Tetrahedron Vol. 49, No. 42, pp. 9501-9516, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Stereodivergent Synthesis of *cis* Epoxides Derived from Asymmetrized 2-Alkenyl-1,3-propanediols

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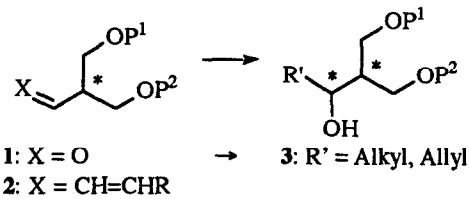
(*Received in UK* 29 *June* 1993; *accepted* 30 *July* 1993)

Abstract: *Cis* epoxides of any desired absolute stereochemistry have been obtained in a high enantio- and diastereodivergent manner *via* diastereospecific epoxidation of asymmetrized (Z)-2-alkenyl-1,3-propanediols, in turn obtained through a chemoenzymatic route, and a protection-deprotection 'trick' on hydroxy groups.

Differently protected *bis*(hydroxymethyl)acetaldehyde (BHYMA*)[1] **1**, recently prepared by us in high enantiomeric excess by a chemoenzymatic procedure, is a new C_4 polyfunctionalized chiral building block available in both enantiomeric forms by a simple protecting group exchange at the two hydroxymethyl branches (*enantiodivergency*).[1] With the purpose to show the high chemical and stereochemical versatility of this new chiral precursor, we have studied some nucleophilic additions and we have found that a suitable choice of both protecting groups on the two hydroxymethyls and of the reaction conditions allows to control the stereochemistry of the addition of various C-nucleophiles and to obtain adducts (**3**, Scheme 1) in high diastereomeric and enantiomeric excess.[2] Moreover, thanks to the residual 'latent symmetry'[2a] present in the right moiety of **3**, we have shown that it is possible to transform one diastereoisomer into its epimer using the same protecting groups interchange 'trick' before mentioned, thus obtaining both diastereoisomeric adducts exploiting a single type of stereocontrol in the addition step (*diastereodivergency*).[2]

Scheme 1



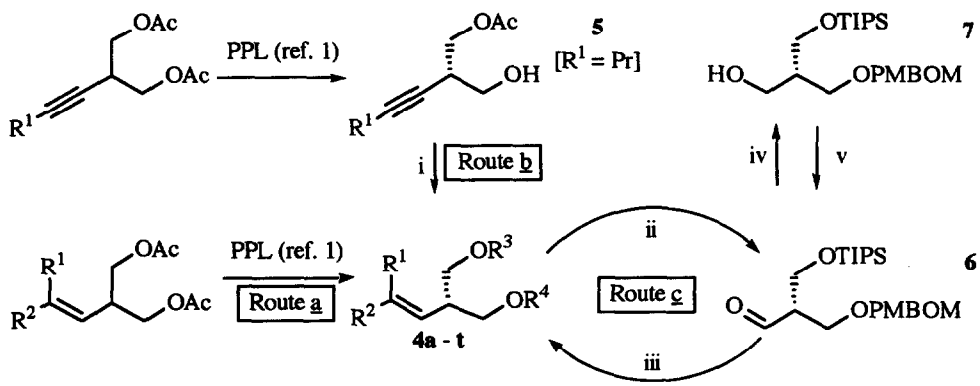
1: X = O
2: X = CH=CHR
→ **3**: R' = Alkyl, Allyl

We have now turned our attention to 2-alkenyl derivatives of 1,3-propanediol (**2**), which are homoallylic diols having both hydroxy groups on the same side and at the same distance with respect to the double bond. These substrates can undergo nucleophilic, electrophilic and radical additions and we were particularly interested in defining the role played by the protections of the two similar appendages on the stereochemistry of these reactions, in view of the many important products achievable through these transformations.

Continuing our researches on new polyfunctionalized chiral building blocks in organic synthesis,[1] we report here our results on the preparation of some (*E*) and (*Z*) asymmetrized 2-alkenyl-1,3-propanediols (**4a - p**)[3] by a chemoenzymatic procedure and on their transformation into the corresponding epoxides[4] which are useful intermediates for the construction of many important chiral targets.[5]

The epoxidation was studied on monoprotected derivatives since the ability of a homoallylic hydroxy group to affect the rate and the stereochemistry of this reaction is well known.[5]

Scheme 2



i) H_2, Lindlar Pd, EtOH, r. t.. ii) O_3, CH_2Cl_2 / MeOH, -78°C, then Me_2S, pyridine, r. t.. iii) $Ph_3P{=}CHR^1$, THF, -78°C. iv) $NaBH_4$, MeOH, -78°C → r.t.. v) DMSO, *i*-Pr_2NEt, -78°C → -30°C.

Comp	R^1	R^2	R^3	R^4	Route
4a	H	Pr	Ac	H	a
4b	H	Pr	Bn	H	a
4c	H	Pr	TBDMS	H	a[a]
4d	-$(CH_2)_5$-		Ac	H	a
4e	-$(CH_2)_5$-		TBDMS	H	a[a]
4f	Pr	H	Ac	H	b
4g	Pr	H	Bn	H	b
4h	Pr	H	TBDMS	H	b[a]
4i	Pr	H	TBDPS	H	b[a]
4l	Pr	H	Tr	H	b[a]
4m	Pr	H	PMBOM	H	c[a]
4n	Pr	H	TIPS	H	c
4o	Me	H	PMBOM	H	c[a]
4p	Me	H	TIPS	H	c
4q	H	Pr^i	Ac	H	a
4r	H	Pr^i	TIPS	PMBOM	a
4s	Pr	H	TIPS	PMBOM	c
4t	Me	H	TIPS	PMBOM	c

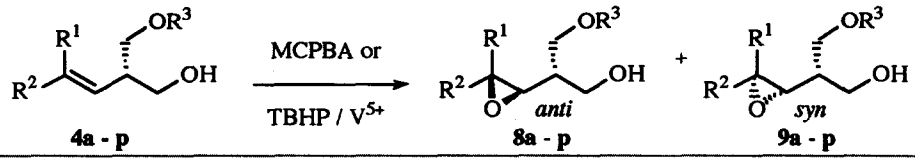
Bn = $PhCH_2$; TBDMS = *t*-$BuMe_2Si$; PMBOM = 4-$MeO(C_6H_4)CH_2OCH_2$; Tr = Ph_3C; TBDPS = *t*-$BuPh_2Si$; TIPS = $(Me_2CH)_3Si$; Pr = $Me(CH_2)_2$; Pr^i = Me_2CH

[a] The enantiomer was synthesised.

With the aim at defining the best protocol to obtain the alkenyl substrates in high enantiomeric and diastereoisomeric excess, we followed three different routes (Scheme 2): a) PPL catalyzed monohydrolysis of 2-alkenyl-1,3-propanediacetates[1] (for **4a - e**); b) hydrogenation of asymmetrized 2-alkynyl-1,3-propanediacetates, in turn obtained by PPL catalyzed monohydrolysis of the corresponding diacetates[1] (for **4f - l**); c) Wittig condensation of asymmetrized BHYMA* **6** with phosphorus ylides (for **4m - p**). In each process, the eventual manipulation of protecting groups afforded the desired monoprotected diol.

Although the first procedure apparently was the most straightforward, unfortunately appreciable changes of enantiomeric excess with the structure of substrates were found to occur in PPL catalyzed hydrolysis[1] and, especially in the asymmetrization of (Z) 2-alkenyl-1,3-diacetoxypropane, the enantiomeric excess was generally rather poor (e. e. 55%). For (Z) substrates the procedure b appeared to be more convenient, since alkynyl substrates were in general better (e. e. ≥ 83%) accepted by PPL than (Z) alkenyl ones and the subsequent hydrogenation of the triple bond generally proceeded in good chemical and stereochemical yields. Finally, a further

Scheme 3

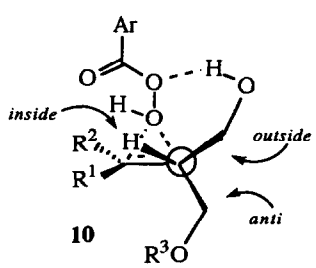


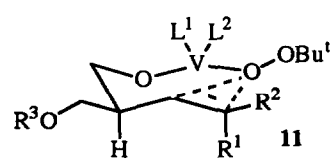
4a - p **8a - p** **9a - p**

Table 1. Epoxidation of monoprotected homoallylic diols **4a - p**

Entry	Subs	Conf	R^3	Method[a]	Yield (%)[b]	*anti* : *syn* ratio[c, d]
1	**4a**	*E*	Ac	A	84	54 : 46
2	**4a**	*E*	Ac	B	58	50 : 50
3	**4b**	*E*	Bn	A	86	51 : 49
4	**4c**	*E*	TBDMS	A	77	57 : 43
5	**4c**	*E*	TBDMS	B	96	68 : 32
6	**4d**	-	Ac	A	50	85 : 15
7	**4d**	-	Ac	B	43	84 : 16
8	**4e**	-	TBDMS	A	19	> 95 : 5
9	**4e**	-	TBDMS	B	66	> 95 : 5
10	**4f**	*Z*	Ac	A	82	64 : 36
11	**4f**	*Z*	Ac	B	38	72 : 28
12	**4g**	*Z*	Bn	A	71	80 : 20
13	**4g**	*Z*	Bn	B	56	> 95 : 5
14	**4h**	*Z*	TBDMS	A	79	70 : 30
15	**4h**	*Z*	TBDMS	B	63	> 95 : 5
16	**4i**	*Z*	TBDPS	A	72	85 : 15
17	**4i**	*Z*	TBDPS	B	57	> 95 : 5
18	**4l**	*Z*	Tr	A	95	79 : 21[e]
19	**4l**	*Z*	Tr	B	90	> 95 : 5[e]
20	**4m**	*Z*	PMBOM	B	74	> 95 : 5
21	**4n**	*Z*	TIPS	B	61	> 95 : 5
22	**4o**	*Z*	PMBOM	B	90	> 95 : 5
23	**4p**	*Z*	TIPS	B	98	> 95 : 5

[a] Method A: MCPBA, anhydrous CH_2Cl_2; Method B: *t*-BuOOH, $VO(acac)_2$, anhydrous CH_2Cl_2. [b] Isolated (*anti* + *syn*) yields. [c] Determined by ^1H NMR spectroscopy. In some cases, diastereoisomeric ratio was confirmed by isolating (flash chromatography) and weighing single diastereoisomers. [d] For a definition of *anti* isomer, see Text. For the determination of stereochemistry and optical purity of products see Text and Experimental. [e] Determined by TLC spectrodensitometry (λ 254 nm).





improvement in the enantiomeric excess of the (Z) derivatives was achieved by strategy c. This strategy star from 2-isopentenyl-1,3-diacetoxypropane, which seemed to be the best substrate accepted by PPL.[1] This di etate, once asymmetrized by the enzyme to **4q** (e. e. > 95%), was transformed into a BHYMA* and then c densed with phosphorus ylides to furnish the required alkenyl derivative. The advantage of this route is that same PPL asymmetrized precursor (**4q**) could be used for the preparation of any olefinic derivative. The o problem was to ensure the enantiospecificity of all the steps that follow the enzyme catalyzed asymmetrizat and the diastereocontrol of the Wittig reaction. This aim was reached by a proper choice of the protect groups (TIPS and PMBOM, see **4r**) for the asymmetrized alkenediol before performing the ozonolysis and purifying the corresponding aldehyde by fast column chromatography in the presence of traces of pyridine[6] fore the Wittig condensation, which was performed using two unstabilized ylides.[7] The optical purity of two (Z) alkenes (**4s** and **4t**) was checked *via* ozonolysis, followed by $NaBH_4$ reduction of the resulting al hyde, and ^1H NMR analysis of Mosher's esters[8] derived from the corresponding alcohol (**7**).

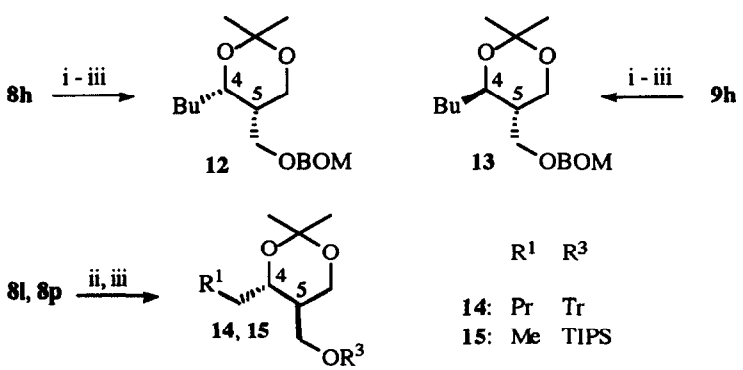
The monoprotected alkenes were finally obtained either from monoacetates **4a**, **d**, **f** or from diprotec alkenes **4s** and **4t** through protection-deprotection procedures. The various protecting groups were selected the basis of the mildness of the conditions required for their introduction and removal and taking into acco their different electronic properties ('chelating' or 'non-chelating').[1] The overall sequences were found to b general non-racemizing, as judged from NMR analysis of Mosher's esters derived from monoprotected alke themselves. Only in the case of benzylation we found some difficulties, working both under basic or acid conditions. In the former case, chemical yield were good, but racemisation was observed (complete when b zylation was performed on monoacetates **4a** or **4d**, partial when performed on monosilylated diols **4c** or 4 in the latter case, no trace of desired product was observed starting either from monoacetates or monosilyla diols.

Having in our hands good methodologies to obtain monoprotected (*E*) and (Z) 2-alkenyl-1,3-propane ols in an enantiospecific manner, we turned our attention to the epoxidation reaction,[10, 11] which was stud using two different sets of oxidative conditions: 3-chloroperoxybenzoic acid in anhydrous CH_2Cl_2 (Method and *t*-BuOOH and $VO(acac)_2$ in anhydrous CH_2Cl_2 (Method B). Chemical and stereochemical results for variously protected 2-alkenyl-1,3-propanediols are reported in Table 1: *anti* epoxides are herein defined as ones having the oxygen of the oxiranic ring and the alkoxymethyl substituent on the opposite side in the zig- drawing, as indicated in Scheme 3.

An examination of the data shows that, in accordance with previously reported literature data for epoxi tion of homoallylic alcohols having a chiral centre in the α position,[5b, 11a, b, f, i, l, 12] the *anti* epoxide is ge ally obtained as the main diastereoisomer.

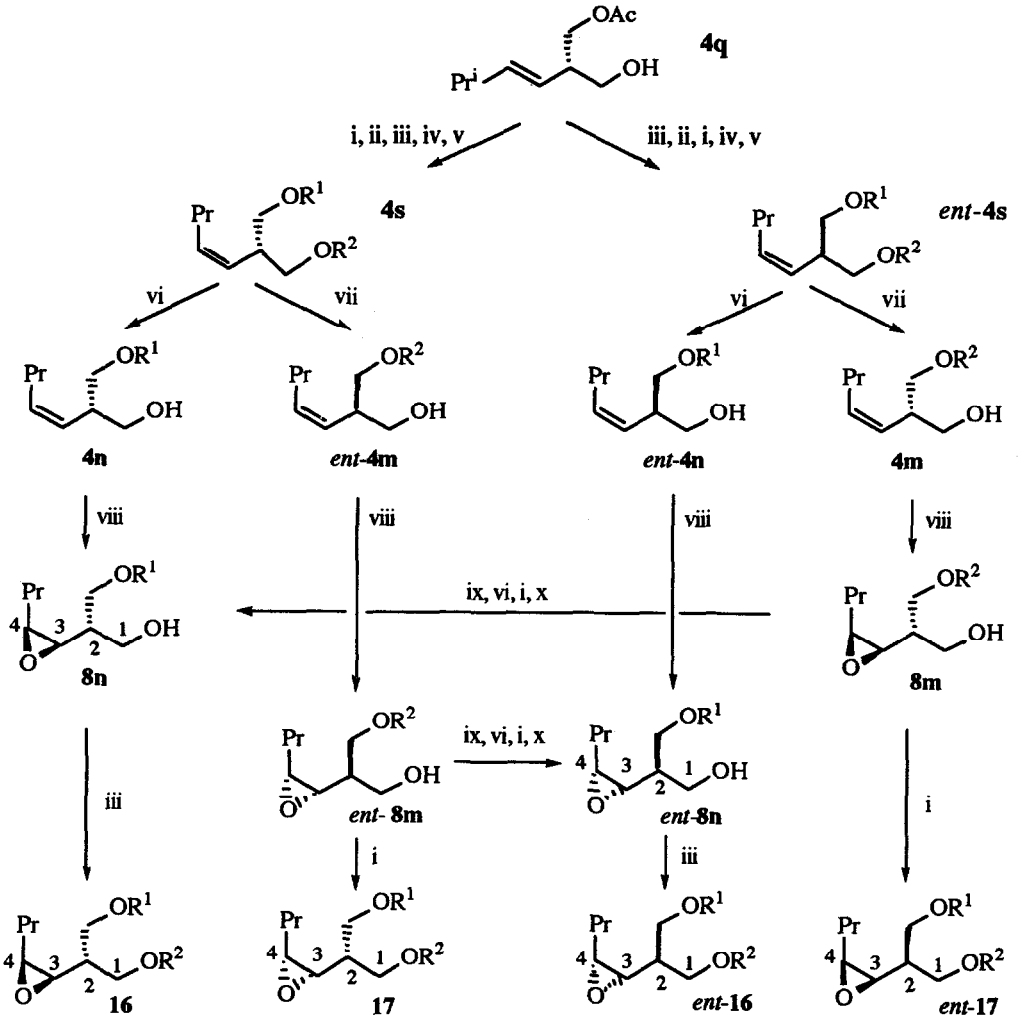
The more pronounced stereoselectivity obtained using *t*-BuOOH / $VO(acac)_2$ could be ascribed t

Scheme 4



i) $PhCH_2OCH_2Cl$, *i*-Pr_2NEt, CH_2Cl_2. ii) $LiAlH_4$, THF or Et_2O / THF. iii) 2-Methoxypropene, PTSA, CH_2Cl_2.

Scheme 5



i) *i*-Pr_3SiCl, imidazole, DMF or *i*-$Pr_3SiOSO_2CF_3$, 2,6-lutidine, CH_2Cl_2. ii) KOH, MeOH. iii) 4-$MeOC_6H_4CH_2OCH_2Cl$, *i*-Pr_2NEt, CH_2Cl_2. iv) O_3, MeOH-CH_2Cl_2, then Me_2S, pyridine. v) $Ph_3P{=}CH(CH_2)_2Me$, THF. vi) DDQ, CH_2Cl_2, *t*-BuOH, pH 7 buffer. vii) TBAF, THF. viii) *t*-BuOOH, VO(acac)2, CH_2Cl_2. ix) $PhCH_2OCH_2Cl$, *i*-Pr_2NEt, CH_2Cl_2. x) H_2, 10% Pd/C, $CaCO_3$, MeOH.

stronger interaction between the hydroxy group in the substrate and the oxidising agent through formation of a cyclic vanadate ester in the transition state.[11b] The higher selectivity observed with (*Z*) alkenes with either employed oxidising systems was also in accordance both with the coordinated transition state[11a, c, 13] (**10**) generally proposed for MCPBA oxidations of olefins and with the 'chair-like' cyclic transition state[11b] (**11**) suggested for vanadium-catalyzed epoxidations. In the former case, the hydroxyalkyl group can occupy either the

anti or the *inside* position for *E* alkenes, but experiences severe steric interactions in the *inside* position for *Z* isomers (R^1 = Alkyl); in the latter case only *E* isomers (R^1 = H) can achieve an energetically competitive boa conformation, leading to *syn* product. High stereoselectivity in the epoxidation of (*E*) homoallylic alcohols ha indeed previously been reported only when the olefinic double bond is trisubstituted.[11a, d] The usually hig selectivity in vanadium-catalyzed epoxidations seems independent both of R^1 (*e. g.*, entries 20 - 21 *vs* 22 - 23) and of R^3 (*e. g.*, entries 13 *vs* 15, 20 *vs* 21), provided that R^3 is not very small: in our opinion, the generally low diastereoselectivity exhibited by homoallylic monoacetates **4a**, **d**, **f** could be ascribed to the small encumbrance of the acetyl group rather than to its coordinating properties.[11d]

Relative configurations of products were determined by converting some of the epoxides into cyclic derivatives, *i. e.* dioxolanes **12** - **15** (Scheme 4)[14] and examining their NMR spectra: both proton and carbon-13 signals were in accord with proposed stereochemistry.[4, 15] Chromatographic and spectroscopic analogies were used to correlate other epoxides. Retention of configurational integrity in the epoxy alcohols was confirmed by ^{1}H NMR analysis of Mosher's esters[8] derived from some of the epoxy alcohols themselves.

We have thus shown how it is possible to obtain *anti* epoxides in an enantiospecific and diastereoselective manner, but it is well known that a major problem in the epoxidation of (*Z*) homoallylic alcohols is the stereoselective achievement of *syn* isomers and only recently some practical methods have been reported, using either a removable C-trimethylsilyl group to mimic a trisubstituted double bond[11d] or a very bulky non-coordinating hydroxyl protecting group and a tungsten-based oxidising agent to reverse the selectivity.[11f]

In our case, thanks to the latent σ-symmetry in the propanediol moiety of our products, no particular chemical device was necessary to reverse the selectivity: in fact, the stereoselective achievement of the *anti* isomer meant the stereoselective achievement of the *syn* one as well, simply applying a suitable protocol of protecting groups exchange. A straightforward example of the high *enantio-* and *diastereodivergency* of our substrates is shown in Scheme 5, that exemplifies how to obtain, starting from a common chiral precursor (monoacetate **4q**, easily obtained in a multigram scale through an enzyme catalyzed hydrolysis),[1] any of the four possible stereoisomeric *cis* diprotected epoxides (**16** and **17**, and their enantiomers). In fact, using a single diastereoselective Wittig reaction (to obtain **4s**) and a single diastereoselective epoxidation on (*Z*) homoallylic alcohols **4r** and *ent*-**4m**, the two stereoisomeric *cis* diprotected epoxide **16** and **17** (having the same configuration at carbon 2 but opposite configuration at carbon 3 and 4) were obtained through the same number of steps and in similar yields (left half of Scheme 5), simply varying the stage and / or the order of removal and introduction of protecting groups: exactly in the same way, their enantiomers were obtained from *ent*-**4s** (right half of Scheme 5).

Moreover, thanks again to the high latent symmetry of our substrates, it was also possible to obtain the two diastereoisomeric diprotected *cis* epoxides **16** and *ent*-**17** (which are epimeric at carbon 2) through the epoxidation of a single homoallylic alcohol (*e. g.* **4m**, that gives *anti* epoxide **8m**), followed by a suitable protection-deprotection trick, thus "building a bridge" between the right and the left half of Scheme 5. The other two diastereoisomers (*ent*-**16** and **17**) could be in turn obtained starting from *ent*-**4m**.

In this way, we have devised a practical route to obtain all four stereoisomeric diprotected *cis* epoxides (**16** and **17**, and their enantiomers), starting from a single precursor (**4q**), simply through the same optimized diastereoselective reactions and a judicious choice and use of protecting groups.

We wish to thank M.U.R.S.T. and C.N.R. (Progetto Finalizzato Chimica Fine) for financial assistance.

EXPERIMENTAL

General

NMR spectra were recorded as $CDCl_3$ solutions on a Varian Gemini 200 spectrometer using tetramethylsilane (TMS) as internal standard; chemical shifts (δ) are in ppm, coupling constants (J) are in Hz; a * means that the value was obtained through double resonance experiments. ^1H NMR data for homoallylic alcohols **4** are reported in Table 2, data for epoxides **8** and **9** are reported in Table 4 (*anti* epoxides **8**) e Table 5 (*syn* epoxides **9**). Optical rotatory powers ($[\alpha]_D$) were measured as 1 - 2% $CHCl_3$ solutions.

'Usual workup' means that the given reaction mixture was extracted (Et_2O, CH_2Cl_2, or AcOEt), the organic layer was dried (Na_2SO_4), filtered, and evaporated to dryness under reduced pressure.

Tetrahydrofuran (THF) was always freshly distilled from K / Ph_2CO; CH_2Cl_2, Et_2O, PhMe, *N,N*-dimethylformamide (DMF), and PhH were purchased as dry solvents from Aldrich and stored over 4 Å molecular sieves. All reactions requiring dry conditions were run under an inert atmosphere (N_2).

TLC analyses were carried out on silica gel plates, which were developed by spraying a solution of $(NH_4)_4MoO_4 \cdot 4H_2O$ (21 g) and $Ce(SO_4)_2 \cdot 4H_2O$ (1 g) in H_2SO_4 (31 ml) and H_2O (469 ml) and warming. R_f were measured after an elution of 7 - 9 cm. Column chromatographies were run following the method of 'flash chromatography',[16] using 230 - 400 mesh silica gel (Merck).

t-Butylhydroperoxide is abbreviated as TBHP, vanadyl acetylacetonate as $VO(acac)_2$, 3-chloroperoxybenzoic acid as MCPBA, *p*-toluenesulfonic acid as PTSA, and petroleum ether (b. p. 40 - 60°C) as PE.

All compounds gave satisfactory spectroscopic and analytical data: a selection of the latter data is reported in Table 6.

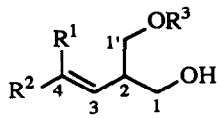
Synthesis of optically active (*S*) monoacetates **4a**, **d**, and **f** through enzymatic hydrolysis of corresponding diacetates has been already reported in Ref. 1, as well as the synthesis of (*S*) alcohol **7** and its enantiomer.

Synthesis of (S)-2-(acetoxymethyl)-3(Z)-hepten-1-ol (4f). - Monoacetate **5** (1 mmol) was dissolved in 96% EtOH (25 ml) and hydrogenated at r.t. and normal pressure over Lindlar Pd for about 15 h. The reaction was followed by GC (RSL 150 capillary column; 120°C, then 3°C/min; t_R = 17.06' for **4f** and 19.06' for **5**). After filtration of the catalyst through a silica gel pad and evaporation of solvent under reduced pressure, pure monoacetate **4f** was obtained as a colourless oil (80%): R_f = 0.38 (PE / AcOEt 7 : 3); ^1H NMR: see Ref. 1.

General procedure for the synthesis of (R)-2-(t-butyldimethylsilyloxymethyl)-3(E)-hepten-1-ol (ent-4c), 2-(t-butyldimethylsilyloxymethyl)-3-cyclohexylidene-1-propanol (ent-4e), and (R)-2-(t-butyldimethylsilyloxymethyl)-3(Z)-hepten-1-ol (ent-4h). - A solution of monoacetate **4a** or **4d** or **4f** (1 mmol) in dry DMF (5 ml), was cooled to 0°C, and treated with *t*-$BuMe_2SiCl$ (1.2 mmol) and imidazole (2.4 mmol). After 10 min the reaction was allowed to reach r.t. and stirred for 2.5 h. After cooling to 0°C, the solution was treated with H_2O (5 ml) and subjected to usual work-up (PE / Et_2O 1 : 1). Crude product was taken up in MeOH (1 ml), cooled to 0°C and treated with a 0.2 M solution of KOH in MeOH (0.7 ml; 1.4 mmol). The solution was stirred for 2 h at 0°C and for 1 h at r.t., then treated with saturated aqueous NH_4Cl (2 ml). Most methanol was evaporated at reduced pressure and the mixture diluted with H_2O and subjected to usual work-up (Et_2O) to give, after chromatography (PE / AcOEt), pure *ent*-**4c** (90%) or *ent*-**4e** (76%) or *ent*-**4h** (88%) as colourless oils: ^1H NMR data: see Table 2. *ent*-**4c**: R_f = 0.34 (PE / Et_2O 9 : 1); $[\alpha]_D$ = +19.6°. *ent*-**4e**: R_f = 0.37 (PE / Et_2O 8 : 2); $[\alpha]_D$ = +14.2°. *ent*-**4h**: R_f = 0.22 (PE / Et_2O 95 : 5); $[\alpha]_D$ = +25.1°.

Synthesis of (R)-2-(t-butyldiphenylsilyloxymethyl)-3(Z)-hepten-1-ol (ent-4i). - It was prepared from **4f** and *t*-$BuPh_2SiCl$ in 70% yield following the same procedure used for *ent*-**4c**, *ent*-**4e**, and *ent*-**4h**: R_f = 0.13 (PE / Et_2O 95 : 5); $[\alpha]_D$ = +23.4°; ^1H NMR: see Table 2.

Table 2. ^{1}H NMR data for homoallylic alcohols **4**.



	=CHC*H* (m, 1 H)[a]	C*H*$_2$OH (2 H)[a]	C*H*$_2$OR (2 H)[a]	=C*H*CH (1 H)[a]	Others
b	2.53-2.70	3.46-3.78[b]		5.28[c] (1.3, 7.6, 15.4)	0.88 (t, 3 H, J 7.2, *Me*CH$_2$); 1.37 (app. sextuplet, 2 H, J 7.4, MeC*H*$_2$); 1.99 (app dq, 2 H, J 1.2 & 6.7, C*H*$_2$CH=); 4.53 (s, 2 H, C*H*$_2$Ph); 5.59 (ddt, 1 H, J 1.4 & 6.0 & 15.7); 7.33 (br s, 5 H, *Ph*).
c	2.47[g] (7.7)	3.58-3.79[b]		5.24[c] (1.4, 8.1, 15.5)	0.07 (s, 6 H, 2 x *Me*Si); 0.88 (t, 3 H, J 7.3, *Me*CH$_2$); 0.90 (s, 9 H, *Me*$_3$C); 1.38 (app sextuplet, 2 H, J 7.5, MeC*H*$_2$); 1.98 (app dq, 2 H, J 1.2 & 6.6, C*H*$_2$CH=); 5.58 (ddt, 1 H, J 0.8 & 6.7 & 15.8, CH$_2$C*H*=); 7.35-7.69 (m, 10 H, 2 x *Ph*).
e	2.72-2.85	3.51-3.76[b]		4.77[h] (9.2)	0.07 & 0.08 (2 s, 3 H each, 2 x *Me*Si); 0.90 (s, 9 H, *Me*$_3$C); 1.10-1.99 (m, 6 H) & 2.06 (t, 2 H, J 5.1) & 2.17 (t, 2 H, J 5.0) (cyclohexane ring C*H*$_2$).
g	2.90-3.08	3.44-3.79[b]		5.16[c] (1.6, 9.5, 10.3)	0.90 (t, 3 H, J 7.3, *Me*CH$_2$); 1.38 (app. sextuplet, 2 H, J 7.4, MeC*H*$_2$); 2.07 (dq, 2 H, J 1.5 & 7.2, C*H*$_2$ CH=); 4.53 (s, 2 H, C*H*$_2$Ph); 5.56 (ddt, 1 H, J 1.0 & 10.9 & 7.4, CH$_2$C*H*=); 7.34 (br s, 5 H, *Ph*).
h	2.77-2.92	3.53-3.79[b]		5.13[c] (1.5, 10.0, 10.6)	0.08 (s, 6 H, 2 x *Me*Si); 0.90 (s, 9 H, *Me*$_3$C); 0.91 (t, 3 H, J 7.3 *Me*CH$_2$); 1.38 (app sextuplet, 2 H, J 7.5, MeC*H*$_2$); 2.07 (dq, 2 H, J 1.5 & 7.3, C*H*$_2$ CH=); 5.55 (dt, 1 H, J 7.4 & 11.0, CH$_2$C*H*=).
i	2.85-2.90	3.60-3.83[b]		5.11[d] (10.9)	0.85 (t, 3 H, J 7.2, *Me*CH$_2$); 1.06 (s, 9 H, *Me*$_3$C); 1.21-1.33 (m, 2 H, MeC*H*$_2$); 1.94 (app q, 2 H, J 7.3, C*H*$_2$CH=); 5.51 (dt, 1 H, J 7.3 & 10.6, CH$_2$ C*H*=); 7.39-7.70 (m, 10 H, 2 x *Ph*).
l	2.80-2.98	3.55 & 3.71[e] (6.0, 7.1, 10.8)	3.10 & 3.21[e] (4.7, 8.0, 9.0)	5.14[c] (1.5, 9.5, 10.2)	0.88 (t, 3 H, J 7.1, *Me*CH$_2$); 1.20-1.41 (m, 2 H, MeC*H*$_2$); 2.01 (app dq, 2 H, J 1.6 & 7.5, C*H*$_2$CH=); 5.54 (dt, 1 H, J 8.3 & 10.1, J*$_{3,4}$ 10.9, CH$_2$C*H*=); 7.22-7.46 (m, 15 H, 3 x *Ph*).
m	2.85-3.05	3.54-3.76[b]		5.20[c] (1.4, 9.7, 11.1)	0.92 (t, 3 H, J 7.2, *Me*CH$_2$); 1.40 (app sextuplet, 2 H, J 7.1, MeC*H*$_2$); 2.08 (app dq, 2 H, J 1.6 & 7.6, C*H*$_2$CH=); 3.81 (s, 3 H, *Me*O); 4.54 (s, 2 H, C*H*$_2$Ar); 4.73 (s, 2 H, OC*H*$_2$O); 5.60 (ddt, 1 H, J 0.8 & 7.3 & 11.0, CH$_2$C*H*=); 6.86-7.30 (m, 4 H, Ar*H*).
n	2.80-2.98	3.58-3.86[b]		5.12[c] (1.5, 9.6, 11.0)	0.91 (t, 3 H, J 7.3, *Me*CH$_2$); 0.98-1.15 (m, 21 H, 3 x *Me*$_2$C*H*); 1.39 (app sextuplet, 2 H, J 7.3, MeC*H*$_2$); 2.07 (app dq, 2 H, J 1.4 & 7.4, C*H*$_2$CH=); 5.55 (ddt, 1 H, J 0.9 & 7.4 & 10.9, CH$_2$C*H*=).
o	2.89-3.06	3.50-3.80[b]		5.23[f] (1.8, 9.4, 10.9)	1.69 (dd, 3 H, J 1.8 & 6.9, *Me*CH); 3.81 (s, 3 H, *Me*O); 4.54 (s, 2 H, C*H*$_2$Ar); 4.74 (s, 2 H, OC*H*$_2$O); 5.68 (ddq, 1 H, J 1.1 & 6.9 & 10.9, MeC*H*=); 6.85-6.91 (m, 2 H, Ar*H*); 7.25-7.34 (m, 2 H, Ar*H*).
p	2.82-3.02	3.56-3.90[b]		5.14[f] (1.7, 9.6, 10.7)	1.00-1.15 (m, 21 H, 3 x *Me*$_2$C*H*); 1.69 (dd, 3 H, J 1.8 & 6.9, *Me*CH); 5.63 (ddq, 1 H, J 1.0 & 6.9 & 10.7, MeC*H*=).

[a] Coupling constants J (Hz) are reported in parentheses. [b] Multiplet, 4 H. [c] Doublet of doublet of triplet. [d] Apparent triplet. [e] AB Part of an ABX system. [f] Doublet of doublet of quadruplet. [g] Apparent sextuplet. [h] Broad doublet.

Synthesis of 2-(benzyloxymethyl)-3(E)-hepten-1-ol (rac-4b). - A solution of **4a** (1 mmol) in dry DMF (1.5 ml) was cooled to 0°C and treated with $PhCH_2Br$ (1.5 mmol) and with NaH (50% in mineral oil; 1.5 mmol). After stirring for 1 h at r.t., saturated aqueous NH_4Cl (15 ml) was added. After usual work-up and chromatographic purification, pure **4b** (85%) was obtained as a colourless oil in almost racemic form: R_f = 0.28 (PE / Et_2O 7 : 3); ^1H NMR: see Table 2.

Synthesis of (S)-2-(benzyloxymethyl)-3(Z)-hepten-1-ol (4g). - A solution of *ent*-**4h** (1 mmol) in dry DMF (1.5 ml) was cooled to 0°C and treated with $PhCH_2Br$ (1.5 mmol) and with NaH (50% in mineral oil; 1.5 mmol).
After stirring for 2 h at 0°C and 1 h at r.t., saturated aqueous NH_4Cl (15 ml) was added. After usual work-up, crude product was dissolved in dry THF (7.5 ml), treated with a 1 M solution of TBAF in THF (1.3 ml; 1.3 mmol) and, after stirring for 40' at r.t., reaction mixture was diluted with brine (15 ml) and water (15 ml) and subjected to usual work-up (Et_2O) to give after chromatography (PE / Et_2O), pure **4g** (85%) as a colourless oil: R_f = 0.33 (PE / AcOEt 8 : 2); $[\alpha]_D$ = -25.9° (e. e. ≈ 56%); ^1H NMR: see Table 2.

Synthesis of (R)-2-(triphenylmethyloxymethyl)-3(Z)-hepten-1-ol (ent-4l). - A solution of monoacetate **4f** (1 mmol) in dry CH_2Cl_2 (3.5 ml) was cooled to 0°C and treated with Et_3N (2.5 mmol), Ph_3CCl (2 mmol) and a catalytic amount of DMAP. After stirring at r.t., water (4 ml) was added. Reaction mixture was diluted with brine (15 ml) and subjected to usual work-up (Et_2O). Crude product was taken up in MeOH (1 ml), cooled to 0°C, and treated with a 0.2 M solution of KOH in MeOH (0.7 ml; 1.4 mmol). The solution was stirred for 4 h at r.t., then treated with saturated aqueous NH_4Cl (4 ml). Most methanol was evaporated at reduced pressure and the mixture diluted with brine and subjected to usual work-up (Et_2O) to give, after chromatography (PE / Et_2O, containing 0.5% of Et_3N), pure *ent*-**4l** (87%) as colourless oil: R_f = 0.54 (PE / Et_2O 6 : 4); $[\alpha]_D$ = +39.5°; ^1H NMR: see Table 2.

Synthesis of (S)-3-(4-methoxybenzyloxymethoxy)-2-(triisopropylsilyloxymethyl)-1-propanol (7). - Di-protected alkene obtained from monoacetate **4q** (that is **4r**) was ozonolyzed to aldehyde **6** as described in Ref. 1, except that an excess of $NaBH_4$ was rapidly added as a solid, instead of Me_2S and pyridine, before allowing reaction mixture to slowly reach r. t.. Saturated aqueous NH_4Cl was added, most methanol was evaporated under reduced pressure, and, after usual work up (AcOEt) and chromatography, pure alcohol **7** (81%) was obtained as a colourless oil; R_f = 0.30 (PE / Et_2O 6 : 4); $[\alpha]_D$ = +2.1°; ^1H NMR: 1.05 - 1.10 (m, 21 H, 3 x Me_2CHSi), 2.03 - 2.12 (m, 1 H, C*H*), 3.69 (app d, J 6.2 Hz, 2 H, CH_2OH), 3.81 (s, 3 H, *Me*O), 3.79 - 3.96 (m, 4 H, 2 x CH_2OR), 4.53 (s, 2 H, CH_2Ar), 4.72 (s, 2 H, OCH_2O), 6.86 - 6.92 (m, 2 H, Ar*H*), 7.25 - 7.29 (m, 2 H, Ar*H*).

The same procedure was applied to convert alkenes **4s** (79%) and **4t** (45%, not optimized) to alcohol **7**, in order to check their enantiomeric purity.

General procedure for the synthesis of Mosher's esters of homoallylic and epoxy alcohols, as well as of alcohol 7. - Alcohol (0.1 mmol) was dissolved in dry CH_2Cl_2 (1 ÷ 2 ml) at 0°C and DMAP (0.6 mmol) and (*R*) or (*S*) Mosher's chloride (0.3 mmol) were added. Reaction was stirred at r. t. until substrate disappeared (2 ÷ 3 h), then directly deposed on a preparative TLC silica gel plate, which was eluted with PE / Et_2O 95 : 5 or 80 : 20. NMR spectra were recorded while irradiating the signal of methine $CH(CH_2OR)_2$ ($\delta \approx 2.22$ ppm for **7**) and AB systems due to methylene CH_2OCO [for **7**: δ 4.40 & 4.50, J_{AB} 10.7 Hz for ester derived from (*R*) Mosher's acyl chloride; δ 4.44 & 4.79, J_{AB} 10.7 Hz for ester derived from (*S*) Mosher's acyl chloride] of the two diastereomeric esters were used for quantitative determination.

Synthesis of S)-1-(4-methoxybenzyloxymethoxy)-2-(triisopropylsilyloxymethyl)- 3(Z)-heptene (4s) and of (S)-5-(4-methoxybenzyloxymethoxy)-4-(triisopropylsilyloxymethyl)-2(Z)-pentene (4t). - To a solution of

aldehyde **6** [obtained through ozonolysis of **4r** as described in ref. 1 and subjected to a rapid chromatography (PE / Et_2O 7 : 3, containing 0.1% of pyridine)] in dry THF containing a small amount of powdered 4 Å molecular sieves and cooled to -78°C, an excess (3 ÷ 6 eq) of a freshly prepared solution of (ethylidene)triphenylphosphorane or (butylidene)triphenylphosphorane in dry THF containing a small amount of powdered 4 Å molecular sieves was added until red-orange colour persisted. Reaction mixture was allowed to reach r.t. and filtered washing with PE, in order to remove most of Ph_3PO. Crude product was chromatographated (PE / Et_2O 98 : 2, containing 0.5% of Et_3N) to give pure **4s** (78%) or **4t** (89%) as colourless oils. No trace of (*E*) stereoisomer was detected in either case.

4s: R_f = 0.79 (PE / Et_2O 7 : 3); $[\alpha]_D$ = -6.9°; ^1H NMR: 0.91 (t, J 7.3 Hz, 3 H, *Me*CH_2), 1.04 - 1.07 (m, 21 H, 3 x *Me*$_2$*CH*Si), 1.20 - 1.45 (m, 2 H, MeCH_2), 2.06 (dq, J 1.1 & 7.3 Hz, 2 H, CH_2CH=), 2.74 - 2.88 (m, 1 H, C*H*CH=), 3.58 & 3.70 (AB part of an ABX system, J 6.0 & 6.0 & 9.5 Hz, 2 H, CHCH_2O), 3.68 (app. d, J 6.8 Hz, 2 H, CH_2O), 3.80 (s, 3 H, *Me*O), 4.52 (s, 2 H, CH_2Ar), 4.72 (s, 2 H, OCH_2O), 5.29 - 5.40 (m, $J_{3/4}$ 11.0* Hz, 1 H, =C*H*CH), 5.46 - 5.58 (m, 1 H, =C*H*CH_2), 6.85 - 6.89 (m, 2 H, Ar*H*), 7.25 - 7.33 (m, 2 H, Ar*H*).

4t: R_f = 0.52 (PE / Et_2O 85 : 15); $[\alpha]_D$ = -6.5°; ^1H NMR: 1.05 - 1.07 (m, 21 H, 3 x *Me*$_2$*CH*Si), 1.67 (dd, J 1.7 & 6.7, 3 H, *Me*CH=), 2.86 (app d of quintuplet, J 6.0 & 9.4 Hz, 1 H, C*H*CH=), 3.58 & 3.72 (AB part of an ABX system, J 5.9 & 6.2 & 9.4 Hz, 2 H, CHCH_2O), 3.66 - 3.76 (m, 2 H, CHCH_2O), 3.81 (s, 3 H, *Me*O), 4.53 (s, 2 H, CH_2Ar), 4.73 (s, 2 H, OCH_2O), 5.36 (ddq, J 1.7 & 9.3 & 10.9 Hz, $J_{3/4}$ 11.5* Hz, 1 H, =C*H*CH), 4.53 - 4.69 (m, 1 H, =C*H*Me), 6.84 - 6.90 (m, 2 H, Ar*H*), 7.25 - 7.34 (m, 2 H, Ar*H*).

General procedure for the synthesis of (R)-2-(4-methoxybenzyloxymethoxy)-3(Z)-hepten-1-ol (ent-4m), and (R)-2-(4-methoxybenzyloxymethoxy)-3(E)-penten-1-ol (ent-4o). - A solution of **4s** or **4t** (1 mmol) in THF (30 ml) was cooled to 0°C and 7 ml of a 0.5 M solution of TBAF in THF (3.5 mmol) were added. After stirring 15 h at r.t., brine (40 ml) and water (40 ml) were added and, after usual work-up (Et_2O) and chromatography (PE / Et_2O 45 : 55, containing 0.5% of Et_3N), pure *ent*-**4m** (92%) or *ent*-**4o** (97%) were obtained as colourless oils. *ent*-**4m**: R_f = 0.34 (PE / Et_2O 4 : 6); $[\alpha]_D$ = +31.8°; *ent*-**4o**: R_f = 0.38 (PE / Et_2O 4 : 6); $[\alpha]_D$ = +26.3°. ^1H NMR: see Table 2.

General procedure for the synthesis of (S)-2-(triisopropylsilyloxymethoxy)-3(Z)-hepten-1-ol (4n), and (S)-2-(triisopropylsilyloxymethoxy)-3(E)-penten-1-ol (4p). - A solution of **4s** or **4t** (1 mmol) in CH_2Cl_2 (15 ml) was added with 0.87 ml of a 0.2 M pH 7 phosphate buffer and 0.87 ml of *t*-BuOH and treated with 2 mmol of DDQ at r.t.. After 2 h, a saturated aqueous solution of $NaHCO_3$ was added. Usual work-up (Et_2O) and chromatography (PE / Et_2O 85 : 15) afforded pure **4n** (62%) or **4p** (95%) as colourless oils. **4n**: R_f = 0.39 (PE / Et_2O 85 : 15); $[\alpha]_D$ = -28.7°. **4p**: R_f = 0.33 (PE / Et_2O 8 : 2); $[\alpha]_D$ = -32.3°. ^1H NMR: see Table 2.

General procedure for epoxidation of homoallylic alcohols 4a - p.

With MCPBA. - Homoallylic alcohol (1 mmol) was dissolved in dry CH_2Cl_2 (10 ml) and treated with 2 mol of MCPBA at 0°C. Reactions were monitored by TLC (PE / Et_2O or PE / AcOEt). A freshly prepared 5% aqueous solution of $NaHSO_3$ (10 - 15 ml) was added and reaction mixture was extracted with Et_2O or AcOEt. The organic layer was washed with a saturated $NaHCO_3$ solution and then with brine, dried over Na_2SO_4, filtered and evaporated to give a crude product which was either rapidly chromatographated through a short silica gel pad ('filtered') (to collect the two diastereoisomeric epoxides together, in order to determine their relative ratio by NMR or GC or TLC techniques) or chromatographated ('flash' chromatography or preparative TLC) to give pure diastereoisomeric epoxides; in either cases the eluant (PE / Et_2O or PE / AcOEt) contained 0.5% of Et_3N. Chemical and stereochemical yields are reported in Table 1. Reaction times, along with details on purification and diastereoisomeric ratio determination and TLC data, are reported in Table 3. ^1H NMR data are reported in Table 4 (*anti* epoxides **8**) and Table 5 (*syn* epoxides **9**).

With VO(acac)$_2$ and TBHP. - Homoallylic alcohol (1 mmol) was dissolved in dry CH_2Cl_2 (10 ml) and

Table 3. Experimental details for syntheses of epoxides **8** and **9**

Epox	React. time (h)		Purification	Rf		Diastereomeric ratio determination
	MCPBA	TBHP		*anti*	*syn*	
a	15	72	F (PE / AcOEt 6 : 4)	0.33		PMR (*Me*CO)
b	4		C (PE / Et_2O 3 : 7)	0.32	0.37	PMR (CH_2Ph & O*H*)
c	4	22	C (PE / Et_2O 6 : 4)	0.29	0.35	PMR [Me_3Si, with Eu(fod)3]; GC
d	20	5	F (PE / Et_2O 3 : 7)	0.25		PMR (*Me*CO)
e	4.5	5	F (PE / Et_2O 6 : 4)	0.25	-	PMR (Me_3Si)
f	15	150	F (PE / Et_2O 6 : 4 → 4 : 6)	0.18 (4 : 6)		PMR (*Me*CO); ^{13}C NMR (*C*=O)
g	7	20	F (PE / Et_2O 4 : 6)	0.30	0.35	PMR (CH_2Ph)
h	15	96	C (PE / Et_2O 7 : 3)	0.18	0.26	PMR (*Me*Si & O*H*); ^{13}C NMR (*C*Me_3); GC
i	5.5	6	C (PE / Et_2O 6 : 4)	0.18	0.25	PMR (Me_3Si in pyridine d-5); GC
l	4	5	TLC (PE / Et_2O 1 : 1)	0.29	0.36	PMR (CH_2OCPh3); SD
m	-	5	TLC (PE / AcOEt 1 : 1)	0.38	-	PMR; TLC
n	-	22	C (PE / Et_2O 7 : 3)	0.24	-	PMR; TLC
o	-	2	C (PE / Et_2O 4 : 6)	0.35	-	PMR; TLC
p	-	22	C (PE / Et_2O 1 : 1)	0.27	-	PMR; TLC

F = Filtration. C = Flash chromatography. TLC = Preparative thin layer chromatography. PMR = ^{1}H NMR.
GC = Gas chromatography (Superox capillary column, T = 130°C, then 3°/min). SD = TLC spectrodensitometry (λ 254 nm).

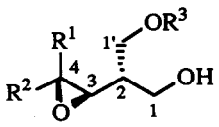
treated with a catalytic amount of $VO(acac)_2$. The mixture was cooled to 0°C, added with TBHP (1.5 mmol), and then allowed to reach r.t.. Reactions were monitored by TLC and worked up as described for MCPBA epoxidations. For details, see Tables 1 and 3 - 5.

*Synthesis of diprotected epoxide **16** from anti epoxide **8n**.* - To a solution of 1 mmol of monoprotected epoxide **8n** ($[\alpha]_D$ = -13.3°) in 30 ml of dry CH_2Cl_2, $(Me_2CH)_2NEt$ (2.3 mmol) and freshly prepared (4-*p*-methoxybenzyloxymethyl)chloride (2 mmol) were added at 0°C and reaction was stirred at r.t. overnight. Et_2NH (0.5 mmol) was added and, after stirring for 15', reaction mixture was diluted with brine and subjected to usual work-up (Et_2O). Chromatography (PE / Et_2O 85 : 15, containing 0.5% of Et_3N) afforded pure **16** (82%) as a colourless oil: R_f = 0.34 (PE / Et_2O 85 : 15); $[\alpha]_D$ = +4.0°; ^{1}H NMR: 0.80 - 1.00 (m, 3 H, *Me*CH_2), 1.00 - 1.10 (m, 21 H, 3 x *Me*$_2$*CH*Si), 1.40 -1.60 (m, 4 H, C*H*$_2$C*H*$_2$), 1.50 - 1.80 (m, 1 H, CH_2*CH*CH_2), 2.90 - 3.05 (m, 2 H, 2 x C*H*O), 3.81 (s, 3 H, *Me*O), 3.81 - 3.86 (m, 4 H, 2 x CHC*H*$_2$), 4.54 (s, 2 H, C*H*$_2$Ar), 4.75 (s, 2 H, OC*H*$_2$O), 6.84 - 7.90 (m, 2 H, Ar*H*), 7.26 - 7.32 (m, 2 H, Ar*H*).

*Synthesis of diprotected epoxide **17** from anti epoxide ent-**8m**.* - To a solution of 1 mmol of monoprotected epoxide *ent*-**8m** ($[\alpha]_D$ = +13.8°) in dry DMF (2 ml), imidazole (3 mmol) and (triisopropylsilyl)chloride (1.5 mmol) were added at 0°C and reaction stirred at r.t. for 6 h. Saturated aqueous NH_4Cl solution (4 ml) and brine were added and reaction mixture was worked up as usual (CH_2Cl_2). Chromatography (PE / Et_2O 9 : 1, containing 0.5% of Et_3N) afforded pure **17** (82%) as a colourless oil: R_f = 0.30 (PE / Et_2O 9 : 1); $[\alpha]_D$ = -2.2°; ^{1}H NMR: 0.99 - 1.90 (m, 8 H, *Me*C*H*$_2$C*H*$_2$ & CH_2*CH*CH_2), 2.95 - 3.01 (m, 2 H, 2 x OC*H*), 3.69 - 3.95 (m, 4 H, 2 x OC*H*$_2$), 3.81 (s, 3 H, *Me*O), 4.52 & 4.72 (2 s, 2 H each, OC*H*$_2$O & OC*H*$_2$Ar), 6.42 - 7.28 (m, 4 H, Ar*H*).

*Synthesis of anti epoxide ent-**8n** from anti epoxide ent-**8m**.* - A solution of 1 mmol of anti epoxide *ent*-

Table 4. ^{1}H NMR data for *anti* epoxides **8**.

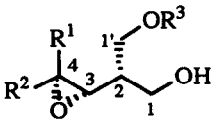


	OCHC*H* (1 H)[a]	OC*H*CH (1 H)[a]	C*H*$_2$OH (2 H)[a]	C*H*$_2$OR (2 H)[a]	Others
a	1.72-1.98[b]	2.77[l] (5.6, 7.6)	3.65[e] (5.7)	4.24[e] (6.5)	0.97 (t, 3 H, J 7.0, *Me*CH$_2$); 1.43-1.59 (m, 4 H, C*H*$_2$C 2.08 (s, 3 H, *Me*CO); 2.83-2.92 (m, 1 H, CH$_2$C*H*O).
b	1.81[m] (6.3)	2.79-2.89[f]	3.76-3.91[b]	3.64[e] (6.0)	0.95 (t, 3 H, J 7.2, *Me*); 1.38-1.58 (m, 4 H, C*H*$_2$C*H*$_2$); 4. 2 H, C*H*$_2$Ph), 7.29-7.36 (m, 5 H, *Ph*).
c	1.65[m] (6.3)	2.76[g] (2.4, 8.0)	3.71-3.88[i]		0.07 (s, 6 H, 2 x *Me*Si); 0.89 (s, 9 H, *Me*$_3$C); 0.96 (t, 3 6.8, *Me*CH$_2$); 1.42-1.57 (m, 4 H, C*H*$_2$C*H*$_2$); 2.85 (dt, 1 2.3 & 5.4, CH$_2$C*H*O).
d	1.86-1.97[b]	2.74[n] (9.4)	3.63-4.00[b]	4.20[e] (6.4)	1.40-1.80 (m, 10 H, cyclohexane ring C*H*$_2$); 2.09 (s, *Me*CO).
e	1.76-1.84[b]	2.75[n] (9.2)	3.80-3.95[b]	3.75[e] (5.2)	0.07 (s, 6 H, 2 x *Me* Si), 0.90 (s, 9 H, *Me*$_3$CSi).1.40-1.8 10 H, cyclohexane ring C*H*$_2$).
f	1.63-1.91[b]	2.97[c] (4.1)	3.79 & 3.86[d] (4.4, 8.4, 12.0)	4.21[e] (6.2)	1.00 (t, 3 H, J 7.0, *Me*CH$_2$); 1.43-1.63 (m, 4 H, C*H*$_2$C 2.09 (s, 3 H, *Me*CO); 3.04-3.07 (m, 2 H, J$_{3/4}$ 4.2*, CH$_2$Cl
g	1.70-1.90[b]	2.92-3.02[f]	3.86 & 3.94[d] (6.0, 6.2, 10.6)	3.59[e] (6.1)	0.96 (t, 3 H, J 6.8, *Me*); 1.40-1.60 (m, 4 H, C*H*$_2$C*H*$_2$); 4 2 H, C*H*$_2$Ph), 7.33-7.34 (m, 5 H, *Ph*).
h	1.72[g] (4.4)	2.91-3.02[f] (J$_{3/4}$ 4.3*)	3.69-3.99[i]		0.07 (s, 6 H, 2 x *Me*Si), 0.90 (s, 9 H, *Me*$_3$CSi); 0.99 (t, 6.9, *Me*CH$_2$); 1.40-1.60 (m, 4 H, C*H*$_2$C*H*$_2$).
i	1.74[g] (4.5)	2.79-2.97[f]	3.79-4.04[b]	3.76[e] (5.8)	0.92 (t, 3 H, J 6.5, *Me*CH$_2$); 1.06 (s, 9 H, *Me*$_3$CSi); 1.3 (m, 4 H, C*H*$_2$C*H*$_2$); 7.38-7.71 (m, 10 H, 2 x *Ph*).
l	1.83[g] (4.5)	2.92-2.98[f]	3.84 & 3.92[d] (6.9, 7.1, 10.9)	3.24[e] (5.8)	0.85-0.97 (m, 3 H, *Me*); 1.25-1.50 (m, 4 H, C*H*$_2$C*H*$_2$); 7.45 (m, 15 H, 3 x *Ph*).
m	1.66-1.87[b]	2.95[c] (4.8)	3.84 & 3.92[d] (5.4, 5.6, 11.0)	3.69[e] (6.0)	0.99 (t, 3 H, J 7.1, *Me*CH$_2$); 1.40-1.60 (m, 4 H, C*H*$_2$C 2.80-3.02 (m, 1 H, CH$_2$C*H*O); 3.81 (s, 3 H, *Me*O), 4.53 H, C*H*$_2$Ar), 4.73 (s, 2 H, OC*H*$_2$ O), 6.87-7.29 (m, 4 H, Ar
n	1.75[h] (2.2, 5.5)	2.96[d] (4.1)	3.78-4.01[i]		0.94 - 1.12 (m, 24 H, 3 x *Me*C*H*Si & *Me*CH$_2$); 1.40 - 1.(4 H, C*H*$_2$C*H*$_2$); 2.98-3.02 (m, 1 H, CH$_2$C*H*O);
o	1.73-1.90[b]	2.95[l] (4.3, 9.3)	3.69[e] (6.0)	3.84 & 3.93[c] (5.3, 5.6, 10.8)	1.32 (d, 3 H, J 5.5, *Me*CHO); 3.12 (dq, 1 H, J 4.3 & MeC*H*O); 3.81 (s, 3 H, *Me*O); 4.54 (s, 2 H, C*H*$_2$Ar); 4.7 H, OC*H*$_2$O); 6.86-6.95 (m, 2 H, Ar*H*); 7.24-7.30 (m, 2 H,
p	1.68-1.83[b]	2.97 (4.3, 9.4)	3.79-4.01[i]		1.00-1.15 (m, 21 H, 3 x *Me*$_2$C*H*Si); 1.33 (d, 3 H, *Me*CHO); 3.12 (dq, 1 H, J 4.3 & 5.5, MeC*H*O).

[a] Coupling constants J (Hz) are reported in parentheses; a * means that the value was obtained through double resonance e ments. [b] Multiplet. [c] AB Part of an ABX system. [d] Apparent triplet. [e] Apparent doublet. [f] Multiplet, 2 H, 2 x C*H*O. [g] App decuplet. [h] Doublet of quintuplet. [i] Multiplet, 4 H. [l] Doublet of doublet. [m] Apparent sextuplet. [n] Doublet.

8m ($[\alpha]_D$ = +13.8°) in dry CH_2Cl_2 (9 ml) was cooled to 0°C and added with i-Pr_2NEt (2.6 mmol PhCH_2OCH_2Cl (2.4 mmol). After stirring at r.t. for 20 h, then Et_2NH (1 mmol) was added and stirring c ued for 15'. Brine was added and reaction was worked up as usual (Et_2O) to give, after chromatographic

Table 5. ^{1}H NMR data for *syn* epoxides **9**.



	OCHC*H* (1 H)[a]	OC*H*CH (1 H)[a]	C*H*$_2$OH (2 H)[a]	C*H*$_2$OR (2 H)[a]	Others
a	1.72-1.98[b]	2.77[i] (5.8, 7.6)	3.73 & 3.77[d] (5.0, 5.0, 11.3)	4.26[f] (5.6)	0.97 (t, 3 H, J 7.0, *Me*CH$_2$); 1.43-1.59 (m, 4 H, C*H*$_2$C*H*$_2$); 2.09 (s, 3 H, *Me*CO); 2.83-2.92 (m, 1 H, CH$_2$C*H*O).
b	1.82[l] (5.6)	2.80-2.89[e]	3.80[c] (5.5)	3.70 & 3.73[d] (J_{gem} 9.2*)	0.96 (t, 3 H, J 7.0, *Me*); 1.42-1.53 (m, 4 H, C*H*$_2$C*H*$_2$); 4.53 (s, 2 H, C*H*$_2$Ph), 7.31-7.36 (m, 5 H, *Ph*).
c	1.52-1.70[b]	2.78[i] (2.4, 7.3)	3.76-3.93[h]		0.08 & 0.08 (2 s, 3 H each, 2 x *Me*Si), 0.90 (s, 9 H, *Me*$_3$CSi); 0.97 (t, 3 H, J 6.8, *Me*CH$_2$); 1.40-1.51 (m, 4 H, C*H*$_2$C*H*$_2$); 2.86 (dt, 1 H, J 2.4 & 5.3, CH$_2$C*H*O).
d	1.86-1.97[b]	2.73[m] (9.5)	3.63-4.00[b]	4.18-4.39[b]	1.40-1.80 (m, 10 H, cyclohexane ring C*H*$_2$); 2.11 (s, 3 H, *Me*CO).
f	1.63-1.91[b]	2.97[c] (4.1)	3.66[c] (5.6)	4.34 & 4.42[d] (4.4, 5.2, 10.6)	1.00 (t, 3 H, J 7.0, *Me*CH$_2$); 1.43- 1.63 (m, 4 H, C*H*$_2$C*H*$_2$); 2.11 (s, 3 H, *Me*CO); 3.04-3.07 (m, 1 H, J$_{3/4}$ 4.2*, CH$_2$C*H*O).
g	1.70-1.90[b]	2.92-3.02[e]	3.76-3.97[b]	3.50- 3.70[b]	0.96 (t, 3 H, J 6.8, *Me*); 1.40-1.60 (m, 4 H, C*H*$_2$C*H*$_2$); 4.57 (s, 2 H, C*H*$_2$Ph), 7.33- 7.34 (m, 5 H, *Ph*).
h	1.52-1.70[b]	2.94-3.06[e]	3.81-3.87[b]	3.92 & 4.01[d] (3.4, 6.2, 10.0)	0.10 & 0.11 (2 s, 3 H each, 2 x *Me*Si), 0.91 (s, 9 H, *Me*$_3$CSi). 0.97 (t, 3 H, J 7.0, *Me*CH$_2$); 1.40-1.51(m, 4 H, C*H*$_2$C*H*$_2$).
i	1.30-2.00[b]	2.98-3.04[e]	3.86[c] (5.7)	3.94-4.15[b]	0.98 (t, 3 H, J 7.0, *Me*CH$_2$); 1.08 (s, 9 H, *Me*$_3$CSi), 1.30-2.00 (m, 4 H, C*H*$_2$C*H*$_2$); 7.38-7.71 (m, 10 H, 2 x *Ph*).
l	1.50-1.90[b]	2.97-3.08[e]	3.70-4.00[b]	3.45[f] (5.1)	0.85-1.02 (m, 3 H, *Me*); 1.25-1.50 (m, 4 H, C*H*$_2$C*H*$_2$); 7.24-7.48 (m, 15 H, 3 x *Ph*).

[a] Coupling constants J (Hz) are reported in parentheses; a * means that the value was obtained through double resonance experiments. [b] Multiplet. [c] Apparent triplet. [d] AB Part of an ABX system. [e] Multiplet, 2 H, 2 x C*H*O. [f] Apparent doublet. [g] Apparent doublet of quintuplet. [h] Multiplet, 4 H. [i] Doublet of doublet. [l] Apparent sextuplet. [m] Doublet.

cation (PE / Et$_2$O 7 : 3), pure diprotected epoxide as a colourless oil: R_f = 0.36 (PE / Et$_2$O 7 : 3); $[\alpha]_D$ = +3.1°; ^{1}H NMR: 0.99 (t, 3 H, J 6.9 Hz, *Me*CH$_2$), 1.36 - 1.70 (m, 4 H, MeC*H*$_2$C*H*$_2$), 1.74 - 1.94 (m, 1 H, C*H*CH$_2$O), 2.93 - 3.04 (m, 2 H, 2 x OC*H*), 3.68 & 3.77 (2 H, AB part of an ABX system, J 3.8 & 6.4 & 9.7 Hz, C*H*$_2$OR), 3.80 (s, 3 H, *Me*O), 3.82 (d, 2 H, J 5.3 Hz, C*H*$_2$OR), 4.52 (s, 2 H, C*H*$_2$Ar), 4.61 (s, 2 H, C*H*$_2$Ph), 4.72 (s, 2 H, OC*H*$_2$OCH$_2$Ar), 4.78 (s, 2 H, OC*H*$_2$OCH$_2$Ph), 6.85 - 6.90 (m, 2 H, Ar*H*), 7.20 - 7.36 (m, 7 H, Ar*H*).

Diprotected epoxide (1 mmol) was dissolved in dry CH_2Cl_2 (12 ml) and treated with 0.85 ml of 0.2 M pH 7 phosphate buffer, 0.85 ml of *t*-BuOH, and 2 mmol of DDQ. After stirring at r.t. for 80', saturated aqueous $NaHCO_3$ was added. Usual work up (Et_2O) and chromatographic purification of crude product (PE / Et$_2$O 4 : 6) afforded pure monoprotected *syn* epoxide as a colourless oil: R_f = 0.31 (PE / Et$_2$O 6 : 4), $[\alpha]_D$ = -6.5°; ^{1}H NMR: 0.80 - 1.00 (m, 3 H, *Me*CH$_2$), 1.40 - 1.70 (m, 4 H, C*H*$_2$C*H*$_2$), 1.68 - 1.82 (m, 1 H, C*H*CH$_2$O), 2.95 - 3.06 (m, 2 H, 2 x C*H*O), 3.72 - 4.00 (m, 4 H, 2 x C*H*$_2$O), 4.63 (s, 2 H, C*H*$_2$Ph), 4.80 (s, 2 H, OC*H*$_2$O), 7.29 - 7.38 (m, 5 H, *Ph*).

Table 6. Analytical data for some selected compounds.

Cpd	Formula	H%		C%	
		Calc	Found	Calc	Found
4b	$C_{15}H_{22}O_2$	9.16	9.00	76.88	77.00
4c	$C_{14}H_{30}O_2Si$	11.70	11.66	65.06	64.87
4e	$C_{16}H_{32}O_2Si$	11.34	10.27	67.55	66.99
4g	$C_{15}H_{22}O_2$	9.16	9.11	76.88	77.01
4h	$C_{14}H_{30}O_2Si$	11.70	11.47	65.06	64.76
4i	$C_{24}H_{34}O_2Si$	8.96	8.92	75.34	75.36
4l	$C_{27}H_{38}O_2$	7.82	7.99	83.90	84.22
4m	$C_{17}H_{26}O_4$	8.90	8.91	69.36	68.96
4n	$C_{17}H_{36}O_2Si$	12.07	12.01	67.94	67.50
4o	$C_{15}H_{22}O_4$	8.33	8.36	67.65	67.05
4p	$C_{15}H_{32}O_2Si$	11.84	11.76	66.11	66.00
4s	$C_{24}H_{42}O_4Si$	10.02	9.98	68.20	68.20
4t	$C_{26}H_{46}O_4Si$	10.29	10.40	69.28	69.55
7	$C_{22}H_{40}O_3Si$	10.59	10.66	69.42	69.36
8a	$C_{10}H_{18}O_4$	8.87	8.99	59.39	59.03
8b	$C_{15}H_{22}O_3$	8.86	8.66	71.97	71.66
8c	$C_{14}H_{30}O_3Si$	11.02	10.97	61.26	61.54

Cpd	Formula	H%		C%	
		Calc	Found	Calc	Found
8d	$C_{12}H_{20}O_4$	8.83	8.78	63.14	63.76
8e	$C_{16}H_{32}O_3Si$	10.73	10.76	63.95	64.65
8f	$C_{17}H_{36}O_3Si$	11.46	11.25	64.50	65.06
8g	$C_{15}H_{22}O_3$	8.86	8.93	71.97	72.06
8h	$C_{14}H_{30}O_3Si$	11.02	11.16	61.26	61.50
8i	$C_{24}H_{34}O_3Si$	8.60	8.66	72.32	72.48
8l	$C_{27}H_{30}O_3$	7.51	7.60	80.56	80.70
8m	$C_{17}H_{36}O_5$	8.44	8.31	65.78	65.88
8n	$C_{17}H_{36}O_3Si$	11.46	11.79	64.50	64.00
8o	$C_{15}H_{22}O_5$	7.85	7.99	63.81	63.99
8p	$C_{15}H_{32}O_3Si$	11.18	11.34	62.45	62.98
8f	$C_{17}H_{36}O_3Si$	11.46	11.25	64.50	65.06
12	$C_{19}H_{30}O_4$	9.38	9.36	70.77	71.00
13	$C_{30}H_{36}O_3$	8.16	7.99	81.04	81.16
14	$C_{20}H_{36}O_3Si$	10.29	10.36	68.13	67.89
15	$C_{26}H_{46}O_5Si$	9.93	9.76	66.91	66.18
16	$C_{26}H_{46}O_5Si$	9.93	9.88	66.91	66.04

Syn monoprotected epoxide (1 mmol) was dissolved in dry DMF (7 ml), cooled to 0°C, and treated witl imidazole (3 mmol) and triisopropylsilylchloride (1.5 mmol). After stirring at r.t. for 6 h, saturated aqueou NH_4Cl (4 ml) and brine were added, and reaction mixture was worked up as usual (CH_2Cl_2) to give, afte chromatographic purification (PE / Et_2O 9 : 1 → 4 : 6), pure diprotected epoxide (55%; quantitative if based o unrecovered substrate) as a colourless oil: R_f = 0.38 (PE / Et_2O 9 : 1); $[\alpha]_D$ = +2.3°; ^{1}N NMR: 0.90 - 1.10 (m 24 H, 3 x *Me*CHSi & *Me*CH_2), 1.10 - 1.80 (m, 5 H, CH_2CH_2 & CHCH_2O), 2.94 - 3.00 (m, 2 H, 2 x CHO 3.82 - 3.86 (m, 4 H, 2 x CH_2O), 4.62 (s, 2 H, CH_2Ph), 4.78 (s, 2 H, OCH_2O), 7.30 - 7.36 (m, 5 H, *Ph*).

Diprotected epoxide (1 mmol) was dissolved in absolute MeOH (35 ml) and hydrogenated overnight a r.t. and normal pressure in the presence of $CaCO_3$ (460 mg) and a catalytic amount of 10% palladium on acti vated charcoal. Filtration through a celite pad and evaporation afforded pure *anti* monoprotected epoxide *ent*-**8i** (73%) as a colourless oil: $[\alpha]_D$ = +10.2°; ^{1}H NMR: see Table 4.

Synthesis of cis dioxolane 12 from anti epoxide 8h and of trans dioxolane 13 from syn epoxide 9h. - A solution of 1 mmol of **8h** in dry CH_2CH_2 (15 ml) was cooled to 0°C and added with *i*-Pr_2NEt (2.8 mmol) an freshly distilled $PhCH_2OCH_2Cl$ (2.5 mmol). After stirring for 29 h at r.t., Et_2NH (0.7 mmol) was added an stirring continued for 15'. Brine was added and, after usual work up (Et_2O) and chromatographic purificatio (PE / Et_2O 9 : 1), pure diprotected epoxide was obtained (87%) as a colourless oil: R_f = 0.23 (PE / Et_2O 9 : 1 $[\alpha]_D$ = +1.4°; ^{1}H NMR: 0.05 (s, 6 H, 2 x *Me*Si), 0.89 (s, 9 H, *Me*$_3$C), 0.99 (t, 3 H, J 6.9 Hz, *Me*CH_2), 1.3 - 1.78 (m, 5 H, CH_2CH_2 & CHCH_2O), 2.92 (app t, 1 H, J 4.6 Hz, CHC*H*O), 2.95 - 3.03 (m, 1 H CH$_2$C*H*O), 3.68 - 3.80 (m, 4 H, 2 x CH_2O), 4.61 (s, 2 H, CH_2Ph), 4.78 (s, 2 H, OCH_2O), 7.31 - 7.36 (m 5 H, *Ph*).

A solution of 1 mmol of diprotected epoxide in dry THF (40 ml) was cooled to 0°C and added to a sus pension of $LiAlH_4$ (1 mmol) in dry THF (60 ml). The reaction mixture was refluxed for about 5 h, then coole

to 0°C and added with NaOH (1 mmol) dissolved in H_2O (1.4 ml). After stirring overnight, the reaction was filtered through a celite pad (washing with Et_2O), dried over anhydrous Na_2SO_4, filtered, and solvent evaporated to give, after chromatographic separation (PE / Et_2O 4 : 6 → 0 : 1), pure monoprotected triol, *i. e.* 2-(benzyloxymethoxymethyl)-1,3-heptanediol (30%): R_f = 0.15 (PE / Et_2O 4 : 6); ^1H NMR: 0.91 (t, 3 H, J 7.0 Hz, *Me*CH_2), 1.29 - 1.68 (m, 6 H, C*H*$_2$C*H*$_2$C*H*$_2$), 1.84 (app sextuplet, 1 H, J 5.5, C*H*CH_2O), 2.18 (t, 1 H, J 5.5, CH_2O*H*), 2.46 (d, 1 H, J 5.6 Hz, CHO*H*), 3.77 - 3.94 (m, 5 H, 2 x C*H*$_2$O & C*H*O), 4.62 (s, 2 H, C*H*$_2$Ph), 4.77 (s, 2 H, OC*H*$_2$O), 7.33 - 7.37 (m, 5 H, *Ph*).

A solution of 1 mmol of monoprotected triol in dry CH_2Cl_2 (30 ml) was cooled to 0°C and treated with 3 mmol of 2-methoxypropene and a catalytic amount (0.02 mmol) of PTSA. After stirring 10' at the same temperature, Et_3N (0.03 mmol) was added and solvent was evaporated under reduced pressure. Chromatographic purification (PE / Et_2O 8 : 2) afforded pure dioxolane **12** (94%): R_f = 0.38 (PE / Et_2O 8 : 2); $[\alpha]_D$ = +14.7°; ^1H NMR: 0.90 (t, 3 H, J 6.1, *Me*CH_2), 1.20 - 1.50 (m, 6 H, C*H*$_2$C*H*$_2$C*H*$_2$), 1.38 & 1.45 (2 s, 3 H each, *Me*$_2$C), 1.55 - 1.65 (m, 1 H, C*H*CH_2OBOM), 3.73 & 3.92 (AB part of an ABX system, 2 H, J 4.7 & 9.5 & 9.7 Hz, C*H*$_2$OBOM), ≈3.90 (m, 1 H, C*H*O), 3.97 & 4.03 (AB part of an ABX system, 2 H, J 1.6 & 2.8 & 11.7 Hz, C*H*$_2$OCMe$_2$), 4.59 & 4.62 (AB part of an ABX system, J_{gem} 11.9* Hz, C*H*$_2$Ph), 4.79 (s, 2 H, OC*H*$_2$O), 7.20 - 7.45 (m, 5 H, *Ph*).

In a similar way **13** was obtained from **9h**: ^1H NMR: 0.90 (t, 3 H, J 6.1, *Me*CH_2), 1.20 - 1.50 (m, 6 H, C*H*$_2$C*H*$_2$C*H*$_2$), 1.38 & 1.43 (2 s, 3 H each, *Me*$_2$C), 1.75 - 1.94 (m, 1 H, C*H*CH_2OBOM), 3.47 & 3.49 (AB part of an ABX system, 2 H, J 2.5 & 8.4 & 10.0 Hz, C*H*$_2$OBOM), ≈3.65 (m, 1 H, C*H*O), ≈3.95 (m, 2 H, C*H*$_2$OCMe$_2$), 4.58 (s, 2 H, C*H*$_2$Ph), 4.71 (s, 2 H, OC*H*$_2$O), 7.20 - 7.45 (m, 5 H, *Ph*).

Synthesis of trans dioxolane 14 from anti epoxides 8l and of trans dioxolane 15 from anti epoxide 8p. - A solution of 1 mmol of *anti* epoxide **8l** in dry THF (40 ml) was cooled to 0°C and added to a suspension of $LiAlH_4$ (1 mmol) in dry THF (60 ml). The reaction mixture was refluxed for about 36 h, then cooled to 0°C and added with NaOH (1 mmol) dissolved in H_2O (1.4 ml). After stirring overnight, the reaction was filtered through a celite pad (washing with Et_2O), dried over anhydrous Na_2SO_4, filtered, and solvent evaporated to give, after preparative TLC (PE / AcOEt 6 : 4), pure monoprotected triol, *i. e.* 2-(triphenylmethoxymethyl)-1,3-heptanediol (31%): R_f = 0.47 (PE / AcOEt 6 : 4); ^1H NMR: 0.88 (t, 3 H, J 7.0, *Me*CH_2), 1.25 - 1.66 (m, 6 H, C*H*$_2$C*H*$_2$C*H*$_2$), 1.75 (app sextuplet, J 5.5 Hz, C*H*$_2$OH), 2.33 - 2.41 (m, 2 H, 2 x O*H*), 3.31 & 3.39 (AB part of an ABX system, 2 H, J 5.1 & 5.7 & 9.5 Hz, C*H*$_2$OH), 3.86 (app q, 1 H, J 4.8 Hz, $J_{2/3}$ 4.4*, $J_{3/4}$ 4.2*, C*H*OH), 3.89 & 3.97 (AB part of an ABX system, J 4.7 & 4.8 & 11.1 Hz, C*H*$_2$OTr), 7.20 - 7.46 (m, 15 H, 3 x *Ph*).

A solution of 1 mmol of monoprotected triol in dry CH_2Cl_2 (30 ml) was cooled to 0°C and treated with 3 mmol of 2-methoxypropene and a catalytic amount (0.02 mmol) of PTSA. After stirring 10' at the same temperature, Et_3N (0.03 mmol) was added and solvent was evaporated under reduced pressure. Chromatographic purification (PE / Et_2O 9 : 1) afforded pure dioxolane **14** (51%): R_f = 0.66 (PE / Et_2O 8 : 2); ^1H NMR: 0.80 - 0.92 (m, 3 H, *Me*CH_2), 1.17 - 1.56 (m, 6 H, C*H*$_2$C*H*$_2$C*H*$_2$), 1.38 & 1.44 (2 s, 3 H each, *Me*$_2$C), 1.70 - 1.94 (m, 1 H, C*H*CH_2OTr), 2.94 & 3.07 (AB part of an ABX system, 2 H, J 4.4 & 6.5 & 9.6 Hz, C*H*$_2$OTr), 3.71 - 3.79 (m, 1 H, OC*H*), 3.88 - 3.92 (m, 2 H, C*H*$_2$OCMe$_2$), 7.23 - 7.44 (m, 15 H, 3 x *Ph*).

In a similar way **15** was obtained from **8p**: R_f = 0.57 (PE / Et_2O 95 : 5); ^1H NMR: 0.94 (t, 3 H, J 7.4, *Me*CH_2), 1.00 - 1.06 (m, 21 H, 3 x *Me*$_2$C*H*), 1.10 - 1.45 (m, 2 H, C*H*$_2$Me), 1.39 & 1.43 (2 s, 3 H each, *Me*$_2$C), 1.60 - 1.83 (m, 1 H, C*H*CH_2O), 3.58 - 4.00 (m, 5 H, 2 x C*H*$_2$O & OC*H*).

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