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Nitration of Halterman porphyrin: a new route for fine tuning chiral iron and manganese porphyrins with application in epoxidation and hydroxylation reactions using hydrogen peroxide as oxidant

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ABSTRACT

A methodology is reported for the regioselective nitration of the phenyl groups of Halterman porphyrin, using $NaNO_2$. These nitro-porphyrins can be reduced to aminoporphyrins and then N-dimethylated to give new optically active porphyrins. Applications to the asymmetric epoxidation of styrene derivatives by H_2O_2 to give optically active epoxides (ee up to 60%) and hydroxylation of alkanes to give optically active secondary alcohols (ee up to 69%) were carried out in organic solvents (dichloromethane/methanol) using chiral iron and manganese porphyrins as catalysts.

1. Introduction

Catalytic asymmetric epoxidation reactions play a major role in organic chemistry since the optically active epoxides are important building blocks.[1–3] In this context, hydrogen peroxide is a very attractive oxidant for sustainable chemistry.[4,5] However, catalytic enantioselective oxidations using transition-metal complexes are still limited when the oxidant is hydrogen peroxide.[6] In particular, catalytic asymmetric reactions in aqueous solutions are attractive, but rare.[7] Recently, there is a revival in developing original and efficient system in asymmetric catalysis. Thus we have now the development of new generations of metal complexes, which are able to selectively catalyze various oxidation reactions using H_2O_2 as oxidant.[3,8,9] A novel and general biomimetic non-haem Fe-catalyzed asymmetric epoxidation of aromatic alkenes by using hydrogen peroxide was reported by Beller and co-workers.[10,11] Other systems including chiral bipyrrolidine,[12] bis-pyridine[13] and Schiff[14] base ligands were also described using iron or manganese as the metal in the active site. Chiral bioinspired iron complexes of N4 ligands based on the ethylenediamine backbone display remarkable levels of enantioselectivity for the first time in the asymmetric epoxidation of α,β-unsaturated ketones using hydrogen peroxide as oxidant (up to 87% ee).[15] Epoxidation catalyzed by non-haem iron and manganese complexes has been reviewed in 2012.[9]

The first asymmetric epoxidation catalyzed by chiral porphyrins was reported by Groves and Myers in 1983.[16] Since then, different chiral iron porphyrins were used by the same author[17] and others.[18–24] The oxidant of choice for these systems is generally iodosyl benzene.[25] It should, however, be emphasized that the extracellular haem-thiolate peroxygenase from *Agrocybe aegerita* (AaeAPO) has been shown to catalyze the epoxidation of styrene derivatives and the hydroxylation of alkylbenzenes with high stereoselectivity using hydrogen peroxide as the terminal oxidant.[26,27]

We previously reported enantioselective sulfoxidation[28] and epoxidation[29] catalyzed by water-soluble iron porphyrin and enantioselective hydroxylation by water-soluble manganese porphyrins using hydrogen peroxide as oxidant.[30] In these results, sulfonation of Halterman porphyrin[31] by sulfuric acid was used to prepare these chiral water-soluble metalloporphyrins. To extend these reactions to organic solvents, preparation of new chiral porphyrins seems to us necessary in order to electronically tune the catalytic activity.[25] We herein report the synthesis of a new generation of chiral porphyrins that bear either a nitro, an amino or a dimethylamino group in the 10-position of the 9-[*anti*-(1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethano-anthracene)]*meso*-

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substituents together with the catalytic oxidation activity of their iron or manganese complexes, using hydrogen peroxide as oxidant.

2. Results and discussion

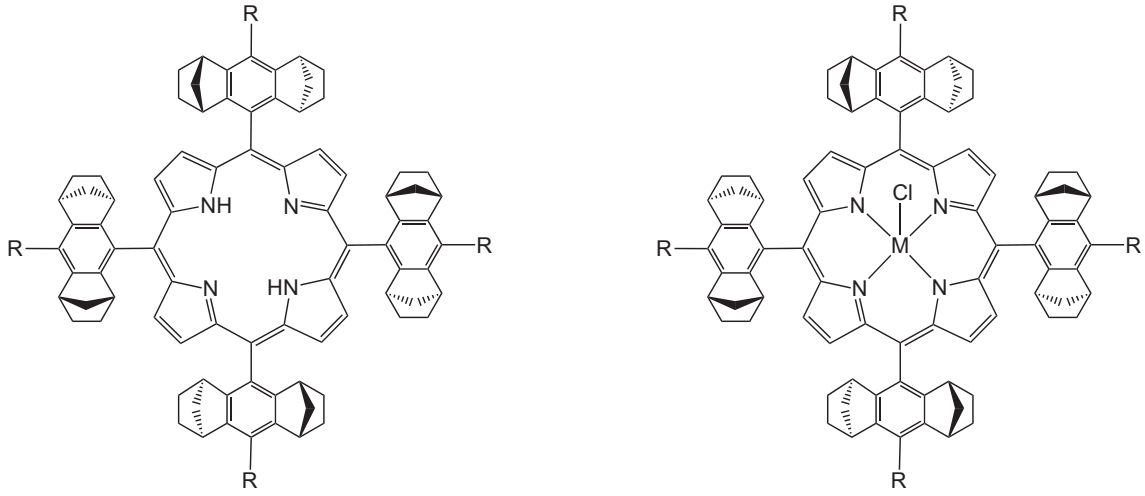
2.1. Synthesis of chiral porphyrins

Several experiments have been previously reported to electronically modified D_4-symmetric metalloporphyrins.[32–34] In all the cases, the key substituted benzaldehyde, which has only the *para*-position open was used for the porphyrin synthesis. However, the efforts were unsuccessful to synthesize the nitro derivative.[32] Thus we decided to test a direct nitration of the porphyrin instead to modify the chiral aldehyde precursor. In 2004, it was reported a nice system for the regioselective nitration of the phenyl group of *meso*-tetraphenylporphyrin, using $NaNO_2$ and trifluoroacetic acid.[35] A similar methodology was herein employed to provide *para*-tetra-nitro Halterman porphyrin. When a concentrated solution of Halterman porphyrin **1** (Fig. 1) in trifluoroacetic acid was treated with 12 equiv of sodium nitrite, the porphyrin **2** was obtained with a good yield (87%). In order to tune the electronic effect of the porphyrin, these nitro-porphyrins were converted to the corresponding aminoporphyrins **3**, by reduction with tin(II) chloride and HCl in 90% yield, as previously reported in the literature for the simplest tetraphenylporphyrins.[36] These chiral porphyrins were then N-dimethylated using iodomethane giving **4** with a method previously described.[37] All the syntheses are summarized in Scheme 1. Classical metallation[38] of these new porphyrins was carried out in DMF, using the corresponding $FeBr_2$ or $MnBr_2$ salts (see Experimental section and Scheme 2).

Following our successful synthesis of the *para*-substituted Halterman iron porphyrins, their catalytic activity was first tested in the epoxidation of styrene derivatives (Scheme 3). Epoxidation was initially catalyzed in presence of imidazole in a mixture of CH_2Cl_2/CH_3OH (1:1 ratio) by the chiral iron complex **5** (R=H, Fig. 1) to obtain a reference. Although the asymmetric induction with **5** is reasonable (39%), the viability of the process is limited owing to a low conversion after 1 h and 2 h were necessary to get 30% conversion. As expected with a ligand bearing electron-donor groups (NMe_2) (compound **7**), epoxidation reactions were also slow with a somewhat increased enantioselectivity (53%). In contrast, epoxidation with nitro derivative **6** was fast and a correct conversion (62%) was obtained after 2 h. The results are summarized in Table 1.

As shown in Table 1, epoxide conversions between 3% and 80% were obtained with enantiomeric excess as high as 60% for 3-methylstyrene and 1,2-dihydronaphthalene. The key role of imidazole in metalloporphyrin-catalyzed oxygenations with H_2O_2, evidenced by Mansuy co-workers[40] in olefin epoxidation with iodosyl benzene is also confirmed herein, since only a very weak conversion (<5%) was detected in absence of this ligand. In these reactions, only traces of aldehydes were also detected as by-products.

Prior to this work, we also reported the asymmetric epoxidation of alkenes to give optically active epoxides in water/methanol solutions using a water-soluble sulfonated Halterman manganese porphyrin.[30] It should also be noted that aqueous hydrogen peroxide has been used once as the oxidant for enantioselective epoxidation using a manganese-glycoconjugated porphyrin as the catalyst in biphasic medium, but the enantioselectivity was modest.[41] For comparison, the herein prepared manganese porphyrins were also tested for epoxidation. The results are summarized in Table 2. As expected, the conversions were generally higher by comparison with the reactions carried out with the iron catalyst. Using the nitro derivative **9** as catalyst, the styrene epoxide was



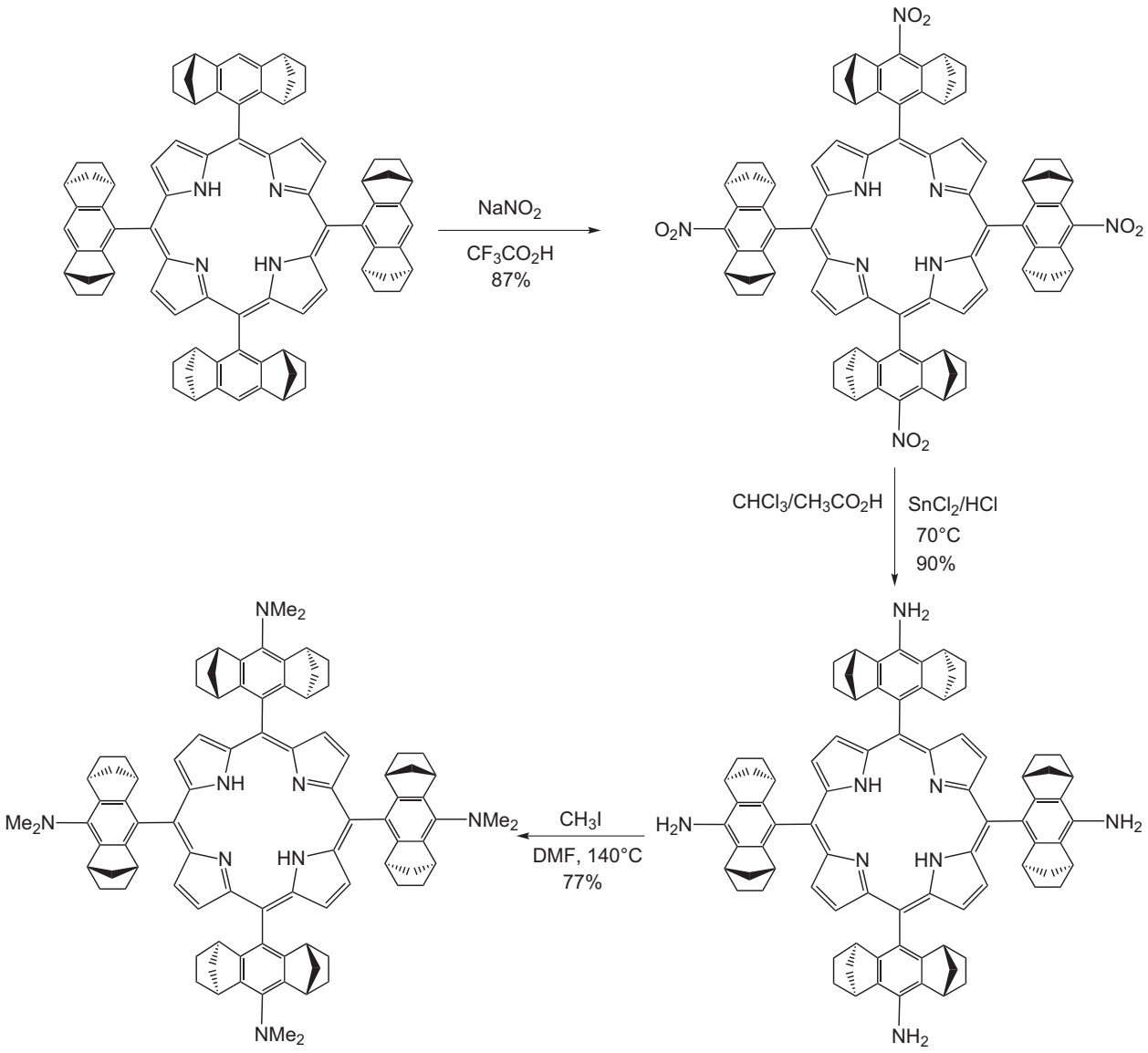
1-R = H (Halt)
2-R = p-NO_2 (Halt p-NO_2)
3-R = p-NH_2 (Halt p-NH_2)
4-R = p-NMe_2 (Halt p-NMe_2)

5-M = Fe, R = H (FeCl Halt)
6-M = Fe, R = p-NO_2 (FeCl Halt p-NO_2)
7-M = Fe, R = p-NMe_2 (FeCl Halt p-NMe_2)
8-M = Mn, R = H (MnCl Halt)
9-M = Mn, R = p-NO_2 (MnCl Halt p-NO_2)
10-M = Mn, R = p-NMe_2 (MnCl Halt p-NMe_2)

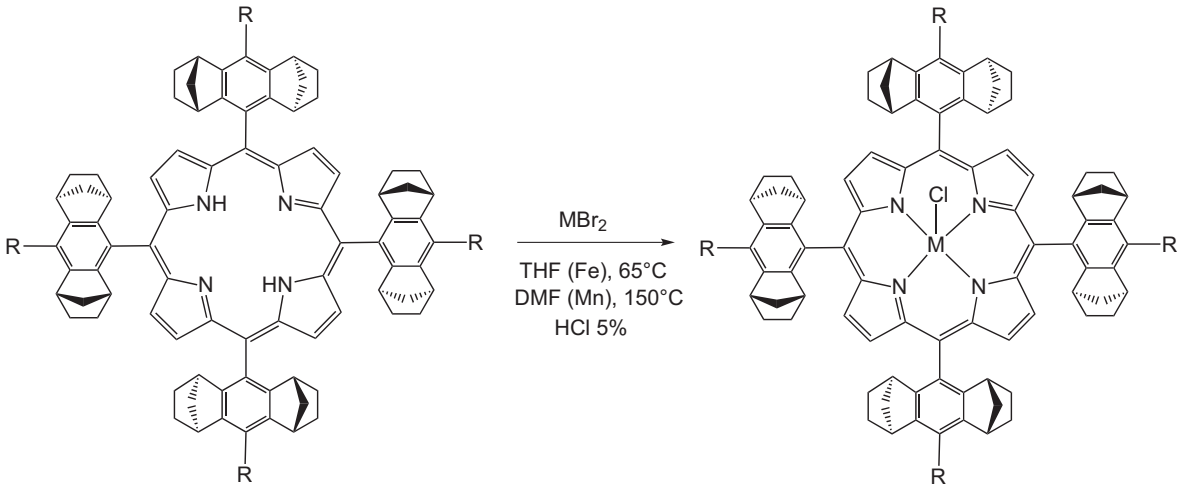
Fig. 1. Structures of chiral porphyrins and metal catalysts.

2.2. Catalytic epoxidation of alkenes

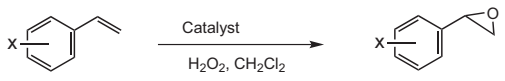
Optically active epoxide-containing compounds are of great interest, particularly to synthetic organic chemists and to bio-organic chemists.[39] Thus the use of hydrogen peroxide has been recently the focus of intense studies as green oxidant for asymmetric oxidation. However, despite a good enantioselectivity, these catalysts suffer from the drawback of moderate stability and there are only few catalytic studies using iron as a metal in the active site.[8]



Scheme 1. Synthesis of modified Halterman porphyrins.



Scheme 2. Metallation of chiral porphyrins.



Scheme 3. Epoxidation of alkenes by hydrogen peroxide.

Table 1
Asymmetric epoxidation of styrene derivatives catalyzed by FeCl Halt *p*-R (R=H (**5**), NO_2 (**6**), NMe_2 (**7**))-H_2O_2-Imidazole system[a]

Entry	Substrate	Catalyst	Conversion[b] (%)	ee[c] (%) (config)[d]
1	Styrene	**5**	30	39 (*S*)
2	Styrene	**6**	62	52 (*S*)
3	Styrene	**7**	34	53 (*S*)
4	4-Methylstyrene	**5**	75	10 (*S*)
5	4-Methylstyrene	**6**	80	8 (*S*)
6	4-Methylstyrene	**7**	79	18 (*S*)
7	4-Chlorostyrene	**5**	46	28 (*S*)
8	4-Chlorostyrene	**6**	18	41 (*S*)
9	4-Chlorostyrene	**7**	19	45 (*S*)
10	2-Methylstyrene	**6**	42	39 (*S*)
11	3-Methylstyrene	**6**	55	60 (*S*)
12	3-Trifluoromethylstyrene	**6**	10	56 (*S*)
13	4-Trifluoromethylstyrene	**6**	3	39 (*S*)
14	1,2-Dihydronaphthalene	**6**	65	60 (1*S*,2*R*)

[a] Reaction conditions: catalyst/imidazole/substrate/H_2O_2 1:10:1000:100 in 1 ml distilled CH_2Cl_2/MeOH mixture (0.5:0.5) under argon for 2 h.
[b] Determined by GC on the crude reaction mixture with traces of aldehyde and based on oxidant.
[c] Determined by GC on a chiral CP-Chirasil-Dex column.
[d] Absolute configuration of the epoxide of styrene was determined by comparison with the authentic optically pure (*R*)-(+)-styrene oxide. Others were deduced from analogy of the GC behavior and of the optical rotatory of (*R*)-(+)-styrene oxide.

Table 2
Asymmetric epoxidation of styrene derivatives catalyzed by MnCl Halt *p*-R (R=H (**8**), NO_2 (**9**), NMe_2 (**10**))−H_2O_2−imidazole system[a]

Entry	Substrate	Catalyst	Conversion[b] (%)	ee[c] (%) (config)[d]
1	Styrene	**8**	39	45 (*S*)
2	Styrene	**9**	98	48 (*S*)
3	Styrene	**10**	7	40 (*S*)
4	4-Methylstyrene	**8**	71	49 (*S*)
5	4-Methylstyrene	**9**	80	13 (*S*)
6	4-Methylstyrene	**10**	12	15 (*S*)
7	4-Chlorostyrene	**8**	24	29 (*S*)
8	4-Chlorostyrene	**9**	84	40 (*S*)
9	4-Chlorostyrene	**10**	10	32 (*S*)
10	2-Methylstyrene	**9**	45	37 (*S*)
11	3-Methylstyrene	**9**	62	51 (*S*)
12	3-Trifluoromethylstyrene	**9**	87	52 (*S*)
13	4-Trifluoromethylstyrene	**9**	80	30 (*S*)
14	1,2-Dihydronaphthalene	**9**	70	55 (1*S*,2*R*)

[a] Reaction conditions: catalyst/imidazole/substrate/H_2O_2 1:24:40:200 in 1 ml distilled CH_2Cl_2 under argon for 2 h.
[b] Determined by GC on the crude reaction mixture with traces of aldehyde.
[c] Determined by GC on a chiral CP-Chirasil-Dex column.
[d] Absolute configuration of the epoxide of styrene was determined by comparison with the authentic optically pure (*R*)-(+)-styrene oxide. Others were deduced from analogy of the GC behavior and of the optical rotatory of (*R*)-(+)-styrene oxide.

formed with very good conversion (98%) after 2 h and 48% enantioselectivity. As anticipated from the reactivity of an electrophilic oxo-Mn(V)-porphyrin as active species, the best conversions were obtained with metalloporphyrins bearing electron-withdrawing substituents (NO_2) whereas no clear trend was evident for optical yields upon changing the *para*-substituent of the Halterman porphyrin ligand. We also investigated the epoxidation of *para*-substituted styrenes. As shown in Table 2, *para*-substitution has a weak effect upon the enantioselectivity of styrene epoxidation, the best ee (55%) being obtained with 1,2-dihydronaphthalene. It should also be noted that the replacement of iron by manganese has a small detrimental effect on the enantioselectivity.

Other factors affecting the catalytic epoxidation of olefins by chiral water-soluble manganese porphyrins and hydrogen peroxide have been recently investigated by us.[30] First, it was recognized the presence of water in methanol can be quite successful and that working in basic buffered solutions increases deeply the efficiency of the system. Thus efficient asymmetric oxidation of alkenes with an equimolar amount of H_2O_2 with respect of the substrate was possible.[30] In contrast, a substrate/H_2O_2 ratio of 1:5 was necessary to get a correct conversion in dichloromethane/methanol solvent (see Table 2), showing a somehow better efficient system in water.

2.3. Hydroxylation of arylalkanes

We then first studied the hydroxylation reaction catalyzed by iron porphyrin **5**, which is clearly an electron-rich iron porphyrin, using H_2O_2 as oxidant. Treatment of ethylbenzene (10 equiv) with hydrogen peroxide (1 equiv) and a catalytic quantity of catalyst **5** in H_2O/MeOH (1:5) at room temperature for 1 h afforded in a very low yield (5% conversion) as a mixture of (*S*)-1-phenyl ethanol (47%) and acetophenone (53%) (Table 3, entry 3). The enantiopurity of the phenyl ethanol was determined to be 15% by chiral capillary GC analysis. Due to this detrimental situation and because iodobenzene diacetate ($PhI(OAc)_2$) is an efficient terminal oxidant in iron(III)porphyrin complex-catalyzed oxygenation reactions in presence of water,[42] similar reactions were undertaken, using $PhI(OAc)_2$ instead of H_2O_2, for comparison with the manganese system (vide infra). The results, which are summarized in Table 3, show that this oxidant converted ethylbenzene to the corresponding secondary alcohol with a better conversion (41%) and higher ee (68%). Similar yields and ees were obtained for the hydroxylation of substituted ethylbenzene and indane (Table 3).

Table 3
Asymmetric hydroxylation catalyzed by FeCl Halt *p*-R (R=H (**5**), NO_2 (**6**), NMe_2 (**7**))−$PhI(OAc)_2$−imidazole system[a]

Entry	Substrate	Catalyst	Conversion (%)[b]	Alcohol/ketone ratio (%)[b]	ee[c] (%) (Config)
1	Ethylbenzene	**5**	41	83:17	68 (*R*)
2	Ethylbenzene	**6**	31	80:20	69 (*R*)
3	Ethylbenzene[d]	**5**	5	47:53	15 (*R*)
4	Ethylbenzene	**7**	35	77:23	56 (*R*)
5	Indane	**5**	98	90:10	53[e] (*R*)
6	Indane	**6**	63	64:36	38[e] (*R*)
7	Indane	**7**	66	70:30	37[e] (*R*)
8	4-Ethyltoluene	**5**	33	91:9	63 (*R*)
9	4-Ethyltoluene	**6**	18	80:20	66 (*R*)
10	4-Ethyltoluene	**7**	16	78:22	59 (*R*)
11	2-Ethyltoluene	**6**	11	60:40	57 (*R*)
12	3-Ethyltoluene	**6**	27	70:30	32 (*R*)

[a] Reaction conditions: catalyst/imidazole/substrate/$PhI(OAc)_2$ 1:10:1000:100 in 1 ml mixture CH_2Cl_2/MeOH/H_2O (0.5:0.4:0.1) under argon for 2 h.
[b] Determined by GC on the crude reaction mixture and based on oxidant.
[c] Determined by GC on a chiral CP-Chirasil-Dex column.
[d] With 1 equiv of hydrogen peroxide and 10 equiv of substrate in H_2O/methanol (1:5).
[e] Determined by chiral HPLC with a chiralcel OB-H column.

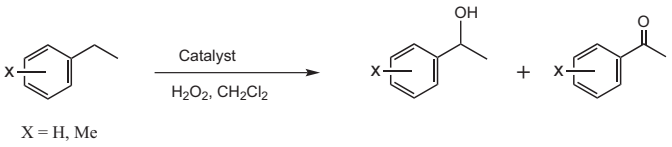
Since it has been reported that Mn(III)porphyrins are much better catalysts than Fe porphyrins for oxygen-atom transfer from H_2O_2 to hydrocarbons,[40] hydroxylation reactions were also carried out with H_2O_2 using the electronically modified Halterman Mn catalysts. The stereoselectivity of catalytic hydroxylation of alkylbenzenes and cycloalkylbenzenes by the manganese catalysts is illustrated in Table 4. The hydrocarbons with saturated side chains, i.e., ethylbenzene and indane, were converted to the corresponding

Table 4
Asymmetric hydroxylation catalyzed by MnCl Halt *p*-R (R=H (**8**), NO_2 (**9**), NMe_2 (**10**))–H_2O_2–imidazole system[a]

Entry	Substrate	Catalyst	Conversion[b] (%)	Alcohol/ketone ratio[b] (%)	ee[c] (%) (config)
1	Ethylbenzene	**8**	3	37:63	3 (*R*)
2	Ethylbenzene	**9**	11	30:70	18 (*R*)
3	Ethylbenzene	**10**	2	54:46	—
4	Indane	**8**	15	70:30	7[d] (*R*)
5	Indane	**9**	11	72:28	33[d] (*R*)
6	Indane	**10**	12	75:25	15[d] (*R*)
7	4-Ethyltoluene	**8**	4	60:40	20 (*R*)
8	4-Ethyltoluene	**9**	18	80:20	38 (*R*)
9	4-Ethyltoluene	**10**	2	51:49	27 (*R*)
10	2-Ethyltoluene	**9**	7	65:35	37 (*R*)
11	3-Ethyltoluene	**9**	33	52:48	21 (*R*)

[a] Reaction conditions: catalyst/imidazole/substrate/H_2O_2 1:24:40:200 in 1 ml mixture CH_2Cl_2 under argon for 2 h.
[b] Determined by GC on the crude reaction mixture.
[c] Determined by GC on a chiral CP-Chirasil-Dex column.
[d] Determined by chiral HPLC with a chiralcel OB-H column.

conjugated secondary benzyl alcohols with ees up to 38% but with a very low conversion. An important amount of α-ketones (up to 70%) was observed. As an example, treatment of ethylbenzene (1 equiv) with hydrogen peroxide (5 equiv) and a catalytic quantity of complex **9** in CH_2Cl_2 at room temperature for 2 h afforded (11% conversion) a mixture of 1-phenyl ethanol (30%) and acetophenone (70%) (Table 4, entry 2). The enantiopurity of the phenyl ethanol was determined to be 18% by chiral capillary GC analysis. As shown in Table 4, 2-, 3-, 4-ethyltoluenes and indane are also effective substrates for the **9**-catalyzed asymmetric hydroxylation and the corresponding 1-arylethanols were produced in low yields and ees of 21–38% (entries 5, 8, 10, 11). As expected for electron-donating group, the conversion (<12%) was much lower when the dimethylamino group was in the *para*-position of the Halterman porphyrin ring (entries 3, 6, 9). An intermediate situation was observed for catalyst **8**. As previously reported with other chiral metalloporphyrins,[17] the manganese porphyrins provided alcohols with the same configuration in excess but with a much lower selectivity than those obtained with the iron analogues. This was explained by the formation of longer lived manganese radical intermediates after hydrogen atom removal[43] (Scheme 4).



Scheme 4. Hydroxylation of arylalkanes by hydrogen peroxide.

3. Conclusion

Our results using complexes **8**–**10** in catalytic epoxidations show large electronic effects for their reactivity. The NO_2-substituted manganese porphyrin catalysts were the best. The better reactivity was attributed to the electron-withdrawing effect of the four NO_2 substituents in *para*-position of the four phenyl rings. A similar suggestion was proposed by Berkessel and co-workers.[33] for the epoxidation of alkenes catalyzed by ruthenium porphyrin bearing CF_3 groups, and using 2,6-dichloropyridine *N*-oxide as oxidant. In contrast, we observe only moderate enantioselectivity changes with the electronically tuned Halterman metalloporphyrins. A different situation was reported in the (salen)Mn-catalyzed asymmetric epoxidation.[44] In this case, enantioselectivity correlates directly with the electronic properties of the ligand substituents, with complexes bearing electron-donating substituents affording highest ees. The results obtained with iron catalysts did not show similar effects and moderated reactivity changes were observed. For a deeper understanding of the role of the porphyrin ligand in the herein reactions, a more detailed analysis of the electronic effect will be necessary for a mechanistic interpretation.

4. Experimental

4.1. General

All reactions were performed under argon. Solvents were distilled from an appropriate drying agent prior to use: CH_2Cl_2 from CaH_2, $CHCl_3$ from K_2CO_3. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Merck precoated aluminium foil sheets (Silica gel 60 with fluorescent indicator UV254). Compounds were visualized with UV light at 254 nm. Column chromatographies were carried out using silica gel from Merck (0.063–0.200 mm) and neutral aluminium oxide, neutral, Brockmann I, 50–200 μm, 60 Å. ^{1}H NMR in $CDCl_3$ were recorded using Bruker (Advance 400dpx spectrometer) at 400 MHz. High resolution mass spectra were recorded on a Thermo-Fisher Q-Exactive spectrometer in ESI positive mode at the CRMPO at Rennes. Liquid UV–visible spectra were recorded on an UVIKON XL from Biotech. All catalytic reactions were controlled on a Varian CP-3380 GC system that was equipped with a CP-Chirasil-Dex Column (25 m, 0.25 mm I.D.) HPLC analysis was realized on a Varian Prostar 218 system equipped with a Chiralcel OB-H column. The enantiomeric excess of epoxides and alcohols was determined on a Varian CP-3380 GC system. The absolute configuration of epoxides and alcohols was obtained from optical rotations on a PerkinElmer model 341 polarimeter. The Halterman porphyrin **1** was synthesized as previously described in the literature.[45]

4.2. Porphyrin and metalloporphyrin syntheses

4.2.1. 5,10,15,20-Tetrakis-(10-nitro-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-dimethano-anthracen-9-yl)-porphyrin ***2***. Porphyrin **1** (150 mg, 0.131 mmol) was dissolved in 9 ml TFA and excess sodium nitrite (109 mg, 1.57 mmol) was added. The mixture was stirred at room temperature for 1 h. The resulting green solution was poured into ice and neutralized with saturated aqueous $NaHCO_3$ until pH 8–9. The resulting purple solution was extracted with chloroform and dried over sulfate magnesium. After evaporation, the resulting precipitate was recovered by vacuum filtration, washed with methanol and dried to give 154 mg of a red-brown solid. Yield: 87%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 8H, β pyrrole), 4.18 (s, 8H, CH), 2.72 (s, 8H, CH), 1.99 (m, 16H, CH_2), 1.53 (m, 8H, CH_2), 1.36 (m, 16H, CH_2), 1.03 (m, 8H, CH_2), −2.65 (s, 2H, NH pyrrole). UV–vis ($CHCl_3$), λ_{max}, nm (ε, M^{-1} cm^{-1}) 424 (395.926×10^3), 516 (20.801×10^3), 550 (7.659×10^3), 590 (5.957×10^3), 645 (2.176×10^3). HRMS [ESI] *m*/*z* calcd for $C_{84}H_{75}N_8O_8$: 1323.5702 $[M+H]^+$, found: 1323.5700.

4.2.2. 5,10,15,20-Tetrakis-(10-amino-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-dimethano-anthracen-9-yl)-porphyrin ***3***. Porphyrin **2** (120 mg, 0.090 mmol) was dissolved in a mixture of 22 ml of $CHCl_3$ and 32 ml of acetic acid. Tin(II) chloride (540 mg, 2.85 mmol) in 32.5 ml concentrated HCl was then added. The mixture was stirred at 70 °C for 40 h. The resulting green solution was poured into ice and neutralized with dilute NH_4OH to pH 8–9. The resulting purple solution was extracted with chloroform and dried over sulfate magnesium. After evaporation, the crude product was purified on neutral aluminium oxide column, using $CHCl_3$ as eluent, to give after evaporation 98 mg of a red-brown solid. Yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 8H, β pyrrole), 3.53 (s, 8H, CH), 2.70 (s, 8H, CH), 1.93 (m, 8H, CH_2), 1.77 (m, 8H, CH_2), 1.30 (m,

24H, CH_2), 0.98 (m, 8H, CH_2), −2.59 (s, 2H, NH pyrrole). UV–vis ($CHCl_3$), λ_{max}, nm (ε, M^{-1} cm^{-1}) 430 (245.200×10^3), 522 (13.176×10^3), 560 (9.179×10^3), 596 (3.664×10^3), 652 (4.520×10^3). HRMS [ESI] *m/z* calcd for $C_{84}H_{83}N_8$: 1203.6735 $[M+H]^+$, found: 1203.6734.

4.2.3. 5,10,15,20-Tetrakis-(10-dimethylamino-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-dimethano-anthracen-9-yl)-porphyrin ***4****.* Porphyrin **3** (100 mg, 0.083 mmol) was dissolved in 10 ml DMF and excess iodomethane (354 mg, 2.5 mmol) and sodium hydride (20 mg, 0.83 mmol) were added. The reaction mixture was stirred for 15 min at room temperature and heated at 140 °C for 30 min. After DMF evaporation under high vacuum, the crude product was purified on neutral aluminium oxide column, using $CHCl_3$ as eluent, to give after evaporation 84 mg of a red-brown solid. Yield: 77%.

^1H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 8H, β pyrrole), 3.83 (s, 8H, CH), 3.10 (s, 24H, NMe_2), 2.66 (s, 8H, CH), 1.90 (m, 8H, CH_2), 1.81 (m, 8H, CH_2), 1.40 (m, 8H, CH_2), 1.25 (m, 16H, CH_2), 1.01 (m, 8H, CH_2), −2.59 (s, 2H, NH pyrrole). UV–vis ($CHCl_3$), λ_{max}, nm (ε, M^{-1} cm^{-1}) 426 (266.797×10^3), 521 (15.299×10^3), 557(8.576×10^3), 593 (4.325×10^3), 650 (3.782×10^3). HRMS [ESI]: *m/z* calcd for $C_{92}H_{99}N_8$: 1315.7987 $[M+H]^+$, found: 1315.7997.

4.2.4. Chloro(5,10,15,20-Tetrakis-(10-nitro-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-dimethano-anthracen-9-yl)-porphyrin) iron(III) ***6****.* Porphyrin **2** (50 mg, 0.037 mmol) in 10 ml THF was heated at 65 °C under argon. $FeBr_2\cdot4H_2O$ (163 mg, 0.75 mmol) was then added and the reaction mixture was stirred until disappearance of the starting material controlled by UV–vis spectroscopy (2 h). The reaction mixture was allowed to cool to room temperature and THF evaporated under vacuum. The crude product was dissolved in 15 ml $CHCl_3$ and stirred for 20 min with 5 ml hydrochloric acid (5%). After phase separation and evaporation of $CHCl_3$, the crude product was purified on silica gel column, using a mixture $CHCl_3/CH_3OH$ (9.5:0.5) as eluent, to give after evaporation 42 mg of a green-brown solid. Yield: 84%.

UV–vis ($CHCl_3$), λ_{max}, nm (ε, M^{-1} cm^{-1}) 424 (70.591×10^3), 509 (9.108×10^3), 579 (2.675×10^3). HRMS [ESI]: *m/z* calcd for $C_{84}H_{72}ClFeN_8O_8$: 1411.4511 $[M]^{+\bullet}$, found: 1411.4509.

4.2.5. Chloro(5,10,15,20-Tetrakis-(10-dimethylamino-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-dimethano-anthracen-9-yl)-porphyrin) iron(III) ***7****.* Porphyrin **4** (40 mg, 0.030 mmol) in 10 ml THF was heated at 65 °C under argon. $FeBr_2\cdot4H_2O$ (129 mg, 0.60 mmol) was then added and the reaction mixture was stirred until disappearance of the starting material controlled by UV–vis spectroscopy (2 h). The reaction mixture was allowed to cool to room temperature and THF evaporated under vacuum. The crude product was dissolved in 15 ml $CHCl_3$ and stirred for 20 min with 5 ml hydrochloric acid (5%). After phase separation and evaporation of $CHCl_3$, the crude product was purified on silica gel column, using a mixture $CHCl_3/CH_3OH$ (9.5:0.5) as eluent, to give after evaporation 30 mg of a green-brown solid. Yield: 68%.

UV–vis ($CHCl_3$), λ_{max}, nm (ε, M^{-1} cm^{-1}) 421 (45.060×10^3), 510 (5.504×10^3), 583(1.686×10^3). HRMS [ESI]: *m/z* calcd for $C_{92}H_{97}ClFeN_8$: 1404.6874 $[M+H]^+$, found: 1404.6863.

4.2.6. Chloro(5,10,15,20-Tetrakis-(10-nitro-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-dimethano-anthracen-9-yl)-porphyrin) manganese(III) ***9****.* Porphyrin **2** (30 mg, 0.022 mmol) in 10 ml DMF and 2,6-lutidine (7–8 mg, 0.07 mmol) were heated at 150 °C under argon. $MnBr_2\cdot4H_2O$ (65 mg, 0.22 mmol) was then added and the reaction mixture was stirred until disappearance of the starting material controlled by UV–vis spectroscopy (8 h). The reaction mixture was allowed to cool to room temperature and DMF evaporated under high vacuum. The crude product was dissolved in 10 ml $CHCl_3$ and stirred for 20 min with 5 ml hydrochloric acid (5%). After phase separation and evaporation of $CHCl_3$, the crude product was purified on silica gel column, using a mixture $CHCl_3$:CH_3OH (19:1) as eluent, to give after evaporation 21 mg of a green solid. Yield: 65%.

UV–vis ($CHCl_3$), λ_{max}, nm (ε, M^{-1} cm^{-1}) 480 (103.453×10^3), 585 (9.073×10^3), 620(8.775×10^3). HRMS [ESI]: *m/z* calcd for $C_{84}H_{72}MnN_8O_8$ 1375.4848 $[M-Cl]^+$, found: 1375.4848.

4.2.7. Chloro(5,10,15,20-Tetrakis-(10-dimethylamino-1,2,3,4,5,6,7,8-octahydro-1,4;5,8-dimethano-anthracen-9-yl)-porphyrin) manganese(III) ***10****.* Porphyrin **4** (50 mg, 0.0379 mmol) in 10 ml DMF and 2,6-lutidine (12–13 mg, 0.11 mmol) were heated at 150 °C under argon. $MnBr_2\cdot4H_2O$ (109 mg, 0.38 mmol) was then added and the reaction mixture was stirred until disappearance of the starting material controlled by UV–vis spectroscopy (8 h). The reaction mixture was allowed to cool to room temperature and DMF evaporated under high vacuum. The crude product was dissolved in 15 ml $CHCl_3$ and stirred for 20 min with 5 ml hydrochloric acid (5%). After phase separation and evaporation of $CHCl_3$, the crude product was purified on silica gel column, using a mixture $CHCl_3/CH_3OH$ (9.5:0.5) as eluent, to give after evaporation 37 mg of a green solid. Yield: 70%.

UV–vis ($CHCl_3$), λ_{max}, nm (ε, M^{-1} cm^{-1}) 480 (70.782×10^3), 586 (7.330×10^3), 624(7.871×10^3). HRMS [ESI]: *m/z* calcd for $C_{92}H_{96}MnN_8$ 1367.7133 $[M-Cl]^+$, found: 1367.7136.

4.3. Catalytic oxidation procedure

4.3.1. General procedure for the catalytic epoxidation reaction of olefins with iron porphyrin catalyst and hydrogen peroxide. Iron porphyrin complex **5** (1.2 mg, 1 μmol) and imidazole (0.34 mg, 10 μmol) were placed in a test tube under argon. Then, 1 ml of distilled CH_2Cl_2/MeOH mixture (0.5:0.5) was added, followed by styrene (104 mg, 1 mmol). Aqueous H_2O_2 (35%) (9.7 mg, 100 μmol) in 0.1 ml MeOH was added over a period of 1 h with a syringe-pump. After the addition of all the H_2O_2, the reaction mixture was allowed to stir for an additional 1 h. The mixture was analyzed by GC for oxidation yield based on H_2O_2, 30%, and for epoxide enantiomeric excess, 39% (conditions used: 80 °C (1 min), 1 °C min^{-1} 80–120 °C, 2.5 °C min^{-1} 120–180 °C). Polarimetric measurement of the oxidation product determined that (*S*)-(−)-styrene epoxide was formed in excess. Only traces of phenylacetaldehyde were detected.

The reaction and analysis of the other substrates and catalysts in Table 1 were carried out in an identical manner with that used for styrene epoxidation.

4.3.2. General procedure for the catalytic epoxidation reaction of olefins with manganese porphyrin catalyst and hydrogen peroxide. Manganese porphyrin complex **8** (1.2 mg, 1 μmol) and imidazole (0.14 mg, 4 μmol) were placed in a test tube under argon. Then, 1 ml of distilled CH_2Cl_2 was added, followed by styrene (4.16 mg, 40 μmol). Aqueous H_2O_2 (35%) (19.4 mg, 200 μmol) and imidazole (0.68 mg, 20 μmol) in 0.1 ml MeOH were added over a period of 1 h with a syringe-pump. After the addition of all the H_2O_2, the reaction mixture was allowed to stir for an additional 1 h. The mixture was analyzed by GC for oxidation yield, 40%, and for epoxide enantiomeric excess, 45% (conditions used: 80 °C (1 min), 1 °C min^{-1} 80–120 °C, 2.5 °C min^{-1} 120–180 °C). Polarimetric measurement of the oxidation product determined that (*S*)-(−)-styrene epoxide was formed in excess. Only traces of phenylacetaldehyde were detected.

The reaction and analysis of the other substrates and catalysts in Table 2 was carried out in an identical manner with that used for styrene epoxidation.

4.3.3. General procedure for the catalytic hydroxylation reaction of arylalkanes with iron porphyrin catalyst and iodobenzene diacetate. Iron porphyrin complex **5** (1.2 mg 1 μmol) and imidazole (0.34 mg,

10 μmol) were placed in a test tube under argon. Then, 1 ml of distilled CH_2Cl_2/MeOH/H_2O mixture (0.5:0.4:0.1) was added, followed by ethylbenzene (106 mg, 1 mmol). $PhI(OAc)_2$ (32 mg, 100 μmol) in 0.1 ml CH_2Cl_2 was added over a period of 1 h with a syringe-pump. After the addition of all the $PhI(OAc)_2$, the reaction mixture was allowed to stir for an additional 1 h. The mixture was analyzed by GC for oxidation yield based on oxidant, 41%, alcohol/ketone ratio, 83:17, and alcohol enantiomeric excess, 68% (conditions used: 80 °C (1 min), 1 °C min^{-1} 80–120 °C, 2.5 °C min^{-1} 120–180 °C). Polarimetric measurement of the oxidation product determined that (*R*)-(+)-1-phenyl ethanol was formed in excess.

The reaction and analysis of the other substrates and catalysts in Table 3 were carried out in an identical manner with that used for ethylbenzene oxidation. Except for indane, the enantiomeric excess was determined by chiral HPLC with a Chiralcel OB-H column: *n*-hexane/isopropanol 95:5; flow rate: 0.5 ml min^{-1}, detection: 220 nm.

4.3.4. General procedure for the catalytic hydroxylation reaction of arylalkanes with manganese porphyrin catalyst and H_2O_2. Manganese porphyrin complex **9** (1.4 mg, 1 μmol) and imidazole (0.14 mg, 4 μmol) were placed in a test tube under argon. Then, 1 ml of distilled CH_2Cl_2 was added, followed by 3-ethyltoluene (4.80 mg, 40 μmol). H_2O_2 (19.4 mg, 200 μmol) and imidazole (0.68 mg, 20 μmol) in 0.1 ml MeOH were added over a period of 1 h with a syringe-pump. After the addition of all the H_2O_2, the reaction mixture was allowed to stir for an additional 1 h. The mixture was analyzed by GC for oxidation yield, 33%, alcohol/ketone ratio, 52:48, and alcohol enantiomeric excess, 21% (conditions used: 80 °C (1 min), 1 °C min^{-1} 80–120 °C, 2.5 °C min^{-1} 120–180 °C).

The reaction and analysis of the other substrates and catalysts in Table 4 was carried out in an identical manner with that used for 3-ethyltoluene oxidation. Except for indane, the enantiomeric excess was determined by chiral HPLC with a Chiralcel OB-H column: *n*-hexane/isopropanol 95:5; flow rate: 0.5 ml min^{-1}, detection: 220 nm.

References and notes

1. Lane, B. S.; Burgess, K. *Chem. Rev.* **2003**, *103*, 2457–2474.
2. Xia, Q. H.; Ge, H. Q.; Ye, C. P.; Liu, Z. M.; Su, K. X. *Chem. Rev.* **2005**, *105*, 1603–1662.
3. De Faveri, G.; Ilyashenko, G.; Watkinson, M. *Chem. Soc. Rev.* **2011**, *40*, 1722–1760.
4. Noyori, R.; Aoki, M.; Sato, K. *Chem. Commun.* **2003**, 1977–1986.
5. Sanderson, W. R. *Pure Appl. Chem.* **2000**, *72*, 1289–1304.
6. Arends, I. W. C. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 6250–6252.
7. (a) Zhuang, W.; Marigo, M.; Jorgensen, K. A. *Org. Biomol. Chem.* **2005**, *3*, 3883–3885; (b) Nicolas, I.; Le Maux, P.; Simonneaux, G. *Coord. Chem. Rev.* **2008**, *252*, 727–735; (c) Simonneaux, G.; Le Maux, P.; Chevance, S.; Srour, H. In *Handbook of Porphyrin Science*; Kadish, K., Smith, K. M., Guilard, R., Eds.; World Scientific: Singapore, 2012; Vol. 21, pp 377–410.
8. Srour, H.; Le Maux, P.; Chevance, S.; Simonneaux, G. *Coord. Chem. Rev.* **2013**, *257*, 3030–3050.
9. (a) Talsi, E. P.; Bryliakov, K. P. *Coord. Chem. Rev.* **2012**, *256*, 1418–1434; (b) Bryliakov, K. P.; Talsi, E. P. *Coord. Chem. Rev.* **2014**, *276*, 73–96.
10. Gelalcha, F. G.; Bitterlich, B.; Anilkumar, G.; Tse, M. K.; Beller, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7293–7296.
11. Gelalcha, F. G.; Anilkumar, G.; Tse, M. K.; Brückner, A.; Beller, M. *Chem.—Eur. J.* **2008**, *14*, 7687–7698.
12. Lyakin, O. Y.; Ottenbacher, R. V.; Bryliakov, K. P.; Talsi, E. P. *ACS Catal.* **2012**, *2*, 1196–1202.
13. White, M. C.; Doyle, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001**, *123*, 7194–7195.
14. Stingl, K. A.; Weiß, K. M.; Tsogoeva, S. B. *Tetrahedron* **2012**, *68*, 8493–8501.
15. Wu, M.; Miao, C.-X.; Wang, S.; Hu, X.; Xia, C.; Kühn, F. E.; Sun, W. *Adv. Synth. Catal.* **2011**, *353*, 3014–3022.
16. Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5791–5796.
17. Groves, J. T.; Viski, P. *J. Org. Chem.* **1990**, *55*, 3628–3634.
18. Rose, E.; Andrioletti, B.; Zrig, S.; Quelquejeu-Etheve, M. *Chem. Soc. Rev.* **2005**, *34*, 573–583.
19. Boitrel, B.; Lecas, A.; Renko, Z.; Rose, E. *J. Chem. Soc., Chem. Commun.* **1985**, 1820–1821.
20. Mansuy, D.; Battioni, P.; Renaud, J. P.; Guerin, P. *J. Chem. Soc., Chem. Commun.* **1985**, 155–156.
21. Collman, J. P.; Zhang, X.; Lee, V. J.; Uffelman, E. S.; Brauman, J. I. *Science* **1993**, *261*, 1404–1411.
22. Gross, Z.; Ini, S. *J. Org. Chem.* **1997**, *62*, 5514–5521.
23. Ferrand, Y.; Daviaud, R.; Le Maux, P.; Simonneaux, G. *Tetrahedron: Asymmetry* **2006**, *17*, 952–960.
24. Naruta, Y.; Tani, F.; Ishihara, N.; Maruyama, K. *J. Am. Chem. Soc.* **1991**, *113*, 6865–6872.
25. Simonneaux, G.; Tagliatesta, P. *J. Porphyrins Phthalocyanines* **2004**, *8*, 1166–1171.
26. Kluge, M.; Ullrich, R.; Scheibner, K.; Hofrichter, M. *Green Chem.* **2012**, *14*, 440–446.
27. Wang, X.; Peter, S.; Kinne, M.; Hofrichter, M.; Groves, J. T. *J. Am. Chem. Soc.* **2012**, *134*, 12897–12900.
28. Le Maux, P.; Simonneaux, G. *Chem. Commun.* **2011**, 6957–6959.
29. Le Maux, P.; Srour, H.; Simonneaux, G. *Tetrahedron* **2012**, *68*, 5824–5828.
30. Srour, H.; Le Maux, P.; Simonneaux, G. *Inorg. Chem.* **2012**, *51*, 5850–5856.
31. Halterman, R. L.; Jan, S. T.; Nimmons, H. L.; Standlee, D. J.; Khan, M. A. *Tetrahedron* **1997**, *53*, 11257–11276.
32. Halterman, R. L.; Jan, S. T.; Abdulwali, A. H.; Standlee, D. J. *Tetrahedron* **1997**, *53*, 11277–11296.
33. Berkessel, A.; Kaiser, P.; Lex, J. *Chem.—Eur. J.* **2003**, *9*, 4746–4756.
34. Ferrand, Y.; Poriel, C.; Le Maux, P.; Rault-Berthelot, J.; Simonneaux, G. *Tetrahedron: Asymmetry* **2005**, *16*, 1463–1472.
35. Luguya, R.; Jaquinod, L.; Fronczek, F. R.; Vicente, M. G. H.; Smith, K. M. *Tetrahedron* **2004**, *60*, 2757–2763.
36. Collman, J. P.; Gagne, R. R.; Reed, C. A.; Halbert, T. H.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 1427–1439.
37. Turk, H.; Erdem, M. *J. Porphyrins Phthalocyanines* **2004**, *8*, 1196–1203.
38. *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, The Netherlands, 1975.
39. Gelalcha, F. G. *Adv. Synth. Catal.* **2014**, *356*, 261–299.
40. Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462–8470.
41. Vilain-Deshayes, S.; Robert, A.; Maillard, P.; Meunier, B.; Momenteau, M. *J. Mol. Catal. A: Chem.* **1996**, *113*, 23–34.
42. In, J. H.; Park, S. E.; Song, R.; Nam, W. *Inorg. Chim. Acta* **2003**, *343*, 373–376.
43. Groves, J. T.; Kruper, W. J.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375–6377.
44. Palucki, M.; Finney, N. S.; Pospisil, P. J.; Galer, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 948–954.
45. Halterman, R. L.; Jan, S. T. *J. Org. Chem.* **1991**, *56*, 5253–5254.