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ScienceDirect
Tetrahedron 64 (2008) 3867–3876
Tetrahedron
www.elsevier.com/locate/tet

Biomimetic transfer hydrogenation of 2-alkoxy- and 2-aryloxyketones with iron–porphyrin catalysts

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Received 24 April 2007; received in revised form 14 January 2008; accepted 19 January 2008
Available online 30 January 2008

Abstract

In situ generated iron porphyrins are applied as homogeneous catalysts in the transfer hydrogenation of α-substituted ketones. Using 2-propanol as hydrogen donor various protected 1,2-hydroxyketones are reduced to the corresponding mono-substituted 1,2-diols in good to excellent yield. Under optimized reaction conditions catalyst turnover frequencies up to 2500 h^{-1} have been achieved.

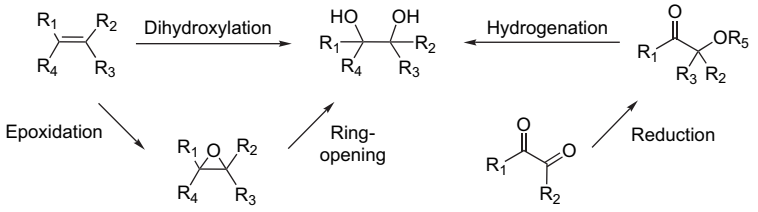
1. Introduction

The relevance of 1,2-diols is impressively shown by the production of ethylene and propylene glycol on multi-million ton scale for the synthesis of polymers and anti-freeze compounds. In addition, more complex 1,2-diols and their derivatives constitute interesting building blocks for a variety of biologically active compounds.

In general, synthetic approaches to 1,2-diols are based on oxidative processes of olefins. Typical processes include the epoxidation of C=C double bonds with peracids or hydroperoxides and subsequent hydrolysis, and the dihydroxylation of olefins in the presence of osmium catalysts (Scheme 1).[1]

A much less explored reaction is the transition metal-catalyzed reduction of 1,2-hydroxyketones. Among the different reductions, the transfer hydrogenation with 2-propanol as nontoxic hydrogen donor is practical and easy to perform.[2,3] Until now only a few number of applications were reported using Rh or Ru based metal catalysts in the reduction of protected 1,2-hydroxyketones, which is in contrast to the well-studied reduction of acetophenone.[4]

A major challenge for catalytic hydrogenations is the substitution of expensive and rare transition metals (Ir, Rh, Ru) by ubiquitous available, inexpensive and less toxic metals. Consequently, the use of iron catalysts is especially desirable.[5] Up to now, homogeneous iron catalysts have been mostly used for



Scheme 1. Possible approaches to 1,2-diols.

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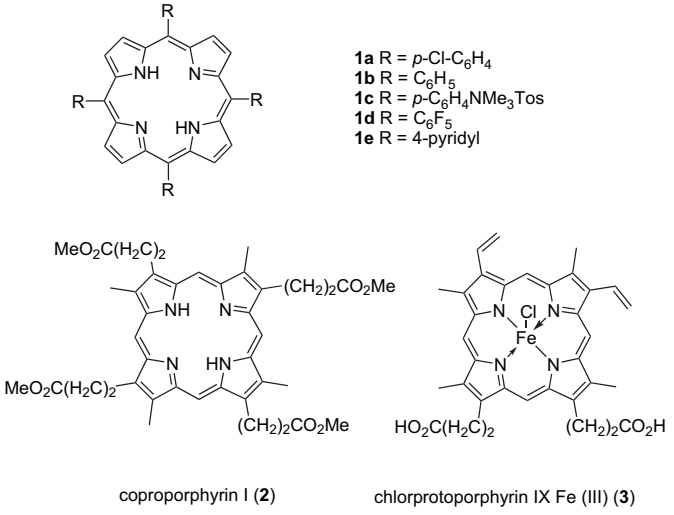
doi:10.1016/j.tet.2008.01.083

carbon–carbon bond formation, such as olefin polymerizations, cross couplings and cycloadditions as well as reduction of nitro compounds.[6] However, much less attention was directed towards iron-catalyzed transfer hydrogenation. Only the groups of Noyori,[7] Vancheesan,[8] Bianchini,[9] Gao,[10] and Morris[11] reported the utilization of iron salts and iron complexes, containing tetradentate phosphines[9] or aminophosphines,[10] in the reduction of ketones and α,β-unsaturated carbonyl compounds to yield alcohols and α,β-saturated carbonyl compounds.[12]

More recently, we established two iron-based methods for the effective transfer hydrogenation of aryl-alkyl as well as alkyl-alkyl ketones utilizing 2-propanol as the hydrogen source.[13] On the one hand we applied a combination of iron salts, tridentate amines and phosphines as catalysts and on the other hand an in situ catalyst composed of an iron salt and porphyrins has been used (Scheme 2).[13] Unfortunately, both catalyst systems faced some difficulties with α-substituted alkyl-aryl ketones. Herein we report for the first time the successful hydrogenation of α-alkoxy- and α-aryloxy-substituted acetophenones in the presence of iron–porphyrin complexes.

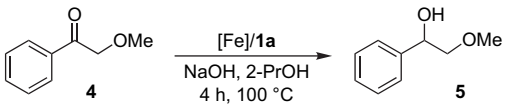
2. Results and discussion

For exploratory experiments the hydrogenation of 2-methoxyacetophenone was used as a model reaction. Typically, the pre-catalyst is prepared by stirring a solution of 1 mol % iron salt and 1 mol % **1a** in 2-propanol (1.0 mL) for 16 h at 65 °C. After addition of 50 mol % base the mixture is heated for 5 min at 100 °C and the substrate 2-methoxyacetophenone **4** is added. At first, the influence of different iron precursors on the reaction rate was studied (Table 1). To our delight full conversion is obtained in all cases within 4 h. Obviously, the formation of the active catalyst is independent from the Fe-salt and is complete for all stated pre-catalysts under standard conditions. Without any Fe present no conversion took place and using $FeCl_2$ without ligand gave only 37% yield. From a point of view of practical convenience we chose $FeCl_2$ as iron source in combination with porphyrin ligands for further investigations.



Scheme 2. Selection of applied porphyrin ligands.[13]

Table 1
Influence of iron salts in the transfer hydrogenation of 2-methoxyacetophenone **4**



Entry	Iron source	Yield[a] [%]
1	—	<1
2	FeF_2	>99
3	$FeCl_2$	>99
4[b]	$FeCl_2$	37
5	$FeCl_3$	>99
6	$FeBr_2$	>99
7	FeI_2	>99
8	$Fe(acac)_2$	>99
9	$Fe(acac)_3$	>99
10	$FeSO_4 \cdot 7H_2O$	>99
11	$CpFe(CO)_2I$	>99
12[c]	Fe(III)citrate·H_2O	>99
13	$Fe_3(CO)_{12}$	>99

Reaction conditions: 0.0038 mmol in situ catalyst (0.0038 mmol Fe-source or 0.0013 mmol $Fe_3(CO)_{12}$ and 0.0038 mmol **1a** in 1.0 mL 2-propanol for 16 h at 65 °C), 0.19 mmol NaOH in 0.5 mL 2-propanol, 0.38 mmol 2-methoxyacetophenone **4** in 0.5 mL 2-propanol, 4 h at 100 °C.

[a] Yield was determined by GC analysis (30 m HP Agilent Technologies 50–300 °C) with diglyme as internal standard.

[b] No ligands are added.

[c] Fe(III)citrate was recrystallized before use.[14]

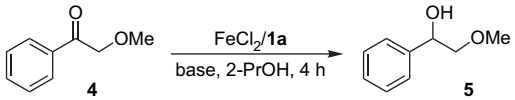
It is well known that type and also amount of base are important parameters for obtaining reasonable quantities of product in transfer hydrogenations. Thus, we investigated frequently used bases, such as NaOH, KOH and KO^{t}Bu. In all cases excellent yields are achieved, except for LiOH and Cs_2CO_3 (Table 2). Diminishing the base of concentration to 5–10 mol % resulted in a decrease of yield of 2-methoxy-1-phenylethanol **5**, while 25 mol % of base still gave excellent yield within 2 h. Noteworthy, in the absence of base no transfer of hydrogen occurred (Table 2, entry 15). In addition, nitrogen-containing bases (e.g., pyridine, NEt_3, DBU) were tested, but only unsatisfactory results were attained (conversion: <1%).

Next, we focused our attention on the influence of the reaction temperature (Table 2, entries 1 and 10–14). An optimal catalyst activity was obtained in the range of 60–100 °C. However, even at lower temperature a moderate yield was attained (40 °C, conversion: 18%). To support the formation of the active catalyst at low temperature two different activation methods were carried out.

On the one hand, substitution of strong coordinating chloride anions by weaker BF_4^- anions via addition of $AgBF_4$ was done. On the other hand activation of the catalyst by light irradiation (Perkin–Elmer PE300BF lamp with hot mirror, ~380–770 nm) has been tried. Surprisingly, both procedures led to complete deactivation of the catalysts with respect to hydrogenation reaction.

In order to further improve the catalyst system we applied different porphyrin ligands (**1a**–**3**) under the optimized

Table 2
Influence of temperature and base in the Fe-catalyzed transfer hydrogenation of 2-methoxyacetophenone **4**



4 **5**

Entry	Base	Base [mol %]	Temp [°C]	Yield[a] [%]
1	NaOH	50	100	>99
2	KOH	50	100	>99
3	LiOH	50	100	49
4	NaO^{i}Pr	50	100	>99
5	KO^{t}Bu	50	100	>99
6[b]	NaO^{t}Bu	50	100	>99
7	K_2CO_3	50	100	>99
8	Na_2CO_3	50	100	97
9	Cs_2CO_3	50	100	37
10[c]	NaOH	50	25	<1
11	NaOH	50	40	18
12[d]	NaOH	50	40	<1
13	NaOH	50	60	>99
14	NaOH	50	80	>99
15[e]	—	—	100	<1
16[e]	NaOH	5	100	17
17[e]	NaOH	10	100	55
18[e]	NaOH	25	100	>99
19[e]	NaOH	50	100	>99

Reaction conditions: 0.0038 mmol in situ catalyst (0.0038 mmol $FeCl_2$ and 0.0038 mmol **1a** in 1.0 mL 2-propanol for 16 h at 65 °C), 0.19 mmol base in 0.5 mL 2-propanol, 0.38 mmol 2-methoxyacetophenone **4** in 0.5 mL 2-propanol, 4 h at described temperature.

[a] Yield was determined by GC analysis (30 m HP Agilent Technologies 50–300 °C) with diglyme as internal standard.

[b] A mixture of solvents was used ^{t}BuOH and 2-propanol 1:4.

[c] Light assisted reaction, thereby only the visible range was applied since the ultraviolet range was shielded.

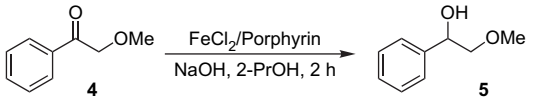
[d] Addition of 2 equiv $AgBF_4$ with respect to $FeCl_2$.

[e] Reaction time: 2 h.

conditions, namely 0.5 or 0.01 mol % Fe catalyst ($FeCl_2$ and the corresponding porphyrin in a ratio of 1:1), sodium hydroxide (25 mol % or 0.5 mol %) at 100 °C (Table 3). In case of 0.5 mol % catalyst loading for all iron–porphyrin catalysts excellent conversion was attained. For 0.01 mol % catalyst loading best performance was achieved with the *meso*-substituted porphyrin **1a** (Table 3, entry 2). Substitution at the *meso*-phenylic system of porphyrin with electron withdrawing groups (**1c** and **1d**) lowered the catalyst activity. Furthermore, an excellent turnover frequency of 1850 h^{-1} was observed with a porphyrin substituted at the β-pyrrolenic positions (Table 3, entry 12). The complex chloroprotoporphyrin IX Fe(III) **3** was utilized without catalysts pre-formation as described for all other representatives, and good turnover numbers were determined (Table 3, entries 13 and 14). Reducing the catalyst loading to 0.01 mol % turnover frequencies up to 2100 h^{-1} were realized (Table 3, entries 1–3).

Notably, the addition of small amounts of water (5–10 mol %) accelerated the transfer hydrogenation compared to the water-free conditions and turnover frequencies up to 2500 h^{-1} were achieved. Higher amounts of water (up to 500 mol %) hampered the reaction (Fig. 1).

Table 3
Screening of different porphyrins in the Fe-catalyzed transfer hydrogenation of 2-methoxyacetophenone **4**



4 **5**

Entry	Ligand	Catalyst loading [mol %]	Yield[a] [%]	TOF[b] [h^{-1}]
1	**1a**	0.5	>99	>99
2	**1a**	0.01	42	*2100*
3	**1b**	0.5	>99	>99
4	**1b**	0.01	30	1500
5	**1c**	0.5	>99	>99
6	**1c**	0.01	18	900
7	**1d**	0.5	>99	>99
8	**1d**	0.01	23	1150
9	**1e**	0.5	>99	>99
10	**1e**	0.01	24	1200
11	**2**	0.5	>99	>99
12	**2**	0.01	37	1850
13	**3**	0.5	>99	>99
14	**3**	0.01	26	1300

Reaction conditions: 0.0019 mmol or 0.038 mmol in situ catalyst (0.0019 mmol or 0.038 μmol $FeCl_2$ and 0.0019 mmol or 0.038 μmol porphyrin in 1.0 mL 2-propanol for 16 h at 65 °C), 0.095 mmol or 0.0019 mmol sodium hydroxide in 0.5 mL 2-propanol, 0.38 mmol 2-methoxyacetophenone **4** in 0.5 mL 2-propanol, 2 h at 100 °C.

[a] Yield was determined by GC analysis (30 m HP Agilent Technologies 50–300 °C) with diglyme as internal standard.

[b] Turnover frequencies were determined after 2 h.

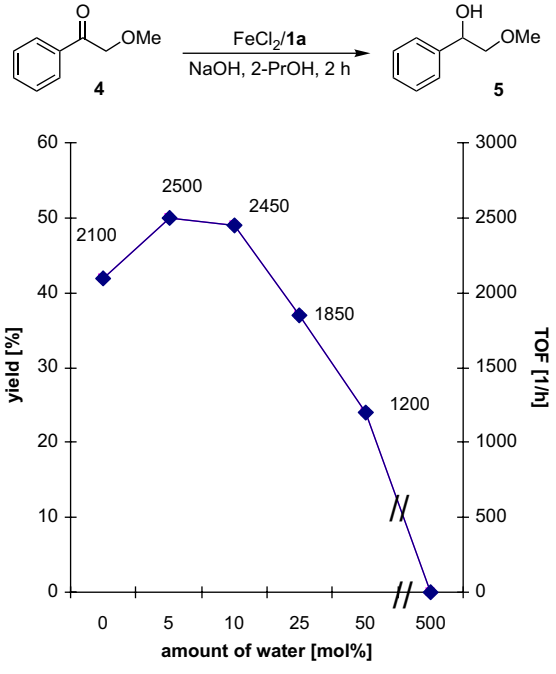


Figure 1. The influence of water addition on hydrogenation of 2-methoxyacetophenone **4**. Reaction conditions: 0.038 μmol in situ catalyst (0.038 μmol $FeCl_2$ and 0.08 μmol **1a** in 1.0 mL 2-propanol for 16 h at 65 °C), 1.9 μmol NaOH in 0.5 mL 2-propanol, the corresponding amount of water, 0.38 mmol substrate in 0.5 mL 2-propanol, temperature: 100 °C, reaction time: 2 h. Yield was determined by GC analysis (30 m HP Agilent Technologies 50–300 °C) with diglyme as internal standard.

Under optimized conditions (vide supra), we compared the activity of the catalytic system for the reduction of acetophenone **6**, *ortho*-methoxyacetophenone **8** and 2-methoxyacetophenone **4**. Here, the yield of 1-phenylethanol **7**, *ortho*-methoxy-1-phenylethanol **9** and 2-methoxy-1-phenylethanol **5** was monitored during the reaction.

The attained curves are shown in Figure 2. The reduction of 2-methoxyacetophenone proceeded without any induction period or deactivation process. Similar behaviour was observed for *ortho*-methoxyacetophenone, albeit a slight deceleration occurred after nearly 100 min. Nevertheless, full conversion was reached after 7 h. In case of acetophenone the reduction process was significantly slower. After 8 h a deactivation took place. Notably, the activities are in agreement with the oxidation potentials of the applied ketones (2-methoxyacetophenone, E_0=213 mV; *ortho*-methoxyacetophenone, E_0=141 mV;[15] acetophenone, E_0=118 mV).

In order to demonstrate the usefulness of our method the catalyst containing ligand **1a** was tested in the hydrogenation of several hydroxy-protected 1,2-hydroxyketones (Table 4).

In general, the substrates were synthesized by reacting 2-bromo ketones with different alcohols in the presence of a base.[16] A first set of experiments was dedicated to the variation of the protecting group. Good to excellent yield was obtained by changing the methoxy group by phenoxy substituents. Best results were achieved with the *p*-chlorophenoxy substituent (Table 4,

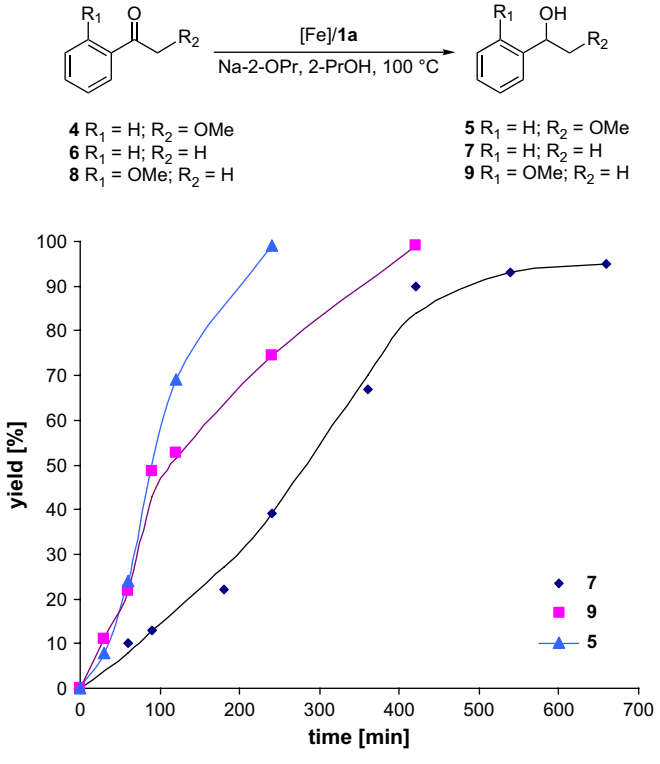
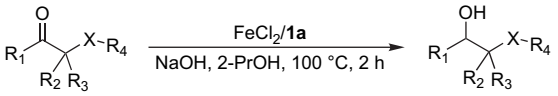


Figure 2. Comparative study between acetophenone **6**, *ortho*-methoxyacetophenone **8** and 2-methoxyacetophenone **4**. Reaction conditions: 0.0038 mmol in situ catalyst (0.0038 mmol $FeCl_2$ and 0.0038 mmol **1a** in 1.0 mL 2-propanol for 16 h at 65 °C), 0.19 mmol base in 0.5 mL 2-propanol, 0.76 mmol substrate in 0.5 mL 2-propanol, temperature: 100 °C. Yield was determined by GC analysis (**7**: 50 m Lipodex E, 95–150 °C, **7**: 50 m Lipodex E, 90–180 °C, **9**: 30 m HP Agilent Technologies 50–300 °C) with diglyme as internal standard.

Table 4
Reduction of α-substituted ketones in the presence of iron catalyst containing porphyrin **1a**



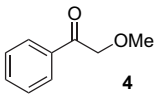
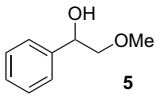
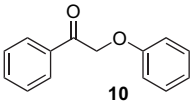
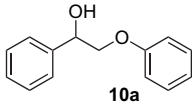
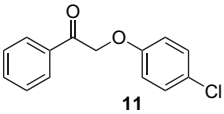
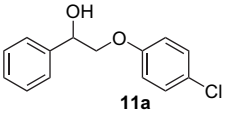
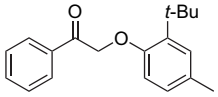
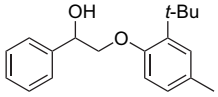
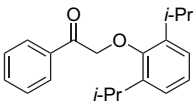
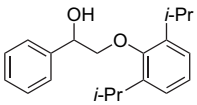
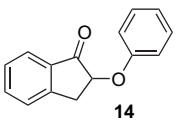
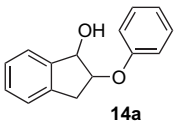
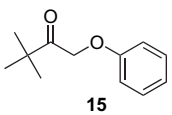
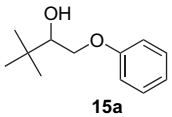
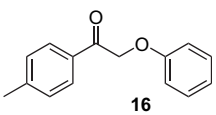
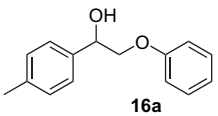
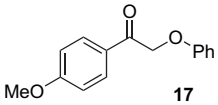
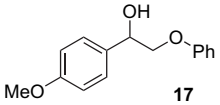
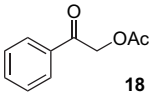
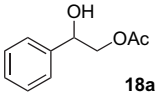
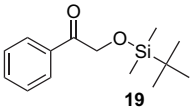
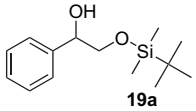
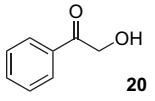
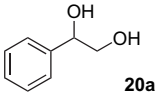
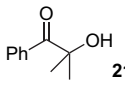
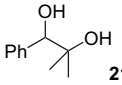
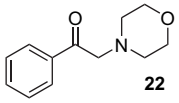
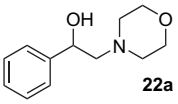
Entry	Substrate	Product	Conv. [%]
1	 **4**	 **5**	>99
2	 **10**	 **10a**	92
3	 **11**	 **11a**	>99[a]
4	 **12**	 **12a**	97
5	 **13**	 **13a**	74[a]
6	 **14**	 **14a**	43
7	 **15**	 **15a**	48
8	 **16**	 **16a**	>99[a]
9	 **17**	 **17**	83[a]
10	 **18**	 **18a**	<1[a]
11	 **19**	 **19a**	<1[a]
12	 **20**	 **20a**	<1[b]

Table 4 (*continued*)

Entry	Substrate	Product	Conv. [%]
13	 **21**	 **21a**	<1[b]
14	 **22**	 **22a**	3 (<1)[c]

Reaction conditions: 0.0019 mmol in situ catalyst (0.0019 mmol $FeCl_2$ and 0.0019 mmol porphyrin in 1.0 mL 2-propanol for 16 h at 65 °C), 0.095 mmol sodium hydroxide in 0.5 mL 2-propanol, 0.34 mmol substrate in 0.5 mL 2-propanol, 2 h at 100 °C. Yield was determined by GC analysis (30 m HP Agilent Technologies 50–300 °C).

[a] ^{1}H NMR.

[b] Decomposition.

[c] Reaction time: 24 h.

entry 3). Increasing the bulkiness at *o*- and *o*′-position the conversion decreased significantly (Table 4, entry 5), while substitution only at *o*-position led to excellent conversion of the desired product (Table 4, entry 4). Substitution on the acetophenone skeleton by a *p*-methyl or *p*-methoxy group gave good to full conversion. In addition, indanone and pinacolin based substrates were synthesized and tested in this transfer hydrogenation, thereby moderate conversions were obtained (Table 4, entries 6 and 7). Unfortunately, variation of the hydroxyl protecting group to the common acetyl and *tert*-butyldimethylsilyl groups displayed an inactivity of the presented catalyst (Table 4, entries 10 and 11). The hydrogenation of 2-hydroxy-acetophenone **20** and 2-hydroxy-2-methyl-1-phenylpropan-1-one **21** were not successful since decomposition was observed. In addition, 2-morpholino-acetophenone **22**, which is a promising precursor for 1,2-amino alcohols, was subjected to the transfer hydrogenation protocol. Unfortunately, no conversion was observed even if the reaction time was extended to 24 h (Table 4, entry 14).

In order to get further informations about the presented catalytic system we carried out electrochemical investigations of the in situ catalysts containing ligands **1a–e**. Cyclic voltammetry has been established as a useful tool for studying the electrochemical properties of porphyrins and metalloporphyrins.[17] The measurement conditions were as close to the reaction conditions as possible. However, under strong basic conditions, no reliable measurements were possible, due to low catalyst solubility at room temperature. Therefore measurements were performed in the absence of base. The temperature dependence of the potentials according to the Nernst equation have to be similar for all Fe-porphyrins and should be in the range of 20–30 mV between room temperature and the reaction temperature of 100 °C. The electrochemical analysis is presented in Figure 3.

All cyclic voltammograms illustrate clearly the oxidation of Fe(II) to Fe(III) in the potential range above ca. 0.2 V versus SCE. The small (negative) reduction currents result probably from Fe(III) contamination of the $FeCl_2$ or from oxidation of $FeCl_2$ from other impurities (e.g., O_2). From the colour of the solutions (light brown to red-brown) and the height of oxidation current (compared to 5 mmol/L $FeCl_2$) the curves

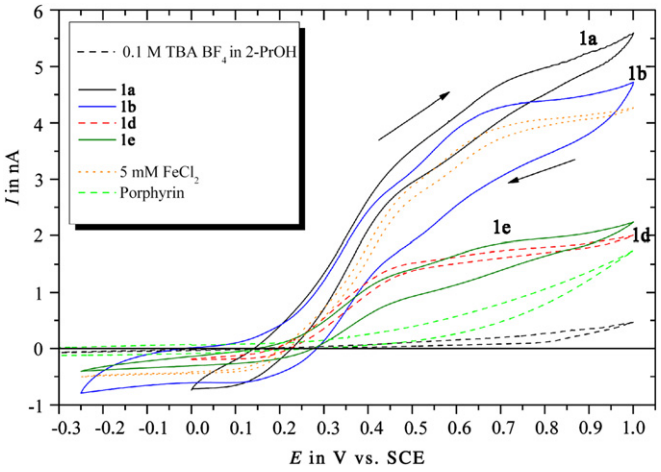


Figure 3. Cyclic voltammograms of porphyrins with $FeCl_2$ in 0.1 mol/L TBA·BF_4 in 2-PrOH. Start at 0 V in positive direction with 10 mV/s at platinum microelectrode.

resulted from free $FeCl_2$ (light yellow coloured solution) or incomplete Fe(II)-porphyrin formation can be excluded.[18]

Most likely the difference in oxidation currents results from different solubilities of the Fe-porphyrins, since the diffusion coefficients should be similar. The porphyrins without $FeCl_2$ (violet coloured solution) generate only a small oxidation current in the region above ca. 0.6 V, which is shown by the cyclic voltammogram of the porphyrin **1a** without $FeCl_2$ (Fig. 3). This oxidation current was also observable in the curves of the Fe(II)-porphyrins in the same potential range.

The second oxidation steps visible in all curves (0.5–0.6 V) cannot clearly be interpreted under the applied conditions. Most likely the second oxidation step is caused by formation of other complexes, since 2-propanol and chloride ions are present in the solution, which are possible ligands for the axial position. During oxidation of Fe(II)- to Fe(III)-porphyrin one anion has to fulfil the unsaturated situation at the Fe(III) centre analogue to compound **3** as shown in Scheme 2. At the same time it has to be considered that Fe(II)-porphyrins can also be coordinated with two axial ligands (six-coordinated Fe(II)).[17,19] The small amount of dissolved chloride results probably in slower kinetics of the Fe(III)-porphyrin formation, seen by the reversible potential values (Table 5).

Due to the influence of the axial ligand a change or different coordination of the porphyrins at the axial positions results in a shift of potential (with an excess of chloride the potentials shift to lower values with higher reversibility).[17] The half-wave potentials for the first oxidation step resulting from the

Table 5
Half-wave potentials and values for reversibility

Compound	TOF	$E_{1/2}$ vs SCE [mV]	Slope [mV]
1d	1150	326	146
1e	1200	339	141
1b	1500	338	152
1a	2100	330	204
$FeCl_2$	—	380	205
Ferrocene	—	525	61

measurements under these conditions are presented in Table 5. Under conditions identical with those for the porphyrins the ferrocenium/ferrocene couple has a half-wave potential of 525 mV and a slope of 61 mV ($E_{1/2}$=480 mV in 0.1 mol/L TBA·PF_6/CH_2Cl_2).[20] With the half-wave potentials of the Fe-porphyrins no correlation with the TOF can be found. In addition following our standard protocol the formation of the pre-catalyst was studied by in situ mass spectroscopy. After stirring $FeCl_2$ and ligand **1a** for 16 h at 65 °C the corresponding iron complex[21] formed by elimination of 2 equiv of HCl was detected, which is in agreement with previous reports.[22] However, the actual active Fe-species is still unclear.

In conclusion, we have demonstrated the successful extension of the Fe-catalyzed transfer hydrogenation to α-hydroxy-protected ketones. Under optimized conditions turnover frequencies up to 2500 h^{-1} were achieved. The scope and limitation of the catalyst were demonstrated on reduction of 10 different ketones with good to excellent yields.

3. Experimental section

3.1. General

^1H and ^{13}C NMR spectra were recorded on Bruker Spectrometer 400 and 300 (^1H: 400.13 MHz, and 300.13 MHz; ^{13}C: 100.6 MHz, and 75.5 MHz). The calibration of ^1H and ^{13}C spectra was carried out either on solvent signals (δ ($CDCl_3$)=7.25 and 77.0) or TMS. Mass spectra were recorded on an AMD 402 spectrometer. IR spectra were recorded as KBr pellets or Nujol mulls on a Nicolet Magna 550. All manipulations were performed under argon atmosphere using standard Schlenk techniques. Unless specified, all chemicals are commercially available and used as received. 2-Propanol was used without further purification (purchased from Fluka, dried over molecular sieves). Sodium 2-propylate and sodium *tert*-butylate were prepared by reacting sodium with 2-propanol or *tert*-butanol, respectively, under an argon atmosphere (stock solution). Ketone **8** was dried over CaH_2, distilled in vacuum and stored under argon. Substrates **18** and **19** were used without further purifications. Porphyrins **1a** and **1d** were synthesized according to literature protocols.[23] Fe(III)-citrate was recrystallized from water/ethanol before use since it was purchased in technical grade.

3.2. General procedure for the synthesis of substrates

A solution of 2-bromo ketone (10.1 mmol), phenol (10.1 mmol), K_2CO_3 (15 mmol) in acetone (15 mL) was refluxed for 3 h. The solvent was removed in vacuum and the residue dissolved in ethyl acetate/diethyl ether and washed with water and brine. After drying over Na_2SO_4 the solvent was removed and the crude product was purified by crystallization.

3.2.1. 2-Phenoxy-acetophenone (*10*)

Flash column chromatography (eluent: ethyl acetate/*n*-hexane 4:1), recrystallized from 2-propanol, 10.1 mmol scale. Yield: 39% (white crystals). Mp=60–61 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=8.02–7.98 (m, 2H); 7.64–7.58 (m, 1H); 7.53–7.46 (m, 2H); 7.31–7.22 (m, 2H); 7.01–6.90 (m, 3H); 5.28 (s, 2H, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=194.5; 157.9; 134.5; 133.8; 129.5; 128.8; 128.1; 121.6; 114.7; 70.7. IR (KBr): 3387 w; 3060 w; 2897 w; 2843 w; 2749 w; 1928 w; 1708 s; 1599 s; 1499 s; 1480 m; 1449 m; 1433 m; 1386 w; 1341 w; 1303 m; 1292 m; 1250 s; 1228 s; 1189 m; 1175 m; 1094 m; 1076 m; 1028 w; 1001 m; 975 m; 921 w; 886 w; 872 m; 751 s; 688 s; 665 m; 614 w; 584 w; 555 w; 511 m; 414 w. MS (EI): *m/z* (%)=212 ([M^+], 26); 105 (100); 77 (43); 51 (12). HRMS calculated for $C_{14}H_{14}O_2$: 214.09883; found: 214.098506.

3.2.2. 2-(4-Chlorophenoxy)-acetophenone (*11*)

Refluxing time: 12 h, crystallized from 2-propanol, 7.8 mmol scale. Yield: 73% (white plates). Mp=87–88 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=8.01–7.96 (m, 2H); 7.66–7.56 (m, 1H); 7.54–7.47 (m, 2H); 7.26–7.20 (m, 2H); 6.90–6.83 (m, 2H); 5.26 (s, 2H, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=194.0; 156.6; 134.3; 134.0; 129.4; 128.9; 128.0; 126.5; 116.1; 70.9. IR (KBr): 3375 w; 3060 w; 2901 w; 2851 w; 2737 w; 1699 s; 1596 s; 1581 m; 1490 s; 1448 m; 1437 s; 1409 w; 1385 w; 1338 w; 1317 w; 1289 s; 1231 s; 1172 m; 1106 m; 1096 m; 1089 m; 1075 m; 1001 m; 983 s; 921 w; 870 w; 830 s; 813 m; 786 w; 756 s; 701 w; 686 s; 634 w; 587 m; 508 m; 476 w; 457 w; 441 w; 422 w; 406 w. MS (EI): *m/z* (%)=246 ([M^+], 15); 105 (100); 77 (30). HRMS calculated for $C_{14}H_{11}ClO_2$: 246.04421; found: 246.044678.

3.2.3. 2-(2-tert-Butyl-4-methylphenoxy)-acetophenone (*12*)

Refluxing time: 12 h, crystallized from 2-propanol, 6.0 mmol scale. Yield: 44% (white needles). Mp=94–95 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=8.05–8.00 (m, 2H); 7.66–7.59 (m, 1H); 7.55–7.48 (m, 2H); 7.13 (d, 1H, J=2.26 Hz); 6.96 (ddd, 1H, J=8.10, 2.26, 0.75 Hz); 6.76 (d, 1H, J=8.22 Hz); 5.29 (s, 2H, CH_2); 2.30 (s, 3H, CH_3); 1.43 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=194.5; 154.8; 138.4; 134.7; 133.7; 130.3; 128.8; 128.1; 127.8; 127.1; 112.3; 71.0; 34.7; 29.9; 20.8. IR (KBr): 3399 w; 3051 w; 2958 s; 2901 m; 2856 m; 2733 w; 1709 s; 1598 m; 1581 w; 1499 s; 1448 m; 1439 m; 1404 w; 1386 m; 1357 w; 1287 m; 1266 m; 1244 m; 1226 s; 1181 w; 1156 w; 1107 m; 1074 w; 1020 w; 1001 m; 980 s; 930 w; 919 w; 876 w; 861 m; 802 s; 751 s; 687 s; 655 m; 584 m; 491 m. MS (EI): *m/z* (%)=282 ([M^+], 64); 267 (21); 249 (21); 161 (11); 121 (13); 119 (16); 117 (14); 105 (100); 91 (33); 77 (29). HRMS calculated for $C_{19}H_{22}O_2$: 282.16143; found: 282.162186.

3.2.4. 2-(2,6-Di-iso-propylphenoxy)-acetophenone (*13*)

Refluxing time: 12 h, crystallized from 2-propanol, 5.6 mmol scale. Yield: 34% (yellow crystals). Mp=60–65 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=8.01–7.95 (m, 2H); 7.66–7.59 (m, 1H); 7.55–7.47 (m, 2H); 7.16 (s, 3H); 5.12 (s, 2H, CH_2); 3.34 (sept, 2H, J=6.91 Hz, CH); 1.25 (d, 12H, J=6.87 Hz, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=193.9; 153.0; 141.6; 133.7; 128.8; 127.8; 125.2; 124.3; 76.7; 26.5;

24.1. IR (KBr): 3442 br; 3063 w; 3028 w; 2967 s; 2868 m; 1706 s; 1597 m; 1580 w; 1451 m; 1429 m; 1381 w; 1371 w; 1360 m; 1334 m; 1255 m; 1227 m; 1185 s; 1163 m; 1100 m; 1085 m; 1075 w; 1058 w; 1042 w; 1001 w; 992 w; 972 m; 934 w; 854 w; 801 m; 763 m; 755 s; 692 m; 648 w; 617 w; 586 w; 556 w; 521 w; 472 w; 434 w. MS (EI): *m/z* (%)=296 ([M^+], 10); 176 (83); 161 (100); 147 (20); 133 (16); 105 (59); 91 (44); 77 (28); 43 (11). HRMS calculated for $C_{20}H_{24}O_2$: 296.17708; found: 296.176483.

3.2.5. 2-Phenoxy-2,3-dihydro-1H-inden-1-one (**14**)

Refluxing time: 16 h, 9.5 mmol scale. Yield: 56% (off-white crystals). Mp=75–78 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.85 (d, 1H, J=7.72 Hz); 7.67 (dt, 1H, J=7.44, 1.13 Hz); 7.50–7.41 (m, 2H); 7.37–6.99 (m, 2H); 7.10–6.99 (m, 3H); 5.09 (dd, 1H, J=7.54, 4.52 Hz, CH); 3.73 (dd, 1H, J=7.54, 16.95 Hz, CH_2); 3.19 (dd, 1H, J=16.95, 4.33 Hz, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=201.7; 157.9; 150.6; 135.9; 134.6; 129.5; 128.2; 126.7; 124.6; 121.7; 115.7; 77.8; 34.1. IR (KBr): 3413 br; 3063 w; 3039 w; 3028 w; 2916 w; 2906 w; 1716 s; 1608 m; 1597 m; 1587 m; 1493 m; 1474 m; 1464 m; 1431 w; 1325 w; 1299 m; 1276 m; 1250 m; 1233 s; 1208 w; 1174 w; 1156 w; 1080 m; 1070 m; 1038 w; 1020 w; 1005 m; 956 w; 913 m; 889 w; 753 s; 725 m; 691 m; 618 w; 607 w; 502 w; 455 w. MS (EI): *m/z* (%)=224 ([M^+], 53); 131 (100); 103 (32); 94 (11); 77 (25). HRMS calculated for $C_{15}H_{12}O_2$: 224.08318; found: 224.083160.

3.2.6. 3,3-Dimethyl-1-phenoxybutan-2-one (**15**)

Refluxing time: 16 h, 11.2 mmol scale. Yield: 92% (off-white crystals). Mp=33–36 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.32–7.24 (m, 2H); 7.00–6.93 (m, 1H); 6.91–6.84 (m, 2H); 4.87 (s, 2H, CH_2); 1.25 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=209.4; 158.0; 129.5; 121.4; 114.6; 68.8; 43.1; 26.3. IR (KBr): 3420 br; 3105 w; 3065 w; 3043 w; 2973 m; 2931 m; 2872 w; 2846 w; 2747 w; 1721 s; 1678 w; 1599 m; 1587 m; 1494 s; 1461 m; 1446 m; 1431 m; 1386 w; 1365 m; 1329 w; 1291 m; 1234 s; 1179 m; 1152 w; 1113 m; 1078 w; 1052 s; 1026 w; 1000 m; 990 s; 962 m; 935 w; 880 m; 825 m; 766 s; 759 s; 693 m; 587 w; 545 w; 522 m. MS (EI): *m/z* (%)=192 ([M^+], 33); 108 (13); 77 (26); 57 (100); 41 (16). HRMS calculated for $C_{12}H_{16}O_2$: 192.11448; found: 192.114302.

3.2.7. 2-Phenoxy-4′-methylacetophenone (**16**)

Refluxing time: 16 h, crystallized from 2-propanol, 9.4 mmol scale. Yield: 51% (colourless crystals). Mp=62–63 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.94–7.88 (m, 2H); 7.33–7.24 (m, 4H); 7.02–6.91 (m, 3H); 5.25 (s, 2H, CH_2); 2.43 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=194.1; 158.0; 144.8; 132.1; 129.54; 129.48; 128.2; 121.6; 114.6; 70.7; 21.8. IR (KBr): 3441 br; 3063 w; 3036 w; 2919 w; 2902 w; 2847 w; 1695 s; 1606 s; 1587 m; 1576 m; 1498 s; 1455 w; 1433 m; 1411 m; 1385 w; 1292 m; 1254 m; 1236 s; 1208 m; 1192 m; 1174 m; 1149 w; 1124 w; 1113 w; 1092 m; 1075 w; 1044 w; 1027 w; 1001 m; 979 m; 885 m; 871 m; 816 m; 749 s; 711 w; 690 m; 609 w; 584 m; 551 w; 517 w; 498 w; 461 w. MS (EI): *m/z* (%)=226 ([M^+], 15); 119 (100); 91 (24); 77 (10). HRMS calculated for $C_{15}H_{14}O_2$: 226.09883; found: 226.099202.

3.2.8. 2-Phenoxy-4′-methoxyacetophenone (**17**)

Refluxing time: 16 h, crystallized from 2-propanol, 8.7 mmol scale. Yield: 74% (off-white needles). Mp=54–55 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.96–7.89 (m, 2H); 7.24–7.16 (m, 2H); 6.93–6.84 (m, 5H); 5.13 (s, 2H, CH_2); 3.80 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=193.1; 164.0; 158.0; 130.5; 129.0; 127.6; 121.5; 114.7; 114.0; 70.7; 55.5. IR (KBr): 3442 br; 3056 w; 3006 w; 2955 w; 2934 w; 2840 w; 1960 m; 1687 s; 1653 w; 1601 s; 1511 m; 1497 s; 1459 m; 1419 w; 1368 m; 1314 m; 1265 s; 1245 m; 1226 s; 1171 s; 1154 w; 1116 m; 1075 m; 1032 m; 976 s; 884 m; 835 m; 789 m; 769 m; 751 s; 691 m; 631 w; 608 m; 582 m; 543 w; 511 w; 492 w. MS (EI): *m/z* (%)=242 ([M^+], 10); 135 (100); 77 (18). HRMS calculated for $C_{15}H_{14}O_3$: 242.09375; found: 242.093706.

3.2.9. 2-Oxo-2-phenylethyl acetate (**18**)

2-Hydroxy-1-phenylethanone (8.0 mmol) was dissolved in dichloromethane (10 mL) and acetic anhydride (8.0 mmol), pyridine (8.5 mmol) and 4-dimethylaminopyridine (0.08 mmol) were added. The solution was stirred for 2 h under refluxing conditions. The mixture was washed with water and brine. After drying over Na_2SO_4 the solvent was removed and yellow crystals were obtained. Yield: 83%. Mp=48–50 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.93–7.88 (m, 2H); 7.63–7.56 (m, 1H); 7.51–7.44 (m, 2H); 5.34 (s, 2H, CH_2); 2.22 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=192.0; 170.3; 134.1; 133.8; 128.7; 127.6; 65.9; 20.4. IR (KBr): 3460 w; 3375 w; 3064 m; 2982 w; 2937 m; 1741 s; 1699 s; 1599 m; 1581 w; 1493 w; 1452 m; 1423 m; 1374 m; 1321 w; 1280 m; 1244 s; 1228 s; 1185 m; 1087 m; 1077 m; 1047 m; 1020 m; 996 m; 970 m; 849 m; 812 m; 757 m; 688 m; 634 m; 597 m; 566 m; 483 m; 443 w; 414 w. MS (EI): *m/z* (%)=178 ([M^+], 1); 105 (100); 77 (34); 51 (10); 43 (14). HRMS calculated for $C_{15}H_{14}O_3$: 178.06245; found: 178.063004.

3.2.10. 2-(tert-Butyldimethylsilyloxy)-1-phenylethanone (**19**)

2-Hydroxy-1-phenylethanone (8.0 mmol) was dissolved in dichloromethane (10 mL) and imidazole (8.5 mmol) was added. After stirring for 10 min at room temperature *tert*-butyldimethylchlorosilane (8.5 mmol) was added dropwise, while rapidly a white precipitate was formed. The mixture was stirred for 5 h at room temperature. Water was added and the organic layer was washed with water and brine. After removal of the solvent a yellow oil was obtained. Yield: 89%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.95–7.89 (m, 2H); 7.61–7.42 (m, 3H); 4.93 (s, 2H, CH_2); 0.94 (s, 9H, $C(CH_3)_3$); 0.13 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=197.4; 134.9; 132.2; 128.6; 127.9; 67.4; 25.8; 18.5; −5.4. IR (KBr): 2953 w; 2929 m; 2885 w; 2856 m; 1705 s; 1599 m; 1581 w; 1472 m; 1449 m; 1390 w; 1362 w; 1288 m; 1254 m; 1229 m; 1151 s; 1025 w; 1002 m; 974 s; 939 w; 834 s; 777 s; 753 s; 712 m; 688 s; 670

s. MS (EI): *m/z* (%)=251 ([M^++H], 16); 193 (66); 181 (10); 149 (12); 135 (13); 105 (100); 75 (73).

3.2.11. 2-Morpholino-acetophenone (**22**)

Morpholine (62 mmol) was added dropwise to a solution of 2-bromoacetophenone (7.5 mmol) in THF (15 mL). A white precipitate was formed while the mixture was refluxed for one day. An aqueous solution of $NaHCO_3$ was added. After extraction with diethyl ether the organic layer was washed with aqueous solution of NaOH and dried over Na_2SO_4. The crude product was purified by flash column chromatography (eluent: ethyl acetate/*n*-hexane 1:1) to yield a brownish oil. Yield: 89%. ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.02–7.97 (m, 2H); 7.60–7.55 (m, 1H); 7.50–7.43 (m, 2H); 3.83 (s, 2H, C(O)CH_2); 3.79 (m, 4H, CH_2); 2.62 (m, 4H, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=172.0; 160.9; 131.9; 129.6; 128.1; 67.1; 66.4; 64.4; 41.7; 40.6. IR (KBr): 3415 w; 3060 m; 2970 m; 2852 m; 2762 w; 1924 w; 1674 s; 1598 s; 1558 m; 1493 w; 1449 s; 1384 s; 1314 m; 1300 m; 1271 s; 1230 m; 1176 m; 1113 s; 1069 m; 1047 w; 1022 m; 1006 m; 981 w; 931 w; 876 w; 840 w; 812 w; 788 w; 757 w; 722 m; 693 w; 674 w; 593 w; 547 w; 449 w. MS (EI): *m/z* (%)=205 ([M^+], 2); 100 (100); 77 (18); 56 (21). HRMS calculated for $C_{12}H_{15}O_2N$: 205.10973; found: 205.109149. R_f (ethyl acetate/*n*-hexane 1:1)=0.14.

3.3. General procedure for the catalytic transfer hydrogenation

In a 10 mL Schlenk tube, the in situ catalyst (0.0038 mmol) is prepared stirring a solution of $FeCl_2$ (0.0038 mmol) and porphyrin (0.0038 mmol) in 1.0 mL 2-propanol for 16 h at 65 °C. The pre-catalyst system is reacted with sodium hydroxide (0.38 mmol in 0.5 mL 2-propanol) and 2-methoxyacetophenone (0.38 mmol in 0.5 mL 2-propanol) for 2 h at 100 °C. The solution is cooled to room temperature and filtered over a plug of silica. The conversion was measured by GC without further manipulations and the products were isolated by column chromatography or crystallization.

3.3.1. 2-Phenoxy-1-phenylethanol (**10a**)

Mp=48–50 °C (white crystals). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.40–7.15 (m, 7H, Ph); 6.92–6.80 (m, 3H, Ph); 5.03 (dd, 1H, *J*=8.67, 3.20 Hz, CH); 4.03–3.88 (m, 2H, CH_2); 2.55 (br, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=158.3; 139.6; 129.5; 128.5; 128.2; 126.3; 121.3; 114.6; 73.2; 72.5. IR (KBr): 3302 br; 3060 w; 3028 w; 2932 w; 2877 w; 1598 s; 1585 m; 1498 s; 1453 m; 1389 w; 1346 w; 1303 m; 1292 m; 1249 s; 1196 m; 1172 m; 1152 w; 1098 m; 1078 m; 1067 m; 1046 m; 1028 m; 995 w; 917 m; 884 w; 863 m; 792 w; 754 s; 701 s; 692 s; 637 m; 615 m; 594 m; 541 m; 512 m. MS (EI): *m/z* (%)=214 ([M^+], 12); 108 (100); 94 (46); 79 (60); 51 (18). HRMS calculated for $C_{14}H_{14}O_2$: 214.09883; found: 214.098407.

3.3.2. 2-(4-Chlorophenoxy)-1-phenylethanol (**11a**)

Mp=46–48 °C (white crystals). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.48–7.19 (m, 7H); 6.87–6.80 (m, 2H); 5.11 (dd, 1H, *J*=8.48, 3.38 Hz, CH); 4.08–3.95 (m, 2H, CH_2); 2.70 (br, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=157.0; 139.4; 129.4; 128.6; 128.3; 126.2; 126.1; 115.8; 72.6; 72.5. IR (KBr): 3313 br; 3059 w; 3032 w; 2933 w; 2875 w; 1596 m; 1581 m; 1491 s; 1453 m; 1388 w; 1345 w; 1290 m; 1242 s; 1196 w; 1169 m; 1093 m; 1066 m; 1039 m; 1006 m; 914 m; 864 w; 825 m; 801 m; 749 m; 700 m; 671 m; 633 w; 616 m; 559 w; 507 m. MS (EI): *m/z* (%)=248 ([M^+], 21); 142 (34); 128 (70); 107 (100); 91 (12); 79 (31). HRMS calculated for $C_{14}H_{13}ClO_2$: 248.05986; found: 248.059204.

3.3.3. 2-(2-tert-Butyl-4-methylphenoxy)-1-phenylethanol (**12a**)

Mp=61–64 °C (colourless crystals). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.53–7.32 (m, 5H, Ph); 7.13 (d, 1H, *J*=2.13 Hz, Ph); 6.98 (ddd, 1H, *J*=8.29, 2.26, 0.75 Hz, Ph); 6.78 (d, 1H, *J*=8.09 Hz, Ph); 5.21 (dd, 1H, *J*=7.35, 4.71 Hz, CH); 4.18–4.08 (m, 2H, CH_2); 2.67 (br, 1H, OH); 2.31 (s, 3H, CH_3); 1.41 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=155.0; 139.9; 137.7; 129.9; 128.5; 128.1; 127.7; 127.1; 126.3; 112.2; 73.5; 72.9; 34.7; 30.0; 20.8. IR (KBr): 3570 m; 3030 w; 2994 w; 2856 m; 2917 m; 2867 m; 1605 w; 1581 w; 1497 s; 1451 s; 1406 m; 1389 m; 1359 m; 1327 w; 1294 m; 1264 m; 1228 s; 1198 m; 1151 m; 1095 m; 1060 m; 1033 s; 1001 w; 934 w; 911 m; 881 w; 854 m; 809 m; 764 m; 702 s; 624 w; 602 w; 592 w; 553 w; 516 w; 493 w. MS (EI): *m/z* (%)=284 ([M^+], 27); 164 (31); 149 (100); 121 (18); 107 (17); 91 (21); 77 (16). HRMS calculated for $C_{19}H_{24}O_2$: 284.17708; found: 284.176978.

3.3.4. 2-(2,6-Di-iso-propylphenoxy)-1-phenylethanol (**13a**)

Mp=67–69 °C (colourless crystals). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.46–7.26 (m, 5H); 7.09 (s, 3H); 5.16 (dd, 1H, *J*=7.53, 4.40 Hz, CH); 3.92–3.82 (m, 2H, CH_2); 3.29 (sept, 2H, *J*=6.91 Hz, $CH(CH_3)_2$); 3.10 (br, 1H); 1.22 (dd, 12H, *J*=6.90, 1.29 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=152.4; 141.6; 139.8; 128.4; 128.0; 126.1; 125.8; 124.9; 79.3; 73.3; 26.4; 24.04; 24.00. IR (KBr): 3064 m; 3030 m; 2963 s; 2927 s; 2868 m; 1604 w; 1589 w; 1454 s; 1384 m; 1362 m; 1327 m; 1255 m; 1182 s; 1100 m; 1047 s; 1020 s; 936 w; 913 m; 861 w; 834 w; 802 m; 755 m; 700 s; 682 w; 623 w; 590 w; 527 w. MS (EI): *m/z* (%)=298 ([M^+], 8); 178 (51); 163 (100); 107 (15); 91 (16); 77 (11). HRMS calculated for $C_{20}H_{26}O_2$: 298.19273; found: 298.192353.

3.3.5. 2-Phenoxy-2,3-dihydro-1H-inden-1-ol (**14a**)

Colourless crystals. During the reaction a mixture of diastereomers were formed in a ratio of 1:3 (D1/D2). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.56–6.93 (m); 5.34 (d, 1H, *J*=4.12 Hz, D1); 5.28 (d, 1H, *J*=5.22 Hz, D2); 5.08–5.02 (m, 1H, D2); 4.98–4.89 (m, 1H, D1); 3.53 (dd, 1H, *J*=16.37, 6.92 Hz, D1); 3.20 (d, 2H, *J*=4.40 Hz, D2); 2.98 (dd, 1H, *J*=16.37, 5.32 Hz, D1); 2.81 (br, OH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=157.7; 142.4; 139.5; 139.2; 129.6; 129.5; 128.9; 128.6; 127.3; 125.1; 125.0; 124.8; 124.5; 121.7; 121.6; 121.0; 115.8; 115.5; 85.4; 80.3; 75.6; 36.4;

35.9. IR (Nujol): 3182 w; 2723 w; 1598 m; 1585 m; 1496 m; 1459 s; 1377 s; 1291 m; 1250 s; 1207 w; 1170 w; 1155 w; 1118 m; 1073 w; 1050 w; 1020 w; 1001 w; 879 w; 849 w; 779 w; 746 s; 723 m; 693 m; 639 w; 511 w; 413 w. MS (EI): *m/z* (%)=226 ([M^+], 19); 133 (100); 115 (21); 103 (21); 94 (61); 77 (29); 65 (11). HRMS calculated for $C_{15}H_{14}O_2$: 226.09883; found: 226.099031.

*3.3.6. 3,3-Dimethyl-1-phenoxybutan-2-ol (**15a**)*

Mp=31–33 °C (colourless crystals). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.33–7.24 (m, 2H); 7.00–6.88 (m, 3H); 4.14 (dd, 1H, *J*=9.23, 2.45 Hz, CH); 3.86 (m, 2H, CH_2); 2.35 (br, 1H, OH); 1.01 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=158.6; 129.5; 121.1; 114.6; 77.2; 69.3; 33.5; 26.0. IR (KBr): 3272 br; 3035 w; 2954 s; 2876 m; 1601 m; 1586 m; 1499 s; 1459 m; 1393 w; 1366 m; 1338 m; 1296 m; 1245 s; 1190 w; 1174 m; 1152 w; 1095 m; 1079 m; 1044 m; 1020 m; 1020 m; 1005 m; 992 w; 942 w; 926 m; 902 m; 895 m; 821 w; 754 s; 692 m; 598 w; 572 w; 513 m; 402 w. MS (EI): *m/z* (%)=194 ([M^+], 26); 119 (10); 108 (63); 94 (100); 87 (19); 77 (22); 69 (14); 57 (24); 41 (17). HRMS calculated for $C_{12}H_{18}O_2$: 194.13013; found: 194.129870.

*3.3.7. 2-Phenoxy-1-(4′-methylphenyl)ethanol (**16a**)*

Mp=50–51 °C (colourless crystals). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.34–7.14 (m, 6H); 6.98–6.85 (m, 3H); 5.05 (dd, 1H, *J*=8.64, 3.36 Hz, CH); 4.04–3.97 (m, 2H, CH_2); 2.87 (br, 1H, OH); 2.34 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=158.3; 137.8; 136.7; 129.5; 129.2; 126.2; 121.1; 114.5; 73.2; 72.3; 21.1. IR (KBr): 3297 br; 3027 w; 2912 w; 2880 w; 1932 w; 1599 m; 1586 m; 1514 m; 1498 s; 1460 m; 1388 m; 1340 m; 1293 m; 1250 s; 1195 m; 1180 m; 1172 m; 1151 w; 1090 s; 1045 m; 1021 m; 995 w; 975 w; 943 w; 916 m; 886 w; 868 m; 838 w; 815 m; 756 s; 716 w; 693 m; 616 w; 597 m; 575 w; 537 m; 513 m; 487 w; 464 w; 403 w. MS (EI): *m/z* (%)=228 ([M^+], 6); 121 (100); 108 (68); 105 (15); 65 (11). HRMS calculated for $C_{15}H_{16}O_2$: 228.11448; found: 228.114429.

*3.3.8. 2-Phenoxy-1-(4′-methoxyphenyl)ethanol (**17a**)*

Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.32–7.15 (m, 4H); 6.92–6.77 (m, 5H); 4.98 (dd, 1H, *J*=8.67, 3.39 Hz, CH); 4.00–3.87 (m, 2H, CH_2); 3.73 (s, 3H, CH_3); 2.77 (br, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=159.4; 158.3; 131.7; 129.5; 127.5; 121.2; 114.6; 113.9; 73.2; 72.1; 55.3. IR (KBr): 3440 br; 3072 w; 3044 w; 2999 w; 2929 m; 2831 w; 1728 w; 1612 m; 1600 m; 1587 m; 1514 s; 1497 s; 1456 m; 1303 m; 1245 s; 1174 m; 1154 w; 1114 w; 1080 m; 1036 m; 912 w; 867 w; 832 m; 755 m; 692 m; 639 w; 596 w; 552 w; 511 w. MS (EI): *m/z* (%)=244 ([M^+], 2); 137 (100); 121 (10); 108 (23); 94 (12); 77 (21). HRMS calculated for $C_{15}H_{16}O_3$: 244.10940; found: 244.109218.

3.4. Electrochemical measurements

The electrochemical workstation is composed of an Autolab PGSTAT 10 potentiostat from ECO Chemie and a P-450 PC with GPES 4.9 software. A three-electrode arrangement with a platinum microelectrode (25 μm diameter) as the working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum counter electrode (16 mm^2 area) was used. All potentials in the following are cited against SCE. All measurements were carried out in 2-PrOH at room temperature. As supporting electrolyte we used 0.1 mol/L tetra-*n*-butylammonium tetrafluoraborate. Due to the low solubility at room temperature all solutions of porphyrins with $FeCl_2$ were saturated solutions. For some porphyrins (e.g., compound **3**) solubility was too low to see any currents. Reversibility was determined by plotting E versus $\log[(I_a-I)/I-I_c]$ for the nearly linear range of the forward scan and determining the slope for the quasi-reversible electrode reactions. Anodic diffusion current (I_a) and cathodic diffusion current (I_c) are determined from the results of a sigmoidal fit with Microcal Origin 7.5.

Acknowledgements

We thank Mrs. S. Buchholz and Dr. C. Fischer (both Leibniz-Institut für Katalyse e.V. an der Universität Rostock) for excellent analytical assistance and Prof. Jeroschewski for general discussions. Generous financial support from the state of Mecklenburg-Western Pomerania and the BMBF as well as the Deutsche Forschungsgemeinschaft (Leibniz-price) are gratefully acknowledged.

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