Asymmetric Synthesis of α,γ-Substituted γ-Sultones via Allylation of Chiral Lithiated Sulfonates

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Dedicated to Professor Helmut Schwarz on the occasion of his 60th birthday

Keywords: Sultones / Asymmetric synthesis / Chiral auxiliaries / Sulfonates / One-pot reaction / Cyclization

The first auxiliary controlled asymmetric synthesis of enantiopure α,γ-substituted γ-sultones via α-allylation of lithiated sulfonates by using 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose as chiral auxiliary is described. The high asymmetric inductions of the α-allylations were reached in good to excellent yields. Successive epimerization-free cleavage of the auxiliary and diastereoselective ring closure of the sulfonic acid intermediates in a one-pot procedure led to the title compounds in good to excellent yields and diastereo- and enantiomeric excesses (*de*, *ee* ≥ 98%).

Introduction

Sultones are synthetically useful heterocycles which can react with a variety of compounds to introduce the alkylsulfonic acid function and offer novel possibilities for stereoselective transformations.[1] There have been several new developments for the synthesis of sultones which have also been applied in total syntheses of natural products. A novel synthetic route for the synthesis of α,β-unsaturated γ-sultones and their application in Diels−Alder reactions have been reported.[2] Moreover, unsaturated sultones with normal, medium and large ring sizes can be prepared easily by ring-closing metathesis of sulfonates.[3] Only a few diastereoselective syntheses of γ-sultones have been reported. For example, palladium-catalyzed rearrangement of cyclic allylic sulfites selectively provided *trans*-α,β-disubstituted γ-sultones.[4] An intramolecular Michael reaction of γ-alkylsulfonyloxy-α,β-unsaturated esters using higher order cyano copper or silver amides as a base gave γ-sultones stereoselectively.[5] Considering the reported methods, only a few synthetic routes to enantiopure sultones and their applications in synthesis have been reported. Various mixed disulfonate ester derivatives of carbohydrates led to chiral products in which a sultone is fused to a sugar ring via intramolecular displacement reactions.[6] In the same manner nucleoside sultones have been prepared as building blocks for the preparation of novel nucleotide analogues.[7] Metz et al. have developed an efficient and highly stereoselective intramolecular Diels−Alder reaction of vinylsulfonates possessing a diene moiety, followed by flexible elaboration with cleavage of the resultant sultones.[8] Moreover, they have shown a powerful application of the sultone route in the synthesis of methyl nonactate, the monomeric subunit of the mactrotetrolides,[9] and the total synthesis of the macrodiolide antibiotic pamamycin-607.[10] A further application in an enantioselective synthesis of the sesqiterpenoid alcohol (−)-myltaylenol employing a sultone as a key intermediate has been reported by Winterfeldt et al.[11] Camphenesultone as a starting material for the total synthesis of β-santalol has been described by Wolinsky et al.[12] Camarasa et al. have discovered a novel class of potent and specific *anti*-HIV-1 agents, called TSAO derivatives containing a sultone moiety and their projects focused on the modification and synthesis of the analogues of 3′-spiro sultone nucleosides and adamantane spiro sultones.[13]

To the best of our knowledge, no chiral auxiliary controlled methodology for the asymmetric synthesis of sultones has been reported so far. Based on the results of our communication,[14] we now wish to describe in detail the efficient asymmetric synthesis of α,γ-substituted γ-sultones via α-allylation of chiral lithiated sulfonates.

Results and Discussion

In previous communications and a full paper we have described highly efficient asymmetric electrophilic α-substitutions of sulfonates bearing 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose as a chiral auxiliary with various alkyl halides and nitroolefins.[15] We have now extended our methodology to the enantioselective synthesis of α,γ-substituted γ-sultones by using allylic halides as electrophiles. The chiral substrate **1a** (Figure 1) was prepared by the reaction of the

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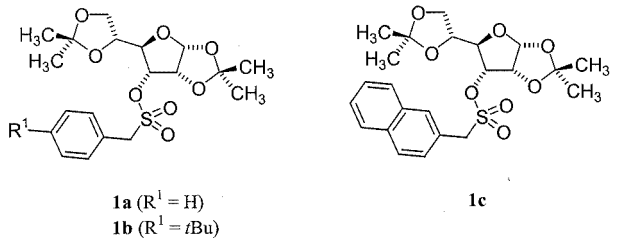
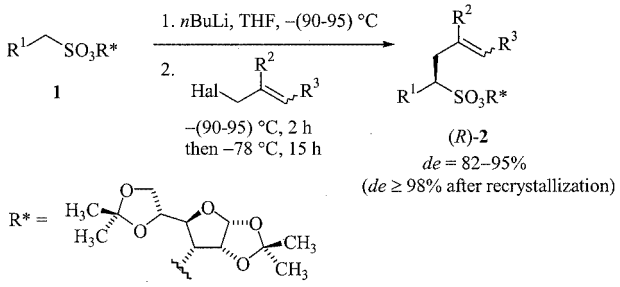


Figure 1. The enantiopure sulfonates **1a**−**c**

chiral auxiliary with benzylsulfonyl chloride which is commercially available, while the syntheses of **1b** and **1c** were started from the corresponding sodium sulfonates, which were prepared according to known procedures.[16]

The enantiopure sulfonates **1** were lithiated with one equivalent of *n*-butyllithium in tetrahydrofuran at −90 to −95 °C and reacted with different allylic halides at this temperature for 2 h and then at −78 °C for 15 h. Decreasing the amount of THF to 10 mL per mmol of substrates led to the highest yield and diastereoselectivity. The α-allylated sulfonates **2a**−**g** were obtained in good to excellent yields (72−98%) with high diastereomeric excesses (*de* = 82−95%) (Scheme 1, Table 1). In all cases diastereomerically pure α-allylated sulfonates could be obtained by recrystallization (*de* ≥ 98%). For **2f** and **2g**, recrystallization produced a 1:13 and 1:4 mixture of the enantiopure (*Z*)- and (*E*)-sulfonates, respectively. The isomeric mixture could be used for the next step without separation.



Scheme 1. Asymmetric α-allylation of chiral sulfonates **1** to afford the product (*R*)-**2**

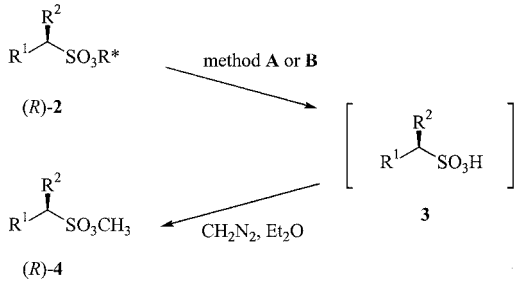
Table 1. Asymmetric α-allylation of chiral sulfonates **1** to afford the product (*R*)-**2a**−**g**

(*R*)-**2**	R^1	R^2	R^3	Yield [%]	*de* [%][a]
a	4-*tert*-Butylphenyl	CH_3	H	80	90 (98)
b	Phenyl	CH_3	H	72	88 (98)
c	Phenyl	H	H	98	94 (98)
d	4-*tert*-Butylphenyl	H	H	98	95 (98)
e	2-Naphthyl	H	H	98	90 (98)
f	4-*tert*-Butylphenyl	H	CH_3	93	90 (98[b])
g	Phenyl	H	CH_3	78	82 (98[b])

[a] Determined by ^{13}C NMR; in parentheses: after recrystallization. [b] Obtained as a 1:13 and 1:4 mixture of the enantiopure *cis* and *trans* sulfonates **2f** and **2g**, respectively.

The absolute configuration of the newly formed stereogenic center was assigned to be (*R*) in analogy to the results shown in the previous report on the synthesis of α-alkylated analogues[15a] and also confirmed by X-ray crystallography of a corresponding sultone (vide infra).

In analogy to the procedure reported in the previous communication,[15a] removal of the chiral auxiliary to form the corresponding sulfonic acids **3** was achieved by refluxing the sulfonates **2** in an EtOH/H_2O solution containing 15 mol % $Pd(OAc)_2$ for 4 days (method **A**). As an alternative method for cleaving the chiral auxiliary without epimerization at the α-position of the sulfonyl group, refluxing the diastereomerically pure sulfonates in ethanol containing 2% TFA for 24 h led to the corresponding sulfonic acids **3** (method **B**). In order to facilitate the purification of the sulfonic acids, they were directly converted into the corresponding methyl sulfonates (*R*)-**4** with diazomethane (Scheme 2). The methyl sulfonates **4a**−**e** were obtained in very good yields and enantiomerically pure (Table 2). A comparison of the two methods concluded that in the case of alkylation product **4a** the cleavage method using TFA results in only slightly lower yields. In contrast, cleavage of the allylated sulfonates **4b**,**c** using TFA gave significantly lower yields of the corresponding acids. This could be attributed to the cyclization to the corresponding sultones which could be detected in a small amount in the crude reaction mixture. Care must be taken when the reaction is performed in ethanol, which can cause the ring opening of sultones. To reduce this side reaction, the reaction time had to be limited to 24 h reflux.



Scheme 2. Removal of the chiral auxiliary to form the methyl sulfonates (*R*)-**4**: Method **A**: $Pd(OAc)_2$, EtOH/H_2O, reflux, 4 days. Method **B**: 2% TFA/EtOH, reflux, 24 h

Cleavage of the chiral auxiliary using TFA liberated the sulfonic acids **3** whose cyclization to the desired sultones **5** had to be optimized (Scheme 3, Table 3). The most reactive substrate in the cyclization reaction was the α-allylsulfonic acid **3a** obtained from (*R*)-**2a** after cleavage of the chiral auxiliary. Refluxing in a 2% TFA/CH_2Cl_2 solution for 22 h gave the geminal disubstituted **5a** in very good yield and excellent enantiomeric excess. Under the same conditions, sultone **5b** was obtained in excellent yield (90%). In contrast, (*R*)-**2c** yielded **5c** in a lower yield of only 29%, which could be significantly improved by increasing the concentration of the TFA solution. Sultones **5c**−**e** could be synthesized in good yields (64−72%) and high diastereoselectivities (*ds* = 89−90%) by refluxing the corresponding crude

Table 2. Removal of the chiral auxiliary to form the methyl sulfonates **4**

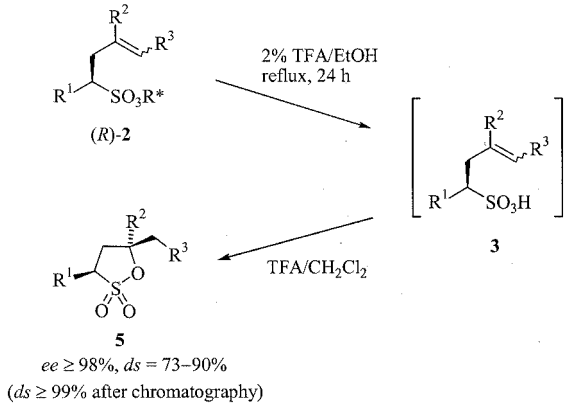
(*R*)-**4**	R^1	R^2	Yield [%] Method **A**	Method **B**	*ee* [%][a]
a	4-*tert*-Butylphenyl	(2-Naphthyl)methyl	86	83	≥98
b	Phenyl	Allyl	85	73[b]	≥98
c	4-*tert*-Butylphenyl	Allyl	80	65[b]	≥98
d	Phenyl	Crotyl	–	80	≥98
e	4-*tert*-Butylphenyl	Crotyl	–	81	≥98

[a] Determined by HPLC using a chiral stationary phase (see Exp. Sect.). [b] The crude product contained a small amount of the corresponding sultone.

Table 3. Removal of the auxiliary and cyclization of the sulfonic acid **3** to afford the γ-sultones **5**

5	R^1	R^2	R^3	Cyclization conditions % TFA/CH_2Cl_2	Temp., time	Yield [%]	*ds* [%][a]	*ee* [%][b]
a	4-*tert*-Butylphenyl	CH_3	H	10	r.t., 3 d	29	–	≥98
				2	reflux, 22 h	82	–	≥98
b	Phenyl	CH_3	H	2	reflux, 20 h	90	–	≥98
c	Phenyl	H	H	2	reflux, 3 d	29	89 (99)	≥98
				10	reflux, 30 h	33	89 (99)	≥98
				10	reflux, 3 d	45	90 (99)	≥98
				20	reflux, 24 h	72	90 (99)	≥98
d	4-*tert*-Butylphenyl	H	H	20	reflux, 24 h	64	89 (99)	≥98
e	2-Naphthyl	H	H	20	reflux, 24 h	77	89 (99)	≥98
f	4-*tert*-Butylphenyl	H	CH_3	20	reflux, 24 h	51	73[c] (99)	≥98
				30	reflux, 16 h	64	78[c] (99)	≥98
g	Phenyl	H	CH_3	30	reflux, 16 h	71	73[c] (99)	≥98
				40	reflux, 16 h	69	73[c] (99)	≥98

[a] Determined by ^{13}C NMR, in parentheses: after column chromatography or HPLC. [b] Determined by HPLC using a chiral stationary phase (see Exp. Sect.). [c] The product mixture consisted of two diastereomeric γ-sultones and small amounts of two diastereomeric δ-sultones.



Scheme 3. Removal of chiral auxiliary and cyclization of the sulfonic acid **3** to afford the γ-sultones **5**

sulfonic acids **3** in a CH_2Cl_2 solution containing 20% TFA for 24 h. Under these conditions, however, **5f** could only be obtained in 51% yield. A further increase of the TFA concentration in solution and a small decrease of reaction time overcame this problem and led to higher yields of **5f** and **5g** of 64% and 71%, respectively. The yield of **5g** could not be increased by using an even higher concentration of TFA. Removal of the chiral auxiliary and cyclization of the sulfonates **2f**,**g** led to a product mixture consisting of two diastereomeric γ-sultones and small amounts of two diastereomeric δ-sultones. In all cases the diastereomerically and enantiomerically pure sultones **5a**–**g** could be obtained by flash column chromatography or HPLC (*de, ee* ≥ 98%).

NOE investigations of the products revealed that the protons at the α- and γ-position are *cis* to each other. The absolute configuration of the newly formed stereogenic center was established unambiguously as (*R*) by X-ray crystallography in the case of product **5c** and again shows that the protons at the α- and γ-position are *cis* to each other (Figure 2). The stereochemistry of the major diastereomer of other sultones is also expected to be (*R*,*R*) based on the assumption of a uniform reaction mechanism operating during the allylation and cyclization reactions.

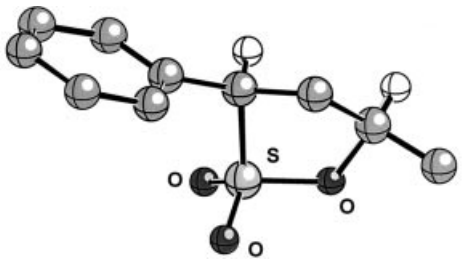


Figure 2. X-ray crystal structure of **5c**

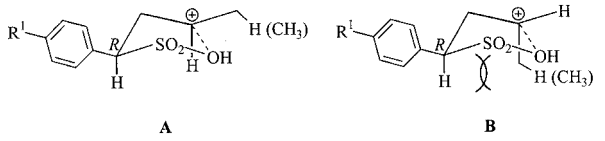


Figure 3. Proposed transition state of the cyclization of sulfonic acids

To explain the stereochemical outcome of the sultone formation we assume a Markownikov protonation of the olefinic double bond under the acidic reaction conditions. The cyclization can proceed via two possible transition states as depicted in Figure 3. Transition state **A** should be more favored than **B** owing to its lower 1,3-steric interaction between the alkyl group and the benzylic H-atom. This transition state model can account for the preferred *cis*-configuration of the α,γ-substituted γ-sultones.

Conclusion

In summary, a highly efficient diastereo- and enantioselective route to α,γ-substituted γ-sultones via α-allylation of lithiated chiral sulfonates has been developed. Acid-catalyzed cleavage of the chiral auxiliary and diastereoselective ring closure of the sulfonic acid intermediates were carried out following a one-pot procedure. Applications of these enantiopure compounds as enantiopure synthetic intermediates will be the subject of further investigations in our laboratories.

Experimental Section

General Remarks: All moisture-sensitive reactions were carried out using standard Schlenk techniques unless stated otherwise. Solvents were dried and purified by conventional methods prior to use. THF was freshly distilled from sodium−lead alloy under argon. Reagents of commercial quality were used from freshly opened containers or purified by common methods. *n*BuLi (1.6 M in hexane) was purchased from Merck, Darmstadt. Preparative column chromatography used Merck silica gel 60, particle size 0.040−0.063 mm (230−240 mesh, flash). Analytical TLC used silica-gel 60 F_{254} plates from Merck, Darmstadt. Optical rotation values were measured with a Perkin−Elmer P241 polarimeter. Microanalyses were obtained with a Vario EL element analyzer. Mass spectra were acquired with a Finnigan SSQ7000 (CI, 100 eV, EI 70 eV) spectrometer. High-resolution mass spectra were recorded with a Finnigan MAT95 spectrometer. IR spectra were taken with a Perkin−Elmer FT/IR 1760 instrument. ^{1}H and ^{13}C NMR spectra were recorded with Gemini 300 or Varian Inova 400 instruments and all measurements were performed with tetramethylsilane as internal standard. Melting points were determined with a Tottoli melting point apparatus and are uncorrected.

α-Allylated Chiral Sulfonates (*R*)-2a−g. General Procedure 1 (GP 1): The enantiopure sulfonate **1** (1.0 equiv.) was dissolved in dry THF (10 mL per mmol) and cooled to between −90 and −95 °C under argon. *n*BuLi (1.0 equiv.) was added dropwise. After stirring for 1 h, the allylic halide (1.5 equiv.) was added dropwise. The reaction mixture was stirred at −90 to −95 °C for 2 h, then stirring was continued at −78 °C overnight. The mixture was quenched with water. After separation of the organic layer the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with water, brine and dried with $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography (SiO_2, *n*-pentane/diethyl ether) to give the product **2**.

Removal of the Chiral Auxiliary to Give the α-Allylated Methyl Sulfonates (*R*)-4a−e. Method B: General Procedure 2 (GP 2): The mixture of the sulfonate (*R*)-**2** (0.5 mmol) and a 2% TFA/EtOH solution (20 mL) was refluxed for 24 h. The resulting colorless solution was treated with an ethereal solution of diazomethane until the yellow color persisted. The solvent was evaporated under reduced pressure and the crude product was purified by flash column chromatography (SiO_2, diethyl ether/*n*-pentane).

Removal of the Chiral Auxiliary and Cyclization to Give the γ-Sultones (*R*,*R*)-5a−g. General Procedure 3 (GP 3): The mixture of the sulfonate (*R*)-**2** (1.0 mmol) and a 2% TFA/EtOH solution (40 mL) was refluxed for 24 h, the solvent was removed under reduced pressure and the crude sulfonic acid was used in the next reaction step without further purification. The crude product **3** was dissolved in a TFA/CH_2Cl_2 solution (20 mL) and the reaction mixture was refluxed. The mixture was quenched with water. After separation of the organic layer the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution. After drying over $MgSO_4$ the solvent was evaporated and the crude product was purified by flash column chromatography (SiO_2, diethyl ether/ *n*-pentane).

(*R*)-1-(4-*tert*-Butylphenyl)-3-methyl-3-butene-1-sulfonate (2a): According to GP 1, sulfonate **1b** (2.35 g, 5 mmol) was deprotonated with *n*BuLi (3.13 mL, 1.6 M) and reacted with 3-bromo-2-methylpropene (0.76 mL, 7.5 mmol). Workup and flash column chromatography (Et_2O/pentane, 1:4) gave (*R*)-**2a** (2.10 g, 80%); *de* = 90% (NMR). The major diastereomer was obtained as a colorless solid after recrystallization from 2-propanol; *de* ≥ 98% (NMR); m.p. 109 °C; $[\alpha]_D^{24}$ = +79.13 (*c* = 1.0; $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2980 (vs), 2938 (s), 2904 (s), 1655 (m), 1614 (w), 1516 (m), 1458 (m), 1416 (w), 1373 (vs), 1315 (w), 1234 (s), 1217 (s), 1168 (vs), 1119 (s), 1049 (vs), 1018 (vs), 931 (m), 875 (vs), 828 (vs), 789 (m), 743 (w), 606 (vs), 548 (m), 522 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 [s, 9 H, C(CH_3)$_3$], 1.33, 1.36, 1.46, 1.56 [each s, 3 H, (O)$_2$C(CH_3)$_2$], 1.62 (s, 3 H, CH_3C=CH$_2$), 2.93 [dd, *J* = 11.5, 14.3 Hz, 1 H, C*H*HC(CH$_3$)=CH$_2$], 3.16 [dd, *J* = 3.3, 14.3 Hz, 1 H, CH*H*C(CH$_3$)=CH$_2$], 3.90 (dd, *J* = 6.6, 8.3 Hz, 1 H, C*H*HOC), 4.04 (dd, *J* = 6.9, 8.3 Hz, 1 H, CH*H*OC), 4.15 [dd, *J* = 4.1, 8.5 Hz, 1 H, C*H*(OC)CH(OC)CH$_2$O], 4.23 [app. t, *J* = 4.4 Hz, 1 H, C*H*(OC)CH(OC)$_2$], 4.30 (dt, *J* = 4.1, 6.6 Hz, 1 H, C*H*(OC)CH$_2$O], 4.52 (dd, *J* = 3.6, 11.5, 1 H, C*H*SO$_3$), 4.64 (br. s, 1 H, C*H*H=CCH$_3$), 4.66 (dd, *J* = 4.7, 8.5 Hz, 1 H, C*H*OSO$_2$), 4.71 (br. s, 1 H, CH*H*=CCH$_3$), 5.69 [d, *J* = 3.6 Hz, 1 H, C*H*(OC)$_2$], 7.35 (s, 4 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1 (*C*H$_3$C=CH$_2$), 25.3, 26.2, 26.6, 26.6 [(O)$_2$C(*C*H$_3$)$_2$], 31.2 [C(*C*H$_3$)$_3$], 34.6 [*C*(CH$_3$)$_3$], 37.6 [*C*H$_2$C(CH$_3$)=CH$_2$], 65.1 (*C*H$_2$OC), 66.5 (*C*HSO$_3$), 74.5, 76.6, 76.7, 77.4 (*C*HO), 103.5 [*C*H(OC)$_2$], 109.9, 113.3 [(O)$_2$*C*(CH$_3$)$_2$], 114.2 [CH$_2$=C(CH$_3$)], 125.4, 127.9 (Ar*C*), 129.4 (Ar*C*H), 139.5 [*C*(CH$_3$)=CH$_2$], 151.9 (Ar*C*) ppm. MS (CI, 100 eV, isobutane): *m*/*z* (%) = 525 (43) [M$^+$ + 1], 471 (3), 243 (41), 201 (100). $C_{27}H_{40}O_8S$ (524.67): calcd. C 61.81, H 7.68; found C 61.72, H 7.99.

(*R*)-3-Methyl-1-phenyl-3-butene-1-sulfonate (2b): According to GP 1, sulfonate **1a** (2.07 g, 5 mmol) was deprotonated with *n*BuLi

(3.13 mL, 1.6 M) and reacted with 3-bromo-2-methylpropene (0.76 mL, 7.5 mmol). Workup and flash column chromatography (Et_2O/pentane, 1:4) gave (*R*)-**2b** (1.68 g, 72%); *de* = 88% (NMR). The major diastereomer was obtained as a colorless solid after recrystallization from 2-propanol; *de* ≥ 98% (NMR); m.p. 132 °C; $[\alpha]_D^{24}$ = +90.69 (*c* = 1.0; $CHCl_3$). IR (KBr): ($\tilde{\nu}$ = 2984 (vs), 2936 (s), 2902 (m), 1653 (m), 1497 (w), 1456 (m), 1370 (vs), 1314 (w), 1218 (s), 1167 (vs), 1116 (s), 1082 (m), 1047 (vs), 1015 (vs), 931 (m), 876 (vs), 828 (vs), 798 (m), 734 (w), 697 (s), 628 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33, 1.36, 1.46, 1.56 [each s, 3 H, $(O)_2C(CH_3)_2$], 1.62 (s, 3 H, $CH_3C{=}CH_2$), 2.95 [ddd, *J* = 0.6, 11.8, 14.3 Hz, 1 H, C*H*HC(CH_3)=CH_2], 3.17 [dd, *J* = 3.3, 14.3 Hz, 1 H, CH*H*C(CH_3)=CH_2], 3.89 (dd, *J* = 6.6, 8.5 Hz, 1 H, C*H*HOC), 4.04 (dd, *J* = 6.6, 8.5 Hz, 1 H, CH*H*OC), 4.14 [dd, *J* = 3.9, 8.5 Hz, 1 H, C*H*(OC)CH(OC)CH_2O], 4.29 [m, 2 H, C*H*(OC)CH$(OC)_2$ and C*H*(OC)CH_2O], 4.53 (dd, *J* = 3.6, 11.8 Hz, 1 H, C*H*SO_3), 4.62 (br. s, 1 H, C*H*H=CCH_3), 4.68 (dd, *J* = 4.7, 8.8 Hz, 1 H, C*H*OSO_2), 4.71 (m, 1 H, CH*H*=CCH_3), 5.70 [d, *J* = 3.6 Hz, 1 H, C*H*$(OC)_2$], 7.35−7.39 (m, 3 H, Ar*H*), 7.43−7.47 (m, 2 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1 (*C*$H_3C{=}CH_2$), 25.2, 26.2, 26.6, 26.7 [2 × $(O)_2C(CH_3)_2$], 37.7 [*C*$H_2C(CH_3){=}CH_2$], 65.2 (*C*H_2OC), 66.8 (*C*HSO_3), 74.6, 76.6, 76.7, 77.4 (*C*HO), 103.5 [*C*H$(OC)_2$], 109.9, 113.4 [$(O)_2C(CH_3)_2$], 114.4 (*C*H_2=C(CH_3), 128.5, 129.0, 129.8 (Ar*C*H), 131.1 (Ar*C*), 139.4 [*C*(CH_3)=CH_2] ppm. MS (CI, 100 eV, isobutane): *m*/*z* (%) = 469 (100) [M^+ + 1], 243 (44), 203 (15). 145 (12). $C_{23}H_{32}O_8S$ (468.57): calcd. C 58.96, H 6.88; found C 58.78, H 6.94.

(*R*)-1-Phenyl-3-butene-1-sulfonate (2c): According to GP 1, sulfonate **1a** (2.07 g, 5 mmol) was deprotonated with *n*BuLi (3.13 mL, 1.6 M) and reacted with allyl iodide (0.75 mL, 7.5 mmol). Workup and flash column chromatography (Et_2O/pentane, 1:4) gave (*R*)-**2c** (2.22 g, 98%); *de* = 95% (NMR). The major diastereomer was obtained as a colorless solid after recrystallization from 2-propanol; *de* ≥ 98% (NMR); m.p. 149 °C; $[\alpha]_D^{24}$ = +77.00 (*c* = 1.0; $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2978 (w), 2934 (w), 1497 (w), 1457 (m), 1370 (vs), 1355 (s), 1313 (m), 1255 (s), 1220 (s), 1172 (vs), 1115 (s), 1054 (s), 1038 (s), 1015 (vs), 1001 (s), 933 (m), 880 (s), 864 (m), 840 (s), 810 (m), 698 (m), 627 (m), 571 (m), 503 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33, 1.37, 1.46, 1.57 [each s, 3 H, $(O)_2C(CH_3)_2$], 2.96 (m, 1 H, C*H*HCH=CH_2), 3.21 (m, 1 H, CH*H*CH=CH_2), 3.89 (dd, *J* = 6.6, 8.5 Hz, 1 H, C*H*HOC), 4.04 (dd, *J* = 6.9, 8.5 Hz, 1 H, CH*H*OC), 4.14 [dd, *J* = 3.9, 8.5 Hz, 1 H, C*H*(OC)CH(OC)CH_2O], 4.26−4.32 [m, 2 H, C*H*(OC)CH$(OC)_2$ and C*H*(OC)CH_2O], 4.37 (dd, *J* = 4.1, 11.3, 1 H, C*H*SO_3), 4.68 (dd, *J* = 4.7, 8.8 Hz, 1 H, C*H*OSO_2), 5.01 (dd, *J* = 1.4, 10.2 Hz, 1 H, C*H*H=CH), 5.08 (dd, *J* = 1.4, 17.0 Hz, 1 H, CH*H*=CH), 5.54 [ddt (ABX_2 system), *J* = 6.9, 10.2, 17.0 Hz, 1 H, $CH_2CH{=}CH_2$], 5.72 [d, *J* = 3.9 Hz, 1 H, C*H*$(OC)_2$], 7.36−7.41 (m, 3 H, Ar*H*), 7.43−7.48 (m, 2 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 26.2, 26.6, 26.6 [2 × $(O)_2C(CH_3)_2$], 34.2 (*C*$H_2CH{=}CH_2$), 65.2 (*C*H_2OC), 67.8 (*C*HSO_3), 74.6, 76.8, 77.2, 77.4 (*C*HO), 103.6 [*C*H$(OC)_2$], 110.0, 113.4 [$(O)_2C(CH_3)_2$], 118.5 (*C*H_2=CH), 128.6, 129.0, 129.8 (Ar*C*H), 131.1 (Ar*C*), 132.4 (*C*H=CH_2) ppm. MS (CI, 100 eV, isobutane): *m*/*z* (%) = 455 (100) [M^+ + 1], 439 (4), 415 (30), 397 (12), 357 (4), 203 (5), 131 (12), 101 (2). $C_{22}H_{30}O_8S$ (454.53): calcd. C 58.13, H 6.65; found C 57.78, H 6.61.

(*R*)-1-(4-*tert*-Butylphenyl)-3-butene-1-sulfonate (2d): According to GP 1, sulfonate **1b** (2.35 g, 5 mmol) was deprotonated with *n*BuLi (3.13 mL, 1.6 M) and reacted with allyl iodide (0.75 mL, 7.5 mmol). Workup and flash column chromatography (Et_2O/pentane, 1:4) gave (*R*)-**2d** (2.50 g, 98%); *de* = 95% (NMR). The major diastereomer was obtained as a colorless solid after recrystallization from 2-propanol; *de* ≥ 98% (NMR); m.p. 92 °C; $[\alpha]_D^{24}$ = +70.00 (*c* = 1.0; $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2965 (vs), 2906 (s), 1642 (m), 1616 (m), 1513 (m), 1459 (m), 1416 (w), 1372 (vs), 1317 (w), 1219 (vs), 1169 (vs), 1119 (m), 1020 (vs), 925 (s), 874 (vs), 829 (vs), 738 (w), 608 (s), 537 (m), 517 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.31 [s, 9 H, $C(CH_3)_3$], 1.33, 1.37, 1.46, 1.57 [each s, 3 H, $(O)_2C(CH_3)_2$], 2.95 (m, 1 H, C*H*HCH=CH_2), 3.20 (m, 1 H, CH*H*CH=CH_2), 3.89 (dd, *J* = 6.6, 8.5 Hz, 1 H, C*H*HOC), 4.03 (dd, *J* = 6.8, 8.5 Hz, 1 H, CH*H*OC), 4.15 [dd, *J* = 3.9, 8.5 Hz, 1 H, C*H*(OC)CH(OC)CH_2O], 4.22 [app. t, *J* = 4.3, 1 H, C*H*(OC)-CH$(OC)_2$], 4.32 [dt, *J* = 3.9, 6.6, 1 H, C*H*(OC)CH_2O], 4.36 (dd, *J* = 3.9, 11.3, 1 H, C*H*SO_3), 4.66 (dd, *J* = 4.7, 8.5 Hz, 1 H, C*H*OSO_2), 5.00 (dd, *J* = 1.4, 10.2 Hz, 1 H, C*H*H=CH), 5.09 (dd, *J* = 1.4, 17.0 Hz, 1 H, CH*H*=CH), 5.55 [ddt (ABX_2 system), *J* = 6.9, 10.2, 17.0 Hz, 1 H, $CH_2CH{=}CH_2$], 5.71 [d, *J* = 3.9 Hz, 1 H, C*H*$(OC)_2$], 7.35−7.42 (m, 4 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3, 26.2, 26.6 [2 × $(O)_2C(CH_3)_2$], 31.2 [$C(CH_3)_3$] 34.2 (*C*$H_2CH{=}CH_2$), 34.6 [*C*$(CH_3)_3$], 65.1 (*C*H_2OC), 67.6 (*C*HSO_3), 74.6, 76.7, 77.2, 77.4 (*C*HO), 103.6 [*C*H$(OC)_2$], 109.9, 113.3 [$(O)_2C(CH_3)_2$], 118.3 (*C*H_2=CH), 125.5 (Ar*C*H), 127.9 (Ar*C*), 129.4 (Ar*C*H),), 132.6 (*C*H=CH_2), 152.1 (Ar*C*) ppm. MS (CI, 100 eV, isobutane): *m*/*z* (%) = 511 (93) [M^+ + 1], 495 (6), 261 (9), 203 (23), 187 (100). $C_{26}H_{38}O_8S$ (510.65): calcd. C 61.15, H 7.50; found C 61.14, H 7.89.

(*R*)-1-(Naphth-2-yl)-3-butene-1-sulfonate (2e): According to GP 1, sulfonate **1c** (0.83 g, 1.8 mmol) was deprotonated with *n*BuLi (1.13 mL, 1.6 M) and reacted with allyl iodide (0.25 mL, 2.7 mmol). Workup and flash column chromatography (Et_2O/pentane, 1:4) gave (*R*)-**2e** (0.88 g, 98%); *de* = 90% (NMR). The major diastereomer was obtained as a colorless solid after recrystallization from 2-propanol; *de* ≥ 98% (NMR); m.p. 102 °C; $[\alpha]_D^{24}$ = +70.50 (*c* = 0.9; $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3062 (w), 2985 (s), 2937 (m), 2904 (m), 1642 (w), 1600 (w), 1510 (w), 1458 (w), 1370 (vs), 1316 (m), 1218 (s), 1171 (vs), 1116 (s), 1047 (vs), 1014 (vs), 928 (m), 875 (s), 838 (s), 746 (m), 655 (m), 601 (m), 480 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.19, 1.37, 1.46, 1.50 [each s, 3 H, $(O)_2C(CH_3)_2$], 3.09 (m, 1 H, C*H*HCH=CH_2), 3.28 (m, 1 H, CH*H*CH=CH_2), 3.89 (dd, *J* = 6.6, 8.5 Hz, 1 H, C*H*HOC), 4.03 (dd, *J* = 6.9, 8.5 Hz, 1 H, CH*H*OC), 4.13 [dd, *J* = 4.1, 8.5 Hz, 1 H, C*H*(OC)CH(OC)CH_2O], 4.21 [app. t, *J* = 4.3 Hz, 1 H, C*H*(OC-)CH$(OC)_2$], 4.28 [dt, *J* = 4.1, 6.6 Hz, 1 H, C*H*(OC)CH_2O], 4.55 (dd, *J* = 4.1, 11.3 Hz, 1 H, C*H*SO_3), 4.66 (dd, *J* = 4.9, 8.5 Hz, 1 H, C*H*OSO_2), 4.88 (dd, *J* = 1.4, 10.2 Hz, 1 H, C*H*H=CH), 5.09 (dd, *J* = 1.4, 17.0 Hz, 1 H, CH*H*=CH), 5.55 [ddt (ABX_2 system), *J* = 6.9, 10.2, 17.0 Hz, 1 H, $CH_2CH{=}CH_2$], 5.72 [d, *J* = 3.8 Hz, 1 H, C*H*$(OC)_2$], 7.48−7.55 (m, 2 H, Ar*H*), 7.59 (dd, *J* = 1.7, 8.5 Hz, 1 H, Ar*H*), 7.82−7.89 (m, 3 H, Ar*H*), 7.92 (br. s, 1 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 26.2, 26.5, 26.6 [2 × $(O)_2C(CH_3)_2$], 34.2 (*C*$H_2CH{=}CH_2$), 65.2 (*C*H_2OC), 68.1 (*C*HSO_3), 74.6, 76.8, 77.2, 77.4 (*C*HO), 103.5 [*C*H$(OC)_2$], 110.0, 113.4 [$(O)_2C(CH_3)_2$], 118.6 (*C*H_2=CH), 126.2, 126.3, 126.7, 127.5, 128.0, 128.4 (Ar*C*H), 128.5 (Ar*C*), 130.0 (Ar*C*H), 132.3 (*C*H=CH_2), 132.9, 133.3 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 504 (4) [M^+], 489 (14), 282 (10), 267 (10), 217 (7), 203 (8), 181 (100), 161 (41), 58 (36). $C_{26}H_{32}O_8S$ (504.59): calcd. C 61.89, H 6.39; found C 61.80, H 6.48.

(*R*)-1-(4-*tert*-Butylphenyl)-3-pentene-1-sulfonate (2f): According to GP 1, sulfonate **1b** (2.35 g, 5 mmol) was deprotonated with *n*BuLi (3.13 mL, 1.6 M) and reacted with 85% (*E*)-crotyl bromide (0.8 mL, 7.5 mmol). Workup and flash column chromatography (Et_2O/pentane, 5:1) gave (*R*)-**2f** (2.44 g, 93%); *de* = 90% (NMR). A 1:13 mixture of the enantiopure (*Z*)- and (*E*)-sulfonate (*R*)-**2f** was obtained

as a colorless solid after recrystallization from 2-propanol; *de* ≥ 98% (NMR); m.p. 103 °C. IR (KBr): $\tilde{\nu}$ = 2980 (vs), 2902 (s), 1614 (w), 1517 (w), 1457 (m), 1370 (vs), 1313 (w), 1218 (s), 1168 (vs), 1118 (s), 1052 (vs), 1018 (vs), 969 (m), 877 (vs), 834 (vs), 612 (s), 550 (m), 505 (m) cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$, (*E*)-isomer]: δ = 1.32 [s, 9 H, $C(CH_3)_3$], 1.33, 1.36, 1.45, 1.56 [each s, 3 H, $(O)_2C(CH_3)_2$], 1.56 [s, 6 H, $(O)_2C(CH_3)_2$ and $CH_3CH{=}CH$], 2.88 (m, 1 H, $CHHCH{=}CHCH_3$), 3.11 (m, 1 H, $CHHCH{=}CHCH_3$), 3.88 (dd, *J* = 6.6, 8.5 Hz, 1 H, $CHHOC$), 4.03 (dd, *J* = 6.8, 8.5 Hz, 1 H, $CHHOC$), 4.15 [dd, *J* = 3.9, 8.5 Hz, 1 H, $CH(OC)CH(OC)CH_2O$], 4.21 [app. t, *J* = 4.3, 1 H, $CH(OC)CH(OC)_2$], 4.29 [m, 2 H, $CH(OC)CH_2O$) and $CHSO_3$), 4.64 (dd, *J* = 4.7, 8.5 Hz, 1 H, $CHOSO_2$), 5.16 (m, 1 H, $CH_2CH{=}CHCH_3$), 5.51 (m, 1 H, $CH_2CH{=}CHCH_3$), 5.69 [d, *J* = 3.9 Hz, 1 H, $CH(OC)_2$], 7.35−7.41 (m, 4 H, Ar*H*) ppm. ^{13}C NMR [100 MHz, $CDCl_3$, (*E*)-isomer]: δ = 17.9 ($CH_3CH{=}CH$), 25.3, 26.2, 26.7,[2 × $(O)_2C(CH_3)_2$], 31.2 ($CH_2CH{=}CH$), 34.6 [$C(CH_3)_3$], 65.1 (CH_2OC), 68.1 ($CHSO_3$), 74.5, 76.6, 78.0, 77.3 (*C*HO), 103.5 [$CH(OC)_2$], 110.0, 113.3 [$(O)_2C(CH_3)_2$], 125.0 ($CH_2CH{=}CHCH_3$), 125.5 (Ar*C*H), 128.1 (Ar*C*), 129.0 ($CH_2CH{=}CHCH_3$), 129.4 (Ar*C*H), 152.0 (Ar*C*) ppm. MS (CI, 100 eV, isobutane): *m*/*z* (%) = 525 (74) [M^+ + 1], 509 (5), 403 (7), 261 (23), 243 (7), 201 (100), 143 (21). $C_{27}H_{40}O_8S$ (524.67): calcd. C 61.81, H 7.68; found C 61.73, H 8.00.

(*R*)-1-Phenyl-3-pentene-1-sulfonate 2g: According to GP 1, sulfonate **1a** (2.06 g, 5 mmol) was deprotonated with *n*BuLi (3.13 mL, 1.6 M) and reacted with 85% (*E*)-crotyl bromide (0.8 mL, 7.5 mmol). Workup and flash column chromatography (Et_2O/pentane, 1:4) gave (*R*)-**2g** (1.81 g, 78%); *de* = 82% (NMR). A 1:4 mixture of the enantiopure (*Z*)- and (*E*)-sulfonate (*R*)-**2g** was obtained as a colorless solid after recrystallization from ethanol; *de* ≥ 98% (NMR); m.p. 143 °C. IR (KBr): $\tilde{\nu}$ = 3068 (w), 2987 (s), 2937 (m), 2902 (m), 1498 (w), 1457 (m), 1370 8vs), 1314 (w), 1255 (s), 1219 (s), 1169 (vs), 1117 (s), 1047 (vs), 1015 (vs), 879 (s), 840 (s), 697 (m), 629 (m), 577 (m), 505 (m) cm^{-1}. ^1H NMR [400 MHz, $CDCl_3$, (*E*)-isomer]: δ = 1.32, 1.36, 1.46, 1.56 [each s, 3 H, $(O)_2C(CH_3)_2$], 1.55 [m, 6 H, $(O)_2C(CH_3)_2$ and $CH_3CH{=}CH$], 2.88 (m, 1 H, $CHHCH{=}CHCH_3$), 3.14 (m, 1 H, $CHHCH{=}CHCH_3$), 3.88 (dd, *J* = 6.6, 8.5 Hz, 1 H, $CHHOC$), 4.03 (dd, *J* = 6.6, 8.5 Hz, 1 H, $CHHOC$), 4.14 [dd, *J* = 3.9, 8.5 Hz, 1 H, $CH(OC)CH(OC)CH_2O$], 4.29 [m, 3 H, $CH(OC)CH_2O$) and $CH(OC)CH(OC)_2$ and $CHSO_3$], 4.66 (dd, *J* = 4.7, 8.5 Hz, 1 H, $CHOSO_2$), 5.14 (m, 1 H, $CH_2CH{=}CHCH_3$), 5.49 (m, 1 H, $CH_2CH{=}CHCH_3$), 5.70 [d, *J* = 3.9 Hz, 1 H, $CH(OC)_2$], 7.35−7.40 (m, 3 H, Ar*H*), 7.42−7.48 (m, 2 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9 [(*Z*)] and 17.8 [(*E*), ($CH_3CH{=}CH$)], 25.2, 26.2, 26.6, 26.6 [2 × $(O)_2C(CH_3)_2$], 27.8 [(*Z*)] and 33.2 [(*E*), ($CH_2CH{=}CH$)], 65.1 (CH_2OC), 67.9 [(*Z*)] and 68.3 [(*E*), ($CHSO_3$)], 74.6, 76.8, 77.1, 77.4 (*C*HO), 103.6 [$CH(OC)_2$], 109.9, 113.4 [$(O)_2C(CH_3)_2$], 124.0 [(*Z*)] and 124.8 [(*E*), ($CH_2CH{=}CHCH_3$)], 127.4 [(*Z*)], 128.5, 128.9 (Ar*C*H), 129.2 ($CH_2CH{=}CHCH_3$), 129.8 (Ar*C*H), 131.3 [(*E*)] and 131.5 [(*Z*), (Ar*C*)] ppm. MS (EI, 70 eV): *m*/*z* (%) = 468 (2) [M^+], 453 (87), 251 (2), 145 (100), 129 (12), 113 (26), 101 (33), 91 (9), 55 (7). $C_{23}H_{32}O_8S$ (468.57): calcd. C 58.96, H 6.88; found C 59.14, H 7.09.

Methyl (*R*)-1-(4-*tert*-Butylphenyl)-2-(naphth-2-yl)ethanesulfonate (4a): According to GP 2, the corresponding (*R*)-sulfonate (0.35 g, 0.6 mmol) was refluxed in a 2% TFA/EtOH solution (25 mL) for 24 h. Workup and flash column chromatography (*n*-pentane/diethyl ether, 9:1) gave (*R*)-**4a** as a colorless solid (0.18 g, 83%); *ee* ≥ 98% (HPLC, Daicel OD); m.p. 94 °C; $[\alpha]_D^{24}$ = −108.2 (*c* = 1.0; $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2962 (m), 1599 (w), 1560 (w), 1508 (w), 1351 (vs), 1162 (vs), 994 (vs), 960 (m), 859 (m), 827 (s), 809 (w), 777 (s), 765 (vs), 749 (m), 673 (m), 603 (vs), 518 (m), 484 (m), 474 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.27 [s, 9 H, $C(CH_3)_3$], 3.58 (dd, *J* = 11.0, 14.0 Hz, 1 H, $CHHAr$), 3.63 (s, 3 H, CH_3O), 3.88 (dd, *J* = 3.9, 14.0 Hz, 1 H, $CHHAr$), 4.53 (dd, *J* = 3.9, 10.7 Hz, 1 H, $CHSO_3$), 7.10−8.00 (m, 11 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2 [$C(CH_3)_3$], 34.6 [$C(CH_3)_3$], 36.5 (CH_2Ar), 56.8 (CH_3O), 68.1 ($CHSO_3$), 125.8, 126.0, 126.1, 127.0, 127.6, 127.6, 127.9, 128.1, (Ar*C*H), 128.5 (Ar*C*), 129.4 (Ar*C*H), 132.3, 133.3, 134.1, 152.3 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 382 (39) [M^+], 287 (100), 231 (12), 153 (16), 141 (22), 122 (26), 57 (88). $C_{23}H_{26}O_3S$ (382.52): calcd. C 72.22, H 6.85; found C 71.84, H 6.71.

Methyl (*R*)-1-Phenyl-3-butene-1-sulfonate (4b): According to GP 2, sulfonate (*R*)-**2c** (0.22 g, 0.5 mmol) was refluxed in a 2% TFA/EtOH solution (20 mL) for 24 h. Workup and flash column chromatography (*n*-pentane/diethyl ether, 9:1) gave (*R*)-**4b** as a colorless solid (0.08 g, 73%); *ee* ≥ 98% (HPLC); m.p. 58 °C; $[\alpha]_D^{28}$ = −6.30 (*c* = 1.0; $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2959 (w), 2944 (w), 2922 (w), 1643 (m), 1456 (m), 1350 (vs), 1320 (s), 1228 (m), 1163 (vs), 993 (vs), 939 (s), 835 (s), 767 (s), 734 (s), 700 (s), 654 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.95 (m, 1 H, $CHHCH{=}CH_2$), 3.13 (m, 1 H, $CHHCH{=}CH_2$), 3.64 (s, 3 H, CH_3O), 4.26 (dd, *J* = 4.7, 11.0 Hz, 1 H, $CHSO_3$), 5.02 (d, *J* = 10.2 Hz, 1 H, $CHH{=}CH$), 5.10 (d, *J* = 17.0 Hz, 1 H, $CHH{=}CH$), 5.57 (m, 1 H, $CH{=}CH_2$), 7.36−7.44 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.1 ($CH_2CH{=}CH_2$), 56.8 (CH_3O), 66.7 ($CHSO_3$), 118.6 ($CH_2{=}CH$), 128.7, 129.0 (Ar*C*H), 129.5 (Ar*C*), 132.3 ($CH{=}CH_2$) ppm. MS (EI, 70 eV): *m*/*z* (%) = 181 (100) [$M^+ - SO_2OCH_3$], 103 (5), 91 (28) [$C_7H_7^+$]. $C_{11}H_{14}O_3S$ (226.29): calcd. C 58.39, H 6.24; found C 58.30, H 6.32.

Methyl (*R*)-1-(4-*tert*-Butylphenyl)-3-butene-1-sulfonate (4c): According to GP 2, sulfonate (*R*)-**2d** (0.25 g, 0.5 mmol) was refluxed in a 2% TFA/EtOH solution (20 mL) for 24 h. Workup and flash column chromatography (*n*-pentane/diethyl ether, 9:1) gave (*R*)-**4c** as a colorless liquid (0.09 g, 65%); *ee* ≥ 98% (HPLC, Daicel OD); $[\alpha]_D^{25}$ = −10.69 (*c* = 1.0; $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3080 (w), 2964 (vs), 2906 (m), 2870 (m), 1643 (w), 1612 (w), 1514 (m), 1464 (m), 1416 (w), 1356 (vs), 1270 (m), 1168 (vs), 1111 (m), 991 (vs), 856 (m), 761 (s), 601 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.32 [s, 9 H, $C(CH_3)_3$], 2.95 (m, 1 H, $CHHCH{=}CH_2$), 3.10 (m, 1 H, $CHHCH{=}CH_2$), 3.63 (s, 3 H, CH_3O), 4.26 (dd, *J* = 4.4, 10.7 Hz, 1 H, $CHSO_3$), 5.01 (dd, *J* = 1.4, 10.2 Hz, 1 H, $CHH{=}CH$), 5.11 (dd, *J* = 1.6, 17.0 Hz, 1 H, $CHH{=}CH$), 5.59 [ddt (ABX_2 system), *J* = 6.9, 10.2, 17.0 Hz 1 H, $CH_2CH{=}CH_2$], 7.34 and 7.41 [each d (AB system), *J* = 8.5 Hz, 2 H, Ar*H*] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2 [$C(CH_3)_3$], 34.0 ($CH_2CH{=}CH_2$), 34.5 [$C(CH_3)_3$], 56.7 (CH_3O), 66.1 ($CHSO_3$), 118.4 ($CH_2{=}CH$), 125.5 (Ar*C*H), 128.3 (Ar*C*), 129.0 (Ar*C*H), 132.3 ($CH{=}CH_2$), 151.9 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 282 (1) [M^+], 267 (2), 187 (31), 157 (5), 129 (16), 115 (6), 91 (5), 57 (100).$C_{15}H_{22}O_3S$ (282.40): calcd. C 63.80, H 7.85; found C 63.69, H 8.08.

Methyl (*R*)-1-Phenyl-3-pentene-1-sulfonate (4d): According to GP 2, sulfonate (*R*)-**2g** (a 1:4 mixture of the enantiopure (*Z*) and (*E*), 0.22 g, 0.5 mmol) was refluxed in a 2% TFA/EtOH solution (20 mL) for 24 h. Workup and flash column chromatography (*n*-pentane/diethyl ether, 9:1) gave (*R*)-**4d** as a colorless liquid (0.09 g, 80%); *ee* ≥ 98% (HPLC). IR ($CHCl_3$): $\tilde{\nu}$ = 3065 (w), 3030 (m), 2960 (m), 2920 (m), 2856 (w), 1497 (m), 1455 (m), 1356 (vs), 1218 (m), 1166 (vs), 990 (vs), 832 (m), 760 (vs), 699 (s), 626 (m), 614 (m), 579 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.55 [dd, *J* = 1.4, 6.6 Hz, 3 H, (*E*) $CH_3CH{=}CH$], 1.59 [m, 3 H, (*Z*) $CH_3CH{=}CH$], 2.88 [(*E*)] and 2.95 [each m, 1 H, (*Z*) $CHHCH{=}CHCH_3$], 3.05 [(*E*)] and 3.13 [each m, 1 H, (*Z*) $CHHCH{=}CHCH_3$], 3.62 [(*E*)] and 3.64 [each s, 3 H, (*Z*) SO_3CH_3], 4.21 (dd, *J* = 4.4, 10.7 Hz, 1 H,

C*H*SO_3), 5.16 (m, 1 H, CH_2CH=CHCH$_3$), 5.51 (m, 1 H, CH_2CH=C*H*CH_3), 7.36−7.43 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9 [(*Z*)] and 17.8 [(*E*) *C*H_3CH=CH], 27.5 (*Z*) and 33.0 [(*E*), *C*H_2CH=CH], 56.7 (SO_3CH_3), 66.7 [(*Z*)] and 67.1 [(*E*), *C*HSO$_3$)], 124.0 [(*Z*)] and 124.7 [(*E*), CH_2CH=CHCH$_3$], 127.5 [(*Z*), 128.6, 128.9, 128.9 [(*Z*)], 129.4, 129.4, 129.5 (CH_2CH=*C*HCH$_3$ and Ar*C*H), 131.8 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 240 (0.2) [M$^+$], 186 (7), 145 (100), 129 (18), 117 (23), 105 (7), 91 (24), 77 (6), 65 (5), 55 (6). $C_{12}H_{16}O_3S$ (240.32): calcd. C 59.97, H 6.71; found C 59.91, H 6.74.

Methyl (*R*)-1-(4-*tert*-Butylphenyl)-3-pentene-1-sulfonate (4e): According to GP 2, sulfonate (*R*)-**2f** (a 1:13 mixture of the enantiopure (*Z*) and (*E*), 0.22 g, 0.4 mmol) was refluxed in a 2% TFA/EtOH solution (20 mL) for 24 h. Workup and flash column chromatography (*n*-pentane/diethyl ether, 9:1) gave (*R*)-**4e** as a colorless liquid (0.10 g, 81%); *ee* ≥ 98% (HPLC, Daicel OD). IR ($CHCl_3$): ṽ = 3031 (m), 2962 (vs), 2869 (m), 1612 (w), 1512 (m), 1450 (m), 1416 (w), 1356 (vs), 1295 (m), 1167 (vs), 1111 (m), 990 (vs), 856 (m), 762 (s), 605 (s) cm^{-1}. ^{1}H NMR [400 MHz, $CDCl_3$, (*E*)-isomer]: δ = 1.32 [s, 9 H, C(C*H*$_3$)$_3$], 1.56 (dd, *J* = 1.4, 6.6 Hz, 3 H, C*H*$_3$CH=CH), 2.87 (m, 1 H, C*H*HCH=CHCH$_3$), 3.02 (m, 1 H, CH*H*CH=CHCH$_3$), 3.63 (s, 3 H, SO_3CH_3), 4.18 (dd, *J* = 4.4, 10.7 Hz, 1 H, C*H*SO$_3$), 5.19 (m, 1 H, CH_2CH=CHCH$_3$), 5.53 (m, 1 H, CH_2CH=C*H*CH$_3$), 7.32, 7.40 [each d (AB system), *J* = 8.5 Hz, 2 H, Ar*H*] ppm. ^{13}C NMR [100 MHz, $CDCl_3$, (*E*)-isomer]: δ = 17.8 (*C*H$_3$CH=CH), 31.2 [C(*C*H$_3$)$_3$], 33.0 (*C*H$_2$CH=CH), 34.6 [*C*(CH$_3$)$_3$], 56.6 (SO_3CH_3), 66.7 (*C*HSO$_3$), 125.0 (CH_2CH=CHCH$_3$), 125.5, 129.1 (Ar*C*H), 129.1 (CH_2CH=*C*HCH$_3$), 151.9 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 296 (7) [M$^+$], 281 (3), 227 (1), 201 (22), 186 (2), 171 (2), 143 (27), 129 (5), 117 (3), 91 (3), 79 (4), 57 (100). $C_{16}H_{24}O_3S$ (296.37): calcd. C 64.84, H 8.16; found C 64.60, H 8.49.

(3*R*)-3-(4-*tert*-Butylphenyl)-5,5-dimethyl-1,2-oxathiolane 2,2-Dioxide [(*R*)-5a]: According to GP 3, sulfonate (*R*)-**2a** (0.25 g, 0.5 mmol) was refluxed in a 2% TFA/EtOH solution (20 mL) for 24 h. After removal of solvent under reduced pressure, the crude sulfonic acid **3** was refluxed in a 2% TFA/CH_2Cl_2 solution (20 mL) for 22 h. Workup and flash column chromatography (*n*-pentane/diethyl ether, 4:1) gave (*R*)-**5a** as a colorless solid (0.11 g, 82%); *ee* ≥ 98% (HPLC, Daicel OD); m.p. 186 °C; $[\alpha]_D^{24}$ = −37.9 (*c* = 1.0; $CHCl_3$). IR (KBr): ṽ = 2966 (s), 2875 (m), 1513 (m), 1464 (m), 1340 (vs), 1303 (m), 1276 (m), 1184 (vs), 1148 (s), 1125 (m), 1105 (m), 1022 (w), 977 (w), 931 (m), 886 (m), 839 (vs), 770 (m), 588 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 [s, 9 H, C(C*H*$_3$)$_3$], 1.60, 1.65 (each s, 3 H, CH_3), 2.58 (dd, *J* = 7.1, 13.2 Hz, 1 H, C*H*H), 2.81 (t, *J* = 13.6 Hz, 1 H, CH*H*), 4.58 (dd, *J* = 7.1, 13.7 Hz, 1 H, C*H*Ar), 7.38−7.41 (m, 3 H, Ar*H*), 7.39−7.45 (m, 4 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.0, 29.1 (CH_3), 31.2 [C(C*H*$_3$)$_3$], 41.5 (*C*H$_2$), 61.5 (*C*HAr), 85.7 (*C*OSO$_2$), 128.5 (Ar*C*), 125.8, 128.3 (Ar*C*H), 152.4 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 282 (27) [M$^+$], 267 (41)], 160 (53), 145 (100), 117 (11), 91 (5), 57 (7). $C_{15}H_{22}O_3S$ (282.40): calcd. C 63.80, H 7.85; found C 63.83, H 7.72.

(3*R*)-5,5-Dimethyl-3-phenyl-1,2-oxathiolane 2,2-Dioxide [(*R*)-5b]: According to GP 3, sulfonate (*R*)-**2b** (0.23 g, 0.5 mmol) was refluxed in a 2% TFA/EtOH solution (20 mL) for 24 h. After removal of solvent under reduced pressure, the crude sulfonic acid **3** was refluxed in a 2% TFA/CH_2Cl_2 solution (20 mL) for 20 h. Workup and flash column chromatography (*n*-pentane/diethyl ether, 4:1) gave (*R*)-**5b** as a colorless solid (0.10 g, 90%); *ee* ≥ 98% (HPLC, Daicel OJ); m.p. 119 °C; $[\alpha]_D^{25}$ = −44.22 (*c* = 1.0; $CHCl_3$). IR (KBr): ṽ = 2985 (m), 2935 (m), 1602 (w), 1585 (w), 1498 (m), 1456 (m), 1389 (m), 1379 (m), 1336 (vs), 1304 (m), 1278 (m), 1237 (m), 1219 (m), 1200 (m), 1185 (vs), 1148 (vs), 1106 (s), 1076 (m), 978 (m), 933 (m), 881 (m), 830 (vs), 773 (s), 699 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58, 1.63 (each s, 3 H, CH_3), 2.58 (dd, *J* = 7.1, 13.2 Hz, 1 H, C*H*H), 2.80 (t, *J* = 13.6 Hz, 1 H, CH*H*), 4.58 (dd, *J* = 7.1, 13.7 Hz, 1 H, C*H*Ar), 7.38−7.41 (m, 3 H, Ar*H*), 7.43−7.48 (m, 2 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.0, 29.1 (CH_3), 41.4 (*C*H$_2$), 61.7 (*C*HAr), 86.0 (*C*OSO$_2$), 128.6 (Ar*C*H), 128.6 (Ar*C*), 128.8, 129.3 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 226 (6) [M$^+$], 161 (10), 145 (7), 131 (34), 104 (100), 91 (13). $C_{11}H_{14}O_3S$ (226.29): calcd. C 58.39, H 6.24; found C 58.31, H 6.21.

(3*R*,5*R*)-5-Methyl-3-phenyl-1,2-oxathiolane 2,2-Dioxide [(*R*,*R*)-5c]: According to GP 3, sulfonate (*R*)-**2c** (0.45 g, 1 mmol) was refluxed in a 2% TFA/EtOH solution (40 mL) for 24 h. After removal of solvent under reduced pressure, the crude sulfonic acid **3** was refluxed in a 20% TFA/CH_2Cl_2 solution (20 mL) for 24 h. The crude product, which consisted of a 90:10 mixture of *cis*:*trans* diastereomers, was purified by flash column chromatography (*n*-pentane/diethyl ether, 4:1) and gave (*R*,*R*)-**5c** as a colorless solid (0.15 g, 72%); *ds* ≥ 99% (NMR); *ee* ≥ 98% (GC, Chirasil-Dex); m.p. 134 °C; $[\alpha]_D^{24}$ = −11.29 (*c* = 1.0; $CHCl_3$). IR (KBr): ṽ = 3035 (w), 2995 (w), 2973 (w), 1498 (m), 1459 (m), 1387 (m), 1331 (vs), 1252 (m), 1194 (m), 1165 (vs), 1130 (w), 1113 (w), 1026 (s), 942 (w), 910 (w), 858 (m), 820 (vs), 795 (vs), 770 (m), 698 (s), 598 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (d, *J* = 6.0 Hz, 3 H, C*H*$_3$CHO), 2.56 (dt, *J* = 10.4, 13.2 Hz, 1 H, C*H*H), 2.79 (ddd, *J* = 5.5, 6.9, 13.2 Hz, 1 H, CH*H*), 4.54 (dd, *J* = 6.9, 13.2 Hz, 1 H, C*H*Ar), 4.78 (m, 1 H, CH_3CHO), 7.36−7.45 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8 (*C*H$_3$), 37.6 (*C*H$_2$), 63.3 (*C*HAr), 77.4 (*C*HO), 128.6, 128.8, 129.3 (Ar*C*H), 129.3 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* = 212 (10) [M$^+$], 148 (14), 104 (100), 91 (5), 78 (10). $C_{10}H_{12}O_3S$ (212.27): calcd. C 56.59, H 5.70; found C 56.48, H 5.65.

(3*R*,5*R*)-3-(4-*tert*-Butylphenyl)-5-methyl-1,2-oxathiolane 2,2-Dioxide [(*R*,*R*)-5d]: According to GP 3, sulfonate (*R*)-**2d** (0.52 g, 1 mmol) was refluxed in a 2% TFA/EtOH solution (40 mL) for 24 h. After removal of solvent under reduced pressure, the crude sulfonic acid **3** was refluxed in a 20% TFA/CH_2Cl_2 solution (20 mL) for 24 h. The crude product, which consisted of an 89:11 mixture of *cis*:*trans* diastereomers, was purified by flash column chromatography (*n*-pentane/diethyl ether, 4:1) and gave (*R*,*R*)-**5d** as a colorless solid (0.17 g, 64%); *ds* ≥ 99% (NMR); *ee* ≥ 98% (HPLC, Daicel AD); m.p. 153 °C; $[\alpha]_D^{24}$ = −8.6 (*c* = 1.2; $CHCl_3$). IR (KBr): ṽ = 2963 (s), 2870 (m), 1614 (w), 1514 (m), 1475 (m), 1454 (m), 1387 (m), 1334 (vs), 1251 (m), 1193 (s), 1164 (vs), 1129 (m), 1099 (m), 1031 (s), 940 (m), 916 (m), 865 (m), 825 (vs), 794 (vs), 706 (m), 677 (w), 603 (s), 568 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 [s, 9 H, C(C*H*$_3$)$_3$], 1.59 (d, *J* = 6.3 Hz, 3 H, C*H*$_3$CHO), 2.59 (dt, *J* = 10.4, 13.2 Hz, 1 H, C*H*H), 2.81 (ddd, *J* = 5.5, 6.9, 13.2 Hz, 1 H, CH*H*), 4.54 (dd, *J* = 7.2, 13.2 Hz, 1 H, C*H*Ar), 4.82 (m, 1 H, CH_3CHO), 7.38 and 7.44 [each d (AB system), *J* = 8.5 Hz, 2 H, Ar*H*] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9 (*C*H$_3$), 31.2 [C(*C*H$_3$)$_3$], 34.6 [*C*(CH$_3$)$_3$], 37.7(*C*H$_2$), 63.0 (*C*HAr), 77.2 (*C*HO), 125.9 (Ar*C*H), 126.2 (Ar*C*), 128.3 (Ar*C*H), 152.5 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 268 (22) [M$^+$], 253 (30), 160 (51), 145 (100), 117 (13), 91 (5). $C_{14}H_{20}O_3S$ (268.38): calcd. C 62.66, H 7.51; found C 62.43, H 7.05.

(3*R*,5*R*)-5-Methyl-3-(naphth-2-yl)-1,2-oxathiolane 2,2-Dioxide [(*R*,*R*)-5e]: According to GP 3, sulfonate (*R*)-**2e** (0.50 g, 1 mmol) was refluxed in a 2% TFA/EtOH solution (40 mL) for 24 h. After removal of solvent under reduced pressure, the crude sulfonic acid

3 was refluxed in a 20% TFA/CH_2Cl_2 solution (20 mL) for 24 h. The crude product, which consisted of an 89:11 mixture of *cis*:*trans* diastereomers, was purified by HPLC (*n*-pentane/EtOAc, 1:1) and gave (*R*,*R*)-**5e** as a colorless solid (0.20 g, 77%); *ds* ≥ 99% (NMR); *ee* ≥ 98% (HPLC, Daicel OD); m.p. 166 °C; $[\alpha]_D^{24} = -17.27$ (*c* = 1.0; $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3055 (w), 2989 (w), 2932 (w), 1600 (w), 1508 (w), 1448 (w), 1388 (m), 1371 (m), 1338 (vs), 1252 (m), 1196 (m), 1168 (vs), 1132 (m), 1109 (m), 1034 (s), 862 (m), 814 (vs), 746 (s), 606 (m), 479 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56 (d, *J* = 6.2 Hz, 3 H, CH_3CHO), 2.72 (dt, *J* = 10.4, 12.9 Hz, 1 H, C*H*H), 2.89 (ddd, *J* = 5.8, 7.1, 12.9 Hz, 1 H, CH*H*), 4.72 (dd, *J* = 7.2, 12.9 Hz, 1 H, C*H*Ar), 4.85 (m, 1 H, CH_3CHO), 7.48−7.58 (m, 3 H, Ar*H*), 7.80−7.91 (m, 4 H, Ar*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6 (*C*H_3), 37.9 (*C*H_2), 63.7 (*C*HAr), 77.4 (*C*HO), 125.4, 126.8 (Ar*C*H), 126.9 (Ar*C*), 127.0, 127.7, 128.1, 128.7, 129.0 (Ar*C*H), 133.1, 133.6 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* = 262 (31) [M^+], 154 (100). HRMS (EI, M^+): *m*/*z* calcd. for $C_{14}H_{14}O_3S$: 262.0664; found 262.0663.

(3*R*,5*R*)-3-(4-*tert*-Butylphenyl)-5-ethyl-1,2-oxathiolane 2,2-Dioxide [(*R*,*R*)-5f]: According to GP 3, sulfonate (*R*)-**2f** (0.26 g, 0.5 mmol) was refluxed in a 2% TFA/EtOH solution (20 mL) for 24 h. After removal of solvent under reduced pressure, the crude sulfonic acid **3** was refluxed in a 30% TFA/CH_2Cl_2 solution (10 mL) for 16 h. The crude product, which consisted of a 78:4:4:14 mixture of *cis*:*trans* diastereomers of the corresponding γ-sultone and δ-sultone respectively, was purified by preparative HPLC and gave (*R*,*R*)-**5f** as a colorless solid (0.09 g, 64%); *ds* ≥ 99% (NMR); *ee* ≥ 98% (HPLC, Chiralpak AD); m.p. 111 °C; $[\alpha]_D^{24} = -0.70$ (*c* = 1.0; $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 2964 (s), 2871 (m), 1657 (w), 1515 (m), 1464 (m), 1420 (w), 1384 (s), 1341 (vs), 1169 (vs), 983 (m), 926 (m), 870 (m), 838 (vs), 818 (vs), 621 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.09 (t, *J* = 7.4 Hz, 3 H, CH_2CH_3), 1.32 [s, 9 H, C(CH_3)$_3$], 1.83 (m, 1 H, C*H*HCH$_3$), 1.98 (m, 1 H, CH*H*CH$_3$), 2.62 (dt, *J* = 10.4, 13.2 Hz, 1 H, C*H*HCHO), 2.78 (ddd, *J* = 5.8, 7.1, 13.2 Hz, 1 H, CH*H*CHO), 4.53 (dd, *J* = 7.1, 13.2 Hz, 1 H, C*H*Ar), 4.82 (m, 1 H, CH_2CHO), 7.38, 7.44 [each d (AB system), *J* = 8.5 Hz, 2 H, Ar*H*] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.4 (CH_2CH_3), 28.4 (CH_2CH_3), 31.2 [C(CH_3)$_3$], 34.7 [*C*(CH_3)$_3$], 35.8 (*C*H_2CH), 62.7 (*C*HAr), 81.9 (*C*HO), 125.9 (Ar*C*H), 126.2 (Ar*C*), 128.3 (Ar*C*H), 152.5 (Ar*C*) ppm. MS (EI, 70 eV): *m*/*z* (%) = 282 (24) [M^+], 267 (27), 189 (6), 160 (62), 145 (100), 117 (13), 91 (7), 57 (34). $C_{15}H_{22}O_3S$ (282.40): calcd. C 63.80, H 7.85; found C 63.57, H 8.04.

(3*R*,5*R*)-5-Ethyl-3-phenyl-1,2-oxathiolane 2,2-Dioxide [(*R*,*R*)-5g]: According to GP 3, sulfonate (*R*)-**2g** (0.32 g, 0.7 mmol) was refluxed in a 2% TFA/EtOH solution (30 mL) for 24 h. After removal of solvent under reduced pressure, the crude sulfonic acid **3** was refluxed in a 30% TFA/CH_2Cl_2 solution (10 mL) for 16 h. The crude product, which consisted of a 73:4:7:16 mixture of *cis*:*trans* diastereomers of the corresponding γ-sultone and δ-sultone respectively, was purified by preparative HPLC and gave (*R*,*R*)-**5g** as a colorless solid (0.11 g, 71%); *ds* ≥ 99% (NMR); *ee* ≥ 98% (HPLC, Daicel OD); m.p. 106 °C; $[\alpha]_D^{23} = -3.41$ (*c* = 0.8; $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3068 (w), 3040 (w), 2978 (m), 2943 (m), 2884 (w), 1500 (m), 1454 (m), 1383 (m), 1337 (vs), 1244 (m), 1160 (vs), 1053 (m), 963 (m), 926 (m), 860 (m), 822 (vs), 778 (m), 759 (m), 702 (m), 602 (m), 555 (m), 532 (m), 491 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.09 (t, *J* = 7.4 Hz, 3 H, CH_2CH_3), 1.84 (m, 1 H, C*H*HCH$_3$), 1.97 (m, 1 H, CH*H*CH$_3$), 2.62 (dt, *J* = 10.4, 13.1 Hz, 1 H, C*H*HCHO), 2.80 (ddd, *J* = 5.4, 6.9, 13.1 Hz, 1 H, CH*H*CHO), 4.54 (dd, *J* = 6.9, 13.1 Hz, 1 H, C*H*Ar), 4.63 (m, 1 H, CH_2CHO), 7.39−7.48 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.5 (CH_2CH_3), 28.5 (CH_2CH_3), 35.8 (*C*H_2), 63.0 (*C*HAr), 82.0 (*C*HO), 128.8, 129.1, 129.5 (Ar*C*H) ppm. MS (EI, 70 eV): *m*/*z* (%) = 226 (6) [M^+], 161 (13), 145 (3), 133 (3), 117 (7), 104 (100), 91 (5), 77 (8). $C_{11}H_{14}O_3S$ (226.29): calcd. C 58.39, H 6.24; found C 58.22, H 6.63.

X-ray Crystallographic Study of 5c: The compound ($C_{10}H_{12}O_3S$; M_r = 212.27) crystallizes in orthorhombic space group $P2_12_12_1$ (No.19) with cell dimensions *a* = 5.9209(7), *b* = 11.219(3), and *c* = 15.264(2) Å. A cell volume of *V* = 1013.9(3) Å^3 and *Z* = 4 results in a calculated density of $d_{calcd.}$ = 1.391 g·cm^{-3}. 4090 reflections have been collected at *T* = 150 K on an ENRAF-NONIUS CAD4 diffractometer employing graphite-monochromated Cu-K_α-radiation (λ = 1.54179 Å) in the ω/2Θ mode. Data collection covered the range $-7 \le h \le 7$, $-13 \le k \le 13$, and $-14 \le l \le 14$ up to $\Theta_{max.}$ = 72.8°. Lorentz and polarization corrections have been applied to the diffraction data but no absorption correction (μ = 2.678 mm^{-1}) The structure has been solved by direct methods as implemented in the Xtal3.7 suite of crystallographic routines[17] where GENSIN has been used to generate the structure-invariant relationships and GENTAN for the general tangent phasing procedure. 1848 observed reflections [$I > 2\sigma(I)$] have been included in the final full-matrix least-squares refinement on *F* involving 127 parameters and converging at $R(R_w) = 0.067(0.077, w = \sigma^2)$, a final shift/error < 0.0003, *S* = 3.544, and a residual electron density of −1.37/0.95 e·Å^{-3}. $X_{abs.} = -0.05(5)$[18] for the structure shown in Figure 2. Most of the hydrogen positions have been calculated. Their isotropic displacement parameters have been fixed at 1.5 times the value of the relevant heavy atom. All hydrogen parameters have been kept fixed in the refinement.

CCDC-205259 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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