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# The Epoxy-Ramberg–Bäcklund Reaction (ERBR): A Sulfone-Based Method for the Synthesis of Allylic Alcohols

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**Keywords:** Epoxy-Ramberg–Bäcklund reaction / Allylic alcohols / Vinyl sulfones / Nucleophilic epoxidation

The epoxy-Ramberg–Bäcklund reaction (ERBR) is outlined, in which α,β-epoxy sulfones are converted into a range of mono-, di- and tri-substituted allylic alcohols, on treatment with base. Modification of this method enabled the preparation of enantio-enriched allylic alcohols following the diastereoselective epoxidation of enantio-enriched vinyl sulfones that were accessed efficiently from the chiral pool. The scope, optimisation and limitations of the ERBR as a method for the preparation of allylic alcohols are discussed.

## Introduction

The base-mediated transformation of sulfones, substituted with a leaving group in the α-position, into regiodefined alkenes – the Ramberg–Bäcklund reaction (Figure 1), is a valuable method for carbon–carbon bond formation.[1–6] Although some control in the geometry of the double bond formed can be achieved, in acyclic examples mixtures of *cis*- and *trans*-alkenes are often formed.[1–6] Typically α-chloro and bromo sulfones, preformed[1–6] or generated in situ,[1–9] are employed and mechanistically this halide leaving group is essential, enabling the rate-determining episulfone ring-closure process to occur.

Although other common leaving groups, e.g. iodide,[1–6,10,11] sulfonate[1–6,12] and sulfinate[1–6,13–17] esters have all been used successfully in Ramberg–Bäcklund-type reactions, not a great deal of research into the use of different leaving groups in this process has been reported.

We envisaged a new variant of the Ramberg–Bäcklund reaction in which the leaving group is incorporated into a three-membered heterocyclic ring (Figure 2) and have described preliminary studies in this area.[18] This process represents a novel variant of the classic Ramberg–Bäcklund reaction enabling the synthesis of allylic alcohols. Alkenes possessing allylic substituents are valuable chemical building blocks and are substrates for important chemical methodologies. Additionally, as a structural motif they are present in a variety of diverse natural products and compounds of biological importance. The key stage in this reaction would involve a favoured 3-*exo*-*tet* ring opening but proceeds via a strained 1-hetero-4-thiaspiro[2.2]pentane transition state. The major advantage of this variant compared to the traditional Ramberg–Bäcklund rearrangement is that the alkene formation is accompanied by the introduction of valuable allylic functionality.

The successful implementation of this process is described herein for the transformation of α,β-epoxy sulfones into a range of allylic alcohols possessing different alkenyl substitution patterns.

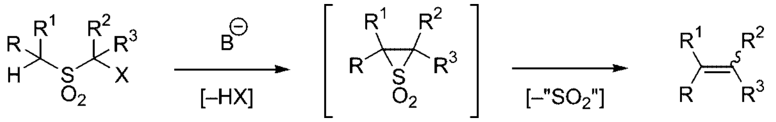

Figure 1. The Ramberg–Bäcklund Reaction [X = Cl, Br etc.; B = Base].

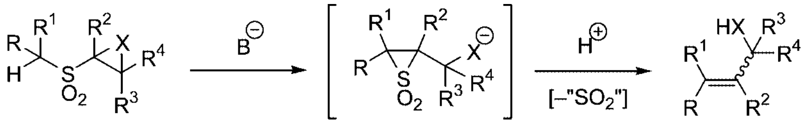

Figure 2. The epoxide (X = O), aziridine (X = NR$^5$) and episulfide (X = S) variants of the Ramberg–Bäcklund reaction.

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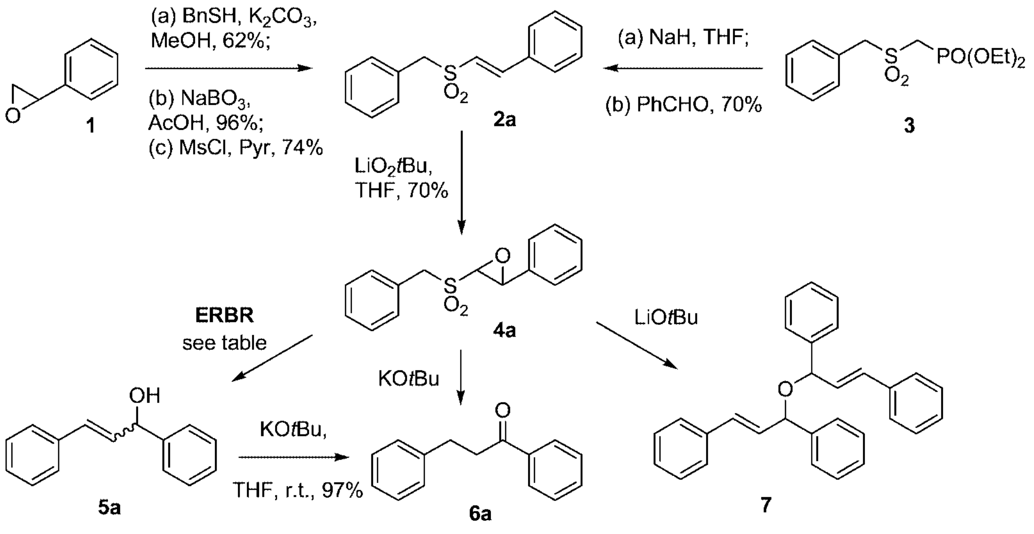
## Results and Discussion

The epoxides required for this study were prepared using the nucleophilic epoxidation of the corresponding vinyl sulfones (α,β-unsaturated sulfones) via the reliable *tert*-butyl hydroperoxide (TBHP)/*n*BuLi procedure reported by Meth-Cohn et al.[19,20] In turn, the vinyl sulfones were prepared following several established protocols.[21,22] Generally, these routes may be broadly grouped into 2 sets; either (a) elimination of β-hydroxy/halo sulfones; or (b) via a Horner–Wadsworth–Emmons reaction between a sulfonyl phosphonate and various aldehydes; this latter method has the advantage of being more convergent (see below).

Initial investigations of the feasibility of the proposed ERBR process involved a study of the behaviour of the epoxide **4a** under basic conditions. This compound was selected because of a combination of its relatively acidic α-benzylic protons and because it was readily prepared by nucleophilic epoxidation of the vinyl sulfone **2a**, which was prepared in turn either (a) by a three-step route from benzyl mercaptan and styrene oxide (**1**) in 44% overall yield; or (b) from benzaldehyde and (benzylsulfonylmethyl)phosphonate **3** in 70% yield. During these optimization studies it became clear that under a variety of basic conditions (Figure 3, Entries 1–5) the desired process was indeed realised, and the hoped-for allylic alcohol **5a** was formed. Thus, the treatment of **4a** with 2 equiv. of LiO*t*Bu in DMSO (Entry 1) initiated a relatively rapid reaction after which **5a** was isolated in 82% yield. However, no double-bond discrimination was observed and a 50:50 mixture of isomers was evident on inspection of the $^1$H NMR spectrum of the unpurified product. Amide bases in THF were also investigated; LHMDS (Entry 2) in particular was found to effectively generate **5a** in yields up to 63% with a selectivity for the *trans*-alkene (*E*:*Z*, 82:18). However, the yields obtained with this base were found to fluctuate. This was in part due to loss of some material from accompanying *O*-silylation of the allylic alcohol **5a** by the base. Other amide bases including LDA (Entry 3), LTMP (Entry 4) and Schlosser's base[23] (Entry 5) all gave the desired product albeit in lower yield than LHMDS, or LiO*t*Bu in DMSO. It became apparent that the use of 2 equiv. of base was optimal, possibly because of the formation of the anion, necessary to form the episulfone, in equilibrium amounts.

Interesting results were obtained when the more standard Ramberg–Bäcklund conditions were employed.[1–6] For example, KO*t*Bu (2 equiv.) in THF (Entry 6) gave the ketone **6a** in good yield. This product apparently arises from an initially successful ERBR affording **5a**, and then this species participates in a precedented allylic anion/enolate isomeris-



| Entry | Conditions | Product, yield (%)[a] | *E*:*Z*[b] |
|---|---|---|---|
| 1 | 2 LiO*t*Bu, DMSO, r.t. | **5a**, 82% | 50:50 |
| 2 | 2 LHMDS, THF, 0 °C to r.t. | **5a**, 63% | 82:18 |
| 3 | 2 LDA, THF, -78 °C to r.t. | **5a**:**4a**, 65:35[b] | 50:50 |
| 4 | 2 LTMP, THF, r.t. | **5a**, 34% | 60:40 |
| 5 | LDA, KO*t*Bu, THF, r.t. | **5a**, 48% | 88:12 |
| 6 | 2 KO*t*Bu, THF, r.t. | **6a**, 65% | — |
| 7 | 2 LiO*t*Bu, THF, r.t. | **7**, 81% | >95:5 |

[a] Yield following purification by flash column chromatography.
[b] Ratio determined by $^1$H-NMR spectroscopy.

Figure 3. Optimisation studies in the ERBR of benzylic α,β-epoxy sulfone **4a**.

ation process.[24] Support for this hypothesis was obtained when the ERBR product **5a** was treated with 1 equiv. of KO*t*Bu in THF, which gave the ketone **6a** in 97% yield after 2 hours. Surprisingly, the identical experiment using LiO*t*Bu did not give this rearrangement – nor did the formally more basic amides. Use of LiO*t*Bu (2 equiv.) in THF (Entry 7) gave the dimer **7** as the sole isolable product in high and reproducible yield as a 1:1 mixture of diastereomers. Following this reaction only the *E*,*E*-allylic ethers were detected, which is perhaps indicative of a delocalised π-allylic intermediate species. The likelihood is that **7** was formed during the work-up procedure as it was found that after partitioning **7** between 1 M HCl and dichloromethane for 1 hour a 1:1 mixture of **7** and **5a** was observed.

In summary, these initial studies indicated that the proposed reaction was indeed viable, but that the presence of the β-phenyl substituent appears to complicate the formation of the desired allylic alcohol.

In order to probe these effects further, we used the Horner–Wadsworth–Emmons reaction[25–27] to obtain variation of the β-substituent whilst maintaining the benzylic sulfonyl moiety. Two alternative methods for the synthesis of the phosphonate **3** are shown in Figure 4.[28,29]

Treatment of **3** with sodium hydride, followed by addition of a variety of aromatic aldehydes gave the requisite vinyl sulfones **2b**–**i** in both high yield and *trans*-stereoselectivity. Epoxidation ($LiO_2tBu$) then gave the corresponding epoxides **4b**–**g**. Interestingly, when the epoxidation reaction was attempted with vinyl sulfones prepared from electron-rich aromatic aldehydes (for example: 2-methoxybenzaldehyde **2h** and furfuraldehyde **2i**) none of the desired epoxide was obtained. In the case of **2h** the vinyl sulfone was recovered, whereas attempted epoxidation of **2i** only resulted in unidentified decomposition products. These observations apparently reflect the diminished electrophilicity of the β-carbon, and/or that the so-formed epoxides are intrinsically unstable.

Application of the optimised ERBR conditions (2 equiv. LiO*t*Bu, THF, 25 °C) to the epoxides **4b**–**g** gave the allylic alcohols **5b**–**g** in moderate to good yield. In these instances, the ERBR processes were found to be generally highly selective for the *E*-isomer (*E*:*Z*, >95:5) and none of the allylic ether dimer **7** (see Figure 3) was encountered. It seems likely that the electron-withdrawing properties of the β-aryl substituents shown in Figure 5 serve to disfavour the allylic carbocation implicated in the formation of **7**.

One anomaly is the 2-pyridyl epoxide **4e**: when treated with LiO*t*Bu this gave a mixture of **5e** (26%, *E*:*Z*, 55:45) and the ketone **6e** (28%), which were separated by flash column chromatography. Based on the previous observation (Figure 3) it seems reasonable to assume that **6e** arises through the allylic anion/enolate isomerisation, facilitated

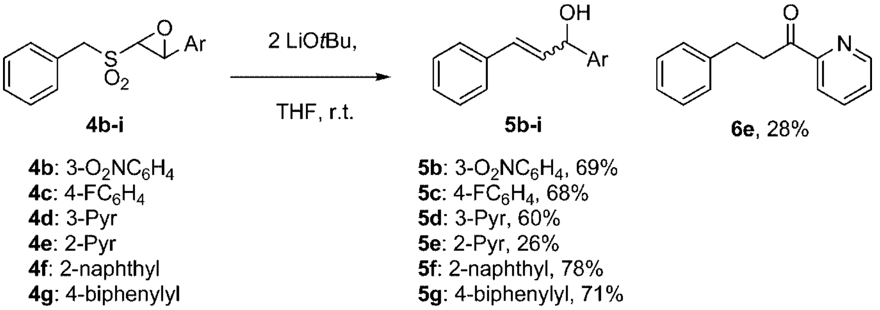


Figure 5. ERBR of benzylic α,β-epoxy aryl sulfones **4b**–**g**.

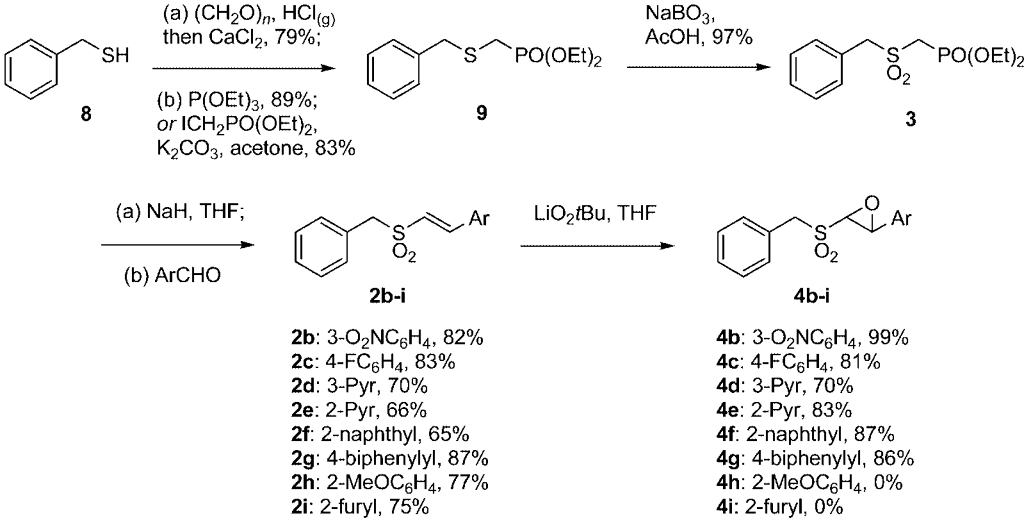


Figure 4. Synthesis of sulfonyl phosphonate **3** and its use in the preparation of aryl α,β-epoxy sulfones **4b**–**g**.

in this instance by the 2-pyridyl heterocycle. Furthermore, the mixture of double-bond isomers encountered, in contrast to the other cases in this series, implies that this tautomerisation may occur more readily on the *trans*-isomer of **5e**.

In order to further demonstrate the scope and limitations of the ERBR as a means of preparing allylic alcohols with different alkenyl substitution patterns, the α,β-epoxy sulfones **4j–m** were prepared by a four-step sequence beginning from the ring opening of an epoxide using benzyl mercaptan (**8**) (Figure 6). It was found that during the preparation of the *cis*-epoxide **4k** the one-pot mesylation–elimination procedure gave a mixture of *cis*- and *trans*-vinyl sulfones (*Z*:*E*, 66:33). However, the modification of this process following the preparation and isolation of the mesylate and subsequent treatment with KO*t*Bu gave the *trans*-vinyl sulfone selectively (see preparation of **4m**). This stereoselective elimination was also observed for the benzylic analogue, enabling the preparation of the *trans*-epoxide **4k** (not shown).

When the α-protons to the sulfonyl group were benzylic, such as in **4j–l**, the ERBR proceeded smoothly and none of the by-products previously ascribed to the β-phenyl group were detected. For example, treatment of *cis*-**4k** with LiO*t*Bu (2 equiv. in THF) gave the corresponding trisubstituted allylic alcohol **5k** in 92% yield as one detectable double-bond isomer. The *trans*-alkene geometry was assigned on the basis of chemical shift values reported in the literature[30] and nOe studies. Similarly, the phenyl derivative **4l** gave the trisubstituted alkene *trans*-**5l** selectively. These examples clearly demonstrate that the particular mechanistic features of the Ramberg–Bäcklund reaction facilitate what is formally an $S_N2$-type process at a tertiary carbon atom to occur during the episulfone formation (see Figure 2).

However, in the case of the epoxide **4m**, which does not possess an activated α-sulfonyl proton, none of the desired alcohol **5m** was detected under the standard LiO*t*Bu ERBR conditions. Use of the stronger base LHMDS did generate the hoped-for product, albeit in low yield.

If the ERBR was to constitute a synthetically useful method for the preparation of allylic alcohols, it was felt that additional structural functionality would need to be compatible with the basic reaction conditions. To this end, the silyl-protected epoxide **4o** and its alcohol precursor **4n** were prepared and their behaviour in the ERBR evaluated. The epoxy sulfones **4n** and **4o** were prepared from **2n** as shown in Figure 7 following the modification of a literature report.[31] On treatment with LiO*t*Bu, compound **4n** gave

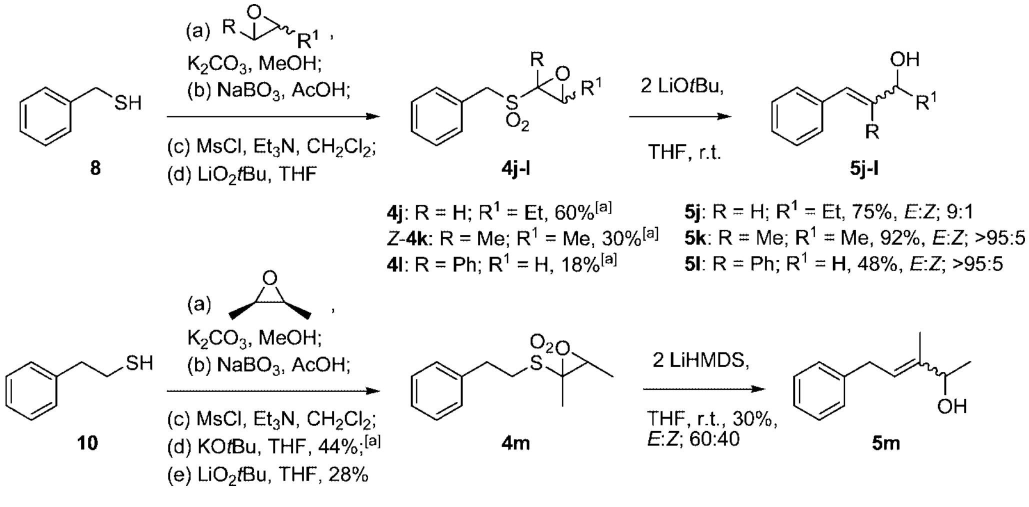


Figure 6. Preparation and ERBR of α,β-epoxy sulfones **4j–m** ([a]: overall yields for four steps).

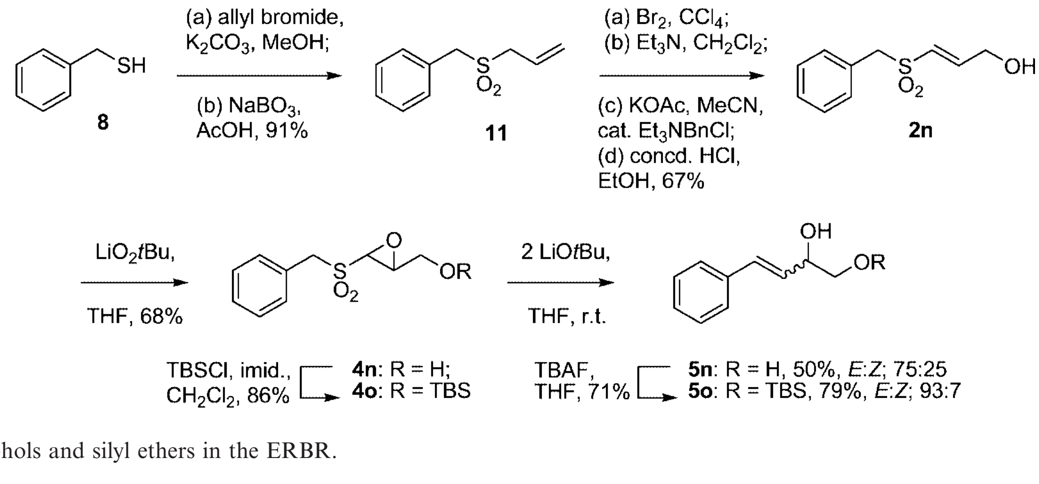


Figure 7. Alcohols and silyl ethers in the ERBR.

the diol **5n** in 50% yield (*E*:*Z*, 75:25), whereas, under identical conditions, **4o** gave **5o** in 79% yield (*E*:*Z*, 93:7). The stereochemical outcome of these processes are noteworthy; presumably the increased steric bulk of the silyl protecting group explains the increased stereoselectivity observed. TBAF removal of the TBS group in **5o** proceeds in high yield with no alteration of double-bond stereochemistry. One plausible explanation for the lower yield observed for the unprotected primary alcohol could be that the base deprotonates the primary alcohol leading to competing Payne-type rearrangement–sulfinate elimination.[20,32]

Moving from the synthesis of secondary allylic alcohols; the synthesis of primary alcohols from terminal epoxides was investigated. Under identical conditions to those described above, **4p** (prepared in four steps from benzyl bromide **12**) gave cinnamyl alcohol (**5p**) as a mixture of isomers (*E*:*Z*, 65:35) in 35% yield. The related epoxide **4q** was prepared from cinnamyl chloride (**13**). In this case, the epoxidation of the intermediate vinyl sulfone which results from **13** was problematic, and only a 19% yield of **4q** was observed. However, **4q** participated in the ERBR and gave the corresponding conjugated alcohol **5q** in 79% yield. Presumably this improvement compared to **4p**, stems from an increased acidity of the α-sulfonyl protons which is, paradoxically the likely explanation for the difficulties associated with the epoxidation. Proton NMR spectroscopy indicated that the *E*-styryl double bond was retained, and that the double bond formed during the Ramberg–Bäcklund process was a mixture of isomers (*E*,*E*:*E*,*Z*; 60:40). The presence of a substituent which increases the sulfonyl acidity is evidently important to the ERBR process: this point is clearly demonstrated by the last example given in Figure 8. In this instance, treatment of **4r**, prepared from the iodide **14**, with LiO*t*Bu, or the more basic LHMDS fails to generate the alcohol **5r** and only the decomposition of the starting material was detected.

In order to further investigate how structural changes to the benzylic position effect the ERBR the vinyl sulfone **2a** was converted into the α-methyl vinyl sulfone **2s**. Treatment of **2s** with $LiO_2tBu$ gave the epoxide **4s** as an undetermined mixture of diastereomers (*de* 33%), which in turn gave the allylic alcohol on treatment with LiO*t*Bu (see Figure 9). It proved necessary to convert this allylic alcohol into the acetate **15** in order to facilitate the purification of the product from remaining starting material. The overall yield of the trisubstituted allylic acetate was 48%, and in this instance equal amounts of *cis*- and *trans*-alkenes were evident by proton NMR spectroscopy. None of the dimeric allylic ether species (see Figure 3) was encountered in this example. Following a slightly different approach, the α-methyl epoxide **4t** was prepared as a 1:1 mixture of diastereomers from *trans*-**4k** following lithiation and quenching of the resultant anion with MeI.[33] Treatment of this mixture with LiO*t*Bu (2 equiv.) gave the tetrasubstituted allylic alcohol, which was converted into the acetate **16** to facilitate the chromatographic separation from the remaining starting material **4t**. The isolated yield was 19% as an undetermined 90:10 mixture of stereoisomers. The lower yields encountered in these examples indicate that the ERBR process is sensitive to substitution at the carbon atom, which is converted into a carbanion during the reaction. Presumably this observation is explained by increased steric hindrance in both these cases.

Currently there is not a generally applicable method available for the enantioselective epoxidation of prochiral vinyl sulfones.[34] Therefore, a route was designed enabling the synthesis of homochiral allylic alcohols using a substrate-controlled diastereoselective epoxidation. The vinyl

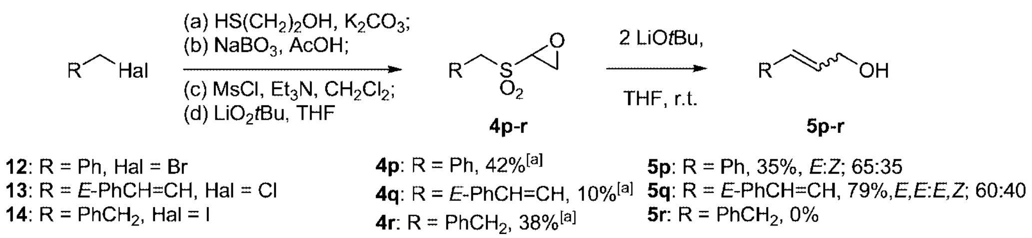


Figure 8. ERBR of terminal α,β-epoxy sulfones **4p** and **4q** ([a]: overall yields for four steps).

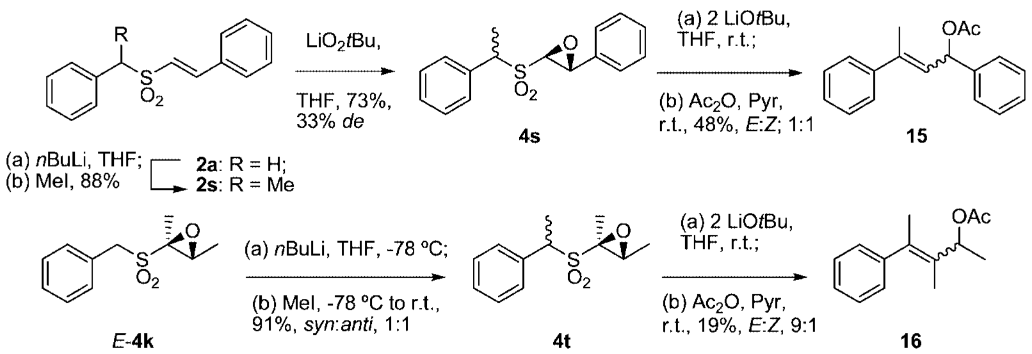


Figure 9. α′-Methylbenzylic α,β-epoxy sulfones **4s** and **4t** in the ERBR.

sulfone **2u**, possessing a γ-oxygen atom was prepared following the Horner–Wadsworth–Emmons reaction of (*R*)-isopropylideneglyceraldehyde, obtained by a Swern oxidation and the phosphonate anion from **3**. This reaction furnished a mixture of geometric isomers (*E*:*Z*, 85:15) in good yield, which were separable by careful flash column chromatography. There is some literature precedent for the diastereoselective epoxidation of similar vinyl sulfones;[35–38] depending on the desired isomer, these reports suggest the use of bulky oxidants with non-oxophilic counterions (i.e. $Na^+$ or $K^+$),[35,36] or manipulation of the γ-oxygen substituent group.[37,38] Thus, the epoxidation of **2u** with Meth-Cohn conditions ($LiO_2t$Bu) gave the epoxide **4u** in good yield but poor diastereoselectivity (*anti*:*syn*, 45:55) (see Figure 10). It is believed that in this case the chelation of the $Li^+$ counterion to the γ-oxygen atom serves to combat the steric repulsion of the approaching oxidant. However, treatment of **2u** with the sodium salt of $Ph_3CO_2H$ gave **4u** in both good yield and diastereoselectivity (80% *de*), from which the *anti*-diastereomer was readily obtained following a single recrystallisation. The ERBR of diastereomerically pure **4u** (LiO*t*Bu, 2 equiv.) gave the allylic alcohol **5u** in 69% yield with no attendant loss in diastereomeric purity. The geometric isomers (*E*:*Z*, 92:8) were separated by recrystallisation and X-ray crystal structural data (see Figure 11)[39] demonstrated the *anti*-relationship between the 2- and 3-oxygenated asymmetric centres, thus confirming the *anti*-selective, sterically controlled epoxidation of **2u**. Removal of the isopropylidene protecting group gave the triol, *anti*-**5v**, whose data corresponded to those reported.[40] By exploiting the balance between steric encumbrance and counterion coordination, the complementary diastereomeric triol, *syn*-**5v** was synthesised. Thus, initial removal of the isopropylidene protecting group and epoxidation ($LiO_2t$Bu) of the diol **2v**, now under coordination control, gave predominantly the *syn*-epoxide **4v** (84%

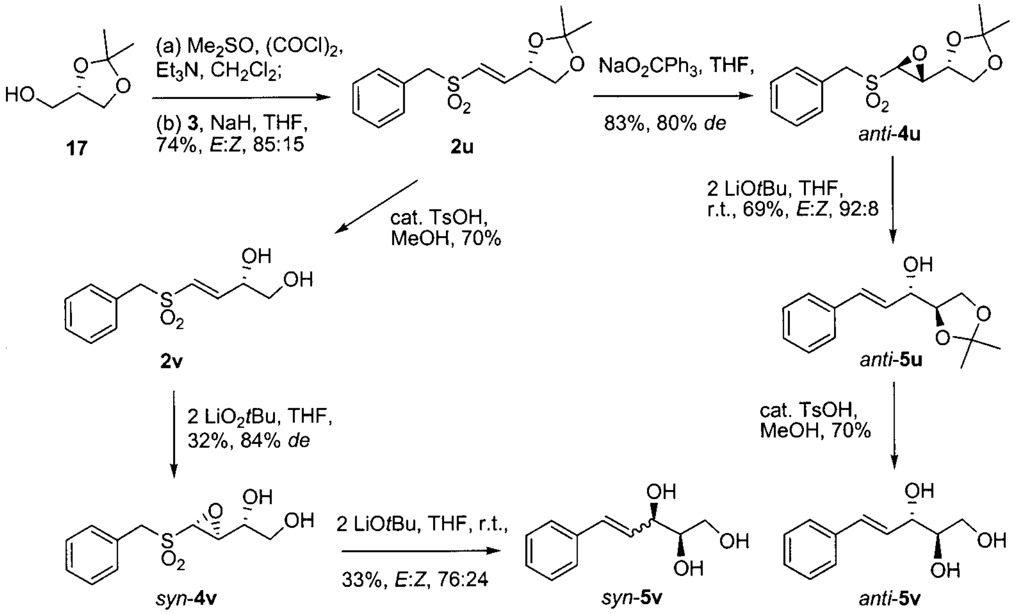


Figure 10. Application of ERBR for the preparation of optically active allylic alcohols.

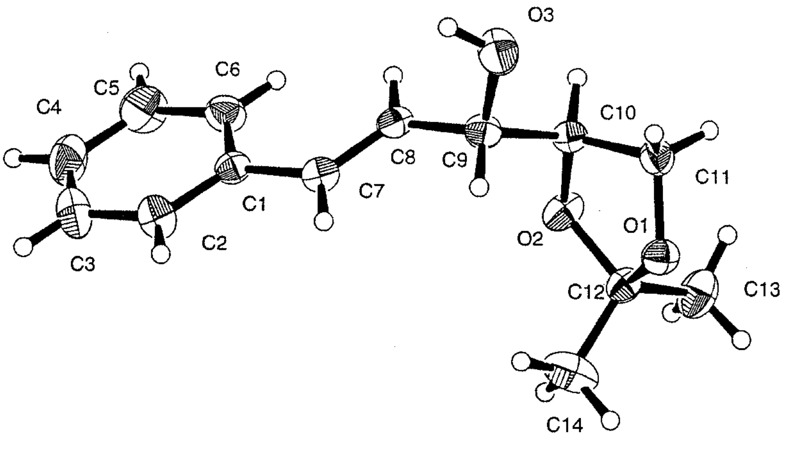


Figure 11. ORTEP representation of *anti*-**5u**.

*de*). Following purification by recrystallisation the Ramberg–Bäcklund reaction under standard conditions gave *syn*-**5v** in low yield. The mixture of geometric isomers proved separable by preparative TLC and comparison of spectral and physical data of the major diastereomeric products, *syn*-**5v** and *anti*-**5v**, demonstrated their non-equivalence.

In summary, the examples discussed demonstrate, that the ERBR is indeed a synthetically viable process, albeit with some limitations. At this stage of optimisation, in order to achieve an efficient conversion, an acidified α-sulfonyl proton is important (represented by the benzylic sulfones used in this study). The compounds studied also indicate that the ERBR is sensitive to substitution patterns around the central α,β-epoxy sulfonyl moiety. For example, it is evident that 1,2-di- and 1,1,2-trisubstituted α,β-epoxy sulfones generate their corresponding alcohols in higher yield than their 1-monosubstituted counterparts; additionally substitution of the α′-position diminishes the yields of ERBR products. Exploration of future applications of this novel technology, particularly in the stereocontrolled synthesis of natural products, is underway in our laboratories.

## Experimental Section

**General Remarks:** The reagents described in the following section were purchased from commercial sources and were used directly. THF was dried with sodium and benzophenone and was distilled prior to use. Similarly, dichloromethane was distilled from over calcium hydride. PE refers to petroleum ether 40–60 °C. Potassium *tert*-butoxide and lithium *tert*-butoxide were used both as solid and as solutions in THF as purchased. LDA and LTMP were generated from dry diisopropylamine and tetramethylpiperidine respectively, via treatment of a THF solution with one equivalent of *n*BuLi at 0 °C. All procedures requiring inert atmospheres were performed in dry glassware under an atmosphere of nitrogen. A dry *tert*-butyl hydroperoxide (TBHP) solution in toluene was prepared from 80% aqueous TBHP by extraction with toluene followed by heating the resultant organic layer at reflux in a Dean–Stark apparatus. The resultant dry TBHP solution was stored under nitrogen at 0 °C and its concentration was calculated from $^1$H NMR spectroscopic analysis.[41,42] TLC analysis was performed using Merck 5554 aluminium backed plates. Compounds were visualised using UV (254 nm) light, iodine, vanillin or a basic aqueous solution of potassium permanganate, where appropriate. Flash column chromatography was performed using ICN 33–64 silica under bellows pressure. Low and high field resolution electron-ionisation (EI) and chemical-ionisation (CI) mass spectrometry were performed with a Fisons Analytical (VG) autospec machine. High resolution molecular ions described are within ± 5 ppm of the required molecular mass. The micro-analytical data quoted are within the margin of error, ± 0.50%, and all data is reported to two decimal places. Infra-red spectroscopy was carried out using a ATI Mattson Genesis FT-IR spectrometer. The samples were either recorded between NaCl plates as neat films, nujol mulls or in solution ($CDCl_3$, or $CHCl_3$). The $^1$H and $^{13}$C NMR spectra were recorded with a Jeol EX270 spectrometer at 270.1 and 67.9 MHz, respectively, at 300.1 MHz and 75.5 MHz with a Bruker AC300 spectrometer and at 500.1 MHz and 125.8 MHz with a Bruker AMX500 spectrometer. The solutions were prepared in suitable deuterated solvents and referencing was accomplished using residual protonated solvent or TMS; all $J$ values are in Hz. Melting points were recorded with a Electrothermal IA9000 Digital Melting Point Apparatus and were uncorrected. Optical rotation values were recorded with a JASCO model DIP-370 digital polarimeter at 20 °C using sodium D line; 589 nm radiation and with units of $10^{-1}$ deg cm$^2$ g$^{-1}$.

**Representative Procedures for the Synthesis of Vinyl Sulfones**

**(a) *trans*-1-Benzylsulfonyl-2-phenylethene (2a):** A dispersion of sodium hydride (60% w/w) in mineral oil (0.40 g, 10.0 mmol, 1 equiv.) was added to a solution of diethyl benzylsulfonylmethylphosphonate (**3**) – prepared as described[43–45] (3.06 g, 10.0 mmol, 1 equiv.) in dry THF (100 mL) under nitrogen at 0 °C. After stirring this mixture for 15 min, benzaldehyde (1.06 g, 1.0 mL, 10.0 mmol, 1 equiv.) was added, and the mixture warmed to room temperature and stirred for a further 1.5 h. Upon disappearance of the starting materials as detected by TLC , saturated aqueous ammonium chloride solution (100 mL) was added to the mixture, which was then extracted into EtOAc (100 mL), washed ($H_2O$, 50 mL) and dried with sodium sulfate, followed by filtration and solvent removal in vacuo yielded the crude product, which was further purified by column chromatography (silica gel, eluted with PE/EtOAc, 4:1) to give **2a** (1.81 g, 70%) as a colourless, crystalline solid, m.p. 142–143 °C [ref.[46] m.p. 145–146 °C] with consistent spectroscopic data.

**(b) *trans*-1-Benzylsulfonyl-2-(3-nitrophenyl)ethene (2b):** Colourless solid; m.p. 186–187 °C [ref.[47] m.p. 184–186 °C] with consistent spectroscopic data.

**(c) *trans*-1-Benzylsulfonyl-2-(4-fluorophenyl)ethene (2c):** Colourless solid; m.p. 170.5–171.5 °C (EtOAc/PE) [ref.[47] m.p. 172–173 °C] with consistent spectroscopic data.

**(d) *trans*-1-Benzylsulfonyl-2-(3-pyridyl)ethene (2d):** Colourless solid; m.p. 145–147 °C (EtOAc). $R_f$ = 0.10 (PE/EtOAc, 4:1). IR (nujol): $\tilde{\nu}$ = 1614, 1568, 1313, 1290, 1124 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 4.34 (s, 2 H), 6.80 (d, $J$ = 15.5 Hz, 1 H), 7.31–7.43 (m, 7 H), 7.71 (dt, $J$ = 2.0, 8.0 Hz, 1 H), 8.63–8.65 (m, 2 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 61.7, 123.8, 126.1, 127.7, 128.1, 128.9, 129.0, 130.8, 134.7, 141.9, 149.8, 151.9 ppm. MS (EI): $m/z$ (%) = 259 (1) [M$^+$], 91 (100) [$C_7H_7^+$]. HRMS: $C_{14}H_{13}NO_2S$ calcd. 259.066701; found 259.066575.

**(e) *trans*-1-Benzylsulfonyl-2-(2-pyridyl)ethene (2e):** Colourless solid; m.p. 119–119.5 °C (EtOAc). $R_f$ = 0.10 (PE/EtOAc, 4:1). IR (nujol): $\tilde{\nu}$ = 1626, 1579, 1304, 1146, 1113. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 4.16 (s, 2 H), 7.10–7.21 (m, 9 H), 7.53 (dt, $J$ = 2.0, 7.5 Hz, 1 H), 8.44–8.46 (m, 1 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 61.4, 125.1, 125.4, 127.6, 128.3, 128.7, 128.8, 130.9, 137.0, 143.6, 150.2, 150.5 ppm. MS (CI): $m/z$ (%) = 260 (6) [MH$^+$], 91 (100) [$C_7H_7^+$]. HRMS: $C_{14}H_{14}NO_2S$ calcd. 260.074526; found 260.074524.

**(f) *trans*-1-Benzylsulfonyl-2-(2-naphthyl)ethene (2f):** Colourless solid; m.p. 161–162 °C (EtOAc). $R_f$ = 0.35 (PE/EtOAc, 4:1). IR (nujol): $\tilde{\nu}$ = 1606, 1311, 1292, 1115cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 4.36 (s, 2 H), 6.80 (d, $J$ = 15.5 Hz, 1 H), 7.39–7.41 (m, 5 H), 7.49–7.61 (m, 4 H), 7.84–7.88 (m, 4 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 62.4, 123.7, 124.3, 127.5, 128.3, 128.4, 128.6, 129.2, 129.3, 129.4, 129.5, 130.1, 131.4, 131.5, 133.55, 135.0, 146.1 ppm. MS (EI): $m/z$ (%) = 308 (15) [M$^+$], 91 (100) [$C_7H_7^+$]. HRMS: $C_{19}H_{16}O_2S$ calcd. 308.087102; found 308.087682.

**(g) *trans*-1-Benzylsulfonyl-2-(4-phenyl)phenylethene (2g):** Colourless solid; m.p. 194–195.5 °C. $R_f$ = 0.30 (PE/EtOAc, 2:1). IR (nujol): $\tilde{\nu}$ = 1622, 1294, 1157, 1119. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 4.35

(s, 2 H), 6.74 (d, $J = 15.5$ Hz, 1 H), 7.40–7.51 (m, 11 H), 7.60–7.66 (m, 4 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta = 61.9$, 123.5, 127.1, 127.7, 128.05, 128.1, 128.9, 129.0, 129.05, 131.0, 131.05, 139.7, 144.1, 145.1. MS (EI): $m/z$ (%) = 334 (9) [$M^+$], 91 (100) [$C_7H_7^+$]. HRMS: $C_{21}H_{18}O_2S$ calcd. 334.102752; found 334.102573.

**(h) *trans*-1-Benzylsulfonyl-2-(2-methoxy)phenylethene (2h):** Colourless solid; m.p. 94–95 °C. $R_f = 0.15$ (PE/EtOAc, 4:1). IR (nujol): $\tilde{\nu}$ = 1597, 1296, 1250, 1111. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta = 3.84$ (s, 3 H), 4.31 (s, 2 H), 6.91–6.99 (m, 3 H), 7.30–7.43 (m, 7 H), 7.61 (d, $J = 15.5$ Hz, 1 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta =$ 55.3, 61.8, 111.2, 120.7, 120.9, 124.7, 128.2, 128.6, 130.8, 130.9, 132.5, 141.2, 158.7 ppm. MS (EI): $m/z$ (%) = 288 (6) [$M^+$], 91 (100) [$C_7H_7^+$]. HRMS: $C_{16}H_{16}O_3S$ calcd. 288.082016; found 288.081964. $C_{16}H_{16}O_3S$ (288.36): calcd. C 66.64, H 5.59; found C 66.66, H 5.40.

**(i) *trans*-1-Benzylsulfonyl-2-(2-furyl)ethene (2i):** Colourless solid; m.p. 130–132 °C. $R_f = 0.15$ (PE/EtOAc, 4:1). IR (nujol): $\tilde{\nu}$ = 1628, 1308, 1257, 1115. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta = 4.30$ (s, 2 H), 6.48 (dd, $J = 2.0$, 3.5 Hz, 1 H), 6.60 (d, $J = 15.0$ Hz, 1 H), 6.64 (d, $J = 3.5$ Hz, 1 H), 7.17 (d, $J = 15.0$ Hz, 1 H), 7.35–7.39 (m, 5 H), 7.50–7.51 (m, 1 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta = 61.8$, 112.5, 117.2, 121.0, 128.0, 128.7, 130.9, 131.5, 145.8, 148.4 ppm. MS (CI): $m/z$ (%) = 266 (100) [$MNH_4^+$]. HRMS: $C_{13}H_{16}NO_3S$ calcd. 266.085090; found 266.085237.

**(j) 2-Benzylsulfanyl-1-phenylethan-1-ol[48,49] and Its Regioisomer 2-Benzylsulfanyl-2-phenylethan-1-ol:[50]** These compounds were prepared from styrene oxide (**1**) and benzyl mercaptan (**8**) according to the procedure described.

**(k) 2-Benzylsulfonyl-1-phenylethan-1-ol:** 2-Benzylsulfanyl-1-phenylethan-1-ol (10.05 g, 41.13 mmol, 1 equiv.) in glacial acetic acid (250 mL) was treated portionwise at room temperature with $NaBO_3\cdot 4H_2O$ (20.12 g, 130.77 mmol, 3.2 equiv.) and stirred for 12 h. The solvent was removed under reduced pressure and the residue was taken up in $H_2O$ (100 mL) and partitioned into EtOAc (100 mL). The resultant aqueous layer was then extracted with EtOAc (3 × 100 mL); the combined organic extracts were washed with $NaHCO_3$ (100 mL), then $H_2O$ (100 mL) and finally brine (100 mL) followed by solvent removal in vacuo to afford the crude sulfone. Recrystallisation from boiling ethanol afforded the title compound (10.89 g, 96%) as a colourless crystalline solid; m.p. 181–182 °C (EtOH). $R_f = 0.05$ (PE/EtOAc, 1:1). IR (nujol): $\tilde{\nu}$ = 3483, 1377, 1175cm$^{-1}$. $^1$H NMR (270.1 MHz, [$D_6$]DMSO): $\delta = 3.19$ (dd, $J = 2.5$, 14.5 Hz, 1 H), 3.48 (dd, $J = 10.0$, 14.5 Hz, 1 H), 4.33 (d, $J = 13.5$ Hz, 1 H), 4.52 (d, $J = 13.5$ Hz, 1 H), 5.12–5.17 (m, 1 H), 7.28–7.44 (m, 10 H) ppm. $^{13}$C NMR (67.9 MHz, [$D_6$]DMSO): $\delta = 59.0$, 59.9, 67.8, 126.0, 127.6, 128.5, 128.7, 131.3, 143.3 ppm. MS (EI): $m/z$ (%) = 276 (1) [$M^+$], 91 (100) [$Bn^+$]. HRMS: $C_{15}H_{16}O_3S$ calcd. 276.0820; found 276.0822. $C_{15}H_{16}O_3S$ (276.35): calcd. C 65.19, H 5.84, S 11.60; found C 65.13, H 5.80, S 11.70.

**(l) *trans*-1-Benzylsulfonyl-2-phenylethene (2a):** 2-Benzylsulfonyl-1-phenylethan-1-ol (1.01 g, 3.65 mmol, 1 equiv.) in dry pyridine (50 mL) was treated with MsCl (0.45 mL, 5.70 mmol, 1.6 equiv.) at 0 °C. The solution was warmed to room temperature and stirring was continued for 12 h. The bulk of the pyridine was removed under reduced pressure and the residue was taken up in EtOAc (50 mL). Partitioning for 0.25 h with $CuSO_4$ (5%, 100 mL) followed by extraction with EtOAc (3 × 50 mL) and washing of the combined organic layers successively with $CuSO_4$ (5%, 25 mL), $H_2O$ (50 mL), brine (50 mL) and drying with $MgSO_4$ gave, on filtration followed by solvent removal in vacuo, the crude vinyl sulfone. Recrystallisation from EtOAc afforded **2a** (0.71 g, 74%) as a colourless crystalline solid with consistent spectroscopic data.[46]

**Representative Procedure for the Synthesis of α,β-Epoxy Sulfones. Meth-Cohn Epoxidation**

**(a) *trans*-1-Benzylsulfonyl-2-phenyloxirane (4a):** *n*-Butyllithium (1.10 mmol, 0.7 mL of a 1.6 M solution in hexanes, 1.1 equiv.) was added to a solution of dry TBHP (1.50 mmol, 0.6 mL of a 2.63 M solution in toluene, 1.5 equiv.) in THF (20 mL) at –78 °C under nitrogen. This solution was stirred for 15 min, before warming to –15 °C. A solution of the vinyl sulfone **2a** (258 mg, 1.00 mmol, 1 equiv.) in dry THF (5 mL) was then added. Stirring was continued for 2 h at –10 to –20 °C, after which time the starting sulfone was judged, by TLC analysis, to be no longer present. Saturated aqueous sodium sulfite (50 mL) was added, and the resultant mixture extracted into ethyl acetate (2 × 100 mL). The combined organic extracts were dried with sodium sulfate. Filtration, concentration in vacuo and column chromatography (eluting with PE/EtOAc, 3:1) gave **4a** (192 mg, 70%) as a colourless crystalline solid. M.p. 145–146 °C. $R_f = 0.30$ (PE/EtOAc, 3:1). IR (nujol): $\tilde{\nu}$ = 1315, 1140, 901, 741, 692cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta = 3.93$ (d, $J = 1.5$ Hz, 1 H), 4.23 (d, $J = 14.0$ Hz, 1 H), 4.39 (d, $J =$ 14.0 Hz, 1 H), 4.43 (d, $J = 1.5$ Hz, 1 H), 7.12–7.43 (m, 10 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta = 56.8$, 58.1, 67.6, 126.1, 126.5, 128.8, 129.2, 129.3, 129.6, 130.9, 132.4 ppm. MS (CI): $m/z$ (%) = 292 (100) [$MNH_4^+$], 276 (7) [$MH^+$], 228 (10), 138 (31), 120 (10), 108 (31), 91 (16). HRMS: $C_{15}H_{14}O_3S$ calcd. 292.1007; found 292.1012. $C_{15}H_{14}O_3S$ (274.33): calcd. C 65.67, H 5.11, S 11.68; found C 65.50, H 5.13, S 11.68.

**(b) *trans*-1-Benzylsulfonyl-2-(3-nitrophenyl)oxirane (4b):** Colourless solid; m.p. 125–126 °C. $R_f = 0.45$ (PE/EtOAc, 1:1). IR (nujol): $\tilde{\nu}$ = 1535, 1352, 1315, 1140, 933, 899cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta = 4.05$ (d, $J = 1.5$ Hz, 1 H), 4.37 (d, $J = 14.0$ Hz, 1 H), 4.50 (d, $J = 14.0$ Hz, 1 H), 4.60 (d, $J = 1.5$ Hz, 1 H), 7.44–7.64 (m, 7 H), 8.06–8.08 (m, 1 H), 8.23 (dt, $J = 2.0$, 7.5 Hz, 1 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta = 55.5$, 58.3, 67.6, 126.2, 129.3, 129.5, 130.0, 130.9, 132.3, 134.9, 148.5 ppm. MS (CI): $m/z$ (%) = 337 (100) [$MNH_4^+$]. HRMS: $C_{15}H_{17}N_2O_5S$ calcd. 337.085819; found 337.085168.

**(c) *trans*-1-Benzylsulfonyl-2-(4-fluorophenyl)oxirane (4c):** Colourless viscous oil. $R_f = 0.30$ (PE/EtOAc, 4:1). IR (nujol): $\tilde{\nu}$ = 1317, 1238, 1142, 906 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta = 3.89$ (d, $J =$ 1.5 Hz, 1 H), 4.24 (d, $J = 14.0$ Hz, 1 H), 4.40 (d, $J = 14.0$ Hz, 1 H), 4.42 (d, $J = 1.5$ Hz, 1 H), 6.94–7.01 (m, 2 H), 7.11–7.19 (m, 2 H), 7.35–7.44 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta =$ 56.3, 58.1, 67.5, 116.0 (d, $J = 20.0$ Hz), 126.5, 128.0, 128.1 (d, $J =$ 12.0 Hz), 129.2, 129.3, 131.0, 159.9 (d, $J = 250.0$ Hz) ppm. MS (CI): $m/z$ (%) = 310 (100) [$MNH_4^+$]. HRMS: $C_{15}H_{17}FNO_3S$ calcd. 310.091319; found 310.091713.

**(d) *trans*-1-Benzylsulfonyl-2-(3-pyridyl)oxirane (4d):** Colourless viscous oil. $R_f = 0.30$ (PE/EtOAc, 1:1). IR (nujol): $\tilde{\nu}$ = 1319, 1144, 906, 829 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta = 4.04$ (d, $J =$ 1.5 Hz, 1 H), 4.34 (d, $J = 14.0$ Hz, 1 H), 4.49 (d, $J = 14.0$ Hz, 1 H), 4.53 (d, $J = 1.5$ Hz, 1 H), 7.30 (dd, $J = 5.0$, 8.0 Hz, 1 H), 7.43–7.54 (m, 6 H), 8.51 (d, $J = 1.5$ Hz, 1 H), 8.61 (dd, $J = 1.5$, 5.0 Hz, 1 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta = 54.9$, 58.3, 67.3, 123.5, 126.3, 128.5, 129.3, 129.4, 130.9, 133.7, 147.9, 150.8 ppm. MS (CI): $m/z$ (%) = 276 (6) [$MH^+$]. HRMS: $C_{14}H_{14}NO_3S$ calcd. 276.069440; found 276.069416.

**(e) *trans*-1-Benzylsulfonyl-2-(2-pyridyl)oxirane (4e):** Colourless viscous oil. $R_f = 0.30$ (PE/EtOAc, 1:1). IR (nujol): $\tilde{\nu}$ = 1325, 1146, 1124, 916, 773 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta = 4.28$ (d, $J = 14.0$ Hz, 1 H), 4.41 (d, $J = 14.0$ Hz, 1 H), 4.45 (d, $J = 1.5$ Hz, 1 H), 4.50 (d, $J = 1.5$ Hz, 1 H), 7.20–7.45 (m, 7 H), 7.65 (dt, $J =$ 2.0, 8.0 Hz, 1 H), 8.50 (ddd, $J = 1.0$, 2.0, 4.5 Hz, 1 H) ppm. $^{13}$C

NMR (67.9 MHz, $CDCl_3$): $\delta$ = 56.3, 58.2, 66.5, 123.2, 124.4, 126.3, 129.2, 129.25, 131.0, 136.9, 151.3 ppm. MS (CI): *m*/*z* (%) = 276 (100) [$MH^+$]. HRMS: $C_{14}H_{14}NO_3S$ calcd. 276.069440; found 276.069647.

**(f) *trans*-1-Benzylsulfonyl-2-(2-naphthyl)oxirane (4f):** Colourless viscous oil. $R_f$ = 0.35 (PE/EtOAc, 4:1). IR (nujol): $\tilde{\nu}$ = 1315, 1138, 896 cm$^{-1}$. $^1H$ NMR (270.1 MHz, $CDCl_3$): $\delta$ = 4.12 (d, *J* = 1.5 Hz, 1 H), 4.35 (d, *J* = 14.0 Hz, 1 H), 4.52 (d, *J* = 14.0 Hz, 1 H), 4.68 (d, *J* = 1.5 Hz, 1 H), 7.22 (dd, *J* = 1.5, 8.0 Hz, 1 H), 7.45–7.56 (m, 7 H), 7.79–7.85 (m, 4 H) ppm. $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 57.1, 58.2, 67.7, 122.3, 126.5, 126.7, 126.8, 127.0, 127.8, 127.9, 128.8, 129.2, 129.3, 129.7, 131.0, 132.8, 133.8 ppm. MS (CI): *m*/*z* (%) = 342 (100) [$MNH_4^+$]. $C_{19}H_{20}NO_3S$ calcd. 342.116391; found 342.117169.

**(g) *trans*-1-Benzylsulfonyl-2-(4-biphenylyl)oxirane (4g):** Colourless solid; m.p. 155–160 °C. $R_f$ = 0.40 (PE/EtOAc, 2:1). IR (nujol): $\tilde{\nu}$ = 1315, 1140, 908 cm$^{-1}$. $^1H$ NMR (270.1 MHz, $CD_3COCD_3$): $\delta$ = 4.26 (d, *J* = 1.5 Hz, 1 H), 4.44 (d, *J* = 14.0 Hz, 1 H), 4.54 (d, *J* = 14.0 Hz, 1 H), 4.55 (d, *J* = 1.5 Hz, 1 H), 7.28–7.41 (m, 10 H), 7.53–7.60 (m, 4 H) ppm. MS (EI): *m*/*z* (%) = 350 (10) [$M^+$], 91 (100) [$C_7H_7^+$]. HRMS: $C_{21}H_{18}O_3S$ requires 350.097666; found 350.098381.

### General ERBR Procedures

**(a) 1,3-Diphenyl-2-propen-1-ol (5a):** A solution of LHMDS in THF (0.88 mL, 1.0 M, 0.88 mmol, 1.9 equiv.) was added dropwise to a solution of **4a** (128 mg, 0.467 mmol, 1 equiv.) in THF (15 mL), at 25 °C under nitrogen. Stirring was continued for 12 h before saturated $NH_4Cl$ (15 mL) was added, followed by extraction into EtOAc (3 × 50 mL). The combined organic layers were washed with brine (20 mL) and dried with $MgSO_4$. Filtration and solvent removal in vacuo gave the crude product, which was purified by column chromatography (PE/EtOAc, 4:1) to yield the allylic alcohol **5a** (62 mg, 63%) as a viscous yellow oil (*E*:*Z*, 65:35) whose data was consistent to that reported.[51]

**(b)** A solution of **4a** (52 mg, 0.189 mmol, 1 equiv.) in dry DMSO (5 mL) was treated at 25 °C with LiO*t*Bu in THF (0.38 mL, 1.0 M, 0.38 mmol, 2 equiv.). Stirring was continued for 2 h. Water (10 mL) was added and extraction was carried out with EtOAc (3 × 20 mL). The combined organic extracts were washed with water (20 mL), brine (20 mL) and dried with $MgSO_4$. Filtration and solvent removal under reduced pressure afforded the crude material which was purified by column chromatography (PE/EtOAc, 4:1). The allylic alcohol **5a** (32 mg, 82%) was obtained as a yellow oil (*E*:*Z*, 50:50).

**(c) 1,3-Diphenyl-1-propanone (6a):** Under nitrogen, **4a** (161 mg, 0.587 mmol, 1 equiv.) in THF (12 mL) was treated dropwise with KO*t*Bu in THF (1.2 mL, 1.0 M, 1.2 mmol, 2 equiv.) at –78 °C. Stirring was continued for 2 h before the reaction mixture was warmed to room temperature and stirring was continued for 12 h before saturated $NH_4Cl$ (10 mL) was added. The resultant mixture was extracted with EtOAc (3 × 25 mL), and the combined organic extracts were washed with brine (50 mL) and dried with $MgSO_4$. The resultant yellow oil obtained after filtration and solvent removal under reduced pressure was purified by flash column chromatography (PE/EtOAc, 3:1) to yield the ketone **6a** (87 mg, 71%) as a colourless solid; m.p 66.5–67.5 °C [ref.[52] m.p. 68–70 °C] whose data was consistent.

**(d) Bis(1,3-diphenyl-3-propenyl) Ether (7):** A solution of **4a** (250 mg, 0.91 mmol, 1 equiv.) in THF (20 mL) was treated with LiO*t*Bu in THF (1.82 mL, 1.0 M, 1.82 mmol, 2 equiv.) dropwise at 25 °C. Stirring was continued for 12 h. Saturated $NH_4Cl$ (15 mL) was added and the mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine (20 mL) and dried with $Na_2SO_4$. Purification of the crude residue obtained after filtration and solvent removal in vacuo by column chromatography (PE/EtOAc, 19:1) furnished the allylic ether **7** (148 mg, 81%) as an inseparable mixture (1:1) of diastereomers. $R_f$ = 0.20 (PE/EtOAc, 19:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3084, 3061, 3028, 2956, 2908, 2856, 1599, 1495, 1450 cm$^{-1}$. $^1H$ NMR (500.1 MHz $CDCl_3$): $\delta$ = 5.11 (d, *J* = 7.0 Hz, 1 H), 5.13 (d, *J* = 7.0 Hz, 1 H), 6.36 (dd, *J* = 7.0, 16.0 Hz, 1 H), 6.38 (dd, *J* = 7.0, 16.0 Hz, 1 H), 6.61 (d, *J* = 16.0 Hz, 1 H), 6.63 (d, *J* = 16.0 Hz, 1 H), 7.23–7.47 (m, 20 H) ppm. $^{13}C$ NMR (67.9 MHz $CDCl_3$): $\delta$ = 79.1, 79.2, 126.6, 127.1, 127.6, 127.7, 127.9, 128.3, 128.5, 130.3, 130.4, 131.4, 131.5, 136.6, 141.1, 141.2 ppm. MS (CI): *m*/*z* (%) = 420 (5) [$MNH_4^+$], 404 (6) [$MH^+$], 193 (100) [$C_{15}H_{13}^+$]. HRMS: $C_{30}H_{30}NO$ calcd. 420.2327; found, 420.2326.

**(e) *trans*-1-(3-Nitrophenyl)-3-phenylprop-2-en-1-ol (5b):** Pale yellow solid; m.p. 45–47 °C [ref.[53] m.p. 46–47 °C] whose data was consistent with literature.

**(f) *trans*-1-(4-Fluorophenyl)-3-phenylprop-2-en-1-ol (5c):** Colourless clear oil.[54] $R_f$ = 0.20 (DCM). IR (film): $\tilde{\nu}$ = 3361, 1603, 1508, 1223, 1157, 966, 744, 692 cm$^{-1}$. $^1H$ NMR (270.1 MHz, $CDCl_3$): $\delta$ = 2.41 (br. s, 1 H), 5.29 (d, *J* = 6.5 Hz, 1 H), 6.28 (dd, *J* = 6.5, 16.0 Hz, 1 H), 6.60 (d, *J* = 16.0 Hz, 1 H), 7.00 (t, *J* = 8.5 Hz, 2 H), 7.17–7.36 (m, 7 H) ppm. $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 74.4, 115.4 (d, *J* = 20.5 Hz), 126.6, 127.9, 128.0 (d, *J* = 8.0 Hz), 128.6, 130.7, 131.3, 136.3, 138.4 (d, *J* = 3.0 Hz), 162.2 (d, *J* = 245.0 Hz) ppm. MS (EI): *m*/*z* (%) = 228 (39) [$M^+$], 209 (6), 133 (7), 123 (100), 115 (7), 105 (22), 95 (15), 77 (17), 51 (9). HRMS: $C_{15}H_{13}FO$ calcd. 228.0950; found 228.0951.

**(g) *trans*-3-Phenyl-1-(3-pyridyl)prop-2-en-1-ol (5d):** Yellow oil whose data was consistent with literature.[55]

(h) ***cis*/*trans*-3-Phenyl-1-(2-pyridyl)prop-2-en-1-ol (5e):** Isolated as colourless oils whose data was consistent with their assigned structures.[56] **3-Phenyl-1-(2-pyridyl)propan-1-one (6e):** Isolated as a colourless oil whose data was consistent with the assigned structure.[57]

**(i) *trans*-1-(2-Naphthyl)-3-phenylprop-2-en-1-ol (5f):** Colourless oil. $R_f$ = 0.35 (PE/EtOAc, 4:1). IR (film): $\tilde{\nu}$ = 3419, 3057, 2856, 1599, 1495, 1448 cm$^{-1}$. $^1H$ NMR (270 MHz, $CDCl_3$): $\delta$ = 5.49 (d, *J* = 6.5 Hz, 1 H), 6.39 (dd, *J* = 6.5, 16.0 Hz, 1 H), 6.67 (d, *J* = 16.0 Hz, 1 H), 7.17–7.49 (m, 8 H), 7.59–7.82 (m, 4 H) ppm. $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 75.2, 124.5, 124.9, 126.0, 126.2, 126.6, 127.7, 127.8, 128.0, 128.4, 128.6, 130.8, 131.3, 133.3, 133.6, 136.5, 140.1 ppm. MS (EI): *m*/*z* (%) = 260 (25) [$M^+$], 155 (100) [$C_{11}H_7O^+$]. HRMS: $C_{19}H_{16}O$ calcd. 260.120115; found 260.120375.

**(j) *trans*-3-Phenyl-1-[(4-phenyl)phenyl]prop-2-en-1-ol (5g):** Colourless solid. m.p. 107–108 °C. $R_f$ = 0.40 (PE/EtOAc, 2:1). IR ($CHCl_3$): $\tilde{\nu}$ = 3413, 3028, 1599, 1487, 1448 cm$^{-1}$. $^1H$ NMR (270 MHz, $CDCl_3$): $\delta$ = 5.46 (d, *J* = 6.5 Hz, 1 H), 6.44 (dd, *J* = 6.5, 16.0 Hz, 1 H), 6.75 (d, *J* = 16.0 Hz, 1 H), 7.24–7.64 (m, 14 H) ppm. $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 74.9, 126.6, 126.8, 127.1, 127.4, 127.5, 127.8, 128.6, 128.8, 130.7, 131.4, 136.6, 140.7, 140.9, 141.8 ppm. MS (EI): *m*/*z* (%) = 286 (50) [$M^+$], 181 (100) [$C_{13}H_9O^+$]. HRMS: $C_{21}H_{18}O$ calcd. 286.135765; found 286.134779.

### Preparation of Allylic Alcohols 5j–m

**(a) 3-Benzylsulfanylbutan-2-ol:** Prepared from *cis*-2,3-epoxybutane following a literature procedure.[58]

**(b) 3-Benzylsulfonylbutan-2-ol:** Colourless solid; m.p. 68.5–69 °C ($Et_2O$) [ref.[59] m.p. 60 °C] data consistent with the assigned structure.

**(c) *cis*/*trans*-2-Benzylsulfonyl-2-butene:** A solution of 3-benzylsulfonylbutan-2-ol (1.66 g, 7.26 mmol, 1 equiv.) in DCM (30 mL) and methanesulfonyl chloride (0.69 mL, 8.71 mmol, 1.2 equiv.) were treated at 0 °C dropwise with triethylamine (1.52 mL, 10.91 mmol, 1.5 equiv.). The reaction mixture was warmed to room temperature and after 3 h the second portion of triethylamine (4.56 mL, 32.67 mmol, 4.5 equiv.) was added. After a further 1 h distilled water (50 mL) was added, and the resultant aqueous layer was extracted with DCM (3 × 50 mL). Washing of the combined organic layers with brine (100 mL) and drying with $MgSO_4$ afforded crude material which was purified by flash column chromatography (PE/EtOAc, 1:1) affording the title compound (1.23 g, 81%) as a clear oil containing a mixture of stereoisomers ($Z^*$:$E^\#$, 3:1). $R_f$ = 0.50 (PE/EtOAc, 1:1). IR (film): ṽ = 3064, 3034, 2978, 2926, 1651, 1497, 1456, 1304, 1113 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.72–1.77$^{*\#}$ (m, 3 H), 1.87–1.92$^{*\#}$ (m, 3 H), 4.17* (s, 2 H), 4.19$^\#$ (s, 2 H), 6.21$^\#$ (qq, $J$ = 1.5, 7.5 Hz, 1 H), 6.52* (qq, $J$ = 1.5, 7.0 Hz, 1 H), 7.28–7.38 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 12.0, 14.1, 14.6, 20.7, 59.1, 60.3, 128.1, 128.5, 128.6, 128.7, 128.75, 130.6, 130.8, 134.2, 135.1, 139.5, 140.2 ppm. MS (CI): $m/z$ (%) = 228 (100) [$MNH_4^+$]. HRMS: $C_{11}H_{18}NO_2S$ calcd. 228.1058; found 228.1064. * Corresponds to the *cis*-stereoisomer; $^\#$ corresponds to the *trans*-stereoisomer whose data has been reported.[60]

**(d) *trans*-2-Benzylsulfonyl-2-butene:** Prepared as a single stereoisomer following isolation of the intermediate mesylate and subsequent treatment with KO*t*Bu. The data for the resultant clear oil was consistent with that described;[60] b.p. 200 °C/1 Torr. $R_f$ = 0.55 (PE/EtOAc, 1:1).

**(e) *cis*-2-Benzylsulfonyl-2,3-dimethyloxirane (4k):** Following the representative Meth-Cohn epoxidation procedure described **4k** was prepared from the mixture of isomeric vinyl sulfones. A toluene solution of TBHP (3.16 M, 4.21 mL, 13.31 mmol, 2 equiv.) was dissolved in THF (40 mL) and treated with *n*BuLi (2.5 M) in hexanes (2.93 mL, 7.32 mmol, 1.1 equiv.) at –78 °C. The mixture of sulfones (1.40 g, 6.66 mmol, 1 equiv.) [$Z$:$E$, 66:33] in THF (30 mL) was then added to the $LiO_2t$Bu solution via cannula. The temperature was raised to –10 °C and stirring was continued for 3 h. Solid $Na_2SO_3$ (ca. 1 g) was added, and the reaction mixture was stirred for a further 0.25 h. Filtration through kieselgur, washing with diethyl ether (2 × 100 mL), concentration in vacuo and purification by flash column chromatography (PE/EtOAc, 1:1, $R_f$ = 0.50) gave an oil which solidified on cooling (1.00 g, 66%). Further purification by recrystallisation afforded the *cis*-epoxide **4k** (0.72 g, 48%) as a colourless solid, m.p. 90 °C (EtOAc/PE). $R_f$ = 0.30 (PE/EtOAc, 3:1). IR (KBr): ṽ = 3080, 3040, 2990, 2920, 1305, 1110 cm$^{-1}$. $^1$H NMR (300.1 MHz, $CDCl_3$): $\delta$ = 2.28 (d, $J$ = 5.0 Hz, 3 H), 2.63 (d, $J$ = 6.0 Hz, 3 H), 3.15 (m, 1 H), 4.22 (d, $J$ = 13.0 Hz, 1 H), 4.38 (d, $J$ = 13.0 Hz, 1 H), 7.30–7.49 (m, 5 H) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta$ = 13.3, 19.4, 58.0, 62.9, 73.4, 126.4, 129.0, 129.1, 131.2 ppm. MS (CI): $m/z$ (%) = 244 (100) [$MNH_4^+$]. HRMS: $C_{11}H_{18}NO_3S$ requires 244.1007; found 244.1004. $C_{11}H_{14}O_3S$ (226.29): calcd. C 58.38, H 6.23; found C 58.58, H 6.47.

**(f) *trans*-2-Benzylsulfonyl-2,3-dimethyloxirane (4k):** The *trans*-vinyl sulfone (3.85 g, 18.0 mmol, 1 equiv.) in THF (100 mL) was added to a solution of $LiO_2t$Bu generated from TBHP in toluene (3.16 M, 8.7 mL, 27.0 mmol, 1.5 equiv.) and *n*BuLi in hexanes (1.6 M, 12.6 mL, 20.0 mmol, 1.1 equiv.) in THF (100 mL) at –78 °C. Stirring was continued for 12 h at room temperature. $^1$H NMR spectroscopic analysis of the crude material obtained after standard celite work-up indicated incomplete conversion. Therefore, the mixture was treated again with $LiO_2t$Bu generated from TBHP in toluene (2.55 M, 4.3 mL, 11.0 mmol, 0.6 equiv.); *n*BuLi in hexanes (1.6 M, 5.7 mL, 9.15 mmol, 0.5 equiv.) at –78 °C to room temperature. Stirring was continued for 24 h before work-up and flash column chromatography (PE/EtOAc, 3:1) afforded the *trans*-epoxide **4k** (1.21 g, 29%) as a colourless viscous oil. $R_f$ = 0.30 (PE/EtOAc, 3:1). IR ($CDCl_3$): ṽ = 3072, 2982, 2930, 1496, 1456, 1321, 1305, 1155, 1104 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.41 (d, $J$ = 5.5 Hz, 3 H), 1.61 (s, 3 H), 3.83 (q, $J$ = 5.5 Hz, 1 H), 4.32 (d, $J$ = 13.5 Hz, 1 H), 4.46 (d, $J$ = 13.5 Hz, 1 H), 7.36–7.52 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 12.7, 13.0, 55.8, 56.7, 72.7, 126.5, 128.8, 129.0, 131.1 ppm. MS (CI): $m/z$ (%) = 244 (100) [$MNH_4^+$]. HRMS: $C_{11}H_{18}NO_3S$ calcd. 244.1007; found 244.1004.

**(g) *trans*-3-Methyl-4-phenyl-3-buten-2-ol (5k):** Clear oil with spectroscopic data consistent with literature.[30]

**(h) 1-Benzylsulfanylbutan-2-ol:** Clear oil with spectroscopic data consistent with literature.[61]

**(i) 1-Benzylsulfonylbutan-2-ol:** Colourless solid; m.p. 93–94 °C (EtOAc). $R_f$ = 0.35 (PE/EtOAc, 1:1). 0.35. IR (nujol): ṽ = 3461, 1377, 1117 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 0.95 (t, $J$ = 7.5 Hz, 3 H), 1.46–1.64 (m, 2 H), 2.88 (dd, $J$ = 1.5, 14.5 Hz, 1 H), 3.04 (dd, $J$ = 10.0, 14.5 Hz, 1 H), 4.13–4.25 (m, 1 H), 4.30 (d, $J$ = 14.0 Hz, 1 H), 4.41 (d, $J$ = 14.0 Hz, 1 H), 7.39–7.46 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 9.4, 29.7, 56.4, 60.9, 67.6, 127.8, 129.1, 129.1, 130.9 ppm. MS (EI): $m/z$ (%) = 228 (1) [$M^+$], 91 (100) [$Bn^+$]. HRMS: $C_{11}H_{20}NO_3S$ calcd. 246.1164; found 246.1167.

**(j) *trans*-1-Benzylsulfonyl-1-butene:** Colourless oil; b.p. 200 °C/0.1 Torr. $R_f$ = 0.20 (PE/EtOAc, 3:1). IR (film): ṽ = 3035, 2976, 2937, 1633, 1315, 1117 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.02 (t, $J$ = 7.5 Hz, 3 H), 2.17–2.28 (m, 2 H), 4.22 (s, 2 H), 6.13 (dt, $J$ = 1.5, 15.0 Hz, 1 H), 6.77 (dt, $J$ = 6.5, 15.0 Hz, 1 H), 7.35–7.40 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 11.6, 24.8, 61.4, 126.1, 128.2, 128.7, 128.8, 130.8, 151.9 ppm. MS (CI): $m/z$ (%) = 228 (55) [$MNH_4^+$], 91 (100) [$Bn^+$]. HRMS: $C_{11}H_{18}NO_2S$ calcd. 228.1058; found 228.1066. $C_{11}H_{14}O_2S$ (210.29): calcd. C 62.83, H 6.71, S 15.25; found C 62.85, H 6.67, S 15.22.

**(k) *trans*-2-Benzylsulfonyl-3-ethyloxirane (4j):** Colourless solid; m.p. 59–61 °C (PE/EtOAc). $R_f$ = 0.30 (PE/EtOAc, 3:1). IR ($CDCl_3$): ṽ = 3091, 3035, 2976, 1331, 1120 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.09 (t, $J$ = 7.5 Hz, 3 H), 1.67–1.83 (m, 2 H), 3.68–3.73 (m, 1 H), 3.82 (d, $J$ = 1.5 Hz, 1 H), 4.33 (d, $J$ = 14.0 Hz, 1 H), 4.49 (d, $J$ = 14.0 Hz, 1 H), 7.36–7.58 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 9.3, 23.4, 58.0, 58.2, 64.5, 126.7, 129.1, 129.15, 130.9 ppm. MS (CI): $m/z$ (%) = 244 (100) [$MNH_4^+$]. HRMS: $C_{11}H_{18}NO_3S$ calcd. 244.1007; found 244.1005.

**(l) 1-Phenyl-1-penten-3-ol (5j):** Clear oil ($E$:$Z$, 90:10) with spectroscopic data consistent with literature.[62]

**(m) 2-Benzylsulfonyl-2-phenylethan-1-ol:** Colourless solid; m.p. 138–138.5 °C (EtOAc). $R_f$ = 0.25 (PE/EtOAc, 1:1). IR (KBr): ṽ = 3500, 3080, 3020, 2995, 2950, 2925, 2885, 1280, 1150 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 4.03 (dd, $J$ = 4.5, 12.5 Hz, 1 H), 4.12 (d, $J$ = 14.0 Hz, 1 H), 4.17 (d, $J$ = 14.0 Hz, 1 H), 4.27 (dd, $J$ = 4.5, 8.0 Hz, 1 H), 4.51–4.61 (m, 1 H), 7.19–7.44 (m, 10 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 58.6, 61.7, 68.5, 127.0, 128.8, 129.0, 129.1, 129.4, 129.6, 130.7, 131.0 ppm. MS (CI): $m/z$ (%) = 294 (100) [$MNH_4^+$]. HRMS: $C_{15}H_{20}NO_3S$ calcd. 294.1164; found 294.1168. $C_{15}H_{16}O_3S$ (276.35): calcd. C 65.19, H 5.84; found C 65.35, H 5.96.

**(n) 1-Benzylsulfonyl-1-phenylethene:** Colourless solid; m.p. 64–65 °C (PE/EtOAc). $R_f$ = 0.30 (PE/EtOAc, 4:1). IR (nujol): ṽ = 1302, 1132 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 4.13 (s, 2 H), 5.98 (s, 1 H), 6.29 (s, 1 H), 7.16–7.66 (m, 10 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 59.2, 128.0, 128.7, 129.1, 129.3, 130.3, 131.3, 133.0, 140.2 ppm. MS (CI): $m/z$ (%) = 276 (100) [$MNH_4^+$]. HRMS: $C_{15}H_{18}NO_2S$ calcd. 276.1058; found 276.1059.

**(o) 2-Benzylsulfonyl-2-phenyloxirane (4l):** Viscous colourless oil. $R_f$ = 0.20 (PE/EtOAc, 4:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3064, 3033, 2994, 2931, 1320, 1124 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 3.00 (d, $J$ = 6.0 Hz, 1 H), 3.88 (d, $J$ = 6.0 Hz, 1 H), 4.09 (d, $J$ = 14.5 Hz, 1 H), 4.25 (d, $J$ = 14.5 Hz, 1 H), 7.26–7.47 (m, 6 H), 7.40–7.74 (m, 4 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 51.7, 55.6, 71.9, 125.5, 128.0, 128.7, 129.0, 130.0, 130.1, 131.2 ppm. MS (CI): $m/z$ (%) = 292 (100) [$MNH_4^+$]. HRMS: $C_{15}H_{18}NO_3S$ calcd. 292.1007; found 292.1008.

**(q) *trans*-2,3-Diphenyl-2-propen-1-ol 5l:** Clear oil with data consistent to literature values.[63]

**(r) 3-(2-Phenylethylsulfanyl)butan-2-ol:** Colourless oil; b.p. 170 °C/1 Torr. $R_f$ = 0.30 (PE/EtOAc, 3:1). IR (film): $\tilde{\nu}$ = 3423, 3062, 3026, 2972, 2925, 2871, 1496, 1452 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.25 (d, $J$ = 6.5 Hz, 3 H), 1.33 (d, $J$ = 6.5 Hz, 3 H), 2.65 (quin, $J$ = 6.5 Hz, 1 H), 2.80–2.95 (m, 4 H), 3.61 (quin, $J$ = 6.5 Hz, 1 H), 7.20–7.36 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 18.02, 19.7, 31.7, 36.5, 49.5, 70.0, 126.4, 128.4, 128.45, 140.2 ppm. MS (EI): $m/z$ (%) = 210 (10) [$M^+$], 105 (100) [$Ph(CH_2)_2^+$]. HRMS: $C_{12}H_{18}OS$ calcd. 210.1078; found 210.1083.

**(s) 3-(2-Phenylethylsulfonyl)butan-2-ol:** Colourless solid; m.p. 80 °C (EtOAc/PE). $R_f$ = 0.25 (PE/EtOAc, 1:1). IR (nujol): $\tilde{\nu}$ = 3423, 1377, 1105 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.31 (d, $J$ 6.5, 3 H), 1.34 (d, $J$ = 7.5 Hz, 3 H), 2.96 (dq, $J$ = 7.5, 8.5 Hz, 1 H), 3.17 (dd, $J$ = 2.0, 10.5 Hz, 1 H), 3.19 (d, $J$ = 10.5 Hz, 1 H), 3.36 (d, $J$ = 10.5 Hz, 1 H), 3.38 (dd, $J$ = 2.0, 10.5 Hz, 1 H), 4.23 (dq, $J$ = 6.5, 8.5 Hz, 1 H), 7.22–7.37 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 10.9, 21.5, 27.9, 54.7, 64.4, 67.4, 127.4, 128.9, 129.3, 138.2 ppm. MS (CI): $m/z$ (%) = 260 (90) [$MNH_4^+$]. HRMS: $C_{12}H_{22}NO_3S$ calcd. 260.1320; found 260.1318. $C_{12}H_{18}O_3S$ (242.33): calcd. C 59.48, H 7.49, S 13.23; found C 59.19, H 7.52, S 13.36.

**(t) *trans*-2-(2-Phenylethylsulfonyl)-2-butene:** Colourless oil; b.p. 200 °C/1 Torr. $R_f$ = 0.30 (PE/EtOAc, 3:1). IR (film): $\tilde{\nu}$ = 3085, 3062, 3028, 2925, 1653, 1496, 1454, 1380, 1115 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.83 (dq, $J$ = 1.5, 7.0 Hz, 3 H), 1.99 (quin, $J$ = 1.5 Hz, 3 H), 3.00–3.10 (m, 2 H), 3.17–3.23 (m, 2 H), 6.81 (qq, $J$ = 1.5, 7.0 Hz, 1 H), 7.16–7.34 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 11.5, 14.1, 28.4, 52.9, 126.8, 128.3, 128.7, 135.6, 137.7, 138.4 ppm. MS (CI): $m/z$ (%) = 242 (60) [$MNH_4^+$], 104 (100) [$Ph(CH_2)_2^+$]. HRMS: $C_{12}H_{20}NO_2S$ calcd. 242.1215; found 242.1214.

**(u) *trans*-2,3-Dimethyl-2-(2-phenylethylsulfonyl)oxirane (4m):** Colourless solid; m.p. 41–42 °C. $R_f$ = 0.35 (DCM). IR (film): $\tilde{\nu}$ = 3085, 3028, 3003, 2935, 1497, 1454, 1317, 1105 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.50 (d, $J$ = 5.5 Hz, 3 H), 1.82 (s, 3 H), 3.23–3.30 (m, 2 H), 3.32–3.43 (m, 2 H), 3.94 (q, $J$ = 5.5 Hz, 1 H), 7.32–7.47 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 12.1, 13.1, 26.9, 50.2, 56.1, 72.6, 127.0, 128.4, 128.9, 137.7 ppm. MS (CI): $m/z$ (%) = 258 (100) [$MNH_4^+$]. HRMS: $C_{12}H_{20}NO_3S$ calcd. 258.1164; found 258.1162. $C_{12}H_{16}O_3S$ (240.32): calcd. C 59.98, H 6.71, S 13.34; found C 60.20, H 6.50, S 13.28

**(v) 3-Methyl-5-phenyl-3-penten-2-ol (5m):** Yellow oil [$E^*$:$Z^\#$, 60:40]. $R_f$ = 0.30 (PE/EtOAc, 3:1). IR (film): $\tilde{\nu}$ = 3357, 3062, 3026, 2974, 2922, 1603, 1493, 1452 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.30* (d, $J$ = 6.5 Hz, 3 H), 1.31$^\#$ (d, $J$ = 6.5 Hz, 3 H), 1.74–1.77* (m, 3 H), 1.79$^\#$ (q, $J$ = 1.5 Hz, 3 H), 3.39–3.45*$^\#$ (m, 2 H), 4.27* (q, $J$ = 6.5 Hz, 1 H), 4.93$^\#$ (q, $J$ = 6.5 Hz, 1 H), 5.40–5.43$^\#$ (m, 1 H), 5.62–5.64* (m, 1 H), 7.18–7.34 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 11.6, 17.2, 21.3, 21.6, 33.3, 33.8, 65.6, 73.2, 123.5, 124.9, 125.2, 125.9, 128.2, 128.5, 128.4, 128.5, 138.8, 139.5, 141.0 ppm. MS (EI): $m/z$ (%) = 176 (20) [$M^+$], 85 (100) [$C_5H_9O^+$]. HRMS: $C_{12}H_{16}O$ calcd. 176.1201; found 176.1199. * Denotes *trans*-isomer; $^\#$ denotes *cis*-isomer.

**Preparation of 4-Phenyl-3-buten-1,2-diol (5n) and 4-Phenyl-1-(*tert*-butyldimethylsilyloxy)-3-buten-2-ol (5o)**

**(a) 1-Benzylsulfanyl-2-propene:** Prepared according to literature procedures.[64]

**(b) 1-Benzylsulfonyl-2-propene (11):** Prepared according to literature procedures.[64]

**(c) *trans*-3-Bromo-1-benzylsulfonyl-1-propene:** Prepared according to literature procedures.[64]

**(d) *trans*-3-Benzylsulfonyl-2-propene acetate:** Prepared according to literature procedures.[64]

**(e) *trans*-3-Benzylsulfonyl-2-propen-1-ol (2n):** Prepared according to literature procedure.[65]

**(f) *trans*-2-Benzylsulfonyl-3-hydroxymethyloxirane (4n):** Compound **2n** (279 mg, 1.31 mmol, 1 equiv.) in THF (15 mL) was converted into the corresponding epoxide **4n** over 1.5 h at –5 °C upon treatment with $LiO_2tBu$ [generated at –78 °C from 2.55 M TBHP in toluene (0.77 mL, 1.97 mmol, 1.5 equiv.) and 1.6 M *n*BuLi in hexanes (0.9 mL, 1.45 mmol, 1.1 equiv.) in THF (15 mL)]. $Na_2SO_3$ (ca. 1 g) was added and the reaction mixture was stirred for a further 0.25 h at –5 °C. Filtration through celite, washing with diethyl ether (2 × 50 mL), evaporation under reduced pressure followed by flash column chromatography (PE/EtOAc, 1:1) gave the epoxide **4n** (203 mg, 68%) as a colourless solid; m.p. 93.5–95 °C. $R_f$ = 0.20 (PE/EtOAc, 1:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3309, 3055, 2983, 2935, 1497, 1456, 1329, 1265. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 3.73 (dd, $J$ = 1.5, 2.5 Hz, 1 H), 3.74 (dd, $J$ = 2.5, 14.0 Hz, 1 H), 3.96 (dd, $J$ = 2.5, 14.0 Hz, 1 H), 4.10 (d, $J$ = 1.5 Hz, 1 H), 4.28 (d, $J$ = 14.0 Hz, 1 H), 4.41 (d, $J$ = 14.0 Hz, 1 H), 7.40–7.43 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 56.8, 58.2, 58.6, 62.2, 126.4, 129.2, 129.3, 130.9 ppm. MS (CI): $m/z$ (%) = 246 (100) [$MNH_4^+$]. HRMS: $C_{10}H_{16}NO_4S$ requires 246.0800; found 246.0801.

**(g) *trans*-2-Benzylsulfonyl-3-(*tert*-butyldimethylsilyloxymethyl)-oxirane (4o):** At room temperature a stirred solution of the epoxide **4n** (42 mg, 0.184 mmol, 1 equiv.) in DCM (3 mL) and TBSCl (36 mg, 0.239 mmol, 1.3 equiv.) were treated with imidazole (30 mg, 0.44 mmol, 2.4 equiv.). Stirring was continued for 2 h before the reaction mixture was concentrated in vacuo and subjected directly to flash column chromatography (PE/EtOAc, 1:1), which yielded the silylated epoxide **4o** as a clear oil (54 mg, 86%). $R_f$ = 0.75 (PE/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3035, 2954, 2931, 2858, 1327, 1142 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 0.02 (s, 6 H), 0.84 (s, 9 H), 3.73 (m, 1 H), 3.81 (ddd, $J$ = 2.5, 3.7 Hz5, 13.0, 1 H), 3.98–4.02 (m, 2 H), 4.25 (d, $J$ = 14.0 Hz, 1 H), 4.42 (d, $J$ = 14.0 Hz, 1 H), 7.39–7.45 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = –5.15, –5.1, 18.6, 26.1, 57.6, 58.6, 59.5, 62.0, 127.2, 129.5, 129.6, 131.3 ppm. MS (CI): $m/z$ (%) = 360 (100) [$MNH_4^+$]. HRMS: $C_{16}H_{30}NO_4SSi$ calcd. 360.1665; found 360.1649.

**(h) 4-Phenyl-3-buten-1,2-diol (5n):** Colourless solid [$E$:$Z$, 75:25] with spectroscopic data consistent with literature.[66]

**(i) *trans*-4-Phenyl-1-(*tert*-butyldimethylsilyloxy)-3-buten-2-ol (5o):** Clear oil [$E$:$Z$, 93:7]. $R_f$ = 0.50 (PE/EtOAc, 3:1). IR (film): $\tilde{\nu}$ = 3419, 2954, 2929, 2858 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta^\ddagger$ = 0.11 (s, 6 H), 0.93 (s, 9 H), 1.27 (br. s, 1 H), 3.55 (dd, $J$ = 7.7 Hz5, 10.0, 1 H), 3.75 (dd, $J$ = 3.5, 10.0 Hz, 1 H), 4.32–4.41 (m, 1 H), 6.18 (dd, $J$ = 6.5, 16.0 Hz, 1 H), 6.70 (d, $J$ = 16.0 Hz, 1 H), 7.25–7.41 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = –5.3, 18.3, 25.8, 67.2, 72.8, 126.4, 127.6, 127.8, 128.5, 131.7, 136.7 ppm. MS (CI): *m/z* (%) = 296 (4) [$MNH_4^+$], 278 (7) [$M^+$], 261 (100) [M – $OH^+$]. HRMS: $C_{16}H_{30}NO_2Si$ requires 296.2046; found 296.2042. ‡ Data given for the major *trans*-isomer only.

**Preparation of 3-Phenyl-2-propen-1-ol (5p) and 5-Phenyl-2,4-pentadien-1-ol (5q):**

**(a) 2-Benzylsulfanylethan-1-ol:** Preparation according to a literature procedure.[67]

**(b) 2-Benzylsulfonylethan-1-ol:** Preparation according to a literature procedure.[67]

**(c) 2-Benzylsulfonylethene:** Preparation according to a literature procedure.[67]

**(d) 2-Benzylsulfonyloxirane (4p):** Colourless solid; m.p. 68–69 °C (EtOAc/PE). $R_f$ = 0.45 (PE/EtOAc, 1:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3091, 3035, 2955, 2930, 2925, 1336, 1153 $cm^{-1}$. $^1H$ NMR (270.1 MHz, $CDCl_3$): $\delta$ = 3.09 (dd, *J* = 3.5, 5.5 Hz, 1 H), 3.42 (dd, *J* = 2.0, 5.5 Hz, 1 H), 3.94 (dd, *J* = 2.0, 3.5 Hz, 1 H), 4.28 (d, *J* = 14.0 Hz, 1 H), 4.43 (d, *J* = 14.0 Hz, 1 H), 7.42–7.46 (m, 5 H) ppm. $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 44.6, 58.3, 59.7, 126.6, 129.2, 129.3, 130.9 ppm. MS (CI): *m/z* (%) = 216 (100) [$MNH_4^+$]. HRMS: $C_9H_{14}NO_3S$ calcd. 216.0694; found 216.0695. $C_9H_{10}O_3S$ (198.24): calcd. C 54.53, H 5.08, S 16.18; found C 54.72, H 5.01, S 16.18.

**(e) 3-Phenyl-2-propen-1-ol (5p):** Clear oil [*E*:*Z*, 65:35] whose data was consistent with that reported in the literature.[68]

**(f) 2-(3-Phenyl-2-propen-1-sulfanyl)ethan-1-ol:** Prepared according to a literature procedure.[64]

**(g) 2-(3-Phenyl-2-propen-1-sulfonyl)ethan-1-ol:** Prepared according to a literature procedure.[64]

**(h) 3-Phenyl-2-propen-1-sulfonylethene:** Prepared according to a literature procedure.[64]

**(i) 2-(3-Phenyl-2-propen-1-sulfonyl)oxirane (4q):** Prepared according to a literature procedure.[64]

**(j) 5-Phenyl-2,4-pentadien-1-ol (5q):** Pale yellow solid [*E*:*E*:*E*:*Z*, 65:35] whose data was consistent with that reported in the literature.[69]

**(k) 2-(2-Phenylethylsulfanyl)ethan-1-ol:** Prepared according to a literature procedure.[70]

**(l) 2-(2-Phenylethylsulfonyl)ethan-1-ol:** Prepared according to a literature procedure.[70]

**(m) 2-(2-Phenylethylsulfonyl)ethene:** Prepared according to a literature procedure.[70]

**(n) 2-(2-Phenylethylsulfonyl)oxirane (4r):** Colourless solid; m.p. 77–79 °C. $R_f$ = 0.35 (PE/EtOAc, 1:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3087, 3078, 3030, 2982, 2931, 1496, 1456, 1317, 1151, 1126 $cm^{-1}$. $^1H$ NMR (270.1 MHz, $CDCl_3$): $\delta$ = 3.05 (dd, *J* = 4.0, 5.5 Hz, 1 H), 3.14–3.28 (m, 2 H), 3.30–3.43 (m, 3 H), 3.95 (dd, *J* = 2.0, 4.0 Hz, 1 H), 7.21–7.35 (m, 5 H) ppm. $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 27.7, 44.2, 53.2, 61.0, 127.1, 128.4, 128.9, 137.2 ppm. MS (CI): *m/z* (%) = 230 (100) [$MNH_4^+$]. HRMS: $C_{10}H_{16}NO_3S$ calcd. 230.0851; found 230.0849. $C_{10}H_{12}O_3S$ (212.26): calcd. C 56.59, H 5.70, S 15.11; found C 56.72, H 5.65, S 14.99.

**Preparation of 1,3-Diphenyl-2-butenyl Acetate (15) and 1,2-Dimethyl-3-phenyl-2-butenyl Acetate (16)**

**(a) *trans*-1-(1-Phenylethylsulfonyl)-2-phenylethene (2s):** Under $N_2$ at –78 °C the vinyl sulfone **2a** (306 mg, 1.18 mmol, 1 equiv.) in dry THF (10 mL) was treated with *n*BuLi in hexanes (2.5 M, 0.52 mL, 1.3 mmol, 1.1 equiv.). Stirring at –78 °C was continued for 10 min before MeI (0.15 mL, 2.41 mmol, 2 equiv.) was added to the red solution. The colour rapidly disappeared and stirring was continued for a further 10 min at –78 °C. Saturated $NH_4Cl$ (10 mL) was added and the mixture was warmed to room temperature before extraction was carried out with EtOAc (3 × 30 mL). The combined extracts were washed with $H_2O$ (20 mL) then brine (50 mL) before drying with $MgSO_4$. Purification of the crude oil obtained after filtration and solvent removal in vacuo, by flash column chromatography (PE/EtOAc, 2:1) afforded the methylated compound **2s** (282 mg, 88%) as a colourless solid; m.p. 94–95 °C (EtOAc/PE). $R_f$ = 0.30 (PE/EtOAc, 3:1). IR ($CHCl_3$): $\tilde{\nu}$ = 3086, 3066, 3041, 3007, 2941, 1614, 1497, 1450, 1309, 1128 $cm^{-1}$. $^1H$ NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.83 (d, *J* = 7.5 Hz, 3 H), 4.25 (q, *J* = 7.5 Hz, 1 H), 6.56 (d, *J* = 16.0 Hz, 1 H), 7.35–7.45 (m, 11 H) ppm. $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 14.0, 65.0, 122.8, 128.3, 128.6, 128.7, 128.8, 128.9, 129.3, 131.1, 132.2, 133.7, 145.6 ppm. MS (CI): *m/z* (%) = 290 (100) [$MNH_4^+$]. HRMS: $C_{16}H_{20}NO_2S$ calcd. 290.1215; found 290.1212.

**(b) *syn*- and *anti*-*trans*-3-(1-Phenylethylsulfonyl)-2-phenyloxirane (4s):** Following the described epoxidation process, TBHP in toluene (2.55 M, 0.57 mL, 1.45 mmol, 1.5 equiv.) in THF (10 mL) and *n*BuLi in hexanes (1.6 M, 0.73 mL, 1.17 mmol, 1.2 equiv.) was used to generate $LiO_2$*t*Bu at –78 °C. The sulfone **2s** (265 mg, 0.973 mmol, 1 equiv.) in THF (10 mL) was added and stirring was continued over 4 h at –20 °C to room temperature. $Na_2SO_3$ (ca. 1 g) was added and after 0.5 h the mixture was filtered through celite and washed with diethyl ether (2 × 30 mL). Concentration of the filtrate in vacuo followed by purification by flash column chromatography (PE/EtOAc, 4:1) afforded **4s** (206 mg, 73%) as a separable mixture of the two diastereomers, 33% *de*. $R_f$ = 0.30 and 0.25 (PE/EtOAc, 4:1). IR ($CHCl_3$): $\tilde{\nu}$ = 3065, 3034, 2987, 2939, 2877, 1495, 1456, 1319, 1138 $cm^{-1}$. $^1H$ NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.85* (d, *J* = 7.5 Hz, 3 H), 1.92# (d, *J* = 7.5 Hz, 3 H), 3.73* (d, *J* = 1.5 Hz, 1 H), 4.10# (d, *J* = 1.5 Hz, 1 H), 4.42# (q, *J* = 7.5 Hz, 1 H), 4.45# (d, *J* = 1.5 Hz, 1 H), 4.46* (d, *J* = 1.5 Hz, 1 H), 4.47* (q, *J* = 7.5 Hz, 1 H), 7.14–7.57 (m, 10 H) ppm. $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 13.7, 15.9, 57.3, 58.0, 63.4, 64.7, 68.5, 68.9, 127.4, 127.5, 129.9, 130.0, 130.1, 130.3, 130.5, 130.8, 130.9, 133.2 133.9, 134.6 ppm. MS (CI): *m/z* (%) = 306 (100) [$MNH_4^+$]. HRMS: $C_{16}H_{20}NO_3S$ calcd. 306.1164; found 306.1171. * Defines major diastereomer; # defines minor diastereomer.

**(c) 1,3-Diphenyl-2-butenyl Acetate (15):** Under nitrogen, LiO*t*Bu in THF (1.28 mL, 1.0 M, 1.28 mmol, 2 equiv.) was added to a solution of the epoxide **4s** (185 mg, 0.64 mmol, 1 equiv.) in THF (15 mL) at 25 °C. Stirring was continued for 24 h before saturated $NH_4Cl$ (5 mL) was added. The resultant mixture was extracted with EtOAc (3 × 20 mL), and the combined extracts were washed with brine (20 mL) and dried with $MgSO_4$. Filtration, evaporation in vacuo and flash column chromatography (PE/EtOAc, 3:1) afforded a yellow oil (111 mg) containing the allylic alcohol and unreacted epoxide **4s**. This residue was taken up in $Ac_2O$ (3 mL) and pyridine (0.1 mL, 1.2 mmol) was added. The reaction mixture was stirred for 12 h before ether (10 mL) and water (10 mL) were added. After partitioning for 10 min and separation the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined ethereal extracts were washed with $NaHCO_3$ (20 mL), water (20 mL) and brine (20 mL) before finally drying with $MgSO_4$. The material obtained after filtration and solvent evaporation under reduced pressure was purified by column chromatography (PE/EtOAc, 6:1) to give the recovered epoxide **4s** (29 mg, 16%) and the allylic acetate **15** (82 mg, 48%) as a clear oil [*E*:*Z*, 50:50]. $R_f$ = 0.50 (PE/EtOAc, 6:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3082, 3061, 3032, 2972, 2916, 1736, 1601, 1495, 1444 $cm^{-1}$. $^1H$ NMR (270.1 MHz, $CDCl_3$): $\delta$ = 2.05 (s, 3 H), 2.10 (d, *J* = 1.5 Hz, 3 H), 2.13 (s, 3 H), 2.24 (d, *J* = 1.5 Hz, 3 H), 5.75 (dq, *J* = 1.5, 9.5 Hz, 1 H), 5.99 (dq, *J* = 1.5, 9.0 Hz, 1 H), 6.18 (d, *J* = 9.5 Hz, 1 H), 6.70 (d, *J* = 9.0 Hz, 1 H), 7.18–7.56 (m, 10 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 16.6, 21.3, 25.9, 73.0, 73.9, 125.2, 125.9, 126.5, 126.6, 126.7, 127.4, 127.5, 127.6, 127.8, 127.9, 128.2, 128.3, 128.5, 128.6, 138.8, 140.1, 140.6, 140.7, 141.3, 142.1, 169.7, 170.2 ppm. MS (EI): *m*/*z* (%) = 266 (10) [M$^+$]. HRMS: $C_{16}H_{16}O_2$ calcd. 266.1307; found 266.1314.

**(d) *syn*- and *anti-trans*-2,3-Dimethyl-2-(1-phenylethylsulfonyl)oxirane (4t):** At –78 °C under nitrogen the *trans*-epoxide **4k** (57.5 mg, 0.254 mmol, 1 equiv.) in THF (5 mL) was treated with *n*BuLi in hexanes (1.6 M, 0.14 mL, 0.224 mmol, 0.9 equiv.) over 5 min. After 10 min methyl iodide (1.6 µL, 0.257 mmol, 1 equiv.) was added. Stirring was continued for a further 10 min at –78 °C, then for 1 h at room temperature. Saturated $NH_4Cl$ (5 mL) was added and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (30 mL) and dried with $MgSO_4$. Filtration followed by solvent removal under reduced pressure afforded the crude product as a mixture of diastereomers which was purified by flash column chromatography (PE/EtOAc, 3:1) yielding **4t** as a separable mixture of clear oils (26 mg, 47%; 24 mg, 44%). $R_f$ = 0.35 and 0.30 (PE/EtOAc, 3:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3064, 2991, 2934, 1496, 1456, 1317, 1300, 1151, 1103 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$) upper spot: $\delta$ = 1.19 (d, *J* = 5.5 Hz, 3 H), 1.20 (s, 3 H), 3.58 (q, *J* = 5.5 Hz, 1 H), 4.44 (q, *J* = 7.5 Hz, 1 H), 7.38–7.52 (m, 5 H) ppm; lower spot: $\delta$ = 1.29 (d, *J* = 5.5 Hz, 3 H), 1.56 (s, 3 H), 1.81 (d, *J* = 7.5 Hz, 3 H), 3.63 (q, *J* = 5.5 Hz, 1 H), 4.42 (q, *J* = 7.5 Hz, 1 H), 7.33–7.50 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$) upper spot: $\delta$ = 13.0, 13.1, 13.5, 56.9, 60.7, 72.6, 128.9, 129.2, 129.6, 133.6 ppm; lower spot: $\delta$ = 14.2, 14.4, 15.9, 56.5, 63.1, 74.1, 130.1, 130.4, 130.6, 134.3 ppm. MS (CI): *m*/*z* (%) = 258 (100) [$MNH_4^+$]. HRMS: $C_{12}H_{20}NO_3S$ calcd. 258.1164; found 258.1161.

**(e) 1,2-Dimethyl-3-phenyl-2-butenyl Acetate (16):** Following the ERBR protocol described, the epoxide **4t** (226 mg, 0.94 mmol, 1 equiv.) in THF (18 mL) was treated with LiO*t*Bu in THF (1.03 mL, 1.0 M, 1.03 mmol, 1.1 equiv.) at 25 °C. Stirring was maintained for 15 h before the standard work-up was implemented. $^1$H NMR spectroscopic analysis revealed a significant amount of starting material. Hence, the residue was taken up in THF (18 mL) and treated again with LiO*t*Bu solution (1.4 mL, 1.4 mmol, 1.5 equiv.). After stirring for a further 48 h satd. $NH_4Cl$ (10 mL) was added, and the standard work-up was carried out. Purification by flash column chromatography (PE/EtOAc, 3:1) afforded an inseparable mixture of **4t** and the tetrasubstituted allylic alcohol. The residue (138 mg) was taken up in $Ac_2O$ (3 mL), and pyridine (0.16 mL, 2 mmol) was added at 25 °C. After 15 h an identical work-up to that described above was implemented. Purification by flash column chromatography (PE/EtOAc, 3:1) afforded the epoxide **4t** (10 mg, 4%) and the title compound **16** (39 mg, 19%) as a yellow oil. The allylic acetate was formed as an undetermined 90*:10$^{\#}$ mixture of stereoisomers. $R_f$ = 0.55 (PE/EtOAc, 3:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3078, 2983, 2933, 2862, 1724, 1601, 1493, 1443. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.22$^{\#}$ (d, *J* = 6.5 Hz, 3 H), 1.38* (d, *J* = 6.5 Hz, 3 H), 1.54* (q, *J* = 1.5 Hz, 3 H), 1.79$^{\#}$ (q, *J* = 1.0 Hz, 3 H), 1.96$^{\#}$ (q, *J* = 1.0 Hz, 3 H), 1.99$^{\#}$ (s, 3 H), 2.05* (q, *J* = 1.5 Hz, 3 H), 2.08* (s, 3 H), 5.34$^{\#}$ (q, *J* = 6.5 Hz, 1 H), 5.95* (q, *J* = 6.5 Hz, 1 H), 7.09–7.36 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 12.0, 13.8, 18.6, 19.0, 20.3, 21.2, 21.3, 21.5, 70.4, 71.9, 126.2, 126.4, 127.8, 128.0, 128.1, 128.2, 129.7, 130.2, 133.3, 134.2, 143.3, 144.5, 170.0, 170.4 ppm. MS (EI): *m*/*z* (%) = 218 (5) [M$^+$]. HRMS: $C_{14}H_{18}O_2$ calcd. 218.1307; found 218.1303. * Denotes major stereoisomer; $^{\#}$ denotes minor stereoisomer.

**Preparation of Enantio-enriched Allylic Alcohols via the ERBR**

**(a) *trans*-2-Benzylsulfonyl-1-(2,2-dimethyl-1,3-dioxolan-4-yl)ethene (2u):** Under nitrogen at –65 °C, DMSO (2 mL, 28.18 mmol, 3.5 equiv.) was added dropwise to a solution of oxalyl chloride (1.2 mL, 13.76 mmol, 1.7 equiv.) in DCM (20 mL). Stirring was continued for 10 min before (*S*)-isopropylideneglycerol (**17**, 1.0 mL, 8.17 mmol, 1 equiv.) was added over 4.5 min. After a further 10 min stirring at –65 °C triethylamine (3.4 mL, 24.39 mmol, 3 equiv.) was added dropwise to the cloudy solution. After 5 min the reaction was warmed to –10 °C for 0.5 h before filtration through celite. The residue was washed with cold DCM (15 mL) and cold ether (2 × 15 mL). The bulk of the solvent was removed under reduced pressure at 25 °C. The resultant crude glyceraldehyde was then added to a pre-prepared solution of the anion, generated from the phosphonate **3** (3.72 g, 12.14 mmol, 1.5 equiv.) and NaH dispersion in oil (60%, 389 mg, 9.72 mmol, 1.2 equiv.) in THF (160 mL). Stirring was continued for 40 min before the addition of water (50 mL) followed by EtOAc (50 mL). The resultant aqueous layer was further extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with water (100 mL) and brine (100 mL) and dried with $Na_2SO_4$. The crude oil obtained after filtration and solvent removal was purified by flash column chromatography (PE/EtOAc, 2:1) affording **2u** as a clear oil (1.72 g, 75%), which proved to be a separable mixture of stereoisomers; *E*:*Z*, 85:15 (PE/EtOAc, 3:1). $R_f$ = 0.17 (*Z*) and 0.15 (*E*) (PE/EtOAc, 3:1). Data for (*E*)-vinyl sulfone. IR (film): $\tilde{\nu}$ = 3064, 3015, 2986, 2937, 2889, 1638, 1496, 1456, 1315, 1117 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.39 (s, 3 H), 1.40 (s, 3 H), 3.52 (dd, *J* = 7.0, 8.5 Hz, 1 H), 4.13 (dd, *J* = 7.0, 8.5 Hz, 1 H), 4.24 (s, 2 H), 4.63 (dddd, *J* = 1.5, 4.0, 7.0 Hz, 8.0, 1 H), 6.50 (dd, *J* = 1.5, 15.0 Hz, 1 H), 6.65 (dd, *J* = 4.0, 15.0 Hz, 1 H), 7.32–7.46 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 25.4, 26.2, 61.2, 68.0, 73.7, 110.5, 127.5, 127.9, 128.7, 130.8, 146.6 ppm. MS (CI): *m*/*z* (%) = 300 (100) [$MNH_4^+$]. HRMS: $C_{14}H_{22}NO_4S$ calcd. 300.1270; found 300.1268. $[\alpha]_D$ = +7.4 (*c* = 1.0, $CHCl_3$).

**(b) *trans*-(2*R*,3*R*)-2-Benzylsulfonyl-3-(2,2-dimethyl-1,3-dioxolan-4-yl)oxirane (*anti*-4u):** A solution of $Ph_3CO_2H$ (498 mg, 1.8 mmol, 3 equiv.) in THF (6 mL) at –78 °C was treated with NaH dispersion in oil (60%, 36 mg, 0.9 mmol, 1.5 equiv.). The mixture was warmed to 25 °C and stirred for 0.5 h before cooling to –78 °C and addition of the vinyl sulfone **2u** (169 mg, 0.597 mmol, 1 equiv.) in THF (6 mL) [washed further, THF (2 mL)] was added. Stirring was continued at –78 °C for 0.25 h and then at –20 °C to –10 °C for 1 h. The reaction mixture was cooled again to –78 °C and $NH_4Cl$ (10 mL) was added. Warming to 25 °C followed by extraction with EtOAc (3 × 20 mL), washing of the combined organic layers with brine (30 mL) and drying with $Na_2SO_4$ afforded the crude epoxide upon filtration and solvent removal. Purification by flash column chromatography (PE/EtOAc, 3:1) gave an inseparable mixture of the diastereomeric epoxides (148 mg, 83%), 80% *de*. The major *anti*-epoxide **4u** was obtained as a colourless solid by recrystallisation; m.p. 102–103 °C (EtOAc/PE). $R_f$ = 0.30 (PE/EtOAc, 3:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3064, 3033, 2987, 2935, 2891, 1496, 1456, 1373, 1325, 1151, 1117 cm$^{-1}$. $^1$H NMR (270.1 MHz, $CDCl_3$): $\delta$ = 1.34 (s, 3 H), 1.40 (s, 3 H), 3.70–3.73 (m, 1 H), 3.83–3.90 (m, 1 H), 3.94 (d, *J* = 1.5 Hz, 1 H), 4.08–4.16 (m, 2 H), 4.28 (d, *J* = 14.0 Hz, 1 H), 4.40 (d, *J* = 14.0 Hz, 1 H), 7.41–7.45 (m, 5 H) ppm. $^{13}$C NMR (67.9 MHz, $CDCl_3$): $\delta$ = 25.0, 26.2, 56.7, 58.3, 63.0, 66.3, 72.7, 110.6, 126.4, 129.1, 129.3, 130.9 ppm. MS (CI): *m*/*z* (%) = 316 (100) [$MNH_4^+$]. HRMS: $C_{14}H_{22}NO_5S$ calcd. 316.1219; found 316.1216. $[\alpha]_D$ = +85.2 (*c* = 0.5, $CHCl_3$).

**(c) (1*S*)-1-[(4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-3-phenyl-2-propen-1-ol (*anti*-5u):** The *anti*-epoxide **4u** (45 mg, 0.15 mmol, 1 equiv.) in

THF (3 mL) was treated with LiO*t*Bu in THF (0.3 mL, 1.0 м, 0.3 mmol, 2 equiv.). Stirring was continued for 36 h before $NH_4Cl$ (5 mL) was added. The resultant mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (15 mL) and dried with $Na_2SO_4$. Filtration and solvent removal under reduced pressure furnished the crude product which was purified by flash column chromatography (PE/EtOAc, 2:1). The title compound **5u** (24 mg, 69%) was obtained as a colourless solid [*E*:*Z*, 92:8], recrystallisation gave the *trans*-stereoisomer, m.p. 59 °C ($Et_2O$/PE). $R_f$ = 0.30 (PE/EtOAc, 3:1). IR ($CHCl_3$): $\tilde{\nu}$ = 3467, 3055, 3010, 2988, 2890, 1653, 1496, 1457 $cm^{-1}$. $^1H$ NMR (500.1 MHz, $CDCl_3$): ‡ $\delta$ = 1.39 (s, 3 H), 1.49 (s, 3 H), 2.25 (br. s, 1 H), 3.98 (dd, *J* = 7.0, 8.0 Hz, 1 H), 4.01 (dd, *J* = 7.0, 8.0 Hz, 1 H), 4.23 (ddd, *J* = 5.0, 7.0, 7.0 Hz, 1 H), 4.49–4.50 (m(br), 1 H), 6.18 (dd, *J* = 6.0, 16.0 Hz, 1 H), 6.73 (d, *J* = 16.0 Hz, 1 H), 7.25–7.41 (m, 5 H) ppm. $^{13}C$ NMR (125.8 MHz, $CDCl_3$): ‡ $\delta$ = 25.1, 26.4, 64.7, 71.7, 78.3, 109.5, 126.5, 126.7, 127.8, 128.5, 132.0, 136.2 ppm. MS (EI): *m*/*z* (%) = 234 (5) [$M^+$], 101 (100) [$C_5H_9O_2^+$]. HRMS: $C_{14}H_{18}O_3$ calcd. 234.1256; found 234.1268. $[\alpha]_D$ = +22.1 (*c* = 0.5, $CHCl_3$). ‡ Data given for the major *trans*-isomer only.

**(d) (2*R*,3*S*)-*trans*-5-Phenyl-4-penten-1,2,3-triol (*anti*-5v):** $TsOH{\cdot}H_2O$ (3 mg, 0.016 mmol, 0.23 equiv.) was added to a solution of the alcohol *anti*-**5u** (16.5 mg, 0.071 mmol, 1 equiv.) in MeOH (2 mL). Stirring was continued for 12 h. Water (10 mL) and EtOAc (10 mL) were added. The resultant aqueous layer was extracted with EtOAc (3 × 15 mL) and the combined organic extracts were washed with $NaHCO_3$ (15 mL), brine (15 mL) and dried with $Na_2SO_4$. The crude colourless solid obtained after filtration and solvent removal in vacuo was recrystallised to afford *anti*-**5v** (9.5 mg, 70%); m.p. 121–122 °C (acetone) [ref.[20] m.p. 123 °C (acetone)]. $R_f$ = 0.20 (EtOAc). IR ($CHCl_3$): $\tilde{\nu}$ = 3619, 3294, 3209, 3018, 2958, 2927, 2856, 1601, 1464 $cm^{-1}$. $^1H$ NMR (270.1 MHz, [$D_6$] acetone): $\delta$ = 3.52 (d, *J* = 5.0 Hz, 1 H), 3.47–3.58 (m, 3 H), 3.72 (d, *J* = 4.5 Hz, 1 H), 4.01 (d, *J* = 5.0 Hz, 1 H), 4.14 (q, *J* = 5.0 Hz, 1 H), 6.43 (dd, *J* = 6.0, 16.0 Hz, 1 H), 6.65 (d, *J* = 16.0 Hz, 1 H), 7.18–7.45 (m, 5 H) ppm. $^{13}C$ NMR (67.9 MHz, [$D_6$]acetone): $\delta$ = 64.5, 74.5, 75.7, 127.1, 128.0, 129.3, 130.9, 131.4, 138.2 ppm. MS (CI): *m*/*z* (%) = 212 (30) [$MNH_4^+$], 177 (100) [$M - OH^+$]. HRMS: $C_{11}H_{18}NO_3$ calcd. 212.1287; found 212.1282. $[\alpha]_D$ = –18.7 (*c* = 0.125, THF).

**(e) (2*S*)-*trans*-4-Benzylsulfonyl-3-buten-1,2-diol (2v):** Following the procedure described above the vinyl sulfone **2u** (144 mg, 0.51 mmol, 1 equiv.) in MeOH (10 mL) was treated with $TsOH{\cdot}H_2O$ (19 mg, 0.10 mmol, 0.2 equiv.) at room temp. for 12 h. Water (10 mL) and EtOAc (10 mL) were added and the subsequent aqueous layer was further extracted with EtOAc (3 × 20 mL). The combined extracts were washed with $NaHCO_3$ (20 mL) and brine (25 mL) and dried with $MgSO_4$. The crude product obtained after filtration followed by solvent removal under reduced pressure was purified by flash column chromatography (PE/EtOAc, 1:1 to EtOAc) to give the diol **2v** (85 mg, 70%) as a colourless crystalline solid; m.p. 110–111 °C ($CHCl_3$/PE). $R_f$ = 0.45 (EtOAc). IR ($CHCl_3$): $\tilde{\nu}$ = 3477, 3057, 2985, 2925, 2875, 1635, 1309, 1117 $cm^{-1}$. $^1H$ NMR (270.1 MHz, $CDCl_3$): $\delta$ = 3.44 (dd, *J* = 6.0, 11.0 Hz, 1 H), 3.68 (dd, *J* = 4.0, 11.0 Hz, 1 H), 4.26 (s, 2 H), 4.39–4.44 (m, 1 H), 6.57 (dd, *J* = 2.0, 15.0 Hz, 1 H), 6.67 (dd, *J* = 3.0, 15.0 Hz, 1 H), 7.33–7.41 (m, 5 H) ppm. $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 61.2, 64.9, 70.9, 127.9, 128.1, 128.9, 129.0, 130.9, 147.9 ppm. MS (CI): *m*/*z* (%) = 260 (100) [$MNH_4^+$]. HRMS: $C_{11}H_{18}NO_4S$ calcd. 260.0957; found 260.0954. $[\alpha]_D$ = –22.1 (*c* = 0.25, $CHCl_3$).

**(f) (3*S*)-*trans*-2-Benzylsulfonyl-3-[(2*R*)-1,2-dihydroxyethyl]oxirane (*syn*-4v):** The vinyl sulfone **2v** (59 mg, 0.24 mmol, 1 equiv.) in THF (2 mL) was treated with a solution of $LiO_2$*t*Bu in THF (3 mL), generated from TBHP in toluene (2.63 м, 0.14 mL, 0.368 mmol, 1.5 equiv.) and *n*BuLi in hexanes (1.6 м, 0.17 mL, 0.272 mmol, 1.1 equiv.) over 3 h at –15 °C to –5 °C. Following the work-up procedure described above the crude product was purified by flash column chromatography (PE/EtOAc, 1:1 to EtOAc) to yield the epoxide **4v** (20 mg, 32%) as a colourless solid, *syn*-**4v**/*anti*-**4v**, 92:8 (84% *de*). Recrystallisation gave the major *syn*-diastereomer as a fine colourless crystalline solid; m.p. 140 °C (EtOAc). $R_f$ = 0.40 (EtOAc). IR ($CHCl_3$): $\tilde{\nu}$ = 3464, 3050, 2958, 2923, 2861, 1458, 1398, 1319, 1109 $cm^{-1}$. $^1H$ NMR (500.1 MHz, $CDCl_3$): $\delta$ = 3.74 (dd, *J* = 2.0, 3.0 Hz, 1 H), 3.75 (dd, *J* = 6.0, 11.0 Hz, 1 H), 3.80 (dd, *J* = 4.0, 11.0 Hz, 1 H), 3.88 (ddd, *J* = 3.0, 4.0, 6.0 Hz, 1 H), 4.09 (d, *J* = 2.0 Hz, 1 H), 4.29 (d, *J* = 14.0 Hz, 1 H), 4.40 (d, *J* = 14.0 Hz, 1 H), 7.40–7.65 (m, 5 H) ppm. $^{13}C$ NMR (67.9 MHz, $CDCl_3$): $\delta$ = 57.2, 58.5, 62.0, 64.5, 68.0, 126.5, 129.2, 129.4, 131.0 ppm. MS (CI): *m*/*z* (%) = 212 (50) [$MNH_4^+$]. HRMS: $C_{11}H_{18}NO_5S$ calcd. 276.0906; found 276.0909. $[\alpha]_D$ = –134.0 (*c* = 0.25, EtOH).

**(g) (2*R*,3*R*)-*trans*-5-Phenyl-4-penten-1,2,3-triol (*syn*-5v):** The *syn*-epoxide **4v** (12 mg, 0.0465 mmol, 1 equiv.) in THF (1 mL) was treated with LiO*t*Bu in THF (0.14 mL, 1.0 м, 0.14 mmol, 3 equiv.) for 12 h at room temp. Saturated $NH_4Cl$ (2 mL) was added and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (15 mL) and dried with $MgSO_4$. Filtration followed by solvent removal in vacuo gave the crude triol (3 mg, 33%) [*E*:*Z*, 76:24] as a clear oil. The *cis* and *trans*-stereoisomers were separated by preparative TLC. $R_f$ = 0.15 (*E*) and 0.20 (*Z*) (EtOAc). $^1H$ NMR (270.1 MHz, $CD_3OD$): $\delta^‡$ = 3.59 (dd, *J* = 6.0, 10.0 Hz, 1 H), 3.63–3.68 (m, 1 H), 3.74 (dd, *J* = 3.5, 10.0 Hz, 1 H), 4.30 (ddd, *J* = 1.0, 5.0, 6.5 Hz, 1 H), 6.37 (dd, *J* = 6.5, 16.5 Hz, 1 H), 6.70 (d, *J* = 16.5 Hz, 1 H), 7.22–7.48 (m, 5 H) ppm. $^{13}C$ NMR (67.9 MHz, $CD_3OD$): $\delta^‡$ = 64.3, 74.21, 76.4, 127.5, 128.6, 129.6, 130.4, 132.6, 138.4 ppm. $[\alpha]_D$ = +10 (*c* = 0.05, EtOH). ‡ Data given for the major *trans*-isomer only.

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[39] Crystal structure for compound *anti*-**5u**: $C_{14}H_{18}O_3$ $M = 234.28$, monoclinic space group $P2_1$, $a = 6.404(9)$ Å, $b = 8.368(7)$ Å, $c = 12.496(7)$ Å, $\beta = 97.95(7)^\circ$, $U = 663.2(12)$ Å$^3$, $T = 293(2)$ K, $Z = 2$, $\lambda$ (Mo-$K_\alpha$) = 0.7107 Å, 1258 reflections collected, $R_{\mathrm{int}} = 3.2\%$. CCDC-290132 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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