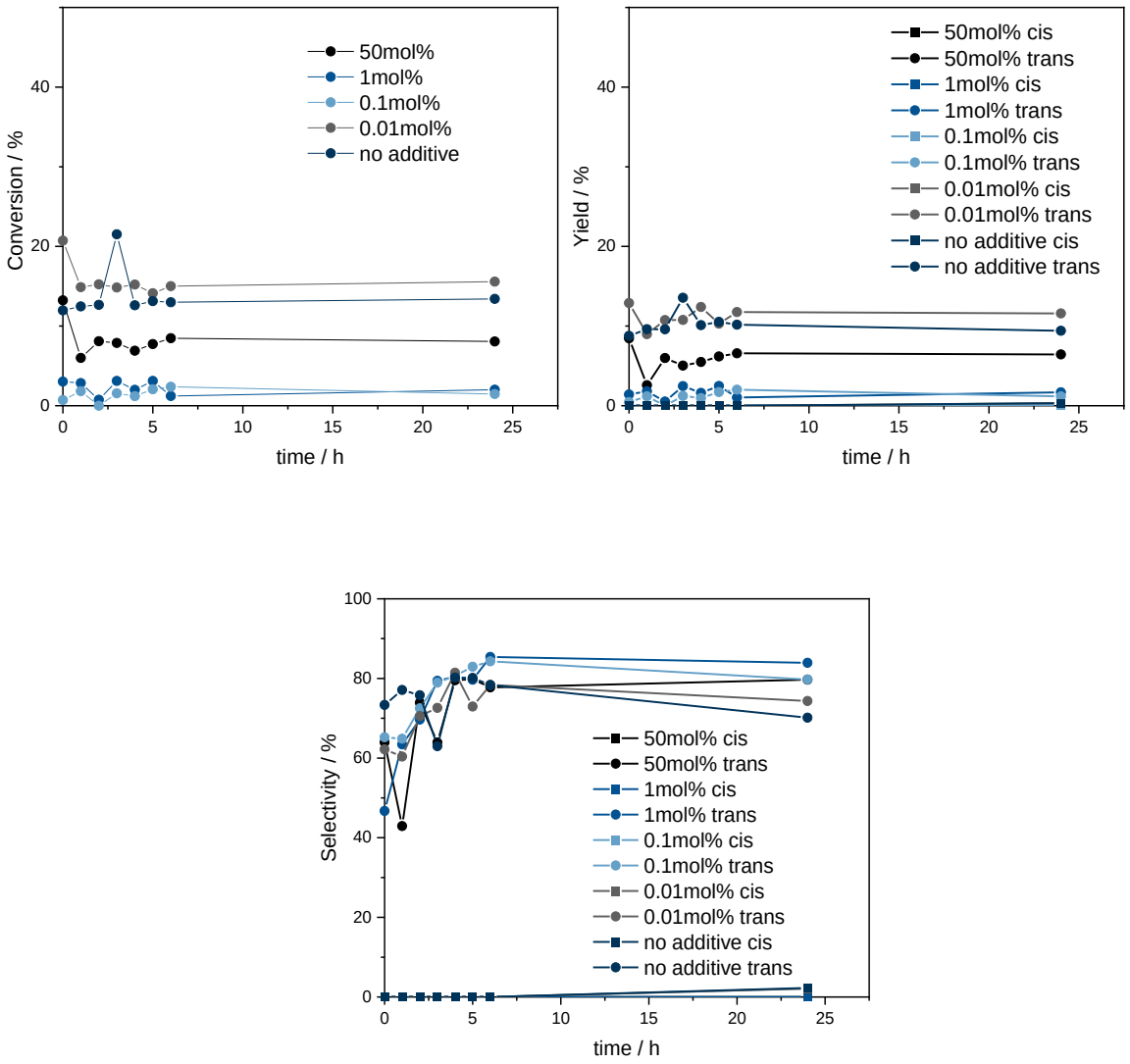


Figure S33: Catalytic performance texts of the cyclopropanation of 4-aminostyrene with EDA adding different concentrations (regarding Rh) of ethylenediamine. Conversion, Yield and Selectivity as a function of reaction time for PCN-222(Rh).

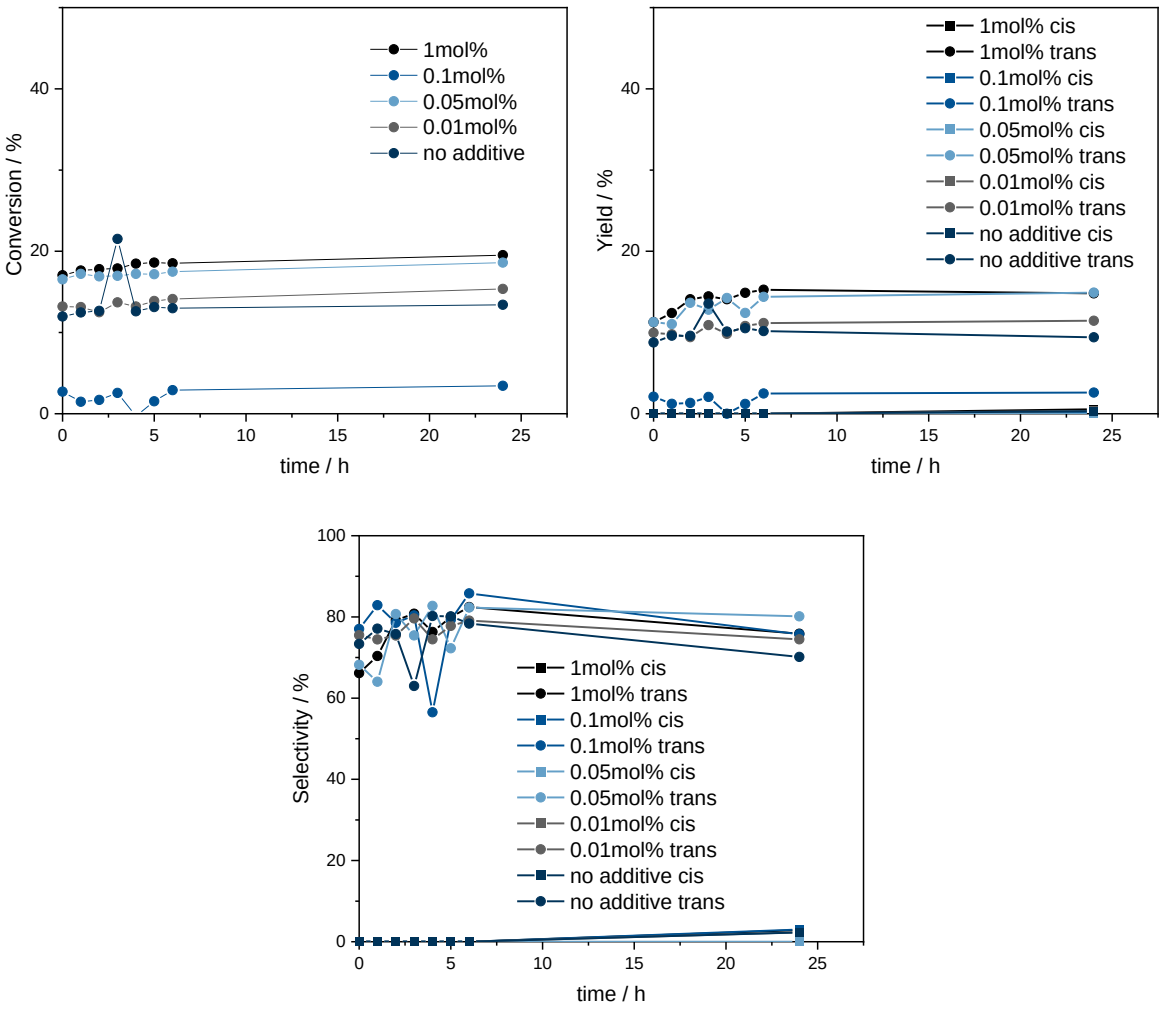


Figure S34: Catalytic performance texts of the cyclopropanation of 4-aminostyrene with EDA adding different concentrations (regarding Rh) of phenol. Conversion, Yield and Selectivity as a function of reaction time for PCN-222(Rh).

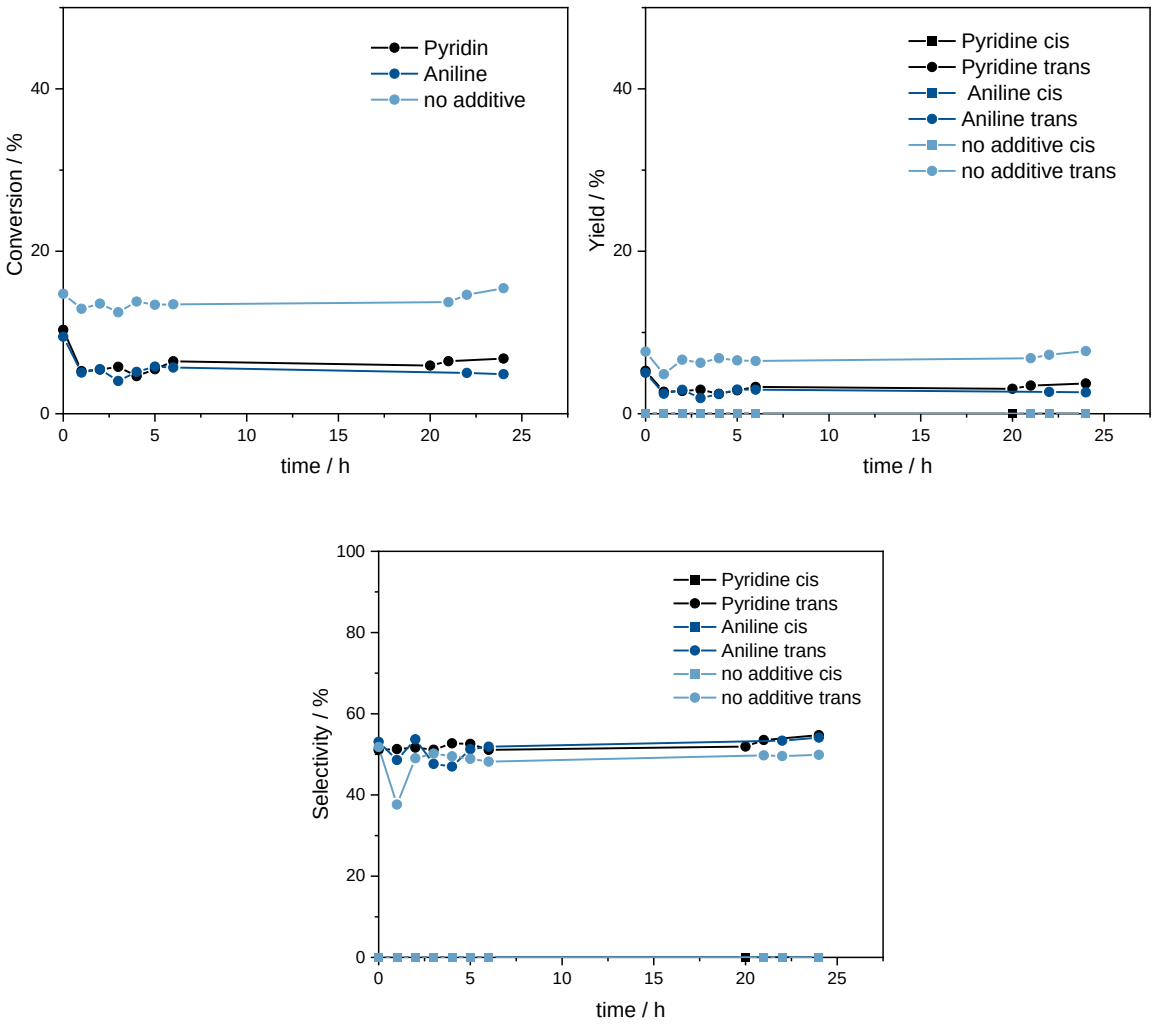


Figure S35: Catalytic performance texts of the cyclopropanation of 4-aminostyrene with EDA and different additives with a concentration of 50 mol% regarding Rh. Conversion, Yield and Selectivity are given as a function of reaction time for PCN-222(Rh).

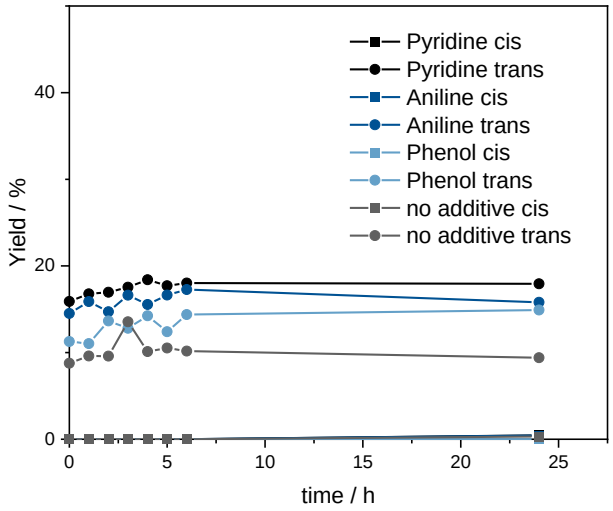
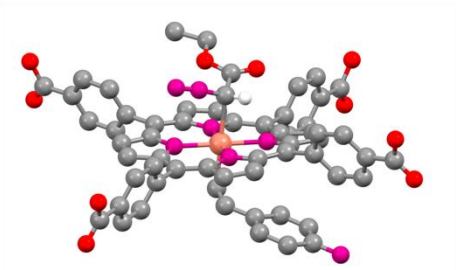


Figure S36: Catalytic performance texts of the cyclopropanation of 4-aminostyrene with EDA and different additives with a concentration of 0.05 mol% regarding Rh. The Yield is given as a function of reaction time for PCN-222(Rh).

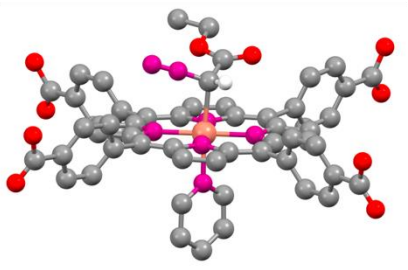
5. DFT calculations

Optimized Geometries on the B3LYP/def2-SVP level of theory

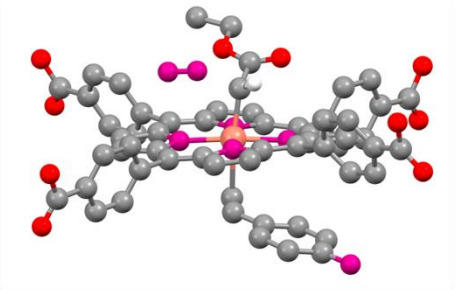
Colour code: grey = carbon; white = hydrogen; pink = nitrogen; red = oxygen; orange = rhodium



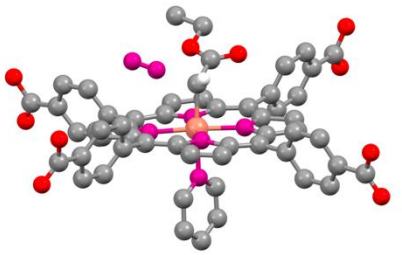
[Rh(Por)(EDA)(Aminostyrene)]



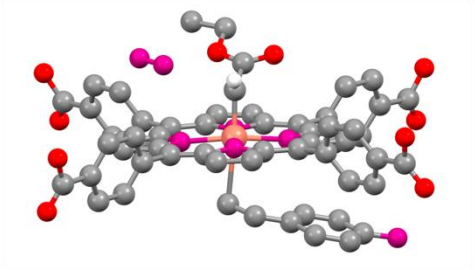
[Rh(Por)(EDA)(Pyridine)]



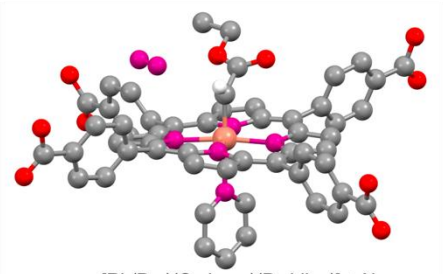
[Rh(Por)(EDA)(Aminostyrene)]‡



[Rh(Por)(EDA)(Pyridine)]‡



[Rh(Por)(Carbene)(Aminostyrene)] + N_2



[Rh(Por)(Carbene)(Pyridine)] + N_2

XYZ Coordinates

[Rh(Por)(EDA)(Aminostyrene)]

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O	-7.455206000	6.804719000	1.377982000
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H	-4.397972000	-5.907737000	3.064893000
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H	7.841306000	-6.965907000	-0.563459000
H	-6.892572000	-8.140746000	2.670540000
H	-8.196539000	7.429773000	1.303368000
H	7.159086000	7.630862000	1.401200000
H	4.586607000	1.713527000	-0.331682000

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C	-1.479449000	0.768939000	2.753496000
O	-1.813163000	1.924329000	2.791703000
O	-2.180577000	-0.268624000	3.202203000
C	-3.494600000	0.014350000	3.753368000
C	-4.156087000	-1.304174000	4.075577000
H	-4.058014000	0.590240000	3.005138000
H	-3.360561000	0.649297000	4.642765000
H	-4.290571000	-1.909565000	3.167846000
H	-5.147411000	-1.119656000	4.516788000
H	-3.561223000	-1.882188000	4.799399000
N	0.277434000	-0.871149000	2.571540000
N	0.602247000	-1.909590000	2.826130000
H	0.603043000	5.238724000	-0.003065000
H	0.613197000	1.084431000	2.152694000
C	0.297904000	0.090652000	-2.690078000
C	-1.010493000	-0.100019000	-2.239360000
C	2.894492000	2.445065000	-3.961153000
C	0.892493000	1.296767000	-3.157719000
C	0.162875000	2.504580000	-3.327817000
C	2.274718000	1.310577000	-3.483535000
C	0.768463000	3.643077000	-3.808124000
C	2.152113000	3.641772000	-4.142237000
N	2.750848000	4.769170000	-4.590063000
H	0.951341000	-0.787693000	-2.687256000
H	2.215360000	5.608041000	-4.771748000
H	-1.406101000	-1.116725000	-2.246533000
H	-1.751876000	0.687497000	-2.386005000
H	3.960610000	2.433661000	-4.198169000
H	2.859692000	0.399175000	-3.340216000
H	0.189744000	4.561600000	-3.930364000
H	-0.896757000	2.540003000	-3.072945000
H	3.727571000	4.771804000	-4.854071000

[Rh(Por)(EDA)(Aminostyrene)]

O	-8.033306000	6.521754000	-0.605474000
O	-7.431314000	6.816909000	1.537606000
N	-2.476813000	-0.031272000	0.113475000
N	-0.546943000	2.141654000	-0.174144000
C	-7.311486000	6.247583000	0.322806000
C	-6.198536000	5.253481000	0.257036000
C	-5.385972000	4.966510000	1.363863000
H	-5.566574000	5.477640000	2.310139000
C	-4.355771000	4.033661000	1.248642000
H	-3.717687000	3.798893000	2.103631000
C	-4.126515000	3.378560000	0.027745000
C	-4.945571000	3.663181000	-1.074777000
C	-5.974730000	4.596561000	-0.961084000
H	-6.620114000	4.835461000	-1.808343000
C	-3.015691000	2.381391000	-0.065704000
C	-1.709031000	2.877825000	-0.167971000
C	-1.372633000	4.283718000	-0.173983000
H	-2.095525000	5.094532000	-0.186414000
C	-3.351640000	1.028857000	0.082841000
C	-4.695066000	0.534131000	0.288708000
H	-5.585909000	1.155922000	0.317918000
C	-3.211199000	-1.177151000	0.306486000
C	0.509348000	3.024342000	-0.122239000
H	-4.769729000	3.152083000	-2.024349000
C	-0.012845000	4.373782000	-0.119401000
C	-4.607858000	-0.820821000	0.438937000
C	-2.705376000	-2.485849000	0.344161000
C	1.871530000	2.688508000	-0.067747000
H	-5.416434000	-1.524248000	0.616327000
C	-3.658597000	-3.606889000	0.596241000
C	-1.357467000	-2.822898000	0.137482000

C	2.872532000	3.791371000	0.031931000
C	2.365168000	1.372594000	-0.130347000
C	-3.549670000	-4.365482000	1.774162000
C	-4.659715000	-3.933168000	-0.334285000
N	-0.308117000	-1.944125000	-0.032571000
C	-0.857774000	-4.174168000	0.024081000
C	2.990786000	4.752519000	-0.986347000
C	3.730797000	3.873935000	1.142128000
C	3.763033000	1.029969000	-0.280942000
N	1.620774000	0.216065000	-0.149762000
C	-4.420476000	-5.426097000	2.021002000
H	-2.772289000	-4.116879000	2.499735000
C	-5.528394000	-4.994860000	-0.092488000
H	-4.742292000	-3.358116000	-1.259080000
C	0.833108000	-2.692490000	-0.241061000
H	-1.466125000	-5.070491000	0.104719000
C	0.484543000	-4.093914000	-0.212843000
H	2.337014000	4.693478000	-1.853579000
C	3.948985000	5.757949000	-0.905048000
H	3.642385000	3.138544000	1.944737000
C	4.686103000	4.886010000	1.231843000
C	3.837994000	-0.327308000	-0.404733000
C	2.489389000	-0.840488000	-0.307805000
C	-5.413900000	-5.747039000	1.085173000
H	-4.334542000	-6.011992000	2.936706000
H	-6.303693000	-5.267572000	-0.810839000
C	2.139860000	-2.197688000	-0.381558000
H	1.187212000	-4.911417000	-0.347522000
H	4.058030000	6.496785000	-1.700808000
C	4.803442000	5.832350000	0.203713000
H	5.345290000	4.949255000	2.098292000
H	4.724912000	-0.935583000	-0.558927000
C	-6.364348000	-6.881907000	1.286850000
C	3.235647000	-3.194785000	-0.578436000
C	5.815509000	6.929480000	0.236336000
O	-6.155238000	-7.537293000	2.444333000
O	-7.228525000	-7.189794000	0.502318000
C	3.344637000	-3.903947000	-1.786389000
C	4.160191000	-3.448469000	0.447405000
O	6.567099000	6.914151000	1.352962000
O	5.955394000	7.748704000	-0.640369000
H	2.629370000	-3.711902000	-2.589488000
C	4.355520000	-4.845985000	-1.963554000
H	4.076824000	-2.905855000	1.391763000
C	5.170601000	-4.394089000	0.275156000
C	5.271961000	-5.098239000	-0.932966000
H	4.454162000	-5.402804000	-2.897238000
H	5.882204000	-4.596158000	1.076365000
C	6.329411000	-6.126593000	-1.170305000
O	7.137912000	-6.297889000	-0.107247000
O	6.454536000	-6.745976000	-2.198928000
Rh	-0.429226000	0.091804000	-0.032388000
H	7.786745000	-6.980013000	-0.351729000
H	-6.811796000	-8.253649000	2.487514000
H	-8.172991000	7.443784000	1.484572000
H	7.190498000	7.657796000	1.287061000
H	4.576873000	1.747731000	-0.324411000
C	-0.275300000	0.432521000	1.896367000
C	-1.506542000	0.752577000	2.701538000
O	-1.839827000	1.908878000	2.802429000
O	-2.151257000	-0.300241000	3.172437000
C	-3.428763000	-0.054516000	3.826371000
C	-4.056146000	-1.393353000	4.131004000
H	-4.042098000	0.548458000	3.141231000
H	-3.237595000	0.541720000	4.731863000
H	-4.239491000	-1.960944000	3.207447000
H	-5.020279000	-1.239093000	4.638815000
H	-3.413033000	-1.993979000	4.792249000
N	0.352451000	-1.107440000	2.708114000

N	0.549881000	-2.193081000	2.729950000
H	0.590768000	5.275018000	-0.073016000
H	0.582678000	1.049478000	2.188654000
C	0.194216000	0.018066000	-2.753637000
C	-1.119680000	-0.109562000	-2.384408000
C	2.965808000	2.263579000	-3.901210000
C	0.878136000	1.209134000	-3.194440000
C	0.223127000	2.448079000	-3.383970000
C	2.264085000	1.154416000	-3.462204000
C	0.909203000	3.562097000	-3.826623000
C	2.299503000	3.495553000	-4.103212000
N	2.977823000	4.607443000	-4.504411000
H	0.808691000	-0.888148000	-2.727795000
H	2.470587000	5.432306000	-4.797148000
H	-1.552377000	-1.102268000	-2.264597000
H	-1.821262000	0.721468000	-2.472804000
H	4.038922000	2.190349000	-4.094710000
H	2.797065000	0.212391000	-3.312115000
H	0.380452000	4.508606000	-3.964813000
H	-0.844531000	2.537474000	-3.177987000
H	3.939739000	4.534004000	-4.808760000

[Rh(Por)(Carbene)(Aminostyrene)] + N_2

O	-7.385635000	6.683089000	-0.899063000
O	-6.772251000	7.136225000	1.213573000
N	-2.184628000	-0.105690000	0.079126000
N	-0.157822000	1.965583000	-0.086157000
C	-6.686023000	6.451940000	0.057694000
C	-5.636578000	5.389382000	0.090696000
C	-4.817331000	5.178854000	1.209250000
H	-4.950055000	5.798814000	2.096578000
C	-3.839944000	4.183702000	1.180791000
H	-3.197931000	4.013060000	2.047978000
C	-3.672262000	3.385282000	0.038378000
C	-4.506948000	3.590205000	-1.072693000
C	-5.478866000	4.587675000	-1.048995000
H	-6.130941000	4.766263000	-1.906058000
C	-2.610825000	2.335641000	0.007730000
C	-1.281059000	2.761883000	-0.072728000
C	-0.873196000	4.144977000	-0.143655000
H	-1.553566000	4.990374000	-0.181041000
C	-3.011782000	0.996072000	0.081522000
C	-4.381858000	0.555618000	0.203583000
H	-5.245037000	1.214768000	0.236462000
C	-2.982649000	-1.224688000	0.178865000
C	0.942708000	2.795588000	-0.102177000
H	-4.385261000	2.963433000	-1.958941000
C	0.489470000	4.166800000	-0.149654000
C	-4.363708000	-0.808868000	0.266948000
C	-2.547550000	-2.556880000	0.202552000
C	2.286757000	2.404424000	-0.044778000
H	-5.211391000	-1.481215000	0.362726000
C	-3.580002000	-3.626866000	0.340345000
C	-1.204643000	-2.953189000	0.120292000
C	3.332338000	3.471509000	-0.048837000
C	2.721356000	1.070205000	0.011671000
C	-3.627698000	-4.412739000	1.504569000
C	-4.518608000	-3.859026000	-0.679252000
N	-0.103499000	-2.126656000	0.068539000
C	-0.758540000	-4.325263000	0.079226000
C	3.515823000	4.292310000	-1.174683000
C	4.153939000	3.663117000	1.074331000
C	4.105923000	0.658360000	-0.054459000
N	1.923495000	-0.049679000	0.067395000
C	-4.597826000	-5.403759000	1.652510000
H	-2.899619000	-4.239682000	2.299501000

C	-5.485732000	-4.851081000	-0.535338000
H	-4.479174000	-3.261638000	-1.592778000
C	1.018991000	-2.926544000	0.029733000
H	-1.413991000	-5.191272000	0.085455000
C	0.606261000	-4.308743000	0.030207000
H	2.878234000	4.151237000	-2.047379000
C	4.504031000	5.273043000	-1.180183000
H	4.011480000	3.036089000	1.957201000
C	5.139485000	4.649875000	1.074438000
C	4.123745000	-0.705860000	-0.040213000
C	2.751136000	-1.151347000	0.037936000
C	-5.533310000	-5.626190000	0.632076000
H	-4.636260000	-6.008558000	2.559143000
H	-6.217188000	-5.047240000	-1.321494000
C	2.352996000	-2.494714000	0.022116000
H	1.282695000	-5.158231000	-0.000429000
H	4.665222000	5.910890000	-2.051198000
C	5.321732000	5.457911000	-0.056707000
H	5.771595000	4.800145000	1.950246000
H	4.986590000	-1.363138000	-0.100884000
C	-6.594326000	-6.673189000	0.736038000
C	3.424434000	-3.535937000	-0.006092000
C	6.367388000	6.522497000	-0.119905000
O	-6.544100000	-7.352185000	1.897798000
O	-7.414417000	-6.894677000	-0.121607000
C	3.646386000	-4.299966000	-1.163994000
C	4.227524000	-3.757110000	1.124117000
O	7.084353000	6.617892000	1.015193000
O	6.558524000	7.227379000	-1.081689000
H	3.028835000	-4.128715000	-2.048602000
C	4.654161000	-5.261092000	-1.191467000
H	4.055417000	-3.169216000	2.028573000
C	5.234601000	-4.721706000	1.100644000
C	5.453521000	-5.476968000	-0.060025000
H	4.844245000	-5.857286000	-2.085824000
H	5.855522000	-4.895182000	1.980140000
C	6.522655000	-6.516984000	-0.145600000
O	7.227611000	-6.635089000	0.995452000
O	6.741294000	-7.184761000	-1.127205000
Rh	-0.125659000	-0.073907000	0.118801000
H	7.894312000	-7.327592000	0.847223000
H	-7.262818000	-8.007154000	1.875037000
H	-7.473272000	7.800853000	1.099940000
H	7.735135000	7.328440000	0.882407000
H	4.952247000	1.334980000	-0.130782000
C	-0.097154000	0.059628000	1.957184000
C	-1.291586000	0.407185000	2.763114000
O	-1.429262000	1.588761000	2.996820000
O	-2.081042000	-0.581273000	3.107027000
C	-3.325546000	-0.247738000	3.793267000
C	-4.091898000	-1.532927000	3.990605000
H	-3.866744000	0.472989000	3.162610000
H	-3.068744000	0.246558000	4.742472000
H	-4.327044000	-2.001799000	3.024146000
H	-5.036712000	-1.320434000	4.513431000
H	-3.515895000	-2.248070000	4.597281000
N	0.226400000	-2.592390000	3.130214000
N	-0.359808000	-3.498071000	3.346458000
H	1.141128000	5.034584000	-0.179776000
H	0.870536000	0.081317000	2.480858000
C	0.471773000	0.540082000	-2.866465000
C	-0.348927000	-0.477542000	-2.481617000
C	0.821016000	4.107367000	-3.981648000
C	0.107207000	1.890845000	-3.234178000
C	-1.224668000	2.364941000	-3.224281000
C	1.112581000	2.799894000	-3.628478000
C	-1.531457000	3.669149000	-3.562105000
C	-0.512607000	4.578910000	-3.944236000
N	-0.811599000	5.873998000	-4.244522000

H	1.546826000	0.328446000	-2.900241000
H	-1.775373000	6.156372000	-4.364207000
H	0.054786000	-1.482920000	-2.368818000
H	-1.436147000	-0.385714000	-2.501558000
H	1.621018000	4.785211000	-4.290169000
H	2.150446000	2.456974000	-3.658540000
H	-2.567571000	4.014151000	-3.526620000
H	-2.034689000	1.694658000	-2.931497000
H	-0.109707000	6.473401000	-4.658149000

[Rh(Por)(EDA)(Pyridine)]

O	-7.356860000	6.758764000	-0.225062000
O	-6.617280000	6.986169000	1.882608000
N	-2.080583000	-0.035605000	-0.084702000
N	-0.040711000	2.018751000	-0.159098000
C	-6.588898000	6.441851000	0.651100000
C	-5.516179000	5.413434000	0.497786000
C	-4.655178000	5.068426000	1.549639000
H	-4.762858000	5.561909000	2.516159000
C	-3.672151000	4.097916000	1.357564000
H	-3.003223000	3.811367000	2.171382000
C	-3.538421000	3.461419000	0.112380000
C	-4.401934000	3.810493000	-0.937510000
C	-5.383773000	4.780923000	-0.746599000
H	-6.062532000	5.068038000	-1.551809000
C	-2.487474000	2.411854000	-0.052589000
C	-1.151496000	2.830292000	-0.113404000
C	-0.729537000	4.212193000	-0.160135000
H	-1.401589000	5.065781000	-0.141513000
C	-2.900637000	1.071457000	-0.065637000
C	-4.278854000	0.635978000	-0.026989000
H	-5.138608000	1.299688000	0.003239000
C	-2.886662000	-1.150074000	-0.061841000
C	1.065038000	2.833797000	-0.225062000
H	-4.298281000	3.319767000	-1.908188000
C	0.632579000	4.215699000	-0.228678000
C	-4.270622000	-0.729341000	-0.031037000
C	-2.463641000	-2.486856000	-0.009109000
C	2.406880000	2.420074000	-0.242772000
H	-5.124533000	-1.400354000	-0.003826000
C	-3.519569000	-3.543441000	0.035463000
C	-1.123649000	-2.900113000	0.030363000
C	3.456526000	3.480234000	-0.332933000
C	2.832276000	1.084613000	-0.160580000
C	-3.733039000	-4.286938000	1.207914000
C	-4.317665000	-3.802362000	-1.091271000
N	-0.013856000	-2.083852000	0.021148000
C	-0.692493000	-4.278706000	0.097748000
C	3.623710000	4.218105000	-1.516851000
C	4.283997000	3.758302000	0.766945000
C	4.214919000	0.660905000	-0.190678000
N	2.026417000	-0.026331000	-0.041609000
C	-4.723187000	-5.268190000	1.256749000
H	-3.117719000	-4.088694000	2.088172000
C	-5.304221000	-4.784587000	-1.047161000
H	-4.153613000	-3.231326000	-2.007834000
C	1.099526000	-2.896717000	0.085098000
H	-1.356836000	-5.138166000	0.107986000
C	0.671556000	-4.275985000	0.146650000
H	2.986289000	4.004161000	-2.377702000
C	4.598093000	5.210057000	-1.598633000
H	4.154376000	3.193306000	1.692796000
C	5.256979000	4.754373000	0.690111000
C	4.225279000	-0.698764000	-0.073505000
C	2.848372000	-1.131315000	0.020303000
C	-5.513043000	-5.522260000	0.126654000

H	-4.890081000	-5.841706000	2.169122000
H	-5.927205000	-5.001862000	-1.916747000
C	2.438581000	-2.472527000	0.100117000
H	1.337272000	-5.131681000	0.214422000
H	4.743587000	5.788008000	-2.513109000
C	5.418424000	5.485079000	-0.495448000
H	5.893206000	4.974012000	1.548075000
H	5.086047000	-1.361774000	-0.069469000
C	-6.583126000	-6.564703000	0.118015000
C	3.501604000	-3.517837000	0.200843000
C	6.443542000	6.562732000	-0.635679000
O	-6.693937000	-7.207633000	1.295841000
O	-7.278517000	-6.813520000	-0.836849000
C	3.741702000	-4.404485000	-0.862296000
C	4.277347000	-3.626824000	1.366367000
O	7.165876000	6.744890000	0.485815000
O	6.615394000	7.208181000	-1.641351000
H	3.147531000	-4.322663000	-1.775321000
C	4.733342000	-5.377319000	-0.761506000
H	4.096001000	-2.942337000	2.198195000
C	5.267846000	-4.602715000	1.473177000
C	5.500237000	-5.483295000	0.407402000
H	4.934573000	-6.069299000	-1.581380000
H	5.864151000	-4.689510000	2.382040000
C	6.548094000	-6.546781000	0.465604000
O	7.207242000	-6.564460000	1.639514000
O	6.786416000	-7.313311000	-0.436023000
Rh	-0.026691000	-0.029907000	-0.066665000
H	7.863557000	-7.280351000	1.586557000
H	-7.406269000	-7.862486000	1.196650000
H	-7.339314000	7.637768000	1.887199000
H	7.800281000	7.458819000	0.301891000
H	5.066208000	1.326812000	-0.301063000
C	0.058452000	0.203707000	2.115878000
C	-1.248442000	0.710806000	2.695928000
O	-1.481499000	1.884345000	2.808632000
O	-2.057712000	-0.292644000	3.013636000
C	-3.383711000	0.049805000	3.502532000
C	-4.157800000	-1.235411000	3.671316000
H	-3.848632000	0.724819000	2.769491000
H	-3.264955000	0.600896000	4.448162000
H	-4.271682000	-1.755377000	2.709013000
H	-5.161723000	-1.010611000	4.062336000
H	-3.656692000	-1.910689000	4.381739000
N	0.407512000	-1.022656000	2.631282000
N	0.637463000	-2.058392000	2.967319000
H	1.296732000	5.074420000	-0.268846000
H	0.890464000	0.903739000	2.253950000
C	-0.861972000	0.664396000	-2.851662000
C	0.818395000	-0.940051000	-2.786964000
C	-0.882269000	0.641447000	-4.243319000
C	0.852453000	-1.015456000	-4.176414000
C	-0.011522000	-0.212238000	-4.922429000
N	-0.025682000	-0.114500000	-2.141321000
H	-1.576697000	1.291001000	-4.778532000
H	-0.005797000	-0.250458000	-6.014113000
H	-1.525479000	1.318071000	-2.289101000
H	1.479203000	-1.548621000	-2.173328000
H	1.553631000	-1.699074000	-4.657638000

[Rh(Por)(EDA)(Pyridine)]

O	-7.093146000	6.751401000	0.098285000
O	-6.153650000	7.044078000	2.116968000
N	-1.798636000	-0.029067000	-0.213699000
N	0.225458000	2.039971000	-0.269510000
C	-6.246335000	6.459138000	0.907677000

C	-5.195410000	5.420725000	0.685294000
C	-4.218687000	5.125141000	1.647155000
H	-4.217947000	5.662708000	2.596092000
C	-3.255407000	4.150977000	1.385867000
H	-2.489866000	3.913681000	2.127825000
C	-3.258456000	3.456167000	0.163539000
C	-4.239785000	3.756509000	-0.794916000
C	-5.199235000	4.733371000	-0.537008000
H	-5.963754000	4.986506000	-1.273872000
C	-2.218282000	2.412092000	-0.075195000
C	-0.887974000	2.841590000	-0.193404000
C	-0.478963000	4.226343000	-0.276021000
H	-1.155310000	5.076181000	-0.253260000
C	-2.624641000	1.068666000	-0.112005000
C	-3.997260000	0.617600000	-0.040627000
H	-4.862413000	1.268135000	0.051556000
C	-2.593405000	-1.150343000	-0.212758000
C	1.323168000	2.860673000	-0.375206000
H	-4.240819000	3.227133000	-1.750502000
C	0.879590000	4.238551000	-0.392433000
C	-3.978821000	-0.745427000	-0.115263000
C	-2.157779000	-2.484061000	-0.233307000
C	2.667161000	2.458548000	-0.400544000
H	-4.825702000	-1.425883000	-0.095092000
C	-3.205205000	-3.550704000	-0.230774000
C	-0.813942000	-2.886666000	-0.205259000
C	3.703704000	3.527427000	-0.530833000
C	3.103708000	1.130396000	-0.274926000
C	-3.429927000	-4.326923000	0.917932000
C	-3.985343000	-3.783669000	-1.375308000
N	0.289428000	-2.061210000	-0.164380000
C	-0.371869000	-4.259474000	-0.133980000
C	3.851704000	4.228983000	-1.739081000
C	4.530640000	3.855799000	0.555377000
C	4.491037000	0.720138000	-0.274751000
N	2.307728000	0.015569000	-0.137168000
C	-4.411372000	-5.317730000	0.925246000
H	-2.831050000	-4.147137000	1.813721000
C	-4.963972000	-4.775067000	-1.372646000
H	-3.814039000	-3.184959000	-2.272690000
C	1.407493000	-2.861636000	-0.045158000
H	-1.026316000	-5.126113000	-0.163674000
C	0.989677000	-4.243390000	-0.013900000
H	3.213856000	3.975219000	-2.588737000
C	4.805586000	5.237052000	-1.857529000
H	4.414070000	3.320120000	1.500117000
C	5.483863000	4.867419000	0.441086000
C	4.513042000	-0.634654000	-0.114204000
C	3.138009000	-1.077922000	-0.033246000
C	-5.182250000	-5.547327000	-0.223178000
H	-4.586693000	-5.917215000	1.819170000
H	-5.573363000	-4.972416000	-2.256483000
C	2.739468000	-2.423026000	0.044194000
H	1.657558000	-5.094711000	0.081520000
H	4.934429000	5.788875000	-2.790474000
C	5.624815000	5.563723000	-0.767639000
H	6.119174000	5.127253000	1.288427000
H	5.380050000	-1.288537000	-0.081538000
C	-6.242189000	-6.598780000	-0.276161000
C	3.810035000	-3.453835000	0.195974000
C	6.623922000	6.660124000	-0.945388000
O	-6.362936000	-7.275977000	0.881343000
O	-6.922624000	-6.826311000	-1.246939000
C	4.082074000	-4.367864000	-0.836492000
C	4.567463000	-3.517692000	1.377209000
O	7.348727000	6.891129000	0.165542000
O	6.774143000	7.281511000	-1.969592000
H	3.507037000	-4.318774000	-1.763925000
C	5.083473000	-5.324484000	-0.688635000

H	4.364222000	-2.809932000	2.184106000
C	5.568094000	-4.476911000	1.530565000
C	5.829961000	-5.386612000	0.496609000
H	5.309036000	-6.036776000	-1.484422000
H	6.149549000	-4.527715000	2.451727000
C	6.888385000	-6.435683000	0.605730000
O	7.530416000	-6.406640000	1.788896000
O	7.147867000	-7.229936000	-0.265536000
Rh	0.255485000	-0.012290000	-0.161207000
H	8.194884000	-7.116684000	1.769037000
H	-7.068015000	-7.933750000	0.753857000
H	-6.868273000	7.701817000	2.169288000
H	7.964611000	7.614327000	-0.043380000
H	5.337007000	1.391104000	-0.395037000
C	0.266225000	0.107798000	1.823319000
C	-0.849284000	0.811499000	2.549486000
O	-0.742448000	2.000059000	2.731526000
O	-1.885154000	0.052141000	2.859659000
C	-3.046900000	0.707461000	3.442744000
C	-4.084575000	-0.356087000	3.710124000
H	-3.397911000	1.462575000	2.724083000
H	-2.723346000	1.229055000	4.356457000
H	-4.368509000	-0.863120000	2.776184000
H	-4.984589000	0.109121000	4.140030000
H	-3.712350000	-1.106440000	4.424236000
N	0.132707000	-1.591304000	2.524865000
N	-0.112874000	-2.589275000	2.918555000
H	1.535178000	5.101105000	-0.471116000
H	1.248079000	0.308218000	2.270841000
C	-0.569492000	0.702812000	-3.023047000
C	1.187368000	-0.808533000	-2.968540000
C	-0.572773000	0.712496000	-4.415812000
C	1.247319000	-0.853610000	-4.359236000
C	0.351775000	-0.079411000	-5.099492000
N	0.295002000	-0.044672000	-2.316963000
H	-1.292849000	1.335470000	-4.948950000
H	0.374246000	-0.092801000	-6.191676000
H	-1.274274000	1.307203000	-2.453060000
H	1.870310000	-1.395770000	-2.355429000
H	1.989378000	-1.487946000	-4.846829000

[Rh(Por)(Carbene)(Pyridine)] + N_2

O	-7.241402000	6.852865000	0.385535000
O	-6.353713000	6.994757000	2.443380000
N	-2.082179000	-0.041076000	-0.066527000
N	-0.045406000	2.001014000	-0.209663000
C	-6.426711000	6.487825000	1.198227000
C	-5.397607000	5.435623000	0.940898000
C	-4.465508000	5.046462000	1.913603000
H	-4.484879000	5.518747000	2.896370000
C	-3.521880000	4.062174000	1.620503000
H	-2.794841000	3.748154000	2.372738000
C	-3.500658000	3.454123000	0.354212000
C	-4.437290000	3.845400000	-0.615138000
C	-5.378252000	4.831295000	-0.324170000
H	-6.110235000	5.154149000	-1.066794000
C	-2.478388000	2.400039000	0.079968000
C	-1.150171000	2.813743000	-0.090549000
C	-0.727808000	4.190476000	-0.192845000
H	-1.395019000	5.046830000	-0.143838000
C	-2.898224000	1.062909000	0.052412000
C	-4.272847000	0.623400000	0.122959000
H	-5.130712000	1.283046000	0.222230000
C	-2.886052000	-1.156325000	-0.085374000
C	1.060480000	2.808136000	-0.345527000
H	-4.419598000	3.379057000	-1.602987000

C	0.626937000	4.187615000	-0.362619000
C	-4.266325000	-0.739360000	0.020904000
C	-2.460215000	-2.492219000	-0.130504000
C	2.402421000	2.395859000	-0.360678000
H	-5.119239000	-1.412468000	0.025892000
C	-3.515113000	-3.550698000	-0.136667000
C	-1.119725000	-2.903191000	-0.103219000
C	3.442187000	3.452660000	-0.544611000
C	2.828643000	1.072814000	-0.163634000
C	-3.733424000	-4.338678000	1.005744000
C	-4.309443000	-3.760398000	-1.275755000
N	-0.011385000	-2.090319000	-0.025717000
C	-0.685007000	-4.280704000	-0.067009000
C	3.565140000	4.114314000	-1.778204000
C	4.292798000	3.814238000	0.512540000
C	4.210552000	0.648363000	-0.119392000
N	2.021129000	-0.027877000	0.016501000
C	-4.725493000	-5.319185000	1.010451000
H	-3.120204000	-4.176752000	1.894627000
C	-5.297025000	-4.742892000	-1.275065000
H	-4.141935000	-3.151984000	-2.167341000
C	1.096870000	-2.896289000	0.116511000
H	-1.344795000	-5.140912000	-0.135693000
C	0.671333000	-4.276385000	0.091222000
H	2.908339000	3.834639000	-2.605000000
C	4.517897000	5.115574000	-1.950044000
H	4.194273000	3.312096000	1.477509000
C	5.244995000	4.819302000	0.344360000
C	4.215811000	-0.696873000	0.113006000
C	2.836197000	-1.125218000	0.181839000
C	-5.510700000	-5.526747000	-0.132526000
H	-4.896804000	-5.928723000	1.898323000
H	-5.917236000	-4.924274000	-2.154796000
C	2.424404000	-2.465111000	0.268393000
H	1.333069000	-5.132699000	0.184700000
H	4.627155000	5.636564000	-2.903005000
C	5.361030000	5.475428000	-0.889234000
H	5.898310000	5.105987000	1.169047000
H	5.074749000	-1.357404000	0.194471000
C	-6.580788000	-6.567981000	-0.188290000
C	3.478389000	-3.494994000	0.511578000
C	6.357001000	6.564467000	-1.123349000
O	-6.701642000	-7.253355000	0.964167000
O	-7.268336000	-6.781005000	-1.157371000
C	3.846240000	-4.413538000	-0.485760000
C	4.120886000	-3.547967000	1.759208000
O	7.105976000	6.828509000	-0.036284000
O	6.484407000	7.153110000	-2.169617000
H	3.359696000	-4.371726000	-1.462923000
C	4.831865000	-5.366295000	-0.238009000
H	3.836930000	-2.836785000	2.538132000
C	5.105546000	-4.502562000	2.011358000
C	5.464604000	-5.417944000	1.012172000
H	5.132407000	-6.083768000	-1.003808000
H	5.598906000	-4.545541000	2.982900000
C	6.511042000	-6.462847000	1.226543000
O	7.045922000	-6.418084000	2.461115000
O	6.848248000	-7.266150000	0.390985000
Rh	-0.026939000	-0.036355000	0.004641000
H	7.710142000	-7.127028000	2.509001000
H	-7.412858000	-7.904218000	0.835118000
H	-7.052474000	7.667290000	2.517383000
H	7.718175000	7.543920000	-0.280088000
H	5.065670000	1.303373000	-0.260889000
C	-0.027684000	0.069125000	1.863876000
C	-1.203127000	0.466159000	2.671541000
O	-1.239457000	1.638743000	2.980225000
O	-2.090567000	-0.463169000	2.928283000
C	-3.315493000	-0.068236000	3.615830000

C	-4.171146000	-1.304063000	3.755683000
H	-3.797207000	0.711799000	3.007650000
H	-3.037271000	0.371318000	4.585731000
H	-4.416091000	-1.722633000	2.768438000
H	-5.110698000	-1.044955000	4.266871000
H	-3.657742000	-2.075943000	4.348812000
N	0.024564000	-2.623625000	3.106209000
N	-0.695881000	-3.451484000	3.184716000
H	1.288024000	5.043292000	-0.467017000
H	0.921666000	0.014294000	2.418907000
C	-0.910447000	0.521943000	-2.940088000
C	0.951185000	-0.853878000	-2.854804000
C	-0.924052000	0.490683000	-4.332768000
C	1.007588000	-0.937291000	-4.244297000
C	0.052586000	-0.252822000	-4.999020000
N	0.009500000	-0.138777000	-2.219892000
H	-1.690101000	1.042863000	-4.879794000
H	0.069452000	-0.297742000	-6.090527000
H	-1.653530000	1.089809000	-2.379383000
H	1.678621000	-1.370778000	-2.228137000
H	1.790813000	-1.529695000	-4.720218000

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