Intramolecular epoxidation in unsaturated ketones and oxaziridines

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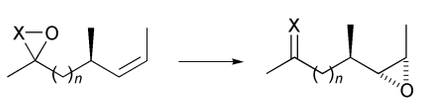
The possibility of intramolecular epoxidation in acyclic unsaturated ketones (*via* dioxiranes) and oxaziridines (*via* oxaziridinium species) has been investigated. Treatment of several acyclic unsaturated ketones with Oxone® led to low levels of regio- and stereocontrol, suggesting that background epoxidation by Oxone® dominates. However, treatment of unsaturated oxaziridines with methyl trifluoromethanesulfonate led to intramolecular epoxidation. This process allowed regioselective epoxidation of a non-conjugated diene. It also proceeded with a high degree of stereocontrol consistent with a stereoelectronic preference for a *spiro*-transition state.

Introduction

Intramolecular reactions often proceed with significant levels of regio- and stereocontrol. Although alkene epoxidation is one of the most useful synthetic transformations, and the directing effects of substituents have been widely studied,[1] there are few examples of intramolecular oxygen transfer to alkenes.[2] This is largely because of the inherent stereoelectronic constraints of such processes. We have been interested in the catalysis of Oxone® epoxidation of alkenes by ketones[3] (*via* dioxiranes)[4] and iminium salts[5] (*via* oxaziridinium species).[6] Most studies of these compounds have been concerned with the development of new chiral reagents for asymmetric alkene epoxidation,[3–7] but we were also attracted to the possibility that intramolecular variants of these processes (Scheme 1) may proceed with a high



1 **2**

X = O or R_2N^+

Scheme 1

degree of regio- and stereocontrol. Moreover, it had already been established that the epoxycarbonyl products **2** (X = O) were useful intermediates in the synthesis of oxygen heterocycles.[8] Here we describe in full[9] our studies of these intramolecular epoxidation reactions.

Results and discussion

(*a*) Oxone® epoxidation of unsaturated ketones

At the outset of our studies, the generation of dioxiranes from ketones and Oxone® (active constituent $KHSO_5$) required a two-phase, CH_2Cl_2–H_2O solvent system in the presence of a tetraalkylammonium salt, presumed to act as a phase-transfer catalyst to take the HSO_5^- anion into the organic phase to react with the ketone.[10] Indeed, Curci and co-workers have reported the epoxidation of hex-5-en-2-one under these conditions in the absence of a separate ketone, although it was not established whether the epoxidation was intramolecular.[10] Subsequent detailed study of this reaction system by Denmark and co-workers[11] underscored the need for careful control of several variables, including pH. We used this two-phase system to study the Oxone® epoxidation of the *Z*-acyclic unsaturated ketones[12] **3**–**5** which would be expected to undergo intramolecular epoxidation with a high degree of diastereoselectivity due to the effect of $A_{1,3}$-strain.[13] However, conversions were low and little or no stereoselectivity was observed. Several pieces of evidence led to the conclusion that the interaction of the $KHSO_5$ and the ketone takes place in the aqueous phase, where direct, background epoxidation of the alkene by Oxone® is rapid.[12b,14] The tetraalkylammonium salt likely plays the role of surfactant, increasing the water solubility of the substrate, rather than acting as phase-transfer catalyst. The complicated solubility requirements of this two-phase solvent system meant that is was largely superseded when Yang introduced an experimentally far more convenient monophasic CH_3CN–H_2O system, in the presence of $NaHCO_3$ to effect pH control.[15] We therefore decided to investigate the possibility of intramolecular epoxidation of acyclic ketoalkenes **3**–**5** in this monophasic system. Even at high dilution (8 mM in ketoalkene), diastereoselectivity never exceeded 1.8 : 1. We suspected that non-stereoselective background epoxidation by Oxone® was competing with any intramolecular dioxirane epoxidation. Indeed, the epoxidation of a simple dialkyl substituted alkene such as decene occurs over a similar time period under the same reaction conditions in the absence of a ketone promoter. We therefore attempted to increase the ketone reactivity by incorporation of an α-chloro substituent, since Yang[16] and ourselves[3b] had shown that chloroacetone promotes epoxidation of (*E*)-stilbene approximately 17 times faster than acetone itself. Disappointingly, however, at 8 mM concentration, diastereoselectivity in the epoxidation of **6**–**8** did not exceed 1.4 : 1. Since it was conceivable that the $A_{1,3}$-strain conformational preference was preventing the preferred *spiro*-TS geometry[17] for dioxirane epoxidation, we decided to remove the allylic stereocentre and use regioselectivity as a probe for intramolecular epoxidation. The non-conjugated dienyl ketone **10** and its α-chloro isomer **11** were prepared as shown in Scheme 2, with the *Z*-geometry of the disubstituted alkene being installed using Ni-catalysed ring opening of dihydropyran with a Grignard reagent.[18] Intramolecular epoxidation would be expected to occur at the disubstituted olefin, closest to the ketone. However, reaction of **10** with 1 equiv. Oxone® under the Yang CH_3CN–H_2O conditions at 40 mM concentration led to exclusive epoxidation at the trisubstituted alkene. Under the same conditions, and also under the Shi higher pH conditions,[19] chloroketone **11** provided a *ca.* 3 : 1 ratio of inseparable epoxides, with reaction on the trisubstituted alkene

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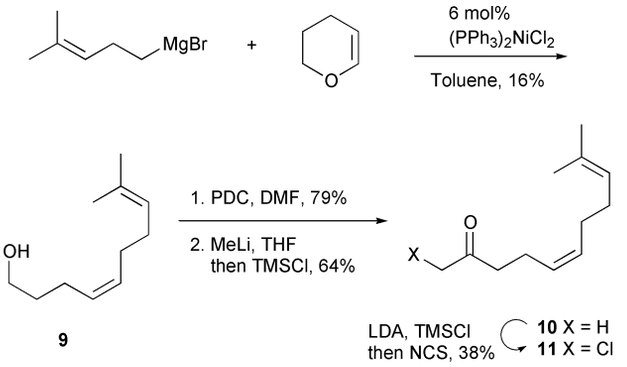
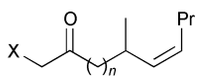


Scheme 2

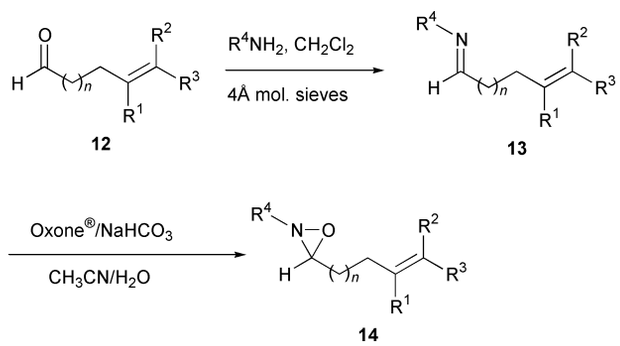
again predominating. This suggested that the desired intramolecular epoxidation may be occurring to a small extent, but not enough to make the reaction useful. For high levels of regio- or stereocontrol to be achieved it seems likely that the reactivity of the olefin component towards Oxone® would have to be substantially reduced (*e.g.* by aromatic substitution), as well as having an activated ketone. The need for heavily biased substrates would clearly limit the scope of this chemistry and would restrict the synthetic utility of any product epoxyketones. Efforts in this area were therefore abandoned.



X = H **3** *n* = 1 X = Cl **6** *n* = 1
4 *n* = 2 **7** *n* = 2
5 *n* = 3 **8** *n* = 3

(*b*) Intramolecular epoxidation of unsaturated oxaziridines

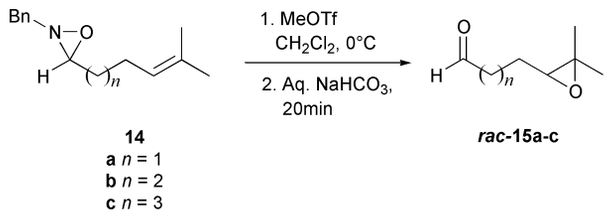
The major problem in the attempted intramolecular dioxirane epoxidations appeared to be competing background epoxidation by Oxone®. The related oxaziridinium epoxidation system offered an attractive alternative since, as well as being accessible by iminium oxidation, these species can be prepared by a non-oxidative method: quaternisation of an *N*-alkyloxaziridine.[6] However, preparation of unsaturated oxaziridines for quaternisation would still require oxidation of the corresponding unsaturated imine in the presence of the alkene. Scattered examples in the literature suggested that this would be possible.[20] For our initial studies, we opted to study aldimines to ensure high *E*/*Z*-selectivity in imine formation. As shown in Scheme 3 and Table 1, a range of unsaturated aldehydes **12** of



Scheme 3

varying tether length and alkene substitution pattern were reacted with achiral primary amines, and indeed provided exclusively the *E*-imine product **13**. Best results for selective imine oxidation were obtained using 0.6 equiv. Oxone® (1.2 equiv. $KHSO_5$) to prevent over-oxidation, leading to the desired unsaturated oxaziridines **14**. The crude oxaziridines required little purification but were found to be stable to flash column chromatography on deactivated (Et_3N) silica. A characteristic triplet at *ca.* 3.90 ppm (^{1}H NMR) and the oxaziridine carbon signal at *ca.* 82 ppm (^{13}C NMR) served to confirm structure.

With the seven novel oxaziridines in hand, attention was focused on the intramolecular epoxidation process. The first substrate to be subjected to *N*-alkylation was **14a**. When a 42 mM dichloromethane solution of **14a** was treated with methyl trifluoromethanesulfonate (MeOTf), formation of a more polar product was observed by TLC. The presumed intermediate epoxy iminium salt was readily hydrolysed by addition of saturated aqueous sodium bicarbonate to the reaction mixture. ^{1}H NMR analysis of the crude reaction product following extraction with dichloromethane showed only the expected epoxyaldehyde (*rac*-**15a**) and *N*-methylbenzylamine to be present (Scheme 4). Despite repeated

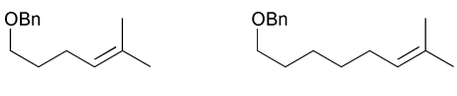


Scheme 4

attempts, the epoxyaldehyde could not be isolated in yields greater than *ca.* 40%. This was attributed mainly to loss during chromatographic purification and isolation due to volatility of the product. The low yields were not due to the presence of trifluoromethanesulfonic (triflic) acid (from hydrolysis of MeOTf) since addition of the hindered base 2,6-di-*tert*-butylpyridine (4 equiv. relative to oxaziridine) had no observable effect on the reaction.

In order to demonstrate that this epoxidation reaction was indeed intramolecular, we designed a crossover experiment in which the epoxidation reaction was repeated in the presence of a second olefin, benzyl ether **16**, expected to be of comparable reactivity. The methylation and hydrolysis of **14a** was carried out as before at the same concentration in the presence of an equimolar amount of **16**. The reaction proceeded as before with no evidence for the epoxidation of **16** by TLC or ^{1}H NMR analysis of the crude reaction product. The main product again was epoxyaldehyde *rac*-**15a** (39%) and **16** was recovered in good yield following flash column chromatography (Table 2, entry 1), indicating that the selective epoxidation of **14a** was due to an intramolecular epoxidation process.

We wished to investigate the range of substrates for which the sequence of oxaziridine formation and intramolecular epoxidation could be applied. In particular, increasing tether length might reduce the rate of intramolecular oxygen transfer relative to intermolecular reaction. Directed epoxidations tend only to be highly selective when the functional groups are close together.[1] If intramolecular selectivity were maintained for longer tether lengths it would represent a considerable achievement. The chain extended homologues **14b** and **14c** were subjected to identical reaction conditions (4 equiv. of MeOTf over 4 hours) followed by hydrolysis. As before, TLC and ^{1}H NMR analysis showed clean transformation to the epoxyaldehydes but the isolated yields were moderate (38% for *rac*-**15b** and 58% for *rac*-**15c**) following chromatography. Crossover experiments were again conducted (Table 2, entries 2 and 3) with the chain-extended benzyl ether **17** present in the case of oxaziridine **14c**. Pleasingly, the reaction proceeded as before in both cases generating the epoxyaldehydes with no evidence for intermolecular epoxidation. Benzyl ethers **16** and **17** were recovered unchanged after purification.



16 **17**

Table 1 Preparation of unsaturated oxaziridines **14** from aldehydes **12**[a]

Substrate **12**	R^1	R^2	R^3	R^4	*n*	Yield for **12** ⟶ **14** (%)
a	H	Me	Me	Bn	1	73
b	H	Me	Me	Bn	2	60
c	H	Me	Me	Bn	3	64
d	nBu	H	H	Bn	1	72
e	H	H	nPr	Bn	1	73
f	H	nBu	H	Bn	1	45
g	H	nBu	H	nPr	1	39

[a] Conditions as shown in Scheme 3.

Table 2 Crossover experiments: conversion of **14a**–**c** to **15a**–**c** in the presence of **16** or **17**[a]

Entry	Substrate **14**	*n*	**14** ⟶ **15** (%)	Recovered alkene
1	**a**	1	39	**16** (73%)
2	**b**	2	41	**16** (96%)
3	**c**	3	55	**17** (90%)

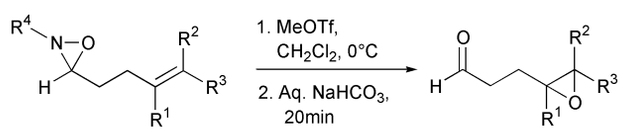
[a] Conditions as shown in Scheme 4, with 1 equiv. **16** or **17**.

Table 3 Conversion of **14d**–**g** to **15d**–**g**[a]

Substrate **14**	R^1	R^2	R^3	R^4	**14** ⟶ **15** (%)
d	nBu	H	H	Bn	39
e	H	H	nPr	Bn	56
f	H	nBu	H	Bn	60
g	H	nBu	H	nPr	48

[a] Conditions as shown in Scheme 5.

These initial studies provided an important proof of concept for the intramolecular oxaziridinium epoxidation. Our attention then turned to variation of the alkene substitution pattern (Scheme 5, Table 3). The representative 1,1-disubstituted (**14d**)

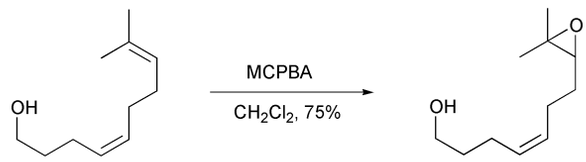


14d-g ***rac*-15d-g**

Scheme 5

and *trans*-(**14e**) and *cis*-(**14f**) 1,2-disubstituted unsaturated oxaziridines were again converted to the epoxyaldehydes **15** upon treatment with MeOTf followed by aqueous bicarbonate work-up. The amine portion was also varied (**14g**). The pure epoxyaldehydes, the major components of the crude reaction mixtures, were isolated in moderate yield following chromatography (Table 3). As expected, only one epoxide isomer was observed for **15e**–**g**, indicating that intramolecular epoxidation is a stereospecific process. This is in agreement with previous studies on intermolecular oxaziridinium epoxidation which have demonstrated retention of alkene configuration,[6] and provide further evidence that oxaziridinium epoxidation is a concerted process.

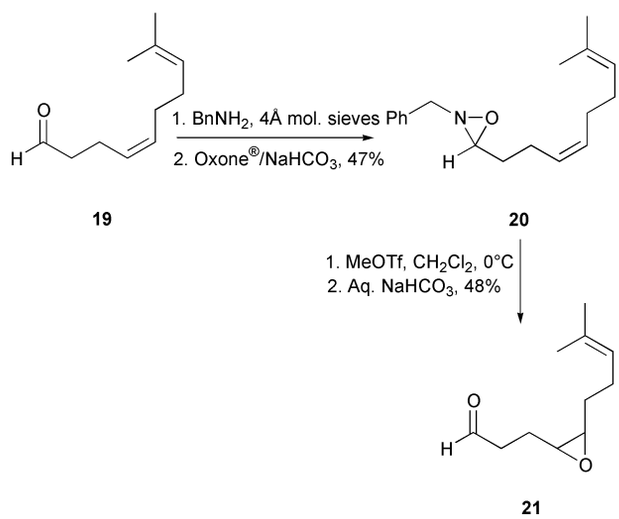
We next investigated the possibility of applying this intramolecular epoxidation to the regioselective epoxidation of a polyene. The previously prepared substrate **9** containing *cis*-disubstituted and trisubstituted alkenes was again chosen. It was proposed that intermolecular epoxidation by an electrophilic oxidant, such as peracid or an oxaziridinium salt, would occur at the trisubstituted alkene whereas intramolecular reaction should be directed to the *cis*-double bond adjacent to the functional group. Indeed, it was found that oxidation of **9** with MCPBA produced the 8,9-epoxide **18** (75% after chromatography) as the sole product (Scheme 6).



9 **18**

Scheme 6

Following the procedure applied to the previous series, aldehyde **19** was reacted with benzylamine followed by imine oxidation to provide **20** (Scheme 7). Oxaziridine **20** was then



19 **20** **21**

Scheme 7

subjected to methylation and hydrolysis resulting solely in epoxidation of the disubstituted alkene. Thus, as expected, intramolecular epoxidation *via* the oxaziridinium salt completely controls the site of oxidation. The yield of this process was not optimised, but the concept of regiocontrol through intramolecular epoxidation had clearly been demonstrated.

(*c*) Stereoselective intramolecular epoxidation in unsaturated oxaziridines

Our attention next turned to the stereochemical aspects of the intramolecular epoxidation process. At this point in our studies, there was no information as to whether alkene epoxidation by oxaziridinium species displayed a stereoelectronic preference for a *spiro* or a *planar* geometry (Fig. 1). This point is important for the rational design of chiral oxaziridinium salts for asymmetric epoxidation. However, inspection of molecular models indicated that for an oxaziridinium of fixed configuration at the ring carbon, these two extreme geometries would lead to intramolecular epoxidation on opposite faces of the olefin (Fig. 1). Thus, study of the stereochemistry of the intramolecular process would provide information on the stereoelectronic preference as well as potentially leading to epoxyaldehydes of high enantiomeric purity. We reasoned that oxidation of an

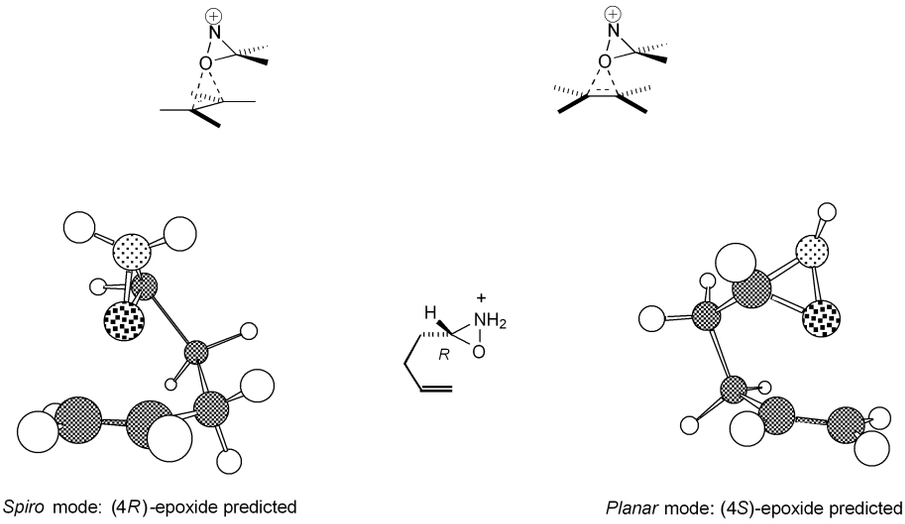
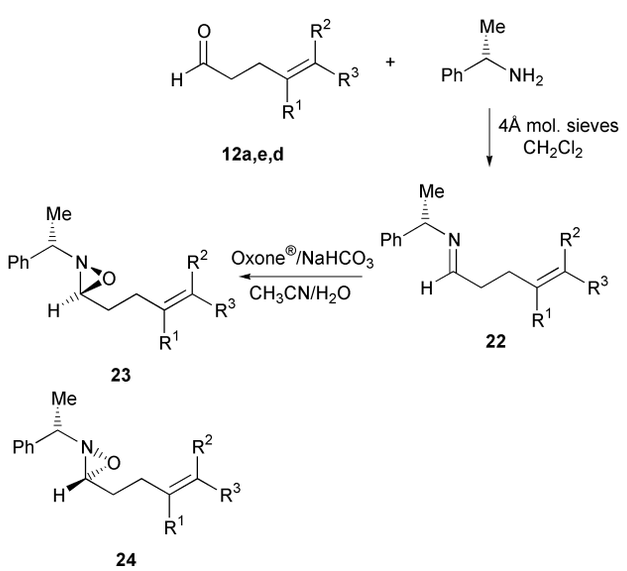


Fig. 1 Stereoelectronics of oxaziridinium epoxidation.

imine derived from an enantiomerically pure chiral primary amine and an unsaturated aldehyde could yield separable diastereomeric oxaziridines, allowing the oxygen transfer process to be studied in each. Thus, reaction of the previously prepared aldehydes **12a**, **12e**, and **12d** with (*S*)-α-methylbenzylamine in the presence of molecular sieves produced the *trans*-imines **22** (Scheme 8). Oxone® oxidation of each imine



Scheme 8

proceeded smoothly to provide a mixture of two diastereomeric oxaziridine products **23** and **24** in good combined yield (>90%). The diastereomeric ratio could be determined by integration of the ^{1}H NMR spectra. However, the similar R_f values of the diastereomers necessitated repeated column chromatography leading to low yields of the isolated diastereomerically enriched oxaziridines. Nevertheless, samples of suitably high diastereoselectivity for further studies were obtained (Table 4). One of the minor oxaziridine ring diastereomers, **24d**, contained an impurity which did not correspond to **23d** by ^{1}H NMR, and which was tentatively assigned as a *cis* oxaziridine isomer. The ^{1}H NMR spectrum of this impurity had a triplet resonance for the oxaziridine ring proton at 4.15 ppm (*cf.* 3.89 for **24d**) and a benzylic quartet at 3.62 ppm (*cf.* 3.14 for **24d**).

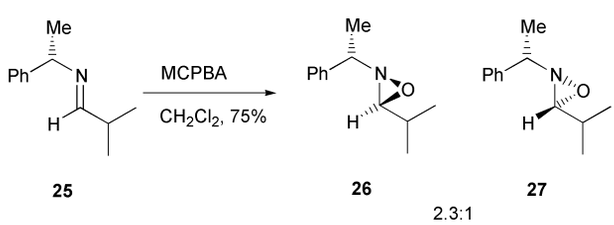
The configuration of the two oxaziridine diastereomers was assigned by comparison to secure literature precedent for the oxidation of imines derived from α-methylbenzylamine.[20a,21] The ring nitrogen is a stereocentre, and inversion does not occur in *N*-alkyloxaziridines at room temperature. There is good

Table 4 Preparation of unsaturated oxaziridines **23** and **24** from aldehydes **12**[a]

Substrate **12**	R^1	R^2	R^3	**23** : **24**[b]	**23** (%)[c]	**24** (%)[c]
a	H	Me	Me	3 : 1	22	14
e	H	H	nPr	4 : 1	21	15
d	nBu	H	H	3 : 1	54	15

[a] Conditions as shown in Scheme 8. [b] Estimated from the crude ^{1}H NMR spectrum. [c] Isolated yields after chromatography. Diastereomeric excess of purified samples as indicated in Table 5.

precedent that imine oxidation will result in products with the *N*-substituent *trans* to the substituent on the ring carbon.[21,22] With regard to configuration at the ring carbon, it has been consistently observed that the main stereoisomeric oxaziridine formed by peracid oxidation of imines bearing an *N*-α-methylbenzyl substituent has *unlike* relative stereochemistry at the nitrogen and α-stereocentres (*cf.* **23**).[21] For example, MCPBA oxidation of **25** was shown to provide a 2.3 : 1 ratio of **26** : **27** (Scheme 9).[21e] We repeated this reaction under



Scheme 9

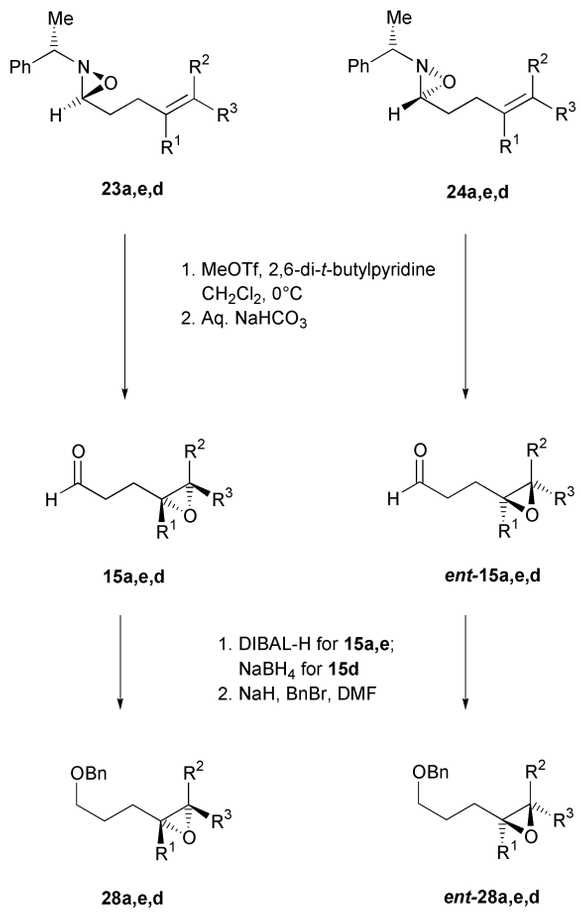
our Oxone® conditions and obtained a 3 : 1 mixture with the same major isomer predominating. In accord with literature precedent,[21e] the oxaziridine ring proton and the proton α to nitrogen are at a higher field in **26** (δ 3.53 and 3.02 respectively) than in the minor isomer **27** (δ 3.59 and 3.10). This correlation was observed for all the oxaziridines **23** and **24** prepared in our studies. For example, the major isomer **23a** was characterised by the upfield resonances of the ring proton and α-proton (3.81 and 3.04) compared with the minor isomer **24a** (3.86 and 3.14, respectively).

Attention was then turned to intramolecular epoxidation in the purified diastereomeric oxaziridines (Scheme 10 and Table 5). These compounds were treated with MeOTf as before; the presence of 2,6-di-*tert*-butylpyridine (4 equiv.) proved to be beneficial to prevent degradation of the starting material and the product epoxide mediated by adventitious triflic acid. Enantiomeric purity of the resulting epoxyaldehydes **15** was then

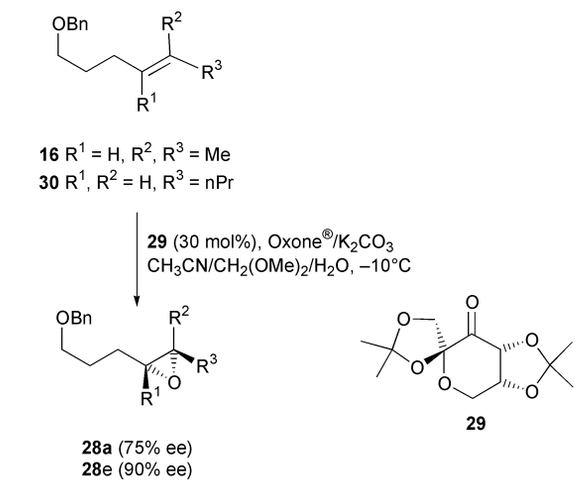
Table 5 Intramolecular epoxidation of **23a**,**d**,**e** and **24a**,**d**,**e**[a]

Substrate **23/24**	R^1	R^2	R^3	**23** De (%)[b]	**28** Ee (%)[c]	**15** Yield (%)	**24** De (%)[b]	*ent*-**28** Ee (%)[c]	*ent*-**15** Yield (%)
a	H	Me	Me	~83	81	60	>90	94	40
e	H	H	nPr	>90	93	35	>90	92	47
d	nBu	H	H	>90	>98	55	~83[d]	84	70

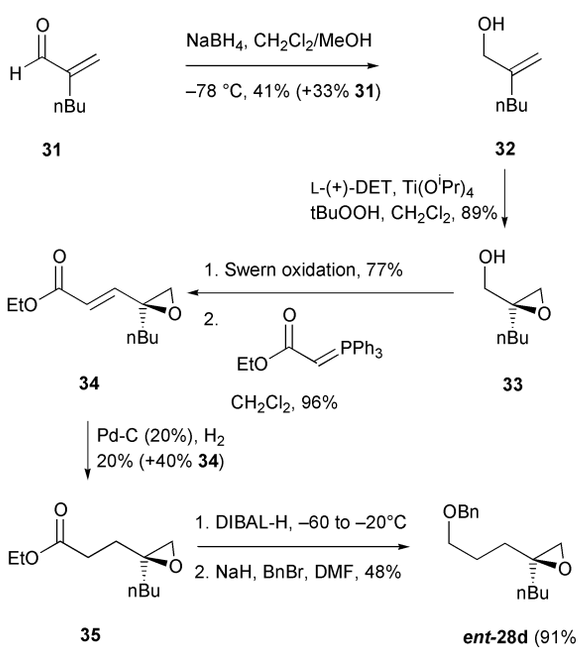
[a] Conditions as shown in Scheme 10. [b] Estimated from the crude ^{1}H NMR spectrum. [c] Measured by chiral HPLC. [d] Sample of **24d** contained an impurity (see text).



Scheme 10



Scheme 11



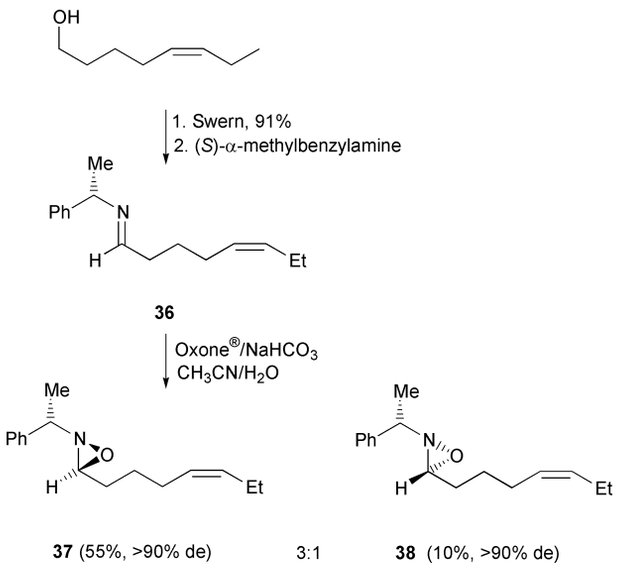
Scheme 12

determined by reduction and conversion to the benzyl ethers **28**, which could be resolved by chiral HPLC. The absolute configuration of the major isomers was determined by preparation of authentic samples for chiral HPLC analysis using reliable methods of asymmetric synthesis. Thus, epoxidation using the Shi fructose-derived ketone **29**[19] provided samples of **28a** and **28e** (Scheme 11). Sharpless epoxidation[23] was the key step in the synthesis of epoxide *ent*-**28d** (Scheme 12).

Several interesting features emerge from the results in Table 5. In all cases, epoxide products were obtained with enantiomeric excess very close to the diastereomeric excess of the starting oxaziridine **23/24**. Thus, the intramolecular epoxidation appears to proceed with a very high level of stereocontrol. Of particular note is the formation of a terminal epoxide, **15d/28d**, of very high enantiomeric excess, since direct asymmetric epoxidation of "unfunctionalised" terminal alkenes is still a difficult transformation. Importantly, epoxides of opposite absolute configuration were obtained from the two oxaziridine diastereomers **23** and **24**, suggesting that it is the ring carbon rather than the chiral α-methylbenzyl unit that determines the stereochemistry of the epoxide. In all cases, the observed major enantiomer is consistent with intramolecular attack *via* a *spiro* transition state, and this work provided the first evidence for such a preference. Following the communication of our results, the first computational study of epoxidations by oxaziridinium salts was reported by Washington and Houk.[24] All calculated transition structures (Becke3LYP/6-31G*) for epoxidations of simple alkenes by substituted oxaziridiniums were indeed found to have *spiro* geometry. Examples of stereoselective oxaziridinium epoxidation were also modelled including the intramolecular epoxidation of **24a** to give epoxyaldehyde *ent*-**15a** in 94% ee. Using *N,N*-dimethyl-3-butenyloxaziridinium as a model it was found that the *spiro* transition state leading to the observed *S*-epoxide was 6.6 kcal mol^{-1} lower in energy than the *planar* mode. It is very pleasing that this *ab initio* study validates our experimental work and supports the proposed *spiro* transition state for epoxidation by oxaziridinium salts.

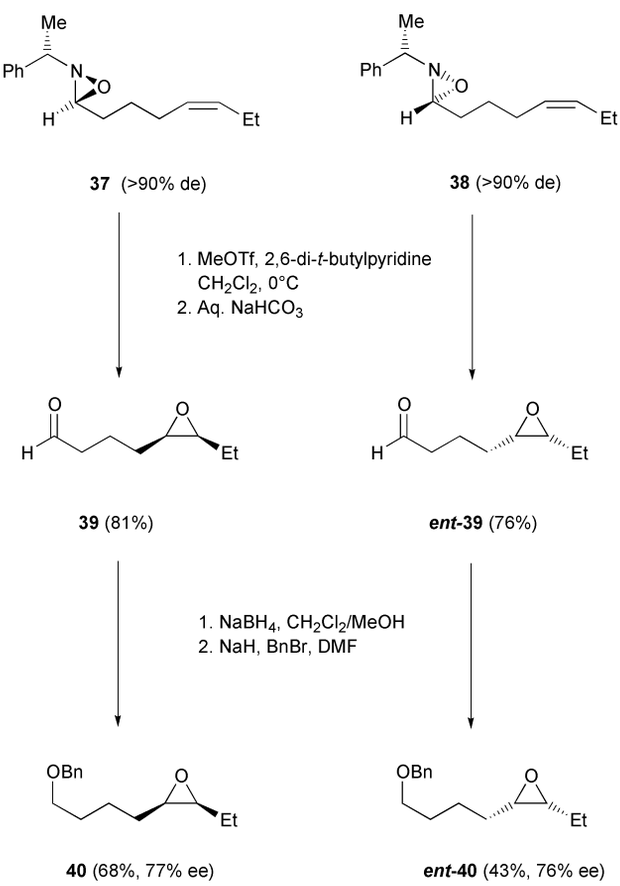
We were interested in expanding the scope of the intramolecular epoxidation methodology further to different alkene substitution patterns and longer tether lengths. (*Z*)-Oct-5-en-1-

ol was oxidised to the aldehyde followed by imine formation and oxidation under standard conditions to generate oxaziridines **37** and **38** in high diastereomeric excess after purification (Scheme 13).



Scheme 13

The intramolecular epoxidation of the oxaziridine pair **37** and **38** was then undertaken. We were pleased to isolate the product epoxyaldehydes **39** in excellent yield (Scheme 14). The



Scheme 14

improved recovery compared with previous reactions with variable yields may be due to the methylation reactions being conducted on a larger scale so that proportionately less material was lost on isolation and purification. The product epoxyaldehydes were then easily transformed into the corresponding benzyl ethers **40** following the established protocol. Chiral HPLC analysis of these epoxide products showed that the epoxide ring had been installed in high and similar enantiomeric excess, with the configuration of the major isomers assigned assuming that a *spiro*-transition state is again preferred. However, given the high de of **37** and **38** it is evident that complete chirality transfer has not occurred. The drop in stereoselectivity in this series could be due to the increased alkyl tether length reducing the difference in transition state energies for epoxidation of opposite alkene faces. Alternatively, the reduced enantiomeric excess could result from an increased *spiro* TS energy for the *Z*-alkene due, for example, to a steric clash between the alkene ethyl substituent and oxaziridine ring hydrogen. Further experiments combined with molecular modelling studies would help clarify this result.

Conclusions

Two different approaches towards selective intramolecular epoxidation have been studied. The first investigated the possibility for ketone-directed oxidation *via* an intermediate dioxirane generated *in situ* from Oxone®. It was found that direct, non-selective epoxidation by Oxone® competed with the intramolecular dioxirane reaction leading to poor levels of diastereo- and regiocontrol in a homogenous solvent system.

New methodology was developed for the synthesis and epoxidation of a range of unsaturated oxaziridines. Treatment with MeOTf followed by hydrolysis yielded epoxyaldehydes, presumably *via* the oxaziridinium salts. Crossover experiments and the completely regioselective epoxidation of a non-conjugated diene provided strong evidence for intramolecular reaction. The use of α-methylbenzylamine as a chiral auxiliary allowed diastereomeric oxaziridines to be isolated. Intramolecular epoxidation was then observed to proceed with extremely high stereoselectivity. The observed stereochemistry for each of the intramolecular epoxidations was consistent with a *spiro*-transition state. This represents the first experimental evidence for the transition state geometry in epoxidation by oxaziridinium salts and may help in the future rational design of chiral catalysts. The intramolecular epoxidation process would now be improved by use of an alternative chiral amine which leads to higher diastereoselectivity in the imine oxidation and therefore higher yields of diastereomerically pure oxaziridine.

Experimental

General details

NMR spectra were recorded on a JEOL EX 270, Bruker WM 250, Bruker AM 400 or Bruker DRX 500 spectrometer using $CDCl_3$ with tetramethylsilane or $CDCl_3$ (δ_C = 77.0) as internal reference. Coupling constants are measured in hertz and are quoted to the nearest 0.5 Hz. Multiplicities in ^{13}C spectra were determined by DEPT experiments. Infrared spectra were recorded on a Perkin-Elmer 1605 FT-IR spectrometer from 4000 to 600 cm^{-1}. Mass spectra were recorded at the University of Nottingham or the EPSRC service at Swansea. Optical rotations were measured using a JASCO DIP-370 digital polarimeter. Diethyl ether (referred to throughout as ether) and tetrahydrofuran (THF) solvents were distilled from sodium benzophenone ketyl. Dichloromethane, acetonitrile, triethylamine and pyridine were distilled from calcium hydride. Toluene and benzene were distilled from sodium and DMF from anhydrous magnesium sulfate. Petrol refers to light petroleum ether of boiling range 40–60 °C which was distilled prior to use. All commercial reagents were used without further purification unless stated otherwise. Flash column chromatography was performed using Merck Kieselgel 60 (230–400 mesh). Where appropriate the silica gel was neutralised by flushing with a 1% solution of triethylamine. Thin layer chromatography was performed using precoated glass-backed

plates (Merck Kieselgel 60 F_{254}) and visualised by ultraviolet light and/or acidic ceric ammonium molybdate or potassium permanganate as appropriate.

Chiral HPLC determinations of enantiomeric excess of **28a**,**d**,**e** and **40** were performed on an HP Series 1100 with diode array detection at 254 nm; Chiracel OD column; eluent: 0.1% isopropyl alcohol–hexane; flow rate: 0.6 ml min^{-1}. Retention times: **28a**, 51.5 min; *ent*-**28a**, 55.2 min; **28e**, 54.2 min; *ent*-**28e**, 58.8 min; **28d**, 52.4 min; *ent*-**28d**, 57.1 min; **40**, 94.3 min; *ent*-**40**, 99.1 min.

Ketones **3**–**5** were prepared as previously described.[12]

(*Z*)-1-Chloro-4-methylnon-5-en-2-one 6

To a stirred solution of diisopropylamine (0.218 ml, 1.56 mmol) in THF (2.0 ml) at 0 °C under nitrogen was added *n*-butyllithium (2.2 M in THF, 0.707 ml, 1.56 mmol) over 10 minutes. The solution was cooled to −78 °C and (*Z*)-4-methylnon-5-en-2-one **3**[12] (200 mg, 1.29 mmol) added dropwise in THF (1.5 ml). After 40 minutes, freshly distilled chlorotrimethylsilane (0.181 ml, 1.42 mmol) was added and stirring continued for 20 minutes before the reaction was allowed to warm to room temperature for 1 hour. The reaction was poured into half-saturated aqueous $NaHCO_3$ (5 ml), the mixture extracted with ethyl acetate (3 × 5 ml) and the combined organics washed consecutively with aqueous $NaHCO_3$ and saturated NaCl and then dried (Na_2SO_4). Filtration and removal of solvent under reduced pressure gave the TMS enol ether as a yellow oil. To a mixture of *N*-chlorosuccinimide (260 mg, 1.94 mmol) and sodium acetate (182 mg, 2.22 mmol) in acetone (5.9 ml) and water (1.2 ml) at −5 °C was added the enol ether in acetone (1.5 ml) over 5 minutes. After 1.5 hours 20% aqueous $NaHSO_3$ solution (3 ml) and saturated NaCl (6 ml) were added and the mixture extracted with dichloromethane. The combined organic extracts were evaporated under reduced pressure, dissolved in dichloromethane, washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4) and filtered. Removal of solvent under reduced pressure gave a yellow oil. Flash column chromatography (petrol–ethyl acetate 15 : 1) yielded the α-chloroketone (140 mg, 58%) as a colourless oil, R_f 0.51 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2959, 1732, 1456, 1402 and 735 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.37–5.31 (1H, m, *H*C=CH), 5.17–5.12 (1H, m, HC=C*H*), 4.05 (2H, s, $ClCH_2C$=O), 3.08–3.04 [1H, m, $CH_2CH(CH_3)$], 2.52 (2H, d, *J* 7.0 Hz, CH_2C=O), 2.04–2.01 (2H, m, CH_2CH=), 1.38–1.35 (2H, m, CH_2CH_3), 1.00 [3H, d, *J* 6.5 Hz, $CH(CH_3)$], 0.90 (3H, t, *J* 7.5 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 201.6 (s), 133.5 (d), 130.0 (d), 48.8 (t), 47.1 (t), 29.4 (t), 28.3 (d), 22.8 (t), 21.2 (q), 13.8 (q); *m*/*z* (CI+) 189 (M + H), 188, 173, 153, 145, 139, 111, 97; observed 188.0964. $C_{10}H_{17}{}^{35}ClO$ (M^+) requires 188.0968.

(*Z*)-1-Chloro-5-methyldec-6-en-2-one 7

This was prepared from **4**[12] using the procedure described above to give **7** (54%) as a colourless oil, R_f 0.54 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2957, 1720, 1456, 1402, 1374 and 738 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 5.38–5.31 (1H, m, *H*C=CH), 5.11–5.02 (1H, m, HC=C*H*), 4.06 (2H, s, $ClCH_2C$=O), 2.58–2.51 (2H, d, *J* 7.0 Hz, CH_2CH_2C=O), 2.47–2.40 [1H, m, $CH_2CH(CH_3)$], 2.04–1.93 (2H, m, CH_2CH=), 1.70–1.64 [1H, m, C*H*HCH-(CH_3)], 1.52–1.43 [1H, m, CH*H*CH(CH_3)], 1.36 (2H, q, *J* 7.0 Hz, CH_2CH_3), 0.96 [3H, d, *J* 6.5 Hz, $CH(CH_3)$], 0.90 (3H, t, *J* 7.0 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 202.6 (s), 134.9 (d), 129.7 (d), 48.2 (t), 37.9 (t), 31.1 (t), 30.8 (d), 29.5 (t), 22.9 (t), 21.4 (q), 13.8 (q); *m*/*z* (CI+) 203 (M + H), 202, 185, 167, 153, 110, 95; observed 202.1119. $C_{11}H_{19}{}^{35}ClO$ (M^+) requires 202.1124.

(*Z*)-1-Chloro-6-methylundec-7-en-2-one 8

This was prepared from **5**[12] using the procedure described above to give **8** (47%) as a colourless oil, R_f 0.56 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2961, 1720, 1459, 1403, 1372 and 737 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.36–5.29 (1H, m, *H*C=CH), 5.09–5.04 (1H, m, HC=C*H*), 4.06 (2H, s, $ClCH_2C$=O), 2.56 (2H, t, *J* 7.5 Hz, CH_2CH_2C=O), 2.46–2.40 [1H, m, $CH_2CH(CH_3)$], 2.06–2.00 (2H, m, CH_2CH=), 1.63–1.52 [4H, m, CH_2CH_2-$CH(CH_3)$], 1.37–1.17 (2H, m, CH_2CH_3), 0.96 (3H, t, *J* 7.5 Hz, CH_2CH_3), 0.94 [3H, d, *J* 6.5 Hz, $CH(CH_3)$]; δ_C (68 MHz, $CDCl_3$) 202.2 (s), 134.9 (d), 130.7 (d), 48.2 (t), 39.8 (t), 36.8 (t), 31.5 (d), 21.7 (t), 21.7 (t), 21.4 (q), 20.8 (t), 14.5 (q); *m*/*z* (CI+) 217 (M + H), 201, 183, 167, 149, 135, 123, 110, 95.

Oxone® epoxidation of unsaturated ketones 3–8

To a solution of ketone (0.30 mmol) stirred in acetonitrile (22.5 ml) was added an aqueous 0.4 mM Na_2EDTA solution (15 ml). To this homogeneous solution was added a mixture of Oxone® (1.84 g, 3.0 mmol) and $NaHCO_3$ (391 mg, 4.65 mmol) in portions over 30 minutes. The reaction was followed to completion by TLC, poured into water (20 ml) and extracted with dichloromethane (3 × 20 ml). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give a yellow oil. Epoxide diastereomeric ratios were then determined by ^1H NMR integration.

(*Z*)-9-Methyldeca-4,8-dien-1-ol 9

To a stirred suspension of magnesium (1.32 g, 54.1 mmol) in ether (25 ml) was added 1-bromo-4-methylpent-3-ene[25] (8.54 g, 52.6 mmol) dropwise under nitrogen and stirring was continued for 2 hours. The ethereal solution was added dropwise to $(PPh_3)_2NiCl_2$ (2.07 g, 3.15 mmol) in toluene (125 ml) and the mixture stirred for 30 minutes. Removal of ether *in vacuo* was followed by slow addition of 3,4-dihydro-2*H*-pyran (4.08 g, 48.5 mmol) after which the mixture was stirred for 4 days. The reaction was quenched by being poured into a vigorously stirred saturated NH_4Cl solution, the layers separated and the aqueous layer extracted with ether (3 × 150 ml). The combined organics were dried ($MgSO_4$) and filtered and the solvent removed under reduced pressure to a yellow oil. Flash column chromatography (petrol–ethyl acetate 2 : 1) yielded the *alcohol* **9** (1.3 g, 16%) as a colourless oil, R_f 0.27 (petrol–ethyl acetate 2 : 1); ν_{max} (film) 3326 (br), 2927, 1673, 1652, 1450, 1376 and 1060 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.45–5.36 (2H, m, *H*C=C*H*), 5.15–5.10 [1H, m, *H*C=C$(CH_3)_2$], 3.66 (2H, t, *J* 6.5 Hz, CH_2OH), 2.21–2.02 (6H, m, 3 CH_2CH=), 1.69 (3H, s, CH_3), 1.66–1.63 (2H, m, $CH_2CH_2CH_2$), 1.61 (3H, s, CH_3), 1.43–1.29 (1H, m, O*H*); δ_C (68 MHz, $CDCl_3$) 133.1 (s), 131.7 (s), 130.5 (d), 125.4 (d), 64.1 (t), 34.0 (t), 29.5 (t), 28.9 (t), 27.1 (q), 25.0 (t), 19.1 (q); *m*/*z* (EI+) 168 (M^+), 153, 125, 109, 96, 81, 69; observed 168.1513. $C_{11}H_{20}O$ (M^+) requires 168.1514.

(*Z*)-10-Methylundeca-5,9-dien-2-one 10

To a solution of (*Z*)-9-methyldeca-4,8-dien-1-ol **9** (700 mg, 4.16 mmol) in DMF (23 ml) under nitrogen was added pyridinium dichromate (6.26 g, 16.6 mmol) in a single portion. After 20 hours the reaction was poured into water (50 ml) and extracted with ether (4 × 25 ml). The combined organics were washed with brine, dried ($MgSO_4$) and filtered and the solvents removed under reduced pressure to afford a pale green oil. Flash column chromatography (petrol–ethyl acetate 1 : 1) yielded (*Z*)-9-methyldeca-4,8-dienoic acid as a white solid (595 mg, 79%), R_f 0.57 (petrol–ethyl acetate 1 : 1); ν_{max} (film) 2918 (br), 1711, 1435, 1282 and 938 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 5.47–5.37 (2H, m, *H*C=C*H*), 5.14–5.11 [1H, m, *H*C=C$(CH_3)_2$], 2.40–2.34 (4H, m, $HO_2CCH_2CH_2CH$=), 2.10–2.02 (4H, m, =$CHCH_2CH_2CH$=), 1.69 (3H, s, CH_3), 1.61 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 178.3 (s), 132.0 (s), 131.3 (d), 127.2 (d), 123.9 (d), 33.9 (t), 28.0 (t), 27.5 (t), 25.7 (q), 22.6 (t), 17.7 (q); *m*/*z* (EI+) 182 (M^+), 150, 139, 122, 69; observed 182.1307. $C_{11}H_{18}O_2$ (M^+) requires 182.1307.

To a solution of the acid (223 mg, 1.22 mmol) in THF (10 ml) under nitrogen at 0 °C was added rapidly methyllithium (1 M in THF, 4.89 ml, 4.89 mmol). After 2.5 hours, the reaction was quenched with freshly distilled chlorotrimethylsilane (3.05 ml, 24.4 ml) and allowed to warm to room temperature. 1 M HCl (10 ml) was then added and the solution stirred for 30 minutes. The mixture was extracted with ether (3 × 20 ml) and the combined organics washed with water, dried ($MgSO_4$), filtered and solvents removed under reduced pressure to a yellow oil. Flash column chromatography (petrol–ethyl acetate 15 : 1) yielded the *ketone* **10** (140 mg, 64%) as a colourless oil, R_f 0.44 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2916, 1718, 1446, 1362 and 1158 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.45–5.27 (2H, m, *H*C=C*H*), 5.12–5.09 [1H, m, *H*C=C(CH_3)$_2$], 2.50–2.45 (2H, m, CH_2C=O), 2.34–2.27 (2H, m, CH_2CH=), 2.14 (3H, s, CH_3C=O), 2.11–2.01 (4H, m, =CHCH_2CH_2CH=), 1.69 (3H, s, CH_3), 1.60 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 208.6 (s), 131.5 (s), 130.8 (d), 127.9 (d), 124.0 (d), 43.6 (t), 30.0 (q), 28.1 (t), 27.5 (t), 25.7 (q), 21.7 (t), 17.7 (q); *m*/*z* (EI+) 180 (M^+), 162, 137, 122, 111, 69; observed 180.1512. $C_{12}H_{20}O$ (M^+) requires 180.1514.

(*Z*)-1-Chloro-10-methylundeca-5,9-dien-2-one 11

This was prepared from **10** using the procedure described above for the preparation of **6**, to give **11** (38%) as a colourless oil, R_f 0.45 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2926, 1718, 1456 and 1400 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.45–5.27 (2H, m, *H*C=C*H*), 5.12–5.09 [1H, m, *H*C=C(CH_3)$_2$], 4.07 (2H, s, ClCH_2C=O), 2.67–2.61 (2H, m, CH_2CH_2C=O), 2.40–2.32 (2H, m, CH_2CH=), 2.09–2.02 (4H, m, =CHCH_2CH_2CH=), 1.69 (3H, m, CH_3), 1.61 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 202.3 (s), 131.7 (s), 131.4 (d), 127.2 (d), 123.9 (d), 48.2 (t), 39.7 (t), 28.0 (t), 27.4 (t), 25.7 (q), 21.5 (t), 17.7 (q); *m*/*z* (EI+) 214 (M^+), 145, 122, 107, 84, 69; observed 214.1125. $C_{12}H_{19}{}^{35}ClO$ (M^+) requires 214.1124.

Oxone® epoxidation of unsaturated ketones 10 and 11

To a stirred solution of ketone (0.30 mmol) in acetonitrile (4.5 ml) was added an aqueous 0.4 mM Na_2EDTA solution (3.0 ml). To this homogeneous solution was added a mixture of Oxone® (184 mg, 0.30 mmol) and $NaHCO_3$ (39 mg, 0.465 mmol) in portions over 30 minutes. The reaction was followed to completion by TLC, poured into water (20 ml) and extracted with dichloromethane (3 × 20 ml). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give a yellow oil. Epoxide regioisomeric ratios were determined by ^{1}H NMR integration.

Unsaturated aldehydes **12a**,[26] **12b**,[27] **12c**,[28] **12d**,[29] **12e**,[30] **12f**,[30] **19**,[31] and (*Z*)-oct-5-enal[32] were prepared according to known procedures and gave spectroscopic data in accord with those in the literature.

General procedure for preparation of unsaturated imines 13

To a stirred solution of unsaturated aldehyde (5.0 mmol) in dichloromethane (5.0 ml) under nitrogen was added benzylamine (536 mg, 5.0 mmol) followed by powdered 4 Å molecular sieves (500 mg). The reaction was stirred for 15 hours, filtered and the sieves washed with dichloromethane. The solvent was removed under reduced pressure to yield the crude imine as a yellow oil which was carried onto the next stage without purification. In all cases ^{1}H NMR showed a single imine, presumed to be the *E*-isomer.

General procedure for preparation of unsaturated oxaziridines

To a stirred solution of imine (4.0 mmol) in acetonitrile (60 ml) was added deionised water (40 ml). To this homogeneous solution was added a mixture of Oxone® (1.48 g, 4.8 mmol $KHSO_5$) and $NaHCO_3$ (627 mg, 7.46 mmol). The reaction was stirred for 30 minutes, poured into water (100 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give a yellow oil. Flash column chromatography (petrol–ethyl acetate 10 : 1 or petrol–dichloromethane 1 : 1) on base-washed silica yielded the oxaziridine.

2-Benzyl-3-(4′-methylpent-3′-enyl)oxaziridine 14a. Colourless oil (73%), R_f 0.42 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2916, 1640, 1496 and 1453 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.37–7.29 (5H, m, Ph), 5.11–5.05 [1H, m, *H*C=C(CH_3)$_2$], 3.90 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.83 (2H, s, PhCH_2N), 2.14–2.06 [2H, m, CH_2CH=C(CH_3)$_2$], 1.74–1.67 [2H, m, CH_2CHN(O)], 1.67 (3H, s, CH_3), 1.58 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 135.5 (s), 132.7 (s), 128.8 (d), 128.6 (d), 127.8 (d), 122.7 (d), 81.8 (d), 65.6 (t), 32.3 (t), 25.6 (q), 22.7 (t), 17.6 (q); *m*/*z* (CI+) 218 (M + H), 200, 174, 159, 146, 132, 126, 106, 91; observed: 218.1544. $C_{14}H_{20}NO$ (M + H) requires 218.1545.

2-Benzyl-3-(5′-methylhex-4′-enyl)oxaziridine 14b. Colourless oil (60%), R_f 0.45 (petrol–ethyl acetate 10 : 1) (Found C: 77.81; H: 9.40; N: 6.10. $C_{15}H_{21}NO$ requires C: 77.88; H: 9.15; N: 6.05%); ν_{max} (film) 2925, 1644, 1496, 1456 and 1376 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.37–7.30 (5H, m, Ph), 5.09–5.03 [1H, m, *H*C=C(CH_3)$_2$], 3.90 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.87 (1H, d, *J* 13.0 Hz, PhC*H*HN), 3.81 (1H, d, *J* 13.0 Hz, PhCH*H*N), 2.03–1.95 [2H, m, CH_2CH=C(CH_3)$_2$], 1.70–1.59 [5H, m, CH_2-CHN(O) and CH_3], 1.57 (3H, s, CH_3), 1.47–1.40 (2H, m, CH_2CH_2CH_2); δ_C (68 MHz, $CDCl_3$) 135.6 (s), 132.5 (s), 129.1 (d), 128.8 (d), 128.1 (d), 124.0 (d), 82.3 (d), 65.8 (t), 32.0 (t), 27.8 (t), 25.9 (q), 24.4 (t), 17.9 (q); *m*/*z* (CI+) 232 (M + H), 214, 174, 146, 132, 106, 91; observed: 232.1709. $C_{15}H_{22}NO$ (M + H) requires 232.1701.

2-Benzyl-3-(6′-methylhept-5′-enyl)oxaziridine 14c. Colourless oil (64%), R_f 0.47 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2926, 1643, 1452, 1377, 1310 and 969 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.36–7.31 (5H, m, Ph), 5.07–5.04 [1H, m, *H*C=C(CH_3)$_2$], 3.89 [1H, t, *J* 4.5 Hz, *H*CN(O)], 3.88 (1H, d, *J* 13.0 Hz, PhC*H*HN), 3.79 (1H, d, *J* 13.0 Hz, PhCH*H*N), 1.97–1.91 [2H, m, CH_2CH=C(CH_3)$_2$], 1.67 (3H, d, *J* 1.0 Hz, CH_3), 1.65–1.62 [2H, m, CH_2CHN(O)], 1.57 (3H, s, CH_3), 1.43–1.29 (4H, m, CH_2CH_2-CH_2CH_2); δ_C (68 MHz, $CDCl_3$) 135.4 (s), 131.6 (s), 128.9 (d), 128.6 (d), 127.9 (d), 124.2 (d), 82.2 (d), 65.6 (t), 32.1 (t), 29.5 (t), 27.8 (t), 25.7 (q), 23.7 (t), 17.7 (q); *m*/*z* (EI+) 245 (M^+), 192, 149, 105, 91; observed: 245.1778. $C_{16}H_{23}NO$ (M^+) requires 245.1780.

2-Benzyl-3-(3′-butylbut-3′-enyl)oxaziridine 14d. Colourless oil (72%), R_f 0.42 (petrol–ethyl acetate 10:1) (Found C: 78.17; H: 9.74; N: 5.66. $C_{16}H_{23}NO$ requires C: 78.32; H: 9.45; N: 5.71%); ν_{max} (film) 2929, 1644, 1496, 1454, 1422 and 890 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.36–7.31 (5H, m, Ph), 4.72 (1H, s, *H*HC=C), 4.69 (1H, s, H*H*C=C), 3.93 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.83 (2H, s, PhCH_2N), 2.15–2.09 (2H, m, one of CH_2C=), 2.02–1.96 (2H, m, one of CH_2C=), 1.86–1.76 [2H, m, CH_2CHN(O)], 1.42–1.26 (4H, m, CH_2CH_2CH$_3$), 0.89 (3H, t, *J* 7.0 Hz, CH_3); δ_C (68 MHz, $CDCl_3$) 148.4 (s), 135.5 (s), 128.9 (d), 128.6 (d), 127.9 (d), 109.4 (t), 81.8 (d), 65.6 (t), 35.7 (t), 30.3 (t), 30.3 (t), 29.9 (t), 22.4(t), 14.0 (q); *m*/*z* (CI+) 246 (M + H), 229, 228, 216, 202, 174, 154, 141, 91; observed: 246.1859. $C_{16}H_{24}NO$ (M + H) requires 246.1858.

(*E*)-2-Benzyl-3-hept-3′-enyloxaziridine 14e. Colourless oil (73%), R_f 0.52 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2958, 1598, 1496, 1454 and 970 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.37–7.31 (5H, m, Ph), 5.44–5.32 (2H, m, *H*C=C*H*), 3.92 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.87 (1H, d, *J* 13.0 Hz, PhC*H*HN), 3.79 (1H, d, *J* 13.0 Hz, PhCH*H*N), 2.15–2.08 (2H, m, one of CH_2CH=), 1.97–1.90 (2H, m, one of CH_2CH=), 1.80–1.62 [2H, m, CH_2-CHN(O)], 1.42–1.28 (2H, m, CH_2CH$_3$), 0.88 (3H, t, *J* 7.5 Hz,

CH_3); δ_C (68 MHz, $CDCl_3$) 135.4 (s), 131.4 (d), 128.9 (d), 128.6 (d), 128.4 (d), 127.8 (d), 81.7 (d), 65.6 (t), 34.6 (t), 32.1 (t), 27.2 (t), 22.6 (t), 13.6 (q); *m/z* (FAB+) 232 (M + H), 214, 202, 188, 176, 136, 106, 91; observed: 232.1712. $C_{15}H_{22}NO$ (M + H) requires 232.1701.

(*Z*)-2-Benzyl-3-oct-3′-enyloxaziridine 14f. Colourless oil (45%), R_f 0.58 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2955, 1496, 1454, 1421 and 1030 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.37–7.30 (5H, m, Ph), 5.49–5.27 (2H, m, *H*C=C*H*), 3.92 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.83 (2H, s, PhCH_2N), 2.20–2.12 (2H, m, one of CH_2CH=), 2.03–1.96 (2H, m, one of CH_2CH=), 1.76–1.68 [2H, m, CH_2CHN(O)], 1.34–1.29 (4H, m, CH_2CH_2CH$_3$), 0.92–0.86 (3H, m, CH_3); δ_C (68 MHz, $CDCl_3$) 135.5 (s), 131.2 (d), 128.8 (d), 128.6 (d), 127.8 (d), 127.6 (d), 81.7 (d), 65.6 (t), 32.2 (t), 31.8 (t), 26.9 (t), 22.3 (t), 21.9 (t), 14.0 (q); *m/z* (FAB+) 246 (M + H), 230, 216, 202, 154, 136, 120, 107, 91; observed: 246.1853. $C_{16}H_{24}NO$ (M + H) requires 246.1858.

(*Z*)-3-Oct-3′-enyl-2-propyloxaziridine 14g. Colourless oil (39%), R_f 0.49 (petrol–ethyl acetate 15 : 1) (Found C: 73.27; H: 12.06; N: 6.87. $C_{12}H_{23}NO$ requires C: 73.04; H:11.75; N: 7.10%); ν_{max} (film) 2959, 1654, 1458, 1421 and 1256 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 5.46–5.36 (2H, m, *H*C=C*H*), 3.72 [1H, t, *J* 5.0 Hz, *H*CN(O)], 2.79 (1H, dt, *J* 12.5, 7.5 Hz, C*H*HN), 2.52 (1H, dt, *J* 12.5, 7.0 Hz, CH*H*N), 2.26–2.17 (2H, m, one of CH_2CH=), 2.08–2.00 (2H, m, one of CH_2CH=), 1.75–1.61 [4H, m, CH_2CHN(O) and CH_2CH$_2$N], 1.39–1.26 (4H, m, CH_2CH_2CH$_3$), 0.99 (3H, t, *J* 7.5 Hz, CH_3), 0.92–0.87 (3H, m, CH_3); δ_C (68 MHz, $CDCl_3$) 131.2 (d), 127.8 (d), 81.8 (d), 63.6 (t), 32.3 (t), 31.8 (t), 26.9 (t), 22.3 (t), 21.9 (t), 21.3 (t), 14.0 (q), 11.8 (q); *m/z* (FAB+) 198 (M + H), 182, 154, 136, 91, 73, 55; observed 198.1862. $C_{12}H_{24}NO$ (M + H) requires 198.1858.

(Z)-2-Benzyl-3-(8′-methylnona-3′,7′-dienyl)oxaziridine 20. Colourless oil (47%), R_f 0.51 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2924, 1496, 1453, 1376 and 1030 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.37–7.30 (5H, m, Ph), 5.39–5.28 (2H, m, *H*C=C*H*), 5.15–5.05 [1H, m, *H*C=C(CH$_3$)$_2$], 3.91 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.83 (2H, s, PhCH_2N), 2.20–2.12 (2H, m, one of CH_2CH=), 2.10–1.95 (4H, m, two of CH_2CH=), 1.76–1.71 [2H, m, CH_2CHN(O)], 1.68 (3H, s, CH_3), 1.60 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 135.5 (s), 131.9 (s), 130.8 (d), 128.8 (d), 128.6 (d), 128.0 (d), 127.8 (d), 124.0 (d), 81.7 (d), 65.6 (t), 32.2 (t), 28.0 (t), 27.4 (t), 25.7 (q), 21.9 (t), 17.7 (q); *m/z* (CI+) 272 (M + H), 256, 242, 228, 214, 202, 188, 174, 159, 149, 136, 121, 106, 91; observed 272.2010. $C_{18}H_{26}NO$ (M + H) requires 272.2014.

General procedure for methylation of oxaziridines and hydrolysis to epoxyaldehydes

To a stirred solution of oxaziridine (0.25 mmol) in dichloromethane (6.0 ml) at 0 °C under nitrogen was added dropwise methyl trifluoromethanesulfonate (0.056 ml, 0.50 mmol). The reaction was followed by TLC with a further amount of methyl trifluoromethanesulfonate (0.50 mmol) added every 90 minutes until reaction was complete. Saturated aqueous $NaHCO_3$ (3.0 ml) was added and the reaction stirred vigorously for 20 minutes before separation and extraction of the aqueous layer with dichloromethane (3 × 10 ml). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to yield a yellow oil. Flash column chromatography (petrol–ethyl acetate 5 : 1) yielded the epoxyaldehyde.

3-(3′,3′-Dimethyloxiranyl)propionaldehyde *rac*-15a. Colourless oil (39%), R_f 0.51 (petrol–ethyl acetate 1 : 1); ν_{max} (film) 2965, 2728, 1724, 1458, 1380, 1252, 1124 and 916 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 9.83 (1H, t, 1.5 Hz, *H*C=O), 2.77 [1H, dd, *J* 7.5, 5.0 Hz, *H*C(O)C(CH$_3$)$_2$], 2.69–2.63 (2H, m, CH_2CHO), 2.03–1.90 [1H, m, C*H*HCH(O)C], 1.80–1.67 [1H, m, CH*H*CH(O)C], 1.32 (3H, s, CH_3), 1.30 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 201.6 (d), 63.4 (d), 59.2 (s), 41.1 (t), 25.0 (q), 21.8 (t), 19.0 (q); *m/z* (EI+) 129 (M + H), 111, 95, 85, 71; observed: 129.0911. $C_7H_{13}O_2$ (M + H) requires 129.0915.

4-(3′,3′-Dimethyloxiranyl)butyraldehyde *rac*-15b. Colourless oil (41%), R_f 0.46 (petrol–ethyl acetate 2 : 1); ν_{max} (film) 2960, 1723, 1458, 1378 and 1120 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 9.80 (1H, t, *J* 1.5 Hz, *H*C=O), 2.72 [1H, t, 6.0 Hz, *H*C(O)C(CH$_3$)$_2$], 2.55–2.52 (2H, m, CH_2CHO), 1.86–1.70 [2H, m, CH_2CH(O)C], 1.67–1.50 (2H, m, CH$_2$CH_2CH$_2$), 1.32 (3H, s, CH_3), 1.26 (3H, d, *J* 1.5 Hz, CH_3); δ_C (68 MHz, $CDCl_3$) 202.0 (d), 63.9 (d), 58.2 (s), 43.4 (t), 28.2 (t), 24.8 (q), 19.1 (t), 18.7 (q); *m/z* (FAB+) 143 (M + H), 141, 125, 113, 95; observed: 143.1072. $C_8H_{15}O_2$ (M + H) requires 143.1072.

5-(3′,3′-Dimethyloxiranyl)pentanal *rac*-15c. Colourless oil (55%), R_f 0.20 (petrol–ethyl acetate 5 : 1); ν_{max} (film) 2929, 2720, 1724, 1459, 1378 and 1118 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 9.78 (1H, t, *J* 1.5 Hz, *H*C=O), 2.71 [1H, t, 6.0 Hz, *H*C(O)C(CH$_3$)$_2$], 2.47 (2H, dt, *J* 7.5, 1.5 Hz, CH_2CHO), 1.73–1.67 [2H, m, CH_2CH(O)C], 1.59–1.48 (4H, m, CH_2CH_2), 1.31 (3H, s, CH_3), 1.27 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 202.4 (d), 64.1 (d), 58.2 (s), 43.8 (t), 28.6 (t), 26.1 (t), 24.9 (q), 21.9 (t), 18.7 (q); *m/z* (EI+) 156 (M+), 138, 113, 109, 98, 85; observed: 156.1155. $C_9H_{16}O_2$ (M^+) requires 156.1150.

3-(2′-Butyloxiranyl)propionaldehyde *rac*-15d. Colourless oil (39%), R_f 0.35 (petrol–ethyl acetate 5 : 1); ν_{max} (film) 2932, 2722, 1724, 1458, 1389 and 1142 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 9.77 (1H, s, *H*C=O), 2.62–2.57 [2H, m, H_2C(O)C], 2.48 (2H, t, *J* 7.5 Hz, CH_2CHO), 2.04 [1H, dt, *J* 15.0, 7.5 Hz, C*H*HC(O)], 1.90 [1H, dt, *J* 15.0, 7.5 Hz, CH*H*C(O)], 1.69–1.60 (1H, m, C*H*HPr), 1.52–1.40 (1H, m, CH*H*Pr), 1.38–1.25 (4H, m, CH_2CH_2CH$_3$), 0.90 (3H, t, *J* 6.5 Hz, CH_3); δ_C (68 MHz, $CDCl_3$) 201.4 (d), 58.5 (s), 51.9 (t), 38.8 (t), 34.5 (t), 27.0 (t), 25.9 (t), 22.7 (t), 14.0 (q); *m/z* (FAB+) 157 (M + H) 139, 125, 109, 83, 73, 69; observed 157.1223. $C_9H_{17}O_2$ (M + H) requires 157.1229.

***trans*-3-(3′-Propyloxiranyl)propionaldehyde *rac*-15e.** Colourless oil (56%), R_f 0.32 (petrol–ethyl acetate 4 : 1); ν_{max} (film) 2961, 2725, 1724, 1458, 1242, 1048 and 906 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 9.81 (1H, t, *J* 1.0 Hz, *H*C=O), 2.76–2.69 [2H, m, *H*C(O)C*H*], 2.60 (2H, dt, *J* 7.0, 1.0 Hz, CH_2CHO), 2.09–1.96 [1H, m, C*H*HCH(O)], 1.80–1.60 [1H, m, CH*H*CH(O)], 1.56–1.35 (4H, m, CH_2CH_2CH$_3$), 0.98–0.92 (3H, m, CH_3); δ_C (68 MHz, $CDCl_3$) 201.2 (d), 58.8 (d), 57.4 (d), 40.0 (t), 33.9 (t), 24.5 (t), 19.2 (t), 13.9 (q); *m/z* (EI+) 142 (M^+), 125, 113, 101, 99, 87, 71; observed 142.0998. $C_8H_{14}O_2$ (M^+) requires 142.0994.

***cis*-3-(3′-Butyloxiranyl)propionaldehyde *rac*-15f.** Colourless oil (60 and 48%), R_f 0.33 (petrol–ethyl acetate 4 : 1); ν_{max} (film) 2958, 2724, 1723, 1458 and 1389 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 9.84 (1H, t, *J* 1.0 Hz, *H*C=O), 2.99–2.92 [2H, m, *H*C(O)C*H*], 2.71–2.64 (2H, m, CH_2CHO), 2.01–1.88 [1H, m, C*H*HCH(O)], 1.80–1.66 [1H, m, CH*H*CH(O)], 1.54–1.30 [6H, m, (CH_2)$_3$CH$_3$], 0.93 (3H, t, *J* 7.0 Hz, *CH*$_3$); δ_C (68 MHz, $CDCl_3$) 201.2 (d), 57.6 (d), 56.0 (d), 40.9 (t), 28.6 (t), 27.4 (t), 22.6 (t), 20.6 (t), 14.0 (q); *m/z* (FAB+) 157 (M + H), 139, 127, 121, 111, 99, 81, 69; observed 157.1223. $C_9H_{17}O_2$ (M + H) requires 157.1229.

***cis*-3-[3′-(4″-methylpent-3″-enyl)oxiranyl]propionaldehyde 21.** Colourless oil (48%), R_f 0.14 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2966, 2724, 1724, 1450 and 1387 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 9.83 (1H, s, *H*C=O), 5.14 [1H, t, *J* 6.5 Hz, *H*C=C(CH$_3$)$_2$], 2.97–2.94 [2H, m, *H*C(O)C*H*], 2.69–2.63 (2H, m, CH_2CHO), 2.17–2.03 [2H, m, CH_2CHC=C(CH$_3$)$_2$], 2.00–

1.87 [2H, m, one of $CH_2CH(O)$], 1.80–1.62 [2H, m, one of $CH_2CH(O)$], 1.70 (3H, s, CH_3), 1.62 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 201.1 (s), 132.6 (s), 123.1 (d), 57.2 (d), 56.1 (d), 40.9 (t), 27.9 (t), 25.7 (q), 25.0 (t), 20.6 (t), 17.7 (q); *m/z* (EI+) 182 (M^+), 164, 138, 96, 82; observed 182.1306. $C_{11}H_{18}O_2$ (M^+) requires 182.1307.

5-Methylhex-4-en-1-ol benzyl ether 16

Sodium hydride as a 60% dispersion in oil (168 mg, 4.20 mmol) was washed with hexane, triturated and dried over a stream of nitrogen. DMF (1.0 ml) was added and the solution cooled to 0 °C. To this was added dropwise 5-methylhex-4-en-1-ol[33] (400 mg, 3.50 mmol) in DMF (0.50 ml) followed, after 10 minutes, by tetrabutylammonium iodide (65 mg, 0.176 mmol) in DMF (0.50 ml) and benzyl bromide (0.46 ml, 3.85 mmol). After 30 minutes the reaction was quenched by addition of water followed by saturated NH_4Cl before separation and extraction of the aqueous layer with ether (3 × 10 ml). The combined organic extracts were washed successively with 2M NaOH, water and brine and dried ($MgSO_4$). Filtration and removal of solvent under reduced pressure gave a yellow oil. Flash column chromatography (petrol–ethyl acetate 15 : 1) yielded the *benzyl ether* **16** (622 mg, 87%) as a colourless oil, R_f 0.58 (10 : 1 petrol–EtOAc); ν_{max} (film) 2926, 1603, 1495, 1453, 1376, 1363 and 1102 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.35–7.24 (5H, m, Ph), 5.14–5.08 [1H, m, *H*C=C(CH_3)$_2$], 4.50 (2H, s, PhCH_2O), 3.46 (2H, t, *J* 6.5 Hz, CH_2OCH_2Ph), 2.11–2.03 (2H, m, CH_2CH=C), 1.68 (3H, d, *J* 1.5 Hz, CH_3), 1.65–1.58 (2H, m, $CH_2CH_2CH_2$), 1.60 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 139.2 (s), 132.4 (s), 128.8 (d), 128.1 (d), 127.9 (d), 124.4 (d), 73.3 (t), 70.4 (t), 30.3 (t), 26.2 (q), 25.1 (t), 18.1 (q); *m/z* (EI+) 204 (M^+), 161, 113, 91, 69; observed: 204.1511. $C_{14}H_{20}O$ (M^+) requires 204.1514.

7-Methyloct-6-en-1-ol benzyl ether 17

Prepared from the alcohol following the procedure described above for **16**. Colourless oil (70%), R_f 0.70 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2929, 1496, 1453, 1362 and 1104 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.36–7.28 (5H, m, Ph), 5.13 [1H, t, *J* 1.5 Hz, *H*C=C(CH_3)$_2$], 4.52 (2H, s, PhCH_2O), 3.48 (2H, t, *J* 6.5 Hz, CH_2OCH_2Ph), 2.02–1.98 (2H, m, CH_2CH=C), 1.70 (3H, d, *J* 1.0 Hz, CH_3), 1.67–1.62 (2H, m, one of CH_2), 1.61 (3H, s, CH_3), 1.40–1.34 (4H, m, two of CH_2); δ_C (68 MHz, $CDCl_3$) 138.7 (s), 131.3 (s), 128.3 (d), 127.8 (d), 127.5 (d), 124.7 (d), 72.9 (t), 70.5 (t), 29.7 (t), 29.7 (t), 28.0 (t), 25.9 (q), 25.7 (t), 17.7 (q); *m/z* (EI+) 232 (M^+), 141, 123, 91; observed: 232.1821. $C_{16}H_{24}O$ (M+) requires 232.1827.

(4*Z*)-7-(3,3-Dimethyloxiranyl)hept-4-en-1-ol 18

To a stirred solution of (*Z*)-9-methyldeca-4,8-dien-1-ol **9** (25 mg, 0.149 mmol) in dichloromethane (3.8 ml) at 0 °C was added 3-chloroperbenzoic acid (82%, 31.2 mg, 0.149 mmol). After 45 minutes the reaction was quenched by addition of saturated aqueous sodium bisulfite (1.0 ml). The organic layer was washed with water, saturated aqueous $NaHCO_3$ and brine before being dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Flash column chromatography (petrol–ethyl acetate 1 : 1) yielded dienol **9** (3.5 mg, 14% recovery) and the epoxy alcohol **18** (20.5 mg, 75%) as colourless oils. Data for **18**: R_f 0.43 (petrol–ethyl acetate 1 : 1); ν_{max} (film) 3430 (br), 2929, 1654, 1457, 1379, 1119 and 1060 cm^{-1}; δ_H (270 MHz, $CDCl_3$) 5.49–5.40 (2H, m, *H*C=C*H*), 3.65 (2H, t, 6.5 Hz, CH_2OH), 2.75 [1H, t, 6.5 Hz, *H*C(O)C(CH_3)$_2$], 2.27–2.13 (4H, m, 2CH_2CHC=), 1.78 (1H, s, O*H*), 1.69–1.56 (4H, m, 2CH_2), 1.31 (3H, s, CH_3), 1.27 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 130.0 (d), 129.1 (d), 64.0 (d), 62.1 (t), 58.6 (s), 32.4 (t), 28.7 (t), 24.8 (q), 24.1 (t), 23.4 (t), 18.7 (q); *m/z* (FAB+) 185 (M + H), 154, 136, 121, 109, 95, 81, 69; observed 185.1530. $C_{11}H_{21}O_2$ (M + H) requires 185.1541.

Preparation of oxaziridines 23, 24, 37 and 38

The diastereomeric unsaturated oxaziridines, prepared following the general procedure described above for **14**, were separated by flash column chromatography (petrol–ethyl acetate or petrol–dichloromethane) on base-washed silica and gave the following data.

(2*R*,3*R*,1′*S*)-3-(4″-Methylpent-3″-enyl)-2-(1′-phenylethyl)-oxaziridine 23a. Colourless oil (22%), R_f 0.38 (petrol–dichloromethane 1 : 1); $[\alpha]_D^{25}$ −36.5 (*c* 1.0, $CHCl_3$); ν_{max} (film) 2970, 1602, 1494, 1452, 1374 and 913 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.36–7.31 (5H, m, Ph), 4.93–4.90 [1H, m, *H*C=C(CH_3)$_2$], 3.81 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.04 [1H, q, *J* 6.5 Hz, PhC*H*(CH_3)N], 1.93–1.88 [2H, m, CH_2CH=C(CH_3)$_2$], 1.71–1.53 [2H, m, CH_2CHN(O)], 1.59 [3H, d, *J* 6.5 Hz, PhCH-(CH_3)N], 1.58 (3H, s, CH_3), 1.46 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 140.1 (s), 132.6 (s), 128.7 (d), 128.0 (d), 127.3 (d), 122.6 (d), 81.7 (d), 70.9 (d), 32.5 (t), 25.6 (q), 22.7 (t), 21.6 (q), 17.5 (q); *m/z* (EI+) 231 (M^+), 213, 171, 149, 119, 105, 77; observed: 231.1622. $C_{15}H_{21}NO$ (M^+) requires 231.1623.

(2*S*,3*S*,1′*S*)-3-(4″-Methylpent-3″-enyl)-2-(1′-phenylethyl)-oxaziridine 24a. Colourless oil (14%), R_f 0.46 (petrol–dichloromethane 1 : 1); $[\alpha]_D^{25}$ −90.5 (*c* 1.0, $CHCl_3$) (Found C: 77.86; H: 9.30; N: 5.73. $C_{15}H_{21}NO$ requires C: 77.88; H: 9.15; N: 6.05%); ν_{max} (film) 2922, 1495, 1447, 1374 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.43–7.27 (5H, m, Ph), 5.18–5.15 [1H, m, *H*C=C(CH_3)$_2$], 3.86 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.14 [1H, q, *J* 7.0 Hz, PhC*H*(CH_3)N], 2.23–2.17 [2H, m, CH_2CHC(CH_3)$_2$], 1.84–1.70 [2H, m, CH_2CHN(O)], 1.71 (3H, s, CH_3), 1.64 (3H, s, CH_3), 1.44 [3H, d, *J* 7.0 Hz, PhCH(CH_3)N]; δ_C (68 MHz, $CDCl_3$) 142.1 (s), 132.8 (s), 128.5 (d), 127.5 (d), 126.8 (d), 122.9 (d), 82.0 (d), 69.7 (d), 32.6 (t), 25.7 (q), 22.9 (t), 19.4 (q), 17.8 (q); *m/z* (EI+) 231 (M^+), 215, 171, 149, 119, 105, 77; observed 231.1625. $C_{15}H_{21}NO$ (M^+) requires 231.1623.

(2*R*,3*R*,1′*S*,3″*E*)-3-(Hept-3″-enyl)-2-(1′-phenylethyl)-oxaziridine 23e. Colourless oil (21%), R_f 0.48 (petrol–dichloromethane 1 : 1); $[\alpha]_D^{20}$ −40.0 (*c* 0.72, $CHCl_3$); ν_{max} (film) 2958, 1494, 1452, 1373, 970, 761 and 701 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.38–7.31 (5H, m, Ph), 5.23–5.13 (2H, m, *H*C=C*H*), 3.82 [1H, dd, *J* 5.5, 4.5 Hz, *H*CN(O)], 3.03 [1H, q, *J* 6.5 Hz, PhC*H*(CH_3)N], 1.97–1.83 (4H, m, 2 CH_2CH=), 1.69–1.64 [1H, m, C*H*HCHN(O)], 1.59 [3H, d, *J* 6.5 Hz, PhCH(CH_3)N], 1.56–1.50 [1H, m, CH*H*CHN(O)], 1.32–1.24 (2H, m, CH_2CH$_3$), 0.84 (3H, t, *J* 7.5 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 140.5 (s), 131.8 (d), 129.2 (d), 128.7 (d), 128.5 (d), 127.8 (d), 81.9 (d), 71.4 (d), 35.0 (t), 32.7 (t), 27.6 (t), 23.0 (t), 22.0 (q), 14.1 (q); *m/z* (CI+) 245 (M^+), 230, 140, 120, 105, 77; observed: 245.1775. $C_{16}H_{23}NO$ (M+) requires 245.1780.

(2*S*,3*S*,1′*S*,3″*E*)-3-(Hept-3″-enyl)-2-(1′-phenylethyl)-oxaziridine 24e. Colourless oil (15%), R_f 0.57 (petrol–dichloromethane 1 : 1); $[\alpha]_D^{20}$ −85.0 (*c* 0.72, $CHCl_3$); ν_{max} (film) 2927, 1685, 1495, 1448, 1360, 969, 758 and 699 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.42–7.27 (5H, m, Ph), 5.54–5.41 (2H, m, *H*C=C*H*), 3.88 [1H, dd, *J* 5.5, 4.5 Hz, *H*CN(O)], 3.14 [1H, q, *J* 7.0 Hz, PhC*H*(CH_3)N], 2.25–2.20 (2H, m, C*H*HCH=), 2.01–1.96 (2H, m, CH*H*CH=), 1.87–1.80 [1H, m, C*H*HCHN(O)], 1.79–1.69 [1H, m, CH*H*CHN(O)], 1.44 [3H, d, *J* 7.0 Hz, PhCH-(CH_3)N], 1.43–1.31 (2H, m, CH_2CH$_3$), 0.89 (3H, t, *J* 7.5 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 142.0 (s), 131.6 (d), 128.5 (d), 128.4 (d), 127.5 (d), 126.8 (d), 81.8 (d), 69.7 (d), 34.6 (t), 32.3 (t), 27.4 (t), 22.6 (t), 19.5. (q), 13.6 (q); *m/z* (FAB+) 246 (M + H), 176, 136, 120, 105, 77; observed: 246.1859. $C_{16}H_{24}NO$ (M + H) requires 246.1858.

(2*R*,3*R*,1′*S*)-3-(3″-Butylbut-3″-enyl)-2-(1′-phenylethyl)-oxaziridine 23d. Colourless oil (54%), R_f 0.44 (petrol–ethyl acetate 15 : 1); $[\alpha]_D^{25}$ −26.7 (*c* 1.07, $CHCl_3$) (Found C: 78.66; H:

9.77; N: 5.67. $C_{17}H_{25}NO$ requires C: 78.72; H: 9.71; N: 5.40%); ν_{max} (film) 2930, 1645, 1493, 1452, 1372 and 890 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.37–7.29 (5H, m, Ph), 4.61 (1H, s, *H*HC=C), 4.50 (1H, s, H*H*C=C), 3.82 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.04 [1H, q, *J* 6.5 Hz, PhC*H*(CH_3)N], 1.93–1.87 (4H, m, 2 CH_2C=), 1.81–1.72 [1H, m, C*H*HCHN(O)], 1.66–1.58 [1H, m, CH*H*CHN(O)], 1.59 [3H, d, *J* 6.5 Hz, PhCH(CH_3)N], 1.31–1.21 (4H, m, $CH_2CH_2CH_3$), 0.87 (3H, t, *J* 7.0 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 148.1 (s), 140.0 (s), 128.7 (d), 128.0 (d), 127.3 (d), 109.2 (t), 81.5 (d), 70.9 (d), 35.6 (t), 30.3 (t), 30.2 (t), 29.8 (t), 22.4 (t), 21.6 (q), 13.9 (q); *m*/*z* (FAB+) 260 (M + H), 244, 154, 136, 120, 105; observed: 260.2024. $C_{17}H_{26}NO$ (M + H) requires 260.2014.

(2*S*,3*S*,1′*S*)-3-(3″-Butylbut-3″-enyl)-2-(1′-phenylethyl)-oxaziridine 24d. Colourless oil (15%), R_f 0.39 (petrol–ethyl acetate 15 : 1); $[\alpha]_D^{25}$ −88.9 (*c* 1.10, $CHCl_3$); ν_{max} (film) 2928, 1644, 1495, 1447, 1370 and 889 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.42–7.27 (5H, m, Ph), 4.79 (2H, s, H_2C=C), 3.89 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.14 [1H, q, *J* 7.0 Hz, PhC*H*(CH_3)N], 2.22 (2H, t, *J* 8.0 Hz, one of CH_2C=), 2.05 (2H, t, *J* 7.5 Hz, one of CH_2C=), 1.95–1.80 [2H, m, CH_2CHN(O)], 1.44 [3H, d, *J* 7.0 Hz, PhCH(CH_3)N], 1.44–1.39 (2H, m, CH_2CH$_2$CH$_3$), 1.32 (2H, q, *J* 7.5 Hz, $CH_2CH_2CH_3$), 0.91 (3H, t, *J* 7.5 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 148.3 (s), 142.0 (s), 128.5 (d), 127.5 (d), 126.8 (d), 109.5 (t), 81.9 (d), 69.7 (d), 35.7 (t), 30.5 (t), 30.5 (t), 29.9 (t), 22.4 (t), 19.4 (q), 14.0 (q); *m*/*z* (FAB+) 260 (M + H), 244, 154, 136, 120, 105; observed: 260.2010. $C_{17}H_{26}NO$ (M + H) requires 260.2014.

(2*R*,3*R*,1′*S*,4″*Z*)-3-(Hept-4″-enyl)-2-(1′-phenylethyl)-oxaziridine 37. Colourless oil (55%), R_f 0.45 (petrol–ethyl acetate 15 : 1); $[\alpha]_D^{26}$ −28.7 (*c* 1.62, $CHCl_3$) (Found C: 78.35; H: 9.59; N: 5.68. $C_{16}H_{23}NO$ requires C: 78.32; H: 9.45; N: 5.70%); ν_{max} (film) 2931, 1493, 1453, 1372, 762 and 701 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.36–7.29 (5H, m, Ph), 5.34–5.29 (1H, m, *H*C=CH), 5.19–5.14 (1H, m, HC=C*H*), 3.80 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.04 [1H, q, *J* 6.5 Hz, PhC*H*(CH_3)N], 1.96–1.87 (4H, m, 2CH_2C=), 1.65–1.60 [1H, m, C*H*HCHN(O)], 1.59 [3H, d, *J* 6.5 Hz, PhCH(CH_3)N], 1.53–1.46 [1H, m, CH*H*CHN(O)], 1.31–1.23 (2H, m, $CH_2CH_2CH_2$), 0.90 (3H, t, *J* 7.5 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 140.0 (s), 132.3 (d), 128.7 (d), 128.1 (d), 128.1 (d), 127.3 (d), 81.8 (d), 71.0 (d), 31.8 (t), 26.5 (t), 24.0 (t), 21.5 (q), 20.4 (t), 14.3 (q); *m*/*z* (EI+) 245 (M^+), 163, 105, 77; observed: 245.1774. $C_{16}H_{23}NO$ (M^+) requires 245.1780.

(2*S*,3*S*,1′*S*,4″*Z*)-3-(Hept-4″-enyl)-2-(1′-phenylethyl)-oxaziridine 38. Colourless oil (10%), R_f 0.40 (petrol–ethyl acetate 15 : 1); $[\alpha]_D^{26}$ −89.9 (*c* 1.27, $CHCl_3$); ν_{max} (film) 2962, 1495, 1451, 1359, 758 and 698 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.42–7.27 (5H, m, Ph), 5.44–5.39 (1H, m, *H*C=CH), 5.35–5.30 (1H, m, HC=C*H*), 3.86 [1H, t, *J* 5.0 Hz, *H*CN(O)], 3.14 [1H, q, *J* 7.0 Hz, PhC*H*(CH_3)N], 2.15–2.10 (2H, m, one of CH_2C=), 2.07–2.00 (2H, m, one of CH_2C=), 1.78–1.66 [2H, m, CH_2CHN(O)], 1.59–1.53 (2H, m, $CH_2CH_2CH_2$), 1.45 [3H, d, *J* 7.0 Hz, PhCH-(CH_3)N], 0.96 (3H, t, *J* 7.5 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 142.0 (s), 132.5 (d), 128.5 (d), 128.1 (d), 127.5 (d), 126.8 (d), 82.1 (d), 69.7 (d), 32.0 (t), 26.8 (t), 24.3 (t), 20.5 (t), 19.5 (q), 14.3 (q); *m*/*z* (EI+) 245 (M^+), 163, 105, 77; observed: 245.1779. $C_{16}H_{23}NO$ (M^+) requires 245.1780.

General procedure for methylation of non-racemic oxaziridines 23, 24 and 37 and hydrolysis to epoxyaldehydes 15 and 39

To a stirred solution of oxaziridine (0.25 mmol) and 2,6-di-*tert*-butylpyridine (0.11 ml, 0.50 mmol) in dichloromethane (6.0 ml) at 0 °C under nitrogen was added dropwise methyl trifluoromethanesulfonate (0.056 ml, 0.50 mmol). The reaction was followed by TLC, with a further amount of methyl trifluoromethanesulfonate (0.50 mmol) added every 2 hours until reaction was complete. Saturated aqueous $NaHCO_3$ (3.0 ml) was added and the reaction stirred vigorously for 20 minutes before separation and extraction of the aqueous layer with dichloromethane (3 × 10 ml). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to yield a yellow oil. Flash column chromatography (petrol–ethyl acetate 5 : 1) yielded the epoxyaldehyde as a colourless oil (**15a** 62%; *ent*-**15a** 40%; **15e** 35%; *ent*-**15e** 47%; **15d** 55%; *ent*-**15d** 70%; **39** 81%; *ent*-**39** 76%). Epoxyaldehydes **15** gave spectroscopic data as described for the racemic series.

4-(3′-Ethyloxiranyl)butyraldehyde 39 and *ent*-39. R_f 0.46 (petrol–ethyl acetate 2 : 1); $[\alpha]_D^{26}$ **39** −2.6 (*c* 0.97, $CHCl_3$), *ent*-**39** +2.3 (*c* 1.2, $CHCl_3$); ν_{max} (film) 2970, 2728, 1723, 1458, 1390 and 906 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 9.80 (1H, t, *J* 1.5 Hz, *H*C=O), 2.95–2.90 [1H, m, *H*C(O)CH], 2.88 [1H, dd, *J* 6.5, 4.0 Hz, HC(O)*CH*], 2.57–2.52 (2H, m, CH_2CHO), 1.87–1.79 [2H, m, one of CH_2CH(O)CH], 1.67–1.59 [2H, m, one of CH_2-CH(O)CH], 1.58–1.48 (2H, m, $CH_2CH_2CH_2$), 1.04 (3H, t, *J* 7.5 Hz, CH_3); δ_C (68 MHz, $CDCl_3$) 202.0 (d), 58.2 (d), 56.8 (d), 43.4 (t), 27.0 (t), 21.1 (t), 19.2 (t), 10.6 (q); *m*/*z* (CI+) 143 (M + H), 141, 123, 100, 95; observed: 143.1061. $C_8H_{15}O_2$ requires 143.1070.

Conversion of epoxyaldehydes 15a,e to benzyl ethers 28a,e: preparation of (3*R*)-3-(3′-benzyloxypropyl)-2,2-dimethyloxirane 28a

To epoxyaldehyde **15a** (20 mg, 0.156 mmol), derived from intramolecular epoxidation of **23a**, in dichloromethane (0.50 ml) at 0 °C under nitrogen was added dropwise DIBAL-H (1.5M in toluene, 0.125 ml, 0.188 mmol). After 20 minutes the reaction was quenched by addition of methanol (0.50 ml) and saturated aqueous potassium sodium tartrate (0.40 ml) before being extracted with dichloromethane (3 × 2.0 ml). The combined organics were washed with brine and dried ($MgSO_4$). Filtration and removal of solvent under reduced pressure gave the alcohol (20 mg) as a colourless oil which was carried onto the next stage without purification. Sodium hydride as a 60% dispersion in oil (3.7 mg, 0.092 mmol) was washed with hexane, triturated and dried over a stream of nitrogen. DMF (0.50 ml) was added and the solution cooled to 0 °C. To this was added dropwise the alcohol (10 mg) in DMF (0.50 ml) followed, after 10 minutes, by Bu_4NI (1.4 mg, 0.005 mmol) in DMF and benzyl bromide (0.010 ml, 0.085 mmol). After 1 hour the reaction was quenched by addition of water followed by saturated NH_4Cl before separation and extraction of the aqueous layer with ether (3 × 5 ml). The combined organic extracts were washed successively with 2 M NaOH, water and brine and dried ($MgSO_4$). Filtration and removal of solvent under reduced pressure gave a yellow oil. Flash column chromatography (petrol–ethyl acetate 10 : 1) yielded the *benzyl ether* **28a** as a colourless oil (5.7 mg, 33%) with spectroscopic data as for **28a** prepared by epoxidation of **16** (*vide infra*), shown by chiral HPLC to be of 81% ee. Retention times: **28a**, 51.5 min; *ent*-**28a**, 55.2 min.

Epoxyaldehydes *ent*-**15a**, **15e** and *ent*-**15e** were converted to the corresponding benzyl ethers *ent*-**28a**, **28e** and *ent*-**28e** respectively following the same procedure. The spectroscopic data were consistent in all cases with those for epoxy ethers **28a** and **28e** prepared by MCPBA and Shi[19] epoxidation of the corresponding alkenes (*vide infra*). Enantiomeric excesses were determined by chiral HPLC: *ent*-**28a** 94% ee; **28e** 93% ee; *ent*-**28e** 92% ee. Retention times: **28e**, 54.2 min; *ent*-**28e**, 58.8 min.

(3*R*)-3-(3′-Benzyloxypropyl)-2,2-dimethyloxirane 28a

To benzyl ether **16** (18.8 mg, 0.092 mmol) in acetonitrile–dimethoxymethane (1.38 ml, 1 : 2 v/v) were added a 0.05 M solution of $Na_2B_4O_7{\cdot}10H_2O$ in aqueous Na_2EDTA (4 × 10^{-4}

M, 0.92 ml), tetrabutylammonium hydrogen sulfate (1.4 mg, 0.0040 mmol), and ketone **29**[19] (7.12 mg, 0.028 mmol) with stirring. The mixture was cooled to −10°C and solutions of Oxone® (78.2 mg, 0.127 mmol) in aqueous Na_2EDTA (4×10^{-4} M, 0.60 ml) and K_2CO_3 (73.6 mg, 0.532 mmol) in water (0.60 ml) were added dropwise separately over 2 hours *via* syringe pumps. The reaction was quenched by addition of pentane and water and the mixture extracted with pentane (3 × 10 ml). The combined organic extracts were washed with brine and dried (Na_2SO_4). Filtration and removal of solvent under reduced pressure gave a yellow oil. Flash column chromatography (petrol–ethyl acetate 10 : 1) yielded the *epoxide* **28a** (17 mg, 84%) as a colourless oil shown by chiral HPLC to be of 75% ee. R_f 0.38 (petrol–ethyl acetate 10 : 1); $[\alpha]_D^{24}$ −36.5 (*c* 0.20, $CHCl_3$); ν_{max} (film) 2958, 1496, 1454, 1378, 1102 and 897 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.37–7.27 (5H, m, Ph), 4.51 (2H, s, PhCH_2O), 3.58–3.48 (2H, m, CH_2OCH_2Ph), 2.74 [1H, dd, *J* 6.5, 6.0 Hz, C*H*(O)C$(CH_3)_2$], 1.74–1.70 [2H, m, CH_2CH(O)C], 1.69–1.56 (2H, m, $CH_2CH_2CH_2$), 1.30 (3H, s, CH_3), 1.26 (3H, s, CH_3); δ_C (68 MHz, $CDCl_3$) 138.5 (s), 128.7 (d), 128.1 (d), 127.6 (d), 72.9 (t), 69.8 (t), 64.2 (d), 58.2 (s), 26.8 (t), 25.7 (t), 24.9 (q), 18.7 (q); *m*/*z* (EI+) 220 (M^+), 149, 113, 91; observed: 220.1467. $C_{14}H_{20}O_2$ (M^+) requires 220.1463.

(*E*)-Oct-4-en-1-ol benzyl ether 30

Prepared from (*E*)-oct-4-en-1-ol following the procedure described above for preparation of **16**. Colourless oil (96%), R_f 0.67 (petrol–ethyl acetate 10 : 1); ν_{max} (film) 2930, 1696, 1454, 1363, 1103 and 967 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.34–7.27 (5H, m, Ph), 5.41–5.38 (2H, m, *H*C=C*H*), 4.50 (2H, s, PhCH_2O), 3.47 (2H, t, *J* 6.5 Hz, CH_2OCH_2Ph), 2.08–2.05 (2H, m, one of CH_2CH=), 1.97–1.93 (2H, m, one of CH_2CH=), 1.71–1.64 (2H, m, $CH_2CH_2CH_2$), 1.35 (2H, q, *J* 7.5 Hz, C$H_2$$CH_3$), 0.87 (3H, t, *J* 7.5 Hz CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 139.1 (s), 131.2 (s), 130.1 (d), 128.8 (d), 128.2 (d), 127.9 (d), 73.3 (t), 70.3 (t), 35.1 (t), 30.1 (t), 29.6 (t), 23.1 (t), 14.1 (q); *m*/*z* (EI+) 218 (M^+), 161, 127, 109, 107, 91; observed: 218.1664. $C_{15}H_{22}O$ (M^+) requires 218.1671.

(2*R*,3*R*)-*trans*-2-(3′-Benzyloxypropyl)-3-propyloxirane 28e

Prepared from **30** with Oxone® and ketone **29** following the procedure described above for **28a** to yield **28e** (75%) as a colourless oil shown by chiral HPLC to be of 90% ee. R_f 0.27 (petrol–ethyl acetate 10 : 1); $[\alpha]_D^{24}$ −2.7 (*c* 0.40, $CHCl_3$); ν_{max} (film) 2960, 1496, 1454, 1363, 1204, 1100 and 909 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.34–7.29 (5H, m, Ph), 4.51 (2H, s, PhCH_2O), 3.54–3.48 (2H, m, CH_2OCH_2Ph), 2.70–2.67 [2H, m, C*H*(O)-C*H*], 1.79–1.67 [2H, m, one of CH_2CH(O)CH], 1.65–1.50 [2H, m, one of CH_2CH(O)CH], 1.49–1.43 (4H, m, C$H_2$$CH_3$ and $CH_2CH_2CH_2$), 0.95 (3H, t, *J* 7.0 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 138.4 (s), 128.3 (d), 127.6 (d), 127.5 (d), 72.9 (t), 69.7 (t), 58.7 (d), 58.5 (d), 34.1 (t), 28.9 (t), 26.3 (t), 19.3 (t), 13.9 (q); *m*/*z* (EI+) 234 (M^+), 216, 191, 173, 143, 127, 107, 91; observed: 234.1629. $C_{15}H_{22}O_2$ (M^+) requires 234.1620.

Conversion of epoxyaldehyde 15d to benzyl ether 28d. Preparation of (2*R*)-2-(3′-benzyloxypropyl)-2-butyloxirane 28d

To sodium borohydride (10 mg, 0.26 mmol) were added dichloromethane (1.5 ml) and methanol (0.75 ml). The reaction was stirred for 5 minutes after which an aliquot (0.95 ml) was removed and added to 3-(2′-butyloxiranyl)propionaldehyde **15d** (14.5 mg, 0.093 mmol) stirred in dichloromethane (0.60 ml) at 0 °C. After 20 minutes the reaction was quenched by addition of acetaldehyde, diluted with dichloromethane, washed with saturated aqueous $NaHCO_3$ and the organic phase dried ($MgSO_4$). Filtration and removal of solvent under reduced pressure gave the alcohol as a colourless oil which was carried onto the next stage without purification. Sodium hydride as a 60% dispersion in oil (4.5 mg, 0.11 mmol) was washed with hexane, triturated and dried over a stream of nitrogen. DMF (0.50 ml) was added and the solution cooled to 0 °C. To this was added dropwise the alcohol in DMF (0.5 ml) followed, after 10 minutes, by Bu_4NI (1.7 mg, 0.0050 mmol) in DMF and benzyl bromide (0.012 ml, 0.10 mmol). After 1 hour the reaction was quenched by addition of water followed by saturated NH_4Cl before separation and extraction of the aqueous layer with ether (3 × 5 ml). The combined organic extracts were washed successively with 2 M NaOH, water and brine and dried ($MgSO_4$). Filtration and removal of solvent under reduced pressure gave a yellow oil. Flash column chromatography (petrol–ethyl acetate 10 : 1) yielded the *epoxide* **28d** (11 mg, 50%) as a colourless oil shown by chiral HPLC to be of >98% ee. R_f 0.40 (petrol–ethyl acetate 10 : 1); $[\alpha]_D^{24}$ +2.2 (*c* 0.86, $CHCl_3$); ν_{max} (film) 2932, 1495, 1454, 1362 and 1101 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.35–7.27 (5H, m, Ph), 4.50 (2H, s, PhCH_2O), 3.50–3.47 (2H, m, CH_2OCH_2Ph), 2.58 [2H, s, H_2C(O)C], 1.70–1.59 [4H, m, 2 CH_2C(O)], 1.52–1.46 (2H, m, one of CH_2), 1.35–1.30 (4H, m, two of CH_2), 0.90 (3H, t, *J* 7.0 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 138.5 (s), 128.4 (d), 127.6 (d), 127.5 (d), 72.9 (t), 70.2 (t), 59.3 (s), 52.5 (t), 34.0 (t), 30.8 (t), 27.0 (t), 25.1 (t), 22.8 (t), 14.0 (q); *m*/*z* (EI+) 248 (M^+), 140, 107, 91; observed: 248.1776. $C_{16}H_{24}O_2$ (M^+) requires 248.1776.

ent-**28d** (47%) was prepared from *ent*-**15d** following the same procedure and was shown by chiral HPLC to be of 84% ee. Retention times **28d**, 52.4 min; *ent*-**28d**, 57.1 min.

(2*S*)-2-(3′-Benzyloxypropyl)-2-butyloxirane *ent*-28d

2-Butylprop-2-en-1-ol[34] **32** was prepared from *n*-butylacrolein by reduction with sodium borohydride.[35] Asymmetric Sharpless epoxidation[23] with L-(+)-DET (diethyl tartrate) generated (2*S*)-(2-butyloxiranyl)methanol[36] **33**. Oxidation using the Swern procedure[37] yielded (2*S*)-2-butyloxirane-2-carbaldehyde as a colourless oil (77%); R_f 0.44 (petrol–ethyl acetate 10 : 1); $[\alpha]_D^{21}$ +56.7 (*c* 0.393, $CHCl_3$); ν_{max} ($CHCl_3$ soln.) 2959, 1732, 1458 and 867 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.90 (1H, s, *H*C=O), 3.02 [2H, s, C(O)CH_2], 1.98–1.91 [1H, m, C*H*HC(O)CH_2], 1.76–1.68 [1H, m, CH*H*C(O)CH_2], 1.41–1.31 (4H, m, CH_2CH_2), 0.90 (3H, t, *J* 7.0 Hz, CH_3); δ_C (68 MHz, $CDCl_3$) 199.2 (d), 61.4 (s), 49.6 (t), 27.3 (t), 26.5 (t), 22.8 (t), 13.9 (q); *m*/*z* (EI+) 128 (M^+), 99, 86, 85, 70; observed: 128.0835. $C_7H_{12}O_2$ (M^+) requires 128.0837. To (2*S*)-2-butyloxirane-2-carbaldehyde (900 mg, 7.02 mmol) stirred in dichloromethane at 0 °C was added (ethoxycarbonylmethylene)triphenylphosphorane (2.69 g, 7.72 mmol). The reaction was stirred for 2.5 hours after which the solvent was removed under reduced pressure to leave a white solid which was slurried with petrol. Filtration and removal of solvent under reduced pressure gave a yellow oil. Flash column chromatography (petrol–ethyl acetate 10 : 1) yielded ester **34** as a colourless oil (1.34 g, 96%); R_f 0.34 (petrol–ethyl acetate 10 : 1); $[\alpha]_D^{21}$ +59.4 (*c* 0.633, $CHCl_3$); ν_{max} (film) 2958, 1720, 1657, 1467, 1367, 1303, 1177, 1036 and 980 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.87 (1H, d, 15.5 Hz, *H*C=CHCO_2Et), 6.04 (1H, d, 15.5 Hz, HC=C*H*CO_2Et), 4.20 (2H, q, 7.0 Hz, OC$H_2$$CH_3$), 2.87 [1H, d, 5.5 Hz, C(O)C*H*H], 2.70 [1H, d, 5.5 Hz, C(O)CH*H*], 1.84–1.78 [1H, m, C*H*HC(O)CH_2], 1.69–1.62 [1H, m, CH*H*C(O)CH_2], 1.46–1.34 (4H, m, CH_2CH_2), 1.29 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 0.91 (3H, t, *J* 7.0 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 166.1 (s), 147.0 (d), 121.9 (d), 60.5 (t), 57.9 (s), 55.6 (t), 33.2 (t), 27.1 (t), 22.7 (t), 14.2 (q), 13.9 (q); *m*/*z* (EI+) 198 (M^+), 180, 170, 152, 125, 109; observed: 198.1259. $C_{11}H_{18}O_3$ (M^+) requires 198.1256. To **34** (400 mg, 2.02 mmol) stirred in ethyl acetate (17 ml) under nitrogen was added 10% palladium on charcoal (42.9 mg). The reaction flask was evacuated and flushed with hydrogen. This process was repeated five times before the reaction was allowed to stir under hydrogen for 18 hours. The reaction was filtered through a Celite pad and solvent removed under reduced pressure to give a colourless oil. Flash column chromatography (petrol–ethyl acetate 10 : 1 and

petrol–ether 10 : 1) yielded unsaturated ester **34** (160 mg, 40% recovery) and (2′*S*)-3-(2′-butyloxiranyl)propionic acid ethyl ester **35** (79 mg, 20%) as colourless oils; data for **35**: R_f 0.29 (petrol–ether 5 : 1); $[\alpha]_D^{21}$ −0.75 (*c* 1.13, $CHCl_3$); ν_{max} (film) 2933, 1736, 1371 and 1180 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.13 (2H, q, 7.0 Hz, OCH_2CH_3), 2.59 [2H, s, $C(O)CH_2$], 2.36–2.32 (2H, m, CH_2CO_2Et), 1.99–1.93 (2H, m $CH_2CH_2CO_2Et$), 1.66–1.61 [1H, m, $CHHC(O)CH_2$], 1.52–1.45 [1H, m, $CHHC(O)CH_2$], 1.36–1.29 (4H, m, CH_2CH_2), 1.26 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 0.90 (3H, t, *J* 7.0 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 174.0 (s), 61.3 (t), 59.4 (s), 52.9 (t), 35.1 (t), 30.3 (t), 29.7 (t), 27.7 (t), 23.6 (t), 15.0 (q), 14.8 (q); *m*/*z* (CI+) 201 (M + H), 183, 171, 155, 127; observed: 201.1472. $C_{11}H_{21}O_3$ (M^+) requires 201.1490. Ester **35** was reduced with DIBAL-H (2 equiv.) using the procedure previously described (preparation of **28a**) and converted to benzyl ether *ent*-**28d** (spectroscopic data as previously prepared **28d**) as a colourless oil (48%), shown by chiral HPLC to be of 91% ee.

cis-2-(4′-Benzyloxybutyl)-3-ethyloxirane 40 and *ent*-40

40 (68%) and *ent*-**40** (43%) were prepared from **39** and *ent*-**39** respectively following the procedure described above for conversion of **15d** to **28d** and were shown to be of 77% ee (**40**) and 76% ee (*ent*-**40**) by chiral HPLC. R_f 0.33 (petrol–ethyl acetate 10 : 1); (Found C: 76.67; H: 9.64. $C_{15}H_{22}O_2$ requires C: 76.88; H: 9.46%); ν_{max} (film) 2935, 1495, 1454, 1361, 1102 and 907 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.39–7.26 (5H, m, Ph), 4.50 (2H, s, $PhCH_2O$), 3.49 (2H, t, *J* 6.5 Hz, CH_2OCH_2Ph), 2.94–2.84 [2H, m, $HC(O)CH$], 1.71–1.65 [2H, m, one of $CH_2CH(O)$], 1.62–1.47 (6H, m, $3CH_2$), 1.03 (3H, t, *J* 7.5 Hz, CH_2CH_3); δ_C (68 MHz, $CDCl_3$) 138.5 (s), 128.3 (d), 127.6 (d), 127.5 (d), 72.9 (t), 70.1 (t), 58.3 (d), 57.2 (d), 29.5 (t), 27.5 (t), 23.3 (t), 21.1 (t), 10.6 (q); *m*/*z* (EI+) 234 (M^+), 216, 187, 143, 125, 107, 91; observed: 234.1612. $C_{15}H_{22}O_2$ (M^+) requires 234.1620. Chiral HPLC retention times **40**, 94.3 min; *ent*-**40**, 99.1 min.

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