A New Practical Method for the Osmium-Catalyzed Dihydroxylation of Olefins using Bleach as the Terminal Oxidant

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Abstract: A general procedure for the osmium-catalyzed dihydroxylation of various olefins using bleach as oxidant is reported for the first time. Aromatic and aliphatic olefins yield the corresponding *cis*-1,2-diols in the presence of dihydroquinine or dihydroquinidine derivatives (Sharpless ligands) with good to excellent chemo- and enantioselectivities under optimized pH conditions. In the presence of a small excess of bleach as reoxidant fast dihydroxylation takes place even at 0 °C. Under optimum reaction conditions it is possible to dihydroxylate terminal aliphatic and aromatic olefins as well as internal olefins. The low price of the oxidant and the simple handling of bleach make this dihydroxylation variant attractive for further applications.

Key words: asymmetric catalysis, dihydroxylation, homogenous catalysis, osmium, oxidations

1,2-Diols constitute important bulk and fine chemicals for the chemical industry. For example ethylene glycol and propylene glycol are manufactured on a million ton scale per annum.[1] Other 1,2-diols such as 2,3-dimethylbutane-2,3-diol, octane-1,2-diol, hexane-1,2-diol, pentane-1,2-diol, butane-1,2-diol, and butane-2,3-diol are produced as fine chemicals. In general, these products are made in industry by a two-step sequence consisting of epoxidation of the terminal olefin with a peracid or peroxide followed by hydrolysis of the resulting epoxide.[2] Enantiomerically pure functionalized aromatic and aliphatic 1,2-diols are of special interest as chiral building blocks for pharmaceuticals and agrochemicals.

The osmium-catalyzed dihydroxylation of olefins is the most reliable method for the synthesis of *cis*-1,2-diols.[3] Here, OsO_4 reacts with olefins to give (dimeric) osmium(VI) glycolates, which subsequently yield the corresponding 1,2-diols and an osmium(VI) species.

In the presence of a suitable oxidant Os(VI) is in situ reoxidized and can be used in catalytic amounts. Based on the introduction of cinchona alkaloid derivatives as ligands for OsO_4 by Sharpless[4] an efficient catalytic asymmetric dihydroxylation (AD reaction) of olefins is possible in the presence of an excess of $K_3[Fe(CN)_6]$ as terminal oxidant. After considerable ligand optimization by the Sharpless group, this reaction constitutes nowadays one of the most useful and versatile methods in asymmetric organic synthesis. Based on this elegant development, an increasing number of applications of asymmetric dihydroxylations in organic synthesis can be found.[5]

Despite the usefulness of the Sharpless AD further improvements are desirable. Here, important goals for the advancement of the method are the increase of catalyst efficiency of the expensive osmium complexes or even better the development of new catalysts based on cheaper and less toxic metals. In addition, the reaction should proceed at high rate and the reoxidant should be cheap and lead to environmentally benign byproducts.

Recently, we and others started a program for the development of new terminal oxidants for the osmium-catalyzed dihydroxylation of olefins. Based on the substantial improvement of enantioselectivities in asymmetric dihydroxylations by using $K_3[Fe(CN)_6]$ as the oxidant, industrial research led to the development of an in situ electrochemical reoxidation of $K_4[Fe(CN)_6]$.[6] More recently, Bäckvall and co-workers developed an elegant H_2O_2 reoxidation process for Os(VI) by using *N*-methylmorpholine together with flavin as cocatalysts in the presence of hydrogen peroxide.[7] 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.[8] At the same time we reported that the osmium-catalyzed dihydroxylation of aliphatic and aromatic olefins proceeds efficiently in the presence of dioxygen at ambient conditions.[9] The latter process with oxygen is clearly the ecologically most favorable procedure, when the production of waste from a stoichiometric reoxidant is considered. Nevertheless, this dihydroxylation variant has also its drawbacks. 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 low. Additionally, the use of oxygen might need special reactor equipment for larger scale applications. Therefore, we are still interested in new industrially viable reoxidants for asymmetric dihydroxylations. Apart from oxygen and hydrogen peroxide, bleach is the most simple and cheap oxidant which can be used in industry without problems. Surprisingly the use of bleach in osmium-catalyzed dihydroxylations has not been studied in detail. To the best of our knowledge this oxidant has only been applied in presence of osmium complexes in two patents in the early 70's

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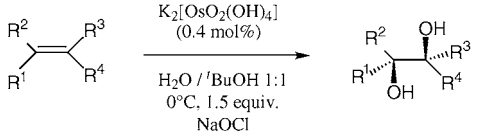
for the oxidation of fatty acids.[10] Herein we describe the first general dihydroxylation procedure of various olefins in the presence of bleach as the reoxidant (Scheme 1).



Scheme1 Osmium-catalyzed asymmetric dihydroxylation of alkenes with bleach

Aromatic olefins are important substrates for the synthesis of pharmaceutically interesting *cis*-1,2-diols.[11] Hence, for our initial investigations we chose α-methylstyrene (Table 1) and 1-phenylcyclohexene (Table 2) as model systems to study their dihydroxylation. As demonstrated by our previous investigations, the dihydroxylation in the presence of osmium tetroxide is largely pH dependant.[12] Hence, the influence of the pH value of the solution, ligands, different biphasic mixtures, and temperature were investigated in detail.

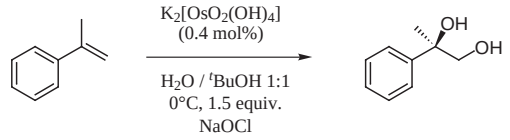
All catalytic experiments were conveniently carried out with 2.0 mmol substrate and 0.4 mol% $K_2[OsO_2(OH)_4]$ in Schlenk tubes using no special inert atmosphere above the solution. In general, a biphasic mixture of organic solvent and water [20 mL H_2O/*t*-BuOH (1:1)] was used as solvent system at room temperature. The pH of the mixture was either kept constant by using different phosphate buffer systems (see experimental section for details) or 2 equivalents of K_2CO_3 were added at the start of the reaction.

In agreement with our results using oxygen or $K_3[Fe(CN)_6]$ as reoxidant, the dihydroxylation of α-methylstyrene in the presence of bleach was significantly influenced by the pH of the water phase. At acidic pH (<7) a fast non-selective oxidation of the olefin to chlorinated compounds occurred due to the formation of *t*-BuOCl. However, already at neutral pH (7.0) a significant amount of 1,2-diol was produced. In the absence of ligand, using a buffered water solution the chemoselectivity increased from 24% at pH 7.0 to 99% at pH 13.

Unfortunately, the conversion of the reaction decreased at the same time from 78% (pH 7) to 42% (pH 13). Hence, the best yield of 2-phenylpropane-1,2-diol (63%) was obtained at pH 12 (Table 1, entries 1–6).

Surprisingly, the use of 2 equivalents of K_2CO_3 instead of a phosphate buffer led to better results (Table 1, entries 7–

Table 1 Osmium-Catalyzed Dihydroxylation of α-Methylstyrene Using Bleach[a]



Entry	pH	NaOCl (equiv)	Time (h)	Ligand (1 mol%)	Conversion (%)	Yield (%)	Selectivity (%)	ee (%)
1	7.0[b]	1.1	0.5[c]	–	78	24	31	–
2	9.0[b]	1.1	0.5[c]	–	74	43	58	–
3	10.4[b]	1.1	0.5[c]	–	74	45	61	–
4	11.2[b]	1.1	0.5[c]	–	69	55	79	–
5	12.0[b]	1.1	0.5[c]	–	66	63	96	–
6	13.0[b]	1.1	0.5[c]	–	42	42	99	–
7	12.7	1.1	0.5[c]	–	79	79	99	–
8	12.7	1.5	0.5[c]	–	84	75	90	–
9	12.7	2.0	0.5[c]	–	82	72	87	–
10	12.7	1.5	1.0[c]	–	95	89	93	–
11	12.7	1.5	1.0	–	80	79	99	–
12	12.7	1.5	1.0	DABCO	73	72	98	–
13	12.7	1.5	1.0	quinuclidine	87	86	98	–
14	12.7	1.5	1.0	$(DHQD)_2PHAL$	100	98	98	77

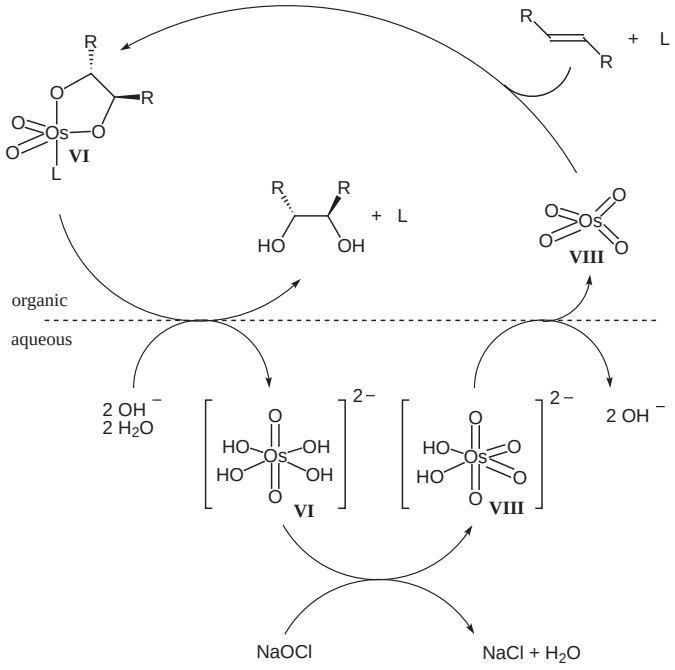
[a] General conditions: 2.0 mmol of substrate, 0.4 mol% of $K_2[OsO_2(OH)_4]$, 20 mL of H_2O/*t*-BuOH (1:1), and 2.0 equiv of K_2CO_3, 0 °C.
[b] Instead of 2.0 equiv K_2CO_3, 10 mL of a buffer solution was used. Buffer solution was prepared by adjusting an aq 0.5 M KH_2PO_4 solution with 2 N aq NaOH solution to proper pH.
[c] Room temperature.

11). Here in contrast to the use of $K_3[Fe(CN)_6]$ as reoxidant, the pH of the water solution remained unchanged at the end of the reaction. Using K_2CO_3 and an excess of bleach (1.5 equiv) at room temperature, 2-phenylpropane-1,2-diol was obtained after 1 hour in 89% yield (93% chemoselectivity, entry 10). At 0 °C the dihydroxylation with bleach proceeded with extremely high chemoselectivity (99%, entry 11), albeit at a somewhat lower rate. Nevertheless the turnover frequency (TOF[13]) at 0 °C was approximately 200 h^{-1}, which is a reasonable level[14] for fine chemical applications. Due to the increased chemoselectivity all further experiments were done at 0 °C. The addition of ligands led to different results. While in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) the reaction rate was decreased, the reaction rate increased (ligand-accelerated catalysis[15]) in the presence of quinuclidine or the Sharpless ligand hydroquinidine 1,4-phthalazinediyl diether [$(DHQD)_2PHAL$]. Thus, a 100% conversion and 98% yield (TOF = 242 h^{-1}) of the desired 1,2-diol were obtained at 0 °C in the presence of 0.4 mol% $K_2[OsO_2(OH)_4]$ and 1 mol% of $(DHQD)_2PHAL$. Interestingly, the yield of 2-phenylpropane-1,2-diol was significantly higher (98%) using bleach compared to literature protocols using *N*-methylmorpholine-*N*-oxide (NMO) (90%)[16] or $K_3[Fe(CN)_6]$ (90%)[4b] at this temperature.

Next, we turned our interest to the asymmetric catalytic dihydroxylation using bleach as oxidant. Sharpless et al. reported an enantioselectivity of 94% ee for the dihydroxylation of α-methylstyrene with $(DHQD)_2PHAL$ as the ligand using $K_3[Fe(CN)_6]$ as reoxidant at 0 °C.[4b] Using our system in the presence of 1 mol% $(DHQD)_2PHAL$ an enantioselectivity of only 77% ee is obtained (Table 2, entry 1). Clearly the catalytic cycle in the presence of bleach should be similar to the one presented by Sharpless et al. for the osmium mediated dihydroxylation with $K_3[Fe(CN)_6]$ as the reoxidant (Scheme 2). Thus, the lower enantioselectivity can be explained by some involvement of the so-called second catalytic cycle as suggested for the dihydroxylation with NMO, with the intermediate Os(VI) glycolate being oxidized to a Os(VIII) species prior to hydrolysis.[17] In general, the second cycle leads to significantly lower enantioselectivities, as the attack of a second olefin molecule on the Os(VIII) glycolate occurs in the absence of chiral ligand. It is likely that the oxidation of the Os(VI) glycolate in the organic phase occurs by minor amounts of *t*-BuOCl, which can be formed by a side reaction of bleach with *t*-BuOH.

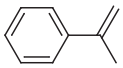
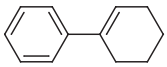
Nevertheless, the enantioselectivity of the reaction was improved by applying a higher ligand concentration (Table 2). In the presence of 5 mol% of $(DHQD)_2PHAL$ a good enantioselectivity is observed for α-methylstyrene and 1-phenylcyclohexene (91 and 95% ee, respectively). Further addition of ligand did not increase the enantioselectivity.

A slow addition mode of 1-phenylcyclohexene to the reaction mixture (Table 2, entry 9) did not improve the stereoselectivity any further. The concentration of ligands, hypochlorite and the different osmium species in the organic phase is very much dependant on the nature of the organic cosolvent. In order to get some more information about the importance of these concentration effects, we studied the model reaction in different biphasic mixtures. As shown in Table 3, the organic cosolvent had indeed a dramatic influence on the outcome of the dihydroxylation of α-methylstyrene.



Scheme 2 Catalytic cycle for the dihydroxylation of olefins with OsO_4 and bleach as the terminal oxidant

Table 2 Asymmetric Dihydroxylation in the Presence of NaOCl[a]

Entry	Substrate	$(DHQD)_2PHAL$ (mol%)	Conversion (%)	Yield (%)	Selectivity (%)	Ee (%)
1		1	100	98	98	77
2	"	2	100	98	98	85
3	"	5	100	99	99	91
4		1	98	88	90	91
5	"	2	100	95	95	92
6	"	5	100	88	88	95
7	"	7[b]	99	87	88	95
8	"	10	98	92	92	95
9	"	1	99	89	90	91[c]
10	"	1	8[d]	0	0	–

[a] General conditions: 2.0 mmol of substrate, 0.4 mol% of $K_2[OsO_2(OH)_4]$, 1 h, then *t*-BuOH (10 mL) + H_2O (10 mL), 0 °C, 1.5 equiv of NaOCl, 2 equiv of K_2CO_3.
[b] 1 Mol% ligand was added after 20 min and 40 min.
[c] Slow addition of substrate over a period of 45 min.
[d] 2 Equiv of $MeSO_2NH_2$ were added.

Table 3 Variation of the Organic Solvent for the Dihydroxylation of α-Methylstyrene[a]

Entry	Solvent	Conversion (%)	Yield (%)	Selectivity (%)	ee (%)
1	H_2O/*t*-BuOH	100	98	98	77
2[b]	H_2O/*t*-BuOH	100	99	99	87
3	H_2O/MIBK	60	60	99	64
4	H_2O/pinacolone	91	90	99	72
5	H_2O/toluene	100	96	96	85
6	H_2O/CH_2Cl_2	73	72	99	64
7	H_2O/MTBE	100	99	99	89
8[c]	H_2O/MTBE	100	99	99	90

[a] General conditions: 2 mmol of α-methylstyrene, 0.4 mol% of $K_2[OsO_2(OH)_4]$, 2 equiv of K_2CO_3, 1.5 equiv of NaOCl, 1 mol% of $(DHQD)_2PHAL$, 0 °C, 1 h.
[b] 10% Aqueous solution of NaCl/*t*-BuOH was used as solvent.
[c] 2 Mol% of $(DHQD)_2PHAL$ was used.

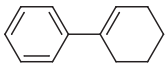
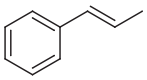
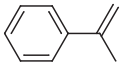
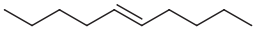
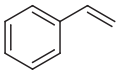
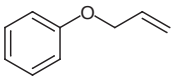
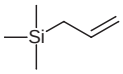
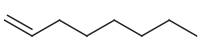
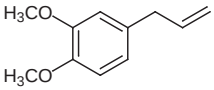
Compared to *t*-BuOH, toluene and *tert*-butyl methyl ether (MTBE) gave comparable yields and better enantioselectivities. Here, the formation of *t*-BuOCl is excluded. Dichloromethane and methyl isobutyl ketone (MIBK) led to lower yields and lower enantioselectivities. The enantioselectivity was increased by increasing the polarity of the water phase by using a 10% aqueous NaCl solution. The increase of enantioselectivity in the presence of salt ('salting-out of the chiral ligand') or using MTBE or toluene can be explained by an increase of the concentration of the chiral ligand in the organic phase. However, so far it is unclear why a decrease of ee is observed in the case of dichloromethane, pinacolone and MIBK.

The new dihydroxylation procedure will be of importance to synthetic organic chemists, only if various kinds of olefins react without problems. Hence, we tested different aliphatic and aromatic olefins, both terminal and internal ones applying our optimized conditions from Table 2. In addition, the reaction of some functionalized olefins was also studied (Table 4).

In all cases, good to excellent yields (84–99%) and chemoselectivities (84–99%) of 1,2-diols were observed. The lowest chemoselectivities were obtained with styrene and 1-phenylcyclohexene. Here, cleavage of the double bond occurred in small amount, which might be prevented by not using an excess of the oxidant. Except for eugenol methyl ether enantioselectivities of 73–95% were realized in the presence of 5.0 mol% $(DHQD)_2PHAL$. These results might be optimized by using other solvent combinations as demonstrated in Table 3.

Despite the slow hydrolysis of the corresponding sterically hindered Os(VI) glycolate, (*E*)-dec-5-ene reacted fast without problems. This result is especially interesting since it is necessary to add stoichiometric amounts of hydrolysis aids to the dihydroxylation of most internal olefins in the presence of other oxidants. Apart from

Table 4 Asymmetric Dihydroxylation of Different Olefins Using NaOCl as Terminal Oxidant[a]

Entry	Substrate	Time (h)	Conversion (%)	Yield (%)	Selectivity (%)	ee (%)	ee (%) Ref.[3b]
1		1	100	88	88	95	99
2		2	93	93	99	95	97
3		1	100	99	99	91	–
4		1	98	92	94	93	97
5		1	100	84	84	91	97
6		2	94	88	94	73	88
7		2	94	87	93	80[b]	–
8		2	100	97	97	73	–
9		2	98	94	96	34[b]	–
10		2	>97	97	>97	80[b]	92

[a] Conditions: 2.0 mmol of substrate, 0.4 mol% of $K_2[OsO_2(OH)_4]$, 5.0 mol% of $(DHQD)_2PHAL$, *t*-BuOH (10 mL), H_2O (10 mL), 1.5 equiv of NaOCl, and 2 equiv of K_2CO_3, 0 °C.
[b] 5.0 Mol% of $(DHQD)_2PYR$ was used instead of $(DHQD)_2PHAL$. Ee value using 5.0 mol% $(DHQD)_2PHAL$ was 20% for entry 9 and 31% for entry 10.

unfunctionalized aromatic and aliphatic olefins, allyl phenyl ether, allyltrimethylsilane, and eugenol methyl ether gave the corresponding 1,2-diol with high chemoselectivity.

In conclusion, we have presented a new variant for the osmium-catalyzed dihydroxylation using bleach as oxidant. In contrast to traditional belief, it is possible to perform dihydroxylations with a variety of olefins to yield the corresponding 1,2-diols in excellent yield and selectivity. Advantageously, the reaction rates are high, even an internal aliphatic olefin reacts fast without the need to add hydrolysis aids. In order to get optimum enantioselectivities a higher ligand concentration (1–5 mol%) has to be applied with respect to the general Sharpless AD procedure. Nevertheless, the new protocol has also distinct advantages. Compared to the dihydroxylation with $K_3[Fe(CN)_6]$ or NMO as oxidant, the procedure has the advantage that the oxidant is cheaper and less harmful byproducts (1.2–1.5 equiv NaCl instead of 3 equiv of Fe salts or 1 equiv of *N*-methylmorpholine) are produced. In addition, the enantioselectivity obtained is considerably higher compared to dihydroxylations using NMO. In comparison to the procedure using hydrogen peroxide, no cocatalysts (flavin, *N*-methylmorpholine) need to be added. Compared to the dihydroxylation using dioxygen this procedure is faster and more easy to perform. Hence, we believe that our new protocol will be valuable for fine chemical synthesis as well as general organic synthesis.

^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer (^1H: 400.1 MHz, ^{13}C: 100.6 MHz). Chemical shifts (δ) are given in ppm and refer to residual solvent as 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). HPLC 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 bis-benzoate 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.[18] The commercial bleach (13% available chlorine) used was obtained from Fluka.

Dihydroxylation of α-Methylstyrene; 2-Phenylpropane-1,2-diol; Typical Procedure

In a 100 mL Schlenk tube, $K_2[OsO_2(OH)_4]$ (2.95 mg, 8 μmol), $(DHQD)_2PHAL$ (77.9 mg, 0.1 mmol), and K_2CO_3 (0.55 g, 4.0 mmol) were dissolved in a mixture of *tert*-BuOH (10 mL) and H_2O (10 mL), then a 13% bleach (1.3 mL, 3.0 mmol) was added. The biphasic mixture was cooled to 0 °C in an ice-bath. Then α-methylstyrene (236 mg, 260 μL, 2.0 mmol) was added by a syringe in one portion and the reaction mixture was stirred vigorously with a magnetic stirring bar. After 1 h, Na_2SO_3 (500 mg) was added and the mixture was warmed to r.t. under stirring. The mixture was then extracted with EtOAc (20 mL). The organic layer was dried ($MgSO_4$) and submitted for GC analysis after addition of diethyleneglycol dibutyl ether (100 μL) as an internal GC standard. For isolation of the product, the solvent was removed under reduced pressure and the crude diol purified by column chromatography (hexane–EtOAc, 2:1) to give 2-phenylpropane-1,2-diol (301 mg, 99%) as a white solid. HPLC analysis of the pure 1,2-diol showed an enantiomeric excess of 91%.

HPLC (diol): (*R*,*R*)-Whelk-O1, 2% EtOH in hexane, flow rate 1.0 mL/min, t_R = 14.4 (*S*), 16.7 (*R*).

^{1}H NMR ($CDCl_3$): δ = 7.23–7.41 (m, 5 H), 3.74 (d, *J* = 11.1 Hz, 1 H), 3.58 (d, *J* = 11.1 Hz, 1 H), 2.39 (br s, 2 H), 1.50 (s, 3 H).

^{13}C NMR: δ = 144.9, 128.4, 127.1, 125.0, 74.8, 71.0, 26.0.

MS (EI, 70 eV): *m*/*z* (%) = 152 ([M]$^+$, 2), 135 (2), 121 (88), 105 (5), 91 (6), 77 (10), 51 (5), 43 (100), 31 (3).

1-Phenylethane-1,2-diol

HPLC (diol): Daicel Chiralcel OB-H, 5% *i*-PrOH in hexane, flow rate 1.0 mL/min, t_R = 12.5 (*R*), 16.2 (*S*).

^{1}H NMR ($CDCl_3$): δ = 7.28–7.34 (m, 5 H), 4.79 (dd, *J* = 3.6, 8.2 Hz, 1 H), 3.72 (dd, *J* = 3.6, 11.4 Hz, 1 H), 3.63 (dd, *J* = 8.2, 11.4 Hz, 1 H), 2.6 (s, 2 H).

^{13}C NMR: δ = 140.4, 128.5, 128.0, 126.0, 74.7, 68.0.

MS (EI, 70 eV): *m*/*z* (%) = 138 ([M]$^+$, 9), 121 (14), 107 (100), 79 (56), 77 (29), 51 (6), 31 (4).

1-Phenylcyclohexane-1,2-diol

HPLC (diol): Whelk (25 cm × 0.46 cm i.d.), 10% *i*-PrOH in hexane, flow rate 1.0 mL/min, t_R = 4.4 (*S*,*S*), t_R = 6.4 (*R*,*R*).

^{1}H NMR ($CDCl_3$): δ = 7.21–7.53 (m, 5 H), 3.96 (dd, *J* = 4.7, 11.1 Hz, 1 H), 1.35–1.89 (m, 11 H).

^{13}C NMR: δ = 146.3, 128.5, 127.0, 125.1, 75.7, 74.5, 38.5, 30.9, 24.3, 21.1.

MS (EI, 70 eV): *m*/*z* (%) = 192 ([M]$^+$, 59), 174 (20), 145 (10), 133 (100), 120 (36), 107 (5), 105 (68), 91 (18), 77 (36), 55 (26).

Decane-5,6-diol

HPLC (bis-benzoate): Daicel Chiralcel OD-H, 0.2% *i*-PrOH in hexane, flow rate 1.0 mL/min, t_R = 6.0 (*S*,*S*), t_R = 7.3 (*R*,*R*).

^{1}H NMR ($CDCl_3$): δ = 3.37–3.39 (m, 2 H), 2.12 (s, 2 H), 1.28–1.50 (m, 12 H), 0.89 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR: δ = 74.5, 33.3, 27.8, 22.7, 14.0.

MS (CI, isobutane): *m*/*z* (%) = 175 ([M + H]$^+$, 2), 157 ([M – OH]$^+$, 100), 139 (15), 117 (2), 97 (5), 87 (12), 86 (11), 83 (14), 69 (19).

3-Phenoxypropane-1,2-diol

HPLC (diol): Daicel Chiralcel OD-H, 20% *i*-PrOH in hexane, flow rate 1.0 mL/min, t_R = 6.7 (*R*), t_R = 11.9 (*S*).

^{1}H NMR ($CDCl_3$): δ = 6.85–7.29 (m, 5 H), 3.99–4.12 (m, 3 H), 3.83, (dd, *J* = 3.7, 11.3 Hz, 1 H), 3.74 (dd, *J* = 5.2, 11.3 Hz, 1 H), 2.10 (br s, 2 H).

^{13}C NMR: δ = 158.3, 129.6, 121.3, 114.5, 70.3, 69.1, 63.7.

MS (EI, 70 eV): *m*/*z* (%) = 168 ([M]$^+$, 27), 119 (9), 94 (100), 77 (17).

3-(Trimethylsilyl)propane-1,2-diol

HPLC (bis-benzoate): Daicel Chiralcel OD-H, 0.2% EtOH in hexane, flow rate 1.0 mL/min, t_R = 9.3 (*S*), t_R = 10.5 (*R*).

^{1}H NMR ($CDCl_3$): δ = 3.68–3.86 (m, 2 H), 3.40–3.58 (m, 2 H), 3.28 (dd, *J* = 11.0, 8.4 Hz, 1 H), 0.76 (dd, *J* = 14.5, 8.1 Hz, 1 H), 0.65 (dd, *J* = 14.5, 4.4 Hz, 1 H), 0.01 (s, 9 H).

^{13}C NMR: δ = 70.3, 68.9, 21.5, –0.9.

MS (CI, isobutane): *m*/*z* (%) = 149 ([M + H]$^+$, 1), 131 ([M – OH]$^+$, 77), 115 (11), 91 (15), 75 {[M – $Si(CH_3)_3$)]$^+$, 100}, 73 (21).

3-(3,4-Dimethoxyphenyl)propane-1,2-diol

^{1}H NMR ($CDCl_3$): δ = 6.8 (d, *J* = 8.13 Hz, 1 H), 6.73–6.75 (m, 2 H), 3.87–3.95 (m, 1 H), 3.86 (s, 3 H), 3.84 (s, 3 H), 3.66–3,71 (m, 1 H), 3.51 (m, 1 H), 2.74 (dd, *J* = 13.78, 5.17 Hz, 1 H), 2.67 (dd, *J* = 13.78, 8.13 Hz, 1 H), 2.06 (d, *J* = 3.44 Hz, 1 H), 1.94 (m, 1 H).

^{13}C NMR: δ = 148.9, 147.7, 130.2, 121.2, 112.4, 111.3, 73, 66, 55.9, 55.8, 39.3.

MS (EI, 70 eV): *m*/*z* = 212 ([M]$^+$, 31), 152 (22), 151 (100), 137 (18).

HPLC (diol): Daicel Chiralcel OF-117, 17.4% *i*-PrOH in hexane, flow rate 2.0 mL/min, t_R = 9.6 (*R*), t_R = 11.4 (*S*).

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