Asymmetric synthesis of α,γ-substituted γ-alkoxy methyl sulfonates *via* diastereospecific ring-opening of sultones

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Dedicated to Professor Binne Zwanenburg on the occasion of his 70th birthday

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Abstract

The diastereospecific alcoholysis of enantiopure α,γ-substituted γ-sultones under mild conditions in the asymmetric synthesis of α,γ-substituted γ-alkoxy methyl sulfonates in excellent yields and enantiomeric excesses (*ee* ≥ 98%) is described.

Keywords: Alcoholysis, sultones, ring-opening, alkoxy sulfonates, asymmetric synthesis

Introduction

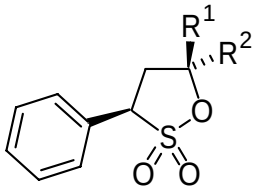
Sultones are valuable heterocyclic intermediates which can react with a variety of compounds to introduce an alkylsulfonic acid functionality. Furthermore, they offer novel possibilities for stereoselective transformations.[1] Several reports have been devoted to the ring-opening reaction of sultones with various nucleophiles cleaving the carbon-oxygen bond.[2] There are many patents covering their use to modify surface properties of a variety of substrates containing nucleophilic functionalities. Very interesting is the use of propanesultone as a cellulose modifier for the production of cation-exchange membranes.[3]

Only a few reports deal with the hydrolysis and alcoholysis of sultones. Helberger et al. have studied the alcoholysis of γ- and δ-sultones.[4] The effects of methyl substituents on the hydrolysis rates of γ-sultone derivatives bearing either no, one or two substitutents in the γ-position have been studied by Bordwell et al. leading to the conclusion that these sultones were hydrolysed predominantly by an unimolecular mechanism.[5] Mori et al. demonstrated that the hydrolysis of propanesultone in $H_2{}^{18}O$ in a strong alkaline medium (pH > 12) led to 86% C–O fission and 14% S–O fission corresponding to unimolecular and bimolecular mechanisms, respectively.[6]

To the best of our knowledge, the diastereoselectivity of the ring-opening reaction of sultones has not been studied so far. We now wish to report mild conditions for the diastereospecific alcoholysis of α,γ-substituted γ-sultones to yield α,γ-substituted γ-alkoxy methyl sulfonates.

Results and Discussion

We have recently reported efficient asymmetric electrophilic α-substitutions of benzylsulfonates bearing 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose as a chiral auxiliary with various alkylhalides and nitroolefins.[7] In a previous communication and a full paper we have shown the extension of this methodology by using allylic halides as electrophiles to the diastereo- and enantioselective synthesis of α,γ-substituted γ-sultones.[8] We now wish to address the issue of the reaction of the enantiopure γ-sultones **1a,b** (figure 1) with alcohols as nucleophiles, the diastereoselectivity of the ring-opening and thus the mechanism of these reactions.

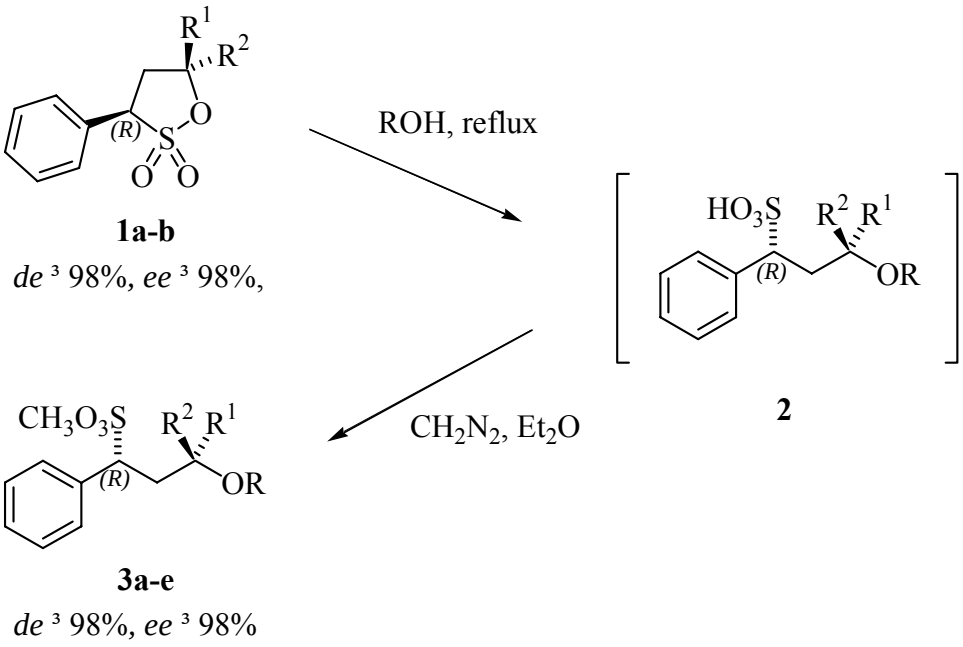


(*R*,*R*)-**1a**, R^1 = Me, R^2 = H
(*R*,*S*)-**1a**, R^1 = H, R^2 = Me
(*R*)-**1b**, R^1 = Me, R^2 = Me

Figure 1. The enantiopure γ-sultones **1**.

As depicted in Scheme 1, the reactions were performed with a large excess of nucleophile by refluxing a solution of the enantio- and diastereomerically pure sultone **1** in the corresponding absolute alcohol for either 3 or 7 days. In order to complete the conversion to the corresponding sulfonic acid **2** the reaction times had to be adjusted and therefore somewhat differ. To obtain the final product in a more accessible form, the sulfonic acids **2** were directly converted to the corresponding methyl sulfonates **3** with diazomethane. In contrast, the reaction of sultone (*R,R*)-**1a** with EtOK in THF at −78 °C for 1 h led to epimerization, resulting in the formation of a mixture of two diastereoisomers of sultone **1a**. No ring-pening product was observed. Methanolysis of (*R,R*)-**1a** and (*R,S*)-**1a** by refluxing the solution for 3 days afforded one single diastereomer (*R,S*)-**3a** and (*R,R*)-**3a**, respectively in excellent yield and enantiomeric excess (Table 1). Since both diastereomers obtained differ from each other and due to the high stereoselectivity of the reaction, it would be reasonable to assume that the reactions proceed *via* a bimolecular nucleophilic substitution with inversion of configuration at the attacked asymmetric carbon atom rather than *via* a unimolecular reaction. Further evidence for the S_N2 mechanism was obtained from the methanolysis of the γ-dimethyl sultone (*R*)-**1b**. Assuming that the S_N2 mechanism holds for this sultone, the reaction should proceed more slowly because the backside attack is hindered for steric reasons. After refluxing the enantiopure sultone (*R*)-**1b** in absolute methanol for 3 days, starting material could be recovered in 75% yield. By increasing the

reaction time to 7 days, (*R*)-**3b** could be obtained in 51% yield. In addition to a small amount of starting material, 29% of the corresponding β,γ-alkenesulfonate was obtained by an elimination reaction. Finally, the absolute configuration of **3a** can be assigned as (1*R*,3*S*) based on a correlation of its ^{1}H NMR spectrum with that obtained from the corresponding (1*R*,3*S*)-γ-hydroxy methyl sulfonate whose absolute configuration was unambiguously established by X-ray crystallography.[9]



1a-b
de ³ 98%, *ee* ³ 98%,

3a-e
de ³ 98%, *ee* ³ 98%

Scheme 1. Alcoholysis of the enantiopure γ-sultones **1** affording the ring-opening products **3**.

Table 1. Alcoholysis of the enantiopure γ-sultones **1** affording the γ-alkoxy methyl sulfonates **3**

Product	R	R^1	R^2	Reaction time, d	Yield (%)	*de* (%)[a]	*ee* (%)[b]
(*R*,*S*)-**3a**	Me	Me	H	3	99	≥ 98	≥ 98
(*R*,*R*)-**3a**	Me	H	Me	3	99	≥ 98	≥ 98
(*R*)-**3b**	Me	Me	Me	3	–[c]	–	–
				7	58 [d,e]	–	≥ 98
(*R*,*S*)-**3c**	Et	Me	H	3	99	≥ 98	≥ 98
(*R*,S)-**3d**	*n*Pr	Me	H	3	99	≥ 98	98
(*R*,*S*)-**3e**	*i*Pr	Me	H	7	94[d]	≥ 98	≥ 98

[a] Determined by ^{1}H-NMR. [b] Determined by HPLC using a chiral stationary phase. [c] The starting material was recovered in 75% yield. (product was not isolated.) [d] The crude product consisted of a small amount of starting material. [e] A yield of 29% of the corresponding β,γ-alkenesulfonate was obtained.

As shown in Table 1, the reactions of the enantiopure sultone (*R*,*R*)-**1a** with ethanol and *n*-propanol were performed by refluxing the solution for 3 days to give (*R*,*S*)-**3c** and (*R*,*S*)-**3d** respectively in excellent yields as well as diastereo- and enantiomeric excesses. For the reaction carried out in the presence of *i*-propanol, (*R*,*R*)-**1a** afforded (*R*,*S*)-**3e** in 94% yield after refluxing the reaction mixture for 7 days. Only a small amount of starting material was observed. It is surmised that the low rate is due to steric hindrance. The absolute configuration of the γ-alkoxy methyl sulfonates **3c-e** is expected to be (1*R*,3*S)* based on the assumption of an uniform reaction mechanism operating in all the substitutions.

In conclusion, alcoholysis of the enantiopure α,γ-substituted γ-sultones under mild conditions provided α,γ-substituted γ-alkoxy methyl sulfonates in excellent yields as well as diastereo- and enantiomeric excesses. The inversion of configuration at the attacked γ-position leads to the conclusion that the reported alcoholyses proceed *via* S_N2 mechanism.

Experimental Section

General Procedures. Absolute methanol was distilled from Mg. Absolute ethanol, *n*-propanol and *i*-propanol were purchased from Merck, Darmstadt. Preparative column chromatography: Merck silica gel 60, particle size 0.040–0.063 mm (230–240 mesh, flash). Analytical TLC: silica gel 60 F254 plates from Merck, Darmstadt. Optical rotation values were measured on a Perkin–Elmer P241 polarimeter. Microanalyses were obtained with a Vario EL element analyzer. Mass spectra were acquired on a Finnigan SSQ7000 (CI 100 eV; EI 70 eV) spectrometer. IR spectra were taken on a Perkin-Elmer FT/IR 1760. ^{1}H and ^{13}C NMR spectra were recorded on Gemini 300 or Varian Inova 400 and all measurements were performed with tetramethylsilane as internal standard. Melting points were determined on a Tottoli melting point apparatus and are uncorrected.

Preparation of α,γ-substituted γ-alkoxy methyl sulfonates 3a-e; General procedure (GP)
The solution of the enantiopure sultone **1** in the corresponding alcohol (30 mL per 0.5 mmol) was refluxed for either 3 or 7 days. The resulting colourless solution was treated with an etheral solution of diazomethane until the yellow colour persisted. The solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography (SiO_2, diethyl ether/*n*-pentane).

(1*R*,3*S*)-Methyl 3-methoxy-1-phenyl-butane-1-sulfonate [*R*,*S*)-3a]. According to GP the solution of the enantiopure sultone (*R*,*R*)-**1a** (0.10 g, 0.5 mmol) in absolute methanol (30 mL) was refluxed for 3 days. The crude product consisting of only one diastereomer was purified by column chromatography (SiO_2, diethyl ether/*n*-pentane, 1:4) to give (*R*,*S*)-**3a** as a colourless solid (0.12 g, 99%); *de* ≥ 98% (NMR); *ee* ≥ 98% (HPLC, Chiralcel OJ, *n*-heptane/*i*-propanol, 9:1); mp 35 ºC; $[\alpha]_D^{25}$ +13.2 (*c* 1.0, $CHCl_3$).

IR (film): 3064 (w), 3033 (w), 2971 (m), 2935 (m), 2826 (m), 1497 (m), 1457 (m), 1353 (s), 1168 (s), 1085 (m), 989 (s), 817 (m), 781 (s), 730 (m), 701 (m), 629 (m), 583 (m) cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 6.2 Hz, 3H, CHC*H*$_3$), 2.25 (dt, *J* = 14.6, 7.3 Hz, 1H, C*H*H), 2.52 (ddd, *J* = 14.4, 6.9, 5.2 Hz, 1H, CH*H*), 3.30 (s, 3H, CHOC*H*$_3$), 3.53 (m, 1H, C*H*OCH$_3$), 3.61 (s, 3H, SO_2OCH_3), 4.49 (t, *J* = 6.9 Hz, 1H, $CH_2CHSO_2OCH_3$), 7.35-7.45 (m, 5H, Ar*H*) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9 (*C*H$_3$), 37.4 (*C*H$_2$), 56.1 (O*C*H$_3$), 56.9 (SO_2OCH_3), 63.3 ($CHSO_2OCH_3$), 73.7 (*C*HOCH$_3$), 128.8, 129.0, 129.4 (Ar*C*H), 133.5 (Ar*C*) ppm.
MS (EI, 70 eV): m/z (%) = 258 (3) [M^+], 226 (4), 162 (10), 147 (6), 131 (5), 115 (4), 104 (6), 91 (5), 77 (3), 59 (100), 51 (4).
Anal. Calcd for $C_{12}H_{18}O_4S$ (258.34): C, 55.79; H, 7.02. Found: C, 55.44; H, 6.84

(1*R*,3*R*)-Methyl 3-methoxy-1-phenyl-butane-1-sulfonate [(*R*,*R*)-3a]. According to GP the solution of the enantiopure sultone (*R*,*S*)-**1a** (0.05 g, 0.25 mmol) in absolute methanol (20 mL) was refluxed for 3 days. The crude product consisting of only one diastereomer was purified by column chromatography (SiO_2, diethyl ether/*n*-pentane, 1:4) to give (*R*,*R*)-**3a** as a colourless solid (0.06 g, 99%); *de* ≥ 98% (NMR); *ee* ≥ 98% (based on the *ee* value of the sultone); mp 51 ºC; $[\alpha]_D^{23}$ +8.03 (*c* 1.2, $CHCl_3$).
IR (KBr): 3062 (m), 3033 (m), 2997 (m), 2955 (m), 2931 (m), 2896 (m), 1500 (m), 1457 (m), 1349 (s), 1238 (w), 1170 (s), 1143 (s), 1075 (s), 987 (s), 924 (w), 833 (s), 778 (m), 722 (m), 699 (m), 623 (m), 589 (s), 506 (m) cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (d, *J* = 6.1 Hz, 3H, CHC*H*$_3$), 2.24 (ddd, *J* = 14.0, 11.8, 2.8 Hz, 1H, C*H*H), 2.40 (ddd, *J* = 14.0, 10.7, 3.3 Hz, 1H, CH*H*), 2.91 (m, 1H, C*H*OCH$_3$), 3.13 (s, 3H, CHOC*H*$_3$), , 3.70 (s, 3H, SO_2OCH_3), 4.61 (dd, *J* = 11.8, 3.3 Hz, 1H, $CH_2CHSO_2OCH_3$), 7.35-7.46 (m, 5H, Ar*H*) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8 (*C*H$_3$), 37.5 (*C*H$_2$), 55.8 (O*C*H$_3$), 56.5 (SO_2OCH_3), 63.4 ($CHSO_2OCH_3$), 72.3 (*C*HOCH$_3$), 128.7, 128.9, 129.4 (Ar*C*H), 131.9 (Ar*C*) ppm.
MS (EI, 70 eV): m/z (%) = 258 (1) [M^+], 226 (1), 162 (19), 147 (4), 131 (3), 115 (2), 104 (4), 91 (3), 79 (2), 59 (100), 51 (1).

(*R*)-Methyl 3-methoxy-3-methyl-1-phenyl-butane-1-sulfonate [(*R*)-3b)]. According to GP the solution of the enantiopure sultone (*R*)-**1b** (0.13 g, 0.5 mmol) in absolute methanol (30 mL) was refluxed for 7 days. The crude product was purified by column chromatography (SiO_2, diethyl ether/*n*-pentane, 1:9) to give (*R*,*S*)-**3b** as a colourless solid (0.09 g, 58%); *ee* ≥ 98% (based on the *ee* value of the sultone); mp 41 ºC; $[\alpha]_D^{24}$ +7.04 (*c* 1.1, $CHCl_3$).
IR (film): 3063 (w), 3033 (m), 2975 (s), 2832 (m), 1496 (m), 1457 (m), 1353 (s), 1223 (m), 1167 (s), 1077 (s), 990 (s), 873 (w), 824 (m), 782 (m), 702 (m), 625 (m), 578 (m), 511 (m) cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 and 1.19 (each s, 3H, C*H*$_3$), 2.31 (dd, J = 14.6, 9.9 Hz, 1H, C*H*H), 2.66 (dd, *J* = 14.6, 1.5 Hz, 1H, CH*H*), 3.10 (s, 3H, CHOC*H*$_3$), 3.62 (s, 3H, SO_2OCH_3), 4.52 (dd, *J* = 9.9, 1.5 Hz, 1H, $CH_2CHSO_2OCH_3$), 7.34-7.42 (m, 3H, Ar*H*), 7.44-7.50 (m, 2H, Ar*H*) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.8 (*C*H_3), 25.9 (*C*H_3), 39.2 (*C*H_2), 49.4 (O*C*H_3), 56.9 (SO_2OCH_3), 63.2 (*C*HSO_2OCH_3), 73.9 (*C*HOCH_3), 128.8, 128.9, 129.9 (Ar*C*H), 134.1 (Ar*C*) ppm.
MS (EI, 70 eV): m/z (%) = 272 (0.3) [M^+], 240 (2), 177 (2), 161 (9), 145 (5), 129 (4), 121 (9), 104 (2), 91 (3), 73 (100).
Anal. Calcd for $C_{13}H_{20}O_4S$ (272.37): C, 57.33; H, 7.40. Found: C, 57.58; H, 7.52.

(1*R*,3*S*)-Methyl 3-ethoxy-1-phenyl-butane-1-sulfonate [(*R*,*S*)-3c]. According to GP the solution of the enantiopure sultone (*R*,*R*)-**1a** (0.11 g, 0.5 mmol) in absolute ethanol (30 mL) was refluxed for 3 days. The crude product consisting of only one diastereomer was purified by column chromatography (SiO_2, diethyl ether/*n*-pentane, 1:4) to give (*R*,*S*)-**3c** as a colourless solid (0.14 g, 99%); *de* ≥ 98% (NMR); *ee* ≥ 98% (HPLC, Chiralcel OD, *n*-heptane/*i*-propanol, 98:2); mp 34.5 ºC; $[\alpha]_D^{26}$ +19.8 (*c* 1.1, $CHCl_3$). IR (KBr): 3063 (w), 3036 (w), 2977 (m), 2871 (m), 1496 (m), 1456 (m), 1355 (s), 1214 (w), 1170 (s), 1143 (m), 1105 (m), 1065 (m), 991 (s), 916 (w), 884 (w), 821 (s), 784 (s), 724 (m), 697 (m), 616 (m), 582 (m), 513 (m), 461 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 6.2 Hz, 3H, CHC*H*$_3$), 1.13 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 2.27 (dt, *J* = 14.3, 7.3 Hz, 1H, C*H*H), 2.51 (ddd, *J* = 14.3, 6.4, 5.4 Hz, 1H, CH*H*), 3.38 and 3.50 [each dq (ABX_3 system), *J* = 9.0, 7.1 Hz, 1H, OCH_2CH_3], 3.59 (m, 1H, C*H*OCH_3), 3.61 (s, 3H, SO_2OCH_3), 4.48 (t, *J* = 6.9 Hz, 1H, $CH_2CHSO_2OCH_3$), 7.35-7.45 (m, 5H, Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.5 (OCH_2CH_3), 19.7 (CH*C*H_3), 37.5 (*C*H_2), 56.9 (SO_2OCH_3), 63.7 (*C*HSO_2OCH_3), 63.8 (OCH_2CH_3), 72.2 (*C*HOCH_2), 128.8, 129.0, 129.5 (Ar*C*H), 133.5 (Ar*C*) ppm. MS (EI, 70 eV): m/z (%) = 272 (5) [M^+], 243 (2), 226 (5), 176 (8), 161 (4), 147 (5), 132 (10), 117 (5), 104 (7), 91 (10), 73 (100), 59 (2), 51 (2). Anal. Calcd for $C_{13}H_{20}O_4S$ (272.37): C, 57.33; H, 7.40. Found: C, 56.94; H, 7.07.

(1*R*,3*S*)-Methyl 3-propoxy-1-phenyl-butane-1-sulfonate [(*R*,*S*)-3d]. According to GP the solution of the enantiopure sultone (*R*,*R*)-**1a** (0.06 g, 0.3 mmol) in absolute *n*-propanol (20 mL) was refluxed for 3 days. The crude product consisting of only one diastereomer was purified by column chromatography (SiO_2, diethyl ether/*n*-pentane, 1:4) to give (*R*,*S*)-**3d** as a colourless liquid (0.08 g, 99%); *de* ≥ 98% (NMR); *ee* ≥ 98% (HPLC, Chiralcel OJ, *n*-heptane/*i*-propanol, 9:1); $[\alpha]_D^{23}$ +18.9 (*c* 1.0, $CHCl_3$). IR (film): 3064 (w), 3044 (w), 2966 (s), 2935 (m), 2875 (m), 1496 (m), 1457 (m), 1354 (s), 1168 (s), 1097 (m), 991 (s), 922 (w), 826 (m), 788 (m), 766 (m), 730 (m), 700 (m), 629 (m), 584 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 1.10 (d, *J* = 6.2 Hz, 3H, CHC*H*$_3$), 1.52 (sextet, *J* = 7.4 Hz, 3H, $OCH_2CH_2CH_3$), 2.27 (dt, *J* = 14.3, 7.4 Hz, 1H, C*H*H), 2.52 (ddd, *J* = 14.3, 6.4, 5.2 Hz, 1H, CH*H*), 3.28 and 3.41 [each dt (ABX_2 system), *J* = 9.2, 6.7 Hz, 1H, OCH_2CH_2), 3.59 (m, 1H, C*H*OCH_3), 3.60 (s, 3H, SO_2OCH_3), 4.49 (t, *J* = 6.9 Hz, 1H, $CH_2CHSO_2OCH_3$), 7.35-7.45 (m, 5H, Ar*H*) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.7 (CH_2CH_3), 19.6 (CH*C*H_3), 23.2 (*C*H_2CH_3), 37.6 (*C*H_2), 56.9 (SO_2OCH_3), 63.7 (*C*HSO_2OCH_3), 70.23 (O*C*H_2), 72.3 (*C*HOCH_2), 128.8, 129.0, 129.5 (Ar*C*H), 133.6 (Ar*C*) ppm. MS (EI, 70 eV): m/z (%) = 286 (8) [M^+], 243 (6), 226 (9), 190 (12), 175 (3), 163 (1), 147 (11), 132 (28), 117 (11), 105 (11), 87 (100), 79 (9), 59 (6). Anal. Calcd for $C_{14}H_{22}O_4S$ (286.39): C, 58.72; H, 7.74. Found: C, 58.71; H, 7.60.

(1*R*,3*S*)-Methyl 3-isopropoxy-1-phenyl-butane-1-sulfonate [(*R*,*S*)-3e]. According to GP the solution of the enantiopure sultone (*R*,*R*)-**1a** (0.11 g, 0.5 mmol) in absolute *i*-propanol (30 mL) was refluxed for 7 days. The crude product consisting of only one diastereomer and a small amount of the sultone was purified by column chromatography (SiO_2, diethyl ether/*n*-pentane, 1:4) to give (*R*,*S*)-**3e** as a colourless solid (0.14 g, 94%); *de* ≥ 98% (NMR); *ee* ≥ 98% (HPLC, Chiralcel OD, *n*-heptane/*i*-propanol, 99:1); mp 39 ºC; $[\alpha]_D^{26}$ +22.2 (*c* 1.1, $CHCl_3$). IR (KBr): 2970 (s), 2932 (m), 2899 (m), 2876 (m), 1497 (m), 1464 (m), 1382 (s), 1352 (s), 1219 (m), 1166 (s), 1123 (s), 1094 (m), 990 (s), 904 (m), 834 (m), 815 (m), 766 (m), 722 (m), 698 (m), 616 (m), 583 (s), 529 (m), 460 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.08, 1.09, 1.10 (each d, *J* = 6.0 Hz, 3H, CHC*H*$_3$), 2.25 (dt, *J* = 14.6, 7.4 Hz, 1H, C*H*H), 2.50 (dt, *J* = 14.6, 5.8 Hz, 1H, CH*H*), 3.60 (s, 3H, SO_2OCH_3), 3.64 (m, 2H, 2 X C*H*O), 4.43 (dd, *J* = 7.4, 6.3 Hz, 1H, $CH_2CHSO_2OCH_3$), 7.35-7.44 (m, 5H, Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 22.4, 23.1 (3 X CH*C*H$_3$), 37.7 (*C*H$_2$), 56.8 (SO_2OCH_3), 63.8 ($CHSO_2OCH_3$), 69.2, 69.7 (2 X O*C*H), 128.6, 128.8, 129.3 (Ar*C*H), 133.3 (Ar*C*) ppm. MS (EI, 70 eV): m/z (%) = 286 (3) [M^+], 243 (9), 226 (7), 190 (4), 163 (3), 147 (24), 131 (38), 117 (17), 105 (32), 87 (100), 79 (16), 69 (17), 59 (11), 45 (45). Anal. Calcd for $C_{14}H_{22}O_4S$ (286.39): C, 58.72; H, 7.74. Found: C, 58.92; H, 7.78.

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