Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron 61 (2005) 3349–3360
Tetrahedron

Superbase-promoted rearrangement of oxiranes to cyclopropanes

Alessandro Mordini,* Daniela Peruzzi, Francesco Russo, Michela Valacchi, Gianna Reginato and Alberto Brandi

Istituto di Chimica dei Composti Organometallici, Dipartimento di Chimica Organica 'U. Schiff', Via della Lastruccia 13, 50019 Sesto Fiorentino, Firenze, Italy

Received 2 November 2004; revised 6 January 2005; accepted 21 January 2005

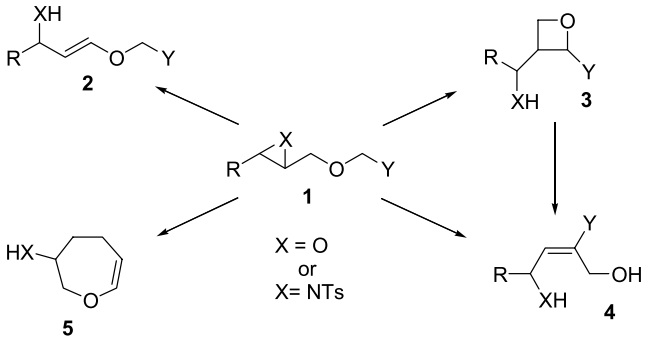
Dedicated to Prof. Manfred Schlosser on the occasion of his 70th birthday

Abstract—Aryl- and alkenyl substituted oxiranes, when submitted to treatment with superbasic reagents, undergo a highly regio- and stereoselective rearrangement leading to cyclopropylmethanol derivatives. The process can also be applied to mono- and dihydroxy substituted substrates thus leading to polyhydroxylated cyclopropanes.

1. Introduction

The usefulness of superbasic reagents[1,2] in promoting small ring heterocycle rearrangements has been clearly shown in recent years. We have indeed demonstrated that alkoxyalkyl oxiranyl-**1** (X=O) and aziridinyl ethers **1** (X=NTs) are efficiently converted into the isomeric hydroxy-[3–7] **2** (X=O) or amino vinylethers **2** (X=NTs),[8,9] respectively. In addition we have shown that benzyl-**1** (X=O, Y=aryl), allyl-**1** (X=O, Y=alkenyl) and propargyl **1** (X=O, Y=alkynyl) oxiranyl ethers can be conveniently rearranged to the corresponding di- or trisubstituted oxetanes **3** (X=O)[10–14] usually with very high regio- and stereoselectivity. Both the benzyl oxiranyl ethers **1** (X=O, Y=C_6H_5) and the rearranged phenyl substituted oxetanes **3** (X=O, Y=C_6H_5) can also be further isomerized to unsaturated 1,4-diols **4** with perfect *Z*-stereocontrol.[13,15] More recently, we have also reported that monosubstituted oxiranyl allyl ethers **1** (X=O, Y=alkenyl, R=H) are regio- and stereoselectively converted into the isomeric disubstituted tetrahydrooxepines **5** (X=O, R=H).[16] All these transformations have been carried out making use of superbases[1,2] and in particular the equimolar mixtures butyllithium/potassium *tert*-butoxide (Schlosser's base, LICKOR)[1] and butyllithium/diisopropylamine/potassium *tert*-butoxide (LIDAKOR)[17] (Scheme 1).

These results clearly show that superbasic reagents are very efficient in promoting 4-*exo* and 7-*endo* ring forming reactions from substituted oxiranyl ethers and this encouraged us to investigate additional possible intramolecular cyclization processes induced by formation of carbanions suitably positioned in oxirane derivatives.



Scheme 1.

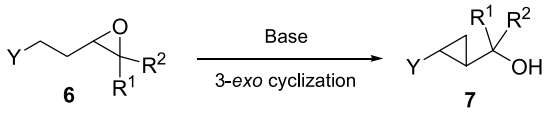
In this paper, we describe our results on the synthesis of cyclopropanes **7** through a 3-*exo* cyclization process performed on alkenyl- or phenyl substituted oxiranes **6** (Y=alkenyl or phenyl) (Scheme 2).

2. Results and discussion

It is well known that cyclopropanes can be obtained from oxiranes through 3-*exo* cyclizations induced by carbanions. Usually the formation of the carbanionic species is

Keywords: Superbase; Cyclopropanes; Rearrangement; 3-*exo* Cyclization.
* Corresponding author. Tel.: +39 055 4573555; fax: +39 055 4573580; e-mail: alessandro.mordini@unifi.it

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.01.102



Scheme 2.

performed on substrates possessing good activating groups (nitriles,[18–20] esters,[21,22] amides,[23] ketones,[24] sulfones,[25–27] sulfides[28]) while very little is known on similar processes performed on oxiranes without a heterosubstituent able to stabilize the carbanionic intermediates. The only known results in this field date back to the 1970s when it was first reported[29,30] that lithium amides in the presence of HMPT as a cosolvent were able to convert a few 1-aryl- and 1-alkenyl-3,4-epoxyalkanes into the corresponding cyclopropanes. Drawbacks of this reaction are the use of the highly toxic HMPT, the low stereoselectivity and the quite limited number of examples. Thus, we decided to see if the use of the superbasic mixtures, LIDAKOR and LICKOR, could positively affect the outcome of the 3-*exo* cyclization reaction on a variety of suitably substituted oxiranes. For this purpose, we synthesized a series of arylethyl oxiranes and we submitted them to reaction with superbasic reagents. The simplest substrate in the series, the 1,2-epoxy-4-phenylbutane **8** easily obtained by epoxidation of 4-phenyl-1-butene, served as a test for finding the best organometallic base and reaction conditions. When **8** was treated with an excess of TMEDA-activated *sec*-butyllithium or with the superbasic mixture LICKOR, it gave no 3-*exo* cyclization products but instead the two olefins **9** and **10**, respectively as the only detected products (Scheme 3).

Such results can be explained by assuming that an initial α-metalation of the oxirane ring is then followed by isomerization to a carbene species which then adds a second organometallic reagent and eventually leads to the olefin via lithium oxide elimination (Scheme 4).[31,32]

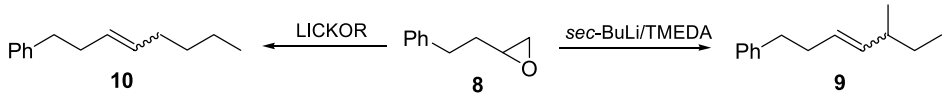
The use of stoichiometric amounts of the base resulted only in recovery of starting material and a decrease of the amount of olefin formed.

On the other hand, the use of the less nucleophilic reagent LIDAKOR, gave only the expected phenyl cyclopropyl methanol **11** in good yields and very good stereoselectivity, the *trans*-cyclopropane being the only detectable product (Scheme 5).

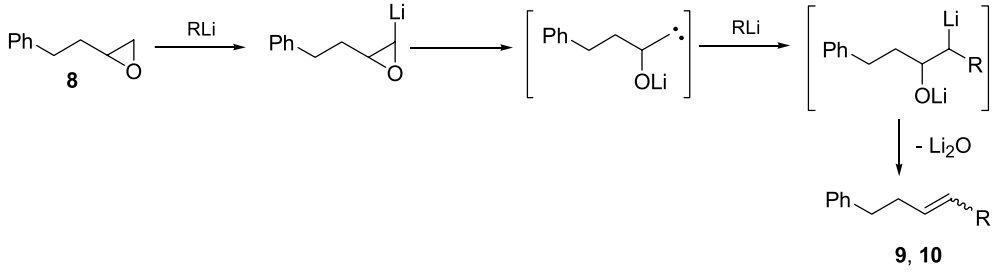
A similar behaviour was observed also with a representative series of di- and trisubstituted oxiranes which were prepared by epoxidation of the corresponding olefins, all synthesized by Wittig olefination. A 67:33 mixture of *cis* and *trans*-3,4-epoxy-2-methyl-6-phenylhexane **12** gave the corresponding cyclopropane **15** in 64% yield as a 67:33 *anti*:*syn* mixture by treatment with 2 equiv LIDAKOR in THF at −50 °C; no *cis* cyclopropanes were detected in the reaction mixture. When the oxirane ring has a methyl substituent as in the 2,3-epoxy-5-phenylpentane **13** and in the 2,3-epoxy-2-methyl-5-phenylpentane **14** cases, treatment with LIDAKOR afforded again the desired *trans*-cyclopropyl derivatives **16** and **17**, respectively in good yields but contaminated by the allylic alcohols **18** and **19**. Their formation is clearly due to a β-elimination process induced by deprotonation of the methyl groups. Interestingly such pathway became exclusive when LICKOR was used, showing the higher efficiency of the metal amide base towards the deprotonation of benzylic positions (Scheme 6).

The LIDAKOR promoted rearrangement leading to cyclopropanes works well even when the intermediate metallic species is of the allylic type.[33] Thus, 5,6-epoxy-1-hexene **20** was converted into *trans*-vinyl cyclopropylmethanol **21** in 75% yield with LIDAKOR in THF at −50 °C (Scheme 7).

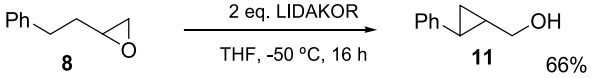
In order to extend the scope of the described 3-*exo* cyclization process we then turned our attention to



Scheme 3.

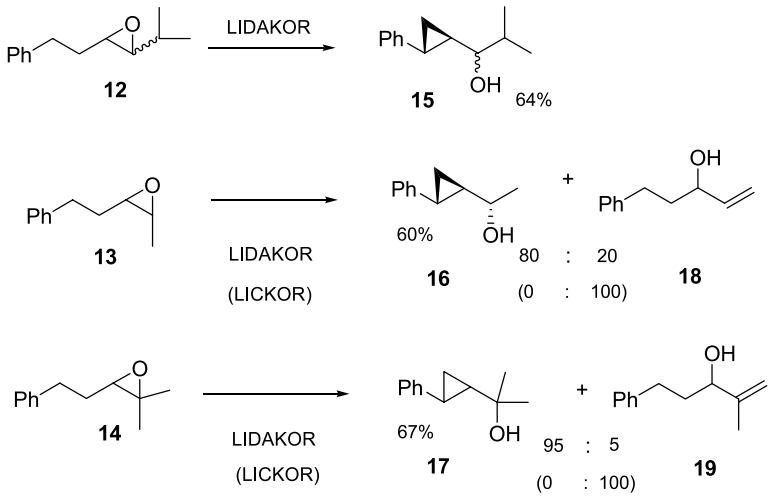


Scheme 4.

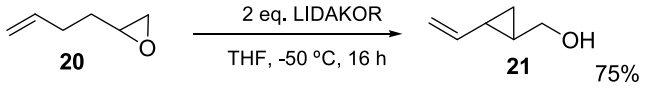


Scheme 5.

functionalized 1-aryl-3,4-epoxy substrates. Methoxy substituted compounds **22**, **23** and **24** derived from the corresponding allylic alcohols via *m*-CPBA epoxidation, were first selected to test their reaction with superbases. The position of the methoxy group is clearly crucial in driving

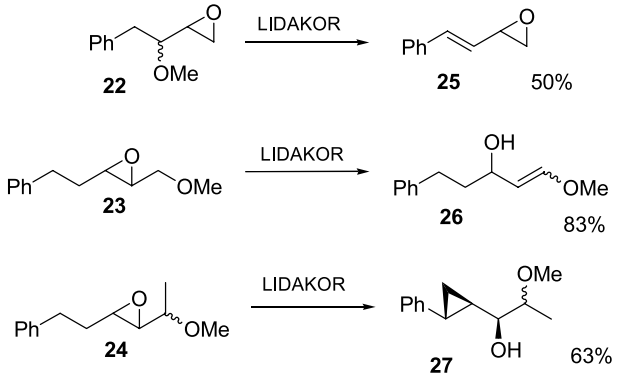


Scheme 6. Reaction conditions: 2 equiv LIDAKOR, THF, −50°C, 16 h; 2 equiv LICKOR, pentane, 25°C, 16 h.



Scheme 7.

the base-promoted reaction. Oxirane **22** was in fact converted into the vinyl oxirane **25** via benzylic metalation followed by elimination of the methoxy group. When the substituent is instead located on the other side of the oxirane



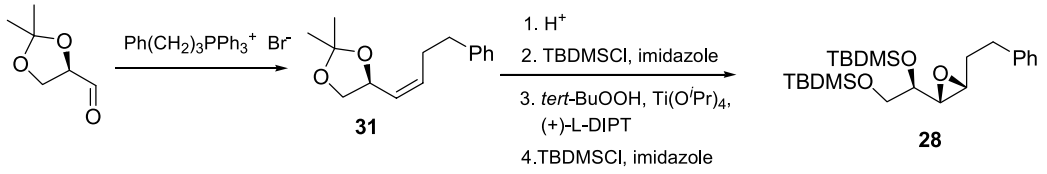
Scheme 8. Reaction conditions: 2 equiv LIDAKOR, THF, −50°C, 16 h.

ring as in **23**, treatment with a superbase produced a ring-opened product **26** derived from deprotonation at the methylene α to the oxirane ring and the methoxy group, followed by β-elimination. No 3-*exo* ring-closure compounds could be detected in both cases while the cyclopropyl derivative **27** became the only observed reaction product when oxirane **24**, derived from a secondary allylic alcohol, was treated with LIDAKOR. In this case the benzylic deprotonation again becomes the predominant pathway due to the decreased availability of the methine proton, and then follows the 3-*exo* cyclization pathway to the cyclopropyl derivative (Scheme 8).

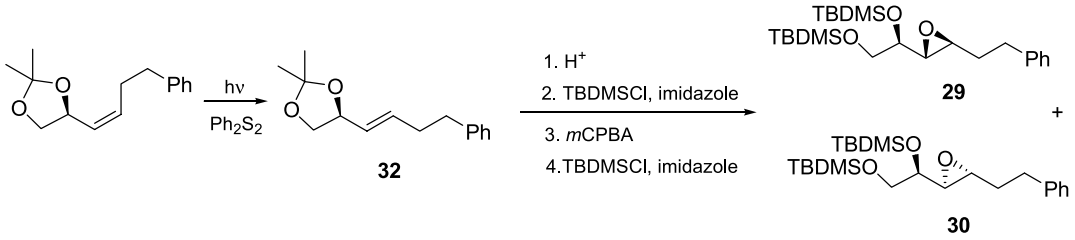
The reaction is again highly stereoselective leading to the *trans*-stereoisomer only, and shows that this can be a convenient way to access cyclopropyl diols or polyols starting from oxiranyl ethers derived from secondary allylic alcohols. In order to further prove this finding and to study in more details the stereochemical outcome of the isomerization reaction, we synthesized the 1,2-di-*tert*-butyldimethylsilyloxy-3,4-epoxy-6-phenylhexane in its diastereomeric forms *syn*,*cis* (**28**, *R*,*R*,*R*), *syn*,*trans* (**29**, *R*,*R*,*S*) and *anti*,*trans* (**30**, *R*,*S*,*R*). Compound **28** was prepared by diastereoselective epoxidation with *tert*-butylhydroperoxide, titanium isopropoxide and (+)-L-diethyl tartrate of the corresponding *cis*-olefin **31** which in turn has been prepared by Wittig olefination of the 2,3-isopropylidene-D-glyceraldehyde[34] with phenylpropyl triphenylphosphonium bromide (Scheme 9).

The two oxiranes **29** and **30** were obtained as a 50:50 mixture by *m*-CPBA epoxidation of the corresponding *trans*-olefin **32** which was prepared by the same Wittig olefination as described above, followed by a photochemically induced isomerization of the double bond in the presence of diphenyl disulfide.[34] The two diastereomers **29** and **30** were separated and then used, together with **28**, in the base-promoted rearrangements (Scheme 10).

Treatment of compounds **28**–**30** with the superbasic reagent LIDAKOR, gave the same result: all diastereoisomers were



Scheme 9.



Scheme 10.

converted into the corresponding *trans*-cyclopropanes **33–35a**,**b** with a perfect stereocontrol thus showing that changes in the configuration of the oxirane ring or in the relative stereochemistry of the silyloxy substituent did not affect the outcome of the rearrangement process.

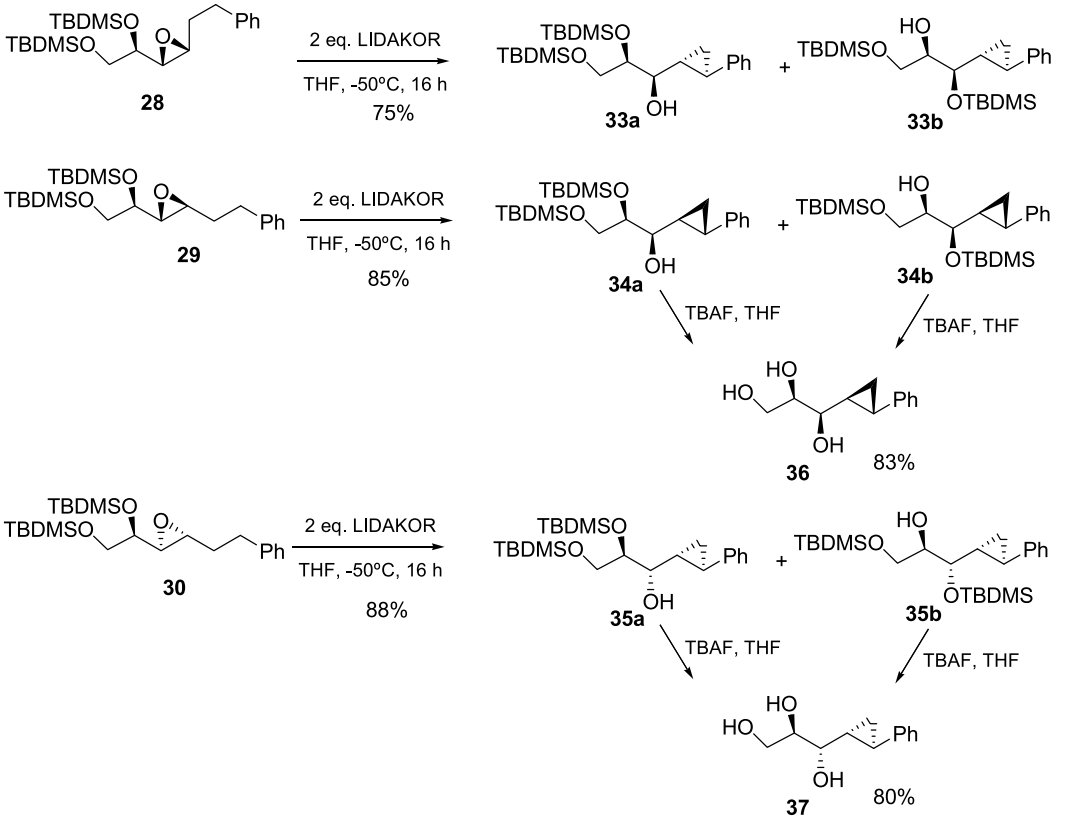
In all cases the reaction mixture contained actually two isomers which, upon a careful NMR investigation, turned out to be those deriving from a *tert*-butyldimethylsilyl group migration from one oxygen to the neighbouring one during the isomerization process. This was then further demonstrated for the cyclopropane derivatives **34a**,**b** and **35a**,**b** which by fluoride deprotection of all the silylated hydroxy groups afforded the triols **36** and **37**, respectively (Scheme 11).

In conclusion, we have found that superbasic mixtures can be conveniently used for the 3-*exo* cyclization of suitably substituted oxiranes lacking strong electron withdrawing substituents. The reaction is highly stereoselective and seems to be of a general applicability allowing the synthesis of functionalized cyclopropanes.

3. Experimental

3.1. General procedures

Air- and moisture-sensitive compounds were stored in Schlenk tubes or in Schlenk burettes. They were protected by and handled under an atmosphere of 99.99% pure nitrogen. Ethereal extracts were dried with sodium sulfate. Purifications by flash column chromatography[35] were performed using glass columns (10–50 mm wide); silica gel 230–400 mesh was chosen as stationary phase (15 cm high), with an elution rate of 5 cm/min. Nuclear magnetic resonance spectra of hydrogen nuclei were recorded at 200 or 400 MHz. Chemical shifts were determined relative to the residual solvent peak ($CHCl_3$: 7.26 ppm). Coupling constants (*J*) are measured in Hz. Coupling patterns are



Scheme 11.

described by abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), dd (doublet of a doublet), m (multiplet), bs (broad singlet), app (apparent). Nuclear magnetic resonance spectra of carbon-13 nuclei were recorded at 50.3 or 100 MHz. Chemical shifts were determined relative to the residual solvent peak ($CHCl_3$: 77.0 ppm). Mass spectra were obtained at a 70 eV ionization potential.

3.2. Materials

Starting materials were commercially available unless otherwise stated. All commercial reagents were used without further purification except diisopropyl amine, which was distilled over calcium hydride. Tetrahydrofuran was obtained anhydrous by distillation over sodium wire after the characteristic blue color of in situ generated sodium diphenylketyl[36] was found to persist. Pentane was stored over lithium aluminum hydride. Methylene chloride was dried over calcium chloride and stored over 4 Å molecular sieves. Petroleum ether, unless specified, was the 40–70 °C boiling fraction.

3.3. Preparation of oxiranes

3.3.1. 1,2-Epoxy-4-phenylbutane 8.[37] *m*-CPBA (1. 035 g, 6.0 mmol, 2 equiv) was added to a cooled (0 °C) solution of the 4-phenyl-1-butene (400 mg, 3.0 mmol, 1 equiv) in 30 mL CH_2Cl_2. The mixture was allowed to reach room temperature and then stirred overnight. The reaction mixture was cooled to −20 °C, and the *m*-chlorobenzoic acid was filtered on Celite. The organic layer was washed twice with satd $Na_2S_2O_3$, once with satd $NaHCO_3$ and dried over Na_2SO_4. The crude product was purified by flash chromatography (petroleum ether:ethyl acetate 10:1) giving 173 mg (39% yield) of oxirane **8** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.38–7.18 (5H, m); 3.05–2.94 (1H, m); 2.93–2.71 (3H, m); 2.51 (1H, dd, J=4.8, 2.6 Hz); 1.95–1.80 (2H, m).

3.3.2. Preparation of *cis*,*trans*-3,4-epoxy-2-methyl-6-phenylhexane 12.[38] *(Z,E)-2-Methyl-6-phenyl-3-hexene*. To a stirred suspension of isobutyltriphenylphosphonium bromide (1.26 g, 1.05 equiv, 3.15 mmol) in 8 mL of dry THF a 1.6 M hexane solution of BuLi (1.96 mL, 1.0 equiv, 3.00 mmol) was added dropwise under N_2 at −78 °C until the mixture became homogeneous and deep red coloured. After 2 h, 3-phenylpropionaldehyde (0.40 mL, 1.0 equiv, 3.00 mmol) was added dropwise. The mixture was allowed to reach room temperature and then stirred for 6 h. Petroleum ether was added and the triphenylphosphine oxide was filtered on Celite. After evaporation of the solvent, 0.52 g (99% yield) of a 67:33 mixture of (*Z*,*E*)-2-methyl-6-phenyl-3-hexene was obtained and used in the next step without any further purification. ^{1}H NMR ($CDCl_3$, 200 MHz) δ *Z*: 7.37–7.20 (5H, m); 5.48–5.18 (2H, m); 2.95–2.67 (4H, m); 2.46–2.35 (1H, appq, J=6.4 Hz); 0.93 (6H, d, J=6.6 Hz). *E*: 7.37–7.20 (5H, m); 5.48–5.18 (2H, m); 2.95–2.67 (4H, m); 2.65–2.47 (1H, m); 1.00 (6H, d, J=7.0 Hz).

cis,trans-3,4-Epoxy-2-methyl-6-phenylhexane **12**. *m*-CPBA (0.69 g, 4.0 mmol, 2 equiv) was added to a cooled (0 °C) solution of the (*E*,*Z*)-2-methyl-6-phenyl-3-hexene (350 mg, 2.0 mmol, 1 equiv) in 20 mL CH_2Cl_2. The mixture was allowed to reach room temperature and then stirred overnight. The reaction mixture was cooled to −20 °C, and the *m*-chlorobenzoic acid was filtered on Celite. The organic layer was washed twice with satd $Na_2S_2O_3$, once with satd $NaHCO_3$ and dried over Na_2SO_4. The crude product was purified by flash chromatography (petroleum ether:ethyl acetate 10:1) giving 215 mg (49% yield) of **12** as a colourless oil in a 67:33 *cis*/*trans* mixture. ^{1}H NMR ($CDCl_3$, 200 MHz) δ *cis*: 7.32–7.17 (5H, m); 3.07–2.96 (1H, m); 2.92–2.70 (2H, m); 2.63 (1H, dd, J=9.2, 4.2 Hz); 1.98–1.69 (2H, m); 1.63–1.38 (1H, m); 1.13 (3H, d, J=6.6 Hz); 0.94 (3H, d, J=6.6 Hz). *trans*: 7.32–7.17 (5H, m); 3.07–2.96 (1H, m); 2.92–2.70 (2H, m); 2.47 (1H, dd, J=6.6, 1.9 Hz); 1.98–1.69 (2H, m); 1.63–1.38 (1H, m); 1.01 (3H, d, J=6.4 Hz); 0.91 (3H, d, J=6.6 Hz).

3.3.3. Preparation of *cis*-2,3-epoxy-5-phenylpentane 13.[37] *(Z)-5-Phenylpent-2-ene*. A solution 1.6 M of BuLi (3.2 mL, 1.0 equiv, 5.1 mmol) in hexane was added, at −78 °C under N_2, to a solution of triphenylethylphosphonium bromide (2.00 g, 1.05 equiv, 5.4 mmol) in 15 mL of dry THF. The mixture was stirred at −78 °C for 2 h and then 3-phenylpropionaldehyde (0.76 mL, 1.13 equiv, 5.8 mmol) was added. The mixture was allowed to reach room temperature and then stirred for 12 h. Petroleum ether was added and the triphenylphosphinoxide was filtered on Celite. After evaporation of the solvent the residue was purified by flash chromatography (petroleum ether:ethyl acetate 10:1) to give 296 mg of (*Z*)-5-phenylpent-2-ene (40% yield) as a colourless oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.39–7.17 (5H, m); 5.49 (2H, appd, J=5.4 Hz); 2.83–2.58 (2H, m); 2.46–2.32 (2H, m); 1.60 (3H, d, J=4.4 Hz).

cis-2,3-Epoxy-5-phenylpentane **13**. *m*-CPBA (0.35 g, 2.0 mmol, 2 equiv) was added to a cooled (0 °C) solution of the (*Z*)-5-phenylpent-2-ene (146 mg, 1.0 mmol, 1 equiv) in 10 mL CH_2Cl_2. The mixture was allowed to reach room temperature and then stirred overnight. The reaction mixture was cooled to −20 °C, and the *m*-chlorobenzoic acid was filtered on Celite. The organic layer was washed twice with satd $Na_2S_2O_3$, once with satd $NaHCO_3$ and dried over Na_2SO_4. After the solvent was evaporated 162 mg (100% yield) of the crude epoxide **13** were obtained and used in the next step without any further purification. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.35–7.17 (5H, m); 3.11–2.65 (4H, m); 1.86 (2H, appquint); 1.21 (3H, d, J=5.6 Hz).

3.3.4. Preparation of 2,3-epoxy-2-methyl-5-phenylpentane 14.[37] *2-Methyl-5-phenylpent-2-ene*. Isopropyltriphenylphosphonium bromide/sodium amide mixture (3.60 g, 8.3 mmol, 1.0 equiv) was poured, under N_2, in 20 mL of dry THF. After 30 min, 3-phenylpropionaldehyde (1.32 mL, 10.0 mmol, 1.2 equiv) was added and the mixture stirred at 40 °C under N_2 overnight. Petroleum ether was then added and the precipitate was filtered on silica. After evaporation of the solvent, 1.55 g (97% yield) of 2-methyl-5-phenylpent-2-ene was obtained as a dark yellow oil and used in the next step without any further purification. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.42–7.18 (5H, m); 5.23 (1H, t, J=6.7 Hz); 2.80–2.62 (2H, m); 2.34 (2H, dt, J=8.8, 6.7 Hz); 1.74 (3H, s); 1.62 (3H, s).

2,3-Epoxy-2-methyl-5-phenylpentane **14**. *m*-CPBA (1.72 g, 10.0 mmol, 2 equiv) was added to a cooled (0 °C) solution of the 2-methyl-5-phenylpent-2-ene (1.60 g, 5.0 mmol, 1 equiv) in 40 mL CH_2Cl_2. The mixture was allowed to reach room temperature and then stirred overnight. The reaction mixture was cooled to −20 °C, and the *m*-chlorobenzoic acid was filtered on Celite. The organic layer was washed twice with satd $Na_2S_2O_3$, once with satd $NaHCO_3$ and dried over Na_2SO_4. The crude product was purified by flash chromatography (petroleum ether:ethyl acetate 10:1) giving 436 mg (50% yield) of **14** as a colourless oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.32–7.10 (5H, m); 2.98–2.61 (3H, m); 1.99–1.65 (2H, m); 1.27 (3H, s); 1.12 (3H, s).

3.3.5. Preparation of *syn,anti*-3,4-epoxy-2-methoxy-1-phenylbutane 22. *1-Phenylbut-3-en-2-ol*. Vinylmagnesium bromide (22.5 mL, 22.5 mmol, 1.5 equiv) was added, at 0 °C under N_2, to a solution of phenylacetaldehyde (1.95 mL, 15 mmol, 1.0 equiv) in 30 mL of dry THF. After the addition was complete the temperature was allowed to reach 25 °C and the mixture was stirred for 2.5 h and then cooled to 0 °C. HCl (10 mL of a 1.0 M solution) was then added and, after 30 min, the precipitate was filtered through Celite. The aqueous layer was extracted with Et_2O, and the organic layer washed with brine and dried over Na_2SO_4. After the solvent was evaporated 2.20 g (100% yield) of 1-phenylbut-3-en-2-ol were obtained. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.42–7.05 (5H, m); 5.94 (1H, ddd, J=17.0, 10.3, 5.8 Hz); 5.34–4.95 (2H, m); 4.62–4.57 (1H, m); 2.87–2.60 (2H, m); 2.40 (1H, bs).

syn,anti-3,4-Epoxy-1-phenyl-2-butanol. *m*-CPBA (1.72 g, 10.0 mmol, 2 equiv) was added to a cooled (0 °C) solution of the 1-phenylbut-3-en-2-ol (740 mg, 5.0 mmol, 1 equiv) in 40 mL CH_2Cl_2. The mixture was allowed to reach room temperature and then stirred overnight. The reaction mixture was cooled to −20 °C, and the *m*-chlorobenzoic acid was filtered on Celite. The organic layer was washed twice with satd $Na_2S_2O_3$, once with satd $NaHCO_3$ and dried over Na_2SO_4. The crude product was purified by flash chromatography (petroleum ether:ethyl acetate 4:1) giving 295 mg (36% yield) of a 1:1 *syn*:*anti* mixture of 3,4-epoxy-1-phenyl-2-butanol as a yellow oil. *First diastereoisomer*: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.40–7.17 (5H, m); 4.07–3.95 (1H, m); 3.08–3.00 (1H, m); 2.99–2.85 (2H, m); 2.83–2.71 (1H, m); 2.61 (1H, dd, J=4.8, 2.6 Hz); 2.48 (1H, bs). *Second diastereoisomer*: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.40–7.17 (5H, m); 3.71 (1H, td, J=6.8, 4.8 Hz); 3.08–3.00 (1H, m); 2.99–2.85 (2H, m); 2.83–2.71 (1H, m); 2.61 (1H, dd, J=4.8, 2.6 Hz); 2.48 (1H, bs).

syn,anti-3,4-Epoxy-2-methoxy-1-phenylbutane **22**. NaH (29 mg, 1.2 mmol, 1.2 equiv) in a 60% dispersion in mineral oil, was suspended in dry THF (1 mL) under N_2 at 0 °C. Then a 0.5 M THF solution of the *syn,anti*-3,4-epoxy-1-phenyl-2-butanol (164 mg, 1.0 mmol, 1.0 equiv) was added and the mixture stirred at 0 °C under N_2 for 45 min. The temperature was allowed to rise to room temperature and methyl iodide (170 mg, 1.2 mmol, 1.2 equiv) was then added. After stirring for 6 h, ice and Et_2O were added and the aqueous layer extracted with Et_2O; the organic layers were washed with brine and dried over Na_2SO_4. The crude product was purified by flash chromatography (petroleum ether:ethyl acetate 4:1) giving 112 mg (52% yield) of a 1:1 *syn*:*anti* diastereomeric mixture of **22** as a yellow oil. First diastereoisomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.41–7.19 (5H, m); 3.49 (3H, s); 3.32–3.20 (1H, m); 3.18–2.73 (4H, m); 2.66 (1H, app t, J=4.4 Hz). Second diastereoisomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.41–7.19 (5H, m); 3.36 (3H, s); 3.32–3.20 (1H, m); 3.18–2.73 (4H, m); 2.25 (1H, dd, J=4.7, 2.5 Hz). MS (*m*/*z*, %): 178 (0.2, M^+); 148 (14); 146 (34, M^+ −OMe− 1); 135 (7); 119 (14); 115 (18); 103 (19); 91 (54); 88 (55); 87 (100); 77 (18); 65 (28); 57 (34).

3.3.6. Preparation of *trans*-2,3-epoxy-1-methoxy-5-phenylpentane 23.[39] *Ethyl 5-phenyl-(E)-2-pentenoate*. NaH (600 mg, 1.15 equiv, 17.2 mmol) in a 60% dispersion in mineral oil, was suspended in 25 mL under N_2 and the mixture was cooled to 0 °C. A solution of diisopropyl-(ethoxycarbonylmethyl)phosphonate (4.1 mL, 1.1 equiv, 16.5 mmol) in 10 mL of dry THF was added slowly; after stirring at room temperature for 30 min, the mixture was cooled to 0 °C and 3-phenylpropionaldehyde (1.98 mL, 1.0 equiv, 15 mmol) in 15 mL of THF was added. After stirring at 0 °C for 1 h, satd NH_4Cl was added and the organic layer was washed twice with satd $NaHCO_3$ and brine, then dried over Na_2SO_4. After the solvent was evaporated 3.0 g (98% yield) of the crude ethyl 5-phenyl-(*E*)-2-pentenoate were obtained as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.40–7.20 (5H, m); 7.07 (1H, dt, J=15.8, 6.8 Hz); 5.91 (1H, dt, J=15.8, 1.7 Hz); 4.24 (2H, q, J=7.1 Hz); 2.84 (2H, t, J=8.4 Hz); 2.58 (2H, tdd, J=8.4, 6.8, 1.7 Hz); 1.34 (3H, t, J=7.1 Hz).

(2E)-5-Phenylpent-2-en-1-ol. A solution of 3.06 g (1.0 equiv, 15 mmol) of 5-phenyl-(*E*)-2-pentenoate in 35 mL of dry CH_2Cl_2 was cooled to −78 °C; 37 mL (2.5 equiv, 37 mmol) of DIBAL-H 1.0 M in CH_2Cl_2 was added and the mixture was stirred under N_2 for 1 h; then 10 mL of H_2O was added and the organic layer was washed twice with a 10% sodium tartrate solution, once with brine, and then dried over Na_2SO_4. Evaporation of the solvent afforded 2.03 g (83% yield) of the crude (2*E*)-5-phenylpent-2-en-1-ol as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.42–7.19 (5H, m); 5.76 (2H, m); 4.13 (2H, bs); 2.77 (2H, t, J=7.4 Hz); 2.50–2.40 (2H, m); 1.77 (1H, bs).

trans-2,3-Epoxy-5-phenylpentan-1-ol.[39] *m*-CPBA (3.44 g, 20.0 mmol, 2 equiv) was added to a cooled (0 °C) solution of the (2*E*)-5-phenylpent-2-en-1-ol (1.62 g, 10.0 mmol, 1 equiv) in 80 mL CH_2Cl_2. The mixture was allowed to reach room temperature and then stirred overnight. The reaction mixture was cooled to −20 °C, and the *m*-chlorobenzoic acid was filtered on Celite. The organic layer was washed twice with satd $Na_2S_2O_3$, once with satd $NaHCO_3$ and dried over Na_2SO_4. After the solvent was evaporated, 1.48 g (83% yield) of the crude colourless oil *trans*-2,3-epoxy-5-phenylpentan-1-ol were obtained and used in the next step without any further purification. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.41–7.18 (5H, m); 3.90 (1H, dd, J=12.6, 2.5 Hz); 3.61 (1H, dd, J=12.6, 4.3 Hz); 3.33 (1H, bs); 3.05 (1H, td, J=5.8, 2.5 Hz); 2.95–2.63 (3H, m); 2.00–1.85 (2H, m).

trans-2,3-Epoxy-1-methoxy-5-phenylpentane **23**. NaH (58 mg, 2.4 mmol, 1.2 equiv) in a 60% dispersion in mineral oil, was suspended in dry THF (2 mL) under N_2 at 0 °C.

Then a 0.5 M THF solution of the *trans*-2,3-epoxy-5-phenylpentan-1-ol (356 mg, 2.0 mmol, 1.0 equiv) was added and the mixture stirred at 0 °C under N_2 for 45 min. The temperature was allowed to rise to room temperature and methyl iodide (340 mg, 2.4 mmol, 1.2 equiv) was then added. After stirring for 6 h, ice and Et_2O were added and the aqueous layer extracted with Et_2O; the organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave 213 mg (55% yield) of the crude **23** as a colourless oil that was used in the next step without any further purification. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.34–7.15 (5H, m); 3.58 (^{1}H, dd, J=11.4, 2.8 Hz); 3.67 (3H, s); 3.31 (1H, dd, J=11.4, 5.3 Hz); 2.91–2.61 (4H, m); 1.89 (2H, td, J=7.7, 5.3 Hz).

3.3.7. Preparation of *syn,anti-trans*-3,4-epoxy-2-methoxy-6-phenylhexane 24. *trans-2,3-Epoxy-5-phenylpentanal*. *trans*-2,3-Epoxy-5-phenylpentan-1-ol (270 mg, 1.0 equiv, 1.5 mmol) was dissolved in 15 mL of dry CH_2Cl_2, and Dess Martin periodinane (950 mg, 1.5 equiv, 2.3 mmol) was added at room temperature under N_2. After 1 h and 30 min Et_2O (5 mL) and satd $Na_2S_2O_3$ (5 mL) were added and the aqueous layer was extracted with Et_2O. The organic layers were washed with satd $NaHCO_3$ and brine, then dried over Na_2SO_4. Evaporation of the solvent gave 260 mg (98% yield) of the crude *trans*-2,3-epoxy-5-phenylpentanal as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 9.02 (1H, d, J=6.2 Hz); 7.39–7.20 (5H, m); 3.29 (1H, td, J=5.5, 1.9 Hz); 3.15 (1H, dd, J=6.2, 1.9 Hz); 2.95–2.77 (2H, m); 2.10–1.92 (2H, m).

syn,anti-trans-3,4-Epoxy-2-hydroxy-6-phenylhexane. *trans*-2,3-Epoxy-5-phenylpentanal (350 mg, 1.0 equiv, 2.0 mmol) was dissolved in 4 mL of dry THF and then cooled to 0 °C. A 3.0 M THF solution of methylmagnesium chloride (0.7 mL, 1.05 equiv, 2.1 mmol) was added and the mixture stirred at 0 °C under N_2 for 1.5 h and for other 45 min at room temperature. 1 M HCl (4 mL) and Et_2O (4 mL) were added and the organic layer was washed with water and brine, then dried over Na_2SO_4. After evaporation of the solvent, 252 mg (65% yield) of the crude *syn,anti-trans*-3,4-epoxy-2-hydroxy-6-phenylhexane were obtained as a yellow oil in a 62:38 *syn*:*anti* ratio. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: *syn*: 7.35–7.15 (5H, m); 3.55 (1H, appquint, J=5.5 Hz); 2.91 (1H, td, J=5.7, 2.3 Hz); 2.84–2.62 (3H, m); 2.11–2.01 (1H, bs); 2.00–1.81 (2H, m); 1.16 (3H, d, J=6.4 Hz) *anti*: 7.35–7.15 (5H, m); 3.94–3.79 (1H, m); 3.00 (1H, td, J=5.6, 2.2 Hz); 2.84–2.62 (3H, m); 2.11–2.01 (1H, bs); 2.00–1.81 (2H, m); 1.14 (3H, d, J=5.9 Hz).

syn,anti-trans-3,4-Epoxy-2-methoxy-6-phenylhexane **24**. NaH (44 mg, 1.8 mmol, 1.2 equiv) in a 60% dispersion in mineral oil, was suspended in dry THF (1.5 mL) under N_2 at 0 °C. Then a 0.5 M THF solution of the *syn,anti-trans*-3,4-epoxy-2-hydroxy-6-phenylhexane (288 mg, 1.5 mmol, 1.0 equiv) was added and the mixture stirred at 0 °C under N_2 for 45 min. Methyl iodide (255 mg, 1.8 mmol, 1.2 equiv) was then added and the temperature was allowed to rise to room temperature. After stirring for 6 h, ice and Et_2O were added and the aqueous layer extracted with Et_2O; the organic layers were washed with brine and dried over Na_2SO_4. The crude product was purified by flash chromatography (petroleum ether:ethyl acetate 4:1) giving 110 mg (36% yield) of a 64:36 *syn*:*anti* diastereomeric mixture as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: *syn*: 7.38–7.18 (5H, m); 3.46 (3H, s); 3.08 (1H, appquint, J=6.6 Hz); 3.01–2.67 (4H, m); 1.92 (2H, td, J=7.0, 6.5 Hz); 1.16 (3H, d, J=6.6 Hz). *anti*: 7.38–7.18 (5H, m); 3.38 (3H, s); 3.20 (1H, appquint, J=6.2 Hz); 3.01–2.67 (4H, m); 1.92 (2H, td, J=7.0, 6.5 Hz); 1.24 (3H, d, J=6.2 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: *syn*: 140.9, 128.3, 128.2, 126.0, 77.5, 61.8, 57.0, 53.8, 33.2, 32.1, 16.7. *anti*: 141.0, 128.3, 128.2, 125.9, 76.1, 60.4, 56.9, 56.8, 33.4, 32.0, 17.0. MS (*m*/*z*, %): 187 (1); 175 (2, M^+-OMe); 173 (6); 147 (8); 129 (9); 128 (13); 117 (91); 103 (35); 91 (100); 77 (23); 58 (100).

3.4. Preparation of oxiranyl ethers from mannitol

3.4.1. Preparation of 2,3-isopropylidene-D-glyceraldehyde.[34] 1,2:5,6-Diisopropylidene-D-mannitol (787 mg, 3 mmol, 1.0 equiv) was dissolved in a mixture of CH_2Cl_2 (7 mL) and a saturated solution of $NaHCO_3$ (0.4 mL); $NaIO_4$ (963 mg, 4.5 mmol, 1.5 equiv) was then slowly added and the mixture stirred at room temperature. After 5 h, Na_2SO_4 was added with vigorous stirring. The resulting suspension was filtered and the filtrate washed with CH_2Cl_2. The organic layers were evaporated to give 709 mg (91% yield) of the crude 2,3-isopropylidene-D-glyceraldehyde as a colourless oil which was immediately used in the next reaction. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.72 (1H, d, J=1.9 Hz); 4.38 (1H, ddd, J=7.4, 4.7, 1.9 Hz); 4.17 (1H, dd, J=8.8, 7.4 Hz); 4.10 (1H, dd, J=8.8, 4.7 Hz); 1.49 (3H, s); 1.42 (3H, s).

3.4.2. Preparation of *syn*-(3,4-*cis*)-(2*R*,3*R*,4*R*)-1,2-di(*tert*-butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexane 28. *(3Z)-(2S)-1,2-Isopropyliden-6-phenylhex-3-enyl-1,2-diol* **31**.[34] To a stirred suspension of 1-phenylpropyltriphenylphosphonium bromide (1.45 g, 3.15 mmol, 1.05 equiv) in 8 mL of dry THF, a 1.6 M hexane solution of BuLi (1.96 mL, 3.00 mmol, 1.0 equiv) was added dropwise, under N_2 at −78 °C, until the mixture became homogeneous and deep red coloured. After 1 h, a solution of 2,3-isopropylidene-D-glyceraldehyde (390 mg, 3.0 mmol, 1.0 equiv) in 2 mL of dry THF was added and the mixture stirred at room temperature, under N_2 overnight. Petroleum ether was added, the precipitate filtered through Celite and the filtrate was washed with petroleum ether. The organic layer was evaporated to give 366 mg (56% yield) of **31** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.34–7.12 (5H, m); 5.67 (1H, dt, J=11.0, 7.4 Hz); 5.41 (1H, dd, J=11.0, 8.5 Hz); 4.70 (1H, ddd, J=8.5, 8.0, 6.0 Hz); 3.77 (1H, dd, J=8.0, 6.0 Hz); 3.35 (1H, appt, J=8.0 Hz); 2.82–2.34 (4H, m); 1.40 (3H, s); 1.36 (3H, s).

(3Z)-(2S)-6-Phenylhex-3-enyl-1,2-diol. To a solution of **31** (349 mg, 1.50 mmol, 1 equiv) in 8.5 mL of THF, 2 mL of 10% HCl were added and the mixture stirred at room temperature overnight. Solid $NaHCO_3$ was then added until CO_2 evolution finished; the mixture was dried over Na_2SO_4. After evaporation of the solvent 218 mg (75% yield) of (3*Z*)-(2*S*)-6-phenylhex-3-enyl-1,2-diol as a white solid were obtained. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.37–7.10 (5H, m); 5.68–5.54 (1H, m); 5.36 (1H, td, J=8.8, 2.2 Hz); 4.37–4.27 (1H, m); 3.36 (2H, d, J=5.9 Hz); 2.70 (2H, td, J=6.6, 2.2 Hz); 2.43 (2H, t, J=6.6 Hz); 1.76 (2H, bs).

(3Z)-(2R)-1-(tert-Butyldimethylsilyloxy)-6-phenylhex-3-en-2-ol. To a stirred solution of (3*Z*)-(2*S*)-6-phenylhex-3-enyl-1,2-diol (200 mg, 1.04 mmol, 1 equiv) in 2 mL of dry CH_2Cl_2, *tert*-butyldimethylsilyl chloride (165 mg, 1.09 mmol, 1.05 equiv) and imidazole (177 mg, 2.6 mmol, 2.5 equiv) were added, under N_2, and the mixture stirred for 5 h. The reaction was quenched with H_2O; the aqueous layer washed with CH_2Cl_2 and the combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave 320 mg of the crude product that was purified by flash chromatography (petroleum ether:ethyl acetate 5:1) to give 151 mg (47% yield) of pure (3*Z*)-(2*R*)-1-(*tert*-butyldimethylsilyloxy)-6-phenylhex-3-en-2-ol as a white solid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.10–7.33 (5H, m); 5.68–5.54 (1H, m); 5.35 (1H, td, $J=8.1$, 1.5 Hz); 4.43–4.33 (1H, m); 3.42–3.26 (2H, m); 2.77–2.62 (2H, m); 2.52–2.30 (2H, m); 1.67 (1H, bs); 0.91 (9H, s); 0.07 (6H, s).

syn-(3,4-cis)-(2S)-1-(tert-Butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexan-2-ol. (+)-L-Diethyl tartrate (80 μL, 1 equiv, 0.46 mmol), titanium (IV) isopropoxide (140 μL, 1 equiv, 0.46 mmol) and (3*Z*)-(2*S*)-1-(*tert*-butyldimethylsilyloxy)-6-phenylhex-3-en-2-ol (140 mg, 1 equiv, 0.46 mmol) were sequentially added to a cooled (−20 °C) suspension of activated 4 Å powdered molecular sieves in 2 mL of dry CH_2Cl_2. After stirring at −20 °C for 15 min, *tert*-butylhydroperoxide (170 μL, 2 equiv, 0.92 mmol), previously dried on activated 4 Å molecular sieves, was added dropwise. After the mixture was stirred for 15 h under N_2 at −20 °C, the reaction was quenched by adding a solution of 400 mg of citric acid and 1.32 g of $FeSO_4 \cdot 7H_2O$ in 4 mL of H_2O at 0 °C. After 10 min the aqueous layer was extracted twice with Et_2O and the combined organic layers were poured into 4 mL of a precooled (0 °C) solution of 30% NaOH (w/v) in saturated brine and stirred for 1 h. The aqueous phase was extracted with Et_2O and the combined organic phases were washed with brine and dried over Na_2SO_4. After the solvent was evaporated 169 mg of the crude product were obtained. Purification by flash chromatography (petroleum ether:ethyl acetate 5:1) led to 80 mg (54% yield) of the pure (3,4-*cis*)-(2*R*)-1-(*tert*-butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexan-2-ol as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.33–7.19 (5H, m); 3.61 (2H, appt, $J=5.1$ Hz); 3.58–3.53 (1H, m); 3.06 (1H, dt, $J=7.8$, 4.4 Hz); 3.00 (1H, dd, $J=6.6$, 4.4 Hz); 2.89 (1H, ddd, $J=14.4$, 8.9, 5.9 Hz); 2.77 (1H, ddd, $J=13.9$, 8.9, 7.22 Hz); 2.42 (1H, bs); 2.00 (1H, dddd, $J=14.0$, 12.1, 7.4, 4.7 Hz); 1.94–1.85 (1H, m); 0.94 (9H, s); 0.11 (6H, s).

syn-(3,4-cis)-(2R,3R,4R)-1,2-di(tert-butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexane **28**. To a stirred solution of -(3,4-*cis*)-(2*S*)-1-(*tert*-butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexan-2-ol (161 mg, 0.5 mmol, 1 equiv) in 1 mL of dry CH_2Cl_2, *tert*-butyldimethylsilyl chloride (113 mg, 0.75 mmol, 1.05 equiv) and imidazole (85 mg, 1.25 mmol, 2.5 equiv) were added, under N_2, and the mixture stirred for 5 h. The reaction was quenched with H_2O; the aqueous layer was washed with CH_2Cl_2 and the combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave 204 mg (94%, yield) of **28** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.37–7.20 (5H, m); 3.69–3.52 (3H, m); 3.10–3.00 (1H, m); 2.97–2.73 (3H, m); 2.15–1.97 (1H, m); 1.81–1.60 (1H, m); 0.94 (9H, s); 0.91 (9H, m); 0.16 (3H, s); 0.11 (3H, s); 0.08 (3H, s); 0.07 (3H, s).

3.4.3. Preparation of *syn*-(3,4-*trans*)-(2*R*,3*R*,4*S*)-1,2-di(*tert*-butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexane 29 and *anti*-(3,4-*trans*)-(2*R*,3*S*,4*R*)-1,2-di(*tert*-butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexane 30. *(3E)-(2S)-6-Phenylhex-3-enyl-1,2-diol*[34] To a stirred solution of **31** (835 mg, 3.6 mmol, 1.0 equiv) in 18 mL of dry cyclohexane, diphenyl sulfide (786 mg, 3.6 mmol, 1.0 equiv) was added under N_2. The solution was irradiated by a water-cooled high-pressure mercury lamp for 11 h at room temperature. The reaction mixture was then concentrated to give 1.6 g of the residue containing **31** and **32** in a 9:91 ratio (by ^{1}H NMR analysis). ^{1}H NMR ($CDCl_3$, 200 MHz) δ, **32**: 7.30–7.10 (5H, m); 5.79 (1H, dt, $J=15.4$, 6.6 Hz); 5.43 (1H, ddt, $J=15.3$, 7.8, 1.4 Hz); 4.42 (1H, ddd, $J=8.0$, 7.8, 6.2 Hz); 4.01 (1H, dd, $J=8.1$, 6.1 Hz); 3.49 (1H, appt, $J=8.0$ Hz); 2.72–2.62 (2H, m); 2.40–2.26 (2H, m); 1.38 (3H, s); 1.34 (3H, s). The crude was dissolved in a solution of 18 mL of THF and 4.5 mL of 10% HCl and the mixture was stirred at room temperature overnight. Solid $NaHCO_3$ was added until CO_2 evolution finished; then the mixture was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography (petroleum ether:ethyl acetate 1:1–1:2) to give 421 mg (61% yield) of (3*E*)-(2*S*)-6-phenylhex-3-enyl-1,2-diol as a white solid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.34–7.13 (5H, m); 5.81 (1H, dtd, $J=15.5$, 6.7, 1.1 Hz); 5.44 (1H, ddt, $J=15.5$, 6.3, 1.4 Hz); 4.18 (1H, ddd, $J=7.0$, 6.3, 3.6 Hz); 3.59 (1H, dd, $J=11.1$, 3.6 Hz); 3.45 (1H, dd, $J=11.1$, 7.0 Hz); 2.76–2.26 (2H, m); 2.45–2.31 (2H, m); 1.98 (1H, bs); 1.81 (1H, bs). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 141.5; 133.1; 129.3; 128.4; 128.3; 125.9; 73.0; 66.5; 35.4; 34.0.

(3E)-(2S)-1-(tert-Butyldimethylsilyloxy)-6-phenylhex-3-en-2-ol. To a stirred solution of (3*E*)-(2*S*)-6-phenylhex-3-enyl-1,2-diol (421 mg, 2.2 mmol, 1 equiv) in 8 mL of dry CH_2Cl_2, *tert*-butyldimethylsilyl chloride (332 mg, 2.2 mmol, 1.0 equiv) and imidazole (373 mg, 5.5 mmol, 2.5 equiv) were added, under N_2, and the mixture stirred at room temperature for 6 h. The reaction was quenched with H_2O; the aqueous layer was washed with CH_2Cl_2 and the combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave 629 mg (93% yield) of (3*E*)-(2*S*)-1-(*tert*-butyldimethylsilyloxy)-6-phenylhex-3-en-2-ol as a white solid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.30–7.13 (5H, m); 5.81 (1H, dtd, $J=15.5$, 6.6, 1.0 Hz); 5.42 (1H, ddt, $J=15.5$, 6.6, 1.4 Hz); 4.16–4.05 (1H, m); 3.59 (1H, dd, $J=10.0$, 3.6 Hz); 3.38 (1H, dd, $J=10.0$, 8.0 Hz); 2.75–2.64 (2H, m); 2.43–2.28 (2H, m); 1.67 (1H, bs); 0.91 (9H, s); 0.07 (6H, s); ^{13}C–NMR ($CDCl_3$, 50 MHz) δ: 141.7; 132.8; 128.8; 128.4; 128.3; 125.8; 72.8; 67.3; 35.5; 34.2; 25.9; 18.3; −5.3.

syn- and anti-(3,4-trans)-(2R)-1-(tert-Butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexan-2-ol. *m*-CPBA (740 mg, 3.0 mmol, 1.5 equiv) was added to a cooled (0 °C) solution of (3*E*)-(2*S*)-1-(*tert*-butyldimethylsilyloxy)-6-phenylhex-3-en-2-ol (610 mg, 2.0 mmol, 1 equiv) in CH_2Cl_2. The mixture was allowed to reach room temperature and then

stirred overnight. The mixture was diluted with CH_2Cl_2, washed twice with satd $Na_2S_2O_3$, twice with 1 M NaOH solution and dried over Na_2SO_4. The crude was purified by flash chromatography (petroleum ether: dichloromethane 1:1), to afford 231 mg (36% yield) of the *syn*-epoxide and 215 mg (33% yield) of the *anti*-epoxide both white solids. *syn*-Epoxide: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.34–7.16 (5H, m); 3.76–3.69 (1H, A part of ABX spin system); 3.69–3.61 (1H, B part of ABX spin system); 3.57–3.44 (1H, m); 3.00 (1H, ddd, J=6.3, 5.1, 2.2 Hz); 2.85–2.69 (2H,m); 2.81 (1H, dd, J=5.3, 2.2 Hz); 2.35 (1H, bs); 2.01–1.79 (2H, m); 0.90 (9H, s); 0.09 (3H, s); 0.08 (3H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 141.1; 128.5; 128.4; 126.1; 71.0; 64.3; 58.2; 56.1; 33.5; 32.2; 25.8; 18.3; −5.4. *anti*-Epoxide: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.32–7.17 (5H, m); 3.65–3.54 (3H, m); 2.99 (1H, ddd, J=5.8, 5.8, 2.3 Hz); 2.87–2.68 (2H, m); 2.82 (1H, dd, J=3.6, 2.3 Hz); 2.21 (1H, d, J=5.7 Hz); 1.93–1.84 (2H, m); 0.90 (9H, s); 0.07 (6H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 141.1; 128.5; 128.4; 126.1; 70.5; 64.5; 58.9; 54.9; 33.4; 32.2; 25.8; 18.2; −5.4, −5.4.

syn-(3,4-trans)-(2R,3R,4S)-1,2-Di(tert-butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexane **29**. To a stirred solution of *syn*-(3,4-*trans*)-(2*R*)-1-(*tert*-butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexan-2-ol (231 mg, 0.72 mmol, 1 equiv) in 7 mL of dry CH_2Cl_2, *tert*-butyldimethylsilyl chloride (163 mg, 1.08 mmol, 1.5 equiv) and imidazole (123 mg, 1.8 mmol, 2.5 equiv) were added, under N_2, and the mixture stirred at room temperature for 2 h. The reaction was quenched with H_2O; the aqueous layer was washed with CH_2Cl_2 and the combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave 325 mg (100% yield) of **29** as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.31–7.16 (5H, m); 3.69 (1H, ddd, J=5.6, 5.4, 3.8 Hz); 3.61 (1H, dd, J=10.2, 5.4 Hz); 3.56 (1H, dd, J=10.2, 5.6 Hz); 2.97 (1H, ddd, J=6.7, 4.8, 2.2 Hz); 2.85 (1H, dd, J=3.8, 2.2 Hz); 2.83–2.67 (2H, m); 1.95–1.75 (2H, m); 0.89 (9H, s); 0.87 (9H, s); 0.05 (9H, s); 0.04 (3H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 141.3; 128.4; 128.3; 125.9; 71.7; 65.8; 59.1; 54.9; 33.7; 32.3; 25.9; 25.8; 18.4; 18.2; −4.6; −4.7; −5.3; −5.4.

anti-(3,4-trans)-(2R,3S,4R)-1,2-Di(tert-butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexane **30**. To a stirred solution of *anti*-(3,4-*trans*)-(2*R*)-1-(*tert*-butyldimethylsilyloxy)-3,4-epoxy-6-phenylhexan-2-ol (215 mg, 0.67 mmol, 1 equiv) in 7 mL of dry CH_2Cl_2, *tert*-butyldimethylsilyl chloride (152 mg, 1.01 mmol, 1.5 equiv) and imidazole (114 mg, 1.68 mmol, 2.5 equiv) were added, under N_2, and the mixture stirred at room temperature for 2 h. The reaction was quenched with H_2O; the aqueous layer was washed with CH_2Cl_2 and the combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave 300 mg (100% yield) of **30** as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.30–7.15 (5H, m); 3.55 (2H, d, J=6.5 Hz); 3.40 (1H, td, J=6.5, 6.0 Hz); 2.93 (1H, ddd, J=6.7, 4.5, 2.2 Hz); 2.80 (1H, dd, J=6.0, 2.2 Hz); 2.77–2.67 (2H, m); 1.96–1.76 (2H, m); 0.89 (9H, s); 0.88 (9H, s); 0.09 (3H, s); 0.06 (3H, s); 0.05 (3H, s); 0.04 (3H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 141.3; 128.4; 128.3; 126.0; 74.2; 65.1; 60.8; 55.6; 33.7; 32.2; 25.9; 25.8; 18.3; 18.2; −4.7; −4.8; −5.4; −5.4.

3.5. Isomerization of oxiranes with LIDAKOR and LICKOR

3.5.1. General procedure. Hexane was stripped off from a solution of BuLi (0.74 mL of a 1.5 M solution, 2 equiv, 1.00 mmol both for LIDAKOR and LICKOR), and precooled THF (1.0 mL) was added at −78 °C under N_2, followed by diisopropylamine (112 mg, 2 equiv, 1.00 mmol for LIDAKOR) and potassium *tert*-butoxide (124 mg, 2 equiv, 1.00 mmol for LIDAKOR, 124 mg, 2 equiv, 1.00 mmol for LICKOR). The mixture was stirred at −78 °C for 45 min and the oxirane (1 equiv, 0.50 mmol) was added and allowed to react at −50 °C; after 15 h the reaction mixture was warmed up to room temperature, quenched with H_2O and extracted twice with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. After evaporation of the solvent the residue was purified.

3.5.2. (*trans*-2-Phenylcyclopropyl)methanol 11.[30] The procedure with 2.2 equiv of LIDAKOR was used on the epoxide **8** obtaining 76 mg of the crude product which was purified by flash chromatography (petroleum ether:ethyl acetate 2:1) giving 60 mg (66% yield) of **11** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.25–6.95 (5H, m); 3.58 (2H, d, J=6.8 Hz); 1.92 (1H, bs); 1.79 (1H, appdt, J=8.0, 5.2 Hz); 1.51–1.33 (1H, m); 0.99–0.85 (2H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 142.3; 128.2; 125.7; 125.5; 66.4; 25.2; 21.2;13.8.

3.5.3. 1-(*trans*-2-Phenylcyclopropyl)-2-methylpropan-1-ol 15.[40] The procedure with 2.2 equiv of LIDAKOR was used on the 67:33 *cis:trans* diasteromeric mixture of epoxide **12** obtaining, after purification by flash chromatography (eluent: CH_2Cl_2), 64 mg (64% yield) of the *anti*-**15** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.34–7.07 (5H, m); 2.95 (1H, appt, J=6.2 Hz); 1.98–1.80 (2H, m); 1.51 (1H, bs); 1.35–1.20 (1H, m); 1.04–0.96 (2H, m); 1.03 (6H, d, J=6.8 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 142.7; 128.3; 125.8; 125.5; 80.5; 34.3; 27.5; 20.3; 18.7; 18.0; 14.4. MS (*m/z*, %): 190 (7, M^+); 173 (1, M^+−OH); 147 (8); 129 (54); 127 (71); 117 (61); 115 (76); 102 (100); 91 (45); 89 (59); 77 (84).

3.5.4. 1-(*trans*-2-Phenylcyclopropyl)ethan-1-ol 16.[41] The procedure with 2.2 equiv of LIDAKOR was used on the epoxide **13** obtaining 97 mg of the crude product which was purified by flash chromatography (petroleum ether:ethyl acetate 5:2) giving 51 mg (60% yield) of **16** as a yellow oil and 13 mg (15% yield) of **18** as a pale yellow oil. **16**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.36–7.08 (5H, m); 3.41 (1H, dq, J=7.4, 6.3 Hz); 2.00–1.87 (1H, m); 1.84 (1H, bs); 1.35 (3H, d, J=6.3 Hz); 1.34–1.24 (1H, m); 1.00–0.88 (2H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 142.6; 128.3; 125.7; 125.5; 71.6; 30.7; 22.3; 21.2; 13.3.

3.5.5. 5-Phenylpent-1-en-3-ol 18. The procedure with 2.2 equiv of LICKOR was used on the epoxide **13** obtaining 62 mg of the crude product which was purified by flash chromatography (petroleum ether:ethyl acetate 3:1) giving 42 mg (52% yield) of **18** as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.38–7.21 (5H, m); 5.95 (1H, ddd, J=17.2, 10.4 Hz); 5.28 (1H, appdt, J=17.2, 1.4 Hz); 5.18 (1H,

appdt, $J=10.4$, 1.4 Hz); 4.24–4.10 (1H, m); 2.76 (2H, td, $J=7.9$, 3.5 Hz); 1.97–1.83 (2H, m); 1.61 (1H, d, $J=$ 4.1 Hz).

3.5.6. 2-(*trans*-2-Phenylcyclopropyl)propan-2-ol 17.[42] The procedure with 2.2 equiv of LIDAKOR was used on the epoxide **14** obtaining 136 mg of the crude product which was purified by flash chromatography (petroleum ether:-ethyl acetate 3:1) giving 105 mg (67% yield) of **17** and 12 mg (7% yield) of **19** both as yellow oils. **17**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.45–7.20 (5H, m); 2.09 (1H, appdt, $J=8.9$, 5.1 Hz); 1.61 (1H, bs); 1.43 (6H, s); 1.42–1.34 (1H, m); 1.19 (1H, ddd, $J=8.9$, 6.0, 5.1 Hz); 0.99 (1H, appdt, $J=$ 8.9, 5.1 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 143.1; 128.2; 125.9; 125.3; 69.4; 34.1; 29.1; 28.9; 19.2; 11.7.

3.5.7. 5-Phenyl-2-methylpent-1-en-3-ol 19. The procedure with 2.2 equiv of LICKOR was used on the epoxide 14 obtaining 59 mg of the crude product which was purified by flash chromatography (petroleum ether:ethyl acetate 3:1) giving 46 mg (57% yield) of **19** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.27–7.05 (5H, m); 4.97 (1H, br s); 4.88 (1H, br s); 4.09 (1H, br t, $J=6.4$ Hz); 2.69 (2H, appq, $J=7.6$ Hz); 1.89 (2H, appquint, $J=7.6$ Hz); 1.74 (1H, bs); 1.29 (3H, s).

3.5.8. (*trans*-2-Vinylcyclopropyl)methanol 21.[30] The procedure with 2.2 equiv of LIDAKOR was used on the commercially available epoxide obtaining 186 mg of the crude product which was purified by flash chromatography (petroleum ether:ethyl acetate 2:1) giving 150 mg (75% yield) of **21** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 5.41 (1H, ddd, $J=17.2$, 10.1, 8.4 Hz); 5.06 (1H, ddd, $J=$ 17.2, 1.8, 0.5 Hz); 4.88 (1H, ddd, $J=10.1$, 1.8, 0.4 Hz); 3.51 (2H, d, $J=6.8$ Hz); 1.49 (1H, bs); 1.41–1.26 (1H, m); 1.25–1.09 (1H, m); 0.72–0.63 (2H, m).

3.5.9. (*E*)-1-Phenyl-3,4-epoxybut-1-en 25. The procedure with 2.2 equiv of LIDAKOR was used on the 1:1 *syn*:*anti* diasteromeric mixture of epoxide **22** obtaining, after purification by flash chromatography (petroleum ether:ethyl acetate 4:1), 40 mg (50% yield) of **25** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.39–7.18 (5H, m); 6.85 (1H, d, $J=16.0$ Hz); 5.90 (1H, dd, $J=16.0$, 8.0 Hz); 3.12–3.02 (1H, m); 2.88–2.74 (2H, m). MS (*m*/*z*, %): 146 (32, M^+); 117 (100); 115 (76); 102 (11); 90 (48); 50 (16).

3.5.10. (*E*,*Z*)-5-Phenyl-1-methoxypent-1-en-3-ol 26. The procedure with 2.2 equiv of LIDAKOR was used on the epoxide **23** obtaining 88 mg (83% yield) of a 20:80 *Z*/*E* diastereomeric mixture of **26** as a yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ: *Z*-**26**: 7.44–7.12 (5H, m); 6.08 (1H, d, $J=5.3$ Hz); 4.73–4.58 (2H, m); 3.50 (3H, s); 2.79 (2H, appt, $J=7.8$ Hz); 2.18–1.82 (3H, m); *E*-**26**: 7.44–7.12 (5H, m); 6.63 (1H, d, $J=12.7$ Hz); 4.93 (1H, dd, $J=12.7$, 8.5 Hz); 4.15 (1H, dt, $J=8.5$, 6.6 Hz); 3.64 (3H, s); 2.79 (2H, appt, $J=7.8$ Hz); 2.18–1.82 (3H, m).

3.5.11. 1-(*trans*-2-Phenylcyclopropyl)-2-methoxypropan-1-ol 27. The procedure with 2.2 equiv of LIDAKOR was used on the 64:36 diasteromeric mixture of epoxide **24** obtaining, after purification by flash chromatography (petroleum ether:ethyl acetate 2:1), 66 mg (63% yield) of a *syn*/*anti* diasteromeric mixture of **27** as a pale yellow oil. Major isomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.38–7.04 (5H, m); 3.42 (3H, s); 3.38–3.25 (1H, m); 3.09–2.90 (1H, m); 2.44 (1H, d, $J=4.1$ Hz); 1.98–1.81 (1H, m); 1.24 (3H, bs); 1.18–0.82 (3H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 142.2; 128.3; 125.6; 125.5; 79.6; 78.1; 56.5; 25.7; 21.1; 14.9; 12.8. MS (*m*/*z*, %): 206 (1, M^+); 188 (5); 175 (10); 147 (21); 131 (52); 129 (100); 118 (72); 103 (69); 91 (100); 77 (84); 59 (100). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.59; H, 8.78. Minor isomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 7.38–7.04 (5H, m); 3.41 (3H, s); 3.38–3.25 (1H, m); 3.09–2.90 (1H, m); 2.56 (1H, d, $J=$ 3.4 Hz); 1.98–1.81 (1H, m); 1.21 (3H, bs); 1.18–0.82 (3H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 142.3; 128.2; 125.7; 125.4; 81.1; 76.2; 56.5; 24.4; 20.7; 13.6; 13.2.

3.5.12. (1*R*,2*R*,1′*R*,2′*R*)-1-(*trans*-2-Phenylcyclopropyl)-2,3-di-*tert*-butyldimethylsilyloxy-propan-1-ol 33a and 1-(*trans*-2-phenylcyclopropyl)-1,3-di-*tert*-butyldimethylsilyloxypropan-2-ol 33b. The procedure with 2.0 equiv of LIDAKOR was used on the *syn*-epoxide **28** (76 mg, 0.17 mmol) obtaining 66 mg of the crude product which was purified by flash chromatography (petroleum ether:-ethyl acetate 3:1) giving 57 mg (75% yield) of a mixture of **33a** and **33b** as a yellow oil in a 67/33 ratio. **33a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.26–7.21 (2H, m); 7.16–7.10 (1H, m); 7.09–7.03 (2H, m); 3.78 (1H, ddd, $J=7.5$, 4.8, 2.7 Hz); 3.70 (1H, dd, $J=9.7$, 7.5 Hz); 3.56 (1H, dd, $J=9.7$, 4.8 Hz); 3.20 (1H, ddd, $J=8.3$, 7.9, 2.7 Hz); 2.53 (1H, d, $J=8.3$ Hz); 2.03 (1H, ddd, $J=8.4$, 5.2, 4.4 Hz); 1.38–1.30 (1H, m); 0.94–0.84 (2H, m); 0.91 (9H, s); 0.89 (9H, s); 0.12 (3H, s); 0.11 (3H, s); 0.09 (6H, s). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 143.0; 128.2; 125.8; 125.4; 75.1; 74.9; 62.2; 26.3; 25.9; 25.8; 21.5; 18.3; 18.1; 13.1; −4.3; −4.8; −5.4; −5.5. Anal. Calcd for $C_{24}H_{44}O_3Si_2$: C, 66.00; H, 10.15. Found: C, 66.19; H, 10.08. **33b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.26–7.21 (2H, m); 7.16–7.10 (1H, m); 7.09–7.03 (2H, m); 3.68–3.55 (3H, m); 3.47 (1H, dd, $J=7.4$; 2.6 Hz); 2.50 (1H, d, $J=6.8$ Hz); 1.88 (1H, ddd, $J=8.6$, 5.2, 4.8 Hz); 1.48 (1H, m); 0.94–0.84 (2H, m); 0.88 (9H, s); 0.87 (9H, s); 0.06 (3H, s); 0.05 (3H, s); 0.04 (3H, s); 0.03 (3H, s). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 142.7; 128.2; 125.7; 125.4; 74.8; 74.4; 63.4; 26.0; 25.9; 25.8; 22.1; 18.2; 18.1; 13.2; −4.0; −4.7; −5.3; −5.4.

3.5.13. (1*R*,2*R*,1′*S*,2′*S*)-1-(*trans*-2-Phenylcyclopropyl)-2,3-di-*tert*-butyldimethylsilyloxy-propan-1-ol 34a and 1-(*trans*-2-phenylcyclopropyl)-1,3-di-*tert*-butyldimethylsilyloxypropan-2-ol 34b. The procedure with 2.0 equiv of LIDAKOR was used on the *syn*-epoxide **29** (87 mg, 0.2 mmol) obtaining 79 mg of the crude product which was purified by flash chromatography (petroleum ether:-ethyl acetate 3:1) giving 50 mg (57% yield) of **34a** and 24 mg (28% yield) of **34b** both as yellow oils. **34a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.27–7.22 (2H, m); 7.17–7.11 (1H, m); 7.07–7.03 (2H, m); 3.75 (1H, ddd, $J=6.7$, 5.4, 4.4 Hz); 3.68 (1H, d, $J=5.4$ Hz); 3.68 (1H, d, $J=6.7$ Hz); 3.45 (1H, bdd, $J=6.8$, 4.4 Hz); 2.88 (1H, bs); 1.94 (1H, ddd, $J=8.8$, 5.1, 5.0 Hz); 1.37 (1H, m); 1.11 (1H, ddd, $J=8.8$, 5.6, 4.9 Hz); 0.94–0.89 (1H, m); 0.88 (9H, s); 0.87 (9H, s); 0.08 (3H, s); 0.07 (3H, s); 0.04 (3H, s); 0.03 (3H, s). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 142.9; 128.3; 125.8; 125.4; 76.3; 75.0; 65.5; 25.9; 25.8; 24.4; 20.3; 18.2; 18.1; 12.7; −4.4; −4.8;

−5.4; −5.5. MS (*m*/*z*, %): 247 (8); 155 (18); 147 (20); 129 (24); 117 (19); 101 (19); 91 (18); 89 (30); 75 (43); 73 (100); 59 (14). Anal. Calcd for $C_{24}H_{44}O_3Si_2$: C, 66.00; H, 10.15. Found: C, 66.11; H, 10.19. **34b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.27–7.22 (2H, m); 7.17–7.11 (1H, m); 7.07–7.04 (2H, m); 3.78–3.70 (2H, m); 3.67–3.60 (1H, m); 3.46 (1H, dd, J=7.2; 4.0 Hz); 2.51 (1H, bs); 1.91 (1H, ddd, J=8.1, 5.9, 4.6 Hz); 1.31 (1H, m); 0.98–0.87 (2H, m); 0.92 (9H, s); 0.89 (9H, s); 0.14 (3H, s); 0.09 (3H, s); 0.05 (3H, s); 0.04 (3H, s). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 142.5; 128.2; 125.7; 125.5; 75.6; 75.5; 63.7; 25.9; 25.9; 25.3; 20.4; 18.3; 18.2; 13.3; −4.0; −4.4; −5.3; −5.3. MS (*m*/*z*, %): 287 (2, M^+-H_2O -OTBDMS); 261 (18); 247 (7); 155 (15); 129 (21); 117 (27); 91 (16); 89 (34); 75 (52); 73 (100); 59 (15).

3.5.14. (1*R*,2*R*,1′*S*,2′*S*)-1-(*trans*-2-Phenylcyclopropyl)-1,2,3-propantriol 36. To a stirred solution of **34a** (26 mg, 0.06 mmol, 1.0 equiv) in THF (1.0 mL), TBAF·3H_2O (57 mg, 0.18 mmol, 3.0 equiv) and 20 μL of water were added. After 12 h at room temperature, evaporation of the solvent gave 30 mg of the crude product that was purified by flash chromatography (ethyl acetate:methanol 10:1) to give 10 mg (80% yield) of pure **36** as a colorless solid. $[\alpha]_D=-98.2°$ (c=0.22; methanol) ^{1}H NMR (CD_3OD, 400 MHz) δ: 7.24–7.19 (2H, m); 7.12–7.06 (3H, m); 3.72 (1H, dd, J=10.3, 4.2 Hz); 3.68 (1H, ddd, J=6.2, 4.8, 4.2 Hz); 3.57 (1H, dd, J=10.3, 6.2 Hz); 3.23 (1H, dd, J=7.8, 4.8 Hz); 1.89 (1H, ddd, J=8.7, 5.0, 4.9 Hz); 1.35 (1H, m); 1.01 (1H, ddd, J=8.7, 5.5, 4.8 Hz); 0.91 (1H, ddd, J=8.7, 5.5, 4.9 Hz). ^{13}C NMR (CD_3OD, 100 MHz) δ: 144.1; 129.3; 126.8; 126.5; 76.5; 76.4; 64.6; 26.1; 21.9; 13.2. MS (*m*/*z*, %): 190 (8, M^+-H_2O); 159 (8); 147 (12); 129 (88); 117 (67); 115 (36); 104 (64); 91 (100, $C_7H_7^+$); 77 (20); 65 (23); 61 (45); 51 (21). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.11; H, 7.82.

To a stirred solution of **34b** (13 mg, 0.03 mmol, 1.0 equiv) in THF (0.5 mL), TBAF·3H_2O (28 mg, 0.09 mmol, 3.0 equiv) and 10 μL of water were added. After 12h at room temperature, evaporation of the solvent gave 20 mg of the crude product that was purified by flash chromatography (ethyl acetate:methanol 10:1) to give 5 mg (80% yield) of pure **36**, identical to that described above.

3.5.15. (1*S*,2*R*,1′*R*,2′*R*)-1-(*trans*-2-Phenylcyclopropyl)-2,3-di-*tert*-butyldimethylsilyloxy-propan-1-ol 35a and 1-(*trans*-2-phenylcyclopropyl)-1,3-di-*tert*-butyldimethylsilyloxypropan-2-ol 35b. The procedure with 2.0 equiv of LIDAKOR was used on the *anti*-epoxide **30** (87 mg, 0.2 mmol) obtaining 82 mg of the crude product which was purified by flash chromatography (petroleum ether:-ethyl acetate 3:1) giving 52 mg (59% yield) of **35a** and 25 mg (29% yield) of **35b** both as yellow oils. **35a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.26–7.21 (2H, m); 7.16–7.11 (1H, m); 7.05–7.01 (2H, m); 3.77 (1H, ddd, J=7.3, 4.8, 2.7 Hz); 3.69 (1H, dd, J=9.7, 7.3 Hz); 3.55 (1H, dd, J=9.7, 4.8 Hz); 3.27 (1H, ddd, J=7.9, 7.7, 2.7 Hz); 2.62 (1H, d, J=7.9 Hz); 1.81 (1H, ddd, J=8.7, 5.0, 4.3 Hz); 1.30 (1H, m); 1.14 (1H, ddd, J=8.7, 5.3, 5.3 Hz); 1.02 (1H, ddd, J=8.4, 5.3, 5.0 Hz); 0.89 (9H, s); 0.86 (9H, s); 0.05 (3H, s); 0.04 (3H, s); 0.03 (3H, s); −0.08 (3H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 142.6; 128.2; 125.5; 125.4; 75.3; 74.3; 64.2; 26.5; 25.9; 25.8; 20.1; 18.3; 18.0; 14.0; −4.3; −5.1; −5.4; −5.5. Anal. Calcd for $C_{24}H_{44}O_3Si_2$: C, 66.00; H, 10.15. Found: C, 66.03; H, 10.10. **35b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.26–7.22 (2H, m); 7.17–7.11 (1H, m); 7.07–7.03 (2H, m); 3.65–3.55 (3H, m); 3.43 (1H, dd, J=7.8, 2.9 Hz); 2.51 (1H, d, J=5.9 Hz); 1.81 (1H, ddd, J=7.1, 6.8, 4.9 Hz); 1.39 (1H, m); 1.00 (2H, appt, J=7.1 Hz); 0.93 (9H, s); 0.88 (9H, s); 0.15 (3H, s); 0.10 (3H, s); 0.05 (3H, s); 0.04 (3H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 142.3; 128.3; 125.9; 125.6; 75.1; 74.9; 63.4; 26.1; 25.9; 25.8; 20.4; 18.2; 18.2; 14.9; −3.8; −4.7; −5.3; −5.4.

3.5.16. (1*S*,2*R*,1′*R*,2′*R*)-1-(*trans*-2-Phenylcyclopropyl)-1,2,3-propantriol 37. To a stirred solution of **35a** (13 mg, 0.03 mmol, 1.0 equiv) in THF (0.5 mL), TBAF·3H_2O (28 mg, 0.09 mmol, 3.0 equiv) and 10 μL of water were added. After 12 h at room temperature, evaporation of the solvent gave 25 mg of the crude product that was purified by flash chromatography (ethyl acetate:methanol 10:1) to give 5 mg (80% yield) of pure **37** as a colourless solid. $[\alpha]_D$ +52.6° (c=0.48; methanol) ^{1}H NMR (CD_3OD, 400 MHz) δ: 7.24–7.19 (2H, m); 7.13–7.06 (3H, m); 3.68 (1H, dd, J=10.1, 3.7 Hz); 3.61 (1H, ddd, J=6.0, 4.8, 3.7 Hz); 3.57 (1H, dd, J=10.1, 6.0 Hz); 3.11 (1H, dd, J=8.4, 4.8 Hz); 1.87 (1H, ddd, J=8.7, 5.1, 4.9 Hz); 1.31 (1H, m); 1.06 (1H, ddd, J=8.7, 5.5, 4.9 Hz); 0.98 (1H, ddd, J=8.5, 5.1, 4.9 Hz). ^{13}C NMR (CD_3OD, 100 MHz) δ: 143.9; 129.3; 126.8; 126.5; 76.6; 76.4; 64.4; 27.3; 21.9; 14.4. MS (*m*/*z*, %): 190 (1, M^+-H_2O); 159 (10); 147 (8); 129 (100); 128 (25); 118 (37); 117 (68); 115 (35); 104 (76); 91 (98, $C_7H_7^+$); 84 (17); 77 (26); 65 (20); 61 (49); 51 (26). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.32; H, 7.69.

To a stirred solution of **35b** (13 mg, 0.03 mmol, 1.0 equiv) in THF (0.5 mL), TBAF·3H_2O (28 mg, 0.09 mmol, 3.0 equiv) and 10 μL of water were added. After 12 h at room temperature, evaporation of the solvent gave 26 mg of the crude product that was purified by flash chromatography (ethyl acetate:methanol 10:1) to give 4 mg (64% yield) of pure **37**, identical to that described above.

Acknowledgements

Ente Cassa di Risparmio di Firenze (Italy) is acknowledged for granting a 400 MHz NMR spectrometer. CINMPIS (Consorzio Interuniversitario Nazionale 'Metodologie e Processi Innovativi di Sintesi') is gratefully acknowledged for the research award to D.P.

References and notes

1. Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9–16.
2. Mordini, A. In Abel, E. W., Stone, F. G. A., Wilkinson, G., McKillop, A., Eds.; Comprehensive Organometallic Chemistry II; Pergamon: Oxford, 1995; Vol. 11, pp 93–128.
3. Mordini, A.; BenRayana, E.; Margot, C.; Schlosser, M. *Tetrahedron* **1990**, *46*, 2401–2410.
4. Degl'Innocenti, A.; Mordini, A.; Pecchi, S.; Pinzani, D.; Reginato, G.; Ricci, A. *Synlett* **1992**, 753–755 (=803–805).

5. Mordini, A.; Valacchi, M.; Pecchi, S.; Degl'Innocenti, A.; Reginato, G. *Tetrahedron Lett.* **1996**, *37*, 5209–5212.
6. Mordini, A.; Pecchi, S.; Capozzi, G.; Capperucci, A.; Degl'Innocenti, A.; Reginato, G.; Ricci, A. *J. Org. Chem.* **1994**, *59*, 4784–4790.
7. Bigi, A.; Mordini, A.; Thurner, A.; Faigl, F.; Poli, G.; Toke, L. *Tetrahedron: Asymmetry* **1998**, *9*, 2293–2299.
8. Mordini, A.; Russo, F.; Valacchi, M.; Zani, L.; Degl'Innocenti, A.; Reginato, G. *Tetrahedron* **2002**, *58*, 7153–7163.
9. Mordini, A.; Sbaragli, L.; Valacchi, M.; Russo, F.; Reginato, G. *Chem. Commun.* **2002**, 778–779.
10. Mordini, A.; Bindi, S.; Pecchi, S.; Degl'Innocenti, A.; Reginato, G.; Serci, A. *J. Org. Chem.* **1996**, *61*, 4374–4378.
11. Mordini, A.; Bindi, S.; Pecchi, S.; Capperucci, A.; Degl'Innocenti, A.; Reginato, G. *J. Org. Chem.* **1996**, *61*, 4466–4468.
12. Mordini, A.; Valacchi, M.; Nardi, C.; Bindi, S.; Poli, G.; Reginato, G. *J. Org. Chem.* **1997**, *62*, 8557–8559.
13. Thurner, A.; Faigl, F.; Toke, L.; Mordini, A.; Valacchi, M.; Reginato, G.; Czira, G. *Tetrahedron* **2001**, *57*, 8173–8180.
14. Faigl, F.; Thurner, A.; Tárkányi, G.; Kovári, J.; Mordini, A. *Tetrahedron: Asymmetry* **2002**, *13*, 59–68.
15. Thurner, A.; Faigl, F.; Mordini, A.; Bigi, A.; Reginato, G.; Toke, L. *Tetrahedron* **1998**, *54*, 11597–11602.
16. Mordini, A.; Bindi, S.; Capperucci, A.; Nistri, D.; Reginato, G.; Valacchi, M. *J. Org. Chem.* **2001**, *57*, 8173–8180.
17. Margot, C.; Schlosser, M. *Tetrahedron Lett.* **1985**, *26*, 1035–1038.
18. Fleming, F. F.; Shook, B. C. *Tetrahedron* **2002**, *58*, 1–23.
19. Lambs, L.; Singh, N. P.; Biellmann, J.-F. *J. Org. Chem.* **1992**, *57*, 6301–6304.
20. Langer, P.; Freifeld, I. *Org. Lett.* **2001**, *3*, 3903–3905.
21. Le Corre, M.; Hercouet, A.; Bessieres, B. *Tetrahedron: Asymmetry* **1995**, *6*, 683–684.
22. Babler, J. H.; Tortorello, A. J. *J. Org. Chem.* **1976**, *41*, 885–887.
23. Majewski, J.; Snieckus, V. *J. Org. Chem.* **1984**, *49*, 2682–2687.
24. Crotti, P.; Di Bussolo, V.; Favero, L.; Macchia, F.; Pineschi, M.; Napolitano, E. *Tetrahedron* **1999**, *55*, 5853–5866.
25. Benedetti, F.; Berti, F.; Fabrissin, S.; Gianferrara, T.; Risaliti, A. *J. Org. Chem.* **1991**, *56*, 3530–3537.
26. Corbel, B.; Durst, T. *J. Org. Chem.* **1976**, *41*, 3648–3650.
27. Gaoni, Y. *J. Org. Chem.* **1982**, *47*, 2564–2571.
28. Narjes, F.; Bolte, O.; Icheln, D.; Konig, A.; Schaumann, E. *J. Org. Chem.* **1993**, *58*, 626–632.
29. Apparu, M.; Barrelle, M. *Tetrahedron Lett.* **1976**, *17*, 2837–2840.
30. Apparu, M.; Barrelle, M. *Tetrahedron* **1978**, *34*, 1691–1697.
31. Doris, E.; Dechoux, L.; Mioskowski, C. *Tetrahedron Lett.* **1994**, *35*, 7943–7946.
32. Hodgson, D. M.; Fleming, M. J.; Stanway, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 12250–12251.
33. Hodgson, D. M.; Chung, Y. K.; Paris, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 8664–8665.
34. Azuma, H.; Takao, R.; Niiro, H.; Shikata, K.; Tamagaki, S.; Tachibana, T.; Ogina, K. *J. Org. Chem.* **2003**, *68*, 2790–2797.
35. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
36. Schlenk, W.; Bergmann, E. *Liebigs Ann. Chem.* **1928**, *464*, 22–34.
37. Mitchell, J. M.; Finney, N. S. *J. Am. Chem. Soc.* **2001**, *123*, 862–869.
38. Shimagaki, M.; Matsuzaki, Y.; Hori, I.; Nakata, T.; Oishi, T. *Tetrahedron Lett.* **1984**, *25*, 4779–4782.
39. Alcón, M.; Poch, M.; Moyano, A.; Pericàs, M. A. *Tetrahedron: Asymmetry* **1997**, *8*, 2967–2974.
40. Charette, A. B.; Lebel, H.; Gagnon, A. *Tetrahedron* **1999**, *55*, 8845–8856.
41. Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12160–12167.
42. Kusuyama, Y. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 685–692.