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Dihydroxylation of olefins using air as the terminal oxidant

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Dedicated to Professor Dr Henri Brunner on the occasion of his 65th birthday

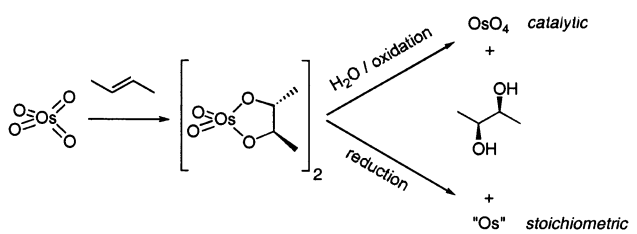
Abstract

A study of the osmium-catalyzed dihydroxylation of various olefins using air as the stoichiometric oxidant is described. Dihydroxylation takes place smoothly at an air pressure of 20 bar, at 50°C and pH 10.4. In the presence of dihydroquinine or dihydroquinidine derivatives (Sharpless ligands) asymmetric dihydroxylations occur with only slightly lower enantioselectivities compared to the classical $K_3[Fe(CN)_6]$ reoxidation system. In the case of stilbene the solvent system is crucial in determining the chemoselectivity of the reaction. The first example of a selective metal catalyzed oxidative cleavage of an olefin with air to give aldehydes is presented.

Keywords: Oxidation; Asymmetric dihydroxylation; Osmium; Air

1. Introduction

The oxidative functionalization of olefins is of major importance for both organic synthesis and the industrial production of bulk and fine chemicals [1]. Among the different oxidation products of olefins, 1,2-diols are used in a wide variety of applications. Ethylene- and propylene-glycol are produced on a multi million ton scale per annum, due to their importance as polyester monomers and anti-freeze agents [2]. A number of 1,2-diols such as 2,3-dimethyl-2,3-butanediol, 1,2-octanediol, 1,2-hexanediol, 1,2-pentanediol, 1,2- and 2,3-butanediol are of interest for the fine chemical industry. In addition chiral 1,2-diols are employed as intermediates for pharmaceuticals and agrochemicals. At present



Scheme 1. Osmylation of olefins.

1,2-diols are manufactured industrially by a two-step sequence consisting of epoxidation of an olefin with a peracid followed by hydrolysis of the resulting epoxide [3]. Compared to this process the dihydroxylation of C=C double bonds constitutes a more atom-efficient and shorter route to 1,2-diols. In general the dihydroxylation of olefins is catalyzed by osmium, ruthenium or manganese oxo species. The osmium-catalyzed variant is the most reliable and efficient method for the synthesis of *cis*-1,2-diols [4]. Since its discovery by Sharpless and co-workers the catalytic asymmetric dihydroxylation has significantly enhanced the utility of osmium-catalyzed dihydroxylation (Scheme 1) [5]. Numerous applications in organic synthesis have appeared in recent years [6].

While the problem of enantioselectivity has largely been solved through extensive synthesis and screening of cinchona alkaloid ligands some features of this general method remain problematic for larger scale applications. Firstly the use of the expensive osmium catalyst must be minimized and an efficient recycling of the metal should be developed. Secondly the applied reoxidants for Os(VI) species are expensive and lead to overstoichiometric amounts of waste.

In the past, several reoxidation processes for osmium(VI) glycolates or other osmium(VI) species have been developed. Historically, chlorates [7] and hydro-

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Table 1
Comparison of the dihydroxylation of α-methylstyrene in the presence of different oxidants

Entry	Oxidant	Yield (%)	Reaction conditions	ee (%)	TON	Waste (oxidant) (kg/kg diol)	Reference
1	$K_3[Fe(CN)_6]$	90	0°C, $K_2[OsO_2(OH)_4]$, ^tBuOH–H_2O	94 [a]	450	8.1 [c]	[5b]
2	NMO	90	0°C, OsO_4, Acetone–H_2O	33 [b]	225	0.88 [d]	[24]
3	$PhSeCH_2Ph$–O_2	89	12°C, $K_2[OsO_2(OH)_4]$, ^tBuOH–H_2O	96 [a]	222	0.16 [e]	[16]
	$PhSeCH_2Ph$–air	87		93 [a]	48	0.16 [e]	
4	NMM–Flavin–H_2O_2	93	RT, OsO_4, Acetone–H_2O		46	0.33 [f]	[9]
5	O_2	96	50°C, $K_2[OsO_2(OH)_4]$, ^tBuOH–aq. buffer	80 [a]	192		[14]

[a] Ligand: hydroquinidine 1,4-phtalazinediyl diether.
[b] Ligand: hydroquinidine *p*-chlorobenzoate.
[c] $K_4[Fe(CN)_6]$.
[d] *N*-Methylmorpholine (NMM).
[e] $PhSe(O)CH_2Ph$.
[f] NMO–Flavin-OOH.

gen peroxide [8] were first applied as stoichiometric oxidants, however in both cases the dihydroxylation proceeds with low chemoselectivity. Recently Bäckvall and coworkers were able to improve significantly the H_2O_2 reoxidation process by using *N*-methylmorpholine together with flavin as co-catalysts in the presence of hydrogen peroxide [9]. Other reoxidants for osmium(VI) are *tert*-butyl hydroperoxide in the presence of Et_4NOH [10] and a range of *N*-oxides such as *N*-methylmorpholine *N*-oxide (NMO) [11] (Upjohn process) and trimethylamine *N*-oxide. $K_3[Fe(CN)_6]$ gave a substantial improvement in the enantioselectivities in asymmetric dihydroxylations when it was introduced as a reoxidant for osmium(VI) species [4b,12,13].

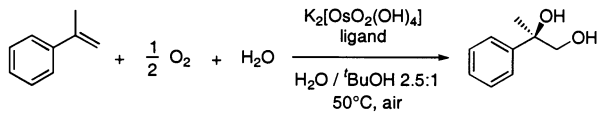
It was demonstrated by several groups that in the presence of OsO_4 and oxygen mainly non-selective oxidation reactions take place [15]. Krief et al. successfully designed a reaction system consisting of oxygen, catalytic amounts of OsO_4 and selenides for the dihydroxylation of α-methylstyrene under irradiation with visible light [16]. More recently we reported that the osmium-catalyzed dihydroxylation of aliphatic and aromatic olefins proceeds efficiently in the presence of dioxygen at ambient conditions [14,17]. As shown in Table 1 the new dihydroxylation procedure constitutes a significant advancement compared to other reoxidation procedures. The yield of the diol remains good to very good (87–96%), independent of the oxidant used. The best enantioselectivities (94–96% ee) are obtained with hydroquinidine 1,4-phthalazinediyl diether ($(DHQD)_2$-PHAL) as the ligand at 0–12°C (Table 1, entries 1 and 3).

The dihydroxylation process with oxygen is clearly the most ecologically favorable procedure (Table 1, entry 5), when the production of waste from a stoichiometric reoxidant is considered. In the presence of $K_3[Fe(CN)_6]$ approximately 8.1 kg of iron salts per kg of product are formed. However, in the case of the Krief (Table 1, entry 3) and Bäckvall procedures (Table 1, entry 4) significant amounts of by-products also arise due to the large amount of co-catalysts and co-oxidants used. It should be noted that only salts and by-products formed from the oxidant have been included in the calculation. Other waste products have not been considered. Nevertheless the numbers presented in Table 1 give a rough estimation of the environmental impact of the reaction.

Despite the advantages of the new procedure the reaction must be improved in order to be applicable on a larger scale. While it is convenient to run our procedure under 1 bar of pure dioxygen gas on a millimolar scale, this process is clearly not yet feasible for kilogram scale applications. On the one hand the concentration of substrates is relatively small (0.2–0.5 molar), on the other hand the turnover frequency of the catalyst is too slow. Additionally the use of pure molecular oxygen might also lead to safety problems. Outlined herein we describe the dihydroxylation of various olefins in the presence of air as the reoxidant as well as the improvement of catalyst efficiency.

2. Results and discussion

Air is the most economical as well as environmentally friendly oxidation reagent known. With regard to the price and safety issues it is significantly more advantageous to use air than pure oxygen gas. Hence, all current bulk oxidation processes, e.g. the oxidation of BTX aromatics or alkanes to give carboxylic acids, and the conversion of ethylene into ethylene oxide, use air and not pure oxygen as the oxidant [18]. In order to investigate the influence of air on the dihydroxylation



Scheme 2. Osmium-catalyzed dihydroxylation of α-methylstyrene.

of aromatic olefins, we studied the reaction of α-methylstyrene as a model system (Scheme 2; Table 2).

As demonstrated by our initial investigations, the dihydroxylation of α-methylstyrene in the presence of 1 bar of pure dioxygen proceeds smoothly (Table 2, entries 1, 2), with the best results being obtained at pH 10.4. In the presence of 0.5 mol% $K_2[OsO_2(OH)_4]$–1.5 mol% DABCO or 1.5 mol% $(DHQD)_2PHAL$ at pH 10.4 and 50°C total conversion was achieved after 16 h or 20 h depending on the ligand. While the total yield and selectivity of the reaction is excellent (97% and 96% respectively), the total turnover frequency of the catalyst is comparatively low (TOF = 10–12 h^{-1}). In the presence of the chiral cinchona ligand $(DHQD)_2PHAL$ an ee of 80% is observed. Sharpless et al. reported an enantioselectivity of 94% for the dihydroxylation of α-methylstyrene with $(DHQD)_2PHAL$ as the ligand using $K_3[Fe(CN)_6]$ as the reoxidant at 0°C [19]. Studies of the ceiling ee at 50°C (88% ee) show that the main difference in the enantioselectivity stems from the higher reaction temperature. Using air instead of pure dioxygen gas gave only 24% of the corresponding diol after 24 h (TOF = 1 h^{-1}; Table 2, entry 3). Although the reaction is slow, it is important to note that the catalyst stays active as shown by the fact that 58% of the product is obtained after 68 h (Table 2, entry 4). Interestingly the chemoselectivity of the dihydroxylation does not significantly decrease after a prolonged reaction time. We assumed that an increase in the oxygen concentration in solution would increase the rate of the reaction. Indeed, at 5–20 bar air pressure the turnover frequency of the catalyst is improved (Table 2, entries 5–11). All pressure experiments were conveniently carried out in a 200 ml steel autoclave (Roth GmbH), equipped with a magnetic stirrer. Similar to the atmospheric pressure reactions a mixture of *tert*-butanol and water was used as the solvent system. The pH of the mixture was kept constant by using a phosphate buffer system (see [17] for details).

As shown in Table 1 full conversion of α-methylstyrene is achieved at an air pressure of 20 bar in the presence of 0.1 mol% of osmium, which corresponds to a turnover frequency of 40 h^{-1} (Table 2, entries 8–11). Thus, by increasing the air pressure to 20 bar, it was possible to reduce the amount of osmium catalyst by a factor of 5. Importantly a decrease of the osmium catalyst *and* the ligand leads to a decrease of the enantioselectivity from 82% to 62% ee. This is explained by the fact that the ligand concentration determines the stereoselectivity of the dihydroxylation reaction (Table 2, entries 7 and 9).

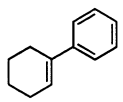
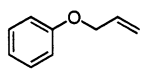
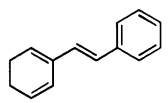
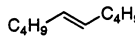
In order to increase the space–time yield of the dihydroxylation, experiments with 10 mmol of substrate were also conducted. While the reaction at this concentration proceeds only sluggishly at 1 bar even with pure oxygen, full conversion is achieved after 24 h at 20 bar of air (Table 2, entries 10, 11 and Table 3,

Table 2
Dihydroxylation of α-methylstyrene with air [a]

Entry	Pressure (bar) [c]	Cat. (mol%)	Ligand	L/Os	[L] (mmol l^{-1})	Time (h)	Yield (%)	Selectivity (%)	ee (%)
1	1 (pure O_2)	0.5	DABCO [d]	3:1	3.0	16	97	97	
2	1 (pure O_2)	0.5	$(DHQD)_2PHAL$ [e]	3:1	3.0	20	96	96	80
3	1	0.5	DABCO	3.1	3.0	24	24	85	
4	1	0.5	DABCO	3.1	3.0	68	58	83	
5	5	0.1	DABCO	3:1	0.6	24	41	93	
6	9	0.1	DABCO	3:1	0.6	24	76	92	
7	20	0.5	$(DHQD)_2PHAL$	3:1	3.0	17	96	96	82
8	20	0.1	$(DHQD)_2PHAL$	3:1	0.6	24	95	95	62
9	20	0.1	$(DHQD)_2PHAL$	15:1	3.0	24	95	95	83
10 [b]	20	0.1	$(DHQD)_2PHAL$	3:1	1.5	24	94	94	67
11 [b]	20	0.1	$(DHQD)_2PHAL$	6:1	3.0	24	94	94	78
12 [b]	20	0.1	$(DHQD)_2PHAL$	15:1	7.5	24	60	95	82

[a] Reaction conditions: $K_2[OsO_2(OH)_4]$, 50°C, 2 mmol olefin, 25 ml buffer solution (pH 10.4), 10 ml *tert*-BuOH.
[b] Reaction conditions: 10 mmol olefin, 50 ml buffer solution (pH 10.4), 20 ml *tert*-BuOH.
[c] The autoclave was purged with air and then pressurized to the given value.
[d] 1,4-Diazabicyclo[2.2.2.]octane.
[e] Hydroquinidine 1,4-phthalazinediyl diether.

Table 3
Dihydroxylation of various olefins with air [a]

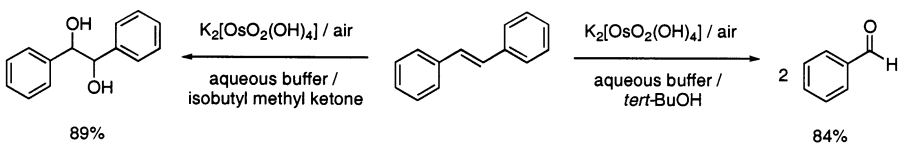
Entry	Olefin	Cat. [mol%]	Ligand	L/Os	[L] [mmol/l]	Time [h]	Yield [%][b]	Selectivity [%][b]	*ee* [%]
1		0.5	$(DHQD)_2PHAL$	3:1	3.0	24	42	42	87
2		0.5	$(DHQD)_2PHAL$	3:1	3.0	16	66	66	86
3		0.5	$(DHQD)_2PHAL$	3:1	3.0	14	76	76	87
4		0.5	$(DHQD)_2PHAL$	3:1	3.0	24	88	88	89
5		0.5	$(DHQD)_2PHAL$	3:1	3.0	24	63	63	67
6		0.5	$(DHQD)_2PHAL$	3:1	3.0	18	68	68	68
7		0.5	$(DHQD)_2PHAL$	3:1	3.0	14	67	67	66
8		0.5	$(DHQD)_2PHAL$	3:1	3.0	9	77	77	68
9		0.5	-	-	-	24	0 (84)	0 (84)	-
10[c]		1.0	DABCO	3:1	1.5	24	4 (77)	5 (87)	-
11[c,d]		1.0	$(DHQD)_2PHAL$	3.1	1.5	24	40 (35)	48 (42)	86
12[c,e]		1.0	$(DHQD)_2PHAL$	3:1	1.5	24	89 (7)	89 (7)	98
13[d]		1.0	$(DHQD)_2PHAL$	3:1	6.0	24	85	85	82
14		0.5	$(DHQD)_2PHAL$	3:1	3.0	18	96	96	63
15		0.1	$(DHQD)_2PHAL$	3:1	0.6	24	95	95	44
16		0.1	$(DHQD)_2PHAL$	15:1	3.0	24	97	97	62
17[f]		0.1	$(DHQD)_2PHAL$	3:1	1.5	24	94	94	47
18[f]		0.1	$(DHQD)_2PHAL$	6:1	3.0	24	95	95	62
19		2.0	$(DHQD)_2PYR$[g]	3:1	12.0	24	55	-	68

[a] Reaction conditions: $K_2[OsO_2(OH)_4]$, 50°C, 2 mmol olefin, 20 bar air, pH = 10.4, 25 ml buffer solution, 10 ml *tert*-BuOH, entries 9-12: 15 ml buffer solution, 20 ml *tert*-BuOH, entries 17-18: 50 ml buffer solution, 20 ml *tert*-BuOH. [b] Values in brackets are for benzaldehyde. [c] 1 mmol olefin. [d] pH = 12. [e] Isobutyl methyl ketone instead of *tert*-BuOH. [f] 10 mmol olefin. [g] Hydroquinidine 2,5-diphenyl-4,6-pyrimidinediyl diether.

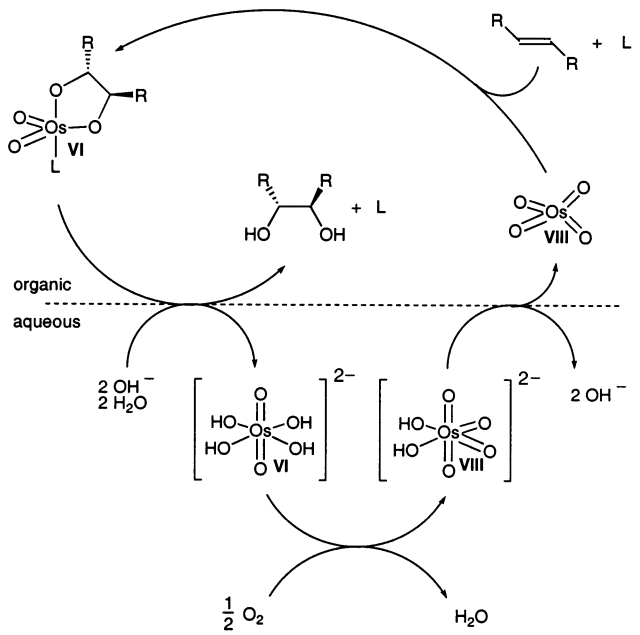
entries 17, 18). In all experiments performed under air pressure the chemoselectivity of the dihydroxylation remained excellent (92–96%).

Clearly the osmium-catalyzed dihydroxylation in the presence of air is of value to organic chemists only if a variety of substrates are tolerated. Hence, to understand the extent to which the structure of the olefin alters the reactivity, we studied the reaction of terminal aromatic (styrene), terminal aliphatic (1-octene), disubstituted (*trans*-5-decene, *trans*-stilbene), trisubstituted (1-phenyl-1-cyclohexene), and functionalized olefins (allyl phenyl ether, 1*H*,1*H*,2*H*-perfluoro-1-octene).

As depicted in Table 3 all olefins gave the corresponding diols in moderate to good yields (48–89%). Applying standard reaction conditions the best yields of diols were obtained with 1-octene (97%), 1-phenyl-1-cyclohexene (88%), *trans*-5-decene (85%), allyl phenyl ether (77%) and styrene (76%). The enantioselectivities varied from 53–98% ee depending on the substrate. Again the concentration of the chiral ligand is crucial to obtain enantioselectivities which are close to the ceiling ee (Table 3, entries 14–18). It is important to note that the chemoselectivity of the reaction decreases under standard conditions in the following substrate



Scheme 3. Osmium-catalyzed oxidative cleavage of stilbene.



Scheme 4. Proposed catalytic cycle for the dihydroxylation of olefins with OsO_4 and oxygen as the terminal oxidant.

order: α-methylstyrene = 1-octene > 1-phenyl-1-cyclohexene > *trans* - 5-decene > 1*H*,1*H*,2*H* - perfluoro - 1-octene > allyl phenyl ether > styrene ≫ *trans*-stilbene. A correlation between the chemoselectivity of the reaction and the sensitivity of the produced diol towards further oxidation is evident, with the main side reaction being the oxidative cleavage of the C=C double bond. Aromatic diols with benzylic hydrogen atoms are especially sensitive to this oxidation reaction. Thus, the dihydroxylation of *trans*-stilbene gave *no* hydrobenzoin in the biphasic mixture water–*tert*-butanol at pH 10.4, 50°C and 20 bar air pressure (Table 3, entry 9). The addition of DABCO as the ligand only slightly improves the reaction (4% hydrobenzoin; Table 3, entry 10). Instead of dihydroxylation a highly selective cleavage of stilbene to give benzaldehyde (84–87% yield) was observed. The stability of benzaldehyde towards further oxidation under 20 bar air pressure is remarkable, with only minor amounts of benzoic acid (< 5%) being produced. *To the best of our knowledge this is the first selective cleavage of an olefin to yield an aldehyde with molecular oxygen or air as the stoichiometric oxidant.*

By changing the pH of the biphasic mixture to 12 (Table 3, entry 11), the reaction becomes slower (full conversion not achieved after 24 h in the presence of 1 mol% $K_2[OsO_2(OH)_4]$), but more selective towards the diol (40%). Due to the competition of hydroxide ions with the chiral cinchona alkaloid ligand the enantioselectivity is lower than obtained with the standard Sharpless procedure using $K_3[Fe(CN)_6]$ (86% versus 99% ee). Interestingly, changing the solvent to isobutyl methyl ketone (Table 3, entry 12) makes it possible to obtain hydrobenzoin in a high yield (89%) and enantioselectivity (98%) at pH 10.4 (Scheme 3).

Although the dramatic effect of the solvent systems is not fully understood so far, it seems possible to tune the reaction pathway for other substrates to promote either oxidative cleavage or dihydroxylation.

Regarding the mechanism of the dihyroxylation reaction we believe that the catalytic cycle is similar to that presented by Sharpless et al. for the osmium catalyzed dihydroxylation with $K_3[Fe(CN)_6]$ as the reoxidant (Scheme 4). We propose that the addition of the olefin to a ligated Os(VIII) species proceeds mainly in the organic phase. Depending on the hydrolytic stability of the resulting Os(VI) glycolate complex, the rate determining step of the reaction is either hydrolysis of the Os(VI) glycolate or the reoxidation of Os(VI) hydroxy species. There must obviously only be a minor involvement of a second catalytic cycle as suggested for the dihydroxylation with NMO [20]. Such a second cycle would lead to significantly lower enantioselectivities, as the attack of a second olefin molecule on the Os(VIII) glycolate would occur in the absence of the chiral ligand. The observed enantioselectivities for the dihydroxylation with air are only slightly lower than the data previously published by the Sharpless group, despite the higher reaction temperature (50°C versus 0°C). Therefore we believe that the direct oxidation of the Os(VI) glycolate to an Os(VIII) glycolate does not represent a major pathway.

In conclusion we have shown that a number of different olefins (1,1-disubstituted, 1,2-disubstituted, terminal aliphatic and aromatic, as well as trisubstituted olefins) react with good to excellent chemoselectivities (76–97%) and sometimes good enantioselectivities (up to 98%) in the presence of an osmium catalyst *and air* to give the corresponding diols. At 20 bar of air dihydroxylations proceed at higher concentrations and with improved catalyst productivities and turnover frequencies compared to the previously described reactions at 1 bar of pure oxygen gas. There are however still improvements needed in order for this procedure to be applied on an industrial scale. Further work in this direction is in progress.

In addition, we have reported the first catalytic oxidative cleavage of an olefin to give aldehydes applying the most environmentally friendly and cost effective oxidant (air). In the future one might expect that careful control of the pH, solvent system and temperature will lead to other examples of this new synthetically useful reaction.

3. Experimental

General: ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker ARX 400 spectrometer (^{1}H 400.1 MHz, ^{13}C

100.6 MHz). Chemical shifts (δ) are given in ppm and refer to residual solvent as an internal standard. Gas chromatography was performed on a Hewlett Packard HP 6890 chromatograph with a HP5 column. Mass spectra were recorded on a AMD 402/3 mass spectrometer. The products were purified on silica gel 60, 230-400 mesh (Merck). High-performance liquid chromatography was carried out using a Hewlett Packard HP 1090 liquid chromatograph equipped with a DAD. Enantiomeric excess values were either determined by HPLC of the isolated diol or its bisbenzoate derivative. (The retention time of the major HPLC peak is printed in bold.) The absolute configurations of the products were either determined by comparison with original samples or are based on the mnemonic device established by Sharpless et al. [21].

General procedure for the dihydroxylation: In a 200 ml steel autoclave (Roth GmbH) equipped with a magnetic stirrer and a glass inline, $K_2[OsO_2(OH)_4]$ (either as a solid or in the form of a freshly prepared 2 mmol l^{-1} solution in aqueous phosphate buffer) and the ligand were dissolved in a mixture of 25 ml aqueous buffer solution and 10 ml *tert*-BuOH. To this was added 2 mmol olefin and the autoclave was closed, pressurized with air and heated to 50°C. After 9–24 h the reaction mixture was cooled to room temperature whilst stirring. A small amount of Na_2SO_3 was added, the mixture was then extracted with 2×20 ml of ethyl acetate. The combined organic layers were dried over $MgSO_4$ and submitted for GC analysis after addition of 100 μl of diethyleneglycol di-*n*-butyl ether as an internal GC standard.

Procedure for the dihydroxylation (10 mmol scale): 10 mmol α-methylstyrene or 1-octene was reacted with 3.7 mg (0.01 mmol) $K_2[OsO_2(OH)_4]$ and 46.1 mg (0.06 mmol) $(DHQD)_2PHAL$ in 50 ml buffer solution and 20 ml *tert*-BuOH as described above.

After 24 h Na_2SO_3 was added and the mixture was extracted with 2×30 ml of ethyl acetate. The combined organic layers were dried over $MgSO_4$, the solvent was removed under reduced pressure and the crude diol purified by column chromatography.

(*R*)-2-Phenyl-1,2-propanediol: Oil, 1.43 g (94% yield), ee 78% (HPLC), $[\alpha]_D^{20}$ −8.8 (c 1.76, $CHCl_3$). Lit. [22]: $[\alpha]_D^{25}$ −10.6 (c 1.76, $CHCl_3$, ee 95%). Anal. Calc. for $C_9H_{12}O_2$ (152.2): C, 71.02; H, 7.95. Found: C, 70.82; H, 7.84%.

(*R*)-1,2-Octanediol: Oil, 1.39 g (95% yield), ee 61% (HPLC, bisbenzoate), $[\alpha]_D^{20}$ 9.6 (c 1.15, EtOH). Lit.. [23]: $[\alpha]_D^{25}$ 15.6 (c 1.15, EtOH). Anal. Calc. for $C_8H_{18}O_2$ (146.5): C, 65.69; H, 12.41. Found: C, 65.39; H, 12.18%.

4. Physical data for diols

2-Phenyl-1,2-propanediol: ^{1}H-NMR ($CDCl_3$): δ = 1.50 (s, 3H), 2.39 (brs, 2H), 3.58 (d, J = 11.1 Hz, 1H), 3.74 (d, J = 11.1 Hz, 1H), 7.23–7.41 (m, 5H). ^{13}C-NMR: δ = 26.0, 71.0, 74.8, 125.0, 127.1, 128.4, 144.9. MS (EI, 70 eV), m/e: 152 ($[M]^+$, 2), 135 (2), 121 (88), 105 (5), 91 (6), 77 (10), 51 (5), 43 (100), 31 (3). HPLC (diol): (*R*,*R*)-Whelk-O1, 2% EtOH in hexane, flow rate 1.0 ml min^{-1}, t_R = 14.4 (*S*), **16.7** (*R*).

1,2-Octanediol: ^{1}H-NMR ($CDCl_3$): δ = 0.85 (t, J = 6.8 Hz, 3H), 1.21–1.29 (m, 10H), 2.25 (brs, 2H), 3.37 (dd, J = 7.7, 11.1 Hz, 1H), 3.50 (dd, J = 2.8, 11.1 Hz, 1H), 3.59–3.65 (m, 1H). ^{13}C-NMR: δ = 14.0, 22.6, 25.5, 29.3, 31.7, 33.1, 66.7, 72.4. MS (EI, 70 eV), m/e: 129 ($[M]^+$), 115, 97, 55. HPLC (bisbenzoate): (R,R)-Whelk-O1, 0.5% ^{i}PrOH in hexane, flow rate 1.0 ml min^{-1}, t_R = **13.6** (*R*), t_R = 15.8 (*S*).

1-Phenyl-1,2-ethanediol: ^{1}H-NMR ($CDCl_3$): δ = 2.6 (s, 2H), 3.63 (dd, J = 8.2, 11.4 Hz, 1H), 3.72 (dd, J = 3.6, 11.4 Hz), 4.79 (dd, J = 3.6, 8.2 Hz, 1H), 7.28–7.34 (m, 5H). ^{13}C-NMR: δ = 68.0, 74.7, 126.0, 128.0, 128.5, 140.4. MS (EI, 70 eV), m/e: 138 ($[M]^+$, 9), 121 (14), 107 (100), 79 (56), 77 (29), 51 (6), 31 (4). HPLC (diol): Daicel Chiralcel OB-H, 5% ^{i}PrOH in hexane, flow rate 1.0 ml min^{-1}, t_R = **12.5** (*R*), 16.2 (*S*).

1-Phenyl-1,2-cyclohexanediol: ^{1}H-NMR ($CDCl_3$): δ = 1.35–1.89 (m, 11H), 3.96 (dd, J = 4.7, 11.1 Hz, 1H), 7.21–7.53 (m, 5H). ^{13}C-NMR: δ = 21.1, 24.3, 30.9, 38.5, 74.5, 75.7, 125.1, 127.0, 128.5, 146.3; MS (EI, 70 eV), m/e: 192 ($[M]^+$, 59), 174 (20), 145 (10), 133 (100), 120 (36), 107 (5), 105 (68), 91 (18), 77 (36), 55 (26). HPLC (diol): Whelk (25 cm × 0.46 cm I.D.), 10% ^{i}PrOH in hexane, flow rate 1.0 ml min^{-1}, t_R = 4.4 (*S*, *S*), t_R = **6.4** (*R*, *R*).

1,2-Diphenyl-1,2-ethanediol: ^{1}H-NMR ($CDCl_3$): δ = 2.73 (brs, 2H), 4.69 (s, 2H), 7.09–7.22 (m, 10H). ^{13}C-NMR: δ = 79.1, 126.9, 127.9, 128.1, 139.8. MS (EI, 70 eV), m/e: 214 ($[M]^+$, 1), 197 (14), 108 (100), 107 (89), 79 (78), 77 (40), 51 (11). HPLC (diol): Daicel Chiralcel OB-H, 10% EtOH in hexane, flow rate 1.0 ml min^{-1}, t_R = **8.0** (*R*, *R*), 10.1 (*S*, *S*).

5,6-Decanediol: ^{1}H-NMR ($CDCl_3$): δ = 0.89 (t, J = 7.2 Hz, 6H), 1.28–1.50 (m, 12H), 2.12 (s, 2H), 3.37–3.39 (m, 2H). ^{13}C-NMR: δ = 14.0, 22.7, 27.8, 33.3, 74.5. MS (CI, isobutane), m/e: 175 ($[M+H]^+$, 2), 157 ($[M-OH]^+$, 100), 139 (15), 117 (2), 97 (5), 87 (12), 86 (11), 83 (14), 69 (19). HPLC (bisbenzoate): Daicel Chiralcel OD-H, 0.2% ^{i}PrOH in hexane, flow rate 1.0 ml min^{-1}, t_R = 6.0 (*S*, *S*), t_R = **7.3** (*R*, *R*).

3-Phenoxy-1,2-propanediol: ^{1}H-NMR ($CDCl_3$): δ = 2.10 (brs, 2H), 3.74 (dd, J = 5.2, 11.3 Hz, 1H), 3.83, (dd, J = 3.7, 11.3 Hz, 1H), 3.99–4.12 (m, 3H), 6.85–7.29 (m, 5H). ^{13}C-NMR: δ = 63.7, 69.1, 70.3, 114.5, 121.3, 129.6, 158.3. MS (EI, 70 eV), m/e: 168 ($[M]^+$, 27), 119 (9), 94 (100), 77 (17). HPLC (diol): Daicel Chiralcel OD-H, 20% ^{i}PrOH in hexane, flow rate 1.0 ml min^{-1}, t_R = 6.7 (*R*), t_R = **11.9** (*S*).

1*H*,1*H*,2*H*-Perfluorooctane-1,2-diol: ^{1}H-NMR (D_6-DMSO): δ = 3.74 (m, 1H), 3.93 (m, 1H), 4.30 (m, 1H), 5.24 (s, 1H), 6.49 (s, 1H). ^{13}C-NMR: δ = 60.2, 76.9,

110.2, 110.9, 112.9, 115.3, 116.8, 119.4; MS (CI, isobutane), m/e: 381 ($[M+H]^+$, 100), 363 ($[M-OH]^+$, 24), 330 (2), 273 (1), 154 (7), 111 (11). HPLC (bisbenzoate): Daicel Chiralcel OD-H, 0.15% EtOH in hexane, flow rate 1.0 ml min^{-1}, $t_R = \mathbf{7.1}$ (S), $t_R = 8.0$ (R).

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