catalysts

Supporting Information: Aerobic Epoxidation of Low-Molecular-Weight and Polymeric Olefins by a Supramolecular Manganese Porphyrin Catalyst

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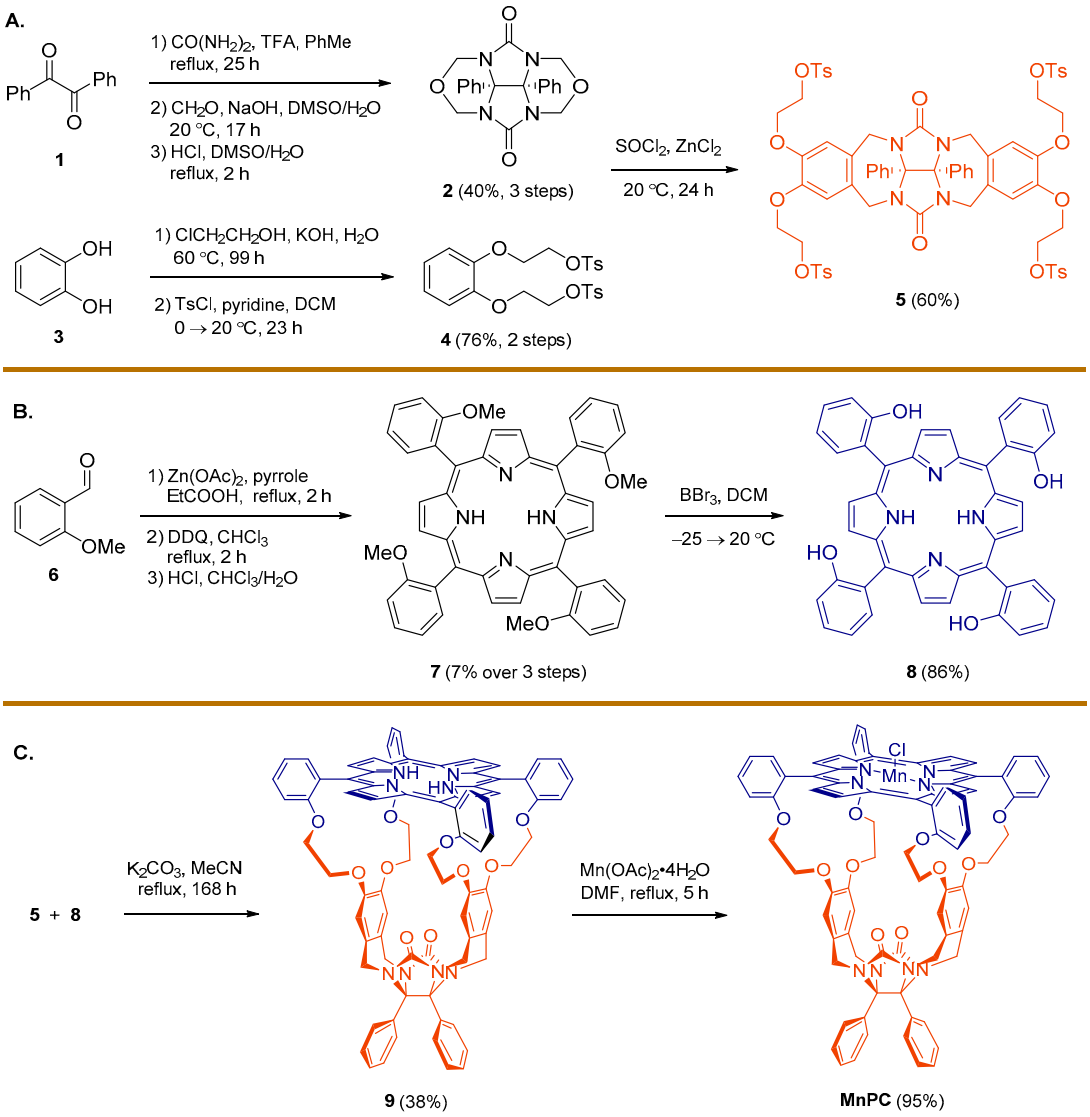
1. Procedures and Methods

1.1. Synthesis of the Manganese Porphyrin Cage Catalyst MnPC

The manganese cage catalyst MnPC was prepared in a multistep procedure developed in our group starting from diphenylglycoluril (**5**) and tetrakis(2-hydroxyphenyl)porphyrin (**8**) (Scheme S1) [1,2]. Thus, the diphenylglycoluril bottom unit was synthesized through the condensation of benzil (**1**) and urea followed by a reaction with formaldehyde and treatment with hydrochloric acid (typical yield 40% over two steps). Next, Friedel–Crafts alkylation of the formed ring ether **2** with the tosyl-protected catechol derivative **4** led to the formation of product **5** in a fair yield (60%). The porphyrin top unit **7** was synthesized by the reaction of 2-methoxybenzaldehyde (**6**) and pyrrole in propionic acid followed by the oxidation with DDQ (up to 7% yield over two steps). The aryl methyl ethers were then cleaved with BBr_3 to give porphyrin **8** in very good yield. Finally, compounds **5** and **8** were connected together while being refluxed in MeCN and in the presence of K_2CO_3 as a base (38% yield). Reaction of the formed macrocycle **9** with $Mn(OAc)_2{\cdot}4H_2O$ in refluxing DMF, followed by oxidation of the manganese center in air, smoothly led to the formation of the metal catalyst MnPC in 95% yield after purification by flash chromatography.

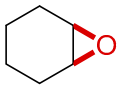


Scheme S1. Preparation of the manganese porphyrin cage catalyst MnPC: (**A**) synthesis of the diphenylglycoluril bottom unit **5**; (**B**) synthesis of tetrakis(2-hydroxyphenyl)porphyrin top unit **8**; (**C**) final connection of the bottom and top units followed by the introduction of manganese into the porphyrin.

1.2. General Procedure for the Catalytic Epoxidation of Olefins to Epoxides

Dioxygen was bubbled through a solution of olefin (0.2 mmol), isobutyraldehyde (2.0 mmol), 4-*tert*-butyl-pyridine (1.0 mmol), and manganese porphyrin (either MnPC or MnTPPCl) (1.0 µmol) in 1,2-dichloroethane (4 mL) at 23 °C. Once the reaction was completed (4–24 h, as checked by TLC or ^{1}H NMR) the solvent was removed under vacuum and the crude reaction mixture was analyzed by ^{1}H NMR to determine the yield of the epoxide and its *cis*:*trans* ratio. Signal assignment of protons of the products in the ^{1}H NMR spectra of the reaction mixture were based on the bibliographical data and yields were calculated by the integration of the corresponding peaks, using furan as and internal standard, which was added to the deuterated solvent [3].

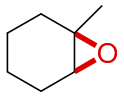
7-Oxabicyclo[4.1.0]heptane



7-Oxabicyclo[4.1.0]heptane was prepared according to the general procedure using 1-methyl-1-cyclohexene (19.6 mg, 0.2 mmol). ^{1}H NMR (400 MHz, δ (ppm), $CDCl_3$) of the main product: 1.15–1.49 (m, 4H), 1.74–2.01 (m, 4H) , 3.12 (s, 2H).

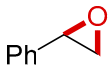
^{13}C NMR (101 MHz, δ (ppm), $CDCl_3$) of the main product: 19.4, 24.4, 52.1. These data were in accordance with those reported in the literature [4].

1-Methyl-7-oxabicyclo[4.1.0]heptane



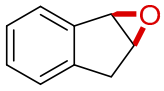
1-Methyl-7-oxabicyclo[4.1.0]heptane was prepared according to the general procedure using 1-methyl-1-cyclohexene (22.4 mg, 1.0 mmol). ^{1}H NMR (400 MHz, δ (ppm), $CDCl_3$) of the main product: 1.15 (m, 1 H), 1.23 (m, 1 H), 1.28 (s, 3 H), 1.32–1.41 (m, 2 H), 1.63 (ddd, *J* = 5.5, 8.0, 14.8 Hz, 1 H), 1.81–1.92 (m, 3 H), 2.93 (d, *J* = 3.5 Hz, 1 H). ^{13}C NMR (101 MHz, δ (ppm), $CDCl_3$) of the main product: 19.7, 20.1, 24.1, 24.8, 30.0, 57.7, 59.7. These data were in accordance with those reported in the literature [5].

2-Phenyloxirane



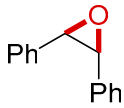
2-Phenyloxirane was prepared according to the general procedure using styrene (24.0 mg, 0.2 mmol). ^{1}H NMR (400 MHz, δ (ppm), $CDCl_3$) of the main product: 2.78 (dd, *J* = 2.6, 5.5 Hz, 1 H), 3.13 (dd, *J* = 4.1, 5.5 Hz, 1 H), 3.87 (dd, *J* = 2.6, 4.1 Hz, 1 H), 7.32–7.38 (m, 5 H). ^{13}C NMR (101 MHz, δ (ppm), $CDCl_3$) of the main product: 51.2, 52.5, 125.5, 128.1, 128.8, 137.5. These data were in accordance with those reported in the literature [6].

1a,6a-Dihydro-6H-indeno[1,2-b]oxirene



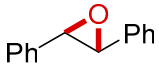
1a,6a-Dihydro-6*H*-indeno[1,2-b]oxirene was prepared the according to general procedure using indene (26.4 mg, 0.2 mmol). ^{1}H NMR (400 MHz, δ (ppm), $CDCl_3$) of the main product: 1.75 (dt, *J* = 5.3, 13.7 Hz, 1 H), 2.39–2.47 (m, 1H), 2.55 (dd, *J* = 5.3, 15.5 Hz, 1 H), 2.77 (dt, *J* = 6.3, 13.7 Hz, 1 H), 3.71–3.77 (m, 1 H), 3.85 (d, *J* = 4.0 Hz, 1H), 7.11 (d, *J* = 6.7 Hz, 1H), 7.19–7.27 (m, 2 H), 7.40 (dd, *J* = 1.3, 7.3 Hz, 1H). ^{13}C NMR (101 MHz, δ (ppm), $CDCl_3$) of the main product: 21.9, 24.4, 53.0, 55.2, 126.3, 128.4, 128.6, 129.7, 132.6, 136.8. These data were in accordance with those reported in the literature [7].

cis-1,2-Diphenyloxirane



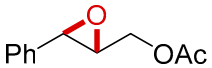
cis-1,2-Diphenyloxirane was prepared according to the general procedure using *cis*-1,2-diphenylethylene (39.3 mg, 0.2 mmol). ^{1}H NMR (400 MHz, δ (ppm), $CDCl_3$) of the main product: 4.33 (s, 2 H), 7.09–7.20 (m, 10 H). ^{13}C NMR (101 MHz, δ (ppm), $CDCl_3$) of the main product: 63.1, 127.0, 127.6, 127.8, 134.5. These data were in accordance with those reported in the literature [8]. By comparing the signal intensity of the epoxide protons, a ratio of *cis*:*trans* stereoisomers of 95:5 was calculated.

trans-1,2-Diphenyloxirane



trans-1,2-Diphenyloxirane was prepared according to the general procedure using *trans*-1,2-diphenylethylene (39.3 mg, 0.2 mmol). ^{1}H NMR (400 MHz, δ (ppm), $CDCl_3$) of the main product: 3.93 (s, 2 H), 7.32–7.41 (m, 10 H). ^{13}C NMR (101 MHz, δ (ppm), $CDCl_3$) of the main product: 63.0, 125.5, 128.2, 128.8, 137.4. These data were in accordance with those reported in the literature [3]. By comparing the signal intensity of the epoxide protons, a ratio of *cis*:*trans* stereoisomers of <1:99 was calculated.

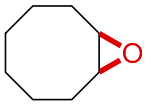
(3-phenyloxiran-2-yl)Methyl acetate



(3-phenyloxiran-2-yl)Methyl acetate was prepared according to the general procedure using cinnamyl acetate (38.4 mg, 0.2 mmol). ^{1}H NMR (400 MHz, δ (ppm), $CDCl_3$) of the main product: 2.02 (s, 3 H), 3.18–3.21 (m, 1 H), 3.71 (d, *J* = 2.0 Hz, 1 H), 4.02 (dd, *J* = 6.7, 12.3 Hz, 1 H), 4.43 (d, *J* = 3.8, 12.3 Hz, 1 H), 7.17–

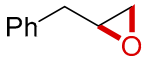
7.28 (m, 5 H). ^{13}C NMR (101 MHz, δ (ppm), $CDCl_3$) of the main product: 20.8, 56.5, 59.2, 64.1, 125.6, 128.4, 128.6, 136.2, 170.7. These data were in accordance with those reported in the literature [9]. By comparing the signal intensity of the epoxide protons, a ratio of *cis*:*trans* stereoisomers of <1:99 was calculated.

9-Oxabicyclo[6.1.0]nonane



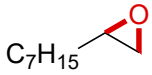
9-Oxabicyclo[6.1.0]nonane was prepared according to the general procedure using *cis*-cyclooctene (25.2 mg, 0.2 mmol). ^{1}H NMR (400 MHz, δ (ppm), $CDCl_3$) of the main product: 1.16–1.59 (m, 10 H), 2.03–2.20 (m, 2 H), 2.81–2.96 (m, 2 H). ^{13}C NMR (101 MHz, δ (ppm), $CDCl_3$) of the main product: 24.9, 26.1, 26.5, 55.7. These data were in accordance with those reported in the literature [10].

2-Benzyloxirane



2-Benzyloxirane was prepared according to the general procedure using 3-phenyl-1-propene (26.8 mg, 0.2 mmol). ^{1}H NMR (400 MHz, δ (ppm), $CDCl_3$) of the main product: 3.10 (dd, J = 7.2, 14.1 Hz, 1 H), 3.30 (dd, J = 7.2, 14.6 Hz, 1 H), 3.65 (dd, J = 5.6, 14.1 Hz, 1H), 3.73 (dd, J = 4.5, 11.3 Hz, 1 H), 4.22–4.33 (m, 1 H), 7.24–7.32 (m, 3 H), 7.33–7.39 (m, 2 H). ^{13}C NMR (101 MHz, δ (ppm), $CDCl_3$): 41.3, 47.3, 59.9, 127.2, 128.6, 129.7, 136.2. These data were in accordance with those reported in the literature [11].

2-Heptyloxirane

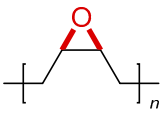


2-Heptyloxirane was prepared according to the general procedure using non-1-ene (28.4 mg, 1.0 mmol). ^{1}H NMR (400 MHz, δ (ppm), $CDCl_3$) of the main product: 0.87 (t, J = 6.5 Hz, 3 H), 1.19–1.58 (m, 12 H), 2.43 (dd, J = 3.0, 4.9 Hz, 1 H), 2.64 (dd, J = 4.1, 4.9 Hz, 1 H), 2.81–2.89 (m, 1 H). ^{13}C NMR (101 MHz, δ (ppm), $CDCl_3$) of the main product: 14.0, 22.1, 25.6, 29.1, 31.4, 32.4, 46.8, 52.2. These data were in accordance with those reported in the literature [12].

1.3. General Procedure for the Catalytic Epoxidation of Polymers

Dioxygen was bubbled through a solution of polymer (0.2 mmol, C=C), isobutyraldehyde (2.0 mmol), 4-*tert*-butyl-pyridine (1.0 mmol), and manganese porphyrin (either MnPC or MnTPPCl) (1.0 μmol) in 1,2-dichloroethane (4 mL) at 23 °C. Once the reaction was completed (8 h, as checked by ^{1}H NMR) the solvent was removed under vacuum and the crude reaction mixture was analyzed by ^{1}H NMR to determine the conversion of the alkene function. Signal assignment of protons of the products in the ^{1}H NMR spectra of the reaction mixture were based on bibliographical data and conversions were calculated by the integration of the corresponding peaks of the starting material and final products. All the epoxidations were repeated three times.

cis-Polybutadiene epoxide



cis-Polybutadiene epoxide was prepared according to the general procedure using *cis*-polybutadiene (11 mg, 0.2 mmol C=C, M_w 200,000~300,000, 98% *cis*). Conversions and stereoselectivities were calculated from the peaks at 5.42 ppm (*cis*-olefin) and 3.01 ppm (*cis*-epoxide) [13], as shown in Figure S1.

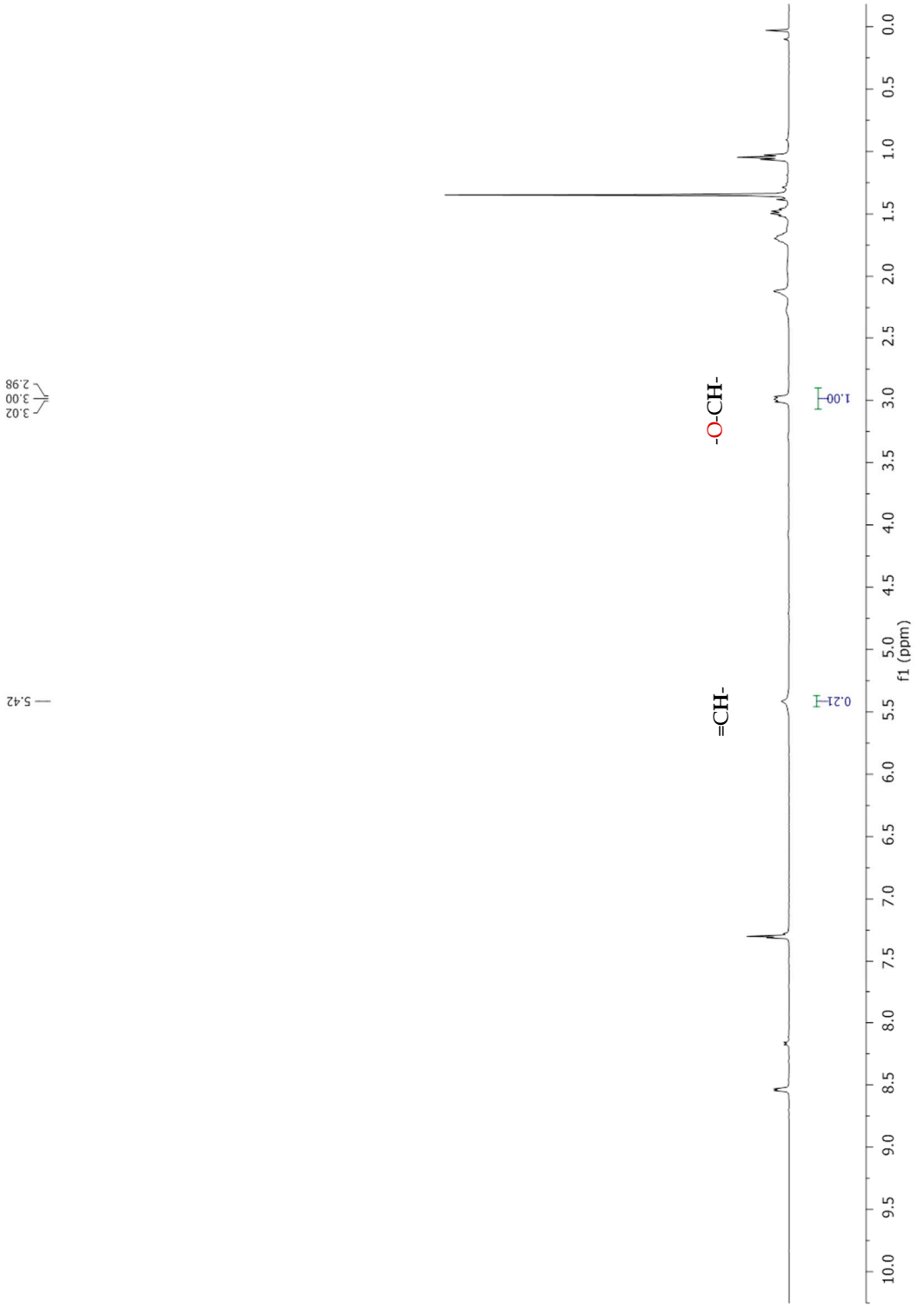
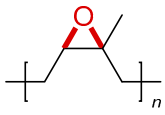


Figure S1. ^{1}H NMR spectrum of a sample of the crude reaction mixture of a catalytic epoxidation of polybutadiene A (M_w = 200,000–300,000; 98% *cis*) after 8 h under the standard conditions, using MnPC as the catalyst.

cis-Polyisoprene epoxide



cis-Polyisoprene epoxide was prepared according to the general procedure using *cis*-polyisoprene (11 mg, 0.2 mmol C=C, 97% *cis*). Conversions and stereoselectivities were calculated from the peaks at 5.11 ppm (*cis*-olefin) and 2.81 ppm (*cis*-epoxide) [14], as shown in Figure S2.

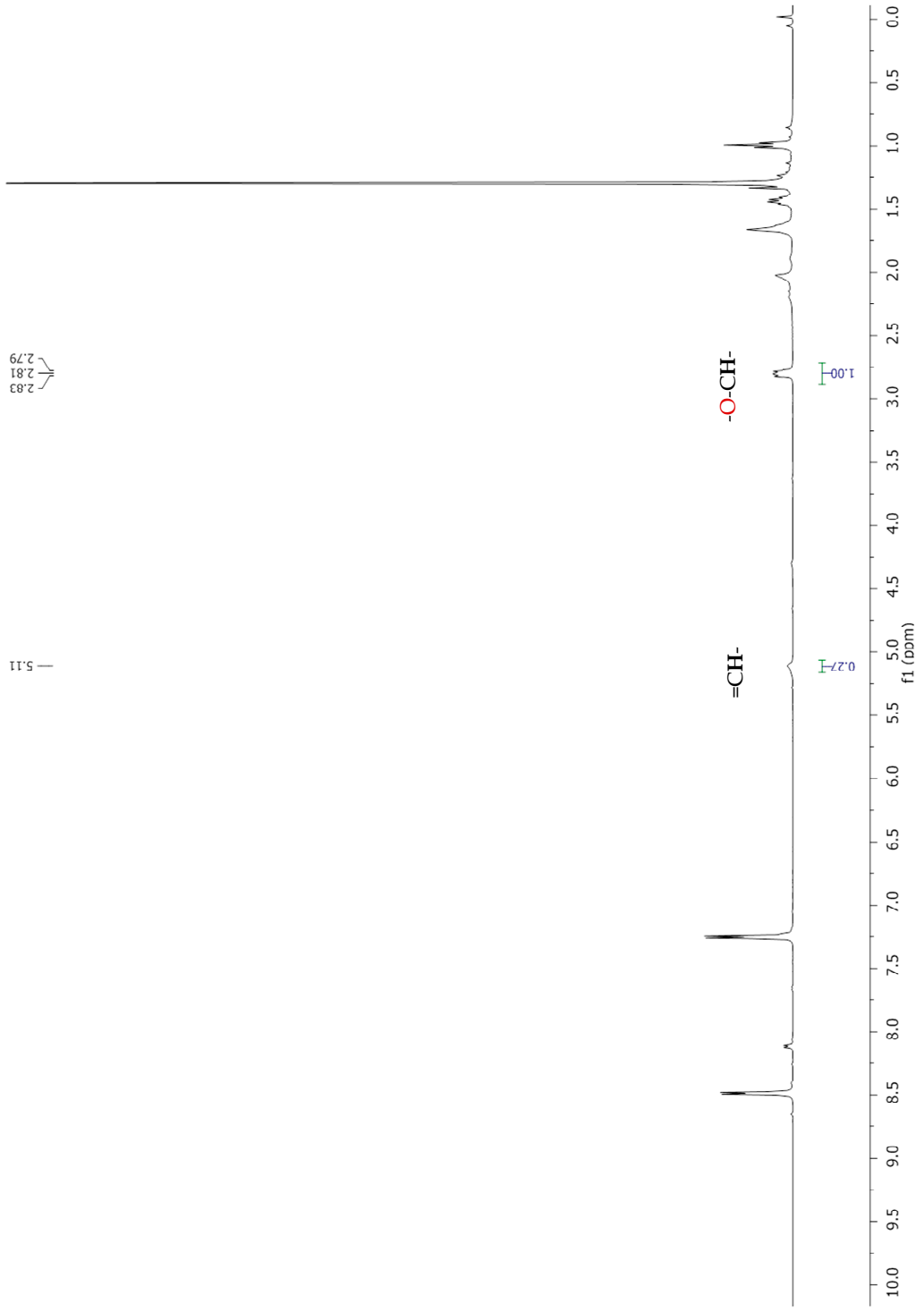


Figure S2. ^{1}H NMR spectrum of a sample of the crude reaction mixture of a catalytic epoxidation of polyisoprene (97% *cis*) after 8 h under the standard conditions, using MnPC as the catalyst.

1.4. Radical Trapping Experiment with BHT

Dioxygen was bubbled to a solution of dichloromethane (5 mL), cyclohexene (0.2 mmol), isobutyraldehyde (2 mmol), 4-*tert*-butyl-pyridine (1.0 mmol), BHT (2 mmol), and manganese porphyrin cage catalyst MnPC (1.0 μmol) at 23 °C. After 8 h of reaction time the solvent was removed under vacuum and the crude product was analyzed by ^{1}H NMR spectroscopy. The corresponding epoxide was formed only in trace amount (<5%).

1.5. In Situ UV–vis Spectra of Manganese Porphyrin Cage Catalyst MnPC

As the reaction proceeded, the absorbance of the Soret band at 480 nm gradually decreased, accompanied by decreases in the absorbance of the bands at 581 nm and 617 nm (Figure S3). At the same time, the color of the reaction mixture changed from green to yellow, indicating the gradual decomposition of the catalyst.

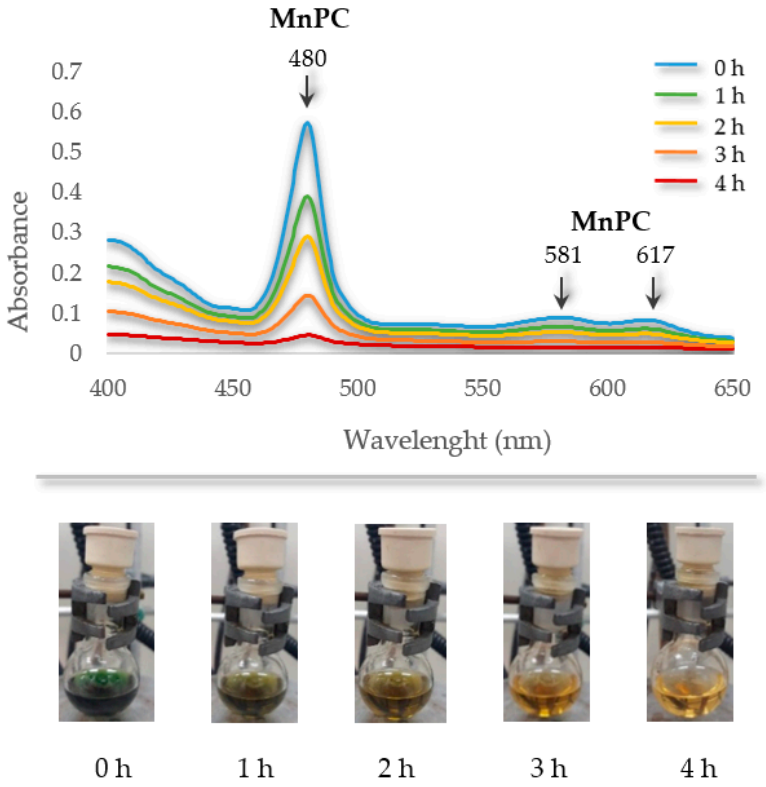


Figure S3. Top: In situ UV-vis spectra of manganese porphyrin cage catalyst MnPC during the aerobic epoxidation of cyclohexene (0.1 mmol) in the presence of isobutyraldehyde (1.0 mmol), 4-*tert*-butyl-pyridine (0.5 mmol), MnPC catalyst (0.5 μmol), DCE (4 mL), O_2-balloon bubbling, 23 °C. Bottom: Color change of the reaction mixture during the epoxidation reaction.

We also recorded the changes in the UV-vis spectra of the reaction mixture in the absence of the substrate (Figure S4). In this case, we also observed a decrease in the absorbance of the Soret and Q bands, but with the concomitant emergence of two new bands at 428 and 525 nm. These new bands provide evidence for the formation of an active manganese oxo species.

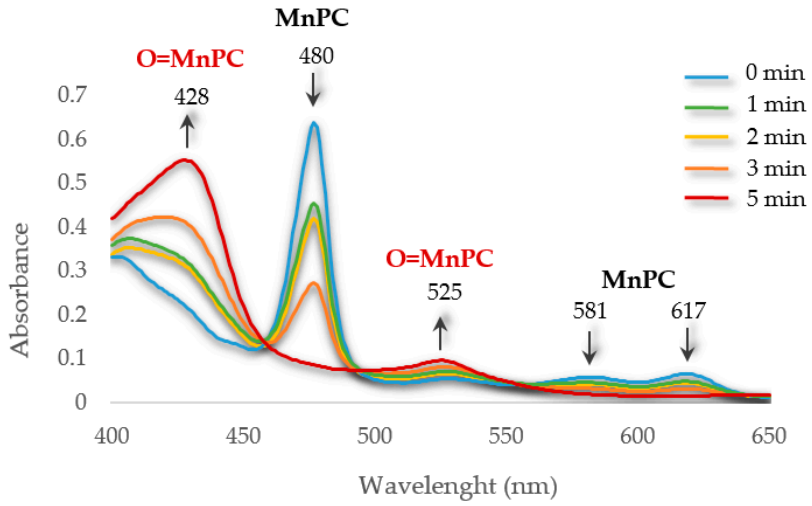


Figure 4. In situ UV-vis spectra of manganese porphyrin cage catalyst MnPC under the aerobic epoxidation conditions in the absence of cyclohexene: isobutyraldehyde (0.1 mmol), 4-*tert*-butyl-pyridine (0.5 mmol), MnPC catalyst (2.0 μmol), DCE (4 mL), O_2-balloon bubbling, 23 °C.

References

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