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RESEARCH ARTICLE

Conjugate addition reactions of vinyl sulfones with hard nucleophiles

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The conjugate addition reactions of several vinyl sulfones with hard oxygen nucleophiles are discussed. In particular a general method for the preparation of β-hydroxy sulfones under Weitz–Scheffer epoxidation conditions is described.

Keywords: Vinyl sulfone; Conjugate addition; Weitz–Scheffer; Nucleophilic epoxidation

1. Introduction

Vinyl sulfones **1** are useful synthetic intermediates which participate in conjugate addition reactions with a variety of both hard and soft nucleophilic species [1–3]. We became interested in the reactions of vinyl sulfones in the context of our development of the epoxy-Ramberg–Bäcklund reaction (figure 1) since this required the preparation of a series of α, β-epoxy sulfones **2** [4].

2. Results and discussion

Two main methods exist for the preparation of epoxysulfones **2**; the Darzens condensation [5, 6] and the nucleophilic epoxidation of vinyl sulfones. Since the Darzens condensation occurs in competition to the standard Ramberg–Bäcklund reaction when the starting material is flanked by a proton on both sides we focused our efforts on the investigation of epoxidation reactions of vinyl sulfones. The nucleophilic epoxidation process using the lithium salt of *tert*-butylhydroperoxide described by Meth–Cohn *et al.* [7, 8], successfully afforded the α, β-epoxy sulfones required for this study (see figure 2) [4]. Generally, this process gave the requisite epoxides **2** in reasonable to good yield, but in the case of the vinyl sulfone **4** the epoxide **5** was

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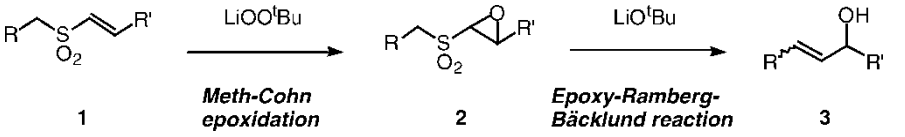


Figure 1. Preparation of α, β-epoxy sulfones and their epoxy Ramberg–Backlund rearrangement.

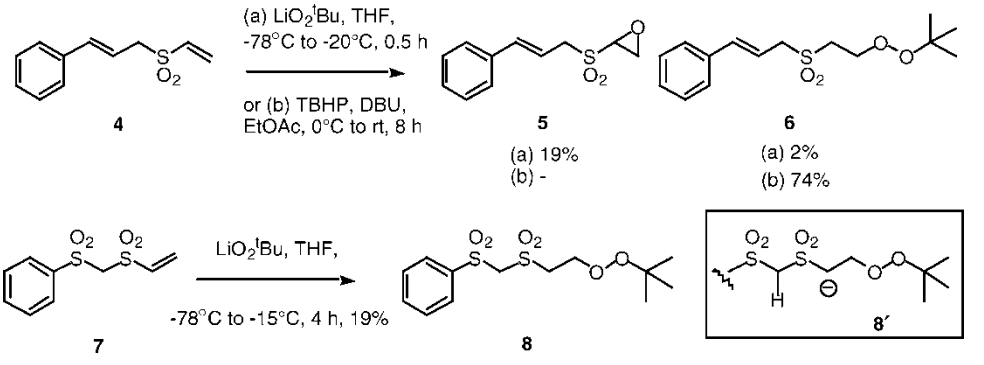


Figure 2. Attempted epoxidation of vinyl sulfones possessing an acidified α-proton.

formed in low yield and this was accompanied by small amounts of the peroxide product **6** from simple conjugate addition. When this reaction was performed using DBU [9] as the base **6** became the only isolable product.

Similarly, when the bis-sulfone **7** was employed, only the peroxide product **8** of conjugate addition was isolated, albeit in low yield. Somewhat to our surprise both **6** and **8** were isolable following column chromatography and appeared to be reasonably stable on prolonged storage at low temperature enabling their complete characterisation.

The likely explanation for the formation of the adducts shown is that the more pronounced acidity of the doubly activated α-sulfonyl position served to protonate the intermediate anion **8** resulting from conjugate addition (or when using DBU, its conjugate base).

In general terms the Meth-Cohn method is a development of the classical Weitz–Scheffer epoxidation reaction of electron deficient olefins [10–12].† Reports also indicate that under modified Weitz–Scheffer conditions (H_2O_2, $NaOH_{(aq)}$, acetone, 40 °C to 45 °C) vinyl sulfones do undergo epoxidation [13–15]. However, when we employed standard Weitz–Scheffer conditions, with methanol as the solvent, to treat vinyl sulfones **9**, **11**, **13** and **15** the only products observed resulted from conjugate addition rather than epoxidation (figure 3). When a reductive work-up was performed (Na_2SO_3) the products are β-hydroxy sulfones **10**, **12**, **14** and **16**. However, if a simple aqueous work-up was carried out the products are the corresponding β-hydroperoxides, which, as with the peroxides **6** and **8**, proved to be reasonably stable to column chromatography and storage in the freezer (−20 °C). The isolation of similar species has been reported previously and confirms that the nucleophilic species performing the conjugate addition is the hydroperoxide anion [19–21].

Along similar lines to the argument used in figure 2, the likely explanation for the formation of the observed products is that methanol protonates the intermediate conjugate adduct before cyclisation occurs generating the α, β-epoxy sulfone. One possible explanation for

†In contrast to α, β-unsaturated carbonyl compounds the epoxidation of vinyl sulfones in our study were not successful using electrophilic epoxidation reagents such as *m*-CPBA [16] and dioxiranes [17, 18].

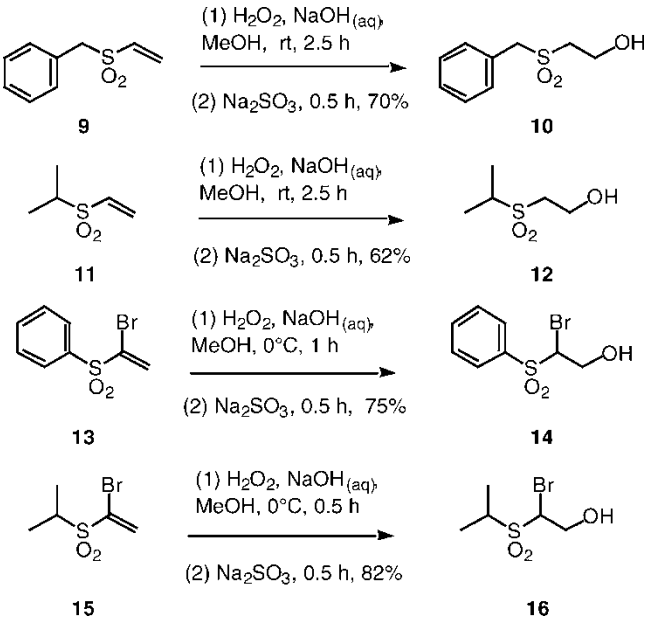


Figure 3. Synthesis of β-hydroxy sulfones via a hydroperoxide conjugate addition reduction sequence.

this behavioural difference to α, β-unsaturated carbonyl compounds is that the pK_a of the α-sulfonyl proton is slightly higher than that of the α-carbonyl proton [1].

Overall this reaction constitutes a simple, high yielding method for the preparation of β-hydroxy sulfones from vinyl sulfones. Attempts to convert the bromohydrins **14** and **16** into the corresponding epoxides under a variety of basic conditions proved unsuccessful possibly due to the field effect of the sulfonyl group.

When hydrogen peroxide was omitted from this type of reaction a rapid reaction ensued and the adducts resulting from the conjugate addition of methanol were isolated in high yield (see figure 4). As a general trend, the α-bromo vinyl sulfones **13** and **15** reacted more rapidly

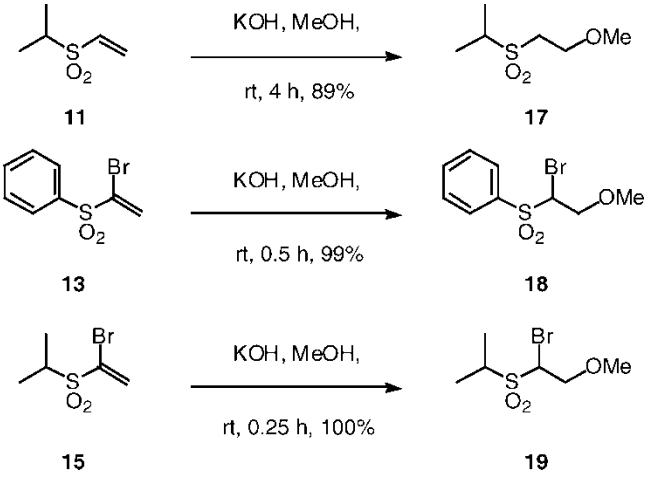


Figure 4. Conjugate addition of methoxide to vinyl sulfones.

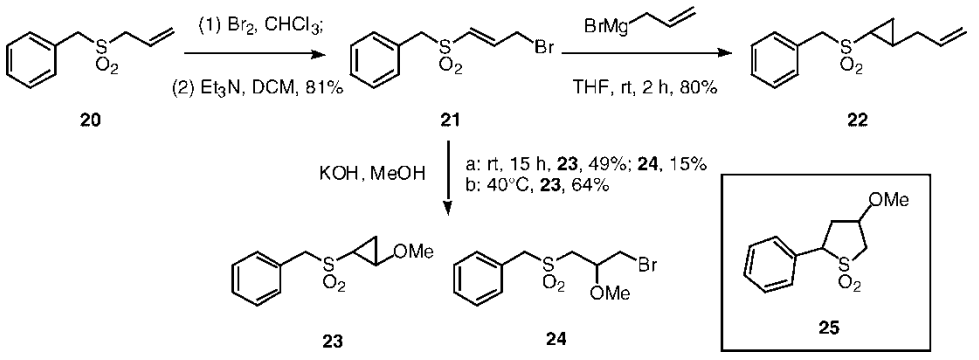


Figure 5. Chemoselective conjugate addition of "hard" nucleophiles to **21**.

than their non-brominated counterparts and the conjugate adducts were isolated in higher yield. These results taken in conjunction with the results described in figure 3 indicate that although the hydroperoxide anion is a better nucleophilic species towards vinyl sulfones than methoxide the conjugate addition of methanol is a synthetically viable and high yielding process. No reaction occurs between vinyl sulfones and methanol at room temperature in the absence of base.

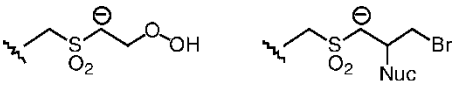
On treatment of base one might expect that compounds **16** and **19** would undergo the Ramberg–Bäcklund rearrangement. However, under the basic reaction conditions we were not able to identify any allylic products stemming from this type of process.

In all the previous cases discussed, the alkenes considered were terminal and did not possess any other reactive groups. Therefore, in order to understand a little more about the chemoselectivity of this type of functional group, the bromo vinyl sulfone **21** was prepared from the corresponding allyl sulfone **20** following a sequence of bromination and elimination [22]. This type of compound has been reported to undergo a conjugate addition – cyclisation process resulting in the formation of sulfonyl substituted cyclopropanes upon treatment with Grignard reagents [22]. We also observed this process when **21** was treated with allylmagnesium bromide and the *trans*-cyclopropane **22** was isolated in good yield. Thus, chemoselective conjugate addition occurs and then, under the aprotic conditions, the α-sulfonyl carbanion undergoes a 3-*exo-tet* cyclisation reaction forming the 3-membered carbocycle (figure 5). Pleasingly, this type of process also occurred when **21** was treated under the basic methanol conditions, and the corresponding cyclopropane **23** was formed along with variable amounts of the conjugate adduct **24**. The yield of **23** was increased when the reaction was conducted under elevated temperature and none of the sulfolane **25** was observed resulting from cyclisation of the benzylic carbon.

This last carbocycle-forming cyclisation process appears to be fundamentally different to the Weitz–Scheffer epoxidation reactions performed in figure 3 – although the conditions for the Weitz–Scheffer reactions were not directly comparable, i.e. H_2O_2 and aqueous NaOH (figure 6). In the former the α-sulfonyl carbanion **26** undergoes protonation rather than carbon-oxygen bond (epoxide) formation, whereas in the later the α-sulfonyl carbanion **27** undergoes carbon-carbon bond (cyclopropane) formation.[‡]

The formation of products **22**, **23** and **24** indicate that there is clearly a preference for the hard organometallic and oxygen nucleophiles to add to the vinylic, β-carbon as opposed to the primary allylic carbon bearing the bromide. In contrast, when softer nucleophiles were

[‡]This hypothesis does not take into account conformational (Thorpe–Ingold type [23]) effects that may be operative in the case of the more substituted anion **27**.



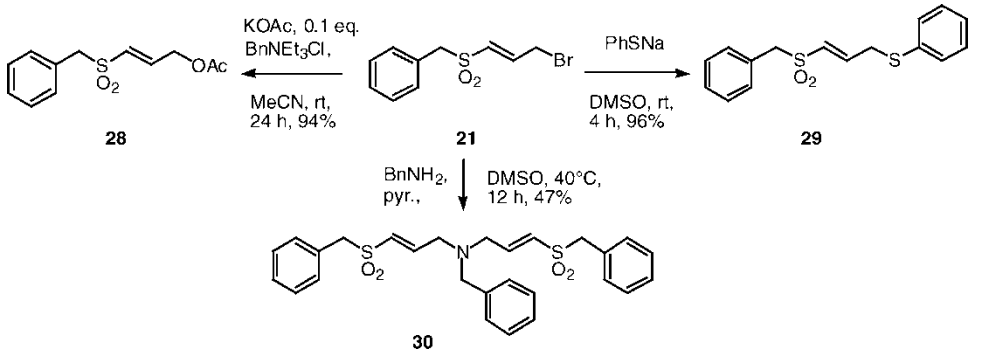
26 **27**

Figure 6. Protonation versus cyclisation of α-sulfonyl carbanionic intermediates **26** and **27**.

employed the products of this latter process were preferentially formed (figure 7). For example, following treatment of **21** with acetate and thiophenoxide only the adducts **28** and **29** were observed. When one equivalent of benzyl amine was used the tertiary amine **30** was isolated, presumably resulting from further reaction of the initially formed secondary amine.

In summary, a series of conjugate addition reactions between vinyl sulfones and oxygen-based nucleophiles, some of which would be formally considered "hard" (e.g. methoxide), result in the formation of the products of conjugate addition in good yield. The treatment of vinyl sulfones under standard Weitz–Scheffer epoxidation conditions results in the formation of β-hydroxy sulfones in good yield (following the reduction of the initially formed β-hydroperoxides). This method represents a synthetically feasible method for the preparation of this compound type. In the context of this report, it should be noted that vinyl sulfones also readily participate in efficient conjugate addition processes with a variety of soft(er) nucleophiles (see figure 8 for example) [24].

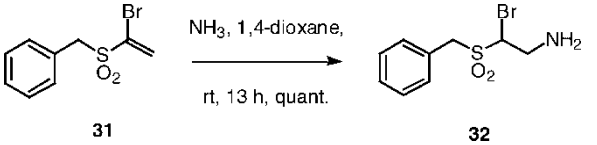
Competitive experiments designed to probe the reactivity preferences between a vinyl sulfone and a primary bromide confirmed these observations. Thus, chemoselective conjugate addition was observed when hard nucleophilic species were used and, in contrast, when soft nucleophiles were used nucleophilic displacement of bromide occurred.



28 **21** **29**

30

Figure 7. Chemoselective addition of "soft" nucleophiles to **21**.



31 **32**

Figure 8. Conjugate addition of ammonia to vinyl sulfone **31**.

3. Experimental

3.1 *General*

The reagents described in the following section were purchased from commercial sources and were used directly unless otherwise stated in the text. THF was dried according to common practice over sodium and benzophenone and were distilled prior to use, DCM was distilled over calcium hydride. The dry TBHP solution in toluene described 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 [25, 26]. 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. Flash chromatography was performed using ICN 33-64 silica under bellows pressure. Short path distillation was carried out using a Kugelrohr apparatus and where applicable the boiling point quoted refers to the oven temperature. Low and high field resolution electron-ionisation (EI) and chemical-ionisation (CI) mass spectrometry was performed by Dr. T. A. Dransfield and Mr. B. R. Glennie using a Fisons Analytical (VG) autospec machine. The values obtained for the high-resolution molecular ions are within ±5 ppm of the required molecular mass. Elemental analyses were performed by Mr. A. Saunders at the University of East Anglia. The 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 ($CHCl_3$ or $CDCl_3$). The ^{1}H and ^{13}C-NMR spectra were recorded on a Jeol EX270 spectrometer at 270.1 and 67.9 MHz respectively. Melting points were recorded on a Electrothermal IA9000 Digital Melting Point Apparatus and were uncorrected.

3.2 *Preparation of 2-(3-phenyl-2-propen-1-sulfonyl)oxirane 5 and 2-(1-phenyl-1-propenyl-3-sulfonyl)-1-tert-butylperoxyethane 6*

3.2.1 2-(3-Phenyl-2-propen-1-sulfanyl)ethan-1-ol. A suspension of 2-mercaptoethanol (5 cm^3, 72.0 mmol, 1 eq.) and K_2CO_3 (20.0 g, 145.0 mmol, 2 eq.) in MeOH (200 cm^3) was treated under N_2 with cinnamyl chloride (10 cm^3, 72.0 mmol, 1 eq.) and heated to reflux for 12 h. H_2O (100 cm^3) and ether (50 cm^3) was added. The phases were separated and the resultant aqueous layer was further extracted with ether (2 × 50 cm^3). The combined ethereal extracts were washed with brine (100 cm^3) and dried over $MgSO_4$. Filtration and solvent removal under reduced pressure afforded *2-(3-phenyl-2-propen-1-sulfanyl)ethan-1-ol* as a yellow oil which was purified by vacuum distillation (11.07 g, 80%), b.p. 155–160 °C/0.05 mmHg. $R_f = 0.60$ (Pet-EtOAc, 1:1); υ_{max} (neat)/cm^{-1} 3379 (OH), 3082, 3059, 3026, 2918, 2873 (CH), 1597, 1576 (C=C), 1495, 1448, 1419 (CH), δ_H (270.1 MHz, $CDCl_3$) 2.72 (2H, t, *J* 6.0, CH_2), 3.34 (2H, d, *J* 7.5, CH_2), 3.75 (2H, t, *J* 6.0, CH_2), 6.20 (1H, dt, *J* 7.5, 15.5, CH), 6.47 (1H, d, *J* 15.5, CH), 7.23–7.43 (5H, m, ArH), δ_C (67.9 MHz, $CDCl_3$) 33.4, 33.7, 60.3 (CH_2), 125.4, 126.1, 127.5, 128.3, 132.3 (CH), 136.3 (C), m/z (EI) 194 (M^+, 10%), 117 ($C_9H_9^+$, 100%); Found 194.0769, $C_{11}H_{14}OS$ requires 194.0765 (−1.9 ppm).

3.2.2 2-(3-Phenyl-2-propen-1-sulfonyl)ethan-1-ol. The allyl sulfide (11.0 g, 0.057 mol, 1 eq.) in AcOH (250 cm^3) was treated with $NaBO_3 \cdot H_2O$ (17.0 g, 0.17 mol, 3 eq.) for 2 days at rt. The AcOH was removed under reduced pressure and the residue was taken up in H_2O (200 cm^3) and EtOAc (100 cm^3). The resultant aqueous layer was extracted with

EtOAc ($3 \times 100\,cm^3$). Washing of the organic extracts with $NaHCO_3$ ($100\,cm^3$) followed by brine ($200\,cm^3$) and drying over $MgSO_4$ afforded *2-(3-phenyl-2-propen-1-sulfonyl)ethan-1-ol* (8.2 g, 65%) as a white solid on filtration and solvent evaporation *in vacuo*. The crude material was purified by recrystallisation, m.p. 126–127 °C (EtOH). $R_f = 0.40$ (Pet-EtOAc, 1:1), υ_{max} (Nujol)/cm^{-1} 3514 (OH), 1277, 1118 (SO_2), δ_H (270.1 MHz, $CDCl_3$) 2.44 (1H, br, OH), 3.23 (2H, t, *J* 5.0, CH_2), 3.99 (2H, d, *J* 7.5, CH_2), 4.14 (2H, t, *J* 5.0, CH_2), 6.2 (1H, dt, *J* 7.5, 15.5, CH), 6.75 (1H, d, *J* 15.5, CH), 7.30–7.44 (5H, m, ArH), δ_C (67.9 MHz, d_6-DMSO) 54.1, 55.1, 58.0 (CH_2), 116.3 (CH), 126.6, 128.3, 128.7 (CH), 135.9 (C), 138.0 (CH), m/z (CI) 244 (MNH_4^+, 100%); Found 244.1012, $C_{11}H_{14}O_3S \cdot NH_4$ requires 244.1007 (−2.0 ppm).

3.2.3 3-Phenyl-2-propen-1-sulfonylethene 4. A mixture of the β-hydoxysulfone (3.42 g, 0.015 mol, 1 eq.) and MsCl ($1.8\,cm^3$, 0.023 mol, 1.5 eq.) in DCM ($150\,cm^3$) was treated with TEA ($6.4\,cm^3$, 0.046 mol, 3 eq.) in a dropwise fashion at 0 °C. Stirring was maintained for 12 h during which time rt was reached. 1 M HCl ($150\,cm^3$) was added to the reaction mixture and the resultant aqueous layer was extracted with DCM ($3 \times 50\,cm^3$). The combined organic extracts were washed with H_2O ($50\,cm^3$) and brine ($100\,cm^3$). Drying over $MgSO_4$ followed by filtration and solvent removal *in vacuo* afforded the crude alkene as a yellow oil. Purification by flash column chromatography (Pet-EtOAc, 1:1) yielded *3-phenyl-2-propen-1-sulfonylethene* **4** (2.99 g, 96%) as a white solid, m.p. 57–58 °C. $R_f = 0.40$ (Pet-EtOAc, 1:1); υ_{max} (Nujol)/cm^{-1} 1623, 1577 (C=C), 1313, 1128 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.90 (2H, d, *J* 7.5, CH_2), 6.19 (1H, d, *J* 10.0, CH), 6.19 (1H, dd, *J* 7.5, 16.0, CH), 6.44 (1H, d, *J* 16.5, CH), 6.66 (1H, d, *J* 16.0, CH), 6.68 (1H, dd, *J* 10.0, 16.5, CH), 7.30–7.42 (5H, m, ArH), δ_C (67.9 MHz, $CDCl_3$) 58.6 (CH_2), 114.7, 126.6, 128.6, 128.7 (CH), 131.1 (CH_2), 135.4 (CH), 135.5 (C), 139.2 (CH); m/z (CI) 226 (MNH_4^+, 100%); Found 226.0899, $C_{11}H_{12}O_2S \cdot NH_4$ requires 226.0902 (+1.1 ppm); [Found C, 63.50; H, 5.74; S, 15.50%, $C_{11}H_{12}O_2S$ requires C, 63.43; H, 5.81; S 15.40%].

3.2.4 2-(3-Phenyl-2-propen-1-sulfonyl)oxirane 5. The sulfone **4** (1.70 g, 8.18 mmol, 1 eq.) in THF ($40\,cm^3$) was treated under the standard conditions for Meth-Cohn epoxidation [4]. Thus, LiO^tBu_2 was generated at −78 °C from 3.16 M TBHP in toluene ($3.9\,cm^3$, 12.32 mmol, 1.5 eq.) and 2.5 M ^{n}BuLi in hexanes ($3.6\,cm^3$, 9.0 mmol, 1.1 eq.) in THF ($80\,cm^3$). The mixture resulting from the addition of the vinyl sulfone solution was stirred at −20 °C for 0.5 h before Na_2SO_3 (*ca.* 2 g) was added. After the mixture was further stirred for a further 0.25 h at −20 °C the reaction mixture was filtered through celite and washed with ether ($2 \times 200\,cm^3$). Concentration *in vacuo* followed by flash column chromatography (Pet-EtOAc, 3:1 to Pet-EtOAc, 1:1) gave *2-(3-phenyl-2-propen-1-sulfonyl)oxirane* **5** (350 mg, 19%) as a pale yellow solid, m.p. 77.5–79 °C (EtOAc-Pet). $R_f = 0.15$ (Pet-EtOAc, 3:1); υ_{max} ($CDCl_3$)/cm^{-1} 3041, 2918 (CH), 1653 (C=C), 1319, 1226 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.13 (1H, dd, *J* 3.5, 5.5, CH), 3.44 (1H, dd, *J* 2.0, 5.5, CH), 3.99 (2H, m, CH_2), 4.22 (1H, dd, *J* 2.0, 3.5, CH), 6.28 (1H, ddt, *J* 6.5, 8.5, 15.5, CH), 6.81 (1H, d, *J* 15.5, CH), 7.32–7.46 (5H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 44.5, 56.2 (CH_2), 60.1, 113.6 (CH), 126.8, 128.8, 128.9 (CH), 135.4 (C), 140.0 (CH); m/z (CI) 242 (MNH_4^+, 100%); Found 242.0846, $C_{11}H_{12}O_3S \cdot NH_4$ requires 242.0810 (+2.1 ppm).

3.2.5 2-(1-Phenyl-1-propenyl-3-sulfonyl)-1-tert-butylperoxyethane 6. At room temperature a mixture of the vinyl sulfone **4** (208 mg, 1.0 mmol, 1 eq.) and 5-6M TBHP in hexane ($0.9\,cm^3$, 5.0–6.0 mmol, 5–6 eq.) in EtOAc ($10\,cm^3$) were treated with DBU (152 mg, 1.0 mmol, 1 eq.). Stirring was continued for 8 h before saturated $FeSO_4$ solution ($10\,cm^3$)

was added. The resultant mixture was extracted with EtOAc ($4 \times 20\,cm^3$) and the combined organic extracts were washed with H_2O ($20\,cm^3$), brine ($50\,cm^3$) and dried over $MgSO_4$. Filtration and solvent removal under reduced pressure afforded the crude peroxide which was purified by flash column chromatography (Pet-EtOAc, 3:1) to give *2-(1-phenyl-1-propenyl-3-sulfonyl)-1-*tert*-butylperoxyethane* **6** (222 mg, 74%) as a white solid. $R_f = 0.25$ (Pet-EtOAc, 1:1); υ_{max} ($CDCl_3$)/cm^{-1} 3060, 2979, 2931 (CH), 1495, 1450 (CH), 1365, 1320, 1124 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 1.36 (9H, s, CH_3), 3.42 (2H, t, *J* 5.0, CH_2), 4.05 (2H, d, *J* 7.5, CH_2), 4.48 (2H, t, *J* 5.0, CH_2), 6.38 (1H, dt, *J* 7.5, 16.0, CH), 6.87 (1H, d, *J* 16.0, CH), 7.34–7.52 (5H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 26.1 (CH_3), 49.5, 58.6, 68.7 (CH_2), 81.0 (C), 115.2, 126.5, 128.2, 128.5 (CH), 135.6 (C), 138.99 (CH); m/z (CI) 316 (MNH_4^+, 100%); Found 316.1588, $C_{15}H_{22}O_4S \cdot NH_4$ requires 316.1583 (−1.8 ppm).

3.3 *Preparation of 2-(phenylsulfonylmethylsulfonyl)-1-tert-butylperoxyethane 8*

3.3.1 2-(Phenylsulfonylmethylsulfonyl)ethan-1-ol. Chloromethyl phenyl sulfide (5.0 g, 31.5 mmol, 1 eq.) and K_2CO_3 (8.7 g, 63.0 mmol, 2 eq.) in MeOH ($100\,cm^3$) under nitrogen were treated with 2-mercaptoethanol ($2.2\,cm^3$, 31.4 mmol, 1 eq.) and the suspension was heated to reflux for 4 h. Ether ($50\,cm^3$) and water ($50\,cm^3$) was added. The resultant aqueous layer was then further extracted with ether ($2 \times 50\,cm^3$). Washing of the ethereal extracts with $NaHCO_3$ ($50\,cm^3$), H_2O ($50\,cm^3$) and brine ($50\,cm^3$) and finally drying over $MgSO_4$ gave on filtration and solvent removal *in vacuo* the sulfide as a clear oil, which was oxidised without further purification. $R_f = 0.40$ (Pet-EtOAc, 1:1). Following the method of oxidation described above sodium perborate (18.9 g, 189.0 mmol, 6 eq.) was added to a solution of *2-(phenylsulfanylmethylsulfanyl)ethan-1-ol*: (*ca.* 31.0 mmol) in AcOH ($200\,cm^3$) afforded the bis-sulfone. The clear oil obtained after standard work-up gradually solidified m.p. 96–98 °C ($CHCl_3$). $R_f = 0.20$ (Pet-EtOAc, 1:1); υ_{max} ($CDCl_3$)/cm^{-1} 3451 (OH), 3061, 2987, 2924 (CH), 1333, 1159, 1138 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.65 (2H, t, *J* 4.5, CH_2), 4.13 (2H, t, *J* 4.5, CH_2), 4.92 (2H, s, CH_2), 7.55–7.73 (3H, m, ArH), 7.92–8.00 (2H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 56.3, 56.6, 73.3 (CH_2), 128.9, 129.4, 134.9 (CH), 138.2 (C); m/z (CI) 282 (MNH_4^+, 100%); Found 282.0462, $C_9H_{12}O_5S_2 \cdot NH_4$ requires 282.0470 (+2.7 ppm).

3.3.2 2-(Phenylsulfonylmethylsulfonyl)ethene 7. The crude bis-sulfone (8.3 g, 31.5 mmol, 1 eq.) in DCM ($100\,cm^3$) was treated with MsCl ($3.7\,cm^3$, 46.9 mmol, 1.5 eq.) followed by TEA ($8.8\,cm^3$, 63.0 mmol, 2 eq.) at 0 °C. After addition stirring was maintained for 15 h at rt. Standard work-up afforded the crude product which was purified by flash column chromatography (Pet-EtOAc, 1:1) to afford *2-(phenylsulfonylmethylsulfonyl)ethene* **7** (1.11 g, 14%, 3 steps) as a white solid, m.p. 97–98 °C (EtOAc-Pet). $R_f = 0.35$ (Pet-EtOAc, 1:1); υ_{max} ($CHCl_3$)/cm^{-1} 3109, 3074, 3029, 2983, 2926 (CH), 1610, 1585 (C=C), 1448, 1387 (CH), 1340, 1165, 1140 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 4.59 (2H, s, CH_2), 6.23 (1H, d, *J* 10.0, CH_2), 6.44 (1H, d, *J* 16.5, CH_2), 6.95 (1H, dd, *J* 10.0, 16.5, CH), 7.53–7.74 (3H, m, ArH), 7.86–8.00 (2H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 73.8 (CH_2), 129.0, 129.4 (CH), 132.4 (CH_2), 135.0, 136.2 (CH), 138.1 (C); m/z (CI) 264 (MNH_4^+, 100%); Found 264.0372, $C_9H_{10}O_4S_2 \cdot NH_4$ requires 264.0364 (−2.8 ppm).

3.3.3 2-(Phenylsulfonylmethylsulfonyl)-1-tert-butylperoxyethane 8. Following the standard epoxidation protocol; under nitrogen **7** (50 mg, 0.24 mmol, 1 eq.) in THF ($1\,cm^3$) was added dropwise to a solution of LiO_2^tBu generated from anhydrous 2.63 M TBHP in toluene ($0.14\,cm^3$, 0.36 mmol, 1.5 eq.) and 1.6 M ^nBuLi in hexanes ($0.16\,cm^3$, 0.26 mmol,

1.1 eq.) in THF (5 cm^3) at −78 °C. After 0.25 h at −78 °C the reaction was warmed to −15 °C and stirring was maintained for 4 h over which period room temperature was attained. The reaction mixture was cooled to −78 °C and saturated NH_4Cl (5 cm^3) was added. Extraction was carried out with EtOAc (3 × 15 cm^3) and the combined organic extracts were washed with brine (25 cm^3) and dried over Na_2SO_4. Filtration followed by solvent removal under reduced pressure and flash column chromatography (Pet-EtOAc, 1:1) afforded the peroxide **8** (15 mg, 19%) as a white solid. $R_f = 0.20$ (Pet-EtOAc, 3:1); υ_{max} ($CDCl_3$)/cm^{-1} 3053, 2985, 2927 (CH), 1475, 1448, 1421 (CH), 1338, 1138 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 1.22 (9H, s, CH_3), 3.71 (2H, t, *J* 5.0, CH_2), 4.34 (2H, t, *J* 5.0, CH_2), 4.75 (2H, s, CH_2), 7.50–7.68 (3H, m, ArH), 7.93–7.98 (2H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 26.2 (CH_3), 52.5, 68.8, 73.1 (CH_2), 81.7 (C), 129.0, 129.3 134.7 (CH), 138.7 (C); m/z (CI) 354 (MNH_4^+, 100%); Found 354.1050, $C_{13}H_{20}O_6S_2 \cdot NH_4$ requires 354.1045 (−1.5 ppm).

3.4 *Preparation of β-hydroxy sulfones from vinyl sulfones*

3.4.1 2-Benzylsulfonylethan-1-ol 10. A solution of benzyl vinyl sulfone **9** (141 mg, 0.77 mmol, 1 eq.) and 30% H_2O_2 (0.44 cm^3, 3.88 mmol, 5 eq.) in MeOH (20 cm^3) at rt were treated dropwise with a solution of NaOH (31 mg, 0.78 mmol, 1 eq.) in H_2O (0.4 cm^3). Stirring was continued for 2.5 h before powdered Na_2SO_3 (*ca.* 0.5 g) was added, and the mixture was further stirred for 0.5 h. Filtration through celite, washing of the residue with MeOH (2 × 50 cm^3) and concentration *in vacuo* followed by column chromatography (Pet-EtOAc, 1:1) afforded *2-benzylsulfonylethan-1-ol* **10** (109 mg, 70%) as a white solid, m.p. 70 °C (EtOAc); lit. m.p. 68–71 °C [27]. $R_f = 0.15$ (Pet-EtOAc, 1:1); υ_{max} (Nujol)/cm^{-1} 3389 (OH), 1377, 1128 (SO_2); δ_H(270.1 MHz $CDCl_3$) 2.51 (1H, br, OH), 3.02 (2H, t, *J* 5.5, CH_2), 4.01 (2H, t, *J* 5.5, CH_2), 4.28 (2H, s, CH_2), 7.07–7.39 (5H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 52.9, 56.4, 61.1 (CH_2), 128.4 (C), 129.0, 129.1, 130.9 (CH); m/z (EI) 200 (M^+, 1%), 91 (Bn^+, 100%); Found 200.0514, $C_9H_{12}O_3S$ requires 200.0507 (−3.3 ppm); [Found C, 54.29; H, 6.12; S, 16.04%, $C_9H_{12}O_3S$ requires C, 53.98; H, 6.04; S, 16.01%].

3.4.2 2-(Propan-2-sulfanyl)ethan-1-ol [28]. Potassium carbonate (6.20 g, 44.86 mmol, 2 eq.), 2-mercaptoethanol (1.73 cm^3, 22.67 mmol, 1 eq.) and catalytic potassium iodide (*ca.* 200 mg) were combined under nitrogen in acetone (100 cm^3). 2-Bromopropane (4.22 cm^3, 44.86 mmol, 2 eq.) was added and the mixture was heated to reflux for 12 h. Upon cooling the precipitate was removed by filtration and the mixture was concentrated under reduced pressure. Water (25 cm^3) was added and extraction carried out with ether (3 × 30 cm^3). The combined organic layers were washed with $NaHCO_3$ (25 cm^3), brine (25 cm^3) and dried over $MgSO_4$. Filtration and solvent removal *in vacuo* afforded the crude product, which was purified by short path distillation to give *2-(propan-2-sulfanyl)ethan-1-ol* (2.24 g, 89%) as a clear oil, b.p. 75 °C/0.5 mmHg. $R_f = 0.45$ (Pet-EtOAc, 1:1); υ_{max} (neat)/cm^{-1} 3390 (OH), 2950, 2926, 2868 (CH); δ_H (270.1 MHz, $CDCl_3$) 1.28 (6H, d, *J* 7.0, CH_3), 2.67 (1H, br, OH), 2.75 (2H, t, *J* 6.0, CH_2), 2.96 (1H, sept, *J* 7.0, CH), 3.72 (2H, q, *J* 6.0, CH_2); δ_C (67.9 MHz, $CDCl_3$) 23.4 (CH_3), 33.5 (CH_2), 34.5 (CH), 60.7 (CH_2); m/z (CI) 121 (MNH_4^+, 100%); Found 121.0691, $C_5H_{12}S \cdot NH_4$ requires 121.0687 (−3.1 ppm).

3.4.3 1-Chloro-2-(propan-2-sulfanyl)ethane [28]. 2-*(Propan-2-sulfanyl)ethan-1-ol* (785 mg, 6.31 mmol, 1 eq.) and pyridine (0.5 cm^3, 6.2 mmol, 0.98 eq.) in DCM (10 cm^3) were treated at 0 °C with thionyl chloride (0.7 cm^3, 9.46 mmol, 1.5 eq.). After the addition of the chlorinating agent the reaction was warmed to rt. Stirring was maintained for 1 h before

addition of water (20 cm^3). The aqueous layer was extracted with DCM (3 × 20 cm^3) the combined organic extracts were washed with water (20 cm^3), a brine solution (20 cm^3) and dried over $MgSO_4$. Filtration and solvent removal *in vacuo* furnished a crude oil which was purified by short path distillation affording *1-chloro-2-(propan-2-sulfanyl)ethane* (980 mg, 91%) as a clear oil b.p. 95 °C/25 mmHg. $R_f = 0.55$ (Pet-EtOAc, 9:1); υ_{max} (neat)/cm^{-1} 2961, 2927, 2867, 1445, 1212 (CH); δ_H (270.1 MHz, $CDCl_3$) 1.27 (6H, d, *J* 7.0, CH_3), 2.86 (2H, t, *J* 8.0, CH_2), 2.97 (1H, sept, *J* 7.0, CH), 3.61 (2H, t, *J* 8.0, CH_2); δ_C (67.9 MHz, $CDCl_3$) 14.9 (CH_3), 35.5 (CH), 51.4, 54.1 (CH_2); m/z (EI) 138 (M^+, ^{37}Cl, 40%), 43 ($^iPr^+$, 100%); Found 138.0276, $C_5H_{11}ClS$ requires 138.0270 (−0.5 ppm).

3.4.4 2-(Propan-2-sulfonyl)ethene 11 [28]. *1-Chloro-2-(propan-2-sulfanyl)ethane* was converted into the corresponding vinyl sulfone **11** in one pot. Thus, the chloride (23.12 g, 0.17 mol, 1 eq.) in acetic acid (100 cm^3) was treated dropwise at 0 °C with 30% aqueous hydrogen peroxide (45 cm^3, 0.40 mol, 2.4 eq.). Stirring was maintained for 12 h during which time the temperature rose to rt. Removal of the solvent and excess oxidising agent under reduced pressure afforded the crude sulfone. The crude sulfone was then dissolved in DCM (200 cm^3) and treated dropwise at 0 °C with triethylamine (47 cm^3, 0.34 mol, 2 eq.). Stirring was maintained for a further 12 h during which period room temperature was reached. Water (200 cm^3) was added and the resultant aqueous layer was extracted with DCM (3 × 100 cm^3). The combined organic extracts were washed with water (100 cm^3), brine (100 cm^3) and dried over $MgSO_4$. Filtration followed by removal of the solvent under reduced pressure furnished the crude product as a pale yellow oil. Purification by short path distillation afforded *2-(propan-2-sulfonyl)ethene* **11** (18.27 g, 76%) as a clear oil, b.p. 100 °C/0.5 mmHg. $R_f = 0.30$ (Pet-EtOAc, 1:1); υ_{max} (neat)/cm^{-1} 3059, 2983, 2941 (CH), 1612 (C=C), 1305, 1128 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 1.24 (6H, d, *J* 7.0, CH_3), 2.98 (1H, sept, *J* 7.0, CH), 6.14 (1H, d, *J* 9.5, CH_2), 6.31 (1H, d, *J* 17.0, CH_2), 6.53 (1H, dd, *J* 9.5, 17.0, CH); δ_C (67.9 MHz, $CDCl_3$) 15.6 (CH_3), 54.2 (CH), 132.0 (CH_2), 134.2 (CH); m/z (CI) 152 (MNH_4^+, 100%); Found 152.0747, $C_5H_{10}O_2S \cdot NH_4$ requires 152.0745 (−0.9 ppm).

3.4.5 2-(Propan-2-sulfonyl)ethan-1-ol 12. Following the procedure described above the vinyl sulfone **157** (107 mg, 0.80 mmol, 1 eq.) and 30% H_2O_2 (0.45 cm^3, 3.99 mmol, 5 eq.) in MeOH (20 cm^3) were treated with NaOH (35 mg, 0.88 mmol, 1.1 eq.) in water (1 cm^3). Stirring was continued for 2.5 h before Na_2SO_3 (*ca.* 1 g) was added. After 0.5 h the solution was filtered through celite, washing with MeOH (2 × 50 cm^3) and concentrated under reduced pressure. Purification by column chromatography (Pet-EtOAc, 1:1) afforded *2-(propan-2-sulfonyl)ethan-1-ol* **12** (75 mg, 62%) as a clear oil. $R_f = 0.20$ (Pet-EtOAc, 1:1); υ_{max} (neat)/cm^{-1} 3484 (OH), 2983, 2941, 2885, (CH), 1290, 1121 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 1.36 (6H, d, *J* 7.0, CH_3), 3.23 (2H, t, *J* 5.5, CH_2), 3.25 (2H, sept, *J* 7.0, CH), 4.12 (2H, m(br), CH_2); δ_C (67.9 MHz, $CDCl_3$) 14.50 (CH_3), 51.20 (CH_2), 53.81 (CH), 55.65 (CH_2); m/z (CI) 170 (MNH_4^+, 100%), 153 (MH^+, 25%); Found 153.0583, $C_5H_{12}O_3S \cdot H$ requires 153.0585 (+1.5 ppm).

3.4.6 1,2-Dibromo-1-phenylsulfonylethane [29]. Phenyl vinyl sulfone (1.75 g, 10.43 mmol, 1 eq.) in CCl_4 (30 cm^3) was treated with bromine (0.58 cm^3, 11.47 mmol, 1.1 eq.) dropwise at rt. Stirring was continued for 24 h before the solvent was removed and water (20 cm^3) and DCM (20 cm^3) were added. The resultant aqueous layer was further extracted with DCM (3 × 20 cm^3). The combined organic extracts were washed with 5% Na_2SO_3 (20 cm^3), brine (20 cm^3) and dried over $MgSO_4$. Filtration and solvent evaporation *in vacuo* afforded the

crude dibromide which was purified by column chromatography (Pet-EtOAc, 5:1) yielding *1,2-dibromo-1-phenylsulfonylethane* (2.96 g, 87%) as a white solid, m.p. 71 °C; lit. m.p. 76–77 °C [29]. $R_f = 0.35$ (Pet-EtOAc, 5:1); υ_{max}(Nujol)/cm^{-1} 1333, 1149 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.58 (1H, dd, *J* 10.0, 11.5, CH_2), 4.28 (1H, dd, *J* 3.5, 11.5, CH_2), 4.94 (1H, dd, *J* 3.5, 10.0, CH), 7.61–7.66 (2H, m, ArH), 7.73–7.79 (1H, m, ArH), 7.79–8.01 (2H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 29.4 (CH_2), 65.0 (CH), 129.4, 130.1 (CH), 134.8 (C), 135.1 (CH); m/z (CI) 346 (MNH_4^+, ^{81}Br, ^{79}Br, 25%); Found 343.8957, $C_8H_8Br_2O_2S \cdot NH_4$ requires 343.8955 (−0.4 ppm).

3.4.7 1-Bromo-1-phenylsulfonylethene 13 [29]. The dibromide (2.51 g, 7.65 mmol, 1 eq.) in DCM (50 cm^3) was treated at rt with Et_3N (1.28 cm^3, 9.19 mmol, 1.2 eq.) and stirring was maintained for 4 h. Water (50 cm^3) was added and the resultant aqueous extract was further extracted with DCM (3 × 30 cm^3). The combined organic layers were washed with brine (50 cm^3) and dried over $MgSO_4$. Filtration and solvent removal under reduced pressure afforded *1-bromo-1-phenylsulfonylethene* **13** (0.83 g, 97%) as a white solid, m.p. 42 °C (EtOAc-Pet); lit. m.p. 46 °C [29]. $R_f = 0.35$ (Pet-EtOAc, 5:1); υ_{max} (neat)/cm^{-1} 3108, 3065, 3019 (CH), 1601 (C=C), 1324, 1161 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 6.29 (1H, d, *J* 3.0, CH_2), 7.13 (1H, d, *J* 3.0, CH_2), 7.56–7.61 (2H, m, ArH), 7.66–7.73 (1H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 129.1 (CH_2), 129.2 (CH), 129.8 (C), 134.3 (CH), 136.4 (C); m/z (CI) 266 (MNH_4^+, ^{81}Br, 100%); Found 263.9685, $C_8H_7BrO_2S \cdot NH_4$ reqiures 263.9694 (+3.3 ppm).

3.4.8 2-Phenylsulfonyl-2-bromoethan-1-ol 14. *1-Bromo-1-phenylsulfonylethene* **13** (637 mg, 2.58 mmol, 1 eq.) and 30% H_2O_2 (1.46 cm^3, 12.89 mmol, 5 eq.) in MeOH (20 cm^3) was converted to *2-Phenylsulfonyl-2-bromoethan-1-ol* **14** (558 mg, 82%) upon treatment with NaOH (124 mg, 3.10 mmol, 1.2 eq.) in H_2O (1 cm^3) at 0 °C. Stirring was continued for 0.5 h. 5% Na_2SO_3 (50 cm^3) was added and the mixture was extracted with DCM (5 × 25 cm^3). The combined organic extracts were washed with water (30 cm^3), brine (50 cm^3) and dried over $MgSO_4$. Filtration, solvent removal under reduced pressure and column chromatography (Pet-EtOAc, 1:1) afforded the desired material as a white solid. $R_f = 0.40$ (Pet-EtOAc, 1:1); υ_{max} (neat)/cm^{-1} 3504 (OH), 3097, 2956, 2877 (CH), 1311, 1149 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.58 (1H, br, OH), 4.00 (1H, dd, *J* 7.0, 13.0, CH_2), 4.16 (1H, dd, *J* 5.5, 13.0, CH_2), 4.94 (1H, t, *J* 7.0, CH), 7.47–7.89 (5H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 62.3 (CH_2), 64.2 (CH), 129.1, 129.7, 134.8 (CH), 135.1 (C); m/z (CI) 284 (MNH_4^+, ^{81}Br, 100%); Found 281.9813, $C_8H_9BrO_3S \cdot NH_4$ requires 281.9800 (−4.7 ppm).

3.4.9 1,2-Dibromo-2-(propan-2-sulfonyl)ethane [28]. Isopropyl vinyl sulfone **11** (14.66 g 0.11 mol, 1 eq.) in CCl_4 (100 cm^3) was treated dropwise at rt with bromine (5.6 cm^3, 0.11 mol, 1 eq.). Stirring was continued for 3 days. DCM (100 cm^3) and water (100 cm^3) were added followed by extraction of the resultant aqueous layer with DCM (3 × 50 cm^3). The combined organic layers were then washed with saturated Na_2SO_3 solution (100 cm^3) and brine (100 cm^3) and dried over $MgSO_4$. Solvent evaporation *in vacuo* gave an oil which was purified by short path distillation to furnish *1,2-dibromo-2-(propan-2-sulfonyl)ethane* (27.90 g, 86%) as a yellow oil, b.p. 150 °C/0.5 mmHg. $R_f = 0.50$ (Pet-EtOAc, 1:1); υ_{max} (neat)/cm^{-1} 3024, 2979, 2940 (CH), 1318, 1134 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 1.48 (3H, d, *J* 7.0, CH_3), 1.50 (3H, d, *J* 7.0, CH_3), 3.81 (1H, dd, *J* 10.0, 12.0, CH_2), 3.93 (1H, sept, *J* 7.0, CH), 4.39 (1H, dd, *J* 3.1, 11.6, CH_2), 5.03 (1H, dd, *J* 3.0, 10.0, CH); δ_C (67.9 MHz, $CDCl_3$) 13.6, 16.2 (CH_3), 28.5 (CH_2), 51.6, 59.2 (CH); m/z (CI) 312 (MNH_4^+, ^{81}Br, ^{81}Br, 100%); Found 309.9111, $C_5H_{10}Br_2O_2S \cdot NH_4$ requires 309.9112 (+0.5 ppm).

3.4.10 1-Bromo-1-(propan-2-sulfonyl)ethene 15 [28]. *1,2-Dibromoethyl isopropyl sulfone* (25.27 g, 86.0 mmol, 1 eq.) in DCM (200 cm^3) was treated at 0 °C with TEA (18 cm^3, 129 mmol, 1.5 eq.). Stirring was maintained for 12 h during which time rt was reached. NH_4Cl (100 cm^3) was added and the resultant aqueous layer was extracted with DCM (3 × 100 cm^3). Washing of the combined organic extracts with water (100 cm^3), brine (100 cm^3) and drying over $MgSO_4$ followed by filtration and solvent evaporation *in vacuo* afforded the crude product. Purification by short path distillation gave *1-bromo-1-(propan-2-sulfonyl)ethene* **15** (17.99 g 98%) as a yellow oil, b.p. 110 °C/0.5 mmHg. $R_f = 0.55$ (Pet-EtOAc, 1:1); υ_{max} (neat)/cm^{-1} 3108, 3017, 2984, 2940, 2878 (CH), 1602 (C=C), 1315, 1147 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 1.31 (6H, d, *J* 7.0, CH_3), 3.50 (1H, sept, *J* 7.0, CH), 6.43 (1H, d, *J* 3.0, CH_2), 6.95 (1H, d, *J* 3.0, CH_2); δ_C (67.9 MHz, $CDCl_3$) 14.4 (CH_3), 49.9 (CH), 125.2 (C), 131.4 (CH_2); m/z (CI) 232 (MNH_4^+, ^{81}Br, 100%); Found 229.9851, $C_5H_9BrO_2S \cdot NH_4$ requires 229.9850 (−0.3 ppm); [Found C, 28.43; H, 4.11; Br, 37.51; S, 15.28%, $C_5H_9BrO_2S$ requires C, 28.18; H, 4.26; Br, 37.50; S, 15.05%].

3.4.11 2-(Propan-2-sulfonyl)-2-bromoethan-1-ol 16. *1-Bromo-1-(propan-2-sulfonyl) ethene* **15** (323 mg, 1.52 mmol, 1 eq.) and 30% H_2O_2 (0.86 cm^3, 7.60 mmol, 5 eq.) in MeOH (8 cm^3) were treated with a solution of NaOH (127 mg, 3.20 mmol, 2 eq.) in H_2O (0.5 cm^3) at 0 °C. Stirring was continued at rt for 1 h before NH_4Cl (15 cm^3) was added. Extraction with EtOAc (3 × 20 cm^3), washing of the combined organic extracts with brine (20 cm^3) and drying over $MgSO_4$ gave the crude product, on filtration and solvent removal *in vacuo*. Purification by column chromatography (Pet-EtOAc, 1:1) afforded *2-(propan-2-sulfonyl)-2-bromoethan-1-ol* **16** (261 mg, 75%) as a clear oil. $R_f = 0.20$ (Pet-EtOAc, 1:1); υ_{max} (neat)/cm^{-1} 3520 (OH), 2989, 2940, 2877, (CH), 1312, 1130 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 1.37 (6H, d, *J* 7.0, CH_3), 2.90 (1H, s(br), OH), 3.68 (1H, sept, *J* 7.0, CH), 4.16 (1H, m(br), CH_2), 4.30 (1H, dd, *J* 7.0, 13.0, CH_2), 4.85 (1H, dd, *J* 4.5, 7.0, CH); δ_C (67.9 MHz, $CDCl_3$) 13.9, 16.5 (CH_3), 52.1, 58.0 (CH), 62.0 (CH_2); m/z (CI) 250 (MNH_4^+, ^{81}Br, 100%).

3.5 *Preparation of β-methoxy sulfones from vinyl sulfones*

3.5.1 1-Bromo-1-phenylsulfonyl-2-methoxyethane 18. Sulfone **13** (74 mg, 0.30 mmol, 1 eq.) in MeOH (5 cm^3) was treated dropwise at rt with a solution of KOH (33 mg, 0.60 mmol, 2 eq.) in MeOH (2 cm^3). After 0.25 h ether (25 cm^3) and NH_4Cl (10 cm^3) were added. Further extraction of the resultant aqueous layer with ether (2 × 15 cm^3), followed by washing of the combined organic phases with brine (50 cm^3) and drying over $MgSO_4$ afforded the crude adduct on filtration and solvent removal *in vacuo*. Purification by column chromatography (Pet-EtOAc, 3:1) gave the *title compound* **18** (83 mg, 99%) as a white solid. $R_f = 0.20$ (Pet-EtOAc, 3:1); υ_{max} (neat)/cm^{-1} 3066, 2937, 2831 (CH), 1324, 1151 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.36 (3H, s, CH_3), 3.85 (1H, dd, *J* 7.0, 11.5, CH_2), 4.11 (1H, dd, *J* 4.5, 11.5, CH_2), 4.93 (1H, dd, *J* 4.5, 7.0, CH), 7.57–7.63 (2H, m, ArH), 7.69–7.75 (1H, m, ArH), 7.95–8.00 (2H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 53.4 (CH), 62.4 (CH_3), 71.3 (CH_2), 129.2, 130.2, 134.6 (CH), 135.8 (C); m/z (CI) 298 (MH_4^+, ^{81}Br, 100%); Found 295.9954, $C_9H_{11}BrO_3S \cdot NH_4$ requires 295.9956 (+0.7 ppm).

3.5.2 2-(Propan-2-sulfonyl)-1-methoxyethane 17. *2-(Propan-2-sulfonyl)-1-methoxy ethane* **17** (246 mg, 89%) was prepared as a clear oil following the previously described protocol from the vinyl sulfone **11** (249 mg, 1.66 mmol, 1 eq.) in MeOH (10 cm^3) and a solution of KOH (209 mg, 3.72 mmol, 2.2 eq.) in MeOH (4 cm^3). Stirring was continued for 4 h

before the reaction mixture was subjected to work-up as described previously. The crude product was purified by column chromatography (Pet-EtOAc, 1:1) yielding **17** as a clear oil. $R_f = 0.25$ (Pet-EtOAc, 1:1); υ_{max} (neat)/cm^{-1} 2985, 2939 (CH), 1313, 1115 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 1.37 (6H, d, *J* 7.0, CH_3), 3.18 (2H, t, *J* 6.0, CH_2), 3.26 (1H, sept, *J* 7.0, CH), 3.36 (3H, s, CH_3), 3.80 (2H, t, *J* 6.0, CH_2); δ_C (67.9 MHz, $CDCl_3$) 14.8 (CH_3), 49.8 (CH_2), 53.8 (CH), 58.7 (CH_3), 65.7 (CH_2); m/z (CI) 184 (MNH_4^+, 100%); Found 184.1003, $C_6H_{14}O_3S \cdot NH_4$ requires 184.1001 (−1.6 ppm).

3.5.3 1-Bromo-1-(propan-2-sulfonyl)-2-methoxyethane 19. The adduct **19** (252 mg, 100%) was prepared from the vinyl sulfone **15** (220 mg, 1.03 mmol, 1 eq.) in MeOH (10 cm^3) upon treatment at rt with a solution of KOH (116 mg, 2.07 mmol, 2 eq.) in MeOH (3 cm^3) after 2 min as a clear oil following the method described above. $R_f = 0.25$ (Pet-EtOAc, 3:1); υ_{max} (neat)/cm^{-1} 2983, 2939, 2833 (CH), 1318, 1132 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 1.32 (3H, d, *J* 7.0, CH_3), 1.35 (3H, d, *J* 7.0, CH_3), 3.38 (3H, s, CH_3), 3.67 (1H, sept, *J* 7.0, CH), 3.86 (1H, dd, *J* 6.0, 11.0, CH_2), 4.06 (1H, dd, *J* 6.0, 11.0, CH_2), 4.90 (1H, t, *J* 6.0, CH); δ_C (67.9 MHz, $CDCl_3$) 14.9, 16.0 (CH_3), 52.5, 57.4 (CH), 59.6 (CH_3), 71.3 (CH_2); m/z (CI) 264 (MNH_4^+, ^{81}Br, 100%); Found 244.9840, $C_6H_{13}BrO_3S \cdot H$ requires 244.9847 (+2.7 ppm).

3.6 *Preparation of 1-benzylsulfonyl-2-(3-propenyl)cyclopropane 22 and 1-benzylsulfonyl-2-methoxycyclopropane 23*

3.6.1 1-Benzylsulfanyl-2-propene [30]. K_2CO_3 (11.77 g, 85.18 mmol, 2 eq.) in MeOH (150 cm^3) and benzyl mercaptan (5 cm^3, 42.59 mmol, 1 eq.) were treated with allyl bromide (4 cm^3, 46.85 mmol, 1.1 eq.) and heated to reflux under N_2 for 1.25 h. The resultant solution was treated with distilled H_2O (200 cm^3) and extracted with ether (3 × 200 cm^3). The combined ethereal layers were then washed with brine (200 cm^3) and dried over $MgSO_4$. Filtration followed by solvent removal under reduced pressure afforded the crude sulfide which was purified by short path distillation yielding *1-benzylsulfanyl-2-propene* (6.39 g, 91%) as a clear oil, b.p. 110 °C/2 mmHg. $R_f = 0.80$ (Pet-EtOAc, 9:1); υ_{max} (neat)/cm^{-1} 3060, 2912 (CH), 1635 (C=C); δ_H (270.1 MHz, $CDCl_3$) 3.02 (2H, d, *J* 7.0, CH_2), 3.63 (2H, s, CH_2), 5.04–5.12 (2H, m, CH_2), 5.73–5.83 (1H, m, CH), 7.20–7.29 (5H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 34.0, 35.5, 117.2 (CH_2), 127.1, 128.4, 128.8, 134.2 (CH), 138.3 (C); m/z (EI) 164 (M^+, 15%), 91 (Bn^+, 100%); Found 164.0660, $C_{10}H_{12}S$ requires 164.06597 (−0.2 ppm).

3.6.2 1-Benzylsulfonyl-2-propene 20 [31]. Allyl benzyl sulfide (6.39 g, 38.90 mmol, 1 eq.) was quantitatively oxidised into the corresponding sulfone **20** (7.63 g, 100%) with $NaBO_3 \cdot 4H_2O$ (18.32 g, 116.7 mmol, 3 eq.) in AcOH (200 cm^3) in 48 h. After this period most of the solvent was removed under reduced pressure and EtOAc (100 cm^3) was added along with H_2O (100 cm^3). The resultant aqueous layer was extracted with EtOAc (3 × 100 cm^3). The combined organic layers were then washed with $NaHCO_3$ (100 cm^3), brine (100 cm^3) and dried over $MgSO_4$ before filtration and solvent removal *in vacuo* afforded a white solid. Recrystallisation gave *1-benzylsulfonyl-2-propene* **20**, m.p. 57–58 °C (EtOAc-Pet); lit. m.p. 63–64 °C, [31]. $R_f = 0.55$ (Pet-EtOAc, 1:1); υ_{max} (Nujol)cm^{-1} 1317, 1138 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.59 (2H, d, *J* 7.5, CH_2), 4.22 (2H, s, CH_2), 5.42 (1H, dd, *J* 1.0, 17.0, CH_2), 5.52 (1H, d, *J* 10.0, CH_2), 5.90 (1H, ddt, *J* 7.5, 10.0, 17.0, CH), 7.40 (5H, s, ArH); δ_C (67.9 MHz, $CDCl_3$) 55.8, 57.8 (CH_2), 124.7, 124.8 (CH), 127.6 (C), 128.9, 130.7, 130.9 (CH); m/z (CI) 214 (MNH_4^+, 100%); Found 214.0898, $C_{10}H_{12}O_2S$ requires 214.0902 (+1.6 ppm).

3.6.3 trans-3-Bromo-1-benzylsulfonyl-1-propene 21 [32]. Under stirring the sulfone **20** (3.76 g, 19.16 mmol, 1 eq.) was treated with bromine (0.98 cm^3, 19.16 mmol, 1 eq.) in CCl_4 (80 cm^3) over 15 h at rt. DCM (100 cm^3) and 5% Na_2SO_3 (150 cm^3) were added. The aqueous layer was then further extracted with DCM (100 cm^3) and then combined organic extracts were washed with brine (100 cm^3) and dried over $MgSO_4$. Filtration and solvent removal under reduced pressure afforded the intermediate dibromide quantitatively as a pale yellow oil which gradually solidified upon standing yielding a white solid. $R_f = 0.30$ (Pet-EtOAc, 3:1). The crude dibromide (*ca.* 19.16 mmol) in DCM (200 cm^3) was treated without further purification with TEA (2.67 cm^3, 19.18 mmol, 1.05 eq.) at 0 °C. Stirring was continued for 0.5 h before the reaction mixture was allowed to reach room temperature and stirring was maintained for 15 h. H_2O (100 cm^3) was added and the aqueous layer was acidified with 2 M HCl (20 cm^3). Extraction with DCM (3 × 50 cm^3), washing of the combined organic extracts with brine (100 cm^3) and drying over $MgSO_4$ afforded the crude product after filtration and solvent removal *in vacuo*. This material was filtered through silica (Pet-EtOAc, 3:1); *E:Z*, 90:10, and the resultant solid was recrystallised to afford the *trans*-bromide **21** (4.25 g, 81%) as a white fluffy solid, m.p. 95 °C (EtOAc-Pet); lit. m.p. 95–97 °C [32]. $R_f = 0.30$ (Pet-EtOAc, 3:1); υ_{max} (Nujol)/cm^{-1} 1635 (C=C), 1278, 1120 (SO_2); δ_H (300.1 MHz, $CDCl_3$) 3.94 (2H, d, *J* 6.5, CH_2), 4.25 (2H, s, CH_2), 6.41 (1H, d, *J* 15.0, CH), 6.79 (1H, dt, *J* 6.5, 15.0, CH), 7.32–7.40 (5H, m, ArH); δ_C (75.5 MHz, $CDCl_3$) 27.0, 61.5 (CH_2), 127.5 (C), 129.0, 129.1, 130.8, 130.9, 143.0 (CH); m/z (CI) 294 (MNH_4^+, ^{81}Br, 100%), 91 (Bn^+, 45%); Found 292.0006, $C_{10}H_{11}BrO_2S \cdot NH_4$ requires 292.0007 (+0.2 ppm); [Found C, 43.59; H, 3.98%, $C_{10}H_{11}BrO_2S$ requires C, 43.65; H, 4.02%].

3.6.4 1-Benzylsulfonyl-2-(3-propenyl)cyclopropane 22. Under nitrogen at rt the sulfone **21** (101 mg, 0.37 mmol, 1 eq.) in THF (10 cm^3) was treated dropwise with 1.0 M magnesium allyl bromide in THF (0.4 cm^3, 0.40 mmol, 1.1 eq.). Stirring was maintained for 2 h before TLC analysis indicated the consumption of **21**. NH_4Cl (5 cm^3) was added followed by EtOAc (15 cm^3) and H_2O (10 cm^3). Further extraction of the aqueous layer with EtOAc (2 × 15 cm^3), washing of the combined organic extracts with brine (20 cm^3) and drying over $MgSO_4$ afforded the crude product upon filtration and solvent removal. The oil obtained was purified by flash column chromatography (Pet-EtOAc, 3:1) to yield *1-benzylsulfonyl-2-(3-propenyl)cyclopropane* **22** (68 mg, 80%) as a clear oil which slowly solidified, m.p. 34 °C. $R_f = 0.25$ (Pet-EtOAc, 3:1); υ_{max} (neat)/cm^{-1} 3066, 3035, 2979, 2922 (CH), 1641 (C=C), 1309, 1119 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 0.71–0.80 (1H, m, CH), 1.20 (1H, dt, *J* 5.0, 9.5, CH), 1.46–1.58 (1H, m, CH), 1.96–2.15 (3H, m, CH, CH_2), 4.26 (2H, s, CH_2), 5.02–5.12 (2H, m, CH_2), 5.96 (1H, ddt, *J* 7.5, 10.0, 17.0, CH), 7.37–7.44 (5H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 11.2 (CH_2), 18.2, 34.2 (CH), 35.1, 60.6, 117.3 (CH_2), 128.7 (C), 129.2, 131.1, 135.0 (CH); m/z (CI) 254 (MNH_4^+, 100%); Found 254.1213, $C_{13}H_{16}O_2S \cdot NH_4$ requires 254.1215 (+0.8 ppm).

3.6.5 1-Benzylsulfonyl-2-methoxycyclopropane 23. trans-*3-Bromo-1-benzylsulfonyl-1-propene* **21** (188 mg, 0.68 mmol, 1 eq.) in MeOH (15 cm^3) was treated at rt with KOH (38 mg, 0.68 mmol, 1 eq.) in MeOH (2 cm^3) with stirring for 15 h. The bulk of the solvent was removed before EtOAc (20 cm^3) and NH_4Cl (20 cm^3) were added. The aqueous phase was extracted with EtOAc (3 × 20 cm^3) and the combined organic layers were washed with brine (50 cm^3). Drying over $MgSO_4$ afforded the mixture of products on filtration and solvent removal *in vacuo*. Flash column chromatography (Pet-EtOAc, 3:1) gave *1-benzylsulfonyl-2-methoxycyclopropane* **23** (75 mg, 49%) as a clear oil. $R_f = 0.15$ (Pet-EtOAc, 3:1); υ_{max} ($CDCl_3$)/cm^{-1} 3091, 3039, 2993, 2935, 2837 (CH), 1309, 1120 (SO_2); δ_H (300.1 MHz, $CDCl_3$) 1.30–1.36 (1H, m, CH_2),

1.35 (1H, dt, *J* 2.0, 8.0, CH_2), 2.31 (1H, dd, *J* 2.0, 8.0, CH), 3.33 (2H, s, CH_3), 3.70 (1H, dt, *J* 2.0, 6.0, CH), 4.27 (2H, s, CH_2), 7.39–7.43 (5H, m, ArH); δ_C (75.5 MHz, $CDCl_3$) 13.4 (CH_2), 34.4, 58.3 (CH), 58.7 (CH_3), 60.2 (CH_2), 128.1 (C), 129.0, 130.8 (CH); m/z (CI) 244 (MNH_4^+, 100%); Found 244.1012, $C_{11}H_{14}O_3S \cdot NH_4$ requires 244.1007 (−1.8 ppm); [Found C, 58.15; H, 6.36%, $C_{11}H_{14}O_3S$ requires C, 58.38; H, 6.24%]. The conjugate adduct *1-benzylsulfonyl-3-bromo-2-methoxypropane* **24** (31 mg, 15%) was also isolated as a viscous oil. $R_f = 0.20$ (Pet-EtOAc, 3:1); υ_{max} ($CHCl_3$)/cm^{-1} 3085, 3034, 2985, 2933, 2833 (CH), 1495, 1456 (CH), 1306, 1119 (SO_2); δ_H (300.1 MHz, $CDCl_3$) 2.94 (1H, dq, *J* 1.0, 15.0, CH_2), 3.30 (1H, dd, *J* 9.0, 15.0, CH_2), 3.44 (1H, dd, *J* 3.5, 11.0, CH_2), 3.52 (3H, s, CH_3), 3.53 (1H, dd, *J* 5.0, 6.0, CH_2), 4.00–4.07 (1H, m, CH), 4.23 (1H, dd, *J* 1.0, 14.0, CH_2), 4.40 (1H, d, *J* 14.0, CH_2), 7.29–7.41 (5H, m, ArH); δ_C (75.5 MHz, $CDCl_3$) 32.0, 53.9 (CH_2), 57.5 (CH_3), 61.4 (CH_2), 75.1 (CH), 128.0 (C), 128.8, 128.9, 131.1 (CH); m/z (CI) 326 (MNH_4^+, ^{81}Br, 100%), 324 (MNH_4^+, ^{79}Br, 100%); Found 324.0273, $C_{11}H_{15}BrO_3S \cdot NH_4$ requires 324.0269 (−1.3 ppm).

3.6.6 trans-3-Benzylsulfonyl-2-propene acetate 28. Anhydrous KOAc (1.96 g, 10 mmol, 1.5 eq.), $BnNEt_3Cl$ (300 mg, *ca.* 1 mmol, 0.1 eq.) and ground molecular sieves 4 Å (0.5 g) were stirred in dry acetonitrile (10 cm^3) under N_2 at rt for 24 h. The *trans*-vinyl sulfone **28** (2.75 g, 10 mmol, 1 eq.) in dry acetonitrile (5 cm^3) was added dropwise. Stirring was continued for a further 48 h at rt. EtOAc (50 cm^3) was added along with H_2O (50 cm^3) and the resultant aqueous layer was extracted with EtOAc (3 × 25 cm^3). The combined organic layers were washed with brine (50 cm^3) and dried over $MgSO_4$. Filtration followed by solvent removal under reduced pressure afforded the crude acetate. Flash column chromatography (Pet-EtOAc, 2:1) followed by recrystallisation yielded trans-*3-benzylsulfonyl-2-propene acetate* **28** (2.13 g, 94%) as a white solid, m.p. 80–81 °C (EtOAc-Pet). $R_f = 0.35$ (Pet-EtOAc, 2:1); υ_{max} (Nujol)/cm^{-1} 1745 (CO), 1636 (C=C), 1237, 1124 (SO_2); δ_H (300.1 MHz, $CDCl_3$) 2.08 (3H, s, CH_3), 4.22 (2H, s, CH_2), 4.70 (2H, dd, *J* 2.0, 4.0, CH_2), 6.35 (1H, d, *J* 15.5, CH), 6.71 (1H, dt, *J* 4.0, 15.5, CH), 7.30–7.38 (5H, m, ArH); δ_C (75.5 MHz, $CDCl_3$) 20.6 (CH_3), 61.35, 61.4 (CH), 127.8, 128.9, 129.0, 131.0 (CH), 143.0 (C), 169.9 (CO); m/z (CI) 272 (MNH_4^+, 100%); Found 272.0958, $C_{12}H_{14}O_4S \cdot NH_4$ requires 272.0957 (−0.5 ppm); [Found C, 56.94; H, 5.43%, $C_{12}H_{14}O_4S$ requires C, 56.68; H, 5.55%].

3.6.7 1-Benzylsulfonyl-3-phenylsulfanyl-1-propene 29. Thiophenol (0.30 cm^3, 2.92 mmol, 1 eq.) in dry DMSO (5 cm^3) was treated with 60% NaH dispersion in oil (117 mg, 2.93 mmol, 1 eq.) with stirring at rt for 0.5 h. The bromide **21** (803 mg, 2.92 mmol, 1 eq.) in DMSO (10 cm^3) was added to this solution and stirring was continued for 4 h. H_2O (50 cm^3) was added and the resultant mixture was extracted with DCM (3 × 25 cm^3). The combined organic extracts were washed with H_2O (25 cm^3), brine (50 cm^3) and dried over $MgSO_4$. Filtration followed by solvent removal under reduced pressure gave the crude vinyl sulfone as a viscous oil. Purification by column chromatography (Pet-EtOAc, 1:1) afforded *1-benzylsulfonyl-3-phenylsulfanyl-1-propene* **29** (850 mg, 96%) as a yellow solid, m.p. 66–69 °C. $R_f = 0.30$ (Pet-EtOAc, 3:1); υ_{max} (neat)/cm^{-1} 3057, 2978, 2924 (CH), 1628 (C=C), 1495, 1481, 1438 (CH), 1315, 1117 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.64 (2H, dd, *J* 1.5, 6.5, CH_2), 4.15 (2H, s, CH_2), 6.27 (1H, d, *J* 15.0, CH), 6.84 (1H, dt, *J* 6.5, 15.0, CH), 7.21–7.28 (2H, m, ArH), 7.34–7.60 (8H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 34.6, 61.2 (CH), 127.2 (CH), 127.6 (C), 128.7, 128.9, 129.1, 129.3, 130.7, 131.0 (CH), 133.6 (C), 143.9 (CH); m/z (CI) 322 (MNH_4^+, 60%); Found 322.0932, $C_{16}H_{16}O_2S_2 \cdot NH_4$ requires 322.0935 (+1.0 ppm).

3.6.8 Benzyl bis-(1-benzylsulfonyl-1-propenyl)amine 30. Sulfone **21** (166 mg, 6.04 mmol, 1 eq.) in DMSO (5 cm^3) was treated at rt with benzylamine (66 μL, 6.04 mmol, 1 eq.) and pyridine (49 μL, 6.06 mmol, 1 eq.). Stirring was continued for 4 h before the temperature was raised to 40 °C for 12 h. The reaction mixture was cooled to rt and H_2O (10 cm^3) was added. Extraction with DCM (3 × 15 cm^3), washing of the combined organic extracts with H_2O (20 cm^3), brine (20 cm^3) and drying over $MgSO_4$ gave the crude product after filtration and solvent evaporation under reduced pressure. Purification by flash column chromatography (Pet-EtOAc, 1:1) afforded *benzyl* bis-*(1-benzylsulfonyl-1-propenyl)amine* **30** (140 mg, 47%) as a white solid, m.p. 163–164 °C. $R_f = 0.25$ (Pet-EtOAc, 1:1); υ_{max} ($CHCl_3$)/cm^{-1} 3053, 3030, 3006, 2927, 2852 (CH), 1620 (C=C), 1495, 1429, 1402 (CH), 1319, 1149, 1117 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.05 (4H, d, *J* 5.0, CH_2), 3.37 (2H, s, CH_2), 4.22 (4H, s, CH_2), 6.33 (2H, d, *J* 15.0, CH), 6.61 (2H, dt, *J* 5.0, 15.0, CH), 7.13–7.31 (15H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 53.5, 58.4, 61.3 (CH_2), 127.7 (CH), 128.1 (C), 128.3, 128.4, 128.6, 128.9, 129.0, 130.7 (CH), 137.3 (C), 146.6 (CH); m/z (CI) 496 (MH^+, 5%); Found 496.1609, $C_{27}H_{29}NO_4S_2 \cdot H$ requires 496.1616 (+1.5 ppm); m/z (FAB) 518 (MNa^+, 15%).

3.7 *Preparation of 2-benzylsulfonyl-2-bromoethylamine 32*

3.7.1 1-Benzylsulfonyl-1,2-dibromoethane [33]. At rt vinyl sulfone **9** (361 mg, 1.98 mmol, 1 eq.) in CCl_4 (10 cm^3) and DCM (2 cm^3) was treated dropwise with bromine (0.12 cm^3, 2.18 mmol, 1.1 eq.). Stirring was continued for 48 h. The solvent was removed under reduced pressure and the crude product was purified directly by column chromatography (Pet-EtOAc, 3:1), affording *1-benzylsulfonyl-1,2-dibromoethane* (676 mg, 100%) as a white solid, m.p. 117–118 °C; lit. m.p. 115–116 °C [33]. $R_f = 0.30$ (Pet-EtOAc, 3:1); υ_{max} (Nujol)/cm^{-1} 1321, 1128 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.71 (1H, dd, *J* 10.0, 11.5, CH_2), 4.26 (1H, dd, *J* 3.0, 11.5, CH_2), 4.56 (1H, d, *J* 14.0, CH_2), 4.76 (1H, dd, *J* 3.0, 10.0, CH), 4.86 (1H, d, *J* 14.0, CH_2), 7.49–7.61 (5H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 28.3, 57.2 (CH_2), 60.3 (CH), 126.2 (C), 129.3, 129.7, 130.8 (CH); m/z (CI) 360 (MNH_4^+, ^{81}Br, ^{81}Br, 10%), 91 (Bn^+, 100%); Found 357.9106, $C_9H_{10}Br_2O_2S \cdot NH_4$ requires 357.9112 (+1.6 ppm); [Found C, 32.02; H, 2.81; S, 9.14%, $C_9H_{10}Br_2O_2S$ requires C, 31.60; H, 2.95; S, 9.38%].

3.7.2 1-Benzylsulfonyl-1-bromoethene 31 [33]. *1-Benzylsulfonyl-1,2-dibromoethane* (302 mg, 0.88 mmol, 1 eq.) in DCM (10 cm^3) was treated with TEA (0.18 cm^3, 1.30 mmol, 1.5 eq.) at rt and stirred for 12 h. Addition of NH_4Cl (15 cm^3) followed by extraction of the resultant aqueous layer with DCM (3 × 20 cm^3) and washing of the combined organic layers successively with water (20 cm^3) and brine (30 cm^3) and drying over $MgSO_4$ afforded the crude vinyl bromide on filtration and solvent removal *in vacuo*. Purification by column chromatography (Pet-EtOAc, 3:1) yielded *1-benzylsulfonyl-1-bromoethene* **31** (229 mg, 99%) as a white solid, m.p. 61–62 °C; lit. m.p. 69–70 °C [33]. $R_f = 0.30$ (Pet-EtOAc, 3:1); υ_{max} (neat)/cm^{-1} 3108, 3064, 3032, 2980, 2923 (CH), 1601 (C=C), 1322, 1154 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 4.43 (2H, s, CH_2) 6.25 (1H, d, *J* 3.0, CH_2) 6.68 (1H, d, *J* 3.0, CH_2), 7.39 (5H, s, ArH); δ_C (67.9 MHz, $CDCl_3$) 56.6 (CH_2), 125.6, 126.9 (C), 128.8, 129.0, 130.7, 132.1 (CH); m/z (CI) 278 (MNH_4^+, ^{81}Br, 100%); Found 277.9853, $C_9H_9BrO_2S \cdot NH_4$ requires 277.9850 (−1.1 ppm); [Found C, 41.40; H, 3.33; Br, 30.67; S, 12.17%, $C_9H_9BrO_2S$ requires C, 41.40; H, 3.47; Br, 30.60; S, 12.28%].

3.7.3 2-Benzylsulfonyl-2-bromoethylamine 32. A solution of the sulfone **31** (162 mg, 0.62 mmol, 1 eq.) in 1,4-dioxane (8 cm^3) was treated with concentrated (0.88) NH_3 solution

($0.3\,cm^3$, *ca.* 6.2 mmol, *ca.* 10 eq.). Stirring was continued at rt for 13 h before water ($15\,cm^3$) was added. The mixture was extracted with EtOAc ($3 \times 20\,cm^3$). The combined organic extracts were washed with water ($10\,cm^3$) and brine ($20\,cm^3$) and dried over $MgSO_4$. Filtration and removal of the solvent under reduced pressure afforded *2-benzylsulfonyl-2-bromoethylamine* **32** (172 mg, 100%) as a waxy white solid, m.p. 59–61 °C. $R_f = 0.05$ (Pet-EtOAc, 3:1); υ_{max} (neat)/cm^{-1} 3390 (NH), 3086, 3034, 2926, 2862 (CH), 1495, 1456 (CH), 1315, 1120 (SO_2); δ_H (270.1 MHz, $CDCl_3$) 3.32 (1H, dd, *J* 6.0, 15.0 CH_2), 3.39 (1H, dd, *J* 5.0, 15.0, CH_2), 4.35 (1H, d, *J* 14.0, CH_2), 4.43 (1H, dd apparent t, *J* 5.5, CH), 4.68 (1H, d, *J* 14.0, CH_2), 7.19–7.45 (5H, m, ArH); δ_C (67.9 MHz, $CDCl_3$) 42.3, 57.0 (CH_2), 62.6 (CH), 126.6 (C), 128.9, 129.2, 130.7 (CH); m/z (CI) 280 (MH^+, ^{81}Br, 70%), 278 (MH^+, ^{79}Br, 70%), Found 277.9857, $C_9H_{12}BrNO_2S \cdot H$ requires 277.9850 (−2.5 ppm).

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