

Halide-free CO₂ cycloaddition onto styrene oxide catalysed by first row transition-metal derivatives of polyoxotungstates

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Supplementary Informations

1. Materials and methods

IR spectra were obtained from KBr pellets on a Jasco FT/IR-4100 spectrometer, or by Attenuated Total Reflection Infra-Red spectroscopy, using a Tensor R27 FTIR equipped with a ZnSe crystal with resolution better than 1 cm⁻¹. The ¹H NMR solution spectra were recorded in 5 mm o.d. tubes on Bruker Avance II 300 or 400 spectrometers equipped with a QNP probehead. Chemical shifts were referenced to tetramethylsilane (TMS) for ¹H NMR. Thermogravimetric analyses (TGA/DSC) were performed under air with a TA-Instrument SDT Q600, between 20 and 800°C (air flow rate: 100.0 mL.min⁻¹, ramp: 10°C.min⁻¹). High-resolution mass spectra (matrix-assisted laser desorption/ionization-time-of-flight - MALDI-TOF) were measured by the Service de Spectrométrie de Masse of Sorbonne Université. Gas chromatography analyses were performed on a Shimadzu NEXIS-GC-2030 AF instrument equipped with a split/splitless (SPL) injector, a flame ionization detector and a GC Capillary Column SH-Rxi-5MS (ID: 0.25 mm; film thickness: 0.25 µm; Length: 30 m) using He as a vector gas (1.5 mL min⁻¹) and the following temperature conditions: ramp from 70 to 250°C at 10°C min⁻¹, then an isotherm at 250°C during 10 min).

For each catalytic experiment, each tetraalkylammonium salt of TM-polyoxometalate used as Cy-Cat catalyst (0.1 mmol) was dissolved in a mixture of 0.7 mL of benzonitrile and 1.4 mL of styrene oxide (SO, 12.2 mmol) in a 45 mL teflon beaker and put in the autoclave. The autoclave was then filled three times with 15 bar of CO₂ to expel the air. The final CO₂ pressure was fixed at 11 bar at room temperature. The autoclave was put in an oil bath and was heated until the internal temperature probe reaches the set temperature (80, 100 or 120°C) which usually took around 30 minutes to one hour. The time t = 0 was taken from the moment when the internal sensor indicated the set temperature. At the end of the experiment, the autoclave was put in a cold water bath, and was opened when the temperature reached ca. 30°C. The composition of the final mixture was analyzed by Gas chromatography and by ¹H NMR. The determination of the SO/SC/polymers ratio was obtained by careful integration of the different peaks observed in the NMR spectrum as indicated on figure S3.

2. Preparation of materials

0-1: K₈[SiW₁₁O₃₉]•15H₂O. Yield: 57.34 g

Sodium metasilicate (5.502 g, 0.045 mol) was dissolved in 50 mL of distilled water (solution A). In parallel, sodium tungstate dihydrate (82.5 g, 0.25 mol) was dissolved in 150 mL of boiling distilled water (solution B). A HCl solution (4 mol.L⁻¹, 82.5 mL) was added dropwise into solution B in 30 min. After that, solution A was quickly dropped to solution B, followed by subsequent 25 mL of a 4 mol/L HCl solution. The pH of mixture should be at 5~6. The mixture was kept boiling for 1 h, then cooled to room temperature. If the solution is not clear, it should be filtered at this stage. Potassium chloride (7.5 g) was added into the filtrate and the suspension stood overnight. The next day, the mixture was filtered, and colorless crystals of K₈[SiW₁₁O₃₉]•15H₂O were collected, washed with ethanol or acetone twice, finally dried in air.

0-2: K₇[PW₁₁O₃₉]•15H₂O. Yield: 67.56 g

Sodium tungstate dihydrate (90.75 g, 0.27 mol) was dissolved in 150 mL distilled water. Phosphoric acid (1.7 mL of which density is 1.7 g.cm³) and acetic acid (44 mL) were successively added into the Na₂WO₄•2H₂O solution. After that, the mixture was refluxed for 1 h. Then 30 g of solid potassium chloride (0.41 mol) was added into the mixture. The suspension was cooled to room temperature, then stood overnight. The next day, the mixture was filtered, and colorless crystals of K₇[PW₁₁O₃₉]•15H₂O were collected, washed with ethanol twice, finally dried in air.

1-1: K₆[SiW₁₁O₃₉Co(H₂O)]•15H₂O Yield: 5.13 g

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.405 g, 1.70 mmol) was dissolved in 3.5 mL of distilled water. Then, $\text{K}_8[\text{SiW}_{11}\text{O}_{39}] \cdot 15\text{H}_2\text{O}$ (5.000 g, 1.54 mmol) was added to the solution. The mixture was stirred at 70 °C for 2 h, cooled down to room temperature, then stayed overnight to crystallize. The next day, the mixture was filtered, and a purple precipitate of $\text{K}_6[\text{SiW}_{11}\text{O}_{39}\text{Co}] \cdot 15\text{H}_2\text{O}$ was collected, washed with ethanol, finally dried in air.

1-2: $\text{K}_5[\text{SiW}_{11}\text{O}_{39}\text{Cr}(\text{H}_2\text{O})] \cdot 15\text{H}_2\text{O}$ Yield: 2.27 g

A sample of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.400 g, 1 mmol) was dissolved in 15 mL of distilled water. Then, $\text{K}_8[\text{SiW}_{11}\text{O}_{39}] \cdot 15\text{H}_2\text{O}$ (3.235 g, 1.00 mmol) was added to the solution. The mixture was boiled for 1 h, cooled down to room temperature, then stayed overnight for crystallizing. The next day, the mixture was filtered, and a green precipitate of $\text{K}_5[\text{SiW}_{11}\text{O}_{39}\text{Cr}] \cdot 15\text{H}_2\text{O}$ was collected, washed with ethanol, finally dried in air.

1-3: $\text{K}_6[\text{SiW}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})] \cdot 8\text{H}_2\text{O}$ Yield: 1.86 g

A sample of $\text{K}_8[\text{SiW}_{11}\text{O}_{39}] \cdot 15\text{H}_2\text{O}$ (2.684 g, 0.82 mmol) was dissolved in 10 mL of distilled water, then heated to 90 °C. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.396 g, 1.67 mmol) was dissolved in 10 mL of distilled water and then added into the previous hot solution. The mixture was stirred at 90 °C for 1 h. After stirring, the mixture was filtered when it was hot, and 10 mL of saturated KCl solution was added to the hot filtrate. The solution was stayed overnight for crystallizing. The next day, the mixture was filtered, and a pale yellow precipitate of $\text{K}_6[\text{SiW}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})] \cdot 8\text{H}_2\text{O}$ was collected, washed with ethanol, finally dried in air.

1-4: $\text{K}_6[\text{SiW}_{11}\text{O}_{39}\text{Zn}(\text{H}_2\text{O})] \cdot 15\text{H}_2\text{O}$ Yield: 9.10 g

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.594 g, 2.00 mmol) was dissolved in 20 mL of distilled water. Then, $\text{K}_8[\text{SiW}_{11}\text{O}_{39}] \cdot 15\text{H}_2\text{O}$ (6.494 g, 2.00 mmol) was added to the Zn^{2+} solution. The mixture was stirred at 80 °C for 2 h, cooled down to room temperature, then stayed overnight for crystallizing. The next day, the mixture was filtered, and a white precipitate of $\text{K}_6[\text{SiW}_{11}\text{O}_{39}\text{Zn}(\text{H}_2\text{O})] \cdot 15\text{H}_2\text{O}$ was collected, washed with ethanol, finally dried in air.

1-5: $\text{K}_6[\text{SiW}_{11}\text{O}_{39}\text{Ni}(\text{H}_2\text{O})] \cdot 9\text{H}_2\text{O}$ Yield: 5.50 g

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.378 g, 1.30 mmol) was dissolved in 20 mL of distilled water. Then, $\text{K}_8[\text{SiW}_{11}\text{O}_{39}] \cdot 15\text{H}_2\text{O}$ (5.00 g, 1.54 mmol) was added to the Ni^{2+} solution. The mixture was stirred at 80 °C for 2 h, cooled down to room temperature, then stayed overnight for crystallizing. The next day, the mixture was filtered, and a green precipitate of $\text{K}_6[\text{SiW}_{11}\text{O}_{39}\text{Ni}(\text{H}_2\text{O})] \cdot 9\text{H}_2\text{O}$ was collected, washed with ethanol, finally dried in air.

2-1: $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})] \cdot 14\text{H}_2\text{O}$ Yield: 7.29 g

A sample of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.810 g, 3.40 mmol) was dissolved in 7 mL of distilled water. Then, 9.890 g (3.00 mmol) of $\text{K}_7[\text{PW}_{11}\text{O}_{39}] \cdot 15\text{H}_2\text{O}$ was added to the Co^{2+} solution. The mixture was stirred at 70 °C for 2 h, cooled down to room temperature, and then stay it overnight for crystallizing. The next day, the mixture was filtered, and a purple precipitate of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})] \cdot 14\text{H}_2\text{O}$ was collected, washed with ethanol, finally dried in air.

2-2: $\text{K}_4[\text{PW}_{11}\text{O}_{39}\text{Cr}(\text{H}_2\text{O})] \cdot 9\text{H}_2\text{O}$ Yield: 6.03 g

$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.800 g, 2.00 mmol) was dissolved in 30 mL of distilled water. Then, 6.470 g (2.00 mmol) of $\text{K}_7[\text{PW}_{11}\text{O}_{39}] \cdot 15\text{H}_2\text{O}$ was added to the Cr^{3+} solution. The boiling mixture was stirred for 1 h, cooled down to room temperature, and then stay it overnight for crystallizing. The next day, the mixture was filtered, and a green precipitate of $\text{K}_4[\text{PW}_{11}\text{O}_{39}\text{Cr}(\text{H}_2\text{O})] \cdot 14\text{H}_2\text{O}$ was collected, washed with ethanol, finally dried in air.

2-3: $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})] \cdot 14\text{H}_2\text{O}$ Yield: 5.74 g

A sample of $\text{K}_7[\text{PW}_{11}\text{O}_{39}] \cdot 15\text{H}_2\text{O}$ (5.140 g, 1.60 mmol) was dissolved in 20 mL of distilled water, and heated to 90 °C. In parallel, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.936 g, 3.95 mmol) was dissolved in 20 mL of distilled water and then added into the previous hot solution. The mixture was heated to 90 °C and stirred for 1 h. The hot mixture was immediately filtered, and 20 mL of a saturated KCl solution was poured inside when hot. and then stood overnight for crystallizing. The next day, the mixture was filtered, and a pink precipitate of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})] \cdot 14\text{H}_2\text{O}$ was collected, washed with

ethanol, finally dried in air. The solution was stood overnight for crystallizing. The next day, the mixture was filtered, and a light yellow precipitate of $K_5[PW_{11}O_{39}Mn(H_2O)] \cdot 14H_2O$ was collected, washed with ethanol, finally dried in air.

2-4: $K_5[PW_{11}O_{39}Zn(H_2O)] \cdot 9H_2O$ Yield: 2.58 g

A sample of $Zn(NO_3)_2 \cdot 6H_2O$ (0.594 g, 2.00 mmol) was dissolved in 20 mL distilled water. Then, 6.470 g (2.00 mmol) of $K_7[PW_{11}O_{39}] \cdot 15H_2O$ was added in the solution, which was stirred at 80 °C for 2 h. After this, the mixture was cooled down to room temperature, and then stood overnight for crystallization. Finally, the mixture was filtered, and the white precipitate of $K_5[PW_{11}O_{39}Zn(H_2O)] \cdot 14H_2O$ was washed with ethanol, finally dried in air.

2-5: $K_5[PW_{11}O_{39}Ni(H_2O)] \cdot 7H_2O$ Yield: 4.94 g

A sample of $Ni(NO_3)_2 \cdot 6H_2O$ (0.495 g, 1.70 mmol) was dissolved in 20 mL distilled water. Then, 5.142 g (1.60 mmol) of $K_7[PW_{11}O_{39}] \cdot 15H_2O$ was added in the solution, which was stirred at 80 °C for 2 h. After this, the mixture was cooled down to room temperature, and then stood overnight for crystallization. Finally, the mixture was filtered, and the green precipitate of $K_5[PW_{11}O_{39}Ni(H_2O)] \cdot 14H_2O$ was washed with ethanol, finally dried in air.

3-1: $(NOct_4)_6[SiW_{11}O_{39}Co(H_2O)] \cdot 8H_2O$ Yield: 2.45 g^[S1]

A sample of $K_6[SiW_{11}O_{39}Co(H_2O)] \cdot 15H_2O$ (2.00g, 0.67 mmol) was dissolved into 67 mL distilled water and stirred at room temperature. In parallel, $(NOct_4)Br$ (2.200 g, 4.02 mmol) was dissolved in 67 mL of CH_2Cl_2 and the resulting red solution was poured into the previous aqueous solution, resulting in a 2-phases mixture. The aqueous phase rapidly became colorless, and the organic phase became red. The latter was separated from the aqueous solution, and toluene was removed under vacuum to give an oily green product identified as $(NOct_4)_6[SiW_{11}O_{39}Co(H_2O)] \cdot 8H_2O$.

3-2: $(NBu_4)_3K_2[SiW_{11}O_{39}Cr(H_2O)] \cdot 4H_2O$ Yield:

A sample of $K_5[SiW_{11}O_{39}Cr(H_2O)] \cdot 15H_2O$ (0.880 g, 0.27 mmol) was dissolved in 28 mL of distilled water and stirred at room temperature. Then, 0.435 g (1.36 mmol) of $(NBu_4)Br$ was added in the previous solution leading to the precipitation of a green solid identified as $(NBu_4)_3K_2[SiW_{11}O_{39}Cr(H_2O)] \cdot 4H_2O$. The precipitate was filtered, washed twice with ethanol, and dried in air.

3-3: $(NBu_4)_3K_3[SiW_{11}O_{39}Mn(H_2O)] \cdot 4H_2O$ Yield: 0.376 g

A sample of $K_6[SiW_{11}O_{39}Mn(H_2O)] \cdot 8H_2O$ (1.000 g, 0.41 mmol) was dissolved in 34 mL of distilled water and stirred at room temperature. Then, 0.657 g (2.04 mmol) of $(NBu_4)Br$ was added in the previous solution leading to the precipitation of a pale yellow solid identified as $(NBu_4)_3K_3[SiW_{11}O_{39}Mn(H_2O)] \cdot 4H_2O$. The precipitate was filtered, washed twice with ethanol, and dried in air.

3-4: $(NBu_4)_3K_3[SiW_{11}O_{39}Zn(H_2O)] \cdot 11H_2O$ Yield: 0.896 g

A sample of $K_6[SiW_{11}O_{39}Zn(H_2O)] \cdot 15H_2O$ (2.000 g, 0.89 mmol) was dissolved in 67 mL of distilled water and stirred at room temperature. Then, 1.728 g (5.37 mmol) of $(NBu_4)Br$ was added in the previous solution leading to the precipitation of a white solid identified as $(NBu_4)_3K_3[SiW_{11}O_{39}Zn(H_2O)] \cdot 11H_2O$. The precipitate was filtered, washed twice with ethanol, and dried in air.

3-5-1: $(NBu_4)_3K_3SiW_{11}O_{39}Ni(H_2O)] \cdot 5H_2O$ Yield: 0.770 g

A sample of $K_6[SiW_{11}O_{39}Ni(H_2O)] \cdot 9H_2O$ (2.000 g, 0.67 mmol) was dissolved in 67 mL of distilled water and stirred at room temperature. Then, 1.293 g (4.02 mmol) of $(NBu_4)Br$ was added in the previous solution leading to the precipitation of a light green solid identified as $(NBu_4)_3K_3[SiW_{11}O_{39}Ni(H_2O)] \cdot 5H_2O$. The precipitate was filtered, washed twice with ethanol, and dried in air.

3-5-2: $(NHex_4)_6[SiW_{11}O_{39}Ni(H_2O)] \cdot xH_2O$ Yield: 0.760 g

A sample of $K_6[SiW_{11}O_{39}Ni(H_2O)] \cdot 9H_2O$ (2.000 g, 0.67 mmol) was dissolved in 67 mL of distilled water and stirred at room temperature. Then, 1.751 g (4.02 mmol) of $(NHex_4)Br$ was added in the

previous solution leading to the precipitation of a light green solid identified as $(\text{NHex}_4)_6[\text{SiW}_{11}\text{O}_{39}\text{Ni}(\text{H}_2\text{O})]\cdot x\text{H}_2\text{O}$. The precipitate was filtered, washed twice with ethanol, and dried in air.

3-6-1: $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ Yield: 1.801 g

A sample of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 14\text{H}_2\text{O}$ (2.000 g, 0.67 mmol) was dissolved in 67 mL of distilled water and stirred at room temperature. Then, 1.290 g (3.40 mmol) of $(\text{NBu}_4)\text{Br}$ was added in the previous solution leading to the precipitation of a pink solid identified as $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$. The precipitate was filtered, washed twice with ethanol, and dried in air.

3-6-2: $(\text{NEt}_4)_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ Yield: 2.132 g

A sample of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 14\text{H}_2\text{O}$ (2.000 g, 0.67 mmol) was dissolved in 67 mL of distilled water and stirred at room temperature. Then, 0.720 g (3.40 mmol) of $(\text{NEt}_4)\text{Br}$ was dissolved in the same volume of toluene and the resulting solution was added to the previous solution leading to the formation of a 2-phases mixture. The pink solid organic phase was separated and dried under vacuum, leading to an oily red product. This product was washed twice with ethanol, and air-dried for a few days, resulting in a pink/red solid precipitate identified as $(\text{NEt}_4)_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$.

3-6-3: $(\text{NPr}_4)_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot x\text{H}_2\text{O}$ Yield: 2.382 g

A sample of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 14\text{H}_2\text{O}$ (2.000 g, 0.67 mmol) was dissolved in 67 mL of distilled water and stirred at room temperature. Then, 0.905 g (3.40 mmol) of $(\text{NPr}_4)\text{Br}$ was dissolved in the same volume of toluene and the resulting solution was added to the previous solution leading to the formation of a 2-phases mixture. The pink solid organic phase was separated and dried under vacuum, leading to an oily red product. This product was washed twice with ethanol, and air-dried for a few days, resulting in a pink/red solid precipitate identified as $(\text{NPr}_4)_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot x\text{H}_2\text{O}$.

3-6-4: $(\text{NPen}_4)_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot x\text{H}_2\text{O}$ Yield: 3.997 g

A sample of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 14\text{H}_2\text{O}$ (2.000 g, 0.67 mmol) was dissolved in 67 mL of distilled water and stirred at room temperature. Then, 1.292 g (3.40 mmol) of $(\text{NPen}_4)\text{Br}$ was dissolved in the same volume of toluene and the resulting solution was added to the previous solution leading to the formation of a 2-phases mixture. The pink solid organic phase was separated and dried under vacuum, leading to an oily red product. This product was washed twice with ethanol, and air-dried for a few days, resulting in a pink/red solid precipitate identified as $(\text{NPen}_4)_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot x\text{H}_2\text{O}$.

3-6-5: $(\text{NHex}_4)_4\text{K}[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ Yield: 2.857 g

A sample of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 14\text{H}_2\text{O}$ (2.000 g, 0.67 mmol) was dissolved in 67 mL of distilled water and stirred at room temperature. Then, 1.479 g (3.40 mmol) of $(\text{NHex}_4)\text{Br}$ was dissolved in the same volume of toluene and the resulting solution was added to the previous solution leading to the formation of a 2-phases mixture. The pink solid organic phase was separated and dried under vacuum, leading to an oily red product. This product was washed twice with ethanol, and air-dried for a few days, resulting in a pink/red solid precipitate identified as $(\text{NHex}_4)_4\text{K}[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$.

3-6-6: $(\text{NOct}_4)_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ Yield: 3.390 g

A sample of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 14\text{H}_2\text{O}$ (2.000 g, 0.67 mmol) was dissolved in 67 mL of distilled water and stirred at room temperature. Then, 1.860 g (3.40 mmol) of $(\text{NOct}_4)\text{Br}$ was dissolved in the same volume of toluene and the resulting solution was added to the previous solution leading to the formation of a 2-phases mixture. The pink solid organic phase was separated and dried under vacuum, leading to an oily red product. This product was washed twice with ethanol, and air-dried for a few days, resulting in a pink/red sticky precipitate identified as $(\text{NOct}_4)_5[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$.

3-6-7: $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{MeIm})]\cdot 3\text{H}_2\text{O}$ Yield: 0.29 g

A sample of $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ (0.5 g, 0.16 mmol) was dissolved in 10 mL of acetonitrile and 2.80 mL (35 mmol) of methylimidazole (MeIm) was added. The resulting solution was heated for 1h at 80°C. The resulting pink solution was then evaporated until a pink precipitate formed. This precipitate was filtered, washed twice with ethanol, and air-dried for a few hours, resulting in a pink/red solid precipitate identified $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{MeIm})]\cdot 3\text{H}_2\text{O}$.

3-7: $(\text{NBu}_4)_3\text{K}[\text{PW}_{11}\text{O}_{39}\text{Cr}(\text{H}_2\text{O})]\cdot 8\text{H}_2\text{O}$ Yield: 1.850 g

A sample of $\text{K}_4[\text{PW}_{11}\text{O}_{39}\text{Cr}(\text{H}_2\text{O})]\cdot 9\text{H}_2\text{O}$ (2.000 g, 0.69 mmol) was dissolved in 69 mL of distilled water and stirred at room temperature. Then, 0.890 g (2.76 mmol) of $(\text{NBu}_4)\text{Br}$ was added in the solution leading to the precipitation of a light green solid identified as $(\text{NBu}_4)_3\text{K}[\text{PW}_{11}\text{O}_{39}\text{Cr}(\text{H}_2\text{O})]\cdot 8\text{H}_2\text{O}$. The precipitate was filtered, washed twice with ethanol, and dried in air.

3-8: $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$ Yield: 2.361 g

A sample of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})]\cdot 9\text{H}_2\text{O}$ (2.000 g, 0.69 mmol) was dissolved in 69 mL of distilled water and stirred at room temperature. Then, 1.095 g (3.40 mmol) of $(\text{NBu}_4)\text{Br}$ was added in the previous solution leading to the precipitation of a pale yellow solid identified as $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$. The precipitate was filtered, washed twice with ethanol, and dried in air.

3-9: $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Zn}(\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$ Yield: 1.563 g

A sample of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Zn}(\text{H}_2\text{O})]\cdot 9\text{H}_2\text{O}$ (2.000 g, 0.69 mmol) was dissolved in 69 mL of distilled water and stirred at room temperature. Then, 1.093 g (3.39 mmol) of $(\text{NBu}_4)\text{Br}$ was added in the previous solution leading to the precipitation of a white solid identified as $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Zn}(\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$. The precipitate was filtered, washed twice with ethanol, and dried in air.

3-10-1: $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Ni}(\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$ Yield: 2.220 g

A sample of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Ni}(\text{H}_2\text{O})]\cdot 9\text{H}_2\text{O}$ (2.000 g, 0.69 mmol) was dissolved in 69 mL of distilled water and stirred at room temperature. Then, 1.102 g (3.40 mmol) of $(\text{NBu}_4)\text{Br}$ was added in the previous solution leading to the precipitation of a white solid identified as $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Ni}(\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$. The precipitate was filtered, washed twice with ethanol, and dried in air.

3-10-2: $(\text{NHex}_4)_5[\text{PW}_{11}\text{O}_{39}\text{Ni}]\cdot x\text{H}_2\text{O}$ Yield: 2.210 g

A sample of $\text{K}_5[\text{PW}_{11}\text{O}_{39}\text{Ni}(\text{H}_2\text{O})]\cdot 7\text{H}_2\text{O}$ (2.000 g, 0.69 mmol) was dissolved in 68 mL of distilled water and stirred at room temperature. Then, 1.479 g (3.40 mmol) of $(\text{NHex}_4)\text{Br}$ was added in the solution leading to the precipitation of a pale green solid identified as $(\text{NHex}_4)_5[\text{PW}_{11}\text{O}_{39}\text{Ni}]\cdot x\text{H}_2\text{O}$. The precipitate was filtered, washed twice with ethanol and dried in air.

4.1: $\text{N,N}'$ -Bis(salicylidene-ethylenediimine) (salen- H_2).^{S2} Salicylaldehyde (20 mmol, 2.1 mL) and ethylenediamine (10 mmol, 0.7 mL) were refluxed in 25 mL of ethanol for 5 minutes. The mixture was cooled in an ice bath, leading to the formation of bright yellow crystals which were filtered on a glass frit, then washed with ethanol and dried at air, leading to 1.854g (yield 90%) of $\text{N,N}'$ -Bis(salicylidene-ethylenediimine) (salen- H_2).

4-2: $\text{N,N}'$ -Bis(salicylidene-ethylenediimino)-Cobalt (II) [Co(salen)].^{S2} In a 100 mL tricol flask, 3.5 mmol of salen- H_2 (0.94 g) was dissolved in 50 mL of ethanol (95%) under N_2 . The mixture was magnetically stirred under a flow of N_2 and heated at 70-80°C until the salen- H_2 crystals have completely dissolved. Meanwhile, 3.5 mmol of cobalt acetate tetrahydrate (0.87 g) was dissolved in 6 mL of hot water then quickly added to the former solution. A gelatinous brown precipitate immediately forms and the heating (70-80°C) was continued for an hour. The precipitate turns dark red. The solution was cooled in a cold water bath while maintaining the flow of N_2 . The red-brown solid obtained was filtered over a glass frit and then washed with 3 portions of 5 mL distilled water and one portion of 5 mL ethanol. The precipitate was finally dry under vacuum, leading to 0.837g of [Co(salen)] (yield: 75%).

3. Characterization of the compounds

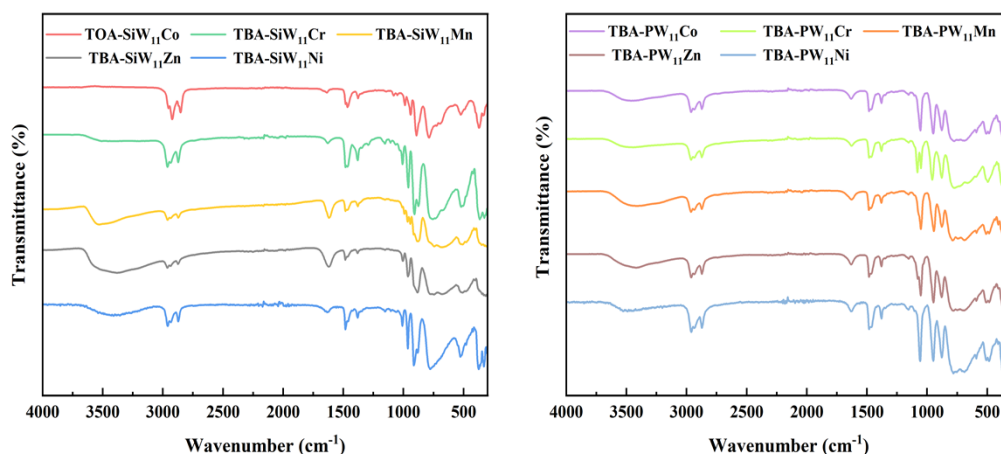


Figure S1. IR spectra of the different tetraalkylammonium salt of the $[SiW_{11}O_{39}\{M(H_2O)\}]^{n-}$ ($M = Cr, n = 5$; $M = Co, Mn, Zn, Ni, n = 6$, left) and $[PW_{11}O_{39}\{M(H_2O)\}]^{n-}$ ($M = Cr, n = 4$; $M = Co, Mn, Zn, Ni, n = 5$ right) transition metal derivatives of polyoxometalates used in the manuscript.

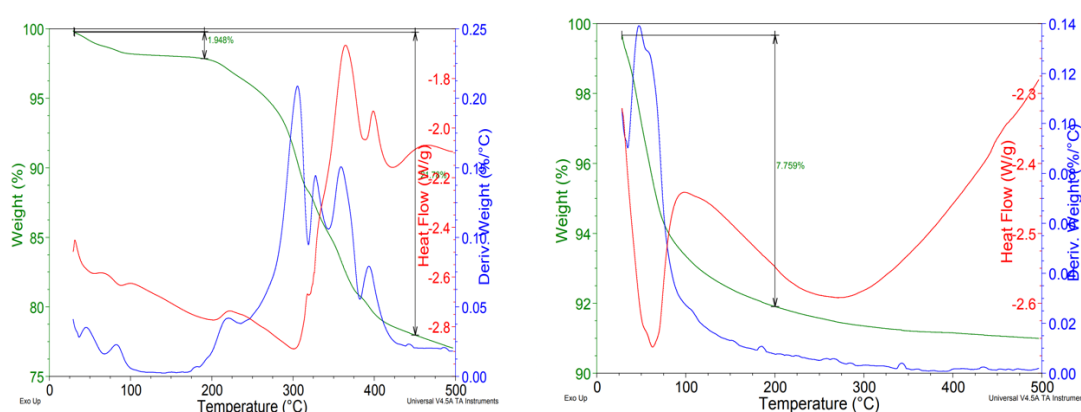


Figure S2: TGA/DSC figures for $K_5[PW_{11}O_{39}Co(H_2O)] \cdot 14H_2O$ and $(NBu_4)_3K_2[PW_{11}O_{39}Co(H_2O)] \cdot 3H_2O$.

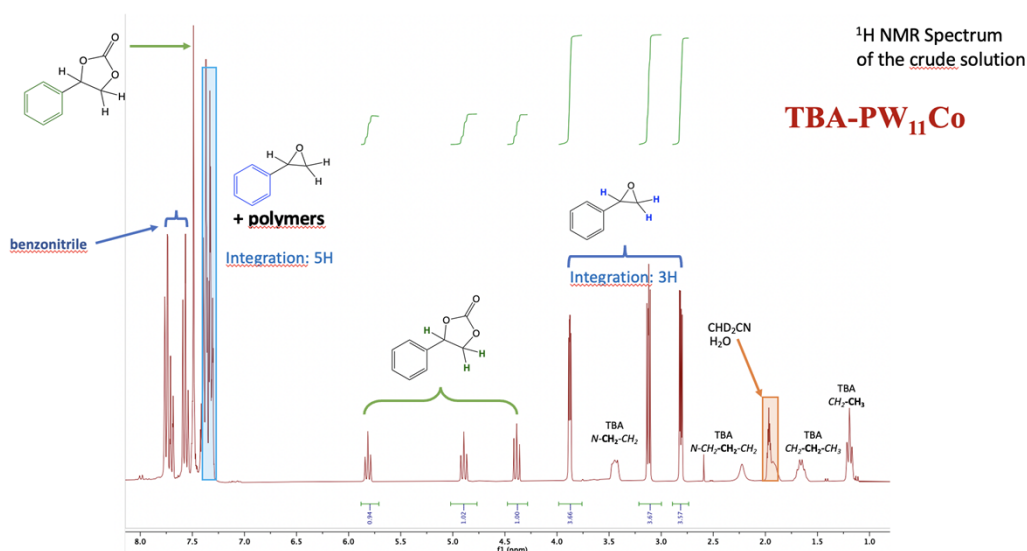


Figure S3: NMR Spectrum of a crude solution (diluted in CD_3CN) obtained after the catalytic reaction performed using the conditions described in Table 1, entry 7, given here as an example. For each sample, the determination of the SO/SC/polymers ratio was obtained by careful integration of the different peaks observed in the 1H NMR spectrum as indicated on the figure above.

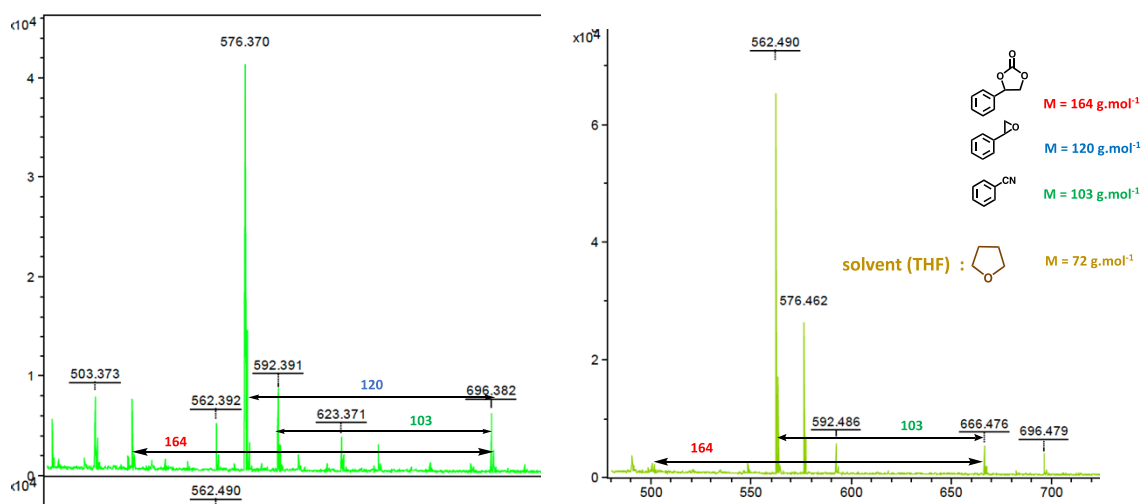


Figure S4: MALDI-TOF mass spectrometry analysis of a crude materials (after dilution in THF) obtained after the catalytic reaction performed using the conditions described in Table 1, entry 3, with $(\text{NBu}_4)_3\text{K}[\text{PW}_{11}\text{O}_{39}\text{Cr}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ CyCat. The arrows added in the spectra between two peaks and the corresponding values are indicative of the m/z differences between these peaks and were attributed to the addition of SO, SC or benzonitrile to the lowest mass molecules.

Table S1. Comparison of the catalytic activity of CyCat in the presence or in the absence of $(\text{NBu}_4)\text{Br}$.

Entry	CyCat	$(\text{NBu}_4)\text{Br}$	SO conv. (%)	SC Yield (%)	Others (%)
1	$(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$	No	17	15	2
2	$(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$	Yes	91	91	0
3	$(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Zn}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$	No	18	14	4
4	$(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Zn}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$	Yes	100	100	0
5	$(\text{NHex}_4)_4\text{K}[\text{PW}_{11}\text{O}_{39}\text{Ni}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$	No			
6	$(\text{NHex}_4)_4\text{K}[\text{PW}_{11}\text{O}_{39}\text{Ni}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$	Yes	94	93	1

$T = 80^\circ\text{C}$, Reaction time: 5h, SO (12.2 mmol, 1.4 mL, CyCat (0.1 mmol), initial $P_{\text{CO}_2} = 11$ bar, benzonitrile (0.7 mL) is used as solvent for the complete dissolution of CyCat and as internal reference.

Table S2. Screening of the catalytic activity of $(\text{NBu}_4)_3\text{K}_2[\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ vs. various epoxides

Entry	Epoxide	Epoxide conv. (%)	Carbonate Yield (%)	Others (%)
1	styrene oxide	17	15	2
2	propylene oxide	10	10	0
3	epichlorhydrin	33	33	0
4	octene-1,2-oxide	1	1	0
5	cyclohexene oxide	0	0	0
6	Limonene oxide	0	0	0

Reaction time: 5h, 80°C , epoxide (12.2 mmol), CyCat (0.1 mmol), initial $P_{\text{CO}_2} = 11$ bar, benzonitrile (0.7 mL) is used as solvent for the complete dissolution of CyCat and as internal reference.

References:

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