ARTICLE

OBC
www.rsc.org/obc

Deprotonation–electrophile trapping of terminal epoxides

David M. Hodgson,*[a] Eirene H. M. Kirton,[a] Steven M. Miles,[a] Stéphanie L. M. Norsikian,[a] Nigel J. Reynolds[a] and Steven J. Coote[b]

[a] *Department of Chemistry, University of Oxford, Chemistry Research Laboratory,*
Mansfield Road, Oxford, UK OX1 3TA
[b] *GlaxoSmithKline, Medicines Research Centre, Gunnels Wood Road, Stevenage, UK SG1 2NY*

Received 25th February 2005, Accepted 29th March 2005
First published as an Advance Article on the web 13th April 2005

Organolithium-induced deprotonation of terminal epoxides in the presence of appropriate diamine ligands allows trapping with a range of electrophiles, yielding functionalised di- and tri-substituted epoxides in good yields and with control of stereochemistry at the epoxide.

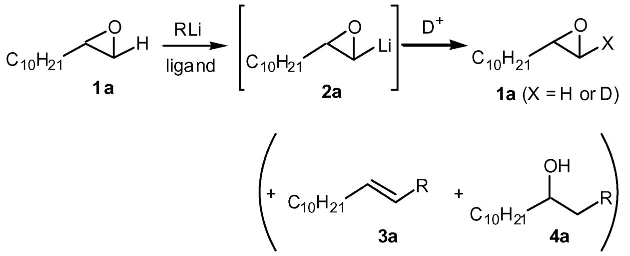
Introduction

In view of the many roles that epoxides play in organic synthesis, efficient (asymmetric) methods for the direct introduction of this important functional group would be highly valued.[1] At the outset of our studies the coupling of oxiranyl organometallics with electrophiles was one method for incorporation of epoxides that had yet to be fully developed, especially as an asymmetric transformation.[2] The first systematic studies of stabilised oxiranyl anions were reported in 1976 by Eisch and Galle.[3] Their pioneering research demonstrated the apparent necessity of an anion-stabilising group attached to the epoxide ring to enhance the facility of metalation of epoxides and to increase the thermal stability of the oxiranyl anions produced. Metalation of *cis*-disubstituted trialkylsilyl epoxides and reaction of the resultant oxiranyl anions with simple electrophiles, such as Me_3SiCl, Me_3SnCl, CO_2, MeI, amides, and D_2O, led to high yields of the desired products, with complete configurational stability being observed. This early work has subsequently been extended in many directions, expanding the range of electrophiles and anion-stabilising groups, and even generating and trapping destabilised (alkyl-substituted) oxiranyl anions by ligand exchange (desulfinylation) of sulfinyloxiranes.[4] Until the last few years it was still generally believed that, as stated in a 1996 review on the synthesis and utility of oxiranyl anions, the "metal–hydrogen exchange reaction is obviously not useful for generation of nonstabilised (H substituent) oxiranyl anions".[2a]

Arising from our studies concerning the lithiation–rearrangement of epoxides,[5] we envisioned that an appropriate ligand might be able to serve the dual role of accelerating deprotonation and reducing the rate of oxiranyl anion decomposition, enabling the direct deprotonation–electrophile trapping of unfunctionalised terminal epoxides. Compared to lithiation–electrophile trapping using epoxides of medium-sized cycloalkenes, terminal epoxides (*e.g.* **1a**) represent a greater challenge due to comparatively reduced epoxide C–H acidity,[6] combined with a higher propensity of both the starting and α-lithiated epoxides to undergo ring-opening reactions. In this paper we report a full account of our studies in this area.[7]

Results and discussion

We started our investigations with a study of various conditions for the deprotonation–deuteration of the simple terminal epoxide 1,2-epoxydodecane **1a** (Scheme 1). The reaction was first carried out in Et_2O in the absence of a ligand. Whilst no reaction occurred at −90 °C, we performed the addition of a solution of **1a** in Et_2O to ^{i}PrLi (2.5 eq.) in Et_2O at −78 °C over a period of 10 min followed after 1.5 min by D_2O quench. This run led after chromatography to recovered **1a** (35% yield, 0% D incorporation), *trans*-alkene **3a** (R = ^{i}Pr, 34%) arising from reductive alkylation,[8] and alcohol **4a** (R = ^{i}Pr, 22%). The same reaction, but carried out in the presence of TMEDA (2.5 eq.) was found to accelerate the deprotonation step. In this case, in Et_2O at −78 °C or −90 °C the alkene dominated the reaction mixture (**1a** (0% D) : **3a** = 20 : 80 and 50 : 50, respectively) with no **4a** (R = ^{i}Pr) detected. On switching from Et_2O to THF, no reaction of **1a** was observed at −90 °C with ^{i}PrLi in the presence of TMEDA.



Scheme 1 Deprotonation–deuteration studies of 1,2-epoxydodecane **1a**.

Significantly, replacing TMEDA with commercially available (−)-sparteine **5** (Fig. 1) as the ligand, we found that D incorporation was possible. When **1a** was added to a mixture of **5** (2.5 eq.) and either ^{n}BuLi, ^{t}BuLi or ^{i}PrLi (2.5 eq.) in Et_2O at −90 °C, followed after 15 min by D_2O quench, **1a** was recovered with 0% D, 10% D and 22% D incorporation, respectively. Increasing the reaction time to 1 h with ^{i}PrLi in Et_2O before D_2O quench led to **1a** in 50% yield with 45% D incorporation, along with **3a** (R = ^{i}Pr, 18%) and **4a** (R = ^{i}Pr, 11%). The reaction performed under the same conditions (^{i}PrLi–**5** at −90 °C for 1 h) but with hexane as solvent allowed us to recover **1a** in 60% yield with the same level of D incorporation but with significantly less **3a** (R = ^{i}Pr, 6%) (Table 1, entry 1). Better results were obtained using ^{s}BuLi in hexane, which after only 15 min at −90 °C gave **1a** in 70% yield with 75% D incorporation (Table 1, entry 3) with 9% of **3a** (R = ^{s}Bu) isolated. Longer reaction times resulted in increased formation of by-products and diminished recovery of **1a** (Table 1, entries 2 and 4). Incorporation of deuterium occurred exclusively *trans* to the alkyl substituent on the oxirane ring.

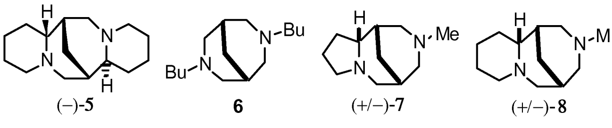


Fig. 1 Diamine ligands used in this study.

The above encouraging results with **5** as ligand prompted us to examine ligands such as **6**–**8**[9] that all possess the 3,7-diazabicyclo[3.3.1]nonane structural feature of **5** (Table 1, entries

DOI: 10.1039/b502888d

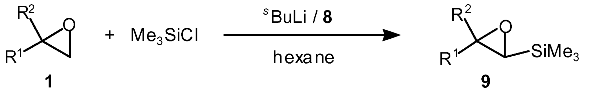
Table 1 Effect of experimental conditions on the lithiation–deuteration of 1,2-epoxydodecane **1a** in hexane at −90 °C

Entry[a]	RLi	Ligand	Time/min	Amount of D[b] in **1a** (%)	Yield[c] of **1a** (%)
1	^{i}PrLi	**5**	60	46	60
2	^{i}PrLi	**5**	180	50	50
3	^{s}BuLi	**5**	15	75	70
4[d]	^{s}BuLi	**5**	60	90	40
5	^{s}BuLi	**6**	15	45	82
6	^{s}BuLi	**7**	15	50	85
7	^{s}BuLi	**7**	60	52	80
8	^{s}BuLi	**8**	15	63	91
9	^{s}BuLi	**8**	60	70	75

[a] Reactions were carried out by the addition over 10 min of a solution of **1a** (1 eq.) in hexane to a mixture of RLi–ligand (2.5 eq. each) in hexane at −90 °C, followed by the addition of CD_3OD after the time indicated. [b] Determined by ^{1}H NMR spectroscopy. [c] Yield following chromatography. [d] **4a** (R = ^{s}Bu) was only observed (5%) in this experiment.

5–8). For these ligands, it was found that the deprotonation step was slower than with **5**. However, in these experiments little or no alkene was formed, which demonstrates the ability of these ligands to stabilise the intermediate oxiranyl anion **2a**. The best results were obtained using ^{s}BuLi–**8** in hexane at −90 °C (Table 1, entries 8 and 9). D_2O quenching after 1 h afforded **1a** in 75% yield with 70% D incorporation along with **3a** (R = ^{s}Bu, 8%). Using ^{s}BuLi–**8** in Et_2O was less effective and provided after 1 h a mixture of **1a** and **3a** (96 : 4 respectively), with only 48% D incorporation in **1a**.

Attempts to trap the intermediate oxiranyl anion **2a** with other external electrophiles (Me_3SiCl, $ClCO_2Me$, PhCHO, EtCHO) were found to be initially unsuccessful under the above conditions. However, reactions carried out with Me_3SiCl present during the generation of the oxiranyl anion led to α,β-epoxysilanes **9** in good yields (Scheme 2, Table 2). α,β-Epoxysilanes are interesting synthons for organic chemistry since, for example, they can be hydrolysed to give carbonyl compounds, undergo regio- and stereospecific α-opening by a range of nucleophiles to give diastereomerically pure β-hydroxysilanes and can serve as vinyl cation equivalents for the preparation of olefins of known stereochemistry.[10]

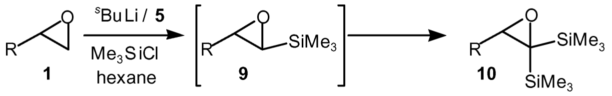


Scheme 2 Silylation of terminal epoxides **1**.

As shown in Table 2, the process is compatible with a variety of functionalised epoxides[11] leading to stereochemically pure *trans*-α,β-epoxysilanes (entries 2–5).[12] The reaction can also be performed with 2,2-disubstituted epoxides affording trisubstituted epoxides (entries 6 and 7).[13] For the unsymmetrical epoxide **1g** (entry 7), silylation was found to proceed with a high degree of selectivity (97 : 3) *trans* to the phenyl substituent.[13b]

Chiral non-racemic ligand **5** could in theory effect kinetic resolution on a racemic epoxide, and this was found to be the case to an extent (entry 8, *ca.* 30% ee for the enantiomer shown based on the specific rotation of the product). When employing 0.6 eq. each of ^{s}BuLi, **5** and Me_3SiCl, the product (1*S*,2*S*)-**9a** was returned in 18% yield and *ca.* 46% ee (based on its specific rotation), along with starting material **1a** (63%) and alkene **3a** (R = ^{s}Bu) from reductive alkylation (5%). Importantly, it was demonstrated that ^{s}BuLi–**5** could be used to silylate either enantiomer of epoxide **1a** in high yield and with complete *trans* selectivity (entries 9 and 10). This is useful given the commercial availability of ligand **5**.

A minor side-reaction of *bis*-silylation was observed in the silylation chemistry with sparteine **5** as the ligand. This led to the formation of an epoxydisilane **10**, presumably *via* lithiation–silylation of **9** (Scheme 3, *ca.* 10% *bis*-silylation observed for R = $C_{10}H_{21}$).[3,10,13a,14]



Scheme 3 Epoxydisilanes **10** *via bis*-silylation of epoxides **1**.

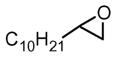
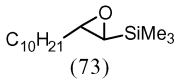
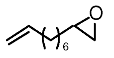
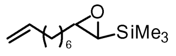
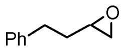
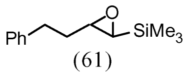
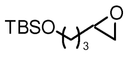
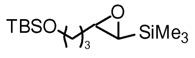
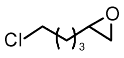
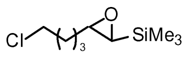
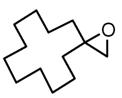
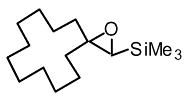
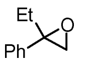
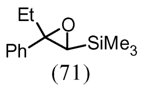
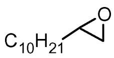
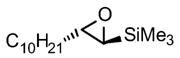
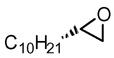
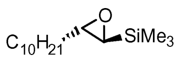
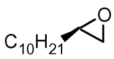
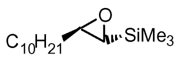
Methods to access epoxydisilanes **10** are of interest, as epoxydisilanes can be readily converted into acylsilanes and 1-halovinylsilanes.[15] Acylsilanes in particular are finding increasing utility in synthesis.[16] With this in mind it was decided to investigate the direct synthesis of epoxydisilanes **10** from readily available terminal epoxides **1**.

Initially, the equivalents of Me_3SiCl and ^{s}BuLi–sparteine complex were increased from the original 1.3 eq. to 3 or 5 eq. This led to a considerable increase in the formation of the epoxydisilane **10a**, however epoxysilane **9a** and traces of the starting terminal epoxide **1a** were still observed by crude ^{1}H NMR analysis (**1a** : **9a** : **10a** returned in ratios of 0.15 : 0.4 : 1 and 0.05 : 0.3 : 1 respectively). On the timescale of the reaction, and in the presence of excess reagents, competitive silylation of the ^{s}BuLi could contribute to incomplete disilylation. It was found that it is important to convert all of the epoxysilane **9** into the epoxydisilane **10**, because of their similar mobility characteristics on column chromatography. Bearing this in mind, the reaction conditions were investigated in more detail.

To avoid observing epoxysilane **9** in the final product profile, it appeared advantageous to obtain complete conversion of the terminal epoxide **1** to the epoxysilane **9**, before the addition of further reagents. To hopefully achieve this, the original reaction conditions (1.3 eq. of reagents at −90 °C, followed by warming to −50 °C over 1 h) were modified by then re-cooling back to −90 °C and adding a further 2 eq. of Me_3SiCl and ^{s}BuLi and leaving for 15 min at −90 °C, then warming to room temperature over 18 h before work-up. Under this protocol, it was found that, as with the monosilylation procedure, hexane proved a better solvent than Et_2O (**1a** : **9a** : **10a** returned in ratios of 0.3 : 1.3 : 1 and 2 : 3 : 1 respectively). To further improve this, instead of just ^{s}BuLi being added after warming to −50 °C and back to −90 °C, ^{s}BuLi–sparteine complex was added. This resulted in an encouraging improvement in the proportion of epoxydisilane **10a** compared to the epoxysilane **9a** (**1a** : **9a** : **10a** returned in ratio of 0 : 0.2 : 1 respectively). Indeed, warming to temperatures above −50 °C as part of a warm–cool cycle led to no epoxysilane **9a** at all in the crude product; however, more noticeable alkenyl signals in the ^{1}H NMR spectra of the crude products suggested that ^{s}BuLi-induced reductive alkylation of epoxides **1a** and **9a** had become a significant side-reaction.[17] A similar trend to the monosilylation chemistry was shown in the effect of ligand with ^{s}BuLi–sparteine complex giving superior results to ^{s}BuLi–TMEDA complex (**1a** : **9a** : **10a** returned in ratio of 0 : 0.2 : 1 and 0.4 : 0.5 : 1 respectively).

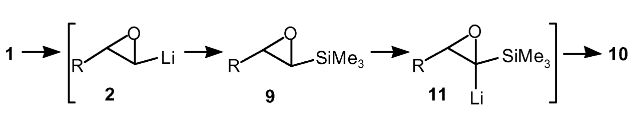
Further insight into the reaction pathway occurring during the above warm–cool protocol was achieved by quenching with

Table 2 Direct synthesis of α,β-epoxysilanes **9** from epoxides **1**

Entry[a]	**1**		Time/h	Yield of **9** (%)[b]	
1		**1a**	2	 (73)	**9a**
2		**1b**	2.5	 (71)	**9b**
3		**1c**	4.5	 (61)	**9c**
4		**1d**	2	 (74)	**9d**
5		**1e**	3	 (65)	**9e**
6		**1f**	4.5	 (67)	**9f**
7		**1g**	3	 (71)	**9g**
8[c]		**1a**	0.25	 (66) 30% e.e.	(1*S*,2*S*)-**9a**
9[c]		(*S*)-**1a**	0.25	 (72)	(1*S*,2*S*)-**9a**
10[c]		(*R*)-**1a**	0.25	 (60)	(1*R*,2*R*)-**9a**

[a] Reactions were carried out at −90 °C (−83 °C for entry 3) for the time indicated, followed by warming to −80 °C over 5 min (to −50 °C over 30 min for entries 1 and 7–10). [b] Yield following chromatography. [c] Ligand **5** used in place of ligand **8**.

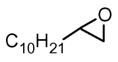
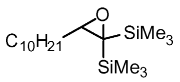
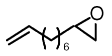
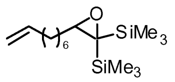
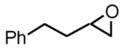
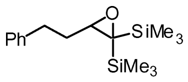
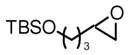
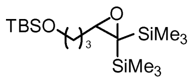
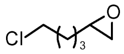
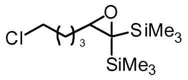
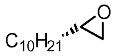
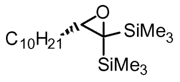
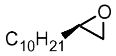
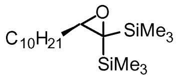
CD_3OD at different stages, followed by GC-MS analysis to determine product ratios (after appropriate calibration graphs had been constructed) and D incorporations. The observation of D incorporation in **1** and/or **9** was expected to indicate the proportion of any oxiranyl anions **2** and **11** (Scheme 4) present at the time the reaction was quenched.



Scheme 4 In-depth studies of the *bis*-silylation reaction.

After only 15 min following the addition of Me_3SiCl and ^{s}BuLi–sparteine complex (all 1.3 eq.) to the epoxide **1a** (R = $C_{10}H_{21}$) at −90 °C a ratio of **1a** : **9a** of 0.5 : 1 with 13% D incorporation in **1a** was obtained. It was established that complete reaction of the terminal epoxide **1a** and **2a** was achieved if the reaction was warmed to −50 °C over 5 min and then left at −50 °C for 1 h. As expected at that point the major compound present was epoxysilane **9a** (traces of alkene signals were also observed by ^{1}H NMR spectroscopy of the crude product). GC-MS analysis indicated a small amount of epoxydisilane **10a** was present (**9a** : **10a** ratio of 10 : 1), and a significant proportion of epoxysilane **9a** was lithiated (29% D incorporation in **9a**). The latter observations are likely to be due to the slight initial excess of ^{s}BuLi–sparteine complex employed. Following subsequent re-cooling to −90 °C and addition of further Me_3SiCl and ^{s}BuLi–sparteine complex (all 2 eq.) and stirring for 15 min, there was a modest change to the product profile (**9a** : **10a** ratio of 5 : 1, 22% of **9a** deuterated). Thus, from epoxysilane **9a** the second deprotonation and silylation do not occur as readily as from the terminal epoxide **1a** since, although the oxiranyl anion **11a** is stabilised by the α-silyl group, the proton that has to be removed to generate **11a** occupies a relatively more hindered site.[12] Compound **11a** is also more hindered than **2a** to subsequent electrophilic trapping. As the reaction warmed from −90 °C to 0 °C over 7 h, the proportion of epoxysilane **9a** gradually fell relative to epoxydisilane **10a** [after 2 h (−60 °C) **9a** : **10a** ratio of 2.5 : 1, with 46% of **9a** deuterated; after 4 h (−30 °C) **9a** : **10a** ratio of 2 : 1, with 62% of **9a** deuterated; after 7 h (0 °C) **9a** : **10a** ratio of 0.1 : 1, with 3% of **9a** deuterated]. Therefore, the majority of the second silylation occurred between −30 °C and 0 °C. The stability observed for **11a** at −30 °C under the current reaction conditions is noteworthy, given the generally accepted thermal lability of oxiranyl anions.[2b] However, Pulido and co-workers have shown

Table 3 Direct synthesis of epoxydisilanes **10** from epoxides **1**

Entry	**1**		**10**		Yield[a] (%)
1		**1a**		**10a**	61
2		**1b**		**10b**	58
3		**1c**		**10c**	53
4		**1d**		**10d**	71
5		**1e**		**10e**	50
6		(*S*)-**1a**		(*S*)-**10a**	55
7		(*R*)-**1a**		(*R*)-**10a**	47

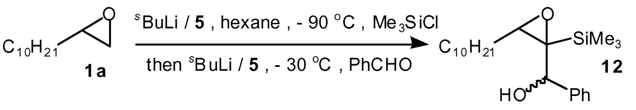
[a] Yield following chromatography (mean value of two runs for entries 1–5).

that ethylene oxide bearing a *tert*-butyldiphenylsilyl group could be lithiated, with BuLi–TMEDA complex in THF followed by efficient trapping (93%) with MeI at −50 °C.[18] At 0 °C, a lower yield of methylated epoxide (31%) together with alkene (48%) from reductive alkylation was obtained.

Application of the optimised disilylation conditions (warm to −50 °C over 5 min, maintain for 1 h then re-cool protocol) to a range of terminal epoxides gave the corresponding epoxydisilanes in good yields (Table 3). It was demonstrated that ^{s}BuLi–**5** could be used to *bis*-silylate either enantiomer of epoxide **1a** (entries 6 and 7).

Interestingly, subjection of two 2,2-disubstituted-1-epoxides (**1f** and **1g**, Table 2) to the reaction conditions led only to the corresponding monosilylated epoxysilanes **9** and it proved impossible to push these reactions past the monosilylation stage.

The introduction of two different electrophiles to a terminal epoxide in a one-flask operation was also possible, albeit in modest yield (37%) by initial silylation followed by addition of benzaldehyde at −30 °C (Scheme 5).



Scheme 5 One-flask introduction of two different electrophiles.

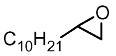
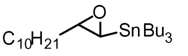
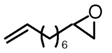
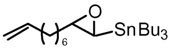
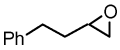
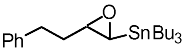
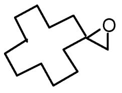
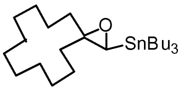
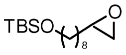
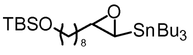
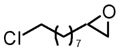
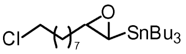
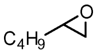
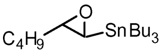
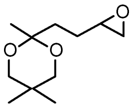
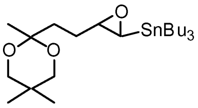
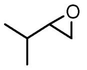
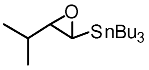
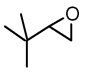
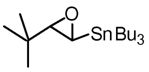
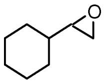
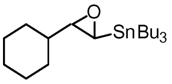
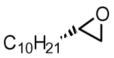
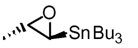
Having established methods for mono-silylation (Me$_3$SiCl present during generation of the oxiranyl anion) and deuteration (CD$_3$OD as external electrophile), attention returned to the reaction of oxiranyl anions with other (external) electrophiles, including C–C bond formation. In the original screen of diamine ligands (Table 1) the use of 3,7-dibutyl-3,7-diazabicyclo[3.3.1]nonane **6** (dibutylbispidine, DBB)–^{s}BuLi[9a,19] (2.5 eq. each) in the lithiation–deuteration of **1a** in hexane at −90 °C for 15 min had afforded 82% recovered epoxide **1a** with only 45% D incorporation (entry 5).

Compared to ^{s}BuLi–(−)-sparteine, ^{s}BuLi–DBB **6** was found to deprotonate **1** at a considerably slower rate, and as other bispidine-type ligands were more efficient, **6** was not studied in more detail at the time. However, further extensive investigations with **6** have revealed that **6** is the preferred ligand for lithiation–electrophile trapping of terminal epoxides.

Initially it was found that employing ^{s}BuLi–**6** over a prolonged reaction time afforded surprising stabilisation of the otherwise labile oxiranyllithium **2a**.[2] Indeed, using ^{s}BuLi–**6** (2.5 eq. each) in hexane at −90 °C for 16 h afforded epoxide **1a** in good isolated yield (66%) with a high level of D incorporation (90%, as judged by ^{1}H NMR), alongside alkene **3a** and alcohol **4a** in relatively small amounts (16% and 10%, respectively). This result was reproducible; under the same conditions a repeat experiment gave an almost identical result (65% yield of **1a** with 90% D, alongside 12% of alkene **3a** and 10% alcohol **4a**). Subsequent studies showed that a good level of D incorporation could be achieved using ^{s}BuLi–**6** (2.5 eq. each) in hexane at −90 °C after 4 h, accompanied by fairly small levels of alkene **3a** and alcohol **4a** by-products. Although the use of Et$_2$O as solvent allowed an enhanced rate of epoxide deprotonation, this was at the expense of slightly increased levels of by-products **3a** and **4a**, while other solvents (cumene, *tert*-butylmethyl ether and THF) and different amounts (eq.) of ^{s}BuLi–**6** gave inferior results.

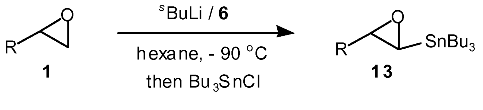
Pleasingly, it was found that following lithiation of epoxide **1a** using ^{s}BuLi–**6** (2.5 eq. each) in hexane at −90 °C for 4 h, addition of Bu$_3$SnCl (2.5 eq., added neat) afforded *trans*-α,β-epoxystannane **13a** in good yield (73% after column chromatography on Florisil®). Since α,β-epoxystannanes are useful for indirect oxiranyl anion generation *via* transmetalation,[4a] and may also allow subsequent introduction of other electrophiles using cross-coupling techniques,[20] an assessment of the stannylation scope was instigated using a range of epoxides.[21] These studies revealed that conducting the reactions at a reduced reactant concentration (0.025 M for **1** rather than 0.050 M) together with

Table 4 Direct synthesis of stannylepoxides **13** from epoxides **1**

Entry[a]	**1**		**13**		Yield[b] (%)
1		**1a**		**13a**	78
2		**1b**		**13b**	67
3		**1c**		**13c**	72
4		**1f**		**13f**	64
5		**1h**		**13h**	83
6		**1i**		**13i**	78
7		**1j**		**13j**	70
8		**1k**		**13k**	72
9		**1l**		**13l**	90
10		**1m**		**13m**	87
11		**1n**		**13n**	73
12		(*S*)-**1a**		(1*S*,2*S*)-**13a**	65
13[c]		(*S*)-**1o**		(1*S*,2*S*)-**13o**	54

[a] Solution of epoxide in hexane was added to ^{s}BuLi–**6** (2.5 eq. each) in hexane at −90 °C, and then stirred at −90 °C for 1 h (1.5 h, entry 1; 4 h, entry 4) before addition of Bu_3SnCl. [b] Yield following chromatography on Florisil® (neutral alumina, entry 4). [c] Epoxide added neat to ^{s}BuLi–**6** (2.5 eq. each) at −100 °C, then reaction continued at −90 °C.

using a shorter lithiation period (1–1.5 h) led to reduced by-product formation and returned the epoxystannane products **13** in good yield (Scheme 6, Table 4).



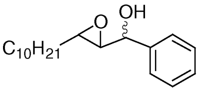
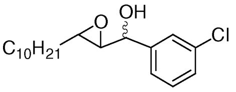
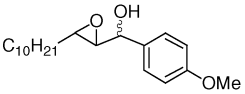
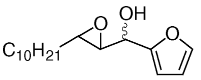
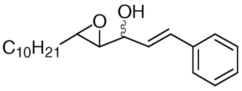
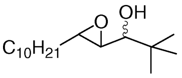
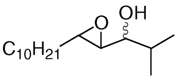
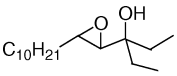
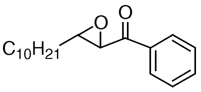
Scheme 6 Direct stannylation of terminal epoxides **1**.

Isopropyl and *tert*-butyl oxiranes gave the best yields of epoxystannanes (entries 9 and 10), but epoxides bearing side-chain functionality were also tolerated (entries 2, 3, 5, 6 and 8). Lithiation of a 2,2-disubstituted epoxide **1f** (entry 4) was significantly slower than the monosubstituted epoxides, requiring a 4 h lithiation period. Commercially available (*S*)-propylene oxide was successfully stannylated (54%, entry 13), as was (*S*)-1,2-epoxydodecane (65%, entry 12).

An investigation of lithiation–electrophile trapping to achieve C–C bond formation was then undertaken. Lithiation of 1,2-epoxydodecane **1a** for 1.5 h, followed by addition of benzaldehyde gave a separable mixture of diastereoisomeric epoxy alcohols[22] (75% combined yield, dr 1 : 1, Table 5, entry 1). The lack of diastereoselectivity is consistent with that observed for other oxiranyl anion reactions.[12] The methodology was extended to other aromatic aldehydes as the electrophile (Table 5, entries 2—4). Non-enolisable aldehydes (cinnamaldehyde and pivaldehyde) were also trapped in good yields (73 and 70% respectively, entries 5 and 6). Potentially enolisable carbonyl electrophiles (isobutyraldehyde and 3-pentanone) were also incorporated, albeit in slightly lower yields (56 and 63% respectively, entries 7 and 8). Acylation using *N*,*N*-dimethylbenzamide also proceeded (50%, entry 9).[23]

In conclusion, we have developed a methodology for the deprotonation–electrophile trapping of unfunctionalised terminal epoxides **1**. This methodology provides a direct and stereocontrolled route to deuterated epoxides, epoxysilanes **9** and epoxystannanes **13**, in addition to epoxydisilanes **10**. The methodology has also been applied to C–C bond formation using carbonyl-based electrophiles. The wide availability of terminal epoxide starting materials, and the robustness of methods for their resolution to highly enantiomerically enriched form,[11e]

Table 5 Direct C–C bond formation from 1,2-epoxydodecane **1a**

Entry[a]	Electrophile	**Product**[b]		Yield[c] (%)
1	PhCHO		**14a**	75
2	3-ClC$_6$H$_4$CHO		**14b**	72
3	4-MeOC$_6$H$_4$CHO		**14c**	57
4	Furfural		**14d**	67
5	Cinnamaldehyde		**14e**	73
6	^{t}BuCHO		**14f**	70
7	^{i}PrCHO		**14g**	56
8	Et$_2$CO		**14h**	63
9	PhCONMe$_2$		**14i**	50

[a] Solution of epoxydodecane **1a** in hexane was added to ^{s}BuLi–**6** (2.5 eq. each) in hexane at −90 °C, and then stirred at −90 °C for 1.5 h before addition of the electrophile. [b] Secondary alcohols obtained with dr 1 : 1. [c] Yield following chromatography (combined yields given for diastereomeric epoxy alcohols which, with the exception of entry 4, were largely chromatographically separable).

renders the methodology described herein as particularly useful. Further research concerning direct epoxide functionalisation and the synthetic utility of the substituted epoxide products is currently underway in our laboratories.

Experimental

General

All reactions requiring anhydrous conditions were conducted in flame- or oven-dried apparatus under an atmosphere of argon. Ethers were distilled from sodium benzophenone ketyl under argon; hexane from CaH$_2$ under argon. External reaction temperatures are reported unless stated otherwise. Reactions were monitored by TLC using commercially available (Merck) aluminium-backed plates, pre-coated with a 0.25 mm layer of silica containing a fluorescent indicator. Following aqueous work-up, organic layers were dried over MgSO$_4$ unless stated otherwise. Light petroleum refers to the fraction with bp 40–60 °C. Specific rotation $[\alpha]_D$ values were recorded at 25 °C and are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded as thin films unless stated otherwise. NMR spectra were recorded in CDCl$_3$ unless stated otherwise with Bruker DPX 250, JEOL EX400 or Bruker AMX500 spectrometers. ^{1}H NMR chemical shifts are reported relative to CHCl$_3$ (δ_H 7.27), ^{13}C NMR chemical shifts are reported relative to CDCl$_3$ (δ_C [central line of three] 77.0) and ^{119}Sn chemical shifts are reported relative to Bu$_4$Sn as external reference. Coupling constants (J) are given in Hz.

Silylation of terminal epoxides employing ligand 8

***trans*-1-(Trimethylsilyl)-1,2-epoxydodecane (9a).** To a solution of ^{s}BuLi (1.3 M in cyclohexane, 0.45 mL, 0.59 mmol) in hexane (4 mL) at −90 °C was added a solution of freshly distilled **8** (116 mg, 0.60 mmol) in hexane (1 mL) and the reaction mixture was allowed to warm to 0 °C. After a few seconds at 0 °C, the mixture was cooled to −90 °C and a solution of 1,2-epoxydodecane (44.1 mg, 0.24 mmol) and chlorotrimethylsilane (36 µL, 0.29 mmol) in hexane (1 mL) was added dropwise over a period of 10 min and the mixture was stirred for 2 h at −90 °C. The reaction mixture was then allowed to warm to −50 °C over 30 min and was quenched with MeOH (1 mL) at −50 °C and then with aqueous 1 N HCl (2 mL) at 0 °C. The two phases were separated and the aqueous one was extracted with Et$_2$O (2 × 5 mL). The combined organic extracts were washed with brine (1 × 5 mL), dried and concentrated *in vacuo*. The crude material was purified by flash chromatography (SiO$_2$, 0.5% Et$_2$O in pentane) to afford *trans*-1-(trimethylsilyl)-1,2-epoxydodecane as a colourless oil (45.1 mg, 73%). υ_{max}/cm^{-1} 2957, 2926, 2855, 1467, 1418, 1249, 870, 841; δ_H (400 MHz, CDCl$_3$) 2.75 (1H, ddd, J 6.0, 5.0, 3.5), 1.96 (1H, d, J 3.5), 1.64–1.25 (18H, m), 0.88 (3H, t, J 7.0), 0.05 (9H, s); δ_C (100 MHz, CDCl$_3$) 56.3, 51.8, 34.2, 32.0, 29.7, 29.7, 29.6, 29.4, 26.5, 22.8, 14.2, −3.6; MS (CI$^+$, NH$_3$) 257 ([M + H]$^+$, 82%), 129 (100%), 90 (30%); HRMS (CI$^+$, NH$_3$ for [M + H]$^+$) found 257.2300, $C_{15}H_{33}OSi$ requires 257.2301.

***trans*-1-(Trimethylsilyl)-1,2-epoxydec-9-ene (9b).** The reaction was performed on 1,2-epoxydec-9-ene (61.7 mg, 0.40 mmol) according to the procedure described for **9a** above but after 2.5 h at −90 °C, the mixture was allowed to warm to −80 °C. Purification by flash chromatography (SiO$_2$, 1% Et$_2$O in pentane) afforded *trans*-1-(trimethylsilyl)-1,2-epoxydec-9-ene as a colourless oil (0.0648 g, 71%). υ_{max}/cm^{-1} 3074, 2957, 2923, 2857, 1636, 1466, 1440, 1415, 1291, 1247, 990, 907, 874, 836, 749, 699; δ_H (400 MHz, CDCl$_3$) 5.90–5.80 (1H, m), 5.05–4.90 (2H, m), 2.80–2.70 (1H, m), 2.05 (2H, m), 1.97 (1H, d, *J* 3.5), 1.70–1.25 (10H, m), 0.06 (9H, s); δ_C (100 MHz, CDCl$_3$) 139.1, 114.2, 56.1, 51.7, 34.0, 33.7, 29.3, 29.0, 28.8, 26.3, −3.7; MS (CI$^+$, NH$_3$) 244 ([M + NH$_4$]$^+$, 25%), 90 (100%); HRMS (CI$^+$, NH$_3$ for [M + NH$_4$]$^+$) found 244.2101, $C_{13}H_{30}NOSi$ requires 244.2097.

***trans*-4-Phenyl-1-(trimethylsilyl)-1,2-epoxybutane (9c).** The reaction was performed on 4-phenyl-1,2-epoxybutane (48.8 mg, 0.33 mmol) according to the procedure described for **9a** above but after 4 h at −90 °C, the mixture was allowed to warm to −80 °C. Purification by flash chromatography (SiO$_2$, 2% Et$_2$O in pentane) afforded *trans*-4-phenyl-1-(trimethylsilyl)-1,2-epoxybutane as a colourless oil (44.3 mg, 61%). υ_{max}/cm^{-1} 3017, 2975, 2954, 2943, 2858, 1604, 1496, 1454, 1416, 1292, 1249, 1031, 864, 840, 747, 699; δ_H (400 MHz, CDCl$_3$) 7.35–7.10 (5H, m), 2.95–2.75 (3H, m), 2.10–1.80 (3H, m), 0.04 (9H, s); δ_C (50 MHz, CDCl$_3$) 141.9, 128.9, 128.8, 128.7, 126.4, 56.1, 52.5, 36.3, 33.1, −3.2; MS (CI$^+$, NH$_3$) 238 ([M + NH$_4$]$^+$, 50%), 90 (100%); HRMS (CI$^+$, NH$_3$ for [M + NH$_4$]$^+$) found 238.1625, $C_{13}H_{24}NOSi$ requires 238.1627.

***trans*-5-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)-1,2-epoxypentane (9d).** The reaction was performed on 5-(*tert*-butyldimethylsiloxy)-1,2-epoxypentane (87.1 g, 0.40 mmol) according to the procedure described for **9a** above but after 2 h at −90 °C, the mixture was allowed to warm to −80 °C. Purification by flash chromatography (SiO$_2$, 2% Et$_2$O in pentane) afforded *trans*-5-(*tert*-butyldimethylsiloxy)-1-(trimethylsilyl)-1,2-epoxypentane as a colourless oil (86.4 mg, 74%). υ_{max}/cm^{-1} 2970, 2960, 2930, 2856, 1470, 1247, 1097, 838, 775; δ_H (400 MHz, CDCl$_3$) 3.75–3.60 (2H, m), 2.85–2.75 (1H, m), 1.98 (1H, d, *J* 3.5), 1.80–1.60 (4H, m), 0.89 (9H, s), 0.07 (15H, apparent s); δ_C (100 MHz, CDCl$_3$) 68.3, 55.6, 51.2, 30.0, 29.9, 25.6, 18.3, −3.4, −5.5; MS (CI$^+$, NH$_3$) 289 ([M + H]$^+$, 50%), 273 (100%), 217 (10%), 164 (10%), 132 (20%), 90 (90%); HRMS (CI$^+$, NH$_3$ for [M + H]$^+$) found 289.2023, $C_{14}H_{33}O_2Si_2$ requires 289.2019.

***trans*-6-Chloro-1-(trimethylsilyl)-1,2-epoxyhexane (9e).** The reaction was performed on 6-chloro-1,2-epoxyhexane (54.6 mg, 0.41 mmol) according to the procedure described for **9a** above but after 3 h at −90 °C, the mixture was allowed to warm to −80 °C. Purification by flash chromatography (SiO$_2$, 3% Et$_2$O in pentane) afforded *trans*-6-chloro-1-(trimethylsilyl)-1,2-epoxyhexane as a colourless oil (54.5 mg, 65%). υ_{max}/cm^{-1} 2969, 2858, 1456, 1418, 1289, 876, 839; δ_H (400 MHz, CDCl$_3$) 3.56 (2H, t, *J* 6.3), 2.80–2.75 (1H, m), 1.98 (1H, d, *J* 3.6), 1.90–1.85 (2H, m), 1.80–1.50 (4H, m), 0.07 (9H, s); δ_C (100 MHz, CDCl$_3$) 55.8, 51.5, 44.8, 33.2, 32.2, 23.7, −3.9; MS (CI$^+$, NH$_3$) 224 ([M + NH$_4$]$^+$, 50%), 90 (100%); HRMS (CI$^+$, NH$_3$ for [M + NH$_4$]$^+$) found 224.1232, $C_9H_{23}NOSiCl$ requires 224.1237.

2-Cyclododecyl-1-(trimethylsilyl)ethylene oxide (9f). The reaction was performed on cyclododecyl ethylene oxide (100 mg, 0.51 mmol) according to the procedure described for **9a** above but after 4.5 h at −90 °C, the mixture was allowed to warm to −80 °C. Purification by flash chromatography (SiO$_2$, pentane) afforded 2-cyclododecyl-1-(trimethylsilyl)ethylene oxide as a colourless oil (91.6 mg, 67%). Data consistent with literature.[13a]

***trans*/*cis*-2-Phenyl-1-(trimethylsilyl)-1,2-epoxybutane (9g).** The reaction was performed on 2-phenyl-1,2-epoxybutane (54.9 mg, 0.37 mmol) according to the procedure described for **9a** above but after 3 h at −90 °C, the mixture was allowed to warm to −50 °C. Purification by flash chromatography (Al$_2$O$_3$, pentane) afforded *trans*- and *cis*-2-phenyl-1-(trimethylsilyl)-1,2-epoxybutane as a colourless oil (97 : 3 inseparable mixture of *trans* and *cis* isomers respectively, 57.4 mg, 71%). Data for the major *trans* product consistent with literature,[13b] minor component assigned tentatively as the *cis* isomer.

Silylation of terminal epoxides employing ligand 5

(1*S*,2*S*)-1-(Trimethylsilyl)-1,2-epoxydodecane [(1*S*,2*S*)-9a]. To a solution of ^{s}BuLi (1.3 M in cyclohexane, 1.0 mL, 1.3 mmol) in hexane (10 mL) at −90 °C was added (−)-sparteine **5** (0.30 mL, 1.3 mmol). The reaction mixture was allowed to warm to 0 °C over 5 min and then re-cooled to −90 °C. A solution of 1,2-epoxydodecane (184 mg, 1.0 mmol) and chlorotrimethylsilane (0.16 mL, 1.3 mmol) in hexane (2 mL) was added dropwise over a period of 15 min and the mixture was stirred for 15 min at −90 °C. The reaction mixture was then allowed to warm to −50 °C over 30 min and was quenched with MeOH (1 mL) at −50 °C and then with aqueous 1 N HCl (5 mL) at 0 °C. Work-up and purification as detailed for the synthesis of **9a** above afforded (1*S*,2*S*)-1-(trimethylsilyl)-1,2-epoxydodecane [(1*S*,2*S*)-**9a**] as a colourless oil (169 mg, 66%). $[\alpha]_D^{25}$ −3.8 (c = 1.1, CHCl$_3$); other data as for racemate **9a**. Specific rotation value indicated 30% ee in favour of the (1*S*,2*S*)-isomer based on comparison with results using enantiopure (>99% ee) (*S*)-1,2-epoxydodecane (see below).

(1*S*,2*S*)-1-(Trimethylsilyl)-1,2-epoxydodecane [(1*S*,2*S*)-9a]. The reaction was performed on (*S*)-1,2-epoxydodecane (130 mg, 0.71 mmol) according to the procedure described for (1*S*,2*S*)-**9a** above to afford (1*S*,2*S*)-1-(trimethylsilyl)-1,2-epoxydodecane as a colourless oil (130 mg, 72%). $[\alpha]_D^{25}$ −12.5 (c = 1.1, CHCl$_3$); other data as for racemate **9a**.

(1*R*,2*R*)-1-(Trimethylsilyl)-1,2-epoxydodecane [(1*R*,2*R*)-9a]. The reaction was performed on (*R*)-1,2-epoxydodecane (184 mg, 1.0 mmol) according to the procedure described for (1*S*,2*S*)-**9a** above to afford (1*R*,2*R*)-1-(trimethylsilyl)-1,2-epoxydodecane as a colourless oil (156 mg, 60%). $[\alpha]_D^{25}$ + 11.2 (c = 1.0, CHCl$_3$); other data as for racemate **9a**.

bis-Silylation of terminal epoxides

1,1-*bis*-(Trimethylsilyl)-1,2-epoxydodecane (10a). To a solution of ^{s}BuLi (1.2 M in cyclohexane, 1.1 mL, 1.3 mmol) in hexane (10 mL) at −90 °C was added (−)-sparteine **5** (0.30 mL, 1.3 mmol). The reaction mixture was allowed to warm to 0 °C over 5 min and then re-cooled to −90 °C. A solution of 1,2-epoxydodecane (0.184 g, 1.0 mmol) and chlorotrimethylsilane (0.16 mL, 1.3 mmol) in hexane (2 mL) was added dropwise maintaining the internal temperature at −90 °C. After 15 min the mixture was warmed to −50 °C over a period of 5 min. The mixture was stirred at −50 °C for 1 h and then re-cooled to −90 °C and chlorotrimethylsilane (0.25 mL, 2.0 mmol) was added. ^{s}BuLi–(−)-sparteine **5** complex (2 mmol) [prepared by adding (−)-sparteine **5** (0.46 mL, 2.0 mmol) dropwise to a solution of ^{s}BuLi (1.2 M in cyclohexane, 1.7 mL, 2.0 mmol) in hexane (8 mL) at −90 °C and allowing the mixture to warm to 0 °C] was added dropwise to the reaction maintaining the internal temperature at −90 °C. After 15 min the mixture was warmed to room temperature over 18 h. Aqueous 1 N HCl (5 mL) was added dropwise at 0 °C and the layers were separated. The aqueous phase was extracted with Et$_2$O (3 × 5 mL) and the combined organic phases were washed with brine (5 mL), dried and concentrated *in vacuo*. Purification by flash chromatography (SiO$_2$, 0.5% Et$_2$O in light petroleum) afforded 1,1-*bis*-(trimethylsilyl)-1,2-epoxydodecane (**10a**) as a pale yellow oil (203 mg, 62%). A second run returned **10a** in 60% yield. $[\alpha]_D^{25}$ −1.2 (c = 1.1, $CHCl_3$); υ_{max}/cm^{-1} 2957, 2926, 2855, 1466, 1408, 1261, 1250, 1051, 891, 859, 842; δ_H (400 MHz, $CDCl_3$) 2.94 (1H, dd, J 7.0, 4.5), 1.69–1.23 (18H, m), 0.88 (3H, t, J 7.0), 0.12 (9H, s), 0.04 (9H, s); δ_C (100 MHz, $CDCl_3$) 62.0, 51.5, 32.0, 31.6, 29.7, 29.7, 29.7, 29.6, 29.4, 27.6, 22.8, 14.2, 0.3, −2.1; MS (CI$^+$, NH_3) 329 ([M + H]$^+$, 68%), 313 (24%), 257 (88%), 90 (100%), 73 (38%); HRMS (CI$^+$, NH_3 for [M + H]$^+$) found 329.2704, $C_{18}H_{41}OSi_2$ requires 329.2696. Specific rotation value indicated 12% ee in favour of the (S)-isomer based on comparison with results using enantiopure (>99% ee) (S)-1,2-epoxydodecane (see below).

1,1-*bis*-(Trimethylsilyl)-1,2-epoxydec-9-ene (10b). The reaction was performed on 1,2-epoxydec-9-ene (154 mg, 1.0 mmol) according to the procedure described for **10a** above to afford 1,1-*bis*-(trimethylsilyl)-1,2-epoxydec-9-ene as a pale yellow oil (182 mg, 61%). A second run returned **10b** in 55% yield. $[\alpha]_D^{25}$ −1.1 (c = 1.1, $CHCl_3$); υ_{max}/cm^{-1} 2959, 2927, 2856, 1414, 1249, 1052, 907, 841; δ_H (400 MHz, $CDCl_3$) 5.92–5.68 (1H, m), 5.07–4.87 (2H, m), 3.01–2.87 (1H, m), 2.16–1.97 (2H, m), 1.29–1.50 (10H, m), 0.12 (9H, s), 0.04 (9H, s); δ_C (100 MHz, $CDCl_3$) 139.0, 114.2, 61.8, 51.3, 33.7, 31.5, 29.0, 20.0, 28.9 27.0, 0.7, −1.9; MS (CI$^+$, NH_3) 299 ([M + H]$^+$, 60%), 255 (20%), 164 (25%), 147 (20%), 90 (100%), 73 (25%); HRMS (CI$^+$, NH_3 for [M + H]$^+$) found 299.2227, $C_{16}H_{35}OSi_2$ requires 299.2226.

4-Phenyl-1,1-*bis*-(trimethylsilyl)-1,2-epoxybutane (10c). The reaction was performed on 4-phenyl-1,2-epoxybutane (148 mg, 1.0 mmol) according to the procedure described for **10a** above to afford 1,1-*bis*-(trimethylsilyl)-1,2-epoxy-4-phenylbutane as a pale yellow oil (161 mg, 55%). A second run returned **10c** in 51% yield. $[\alpha]_D^{25}$ −3.4 (c = 1.1, $CHCl_3$); υ_{max}/cm^{-1} 3027, 2955, 1495, 1454, 1250, 1052, 895, 841; δ_H (400 MHz, $CDCl_3$) 7.38–7.15 (5H, m), 3.10–3.04 (1H, m), 2.95–2.75 (2H, m), 2.07–1.85 (2H, m), 0.14 (9H, s), 0.05 (9H, s); δ_C (100 MHz, $CDCl_3$) 141.2, 61.2, 128.5, 128.4, 125.9, 52.1, 33.6, 33.5, 0.6, −1.9; MS (CI$^+$, NH_3) 293 ([M + H]$^+$, 70%), 277 (55%), 201 (70%), 147 (60%), 90 (100%), 73 (40%); HRMS (CI$^+$, NH_3 for [M + H]$^+$) found 293.1745, $C_{16}H_{29}OSi_2$ requires 293.1757.

5-(*tert*-Butyldimethylsiloxy)-1,1-*bis*-(trimethylsilyl)-1,2-epoxypentane (10d). The reaction was performed on 5-(*tert*-butyldimethylsiloxy)-1,2-epoxypentane (216 mg, 1.0 mmol) according to the procedure described for **10a** above to afford 5-(*tert*-butyldimethylsiloxy)-1,1-*bis*-(trimethylsilyl)-1,2-epoxypentane as a pale yellow oil (263 mg, 73%). A second run returned **10d** in 69% yield. $[\alpha]_D^{25}$ −3.4 (c = 1.1, $CHCl_3$); υ_{max}/cm^{-1} 2955, 2858, 1472, 1251, 1101, 838; δ_H (400 MHz, $CDCl_3$) 3.73–3.57 (2H, m), 2.99–2.93 (1H, m), 1.49–1.80 (4H, m), 0.91 (9H, s), 0.14 (9H, s), 0.06 (6H, s), 0.04 (9 H, s); δ_C (100 MHz, $CDCl_3$) 62.7, 61.6, 32.5, 30.4, 30.3, 25.8, 0.2, −1.4, −5.3; MS (CI$^+$, NH_3) 361 ([M + H]$^+$, 95%), 271 (60%), 229 (40%), 164 (35%), 147 (15%), 90 (100%), 73 (20%); HRMS (CI$^+$, NH_3 for [M + H]$^+$) found 361.2400, $C_{17}H_{41}O_2Si_3$ requires 361.2414.

6-Chloro-1,1-*bis*-(trimethylsilyl)-1,2-epoxyhexane (10e). The reaction was performed on 6-chloro-1,2-epoxyhexane (135 mg, 1.0 mmol) according to the procedure described for **10a** above to afford 6-chloro-1,1-*bis*-(trimethylsilyl)-1,2-epoxyhexane as a pale yellow oil (142 mg, 51%). A second run returned **10e** in 49% yield. $[\alpha]_D^{25}$ −2.3 (c = 1.1, $CHCl_3$); υ_{max}/cm^{-1} 2956, 2855, 1451, 1411, 1250, 1052, 840; δ_H (400 MHz, $CDCl_3$) 3.57 (2H, t, J 7.0), 3.00–2.93 (1H, m), 1.63–1.86 (6H, m), 0.14 (9H, s), 0.06 (9H, s); δ_C (100 MHz, $CDCl_3$) 61.6, 52.4, 44.7, 32.3, 30.7, 24.9, 1.2, −1.9; MS (CI$^+$, NH_3) 279 ([M + H]$^+$, 50%), 263 (30%), 164 (35%), 147 (40%), 90 (100%), 73 (35%); HRMS (CI$^+$, NH_3 for [M + H]$^+$) found 279.1364, $C_{12}H_{28}ClOSi_2$ requires 279.1367.

(S)-1,1-*bis*-(Trimethylsilyl)-1,2-epoxydodecane [(S)-10a]. The reaction was performed on (S)-1,2-epoxydodecane (184 mg, 1.0 mmol) according to the procedure described for **10a** above to afford (S)-1,1-*bis*-(trimethylsilyl)-1,2-epoxydodecane as a pale yellow oil (180 mg, 55%). $[\alpha]_D^{25}$ −10.3 (c = 1.0, $CHCl_3$); other data as for racemate **10a**.

(R)-1,1-*bis*-(Trimethylsilyl)-1,2-epoxydodecane [(R)-10a]. The reaction was performed on (R)-1,2-epoxydodecane (184 mg, 1.0 mmol) according to the procedure described for **10a** above to afford (R)-1,1-*bis*-(trimethylsilyl)-1,2-epoxydodecane as a pale yellow oil (155 mg, 47%). $[\alpha]_D^{25}$ + 10.6 (c = 1.0, $CHCl_3$); other data as for racemate **10a**.

1-Hydroxy-1-phenyl-2-trimethylsilyl-2,3-epoxytridecene (12-1 and 12-2; two diastereoisomers, separable). To a solution of ^{s}BuLi (1.2 M in cyclohexane, 1.1 mL, 1.3 mmol) in hexane (10 mL) at −90 °C was added (−)-sparteine **5** (0.30 mL, 1.3 mmol). The reaction mixture was allowed to warm to 0 °C over 5 min and then re-cooled to −90 °C. A solution of 1,2-epoxydodecane (0.184 g, 1.0 mmol) and chlorotrimethylsilane (0.16 mL, 1.3 mmol) in hexane (2 mL) was added dropwise maintaining the internal temperature at −90 °C. After 15 min the mixture was warmed to −50 °C over a period of 5 min. The mixture was stirred at −50 °C for 1 h and then re-cooled to −90 °C and ^{s}BuLi–(−)-sparteine **5** complex (2 mmol) [prepared by adding (−)-sparteine **5** (0.46 mL, 2.0 mmol) dropwise to a solution of ^{s}BuLi (1.2 M in cyclohexane, 1.7 mL, 2.0 mmol) in hexane (8 mL) at −90 °C and allowing the mixture to warm to 0 °C] was added dropwise to the reaction maintaining the internal temperature at −90 °C. After 15 min the mixture was warmed up slowly to −30 °C (*ca.* 4 h). Benzaldehyde (0.2 mL, 2 mmol) was added and the mixture was allowed to warm to room temperature over 18 h. Aqueous 1 N HCl (5 mL) was added dropwise at 0 °C and the layers were separated. The aqueous phase was extracted with Et_2O (3 × 5 mL) and the combined organic phases were washed with brine (5 mL), dried and concentrated *in vacuo*. Purification by flash chromatography (SiO_2, 5% Et_2O in light petroleum) afforded alcohols **12-1** (76 mg, 21%) and **12–2** (56 mg, 16%) as pale yellow oils (combined yield 132 mg, 37%). Data for **12–1**: υ_{max}/cm^{-1} 3469, 2925, 2854, 1248, 1046, 841, 700; δ_H (400 MHz) 7.49–7.28 (5H, m), 4.84 (1H, s), 2.94 (1H, m), 2.17 (1H, s), 1.73–1.28 (18H, m), 0.90 (3H, t, J 7.0), −0.15 (9H, s); δ_C (100 MHz) 141.6, 128.1, 127.5, 126.4, 68.1, 61.1, 59.0, 34.1, 31.9, 30.3, 29.6, 29.5, 28.9, 28.4, 27.4, 22.9, 14.1, −2.6; HRMS (FI$^+$ for M$^+$) found 362.2642, $C_{22}H_{38}O_2Si$ requires 362.2641. Data for **12-2**: υ_{max}/cm^{-1} 3470, 2925, 2855, 1248, 1047, 841, 701; δ_H (400 MHz) 7.43–7.27 (5H, m), 4.77 (1H, s), 3.06 (1H, m), 2.58 (1H, s), 1.69–1.28 (18H, m), 0.89 (3H, t, J 7.0), −0.17 (9H, s); δ_C (100 MHz) 139.9, 128.2, 127.3, 125.8, 74.8, 62.4, 61.9, 31.9, 29.7, 29.7, 29.5, 29.4, 29.3, 28.9, 27.6, 22.7, 14.1, −2.0; HRMS (FI$^+$ for M$^+$) found 362.2629, $C_{22}H_{38}O_2Si$ requires 362.2641.

Stannylation of terminal epoxides: general procedure

To a solution of DBB **6** (162 mg, 0.68 mmol) in hexane (8.5 mL) at −90 °C was added dropwise ^{s}BuLi (1.40 M in cyclohexane, 0.48 mL, 0.67 mmol) and the mixture was allowed to warm to 0 °C over 5 min. On re-cooling to −90 °C, a solution of the appropriate epoxide **1** (0.27 mmol) in hexane (1 mL + 1 mL wash) was added dropwise over a period of 15 min and the mixture was stirred at −90 °C for 1 h. Tributyltin chloride (0.68 mmol) was then added neat in one portion and the mixture was manually agitated at −90 °C for 10 min before warming to 0 °C over 14 h. After quenching with aqueous 0.5 M H_3PO_4 (2.5 mL), the aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organic phases were washed with H_2O (5 mL), brine (5 mL), dried and concentrated *in vacuo*. Purification of the residue by flash chromatography (Florisil® unless otherwise stated, eluent, petrol–Et_2O) gave the α,β-epoxystannane **13**.

***trans*-1-(Tributylstannyl)-1,2-epoxydodecane (13a).** The reaction was performed on 1,2-epoxydodecane (50 mg, 0.27 mmol) according to the general procedure described above but with a 1.5 h lithiation period. Flash chromatography (0.5% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-1,2-epoxydodecane as a colourless oil (100 mg, 78%). υ_{max}/cm^{-1} 2961, 2925, 2865, 2854, 1464, 1416, 1377, 1340, 1263, 1073, 866; δ_H (400 MHz, CDCl$_3$) 2.83–2.79 (1H, m), 2.46 (1H, d, J 3.6, J_{Sn-H} 99), 1.70–1.20 (30H, m), 0.94–0.86 (18H, m); δ_C (100 MHz, CDCl$_3$) 56.2, 52.8, 34.8, 31.9, 29.6, 29.6, 29.5, 29.3, 29.0, 27.0, 26.3, 22.6, 14.1, 13.6, 8.6 (J_{Sn-C} 330); $\delta^{119}{}_{Sn}$ (186 MHz, CDCl$_3$) −33.2; MS (EI$^+$) 474(M$^+$, <1%), 417 (5%), 291 (10%), 235 (42%), 179 (68%), 121 (20%), 69 (20%), 57 (61%), 41 (100%); HRMS (EI$^+$ for M$^+$) found 474.2884, C$_{24}$H$_{50}$OSn requires 474.2884.

***trans*-1-(Tributylstannyl)-1,2-epoxy-9-decene (13b).** The reaction was performed on 1,2-epoxy-9-decene (50 µL, 0.27 mmol) according to the general procedure described above. Flash chromatography (0.5% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-1,2-epoxy-9-decene as a colourless oil (80 mg, 67%). υ_{max}/cm^{-1} 3077, 2956, 2927, 2871, 2854, 1641, 1464, 1416, 1376, 1340, 1292, 1266, 1182, 1145, 1073, 909, 873, 864, 745; δ_H (400 MHz, CDCl$_3$) 5.87–5.75 (1H, m), 5.03–4.90 (2H, m), 2.85–2.77 (1H, m), 2.46 (1H, d, J 3.8, J_{Sn-H} 98), 2.09–2.00 (2H, m), 1.69–1.26 (22H, m), 1.00–0.85 (15H, m); δ_C (100 MHz, CDCl$_3$) 139.1, 114.1, 56.1, 52.8, 34.8, 33.7, 29.4, 29.0, 28.8, 27.3, 26.3, 13.6, 8.7 (J_{Sn-C} 328); $\delta^{119}{}_{Sn}$ (186 MHz, CDCl$_3$) −33.1; MS (CI$^+$, NH$_3$) 462 ([M + NH$_4$]$^+$, 2%), 386 (2%), 308 (100%), 291 (7%), 268 (4%), 252 (3%), 172 (10%), 154 (7%); HRMS (CI$^+$, NH$_3$ for [M + NH$_4$]$^+$) found 462.2751, C$_{22}$H$_{48}$NOSn requires 462.2752.

***trans*-1-(Tributylstannyl)-1,2-epoxy-4-phenyl-butane (13c).** The reaction was performed on 1,2-epoxy-4-phenyl-butane (40 mg, 0.27 mmol) according to the general procedure described above. Flash chromatography (1% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-1,2-epoxy-4-phenylbutane as a colourless oil (86 mg, 72%). υ_{max}/cm^{-1} 3063, 3027, 2957, 2926, 2865, 2845, 1604, 1586, 1496, 1455, 1416, 1376, 1340, 1268, 1181, 1073, 1030, 870, 748, 698; δ_H (400 MHz) 7.32–7.27 (2H, m), 7.24–7.18 (3H, m), 2.91–2.71 (3H, m), 2.48 (1H, d, J 3.7, J_{Sn-H} 96), 2.02–1.81 (2H, m), 1.62–1.40 (6H, m), 1.32 (6H, m), 1.01–0.81 (15H, m); δ_C (100 MHz) 141.6, 128.4, 128.3, 125.9, 55.6, 53.1, 36.6, 32.6, 29.0, 27.3, 13.7, 8.7 (J_{Sn-C} 332); $\delta^{119}{}_{Sn}$ (186 MHz, CDCl$_3$) −33.4; MS (ES$^+$, NH$_3$) 289 ([M + NH$_4$]$^+$, 12%), 308 (42%), 166 (100%); HRMS (ES$^+$ for [M + NH$_4$]$^+$) found 456.2285, C$_{22}$H$_{42}$NOSn requires 456.2283.

1-(Tributylstannyl)-2-cyclododecyl oxirane (13f). The reaction was performed on cyclododecyl ethylene oxide (53 mg, 0.27 mmol) according to the general procedure described above but with a 4 h lithiation period. Flash chromatography (neutral alumina, 0.5% Et$_2$O in light petroleum) afforded 1-(tributylstannyl)-2-cyclododecyl oxirane as a colourless oil (84 mg, 64%). υ_{max}/cm^{-1} 2951, 2929, 2865, 2851, 1470, 1446, 1376, 1346, 1287, 1073, 1023, 960, 847; δ_H (400 MHz) 2.57 (1H, s, J_{Sn-H} 94), 1.84–1.25 (34H, m), 1.05–0.84 (15 H, m); δ_C (100 MHz) 62.6, 61.2, 32.6, 32.1, 29.0, 27.3, 26.2, 26.1, 25.7, 22.7, 22.4, 22.3, 21.1, 21.0, 13.7, 9.6; $\delta^{119}{}_{Sn}$ (186 MHz) −40.7; MS (EI$^+$) 486 (M$^+$, 2%), 429 (4%), 291 (12%), 235 (37%), 179 (65%), 149 (9%), 135 (25%), 121 (50%), 57 (100%); HRMS (EI$^+$ for M$^+$) found 486.2868, C$_{25}$H$_{50}$OSn requires 486.2878.

***trans*-1-(Tributylstannyl)-1,2-epoxy-10-(*tert*-butyldimethylsilyloxy)decane (13h).** The reaction was performed on 10-(*tert*-butyldimethylsiloxy)-1,2-epoxydecane (80 mg, 0.27 mmol) according to the general procedure described above. Flash chromatography (1% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-1,2-epoxy-10-(*tert*-butyldimethylsilyloxy)-decane as a colourless oil (131 mg, 83%). υ_{max}/cm^{-1} 2956, 2928, 2856, 1464, 1412, 1377, 1360, 1255, 1102, 1006, 836, 775; δ_H (400 MHz) 3.60 (2H, t, J 6.6), 2.83–2.79 (1H, m), 2.46 (1H, d, J 3.8), 1.70–1.24 (26H, m), 1.01–0.82 (24H, m), 0.05 (6H, s); δ_C (100 MHz) 63.3, 56.2, 52.8, 34.8, 32.9, 29.6, 29.5, 29.3, 29.0, 27.3, 26.3, 26.0, 25.8, 18.4, 13.7, 8.7 (J_{Sn-C} 328), −5.3; $\delta^{119}{}_{Sn}$ (186 MHz) −33.2; MS (ES$^+$) 594 ([M + NH$_4$]$^+$, 2%), 308 (40%), 287 (100%), 271 (20%), 252 (6%), 229 (15%), 137 (5%), 132 (20%), 91 (30%); HRMS (ES$^+$ for [M + NH$_4$]$^+$) found 594.3727, C$_{28}$H$_{64}$NO$_2$SiSn requires 594.3723.

***trans*-1-(Tributylstannyl)-1,2-epoxy-10-chlorodecane (13i).** The reaction was performed on 1,2-epoxy-10-chlorodecane (52 mg, 0.27 mmol) according to the general procedure described above. Flash chromatography (1% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-1,2-epoxy-10-chlorodecane as a colourless oil (102 mg, 78%). υ_{max}/cm^{-1} 2955, 2928, 2855, 2845, 1464, 1416, 1376, 1340, 1291, 1266, 1073, 1021, 960, 866, 726; δ_H (400 MHz) 3.54 (2H, t, J 6.8), 2.83–2.79 (1H, m), 2.46 (1H, d, J 3.7, J_{Sn-H} 98), 1.82–1.71 (2H, m), 1.68–1.22 (24H, m) 1.02–0.82 (15H, m); δ_C (100 MHz) 56.2, 52.8, 45.1, 34.8, 32.6, 29.5, 29.4, 29.0, 28.8, 27.3, 26.8, 26.3, 13.7, 8.7 (J_{Sn-C} 330); $\delta^{119}{}_{Sn}$ (186 MHz) −33.2; MS (ES$^+$) 498 ([M + NH$_4$]$^+$, 2%), 308 (100%), 291 (27%), 271 (20%), 252 (10%), 208 (58%), 190 (12%), 155 (5%), 138 (7%), 95 (8%); HRMS (ES$^+$ for [M + NH$_4$]$^+$) found 498.2519, C$_{22}$H$_{49}$ClNOSn requires 498.2519.

***trans*-1-(Tributylstannyl)-1,2-epoxyhexane (13j).** The reaction was performed on 1,2-epoxyhexane (33 µL, 0.27 mmol) according to the general procedure described above. Flash chromatography (0.5% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-1,2-epoxyhexane as a colourless oil (74 mg, 70%). υ_{max}/cm^{-1} 2957, 2928, 2872, 2855, 1465, 1416, 1377, 1340, 1292, 1266, 1152, 1072, 1045, 1021, 863, 750; δ_H (400 MHz) 2.86–2.77 (1H, m), 2.46 (1H, d, J 3.8, J_{Sn-H} 97), 1.71–1.24 (18H, m), 1.01–0.83 (18H, m); δ_C (100 MHz) 56.1, 52.8, 34.5, 29.0, 28.5, 27.3, 22.6, 14.0, 13.6, 8.7 (J_{Sn-C} 329); $\delta^{119}{}_{Sn}$ (186 MHz) −33.2; MS (ES$^+$) 408 ([M + NH$_4$]$^+$, 2%), 332 (2%), 308 (100%), 291 (11%), 268 (5%), 252 (5%), 196 (3%), 155 (3%), 118 (3%); HRMS (ES$^+$ for [M + NH$_4$]$^+$) found 408.2280, C$_{18}$H$_{42}$NOSn requires 408.2283.

***trans*-1-(Tributylstannyl)-1,2-epoxy-5-(5,5-dimethyl[1,3]dioxanyl)hexane (13k).** The reaction was performed on 1,2-epoxy-5-(5,5-dimethyl[1,3]dioxanyl)hexane (54 mg, 0.27 mmol) according to the general procedure described above. Flash chromatography (5% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-1,2-epoxy-5-(5,5-dimethyl[1,3]dioxanyl)hexane as a colourless oil (96 mg, 72%). υ_{max}/cm^{-1} 2955, 2922, 2870, 1464, 1416, 1395, 1374, 1273, 1251, 1212, 1153, 1103, 1043, 1022, 872; δ_H (400 MHz) 3.59–3.41 (4H, m), 2.91–2.82 (1H, m), 2.49 (1H, d, J 3.5, J_{Sn-H} 98), 1.97–1.64 (4H, m), 1.62–1.40 (6H, m), 1.37 (3H, s), 1.30 (6H, m), 1.01 (3H, s), 0.99–0.81 (18H, m); δ_C (100 MHz) 98.6, 70.3, 56.1, 52.8, 34.3, 29.9, 29.0, 28.9, 27.3, 22.7, 22.5, 20.4, 13.7, 8.7 (J_{Sn-C} 330); $\delta^{119}{}_{Sn}$ (186 MHz) −33.2; MS (ES$^+$) 491 ([M + H]$^+$, 4%), 337 (8%), 308 (56%), 291 (16%), 252 (6%), 201 (100%), 183 (90%), 129 (37%); HRMS (CI$^+$, NH$_3$ for [M + H]$^+$) found 491.2543, C$_{23}$H$_{47}$O$_3$Sn requires 491.2542.

***trans*-1-(Tributylstannyl)-1,2-epoxy-3-methylbutane (13l).** The reaction was performed on 1,2-epoxy-3-methyl-butane (28 µL, 0.27 mmol) according to the general procedure described above. Flash chromatography (0.5% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-1,2-epoxy-3-methylbutane[24] as a colourless oil (92 mg, 90%). υ_{max}/cm^{-1} 2957, 2928, 2872, 2854, 1464, 1416, 1377, 1288, 1219, 1072, 937, 879; δ_H (400 MHz) 2.62–2.55 (1H, m), 2.53 (1H, d, J 3.8, J_{Sn-H} 98), 1.66–1.22 (13H, m), 1.07 (3H, d, J 6.6), 1.01–0.83 (18H, m); δ_C (100 MHz) 61.8, 51.8, 33.2, 29.0, 27.3, 19.6, 18.3, 13.7, 8.7 (J_{Sn-C} 328); $\delta^{119}{}_{Sn}$ (186 MHz) −32.6; MS (ES$^+$) 394 ([M + NH$_4$]$^+$, 5%), 308 (100%), 291 (10%), 268 (8%), 252 (5%); HRMS (ES$^+$ for [M + NH$_4$]$^+$) found 394.2127, C$_{17}$H$_{40}$NOSn requires 394.2126.

***trans*-1-(Tributylstannyl)-1,2-epoxy-3,3-dimethylbutane (13m).** The reaction was performed on 1,2-epoxy-3,3-dimethylbutane (33 µL, 0.27 mmol) according to the general procedure described above. Flash chromatography (0.5% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-1,2-epoxy-3,3-dimethylbutane as a colourless oil (92 mg, 87%). υ_{max}/cm^{-1} 2956, 2929, 2872, 2855, 1464, 1418, 1377, 1362, 1293, 1072, 937, 881; δ_H (400 MHz) 2.64 (2H, d, *J* 0.8, J_{Sn-H} 99), 1.65–1.42 (6H, m), 1.38–1.26 (6H, m), 1.02–0.83 (24H, m); δ_C (100 MHz) 64.2, 48.7, 31.5, 29.0, 27.3, 25.6, 13.7, 8.6 (J_{Sn-C} 328); $\delta^{119}{}_{Sn}$ (186 MHz) −31.4; MS (ES$^+$) 408 ([M + NH$_4$]$^+$, 5%), 332 (2%), 308 (100%), 291 (8%), 252 (2%); HRMS (ES$^+$ for [M + NH$_4$]$^+$) found 408.2284, $C_{18}H_{42}NOSn$ requires 408.2283.

***trans*-1-(Tributylstannyl)-2-cyclohexyl oxirane (13n).** The reaction was performed on cyclohexyl oxirane (34 mg, 0.27 mmol) according to the general procedure described above. Flash chromatography (0.5% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-2-cyclohexyl oxirane as a colourless oil (82 mg, 73%). υ_{max}/cm^{-1} 2951, 2925, 2852, 1465, 1450, 1418, 1377, 1340, 1259, 1073, 1024, 960, 869; δ_H (400 MHz) 2.60 (1H, dd, *J* 6.6 and 3.8), 2.53 (1H, d, *J* 3.8, J_{Sn-H} 99), 1.99–1.90 (1H, m), 1.80–1.63 (4H, m), 1.62–1.45 (6H, m), 1.38–1.06 (12H, m), 0.94–0.87 (15H, m); δ_C (100 MHz) 60.7, 51.6, 42.8, 30.3, 29.0, 27.3, 26.4, 25.8, 25.6, 13.7, 8.7 (J_{Sn-C} 328); $\delta^{119}{}_{Sn}$ (186 MHz) −32.7; MS (EI$^+$) 416 (M$^+$, 3%), 359 (19%), 291 (35%), 235 (64%), 179 (100%), 121 (14%); HRMS (EI$^+$ for M$^+$) found 416.2097, $C_{20}H_{40}OSn$ requires 416.2096.

(1*S*,2*S*)-1-(Tributylstannyl)-1,2-epoxydodecane (1*S*,2*S*)-13a. The reaction was performed on (*S*)-1,2-epoxydodecane (50 mg, 0.27 mmol) according to the general procedure described above (1 h lithiation period employed in this reaction, unlike the 1.5 h lithiation used in the synthesis of racemic **13a**). Flash chromatography (0.5% Et$_2$O in light petroleum) afforded *trans*-1-(tributylstannyl)-1,2-epoxydodecane as a colourless oil (83 mg, 65%). $[\alpha]^{25}_D$ −27.8 (*c* = 1.0, CHCl$_3$); other data as for racemate **13a**.

(1*S*,2*S*)-1-(Tributylstannyl)-1,2-epoxypropane (13o). The reaction was performed on (*S*)-propylene oxide (19 µL, 0.27 mmol) according to the general procedure described above but with addition of the neat epoxide to frozen ^{s}BuLi–**6** complex at −100 °C, followed by allowing the mixture to warm to −90 °C, before continuing with the general procedure. Flash chromatography (2% Et$_2$O in light petroleum) afforded (1*S*,2*S*)-1-(tributylstannyl)-1,2-epoxypropane as a colourless oil (51 mg, 54%). $[\alpha]^{25}_D$ −43.0 (*c* = 1.0, CHCl$_3$); υ_{max}/cm^{-1} 2957, 2926, 2872, 1464, 1403, 1376, 1267, 1231, 1072, 1039, 842; δ_H (400 MHz) 2.91 (1H, m), 2.43 (1H, d, *J* 3.8, J_{Sn-H} 98), 1.62–1.45 (6H, m), 1.39 (3H, d, *J* 5.1), 1.37–1.21 (6H, m), 0.98–0.85 (15H, m); δ_C (100 MHz) 54.0, 52.0, 29.0, 27.3, 20.3, 13.7, 8.7 (J_{Sn-C} 329); $\delta^{119}{}_{Sn}$ (186 MHz) −33.6; MS (ES$^+$) 366 ([M + NH$_4$]$^+$, 10%), 349 ([M + H]$^+$, 4%), 308 (100%), 291 (16%), 268 (27%), 250 (8%), 196 (4%); HRMS (ES$^+$ for [M + NH$_4$]$^+$) found 366.1818, $C_{15}H_{36}NOSn$ requires 366.1813.

Lithiation–electrophile trapping with carbonyl-based electrophiles:general procedure

To a solution of DBB **6** (162 mg, 0.68 mmol) in hexane (8.5 mL) at −90 °C was added dropwise ^{s}BuLi (1.40 M in cyclohexane, 0.48 mL, 0.67 mmol) and the mixture was allowed to warm to 0 °C over 5 min. On re-cooling to −90 °C, a solution of 1,2-epoxydodecane **1a** (50 mg, 0.27 mmol) in hexane (1 mL + 1 mL wash) was added dropwise over a period of 15 min and the mixture was stirred at −90 °C for 1.5 h. The electrophile (0.68 mmol) was then added neat in one portion [or dropwise in Et$_2$O (1 mL) for solids] and the mixture was manually agitated at −90 °C for 10 min before warming slowly to 0 °C (over 14 h). After quenching with aqueous 0.5 M H$_3$PO$_4$ (2.5 mL), the aqueous layer was extracted with Et$_2$O (3 × 10 mL) and the combined organic phases were washed with H$_2$O (5 mL), brine (5 mL), dried and concentrated *in vacuo*. Purification of the residue by column chromatography (SiO$_2$ unless otherwise stated) gave the substituted epoxide **14**.

(1*RS*,2*RS*,3*RS*)-1-Phenyl-2,3-epoxytridecan-1-ol (14a-1) and (1*SR*,2*RS*,3*RS*)-1-phenyl-2,3-epoxytridecan-1-ol (14a-2). The general procedure was followed using benzaldehyde as the electrophile. Flash chromatography (10% EtOAc in light petroleum) gave the epoxy alcohols **14a-1** and **14a-2** (59 mg, 75% combined yield, dr 1 : 1). Data for **14a-1**: υ_{max}/cm^{-1} 3436 (br, OH), 2955, 2926, 2855, 1494, 1466, 1455, 1198, 1065, 1027, 904, 756 700; δ_H (400 MHz) 7.41–7.31 (5H, m), 4.89 (1H, d, *J* 3.0) 3.19 (1H, td, *J* 6.0, 2.5), 2.99 (1H, t, *J* 3.0), 2.36 (1H, broad s), 1.65–1.15 (18H, m), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 140.1, 129.0, 128.6, 126.8, 71.4, 61.8, 55.6, 32.3, 31.8, 30.0, 29.9, 29.7, 26.3, 23.1, 14.5; MS (ES$^+$) 308 ([M + NH$_4$]$^+$, 100%), 290 (M$^+$, 7%), 273 (13%), 257 (7%), 202 (2%), 170 (2%), 138 (13%), 120 (5%), 105 (5%); HRMS (ES$^+$ for [M + NH$_4{}^+$]$^+$) found 308.2587, $C_{19}H_{34}NO_2$ requires 308.2590. Data for **14a-2**: υ_{max}/cm^{-1} 3432 (br, OH), 2948, 2926, 2854, 1720, 1466, 1453, 1273, 1113, 1026, 908, 841, 735, 700; δ_H (400 MHz) 7.44–7.30 (5H, m), 4.51 (1H, t, *J* 5.0) 3.05 (1H, td, *J* 5.5, 2.5), 2.98 (1H, dd, *J* 5.0, 2.5), 2.49 (1H, d, *J* 5.0), 1.65–1.16 (18H, m), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 140.8, 129.0, 128.5, 126.6, 74.5, 62.7, 57.8, 32.3, 31.8, 30.0, 29.9, 29.7, 26.3, 23.1, 14.5; MS (ES$^+$) 308 ([M + NH$_4$]$^+$, 96%), 290 (M$^+$, 13%), 273 (14%), 257 (100%), 202 (8%), 170 (7%), 138 (33%), 124 (8%), 105 (12%); HRMS (ES$^+$ for [M + NH$_4$]$^+$) found 308.2593, $C_{19}H_{34}NO_2$ requires 308.2590.

(1*RS*,2*RS*,3*RS*)-1-(3-Chlorophenyl)-2,3-epoxytridecan-1-ol (14b-1) and (1*SR*,2*RS*,3*RS*)-1-(3-chlorophenyl)-2,3-epoxytridecan-1-ol (14b-2). The general procedure was followed using 3-chlorobenzaldehyde as the electrophile. Flash chromatography (10% EtOAc in light petroleum) gave the epoxy alcohols **14b-1** and **14b-2** as colourless oils (32 mg of each, 72% combined yield, dr 1 : 1). Data for **14b-1**: υ_{max}/cm^{-1} 3429 (br, OH), 2925, 2855, 1599, 1576, 1467, 1432, 1197, 1100,1077, 884, 786; δ_H (400 MHz) 7.40 (1H, s), 7.32–7.24 (3H, m), 4.85 (1H, d, *J* 2.5), 3.14 (1H, td, *J* 6.0, 2.5), 2.96 (1H, t, *J* 3.0), 2.45 (1H, br s), 1.65–1.14 (18H, m), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 141.7, 134.5, 129.8, 128.3, 126.4, 124.4, 70.3, 61.1, 55.2, 31.9, 31.3, 29.5, 29.3, 29.2, 25.9, 22.7, 14.1; MS (EI$^+$) 326 ([M(^{37}Cl)]$^+$, 6%), 324 ([M(^{35}Cl)]$^+$, 14%), 306 (26%), 289 (7%), 208 (18%), 185 (33%), 183 (100%), 169 (35%), 167 (74%); HRMS (EI$^+$ for [M(^{35}Cl)]$^+$) found 324.1850, $C_{19}H_{29}ClO_2$ requires 324.1851. Data for **14b-2**: υ_{max}/cm^{-1} 3415 (br, OH), 2925, 2855, 1599, 1575, 1467, 1431, 1195, 1100,1078, 901, 785; δ_H (400 MHz) 7.43 (1H, s), 7.32–7.27 (3H, m), 4.49 (1H, t, *J* 5.0), 3.05 (1H, td, *J* 5.5, 2.5), 2.95 (1H, dd, *J* 5.5, 2.5), 2.60 (1H, br s), 1.67–1.17 (18H, m), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 142.3, 134.6, 129.9, 128.2, 126.4, 124.2, 73.3, 62.0, 57.4, 31.9, 31.4, 29.5, 29.3, 25.8, 22.7, 14.1; MS (ES$^+$) 344 ([M(^{37}Cl) + NH$_4$]$^+$, 35%), 342 ([M(^{35}Cl) + NH$_4$]$^+$, 100%), 326 (9%), 308 (10%), 291 (28%), 200 (5%), 139 (5%); HRMS (ES$^+$ for [M(^{35}Cl) + NH$_4$]$^+$) found 342.2196, $C_{19}H_{33}ClNO_2$ requires 342.2194.

(1*RS*,2*RS*,3*RS*)-1-(4-Methoxyphenyl)-2,3-epoxytridecan-1-ol (14c-1) and (1*SR*,2*RS*,3*RS*)-1-(4-methoxyphenyl)-2,3-epoxytridecan-1-ol (14c-2). The general procedure was followed using 4-methoxybenzaldehyde as the electrophile. Flash chromatography (20% EtOAc in light petroleum) gave the epoxy alcohols **14c-1** and **14c-2** as colourless oils (25 mg of each, 57% combined yield, dr 1 : 1). Data for **14c-1**: υ_{max}/cm^{-1} 3435 (br, OH), 2925, 2854, 1613, 1586, 1514, 1465, 1249, 1174, 1037, 907, 832; δ_H (400 MHz) 7.31 (2H, d, *J* 9.0), 6.91 (2H, d, *J* 9.0), 4.84 (1H, br s), 3.82 (3H, s), 3.18 (1H, td, *J* 5.5, 2.5), 2.95 (1H, t, *J* 2.5), 2.26 (1H, d, *J* 1.5), 1.64–1.16 (18H, m), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 159.5, 131.7, 127.8, 114.0, 70.6, 61.3, 55.3, 55.2, 31.9, 31.5, 29.6, 29.5, 29.3, 25.9, 22.7, 14.1; MS (ES$^+$) 338 ([M + NH$_4$]$^+$, 14%), 320 (M$^+$, 7%), 303 (35%), 287 (20%), 168 (100%), 154 (50%), 137 (23%), 121 (12%); HRMS (ES$^+$ for [M + NH$_4$]$^+$) found 338.2687, $C_{20}H_{36}NO_3$ requires 338.2690. Data for **14c-2**: υ_{max}/cm^{-1} 3381 (br, OH), 2955, 2918, 2849, 1613, 1587, 1515, 1469, 1378, 1251, 1177, 1034, 906, 892; δ_H (400 MHz) 7.34 (2H, d, *J* 8.5), 6.91 (2H, d, *J* 8.5), 4.45 (1H, t, *J* 5.0), 3.82 (3H, s), 3.02 (1H, td, *J* 5.5, 2.5), 2.96 (1H, dd, *J* 5.5, 2.5), 2.44–2.39 (1H, m), 1.65–1.16 (18H, m), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 159.4, 132.6, 127.5, 114.0, 73.7, 62.3, 57.3, 55.3, 31.9, 31.4, 29.6, 29.5, 29.3, 25.9, 22.7, 14.1; MS (ES$^+$) 338 ($[M + NH_4]^+$, 8%), 320 (M^+, 7%), 303 (53%), 287 (25%), 168 (60%), 154 (100%), 137 (47%); HRMS (ES$^+$ for $[M + NH_4]^+$) found 338.2686, $C_{20}H_{36}NO_3$ requires 338.2690.

(1*RS*,2*RS*,3*RS*)-1-(2-Furyl)-2,3-epoxytridecan-1-ol and (1*SR*, 2*RS*,3*RS*)-1-(2-furyl)-2,3-epoxytridecan-1-ol 14d (diastereoisomers not separated). The general procedure was followed using 2-furaldehyde as the electrophile. Flash chromatography (15% EtOAc in light petroleum) gave a mixture of diastereoisomeric epoxy alcohols **14d** as a pale brown oil (21 mg, 67% combined yield, dr 1 : 1). υ_{max}/cm^{-1} 3414 (br, OH), 2925, 2855, 1598, 1504, 1467, 1378, 1226, 1149, 1010, 910, 735; δ_H (400 MHz) 7.44–7.41 (1H, m), 6.38–6.36 (2H, m), 4.90 (0.5H, d, *J* 3.5), 4.63 (0.5H, d, *J* 4.5), 3.19 (0.5H, td, *J* 5.5, 2.5), 3.13 (0.5H, dd, *J* 4.5, 2.5), 3.09–3.03 (1H, m), 2.39 (1H, broad s), 1.69–1.19 (18H, m), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 153.5, 152.4, 142.8, 142.5, 110.3, 108.0, 107.0, 67.1, 65.1, 59.8, 58.8, 56.3, 55.5, 31.9, 31.4, 29.6, 29.5, 29.3, 25.9, 22.7, 14.1; MS (ES$^+$) 298 ($[M + NH_4]^+$, 85%), 280 (M^+, 30%), 263 (53%), 249 (91%), 247 (100%), 214 (18%), 202 (20%), 128 (34%), 114 (95%), 111 (42%); HRMS (ES$^+$ for $[M + NH_4]^+$) found 298.2376, $C_{17}H_{32}NO_3$ requires 298.2377.

(1*RS*,2*RS*,3*RS*)-1-(3-Decyl-oxiranyl)-3-phenyl-prop-2-en-1-ol (14e-1) and (1*SR*,2*RS*,3*RS*)-1-(3-decyl-oxiranyl)-3-phenyl-prop-2-en-1-ol (14e-2). The general procedure was followed using *trans*-cinnamaldehyde as the electrophile. Flash chromatography (10% EtOAc in light petroleum) gave the epoxy alcohols **14e-1** and **14e-2** as pale yellow oils (30 and 33 mg respectively, 73% combined yield, dr 1 : 1). Data for **14e-1**: υ_{max}/cm^{-1} 3412 (br, OH), 2956, 2925, 2854, 1601, 1579, 1495, 1467, 1452, 968, 749; δ_H (400 MHz) 7.45–7.23 (5H, m), 6.72 (1H, d, *J* 16.0), 6.19 (1H, dd, *J* 16.0, 6.5), 4.53–4.47 (1H, m), 3.07 (1H, td, *J* 6.0, 2.5), 2.94 (1H, t, *J* 2.5), 2.11 (1H, d, *J* 2.5), 1.67–1.17 (18H, m), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 136.3, 132.7, 128.6, 128.0, 126.7, 126.6, 70.0, 60.2, 55.2, 31.9, 31.5, 29.6, 29.5, 29.4, 29.3, 26.0, 22.7, 14.1; MS (ES$^+$) 334 ($[M + NH_4]^+$, 35%), 316 (M^+, 15%), 299 ($M - OH^+$, 100%), 283 (18%), 208 (13%), 164 (69%), 150 (73%), 133 (22%), 104 (12%); HRMS (ES$^+$ for $[M + NH_4]^+$) found 334.2737, $C_{21}H_{36}NO_2$ requires 334.2741. Data for **14e-2**: υ_{max}/cm^{-1} 3410 (br, OH), 2956, 2925, 2854, 1601, 1495, 1465, 1453, 968, 749; δ_H (400 MHz) 7.44–7.24 (5H, m), 6.72 (1H, d, *J* 16.0), 6.28 (1H, dd, *J* 16.0, 6.0), 4.23–4.17 (1H, m), 3.02 (1H, td, *J* 5.5, 2.5), 2.92 (1H, dd, *J* 5.5, 2.5), 2.15–2.09 (1H, m), 1.64–1.17 (18H, m), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 136.3, 131.9, 128.6, 128.0, 127.4, 126.6, 72.2, 61.1, 56.8, 31.9, 31.5, 29.6, 29.5, 29.4, 29.3, 25.9, 22.7, 14.1; MS (ES$^+$) 334 ($[M + NH_4]^+$, 23%), 316 (M^+, 13%), 299 ($M–OH^+$, 100%), 283 (14%), 208 (11%), 164 (43%), 150 (100%), 133 (32%), 104 (13%); HRMS (ES$^+$ for $[M + NH_4]^+$) found 334.2742, $C_{21}H_{36}NO_2$ requires 334.2741.

(1*RS*,2*RS*,3*RS*)-1-*tert*-Butyl-2,3-epoxytridecan-1-ol (14f-1) and (1*SR*,2*RS*,3*RS*)-1-*tert*-butyl-2,3-epoxytridecan-1-ol (14f-2). The general procedure was followed using pivaldehyde as the electrophile. Flash chromatography (7.5% EtOAc in light petroleum) gave the epoxy alcohols **14f-2** and **14f-2** as colourless oils (27 mg and 25 mg respectively, 70% combined yield, dr 1 : 1). Data for **14f-2**: υ_{max}/cm^{-1} 3469 (br, OH), 2951, 2926, 2855, 1480, 1467, 1364, 1287, 1246, 1216, 1184, 1117, 1052, 1016, 904; δ_H (400 MHz) 3.50 (1H, t, *J* 2.5), 3.03 (1H, td, *J* 5.5, 2.5), 2.87 (1H, t, *J* 3.0), 1.86 (1H, d, *J* 2.0), 1.64–1.21 (18H, m), 0.99 (9H, s), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 75.5, 58.3, 55.0, 34.2, 31.9, 31.7, 29.6, 29.5, 29.3, 26.0, 22.7, 14.1; MS (ES$^+$) 288 ($[M + NH_4]^+$, 100%), 271 ($[M + H]^+$, 5%), 253 (22%), 183 (11%), 129 (4%); HRMS (ES$^+$ for $[M + NH_4]^+$) found 288.2909, $C_{17}H_{38}NO_2$ requires 288.2897. Data for **14f-2**: υ_{max}/cm^{-1} 3397 (br, OH), 2959, 2918, 2852, 1470, 1362, 1318, 1256, 1192, 1100, 1021, 1007, 906, 895; δ_H (400 MHz) 3.08 (1H, dd, *J* 6.0, 5.0), 2.91–2.84 (2H, m), 2.02–1.98 (1H, m), 1.65–1.19 (18H, m), 0.99 (9H, s), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 78.1, 58.5, 57.2, 34.7, 31.9, 31.6, 29.6, 29.5, 29.3, 25.9, 25.8, 22.7, 14.1; MS (ES$^+$) 288 ($[M + NH_4]^+$, 100%), 270 (M^+, 5%), 253 (15%), 183 (10%), 117 (3%); HRMS (ES$^+$ for $[M + NH_4]^+$) found 288.2892, $C_{17}H_{38}NO_2$ requires 288.2897.

(1*SR*,2*RS*,3*RS*)-1-*iso*-Propyl-2,3-epoxytridecan-1-ol (14g-1) and (1*RS*,2*RS*,3*RS*)-1-*iso*-propyl-2,3-epoxytridecan-1-ol (14g-2). The general procedure was followed using *iso*-butyraldehyde as the electrophile. Flash chromatography (10% EtOAc in light petroleum) gave the epoxy alcohols **14g-1** and **14g-2** as colourless oils (18 mg and 16 mg respectively, 56% combined yield, dr 1 : 1). Data for **14g-1**: υ_{max}/cm^{-1} 3446 (br, OH), 2958, 2926, 2855, 1467, 1379, 1367, 1256, 1177, 1153, 1078, 1025, 906; δ_H (400 MHz) 3.62–3.57 (1H, m), 3.02 (1H, td, *J* 5.5, 2.5), 2.82 (1H, t, *J* 3.0), 1.89–1.78 (2H, m), 1.61–1.20 (18H, m), 1.02 (3H, d, *J* 4.0), 1.00 (3H, d, *J* 4.0), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 72.9, 59.6, 54.9, 31.9, 31.7, 31.6, 29.6, 29.5, 29.4, 29.3, 26.0, 22.7, 18.5, 17.8, 14.1; MS (ES$^+$) 274 ($[M + NH_4]^+$, 100%), 256 (M^+, 35%), 240 (70%), 223 (20%), 202 (30%), 158 (12%), 104 (18%); HRMS (ES$^+$ for $[M + NH_4]^+$) found 274.2743, $C_{16}H_{36}NO_2$ requires 274.2741. Data for **14g-2**: υ_{max}/cm^{-1} 3437 (br, OH), 2958, 2926, 2855, 1467, 1380, 1364, 1246, 1148, 1080, 1025, 902; δ_H (400 MHz) 3.17 (1H, q, *J* 6.0), 2.90 (1H, td, *J* 6.0, 2.5), 2.78 (1H, dd, *J* 5.0, 2.5), 1.97–1.93 (1H, m), 1.83 (1H, sextet, *J* 7.0), 1.61–1.21 (18H, m), 1.02 (3H, d, *J* 7.0), 0.98 (3H, d, *J* 7.0), 0.89 (3H, t, *J* 7.0);δ_C (100 MHz) 76.0, 60.3, 57.1, 32.5, 31.9, 31.6, 29.6, 29.5, 29.4, 29.3, 25.9, 22.7, 18.4, 18.1, 14.0; MS (ES$^+$) 274 ($[M + NH_4]^+$, 94%), 256 (M^+, 27%), 240 (35%), 202 (22%), 158 (34%), 104 (37%); HRMS (ES$^+$ for $[M + NH_4]^+$) found 274.2739, $C_{16}H_{36}NO_2$ requires 274.2741.

(2*RS*,3*RS*)-1,1-Diethyl-2,3-epoxytridecan-1-ol (14h). The general procedure was followed using 3-pentanone as the electrophile. Flash chromatography (7.5% EtOAc in light petroleum) gave recovered 1,2-epoxydodecane **1a** (13 mg, 26%) and epoxy alcohol **14h** as a colourless oil (46 mg, 63%). υ_{max}/cm^{-1} 3481 (br, OH), 2963, 2925, 2855, 1464, 1378, 1304, 1262, 898; δ_H (400 MHz) 2.99 (1H, td, *J* 6.0, 2.5), 2.69 (1H, t, *J* 2.5), 1.73 (1H, s), 1.64–1.20 (22H, m), 0.98–0.84 (9H, m); δ_C (100 MHz) 71.0, 62.9, 54.8, 31.9, 31.7, 29.6, 29.5, 29.3, 28.8, 26.1, 22.7, 14.1, 7.6; MS (ES$^+$) 288 ($[M + NH_4]^+$, 100%), 270 (M^+, 8%), 254 (31%), 237 (53%), 170 (11%), 104 (7%); HRMS (ES$^+$ for $[M + NH_4]^+$) found 288.2898, $C_{17}H_{38}NO_2$ requires 288.2897.

(2*RS*,3*SR*)-1-Phenyl-2,3-epoxytridecan-1-one (14i). The general procedure was followed with *N*,*N*-dimethylbenzamide as the electrophile, added as a solution in Et_2O. Flash chromatography (7.5% EtOAc in light petroleum) gave recovered 1,2-epoxydodecane **1a** (15 mg, 30%) and epoxy ketone **14h** as a white amorphous solid (39 mg, 50%). Mp 100–102 °C; υ_{max}/cm^{-1} 2954, 2918, 2850, 1690 (C=O), 1598, 1580, 1469, 1450, 1232, 1077, 877; δ_H (400 MHz) 8.02 (2H, d, *J* 7.5), 7.63 (1H, d, *J* 7.5), 7.51 (2H, d, *J* 7.5), 4.03 (1H, d, *J* 2.0), 3.15 (1H, td, *J* 5.5, 2.0), 1.84–1.66 (2H, m), 1.59–1.20 (16H, m), 0.89 (3H, t, *J* 7.0); δ_C (100 MHz) 194.7, 135.6, 133.8, 128.8, 128.3, 60.1, 57.4, 32.0, 31.9, 29.5, 29.4, 29.3, 25.8, 22.7, 14.1; MS (CI$^+$, NH_3) 289 ($[M + H]^+$, 50%), 273 (100%), 159 (8%), 133 (5%), 120 (12%), 105 (58%); HRMS (CI$^+$, NH_3 for $[M + H]^+$) found 289.2168, $C_{19}H_{29}O_2$ requires 289.2168.

Acknowledgements

We thank the EPSRC for Research Grants (GR/N26302 and GR/S46789/01), the European Union for a Marie Curie Fellowship (HPMF-CT-1999-00264), the EPSRC and GlaxoSmithKline for a CASE award (to N.J.R.), and the EPSRC National Mass Spectrometry Service Centre for mass spectra. We also thank Dr P. O'Brien (York) for initial test samples of ligands **7** and **8**.

References

1 I. Erden, in *Comprehensive Heterocyclic Chemistry II, vol. 1A*, ed. A. R. Katritzky, C. W. Rees and E. F. V. Scriven, Pergamon, Oxford, 1996, pp. 97.

2 (*a*) T. Satoh, *Chem. Rev.*, 1996, **96**, 3303; (*b*) D. M. Hodgson and E. Gras, *Synthesis*, 2002, 1625; (*c*) D. M. Hodgson, K. Tomooka and E. Gras, in *Topics in Organometallic Chemistry: Organolithiums in Enantioselective Synthesis, vol. 5*, ed. D. M. Hodgson, Springer-Verlag, Heidelberg, 2003, pp. 217–250; (*d*) F. Chemla and E. Vrancken, in *The Chemistry of Organolithium Reagents*, ed. Z. Rappoport and I. Marek, Wiley & Sons, New York, 2004, pp. 1165–1242.

3 J. J. Eisch and J. E. Galle, *J. Am. Chem. Soc.*, 1976, **98**, 4646.

4 (*a*) P. Lohse, H. Loner, P. Acklin, F. Sternfeld and A. Pfaltz, *Tetrahedron Lett.*, 1991, **32**, 615; (*b*) T. Satoh, S. Kobayashi, S. Nakanishi, K. Horiguchi and S. Irisa, *Tetrahedron*, 1999, **55**, 2515.

5 D. M. Hodgson, G. P. Lee, R. E. Marriott, A. J. Thompson, R. Wisedale and J. Witherington, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2151.

6 K. M. Morgan and S. Gronert, *J. Org. Chem.*, 2000, **65**, 1461.

7 Preliminary communications: (*a*) D. M. Hodgson and S. L. M. Norsikian, *Org. Lett.*, 2001, **3**, 461; (*b*) D. M. Hodgson and E. H. M. Kirton, *Synlett*, 2004, 1610; (*c*) D. M. Hodgson, N. J. Reynolds and S. J. Coote, *Org. Lett.*, 2004, **6**, 4187.

8 E. Doris, L. Dechoux and C. Mioskowski, *Synlett*, 1998, 337.

9 (*a*) K. M. Bertini Gross, Y. M. Jun and P. Beak, *J. Org. Chem.*, 1997, **62**, 7679; (*b*) J. R. Harrison, P. O'Brien, D. W. Porter and N. M. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1999, 3623; (*c*) P. Scheiber and P. Nemes, *Liebigs Ann. Chem.*, 1994, 1033.

10 (*a*) P. F. Hudrlik and A. M. Hudrlik, in *Advances in Silicon Chemistry, vol 2*, ed. G. L. Larson, JAI Press Inc., Greenwich, 1993, pp. 1; (*b*) G. H. Whitham, in *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations, vol. 4*, ed. I. Fleming, Thieme, Stuttgart, 2001, pp. 633–646.

11 Epoxides **1** in Table 2 were commercially available or prepared according to (*a*) J. A. Elings, R. S. Downing and R. A. Sheldon, *Eur. J. Org. Chem.*, 1999, 837 (entry 3); (*b*) L. H. Yang, A. E. Weber, W. J. Greenlee and A. A. Patchett, *Tetrahedron Lett.*, 1993, **34**, 7035 (entry 4); (*c*) I. Rothberg, L. Schneider, S. Kirsch and R. Ofee, *J. Org. Chem.*, 1982, **47**, 2675 (entry 5); (*d*) T. J. Michnick and D. S. Matteson, *SYNLETT*, 1991, 631 (entries 6–7); (*e*) S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2002, **124**, 1307 (entries 9–10).

12 G. A. Molander and K. Mautner, *J. Org. Chem.*, 1989, **54**, 4042.

13 (*a*) C. Burford, F. Cooke, G. Roy and P. Magnus, *Tetrahedron*, 1983, **39**, 867 (Table 2, entry 6); (*b*) J. D. Warren and Y. Shi, *J. Org. Chem.*, 1999, **64**, 7675 (Table 2, entry 7).

14 (*a*) J. J. Eisch and J. E. Galle, *J. Organomet. Chem.*, 1988, **341**, 293; (*b*) C. Courillon, J. C. Marie and M. Malacria, *Tetrahedron*, 2003, **59**, 9759.

15 D. M. Hodgson, P. J. Comina and M. G. B. Drew, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2279.

16 (*a*) P. C. B. Page and M. J. McKenzie, in *Science of Synthesis: Houben–Weyl Methods of Molecular Transformations, vol. 4*, ed. I. Fleming, Thieme, Stuttgart, 2001, pp. 513; (*b*) A. E. Mattson, A. R. Bharadwaj and K. A. Scheidt, *J. Am. Chem. Soc.*, 2004, **126**, 2314; (*c*) X. Linghu, J. R. Potnick and J. S. Johnson, *J. Am. Chem. Soc.*, 2004, **126**, 3070.

17 (*a*) Y. Ukaji, A. Yoshida and T. Fujisawa, *Chem. Lett.*, 1990, 157; (*b*) C. Agami, L. Dechoux and C. Mioskowski, *Tetrahedron Lett.*, 1997, **38**, 4071.

18 A. Barbero, P. Cuadrado, I. Fleming, A. M. González, F. J. Pulido and A. Sánchez, *J. Chem. Soc., Perkin Trans. 1*, 1995, 1525.

19 D. M. Hodgson, T. J. Buxton, I. D. Cameron, E. Gras and E. H. M. Kirton, *Org. Biomol. Chem.*, 2003, **1**, 4293.

20 J. R. Falck, R. K. Bhatt and K. M. Reddy, *Synlett*, 1997, 481.

21 Epoxides **1** in Table 4 were either commercially available, prepared as described previously (ref. 11, above) or prepared according to: (*a*) 1,2-epoxy-5-(5,5-dimethyl-[1,3]dioxanyl)hexane was prepared in two steps from 5-hexen-2-one (entry 8); (*b*) cyclohexyl oxirane was prepared according to ref. 11*d*, above.

22 Tentative stereochemical assignments for epoxy alcohol diastereoisomers **14** were made by comparison of NMR spectral data with those of structurally similar compounds in the following reports: (*a*) ref. 12 above; (*b*) T. Kawakami, I. Shibata, A. Baba and H. Matsuda, *J. Org. Chem.*, 1993, **58**, 7608; (*c*) A. E. Lurain, P. J. Carroll and P. J. Walsh, *J. Org. Chem.*, 2005, **70**, 448.

23 Trapping of other electrophiles (allyl bromide, MeI, EtOTf, $PhSO_2F$) has so far been unsuccessful.

24 J. A. Soderquist and C. Lopez, *Tetrahedron Lett.*, 1991, **32**, 6305.