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Useful base promoted elaborations of oxiranyl ethers

Angelika Thurner,[a] Ferenc Faigl,[a,*] László Tőke,[a] Alessandro Mordini,[b] Michela Valacchi,[b] Gianna Reginato[b] and Gábor Czira[c]

[a]*Department of Organic Chemical Technology, Budapest University of Technology and Economics, Müegyetem rkp. 3, H-1111 Budapest, Hungary*

[b]*Dipartimento di Chimica Organica 'U. Schiff', Centro CNR Composti Eterociclici, via G. Capponi 9, I-50121 Firenze, Italy*

[c]*Richter Gedeon Co., H-1103 Budapest, Gyömrői út 19-21, Hungary*

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Abstract—Functionalized oxiranyl ethers can be regio- and stereoselectively converted into hydroxy oxetanes or *cis*-diols by treatment with organometallic bases. These two rearrangements can be conveniently carried out either using different reaction conditions starting from the oxirane or in two consecutive steps from the oxirane via the oxetane.

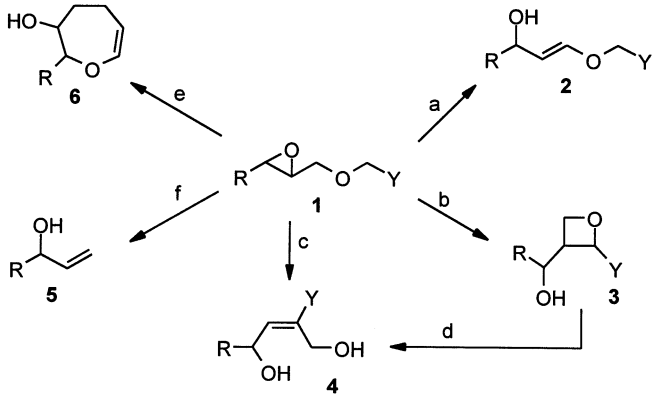
1. Introduction

We have shown in the last few years that oxiranyl ethers **1** can be conveniently elaborated in a number of ways, to afford useful building blocks such as hydroxyvinyl ethers **2**,[1–4] hydroxyoxetanes **3**,[5–7] diols **4**,[8] allylic alcohols **5**[9] and hydroxytetrahydrooxepines **6**[10] (Scheme 1, routes a–f, respectively).

All these transformations have been carried out making use of superbases[11,12] and in particular an equimolar mixture of butyllithium, diisopropylamine and potassium *tert*-butoxide (LIDAKOR)[13] except for the preparation of allylic alcohols which occurs by reductive lithiation[14] of the thiophenyl substituted epoxy ether with the radical anion LDBB[15] via Grob-type fragmentation.[16,17]

2. Results and discussion

Due to the synthetic utility of oxetanes,[18,19] their preparation is still of interest. Furthermore, the recently reported novel stereoselective rearrangement of oxiranes (**1**) or oxetanes (**3**) into *Z*-2-alkene-1,4-diols (**4**) worked only in those cases when R and Y were alkyl and phenyl groups, respectively.[8] The phenyl group is a requisite of the rearrangement process. However, this new reaction would be a convenient route to practically useful building blocks (type **4**) of biologically active sugar and azasugar derivatives[20] if we could extend the method to a series of compounds (**1** and **3**) in which R would be an alkoxymethyl, dialkylaminomethyl or alkenyl group. Therefore, we have undertaken a further study with the aim of extending the scope of the rearrangement sequences. A series of alkyl, alkoxymethyl and



Scheme 1. R=alkyl group, Y=methoxymethyl or phenyl group.

Keywords: oxirane; oxetane; superbase; rearrangement; diol.

* Corresponding author. Tel.: +36-1-463-3652; fax: +36-1-463-3648; e-mail: faigl.oct@chem.bme.hu

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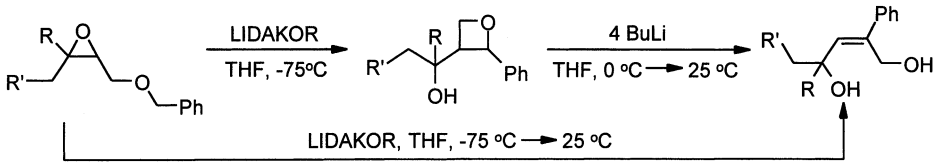

Scheme 2. R and R′ in compounds **7**–**9** are as follows. **a**: R=H, R′=butyl; **b**: R=H, R′=ethyl; **c**: R=methyl, R′=3-methylbut-2-en-1-yl; **d**: R=H, R′=*tert*-butyl-diphenylsilyloxy; **e**: R=H, R′=benzyloxy; **f**: R=H, R′=methoxy; **g**: R=H, R′=triphenylmethyloxy; **h**: R=H, R′=dibenzylamino; **i**: R=H, R′=diethylamino; **l**: R=H, R′=piperidyl.

dialkylaminomethyl group containing oxiranylmethyl benzyl ethers have been synthesized (compounds **7a**–**l**) and then submitted to treatment with the LIDAKOR reagent (Scheme 2).

The benzyl protected octenol- (**7a**), hexenol- (**7b**), geraniol (**7c**) oxides have been obtained via alkene epoxidation and benzylation. The silyl protected diol **7d** has been prepared from 2-buten-1,4-diol via monosilylation[21] followed by epoxidation and benzylation and, similarly, **7e**–**g** via suitable alkylation and epoxidation. 2-Buten-1,4-diol has also been used for the preparation of the three new, amino substituted oxiranyl ethers **7h**, **7i** and **7l** via monobenzylation followed by epoxidation, tosylation and nucleophilic displacement of the tosyl group by the required secondary amine.

All benzyl oxiranyl ethers **7a**–**l** have been clearly converted into the corresponding oxetanes **8a**–**l** (Scheme 2) in good yields and selectivities, as shown in Table 1.

The *cis*/*trans* ratio of the newly formed oxetanes **8c**–**l** is always strongly in favour of the *trans* isomer. The isomeric ratios could be determined on the basis of the ^{1}H NMR spectra as already found in the cases of **8a** and **8b**.[5–7] The transition state for a *cis*-mode 4-*exo* ring closure is indeed clearly more crowded than the transition state for a *trans*-mode and the difference is strikingly higher when a bulky substituent is present on the oxirane in the *cis*-position with respect to the benzyl group.

In order to test the feasibility of the sequence leading to diols **9** (Scheme 2), we have then submitted oxiranes **7** to treatment with the LIDAKOR base in a threefold excess. As reported in Table 1, the results of these experiments show that the conversion to diols is possible and/or synthetically useful only for a limited number of substrates under these reaction conditions. This behaviour can be attributed mainly to the very strongly basic conditions used that are not suitable for highly functionalised substrates. By changing the base from LIDAKOR to butyllithium alone in a large excess (4 equiv.), we have been able to convert most of oxetanes **8** to diols **9** again with a perfect stereocontrol (Scheme 2). The yields of this transformation were significantly better than those obtained via direct superbase isomerisation of the oxiranes (see in Table 1) and in one case (entry 8) the new experimental procedure allowed us to get **9h** while superbase treatment was not effective. The yields of isolated **9** are not always satisfactory and this can be attributed to their low stability at room temperature when trace amount of acids are present, for example in $CDCl_3$ solution or silica gel columns. We have observed that yields can be improved by using florisil instead of silica gel (entry 10).

All the olefins **9** were obtained as pure *Z*-isomers probably owing to a strong interaction between the two O–metal groups in the course of the isomerisation process. The *Z* configuration has been confirmed by NMR (COSY and NOESY) experiments.[8] The free hydroxyl group in oxetane **8** is essential for the diol formation as shown by an attempted isomerisation of 3-(1-methoxybutyl)-2-phenyloxetane **8m** (the O-methylated derivative of **8b**) which failed under both superbase and butyllithium treatment.

In conclusion we have found that a series of benzyl oxiranyl ethers (containing dialkylaminomethyl or alkoxymethyl groups) can be conveniently converted into disubstituted *trans*-oxetanes or new *Z*-2-alkene-1,4-diols. Moreover, we

Table 1. Base induced isomerization of oxiranes

Entry	Oxirane	Transformation of		
		7 to **8** with LIDAKOR (yield[a]; *cis*/*trans*)	**7** to **9** with LIDAKOR (yield[a]; *Z*/*E*)	**8** to **9** with BuLi (yield[a]; *Z*/*E*)
1	**7**	**8a** (70%; 0:100)	**9a** (55%; 100:0)	**9a** (55%; 100:0)
2	**7b**	**8b** (68%; 0:100)	**9b** (52%; 100:0)	**9b** (64%; 100:0)
3	**7c**	**8c** (69%; 0:100)	–	–
4	**7d**	**8d** (64%; 0:100)	**9d** (13%; 100:0)	**9d** (19%[b]; 100:0)
5	**7e**	**8e** (50%; 13:87)	–	–
6	**7f**	**8f** (50%; 0:100)	**9f** (10%; 100:0)	**9f** (22%; 100:0)
7	**7g**	**8g** (66%; 3:97)	**9g** (6%; 100:0)	**9g** (35%; 100:0)
8	**7h**	**8h** (64%; 5:95)	–	**9h** (24%; 100:0)
9	**7i**	**8i** (75%; 5:95)	**9i** (39%; 100:0)	**9i** (35%; 100:0)
10	**7l**	**8l** (59%; 0:100)	**9l** (20%; 100:0)	**9l** (39%[c]; 100:0)

Structures of **8a**–**l** and **9a**–**l** are given in Scheme 2.
[a] Yields of isolated products.
[b] 38% Yield was achieved when the alcoholate of **9d** was quenched with methyl iodide before hydrolysis and workup.
[c] Purification on Florisil; the yield dropped to 20% when Silica gel was used for column chromatography.

have developed a novel, two-step method for the preparation of **9**. In this case the second step is a simple treatment of *trans*-oxetane **8** with an excess of butyllithium. This method provided us **9a** and **9b** in similar yields to those obtained by the one step superbase method. However, the rearrangement process served series of highly functionalized new *Z*-2-alkene-1,4-diols (**9d–l**) in significantly better yields than the LIDAKOR induced reaction. Due to the perfect *Z* selectivity of the reaction, these diols can serve as starting materials for the stereoselective synthesis of sugar and azasugar derivatives.[20]

3. Experimental

3.1. General

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. The temperature of dry ice–ethanol baths is consistently indicated as −78°C, that of ice bath as 0°C and 'room temperature' as 25°C. If no reduced pressure is specified, boiling ranges were determined under ordinary atmospheric conditions (720±35 mmHg). Purifications by flash column chromatography were performed using glass columns (10–50 mm wide); silica gel (230–400 mesh) or Florisil (60–100 mesh) was chosen as stationary phase (15 cm high), with an elution rate of 5 cm/min. All products (**7–9**) were obtained as colourless oils after evaporating of the eluent except **8g**, **8m** and **9g** which are white solids. ^{1}H NMR spectra were recorded at 250 or 500 MHz. Chemical shifts were determined relative to the residual solvent peak ($CHCl_3$ δ: 7.26 ppm) or to tetramethyl silane (TMS δ: 0.00 ppm). Coupling constants (*J*) are measured in Hz. Coupling patterns are described by abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), dd (doublet of a doublet), m (multiplet), bs (broad singlet), bt (broad triplet), bq (broad quartet). All mass spectra were recorded on a Finnigan MAT 95SQ hybrid-tandem mass spectrometer. The electron ionization (EI) spectra were obtained at 70 eV using a heated direct inlet system. A Cs ion gun was used for FAB experiments and the energy of the bombarding Cs^+ beam was 30 keV. The matrix was glycerol. The exact mass determinations were performed at the resolving power of 5000 and using PFK (perfluorokerosene) and glycerol adduct ions as references for EI and FAB measurements, respectively.

3.2. Materials

Starting materials were commercially available unless otherwise stated. All commercial reagents were used without further purification except diisopropylamine, which was distilled over calcium hydride. Anhydrous tetrahydrofuran was distilled from sodium diphenylketyl. Dimethylformamide was distilled over calcium hydride and then stored over 4-Å molecular sieves. 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 oxiranyl ethers 7a–l

Epoxidation. General procedure. *m*-Chloro-perbenzoic acid (1.5 equiv.) in CH_2Cl_2 was added, during a period of 20 min, to a solution of the alkene (1.0 equiv.) in CH_2Cl_2 (total amount to make a 0.5 M solution) at 0°C. The reaction mixture was stirred for 15 h at 25°C then cooled to 0°C. The precipitated *m*-chlorobenzoic acid was rapidly filtered off and washed with cold CH_2Cl_2. The organic solution was washed with saturated aqueous $NaHCO_3$, saturated aqueous $Na_2S_2O_3$, brine and dried. After evaporation of the solvent, the residue was purified by column chromatography (33% ethyl acetate/hexane).

3.4. Preparation of the benzyl ethers

General procedure. NaH (1 equiv., 60% in oil) was washed with pentane and vacuum-dried then dry DMF was added. The resulting suspension was added to a precooled (0°C) solution of the alcohol (1 equiv.; 2.2 equiv. of the diol) in dry DMF (total amount to make a 1.0 M solution). After stirring for 2 h at 25°C the mixture was cooled to 0°C and a solution of benzyl bromide (1 equiv.) in DMF was added during a period of 15 min. The reaction mixture was stirred for 16 h at 25°C, then cautiously poured into ice and extracted with ether. The organic phase was washed with brine. After drying and evaporation of the solvent the residue was purified by flash chromatography (25–33% ethyl acetate/hexane).

3.4.1. (*E*)-1-(Benzyloxy)-2,3-epoxyoctane 7a.[7] Compound **7a** (60%, oil) was prepared according to the general procedure; δ_H ($CDCl_3$): 7.4–7.2 (5H, m, Ph), 4.63 (1H, d, *J*=11.5 Hz, CH_aH$_b$Ph), 4.55 (1H, d, *J*=11.5 Hz, CH$_a$$H_b$Ph), 3.72 (1H, dd, *J*=11.4, 3.4 Hz, CH_aH$_b$O), 3.47 (1H, dd, *J*=11.4, 5.8 Hz, CH$_a$$H_b$O), 2.95 (1H, ddd, *J*=5.8, 3.4, 2.6 Hz, oxirane C*H*), 2.82 (1H, m, oxirane C*H*), 1.6–1.2 (8H, m, CH_2), 0.89 (3H, t, *J*=6.6 Hz, *Me*).

3.4.2. (*E*)-1-(Benzyloxy)-2,3-epoxyhexane 7b.[8] Compound **7b** (65%, oil) was prepared according to the general procedure; δ_H ($CDCl_3$): 7.35–7.22 (5H, m, Ph), 4.65 (1H, d, *J*=12.0 Hz, CH_aH$_b$Ph), 4.50 (1H, d, *J*=12.0 Hz, CH$_a$$H_b$Ph), 3.70 (1H, dd, *J*=11.5, 3.5 Hz, CH_aH$_b$O), 3.45 (1H, dd, *J*=11.5, 5.5 Hz, CH$_a$$H_b$O), 2.93 (1H, m, oxirane C*H*), 2.82 (1H, m, oxirane C*H*), 1.6–1.3 (4H, m, CH_2), 0.95 (3H, t, *J*=6.8 Hz, *Me*).

3.4.3. (*E*)-1-Benzyloxy-2,3-epoxy-3,7-dimethyl-6-octene 7c.[22] Compound **7c** (40%, oil) was prepared according to the general procedure; δ_H ($CDCl_3$): 7.36–7.25 (5H, m, Ph), 5.08 (1H, bt, *J*=7.0 Hz, =C*H*), 4.64 (1H, d, *J*=11.9 Hz, CH_aH$_b$Ph), 4.52 (1H, d, *J*=11.9 Hz, CH$_a$$H_b$Ph), 3.68 (1H, dd, *J*=11.2, 4.5 Hz, CH_aH$_b$O), 3.54 (1H, dd, *J*=11.2, 6.1 Hz, CH$_a$$H_b$O), 3.01 (1H, app t, *J*=5.4 Hz, oxirane C*H*), 2.08 (2H, m, CH_2), 1.71 (3H, s, *Me*–C=), 1.60 (3H, s, *Me*–C=), 1.54 (2H, m, CH_2), 1.46 (3H, s, *Me*).

3.5. Synthesis of 7d

3.5.1. (*Z*)-4-(*tert*-Butyldiphenylsilyloxy)-2-buten-1-ol.[23] Butyllithium (1.6 M in hexane, 10.7 mL, 17.3 mmol) was slowly added to *cis*-2-buten-1,4-diol (1.57 g, 18.2 mmol) in

THF (25 mL) at −78°C. After 10 min, *tert*-butyldiphenylsilyl chloride (4.74 g, 17.3 mmol) was added and the solution warmed to 25°C. After refluxing 7 h, the solvent was evaporated giving 9.8 g of residue which was then purified by column chromatography (25% ethyl acetate/petroleum ether) to 5.0 g (84%, oil) of pure (*Z*)-4-(*tert*-butyldiphenylsilyloxymethyl)-2-buten-1-ol; δ_H ($CDCl_3$): 7.68 (4H, m, Ph), 7.41 (6H, m, Ph), 5.66 (2H, m, =C*H*), 4.25 (2H, d, *J*=4.8 Hz, CH_2OH), 4.01 (2H, d, *J*=4.8 Hz, CH_2OSi), 1.57 (1H, bs, O*H*), 1.05 (9H, s, *Me*$_3$C); *m*/*z* (EI): 269 (2.4, $[M-C_4H_9]^+$), 200 (11), 199 (100), 181 (10), 139 (10), 77 (15), 57 (11).

3.5.2. (*Z*)-4-(*tert*-Butyldiphenylsilyloxy)-2,3-epoxy-1-butanol.[23] The general epoxidation procedure was used giving (*Z*)-4-(*tert*-butyldiphenylsilyloxy)-2,3-epoxy-1-butanol (72%, oil) after purification (25% ethyl acetate/petroleum ether); δ_H ($CDCl_3$): 7.70–7.30 (10H, m, Ph), 3.96–3.67 (4H, m, CH_2OH+CH_2OSi), 3.23 (2H, m, oxirane C*H*), 1.9 (1H, app t, *J*=5.6 Hz, O*H*), 1.05 (9H, s, *Me*$_3$C).

3.5.3. (*Z*)-1-Benzyloxy-4-(*tert*-butyldiphenylsilyloxy)-2,3-epoxy-butane 7d. Compound **7d** (64%, oil) was prepared according to the general benzylation procedure, [Found: C, 75.04; H, 7.53. $C_{27}H_{32}O_3Si$ requires C, 74.96; H, 7.46%]; ν_{max} (liquid film) 3063, 3030, 2972, 1452, 1274 cm^{-1}; δ_H ($CDCl_3$): 7.68–7.27 (15H, m, *Ph*$_2$Si+*Ph*–CH$_2$), 4.57 (1H, d, *J*=11.0 Hz, CH_aH$_b$Ph), 4.43 (1H, d, *J*=11.0 Hz, CH$_a$*H*$_b$Ph), 3.78 (2H, d, *J*=5.2 Hz, OCH_2), 3.59 (1H, dd, *J*=4.5, 11.2 Hz, OCH_aH$_b$), 3.40 (1H, m, OCH$_a$*H*$_b$), 3.21 (2H, m, oxirane C*H*), 1.05 (9H, s, *Me*$_3$C); *m*/*z* (FAB): 455 (8, $[M+Na]^+$), 197 (18), 163 (11), 135 (36), 91 (100).

3.6. Synthesis of 7e

3.6.1. (*Z*)-1,4-Bis(benzyloxy)-2-butene.[24] NaH (1.92 g, 44 mmol, 55% in oil) was washed with hexane (3×5 mL) and vacuum-dried, then dry THF (10 mL) was added. The resulting suspension was added to a precooled (−5°C) solution of *cis*-2-buten-1,4-diol (1.76 g, 20 mmol) in THF (30 mL). After addition of triethylbutylammonium chloride (0.06 g, 0.4 mmol) the mixture was stirred 1 h at −5°C. Benzyl bromide (8.23 g, 48 mmol) was then added, and the reaction mixture was stirred for 16 h at 25°C. The reaction was quenched with ice-water (20 mL) and extracted with diethyl ether (3×15 mL). The organic phase was washed with saturated NH_4Cl (2×15 mL) and brine (15 mL). After drying and evaporation of the solvent and the excess of benzyl bromide, the residue (5.53 g) was purified by column chromatography (25% ethyl acetate/hexane) affording 4.53 g (84%, oil) of pure (*Z*)-1,4-bis(benzyloxy)-2-butene; δ_H ($CDCl_3$): 7.33–7.21 (10H, m, Ph), 5.78 (2H, m, =C*H*), 4.47 (4H, s, CH_2Ph), 4.05 (4H, d, *J*=5.0 Hz, CH_2).

3.6.2. (*Z*)-1,4-Dibenzyloxy-2,3-epoxybutane 7e.[25] The general epoxidation procedure was used giving oxirane **7e** (74%, oil) after purification of the crude product by column chromatography (25% ethyl acetate/hexane); δ_H ($CDCl_3$): 7.41–7.23 (10H, m, Ph), 4.59 (2H, d, *J*=15.5 Hz, CH_2Ph), 4.50 (2H, d, *J*=15.5 Hz, CH_2Ph), 3.67 (2H, dd, *J*=3.5, 11.3 Hz, CH_2O), 3.51 (2H, dd, *J*=6.1, 11.3 Hz, CH_2O), 3.26 (2H, m, oxirane C*H*).

3.7. Synthesis of 7f

3.7.1. (*Z*)-4-Benzyloxy-2-buten-1-ol.[26] The general procedure was used on (*Z*)-2-buten-1,4-diol (7.93 g, 90 mmol) affording 6.48 g of a raw material which was purified by flash chromatography (30% ethyl acetate/petroleum ether) yielding 4.79 g (90%, oil) of (*Z*)-4-(benzyloxy)-2-buten-1-ol; δ_H ($CDCl_3$): 7.41–7.24 (5H, m, Ph), 5.75 (2H, m, =C*H*), 4.51 (2H, s, CH_2Ph), 4.13 (2H, d, *J*=5.6 Hz, CH_2OH), 4.07 (2H, d, *J*=5.7 Hz, CH_2OBn), 2.36 (1H, bs, O*H*).

3.7.2. (*Z*)-1-Benzyloxy-4-methoxy-2-butene.[27] NaH (0.22 g, 5 mmol, 55% in oil) was washed with hexane (3×5 mL) and vacuum-dried then dry THF (8 mL) was added. The resulting suspension was added to a precooled (0°C) solution of (*Z*)-4-(benzyloxy)-2-buten-1-ol (0.75 g, 4.2 mmol) in THF (10 mL). After stirring 1 h at 0°C methyl iodide (1,41 g, 10 mmol) was added, and the reaction mixture was stirred for 16 h at 25°C then quenched with ice-water (20 mL) and extracted with ether (3×15 mL). The organic phase was washed with saturated NH_4Cl (2×10 mL) and brine (10 mL). After drying and evaporation of the solvent 0.76 g (94%, oil) of (*Z*)-1-benzyloxy-4-methoxy-2-butene was obtained, which was used without further purification; δ_H ($CDCl_3$): 7.43–7.25 (5H, m, Ph), 5.76 (2H, m, =C*H*), 4.51 (2H, s, CH_2Ph), 4.09 (2H, d, *J*=5.0 Hz, CH_2OBn), 3.96 (2H, d, *J*=5.2 Hz, CH_2OCH$_3$), 3.23 (3H, s, OCH_3).

3.7.3. (*Z*)-1-Benzyloxy-4-methoxy-2,3-epoxybutane 7f.[26,27] The general epoxidation procedure was used giving oxirane **7f** (72%, oil) after purification by column chromatography (33% ethyl acetate/hexane); δ_H ($CDCl_3$): 7.43–7.25 (5H, m, Ph), 4.62 (1H, d, *J*=11.9 Hz, CH_aH$_b$Ph), 4.53 (1H, d, *J*=11.9 Hz, CH$_a$*H*$_b$Ph), 3.73–3.54 (3H, m, CH_2O+CH_aH$_b$O), 3.40 (3H, s, *Me*), 3.28–3.05 (3H, m, CH$_a$*H*$_b$O+oxirane C*H*).

3.8. Synthesis of 7g

3.8.1. (*Z*)-4-Triphenylmethyloxy-2-buten-1-ol.[28] NaH (0.96 g, 22 mmol, 55% in oil) was washed with pentane (3×5 mL) and vacuum-dried, then dry DMF (15 mL) was added. The resulting suspension was added to a precooled (0°C) solution of *cis*-2-buten-1,4-diol (5.29 g, 60 mmol) in dry DMF (50 mL). After stirring for 2 h at 25°C the mixture was cooled to 0°C and a solution of trityl chloride (5.58 g, 20 mmol) in DMF (12 mL) was added during a period of 20 min. The reaction mixture was stirred for 16 h at 25°C, then cautiously poured into 300 g of ice and extracted with ether (3×100 mL). The organic phase was washed with brine (50 mL). After drying and evaporation of the solvent the residue (6.32 g) was purified by column chromatography (33% ethyl acetate/hexane) affording 3.70 g (56%, oil) of (*Z*)-4-triphenylmethyloxy-2-buten-1-ol; δ_H ($CDCl_3$): 7.46–7.19 (15H, m, Ph), 5.74 (2H, m, =C*H*), 3.98 (2H, d, *J*=5.3 Hz, CH_2OH), 3.68 (2H, d, *J*=5.3 Hz, CH_2OCPh$_3$), 1.69 (1H, bs, O*H*).

3.8.2. (*Z*)-4-Triphenylmethyloxy-2,3-epoxybutan-1-ol.[29] The general epoxidation procedure was used giving the epoxy alcohol (92%, solid) after purification by column chromatography (33% ethyl acetate/hexane).

Crystallization from ethyl acetate afforded 2.84 g of white crystals, mp 115.7–116.8°C; δ_H ($CDCl_3$): 7.46–7.20 (15H, m, Ph), 3.57 (3H, m, C*H*$_2$O+C*H*$_a$H$_b$O), 3.23 (2H, m, oxirane C*H*), 3.03 (1H, m, CH$_a$*H*$_b$O), 1.92 (1H, bs, O*H*).

3.8.3. (*Z*)-1-Benzyloxy-4-triphenylmethyloxy-2,3-epoxybutane 7g.[30] The general epoxidation procedure was used on (*Z*)-4-triphenylmethyloxy-2-buten-1-ol (2.5 g, 7.22 mmol) affording 3.55 g of a crude product which was purified by column chromatography (25% ethyl acetate/hexane) yielding 2.77 g (88%, oil) of **7g**; δ_H ($CDCl_3$): 7.46–7.15 (20H, m, Ph), 4.53 (1H, d, *J*=12.0 Hz, C*H*$_a$H$_b$Ph), 4.42 (1H, d, *J*=12.0 Hz, CH$_a$*H*$_b$Ph), 3.57 (1H, dd, *J*=3.8, 9.5 Hz, C*H*$_a$H$_b$O), 3.39–3.20 (4H, m, C*H*$_2$O+oxirane C*H*), 3.11 (1H, dd, *J*=3.8, 9.5 Hz, CH$_a$*H*$_b$O).

3.9. Synthesis of 7h–l

3.9.1. (*Z*)-4-Benzyloxy-2,3-epoxybutan-1-ol.[26,30] The general epoxidation procedure was used giving the epoxy-alcohol (92%, oil) after purification by column chromatography (33% ethyl acetate/hexane); δ_H ($CDCl_3$): 7.39–7.25 (5H, m, Ph), 4.61 (1H, d, *J*=11.8 Hz, C*H*$_a$H$_b$Ph), 4.46 (1H, d, *J*=11.8 Hz, CH$_a$*H*$_b$Ph), 3.70 (4H, m, C*H*$_2$O), 3.25 (2H, m, oxirane C*H*), 2.30 (1H, bs, O*H*).

3.9.2. (*Z*)-1-Benzyloxy-2,3-epoxy-4-*p*-toluenesulfonyloxybutane.[31] *p*-Toluene-sulfonyl chloride (5.55 g, 29.1 mmol) in dry pyridine (15 mL) was added under nitrogen at −10°C to a solution of 4-benzyloxy-2,3-epoxybutane-1-ol (4.71 g, 24.2 mmol) in dry pyridine (15 mL). The mixture was stirred for 18 h at −10°C and then poured into a mixture of 1 M sulfuric acid (100 mL) and ice (50 g). After stirring for 20 min the mixture was extracted with ether (4×40 mL) and dried. After evaporation of the solvent 7.9 g (94%, oil) of (*Z*)-1-benzyloxy-2,3-epoxy-4-*p*-toluenesulfonyloxybutane was obtained, which was used without further purification; δ_H ($CDCl_3$): 7.78 (2H, d, *J*=8.3 Hz, Ph), 7.34–7.28 (7H, m, Ph), 4.54 (1H, d, *J*=11.8 Hz, C*H*$_a$H$_b$Ph), 4.48 (1H, d, *J*=11.8 Hz, CH$_a$*H*$_b$Ph), 4.24 (1H, dd, *J*=3.8, 11.5 Hz, C*H*$_a$H$_b$OSO$_2$), 4.05 (1H, dd, *J*=6.6, 11.5 Hz, CH$_a$*H*$_b$OSO$_2$), 3.58 (1H, d, *J*=3.6, 11.4 Hz, C*H*$_a$H$_b$O), 3.53 (1H, dd, *J*=5.4, 11.4 Hz, CH$_a$*H*$_b$O), 3.24 (2H, m, oxirane C*H*), 2.44 (3H, s, *Me*–Ph).

3.10. Substitution of tosyl group with amines. General procedure

A solution of (*Z*)-1-benzyloxy-2,3-epoxy-4-*p*-toluenesulfonyloxy-butane (3.48 g, 10 mmol) and potassium iodide (0.83 g, 0.5 mmol) in DMF (40 mL) was cooled to 0°C. Then the amine (20 mmol) was added. The resulting mixture was stirred for 3 days at room temperature then poured into a saturated aqueous solution of $NaHCO_3$ (300 mL). The aqueous phase was extracted with ether (4×50 mL) and the organic phase was washed with brine (50 mL). After drying and evaporation of the solvent the residue was purified by column chromatography.

3.10.1. (*Z*)-1-Benzyloxy-4-dibenzylamino-2,3-epoxybutane 7h. Purification by column chromatography (17% ethyl acetate/petroleum ether) afforded **7h** (85%, oil), [Found: C, 80.04; H, 7.33; N, 3.69. $C_{25}H_{27}NO_2$ requires C, 80.40; H, 7.29; N, 3.75%]; ν_{max} (liquid film) 3060, 3001, 2923, 2860, 1251 cm^{-1}; δ_H ($CDCl_3$): 7.38–7.20 (15H, m, Ph), 4.59 (1H, d, *J*=11.2 Hz, C*H*$_a$H$_b$Ph), 4.47 (1H, d, *J*=11.2 Hz, CH$_a$*H*$_b$Ph), 3.83 (2H, d, *J*=13.6 Hz, NC*H*$_2$Ph), 3.60 (1H, m, C*H*$_a$H$_b$O), 3.50 (2H, d, *J*=13.6 Hz, NC*H*$_2$Ph), 3.39 (1H, m, CH$_a$*H*$_b$O), 3.19 (2H, m, oxirane C*H*), 2.76 (1H, dd, *J*=4.0, 13.0 Hz, C*H*$_a$H$_b$N), 2.44 (1H, dd, *J*=4.0, 13.0 Hz, CH$_a$*H*$_b$N).

3.10.2. (*Z*)-1-Benzyloxy-4-diethylamino-2,3-epoxybutane 7i. Purification by column chromatography (30% petroleum ether/ethyl acetate) afforded **7i** (74%, oil); ν_{max} (liquid film) 3063, 2963, 2933, 2872, 1203 cm^{-1}; δ_H ($CDCl_3$): 7.36–7.28 (5H, m, Ph), 4.64 (1H, d, *J*=11.6 Hz, C*H*$_a$H$_b$Ph), 4.53 (1H, d, *J*=11.6 Hz, CH$_a$*H*$_b$Ph), 3.71 (1H, dd, *J*=4.2, 11.2 Hz, C*H*$_a$H$_b$O), 3.54 (1H, dd, *J*=6.4, 11.2 Hz, CH$_a$*H*$_b$O), 3.18 (2H, m, oxirane C*H*), 2.81–2.38 (6H, m, NC*H*$_2$), 1.03 (6H, t, *J*=6.8 Hz, *Me*); *m/z* (EI): 248 (1, $[M-H]^+$), 234 (2), 158 (3), 128 (3), 91 (25), 86 (100); HRMS (EI): $[M-H]^+$, found 248.1652. $C_{15}H_{22}NO_2$ requires 248.16505.

3.10.3. (*Z*)-1-Benzyloxy-4-piperidino-2,3-epoxybutane 7l. Purification by column chromatography (20% petroleum ether/ethyl acetate) afforded **7l** (54%, oil); ν_{max} (liquid film) 3062, 2933, 2853, 2788, 1206 cm^{-1}; δ_H ($CDCl_3$): 7.36–7.26 (5H, m, Ph), 4.65 (1H, d, *J*=11.8 Hz, C*H*$_a$H$_b$Ph), 4.52 (1H, d, *J*=11.8 Hz, CH$_a$*H*$_b$Ph), 3.70 (1H, dd, *J*=4.1, 11.2 Hz, C*H*$_a$H$_b$O), 3.54 (1H, dd, *J*=6.4, 11.2 Hz, CH$_a$*H*$_b$O), 3.19 (2H, m, oxirane C*H*), 2.66 (1H, dd, *J*=3.3, 13.3 Hz, C*H*$_a$H$_b$N), 2.42 (4H, m, C*H*$_2$N), 2.29 (1H, dd, *J*=6.6, 13.3 Hz, CH$_a$*H*$_b$N), 1.60 (4H, m, C*H*$_2$), 1.44 (2H, m, C*H*$_2$); *m/z* (EI): 260 (1.2, $[M-H]^+$), 170 (3), 98 (100), 91 (15); HRMS (EI): $[M-H]^+$, found 260.1647. $C_{16}H_{22}NO_2$ requires 260.16505.

3.11. LIDAKOR induced isomerisation

General procedure. A solution of potassium *tert*-butoxide in THF was cooled to −78°C then diisopropylamine and a solution of butyllithium in hexane were added and the mixture was stirred for 30 min. After addition of the oxirane derivative **7** the reaction mixture was stirred for 2–16 h at the desired temperature before being diluted with diethyl ether (10 mL) and treated with a saturated aqueous solution of ammonium chloride (10 mL). The aqueous phase was then extracted with ether (3×15 mL) and the organic phase was washed with brine (3×15 mL) and dried. After removal of the solvent either oxetane **8** or 2-penten-1,4-diol **9** was obtained. The crude products were purified by column chromatography.

3.11.1. 3-(1-Hydroxyhexyl)-2-phenyloxetane 8a.[7] The general procedure with LIDAKOR was used leading to **8a** (70%, oil, *cis*/*trans* 0:100) after column chromatography (33% petroleum ether/ether); δ_H ($CDCl_3$): 7.5–7.2 (5H, m, Ph), 5.52 (1H, d, *J*=6.6 Hz, OC*H*Ph), 4.72 (2H, d, *J*=7.6 Hz, C*H*$_2$O), 4.0–3.9 (1H, m, C*H*OH), 2.91 (1H, m, oxetane C*H*), 1.63 (1H, d, *J*=5.4 Hz, O*H*), 1.5–1.2 (8H, m, C*H*$_2$), 0.87 (3H, t, *J*=6.2 Hz, *Me*); *m/z* (EI): 163 (7), 133 (12), 115 (12), 108 (13), 107 (92), 105 (48), 99 (17), 91 (20), 85 (24), 84 (42), 79 (75), 77 (59), 57 (100), 55 (58), 43 (71).

3.11.2. 3-(1-Hydroxybutyl)-2-phenyloxetane 8b.[8] The general procedure with LIDAKOR was used leading to **8b** (68%, oil, *cis*/*trans* 0:100) after purification by column chromatography (33% ethyl acetate/hexane); δ_H ($CDCl_3$): 7.5–7.2 (5H, m, Ph), 5.50 (1H, d, *J*=6.8 Hz, OC*H*Ph), 4.68 (2H, d, *J*=7.8 Hz, CH_2O), 4.0–3.9 (1H, m, C*H*OH), 2.90 (1H, m, oxetane C*H*), 1.98 (1H, br s, O*H*), 1.5–1.2 (4H, m, CH_2), 0.87 (3H, t, *J*=6.6 Hz, *Me*); *m*/*z* (EI): 163 (7), 133 (21), 115 (15), 107 (81), 105 (42), 91 (75); 84 (43), 79 (44), 77 (100), 57 (76).

3.11.3. 3-(2-Hydroxy-6-methyl-hept-5-en-2-yl)-2-phenyloxetane 8c. The general procedure with LIDAKOR was used leading to **8c** (69%, oil, *cis*/*trans* 0: 100) after purification by column chromatography (33% ethyl acetate/hexane), [Found: C, 78.34; H, 9.33; $C_{17}H_{24}O_2$ requires C, 78.42; H, 9.29%]; ν_{max} (in $CHCl_3$) 3585–3295, 3021, 1665, 1557, 1254 cm^{-1}; δ_H ($CDCl_3$): 7.54–7.27 (5H, m, Ph), 5.69 (1H, d, *J*=6.7 Hz, OC*H*Ph), 5.06 (1H, bt, *J*=6.5 Hz, =C*H*), 4.78 (1H, dd, *J*=6.0, 7.2 Hz, CH_aH_bO), 4.63 (1H, dd, *J*=6.0, 8.6 Hz, CH$_a$*H*$_b$O), 2.94 (1H, app q, *J*=7.2 Hz, oxetane C*H*), 2.09 (2H, m, CH_2), 1.67 (3H, s, *Me*), 1.58 (3H, s, *Me*), 1.37 (2H, m, CH_2), 1.26 (3H, s, *Me*). *m*/*z* (EI): 195 (0.4); 169 (10); 134 (41); 131 (12); 115 (45); 107 (11); 105 (75); 103 (32); 102 (12); 92 (80); 91 (100); 78 (44); 77 (62).

3.11.4. 3-[2-(*tert*-Butyldiphenylsilyloxy)-1-hydroxyethyl]-2-phenyloxetane 8d. The general procedure with LIDAKOR was used leading to **8d** (64%, oil, *cis*/*trans* 0:100) after purification by column chromatography (33% ethyl acetate/hexane), [Found: C, 75.01; H, 7.51; $C_{27}H_{32}O_3Si$ requires C, 74.96; H, 7.46%]; ν_{max} (in $CHCl_3$) 3416, 3069–3030, 2997, 1115, 977 cm^{-1}; δ_H ($CDCl_3$): 7.63–7.35 (15H, m, Ph), 5.74 (1H, d, *J*=6.5 Hz, C*H*Ph), 4.49 (2H, m, CH_2O), 4.16 (1H, m, C*H*OH), 3.60 (1H, dd, *J*=4.5 Hz, 11.0, CH_aH_bO), 3.43 (1H, dd, *J*=7.5, 11.0 Hz, CH$_a$*H*$_b$O), 2.86 (1H, quint, *J*=7.5 Hz, oxetane C*H*), 2.55 (1H, bs, O*H*), 1.04 (9H, s, *Me*); *m*/*z* (EI): 241 (61), 223 (30), 197 (8), 183 (11), 181 (17), 163 (100), 105 (38), 91 (27), 77 (26).

3.11.5. 3-(2-Benzyloxy-1-hydroxyethyl)-2-phenyloxetane 8e. The general procedure with LIDAKOR was used leading to **8e** (50%, oil, *cis*/*trans* 13:87) after purification by column chromatography (33% ethyl acetate/hexane), [Found: C, 76.01; H, 7.19; $C_{18}H_{20}O_3$ requires C, 76.03; H, 7.09%]; ν_{max} (film) 3418, 3061–3029, 2882, 1095, 976 cm^{-1}; δ_H ($CDCl_3$) *trans*-(**8e**): 7.47–7.24 (10H, m, Ph), 5.74 (1H, d, *J*=6.5 Hz, oxetane C*H*Ph), 4.72–4.35 (4H, m, CH_2Ph+ oxetane CH_2O), 4.16 (1H, m, C*H*OH), 3.42 (1H, dd, *J*=3.4, 9.4 Hz, OCH_aH_b), 3.28 (1H, dd, *J*=6.8, 9.4 Hz, OCH$_a$*H*$_b$), 2.94 (1H, quint, *J*=7.3 Hz, oxetane C*H*), 2.54 (1H, bs); *cis*-(**8e**): 5.96 (1H, d, *J*=8.2 Hz, oxetane C*H*Ph); *m*/*z* (EI): 207 (4), 145 (6.6), 117 (51), 115 (22), 107 (11), 105 (18), 91 (100), 77 (21).

3.11.6. 3-(1-Hydroxy-2-methoxyethyl)-2-phenyloxetane 8f. The general procedure with LIDAKOR was used leading to **8f** (50%, oil, *cis*/*trans* 0:100) after purification by column chromatography (33% ethyl acetate/hexane), [Found: C, 69.11; H, 7.79; $C_{12}H_{16}O_3$ requires C, 69.21; H, 7.74%]; ν_{max} (film) 3394, 3061, 2927, 2850, 1099, 1066, 968 cm^{-1}; δ_H ($CDCl_3$): 7.45–7.25 (5H, m, Ph), 5.75 (1H, d, *J*=6.2 Hz, C*H*Ph), 4.65 (2H, m, oxetane CH_2O), 4.16 (1H, m, C*H*OH), 3.34 (3H, s, O*Me*), 3.40–3.20 (2H, m, OCH_2), 2.94 (1H, quint, *J*=7.5 Hz, oxetane C*H*), 2.71 (1H, bs, O*H*); *m*/*z* (EI): 163 (5), 133 (51), 121 (27), 115 (37), 107 (66), 105 (55), 91 (41), 77 (100), 70 (44), 57 (52).

3.11.7. 3-[1-Hydroxy-2-(triphenylmethyloxy)ethyl]-2-phenyloxetane 8g. The general procedure with LIDAKOR was used leading to **8g**((66%, white solid, *cis*/*trans* 3:97) after purification by column chromatography (33% ethyl acetate/hexane), mp 48.5–49.9°C; ν_{max} (film) 3440, 3058, 3031, 2878, 1073, 1032, 972 cm^{-1}; δ_H ($CDCl_3$): 7.40–7.21 (20H, m, Ph), 5.66 (1H, d, *J*=6.3 Hz, oxetane C*H*Ph), 4.52 (2H, m, oxetane CH_2O), 4.18 (1H, m, C*H*OH), 3.12 (1H, dd, *J*=3.8, 9.5 Hz, OCH_aH_b), 3.02–2.83 (2H, m, OCH$_a$*H*$_b$+ oxetane C*H*), 2.40 (1H, bs, O*H*). *m*/*z* (FAB): 459 (1, $[M+Na]^+$), 197 (18), 163 (11), 135 (36), 91 (100); HRMS (FAB): $[M+Na]^+$, found 459.1927. $C_{30}H_{28}O_3Na$ requires 459.19355.

3.11.8. 3-(2-Dibenzylamino-1-hydroxyethyl)-2-phenyloxetane 8h. The general procedure with LIDAKOR was used leading to **8h** (64%, oil, *cis*/*trans* 5:95) after purification by column chromatography (33% ethyl acetate/hexane), [Found: C, 80.51; H, 7.35; N, 3.81. $C_{25}H_{27}NO_2$ requires C, 80.40; H, 7.29; N 3.75%]; ν_{max} (film) 3432, 3084, 2939, 1120, 1072, 975 cm^{-1}; δ_H ($CDCl_3$): 7.36–7.23 (15H, m, Ph), 5.56 (1H, d, *J*=6.2 Hz, oxetane C*H*Ph), 4.61 (2H, d, *J*=8.0 Hz, oxetane CH_2O), 4.10 (1H, m, C*H*OH), 3.89 (2H, d, *J*=13.2 Hz, NCH_2Ph), 3.34 (2H, d, *J*=13.2 Hz, NCH_2Ph), 2.78 (1H, m, oxetane C*H*), 2.30 (2H, m, NCH_2), 1.57 (1H, bs, O*H*); *m*/*z*, (EI): 145 (2), 134 (2), 117 (5), 105 (5), 91 (100), 77 (10), 65 (19).

3.11.9. 3-(2-Diethylamino-1-hydroxyethyl)-2-phenyloxetane 8i. The general procedure with LIDAKOR was used leading to **8i** (75%, oil, *cis*/*trans* 5:95) after purification by column chromatography (9% methanol/dichloromethane), [Found: C, 72.11; H, 9.35; N, 5.71. $C_{15}H_{23}NO_2$ requires C, 72.25; H, 9.30; N 5.62%]; ν_{max} (film) 3418, 3060, 2968, 1065, 976 cm^{-1}; δ_H ($CDCl_3$): 7.50–7.27 (5H, m, Ph), 5.79 (1H, d, *J*=6.2 Hz, oxetane C*H*Ph), 4.65 (2H, m, oxetane CH_2O), 3.99 (1H, m, C*H*OH), 2.90–2.08 (7H, m, oxetane C*H*+CH_2N), 1.01 (6H, t, *J*=7.2 Hz, *Me*). *m*/*z* (EI): 200 (21), 199 (100), 181 (5), 115 (3), 105 (11), 86 (42), 77 (25).

3.11.10. 3-[(1-Hydroxy-2-piperidino)ethyl]-2-phenyloxetane 8l. The general procedure with LIDAKOR was used leading to **8l** (59%, oil, *cis*/*trans* 0:100) after purification by column chromatography (9% methanol/dichloromethane); ν_{max} (film) 3417, 3060, 2935, 1119, 978 cm^{-1}; δ_H ($CDCl_3$): 7.48–7.25 (5H, m, Ph), 5.78 (1H, d, *J*=6.3 Hz, oxetane C*H*Ph), 4.64 (2H, m, oxetane CH_2O), 4.06 (1H, m, C*H*OH), 3.50 (1H, bs, O*H*), 2.81 (1H, m, oxetane C*H*), 2.60–2.08 (6H, m, (CH_2N)$_3$), 1.63–1.42 (6H, m, (CH_2)$_3$); *m*/*z* (EI): 261 (0.2, M^+), 260 (0.3), 158 (2.8), 128 (4), 93 (38), 91 (30), 86 (100). HRMS (EI): M^+, found 261.1721. $C_{16}H_{23}NO_2$ requires 261.17288.

3.11.11. 3-(1-Methoxybutyl)-2-phenyloxetane 8m. This compound was prepared from **8b** (64%, white solid, *cis*/*trans* 4:96) by the methylation method described for the

synthesis of (*Z*)-1-Benzyloxy-4-methoxy-2-butene, a precursor of **7f** after purification by column chromatography (33% ethyl acetate/petroleum ether), mp 48.5–49.9°C; ν_{max} (film) 3061, 2958, 2874, 1092, 963 cm^{-1}; δ_H ($CDCl_3$): 7.46–7.29 (5H, m, Ph), 5.50 (1H, d, *J*=6.8 Hz, oxetane C*H*Ph), 4.70 (2H, d, *J*=7.8 Hz, oxetane CH_2O), 3.56 (1H, m, C*H*OMe), 3.41 (3H, s, O*Me*), 2.98 (1H, quint, *J*=6.9 Hz, oxetane C*H*), 1.80–1.24 (4H, m, CH_2), 0.87 (3H, t, *J*=6.6 Hz, *Me*); *m/z* (FAB): 219 (20, $[M-H]^+$), 105 (80), 87 (100); HRMS (FAB): $[M-H]^+$, found 219.1364. $C_{14}H_{19}O_2$ requires 219.1385.

3.12. Butyllithium induced isomerization

General procedure. A solution of the oxetane **8** in THF was cooled to 0°C and a solution of butyllithium in hexane (4 equiv.) was added. The mixture was allowed to warm up to room temperature and stirred for 3 h at this temperature. After being diluted with diethyl ether (10 mL) the mixture was treated with a saturated aqueous solution of ammonium chloride (10 mL). The aqueous phase was then extracted with ether (3×15 mL) and the organic phase was washed with brine (3×15 mL) and dried. After removal of the solvent the residue was purified by column chromatography.

3.12.1. (Z)-2-Phenyl-2-nonen-1,4-diol 9a.[8] The general procedure was used obtaining **9a** (55%, oil) after purification (33% ethyl acetate/hexane), [Found: C 76.79; H 9.42. $C_{15}H_{22}O_2$ requires C 76.88; H 9.46%]; δ_H ($CDCl_3$): 7.5–7.2 (5H, m, Ph); 5.85 (1H, d, *J*=8.0 Hz, =C*H*); 4.65 (1H, d, *J*=12.0 Hz, CH_aH$_b$OH); 4.57 (1H, m, C*H*OH); 4.46 (1H, d, *J*=12.0 Hz, CH$_a$$H_b$OH); 3.62 (2H, bs, O*H*); 1.8–1.2 (8H, m, CH_2); 0.87 (3H, t, *J*=6.6 Hz, *Me*); *m/z* (EI): 217 (3), 203 (13), 163 (27), 133 (35), 101 (100), 77 (42).

3.12.2. (Z)-1,4-Dimethoxy-2-phenyl-2-heptene (O,O′-dimethyl 9b). The general procedure was used obtaining **9b**[8] as a crude product. Then it was treated with 2 equiv. of NaH in dry THF and consecutively with a large excess of iodomethane to get O,O′-dimethyl **9b** (64%, oil, *cis*/*trans* 0:100) after purification by column chromatography (33% ethyl acetate/hexane); ν_{max} (film) 3058, 2959, 2872, 1724, 1095 cm^{-1}; δ_H ($CDCl_3$): 7.47–7.25 (5H, m, Ph), 5.81 (1H, d, *J*=9.5 Hz, =C*H*), 4.36 (2H, s, OCH_2), 4.19 (1H, m, OC*H*), 3.33 (3H, s, O*Me*), 3.32 (3H, s, O*Me*), 1.79–1.20 (4H, m, CH_2), 0.93 (3H, t, *J*=6.7 Hz, *Me*); *m/z* (EI): 233 (23), 219 (22), 206 (37), 147 (35), 129 (36), 121 (77), 105 (100), 91 (61), 87 (94), 77 (42), 45 (76); HRMS (EI): $[M-H]^+$, found 233.1504. $C_{15}H_{21}O_2$ requires 233.15416.

3.12.3. (Z)-5-[(*tert*-Butyldiphenyl)silyloxy]-2-phenyl-2-penten-1,4-diol 9d. The general procedure was used obtaining **9d** (19%, oil, *cis*/*trans* 0:100) after purification by column chromatography (33% ethyl acetate/hexane), [Found: C, 75.04; H, 7.49. $C_{27}H_{32}O_3Si$ requires C, 74.96; H, 7.46%]; ν_{max} (film) 3383, 3070, 2857, 1684, 1080 cm^{-1}; δ_H ($CDCl_3$): 7.68–7.38 (15H, m, Ph), 5.76 (1H, d, *J*=7.4 Hz, =C*H*), 4.69 (1H, q, *J*=6.2 Hz, C*H*OH), 4.53 (1H, d, *J*=12.0 Hz, CH_aH$_b$OH), 4.41 (1H, d, *J*=12.0 Hz, CH$_a$$H_b$OH), 3.72 (2H, m, C$H_2$), 2.95 (1H, bs, O*H*), 1.70 (1H, bs, O*H*), 1.08 (9H, s, *Me*); *m/z* (EI): 160 (5); 145 (5), 133 (63), 129 (13), 128 (13), 115 (49), 107 (39), 105 (16), 103 (17), 91 (100), 79 (29), 78 (22), 77 (57), 65 (36), 63 (21), 33 (69), 51 (43).

3.12.4. (Z)-5-Methoxy-2-phenyl-2-penten-1,4-diol 9f. The general procedure was used obtaining **9f** (22%, oil, *cis*/*trans* 0:100) after purification by column chromatography (50% hexane/ethyl acetate), [Found: C, 69.25; H, 7.76. $C_{12}H_{16}O_3$ requires C, 69.21; H, 7.74%]; ν_{max} (film) 3396, 3058, 2850, 1718, 1194 cm^{-1}; δ_H ($CDCl_3$): 7.48–7.30 (5H, m, Ph), 5.82 (1H, d, *J*=7.9 Hz, =C*H*), 4.79 (1H, q, *J*=7.0 Hz, C*H*OH), 4.55 (1H, d, *J*=12.0 Hz, CH_aH$_b$OH), 4.47 (1H, d, *J*=12.0 Hz, CH$_a$$H_b$OH), 3.46 (2H, m, C$H_2$), 3.41 (3H, s, *Me*), 2.83 (1H, bs, O*H*), 1.55 (1H, bs, O*H*); *m/z* (FAB): 231 (55, $[M+Na]^+$), 173 (100), 129 (33), 115 (36), 105 (40), 91 (75).

3.12.5. (Z)-2 Phenyl-5-trityloxy-2-penten-1,4-diol 9g. The general procedure was used obtaining **9g** (35%, white solid, *cis*/*trans* 0:100) after purification by column chromatography (33% ethyl acetate/hexane), mp 125.5–127.2°C; ν_{max} (film) 3406, 3058, 2920, 1636, 1093 cm^{-1}; δ_H ($CDCl_3$): 7.46–7.21 (20H, m, Ph), 5.72 (1H, d, *J*=7.6 Hz, =C*H*), 4.70 (1H, q, *J*=7.0 Hz, C*H*OH), 4.53 (1H, d, *J*=12.0 Hz, CH_aH$_b$OH), 4.39 (1H, d, *J*=12.0 Hz, CH$_a$*H*-bOH), 3.29 (2H, m, *CH2*O), 2.91 (1H, bs, O*H*), 2.45 (1H, bs, O*H*). *m/z* (FAB): 459 (3, $[M+Na]^+$), 357 (16), 318 (4), 243 (100), 165 (25), 115 (30); HRMS (FAB): $[M+Na]^+$, found 459.1889. $C_{30}H_{28}O_3Na$ requires 459.19355.

3.12.6. (Z)-5-Dibenzylamino-2-phenyl-2-penten-1,4-diol 9h. The general procedure was used obtaining **9h** (14%, oil *cis*/*trans* 0:100) after purification by column chromatography (33% ethyl acetate/hexane); ν_{max} (film) 3379, 3027, 2929, 1650, 1070 cm^{-1}; δ_H ($CDCl_3$): 7.42–7.24 (15H, m, Ph), 5.61 (1H, d, *J*=8.0 Hz, =C*H*), 4.64 (1H, m, C*H*OH), 4.48 (1H, d, *J*=12.0 Hz, CH_aH$_b$OH), 4.37 (1H, d, *J*=12.0 Hz, CH$_a$$H_b$OH), 3.84 (2H, d, *J*=13.0 Hz, CH_2Ph), 3.53 (2H, d, *J*=13.0 Hz, CH_2Ph), 2.75 (1H, bs, O*H*), 2.62 (2H, m, CH_2N), 1.60 (1H, bs, O*H*); *m/z* (FAB): 374 (90, $[M+H]^+$), 210 (14), 147 (16), 106 (15), 98 (100); HRMS (FAB): $[M+H]^+$, found 374.2091. $C_{25}H_{28}NO_2$ requires 374.21201.

3.12.7. (Z)-5-Diethylamino-2-phenyl-2-penten-1,4-diol 9i. The general procedure was used obtaining **9i** (35%, oil, *cis*/*trans* 0:100) after purification by column chromatography (Florisil; 33% hexane/ethyl acetate), [Found: C, 72.31; H, 9.33; N, 5.69. $C_{15}H_{23}NO_2$ requires C, 72.25; H, 9.30; N 5.62%]; ν_{max} (film) 3356, 2970, 2871, 1650, 1070 cm^{-1}; δ_H ($CDCl_3$): 7.52–7.28 (5H, m, Ph), 5.75 (1H, d, *J*=8.0 Hz, =C*H*), 4.60 (1H, q, *J*=7.4 Hz, C*H*OH), 4.48 (1H, d, *J*=12.4 Hz, CH_aH$_b$OH), 4.38 (1H, d, *J*=12.4 Hz, CH$_a$$H_b$OH), 2.64 (1H, bs, O*H*), 2.59 (6H, m, CH_2), 1.45 (1H, bs, O*H*), 1.05 (6H, t, *J*=7.0, *Me*). *m/z* (EI): 177 (13), 163 (15), 133 (25), 103 (11), 77 (100).

3.12.8. (Z)-2-Phenyl-5-piperidino-2-penten-1,4-diol 9l. The general procedure was used obtaining **9l** (39%, oil, *cis*/*trans* 0:100) after purification by column chromatography (Florisil; 33% hexane/ethyl acetate); ν_{max} (film) 3361, 3057, 2935, 1653, 1115 cm^{-1}; δ_H ($CDCl_3$): 7.50–7.27 (5H, m, Ph), 5.77 (1H, d, *J*=7.6 Hz, =C*H*), 4.67 (1H, q, *J*=7.0 Hz, C*H*OH), 4.49 (1H, d, *J*=12.3 Hz, CH_aH$_b$OH),

4.40 (1H, d, J=12.3 Hz, CH_aH_bOH), 2.56–2.38 (7H, m, CH_2N+OH), 1.60–1.23 (7H, m, CH_2+OH); *m/z* (EI): 261 (0.1, M^+), 252 (0.1), 243 (0.1), 230 (0.2), 141 (5), 98 (100); HRMS (EI): M^+, found 261.1717. $C_{16}H_{23}NO_2$ requires 261.17288.

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