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Highly Diastereoselective Methylene Transfer from Diazomethane to the Carbonyl of β-Keto Sulfoxides. A General Approach to Synthetically Versatile Fluorine-Containing Chiral Building Blocks.

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Abstract: This paper describes the reactions of diazomethane with α -alkyl and α -phenyl-substituted (RS)- β -keto sulfoxides bearing difluoro-, trifluoro- and difluorochloromethyl groups on the terminal site, to afford the corresponding diastereo- and enantiomerically pure epoxides. A plausible mechanistic rationale for the origin of the stereochemical preferences in these reactions has been provided. Synthetic versatility of the resultant epoxides has been demonstrated by a series of key transformations of the epoxide ring and the sulfinyl group including ring-opening, reductive desulfurization and syn-elimination reactions. © 1998 Elsevier Science Ltd, All rights reserved.

INTRODUCTION

With the development of catalytic asymmetric methodology for epoxidation of olefins, enantiomerically pure epoxides have gained an eminent position in synthetic organic chemistry as versatile chiral building blocks and key intermediates in natural product synthesis.¹ However, despite the tremendous achievements in this area, enantioselective preparation of fluoro-substituted epoxides remains a challenging synthetic endeavor due to the unique electronic and stereochemical features of fluorine substituents.^{2,3} In particular, it has been shown that an enhanced electrophilicity of fluorinated olefins would generally plague an application of the methods developed for epoxidation of hydrocarbon olefins to their fluorinated analogues.⁴ Nevertheless, the lure of a synthetic versatility of fluorinated epoxides, as chiral building blocks for preparing fluorine-containing compounds of biomedicinal importance,⁵ has stimulated much activity.² For example, the development of biocatalytic⁶ and stoicheiometric⁷ asymmetric approaches to both enantiomers of the trifluoromethyloxirane has provided ready availability of numerous synthetically and biologically valuable trifluoromethyl-containing compounds *via* conventional elaboration of this simple molecule.⁸



As a part of our own goal of developing practical synthetic methods for preparing selectively fluorinated and enantiomerically pure biologically relevant compounds^{9,10} we have examined reactions between enantiopure β keto-γ-fluoro-substituted sulfoxides and diazomethane as a general approach to asymmetric synthesis of the corresponding fluorinated epoxides possessing stereogenic tertiary carbon. The addition of methylene to the carbonyl π -bond of aldehydes and ketones with diazomethane to yield homologated carbonyl compounds and oxiranes is well established.¹¹ However, asymmetric version of this reaction using a chiral auxiliary on the starting carbonyl compound, to the best of our knowledge, has not been reported so far. We have shown¹² that (R_S) - β -keto- γ -fluoroalkyl sulfoxides 1 (Figure 1) readily react with diazomethane under mild conditions (rt) to afford a mixture of the corresponding oxiranes, as major products, in generally good chemical yields. Diastereoselectivity of the oxirane ring formation was found to be controlled by the stereochemistry of the sulfoxide moiety (1,3-asymmetric induction) giving rise to the (S) configured epoxides, with moderate-to-high de, starting from the (R_S) -sulfoxide. Previously, we have studied the reactions of diazomethane with three types of β -keto- γ -fluoroalkyl sulfoxides 1 to afford the corresponding chirons 2-4, and demonstrated their synthetic versatility by preparing a series of fluorinated and enantiomerically pure tertiary alcohols, amino alcohols, hydroxy and amino carboxylic acids 5a-c.¹² Despite the fact that the diastereofacial selectivity in the epoxide formation was common for the all three types of β -keto- γ -fluoroalkyl sulfoxides 1, the reactions featured quite different patterns of reactivity and diastereomeric preferences at the stereogenic center alpha to the sulfoxide moiety. Thus, while the reaction of diazomethane with α -phenyl-substituted (R_S)- β -keto- γ -fluoropropyl sulfoxide 1 (R = Ph; $R_F = CH_2F$) afforded predominantly (1'R,2S,R_S)-configured diastereomer 4,^{12d} the addition of diazomethane to α -alkyl-substituted sulfoxides 1 (R = Alk; R_F = CH₂F) gave a mixture of





 $(1^{2}R_{2}S_{2}R_{3})$ - and $(1^{2}S_{2}S_{3}R_{3})$ -diastereomers **3**, in a ratio dependent on the conditions used.^{12e} Moreover, we have found that an increase of the fluorine substitution for hydrogen on the starting sulfoxide (sulfoxide **1** R_F = CH₂F, CHF₂, CF₃) facilitated the addition reactions (increase in the reaction rates) giving rise to epoxides **2** with a substantially enhanced diastereoselectivity.^{12a,c} Following a systematic study we set about a series of additional experiments to account for the origin of stereogenesis in these reactions and to extend a family of the synthetically valuable chirons, available by this methodology.

In this paper, we a) describe the reactions of diazomethane with α -alkyl and α -phenyl-substituted (R_S)- β keto sulfoxides bearing difluoro-, trifluoro- and difluorochloromethyl groups (Scheme 1); b) provide a plausible rationale for the origin of the stereochemical preferences in these reactions; and c) demonstrate the synthetic versatility of the resultant epoxides by a series of key transformations of the epoxide ring and the sulfinyl group.

RESULTS AND DISCUSSION

Synthesis of (R_S) - β -keto/hydrate- γ -fluoroalkyl sulfoxides 8/9a-h (Scheme 1). The starting (R_S) - β -keto/hydrate- γ -fluoroalkyl sulfoxides 8/9a-h were prepared by the reaction of the α -lithio derivatives of (R)-4-methylphenyl alkyl sulfoxides 6 with the corresponding fluorinated ethyl acetate 7, according to our standard method (Scheme 1).¹³ Monofluoro-substituted derivatives $(3S/R,R_S)$ -8a,f were isolated in keto forms, ^{12d,13} while the difluoro-, chlorodifluoro- and trifluoromethyl compounds were obtained as keto/hydrate mixtures $(3S/R,R_S)$ -8/9b-e,g,h. In all cases, regardless keto/hydrate composition, sulfoxides 8/9a-h were obtained as mixtures of the corresponding $(3S/R,R_S)$ -diastereomers. Isolation of $(3S/R,R_S)$ -8/9a-h by flash chromatography (FC) did not allow separation of the diastereomers, but gave mixtures partially enriched in the $(3S,R_S)$ -configured compounds.

Reactions of sulfoxides 8/9a-h with diazomethane (Scheme 1). The reactions between the diastereometric mixtures of sulfoxides $(3S/R,R_S)$ -8/9a-h and diazomethane were performed under standard

conditions using four different solvents. The reactions of polyfluoro derivatives $(3S/R,R_S)$ -8/9b-e,g,h were found to proceed with notably higher rates as compared with that of monofluoro analogs $(3S/R,R_S)$ -8a,f. Chemical and stereochemical outcomes of the reactions were studied by NMR analysis on crude reaction mixtures. Isolation of the individual reaction products was accomplished by FC. The stereochemistry of the products obtained in the reactions of monofluoro derivatives 8a,f was previously established by X-ray analyses.^{12d,e} Since we have shown that the fluorine substitution for hydrogen does not influence the sense of the diastereochemical preferences in the reactions under study, and on the basis of chemical correlations between diastereomeric and/or enantiomeric products, and similarity in the patterns of NMR spectra of the homochiral compounds, the absolute configurations of epoxides 11-13 were assign as depicted on Scheme 1. In all cases apart from the target epoxides, the corresponding enol ethers 14, presumably resulting from the reactions of enols 10 with diazomethane, were isolated in yields ranging from 4 to *ca* 20%, depending on the substrate and reaction conditions used. The results of the reactions are summarized in Table 1.

As reported previously,^{12e} the stereochemical outcome of the reaction of diazomethane with monofluoro derivative of α -methyl β -keto sulfoxide (3S/R,R_S)-8a was shown to be dependent on the conditions used. Thus, $(1'S, 2S, R_S)$ -configured epoxide 11a was obtained as a major product in the reaction conducted in methanol (Table 1, entry 1), while the reaction in diethyl ether favored a formation of $(1^{2}R_{2}S_{2}R_{3})$ -12a diastereomer (entry 2). The stereoselectivity of the oxirane ring formation was also influenced by the solvent used ranging from 50% to 72% de, entries 1.2, respectively. The same pattern of stereochemical preferences was observed also for the reactions of diazomethane with the corresponding monofluoro derivative of α -n-Pr- β -keto sulfoxide, albeit with lower level of stereoselectivity at both stereogenic centers [in methanol: (1'S/1'R) ratio 60/40, (2S/2R) - 80/20; in diethyl ether: (1'S/1'R) ratio 40/60, (2S/2R) - 78/22].^{12e} In contrast to these data, the reactions of diffuoro derivative $(3S/R,R_S)$ -8/9b afforded $(1'S,2S,R_S)$ -configured epoxide 11b regardless the solvent used (entries 3, 4). The stereoselectivity of the oxirane formation was only slightly influenced by the reaction conditions varying from 60 to 70% de. Introduction of one more fluorine atom on the starting β -keto sulfoxide, the reactions of trifluoromethyl derivatives $(3S/R,R_S)$ -8/9c,d, allowed preparation of the targeted (2S)-configured oxiranes with higher de. Thus, the reaction of diazomethane with trifluoromethyl-containing α -Me- β -keto/hydrate sulfoxide $(3S/R,R_S)$ -8c, performed in methanol, afforded a mixture of (2S)-configured epoxides with 82% de (entry 5). Any appreciable improvement of the diastereoselectivity was not observed by varying reaction conditions such as solvent and temperature (entries 6-9). Substitution of the α -methyl group by a bulkier *n*-Pr one, the reaction of $(3S/R,R_S)$ -8/9d, was found to decrease the stereochemical outcome giving rise to the epoxides with 62-64% de at the α -stereogenic center and only 56-58% de at the oxirane ring (entries 11, 12). In contrast, an increase in a steric bulk on the terminal site of the starting sulfoxide, the reaction of chlorodifluoro derivative $(3S/R, R_S)$ -8/9e, substantially enhanced the stereoselectivity of the process. The reaction of $(3S/R,R_S)$ -8/9e, conducted in a methanol solution (entry 13), gave rise to the corresponding (2S)-configured oxiranes in 90% de and with 74% de at the α -stereogenic center. Finally we investigated the series of α -phenyl substituted derivatives (3S/R,Rs)-**8/9f-h** reactions with diazomethane. Previously we reported that the reaction of α -phenyl- γ -monofluoro- β -keto sulfoxide $(3S/R,R_S)$ -8f gave rise to $(1^2R,2S,R_S)$ -12f diastereomer, as a major product, regardless of the diastereomeric composition of the starting ketone and conditions used (entries 14, 15).^{12d} We have found that the reaction of diffuoro derivative $(3S/R,R_S)$ -8/9g proceeded in more highly diastereoselective manner, in both methanol and diethyl ether solutions, giving rise to oxiranes $(1^{\circ}S_{2}S_{3}R_{5})$ -11g and $(1^{\circ}R_{2}S_{3}R_{5})$ -12g with preferable formation of the latter (70-80% de) (entries 16, 17). The addition of diazomethane to trifluoro-

Entry		Sulfoxides 8/9a-h		Solvent ^a	Yield, ^b	Epoxides ^c				
		R	R _F		(%)	11a-h (1' <i>S</i> ,2 <i>S</i>)	12a-h /(1' <i>R</i> ,2 <i>S</i>)/	13a-h (1' <i>S</i> ,2 <i>R</i>)	ratio (1'S/1'R)	ratio (2 <i>S</i> /2 <i>R</i>)
1	(a)	Me	CH ₂ F ^d	А	87	46	29	23	69/31	75/25
2	(a)	Mie	CH ₂ F ^d	С	75	23	64	10	33/67	86/14
3	(b)	n-Pr	CHF ₂	Α	83	60	20	20	80/20	80/20
4	(b)	n-Pr	CHF ₂	С	80	65	20	15	80/20	85/15
5	(c)	Me	CF ₃	Α	83	68	23	9	77/23	91/9
6	(c)	Me	CF ₃	Ae	87	70	20	10	80/20	90/10
7	(c)	Me	CF ₃	Aſ	80	72	13	15	87/13	85/15
8	(c)	Me	CF ₃	в	88	62	25	13	75/25	87/13
9	(c)	Me	CF ₃	С	75	60	23	17	77/23	73/17
10	(c)	Me	CF ₃	D	78	56	25	19	75/25	81/19
11	(d)	<i>n</i> -Pr	CF ₃	Α	87	60	18	22	82/18	78/22
12	(d)	<i>n</i> -Pr	CF ₃	С	78	60	19	21	81/19	79/21
13	(e)	Allyl	CClF ₂	Α	86	82	13	5	87/13	95/5
14	(f)	Ph	CH ₂ F ^g	А	91	17	78	5	22/78	95/5
15	(f)	Ph	CH ₂ F ^g	С	94	11	79	10	21/79	90/5
16	(g)	Ph	CHF ₂	А	80	10	90	-	10/90	>98/2
17	(g)	Ph	CHF ₂	С	82	15	85	-	15/85	>98/2
18	(h)	Ph	CF ₃	А	88	25	75	-	25/75	>98/2
1 9	(h)	Ph	CF ₃	С	79	33	67	-	33/67	>98/2

Table 1. Reactions of $(3S/R,R_S)$ - β -Keto/hydrate Sulfoxides 8/9a-h with Diazomethane

^{*a*} All reactions were performed by addition of an ethereal solution of the diazomethane to a solution of the corresponding substrate; A = methanol, B = ethanol, C = ethyl ether, D = benzene. ^{*b*} Total yield of all reaction products. ^{*c*} Ratio of epoxides **11-13** determined by NMR on crude reaction mixtures. Apart from the epoxides the corresponding enol ethers **14** were isolated; see experimental part. ^{*d*} See ref. 12e. ^{*e*} The reaction was performed at -70 °C. ^{*f*} Reaction was performed in CH₃OH/H₂O 1:1 (vol) mixture. ^{*g*} See ref. 12d.

substituted sulfoxide $(3S/R,R_S)$ -8/9h also featured virtually complete stereoselectivity of the oxirane ring formation affording only (2S)-configured epoxides 11h and 12h (entries 18, 19). However, the stereoselectivity at the α -stereogenic center was substantially lowed in both methanol and diethyl ether.

On the basis of the previous, $^{12c-e}$ and present results, we attempted to summarize some general features of the stereochemical outcome of the reactions. The most obvious conclusion is that the stereochemistry of the epoxide ring stereogenic center is overwhelmingly controlled by the chirality of the sulfoxide moiety affording the (2S)-configured epoxides as long as the (R_S)-sulfoxide used. Importantly, the sense of stereochemical preferences at C2 of the epoxide ring is not influenced by the pattern of substitution on the starting sulfoxide that renders the present method generally useful for asymmetric synthesis of 2-alkyl-2-fluoroalkyl epoxides, since the stereogenic center alpha to the sulfoxide group has no particular importance from a synthetic point of view, as it might be cleared upon elaboration of the resultant epoxides to the target sulfur-free compounds. The fluorine



substitution for hydrogen increases the reaction rates (an electronic effect) and generally enhances a magnitude of the stereoselectivity (a steric effect) of the epoxide ring formation. Since the carbon stereogenic center on starting β -keto sulfoxides is highly configurationally unstable, prone to racemization through the corresponding enols 10 (Scheme 1),^{12d,e} it would be difficult to rationalize the sense of the stereochemical preferences at this stereogenic center. Thus, the observed $(1^{\prime}S/1^{\prime}R)$ ratio in the resultant epoxides might be a function of a) the starting diastereomeric composition, b) the epimerization rates of the diastereomers and c) the rates of each diastereomer reaction with diazomethane. Obviously, the combined effect of these factors should heavily depend on the nature of substitution on the starting sulfoxide and reaction conditions used. Unfortunately, due to the conformational instability mentioned above, polyfluorinated sulfoxides 8/9 cannot be isolated in diastereomerically pure form. However, considering transition states available for the reactions under study (Figure 2), one can draw some speculative conclusions. For $(3R,R_S)$ -8 diastereomers the most thermodynamically favorable conformation, as supported by molecular mechanics calculations performed for the monofluoro derivatives 8a, f, ^{12d} would be conformation A in which steric interactions between the substituents are minimized. In contrast, for the $(3S,R_S)$ configured diastereomers there is no single thermodynamically favorable conformer as one of the substituents, CO-R_F or R, must occupy a sterically unfavorable position. That is, structures B and C should be considered. Accordingly, the reactions of $(3R,R_S)$ -8 diastereomers with diazomethane could proceed via a single transition state **D**, to afford $(1^{\circ}R, 2S, R_{S})$ -configured oxiranes 12, while for the reactions of $(3S, R_{S})$ -8 diastereomers two transition states E and F should be organized to give oxiranes $(1'S, 2R, R_S)$ -13 and $(1'S, 2S, R_S)$ -11, respectively. It follows, that the reactions of $(3R,R_S)$ -8 diastereomers with diazomethane might afford only one reaction product, oxirane $(1^{2}R, 2S, R_{S})$ -12,^{12d} while the stereochemical outcome of the reactions of $(3S, R_{S})$ -8 diastereomers would reflect a balance between a relative thermodynamic stability of conformers B, C and the corresponding transition states E and F, as a function of the nature of the substitution on the starting β -keto sulfoxide.

Elaboration of the epoxides. Previously we described general routes for elaboration of α unsubstituted polyfluoroalkyl-containing synthons (2*S*,*R*_S)-2 and α -alkyl, α -phenyl-substituted monofluoro synthons (2*S*,*R*_S)-3 and (1'*R*,2*S*,*R*_S)-4 (Figure 1), respectively.¹² As one can assume, the same chemistry might be also applicable to transformations of the synthons available by this study. Therefore, we have studied only key reactions of the oxiranes 11-13, including epoxide ring-opening reactions, reductive desulfurization, and *syn*-elimination reactions, to afford synthetically and biologically interesting compounds. Since the α stereogenic center in epoxides (1'*R*,2*S*,*R*_S)-12 and (1'*S*,2*S*,*R*_S)-11 might be cleared upon their transformation to the target sulfur-free compounds, these epoxides could be elaborated simultaneously in a mixture available directly by the reaction of the corresponding β -keto sulfoxide with diazomethane. However, to obtain stereochemically individual products allowing proper characterization we studied the reactions of the diastereomerically pure compounds.

Epoxide ring-opening reactions. Ring-openings with water (Scheme 2). Recently we have shown that due to a relatively high CH acidity of the proton alpha to the sulfoxide group, base-catalyzed ring-

Scheme 2



Key: (i) HClO₄, H₂O/THF, rt, 5 d; (ii) BnNH₂, THF, rt, 1 d; (iii) Bn₂NH, THF, rt, 3 d



Key: (*i*) Nal, (CF₃CO)₂O, acetone, -20 °C; (*i i*) HClO₄, H₂O/THF, rt, 5 d; (*i i i*) PhCO₂H, DCC, DMAP, CH₂Cl₂, rt; (*i v*)Ni-*Raney*/H₂, EtOH, reflux; (*v*) NaOH, MeOH/H₂O, rt, 5 min.

opening reactions of the synthons 2-4 could be accompanied by the corresponding rearrangement to give openchained allylic alcohols.^{12c-e} Therefore, we developed the acid-catalyzed protocol using HClO₄ in aqueous THF.^{12c-e} Under these reaction conditions trifluoromethyl-containing epoxides (1'S,2S,R_S)-11c and (1'R,2S,R_S)-12e were cleanly transformed to diols (2S,3S,R_S)-15 and (2S,3R,R_S)-16, respectively (Scheme 2). The reactions proceeded slowly (5 d, rt), however the target products were isolated in high yields (80-89%).

Ring-openings with amines (Scheme 2). Due to a particular biomedicinal relevance of 1,2-amino alcohols we used a more wide range of the substrates for preparing the corresponding amino derivatives. All three available diastereomeric trifluoromethyl-containing oxiranes $(1^{\circ}S, 2S, R_S)$ -11c, $(1^{\circ}R, 2S, R_S)$ -12c and $(1^{\circ}S, 2R, R_S)$ -13c, as well as trifluoromethyl 1'-phenyl-containing epoxide $(1^{\circ}S, 2S, R_S)$ -11h, were treated with benzylamine to afford amino alcohols $(2S, 3S, R_S)$ -17, $(2S, 3R, R_S)$ -20, $(2R, 3S, R_S)$ -19 and $(2S, 3S, R_S)$ -21, respectively, in excellent isolated yields. The reactions proceeded with a relatively high rates, as compared with

the acid-catalyzed openings by water, and without any noticeable differences in the behavior of the diastereomeric starting oxiranes. Application of dibenzyl amine for opening the epoxide ring was demonstrated by the transformation of trifluoromethyl 1'-*n*-propyl derivative $(1'S,2S,R_S)$ -11d to amino alcohol $(2S,3S,R_S)$ -18. The reaction occurred slowly to give the *N*,*N*-dibenzyl derivative in a moderate chemical yield. The ring-opening reactions of difluoromethyl-containing oxiranes $(1'S,2S,R_S)$ -11b and $(1'S,2S,R_S)$ -11g showed a similar reactivity giving rise cleanly to the target amino alcohols $(2S,3S,R_S)$ -22 and $(2S,3S,R_S)$ -23, respectively.

All the ring-opening reactions studied featured complete regioselectivity and did not influence the stereochemical integrity of the compounds involved.

Reductive desulfurization (Scheme 3). For reductive desulfurization¹⁴ we followed our standard tworeductive-steps protocol including first transformation of a sulfinyl to a thio group via Oae procedure, ¹⁵ followed by Raney nickel-promoted desulfenylation reaction to afford sulfur-free derivatives. The sulfinyl-to-sulfenyl reduction was studied on three types of substrates, including epoxides and their ring-opened products, the corresponding diols and amino alcohols. Treatment of diastereomeric trifluoromethyl-containing epoxides $(1^{\circ}S, 2S, R_{S})$ -11c and $(1^{\circ}R, 2S, R_{S})$ -12c in an acetone solution with NaI and trifluoroacetic anhydride for 20 min at -20 °C gave sulfenyl derivatives (1'S, 2S)-24 and (1'R, 2S)-25, respectively, in excellent isolated yield; no ring-opened products were detected in the reaction mixtures. Under the same reaction conditions, diol $(2S,3S,R_{S})$ -15 was cleanly reduced to afford product (2S,3S)-26. Its (2S,3R)-diastereomer 27 was prepared by the ring opening of sulfenyl epoxide (1'R,2S)-25 with water to confirm the diastereomeric relations between compounds (2S,3S)-26 and (2S,3R)-27 and their precursors. The reduction of the amino alcohols was demonstrated by preparing also diastereomeric sulfenyl derivatives (2S,3S)-28 and (2S,3R)-29 starting from $(2S,3S,R_S)$ -17 and $(2S,3R,R_S)$ -20, respectively. In this case the reduction was accompanied by trifluoroacetylation of the amino group to afford the corresponding amides. The two-reductive-steps procedure was conducted to show preparation of the enantiomerically pure trifluoromethyl-containing diols and amino alcohols. Sulfoxide diol $(2S,3S,R_S)$ -15 was first benzoylated to afford derivative $(2S,3S,R_S)$ -30 which was reduced under the standard conditions to give sulfenyl (2S,3S)-31. The reductive desulfenylation¹⁶ of (2S,3S)-31 was performed in an ethanol solution in the presence of Raney-Ni under hydrogen atmosphere at 80 °C to afford sulfur-free diol derivative (S)-32 in high isolated yield. The same protocol was applied for preparing sulfur-free amino alcohol (R)-34 through the corresponding sulferyl derivative (2R,3S)-33. Compound (R)-34 was further detrifluoroacetylated under a base-catalyzed conditions to afford (N-benzyl)amino alcohol (R)-35.

syn-Elimination reactions (Scheme 4). Application of the thermal syn-elimination reactions of the ptolyl sulfoxide group¹⁷ to the synthons under study, to afford sulfur-free vinyl compounds, were demonstrated using homochiral trifluoromethyl-containing diol and amino alcohol derivatives. Thus, heating of p-xylene solutions of sulfoxides $(2S,3S,R_S)$ -30 and $(2S,3S,R_S)$ -17 at 150° C for 10 min resulted in elimination of the sulfinyl group to give the corresponding vinyl derivatives (S)-36 and (S)-37, respectively, as major reaction products. Despite the drastic conditions, the reactions occurred quite smoothly to afford compounds (S)-36 and (S)-37 in high isolated yields (78-82%).



Key: (i) p-Xylene, 150 °C, 10 min.

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EXPERIMENTAL SECTION

General. For standard laboratory praxis and techniques see the related papers, ref. 12. Unless otherwise stated, yields refer to isolated yields of products of greater than 95% purity as estimated by ¹H and ¹⁹F NMR spectrometry. All new compounds were characterized by ¹H NMR, ¹⁹F NMR, and elemental analyses. Unless otherwise stated, R_f refers to a hexane/ethyl acetate 4:1 mixture. The product ratios were determined by ¹H and ¹⁹F NMR analyses on crude reaction mixtures. The syntheses of 1,1,1-trifluoro-3-[(4-methylphenyl)sulfinyl]butan-2-one/hydrate **8/9c**,^{13b} 1,1,1-trifluoro-3-[(4-methylphenyl)sulfinyl]hexan-2-one/hydrate **8/9d**,^{13b} 1-chloro-1,1-difluoro-3-[(4-methylphenyl)sulfinyl]hex-5-en-2-one/hydrate **8/9e**,^{13d} and 1,1,1-trifluoro-3-[(4-methylphenyl)sulfinyl]-3-phenylpropan-2-one/hydrate **8/9h**^{13c} were accomplished according to the literature methods.

Reactions of Alkyl p-Tolyl Sulfoxides (RS)-6 with Esters 7. Synthesis of ketones/gemhydrates 8/9. General procedure. To a solution of LDA (10.4 mmol) in THF (10 mL) at -70 °C a solution of sulfoxide (R_S)-6 (10.0 mmol) in THF (10 mL) was added dropwise. Temperature was allowed to reach 0 °C, then the yellow solution was cooled to -60 °C and neat fluorinated ethyl ester 7 (10.0 mmol) was added dropwise by syringe. After 10 min, the reaction was quenched by adding a saturated solution of ammonium chloride, organic layers were extracted by ethyl acetate, dried over anhydrous sodium sulfate and evaporated to dryness.

 $(3R/S,R_S)$ -1,1-difluoro-3-[(4-methylphenyl)sulfinyl]hexan-2-one/hydrate (8b/9b): Starting from (R_S) -1-[(4-methylphenyl)sulfinyl]butane (6), after FC (hexane/ethyl acetate 6:4) product 8b/9b was isolated as a 1:1 mixture of (3R)- and (3S)- diastereoisomers in the keto form 8b and as a 2:1 diastereomeric mixture in the hydrate one 9b; hydrate 9b and ketone 8b were in 1:4 ratio, respectively; 92% yield; $R_f = 0.35$; ketone 8b: ¹H NMR (CDCl₃) δ 0.89-2.40 (7H, m), 2.43 and 2.44 (3H, br.s), 4.17 and 4.43 (1H, m), 5.34 and 5.55 (1H, t, J = 52.5 Hz), 7.2-7.6 (4H, m); ¹⁹F NMR (CDCl₃) δ 0.8-2.4 (7H, m), 2.43 (3H, br.s), 2.80 and 2.97 (1H, m), 5.71 and 5.82 (1H, t, J = 54.0 Hz), 7.2-7.6 (4H, m); ¹⁹F NMR (CDCl₃) δ 0.8-2.4 (7H, m), 2.43 (3H, br.s), 2.80 and 2.97 (1H, m), 5.71 and 5.82 (1H, t, J = 54.0 Hz), 7.2-7.6 (4H, m); ¹⁹F NMR (CDCl₃) δ -141.29 and -132.00 (dd, J = 283.5 and 54.0 Hz), -139.90 and -131.80 (J = 283.5 and 54.0 Hz).

 $(3R/S, R_S)$ -1,1,1-trifluoro-3-[(4-methylphenyl)sulfinyl]butan-2-one/hydrate (8/9c). Starting from (R_S) -[(4-methylphenyl)sulfinyl]ethane (6) and ethyl trifluoroacetate 5 after FC (hexane/ethyl acetate 1:1) the product 8c/9c was isolated as a 4.5:1 mixture of (3R)- and (3S)-diastereoisomers in keto form 8c and as a 18:1 diastereomeric mixture in the hydrate one 9c; hydrate 9c and the ketone 8c were in 10.5:1 ratio, respectively; 95% yield; $R_f = 0.35$; ketone 8c: ¹H NMR (CDCl₃) δ 1.35 and 1.53 (3H, d, J = 7.1 Hz), 2.45 (3H, br.s), 4.07 and 4.40 (1H, q, J = 7.1 Hz), 7.37, 7.50 and 7.71 (4H, m); ¹⁹F NMR (CDCl₃) δ -79.34 and -79.28 (br.s); hydrate 9c: ¹H NMR (CDCl₃) δ 1.09 (3H, d, J = 7.1 Hz), 2.45 (3H, br.s), 3.03 and 3.15 (1H, q, J = 7.1 Hz), 4.61, 5.20 and 5.86 (2H, br.s), 7.37, 7.44 and 7.45 (4H, m); ¹⁹F NMR (CDCl₃) δ -84.04 and -83.54 (br.s).

 $(3R/S,R_S)$ -1,1-difluoro-3-[(4-methylphenyl)sulfinyl]-3-phenylpropan-2-one/hydrate (8g/9g). Starting from (R_S) -[(4-methylphenyl)sulfinyl]phenylmethane (6), after FC (hexane/ethyl acetate 8:2) product 8g/9g was isolated as a 4:1 mixture of (3R)- and (3S)- diastereoisomers in the keto form 8g and as a 10:1 diastereomeric mixture in the hydrate one 9g; hydrate 9g and ketone 8g were in 1:2.4 ratio, respectively; 90% yield; $R_f = 0.35$; ketone 8g: ¹H NMR (CDCl₃) δ 2.42 and 2.43 (3H, br.s), 5.16 and 5.18 (1H, brd, J =2.0 Hz), 5.55 and 5.90 (1H, t, J = 53.0 Hz), 7.0-7.6 (9H, m); ¹⁹F NMR (CDCl₃) δ -130.39 and -127.17 (br.dd, J = 315.0 and 53.0Hz), -130.04 and -127.81 (br.dd, J = 315.0 and 53.0 Hz); hydrate 9g (selected signals): ¹H NMR (CDCl₃) δ 2.42 (3H, br.s), 4.00 and 4.03 (1H, br.d, J = 2.0 Hz), 4.85 (2H, br.m), 5.21 (1H, t, J = 55.0 Hz), and 7.0-7.6 (9H, m); ¹⁹F NMR (CDCl₃) δ -145.10 and -132.68 (br.dd, J = 284.0 and 54.0 Hz), -144.24 and -133.75 (br.dd, J = 284.0 and 54.0 Hz).

Reactions of Keto/Hydrate Sulfoxides 8/9 with Diazomethane. Synthesis of oxiranes 11-13. General procedure. An ethereal solution of diazomethane (CH_2N_2 , *ca* 0.5 M) was added portionwise to a stirred solution of the starting ketone/hydrate **8/9** (10.0 mmol) in the corresponding solvent (80 mL) at 0 °C up to persistence of the diazomethane yellow color. Nitrogen was bubbled to remove the excess of diazomethane and the solvent was then evaporated *in vacuo* to give a mixture of the oxiranes **11-13** and the corresponding enol-ethers **14**. Reaction conditions, yields, and the products ratios are listed in Table 1.

(1'S,2S, R_S)-2-difluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]butyloxirane (11b): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 3, Table 1; yield 48.1%; R_f 0.48; ¹H NMR (CDCl₃) δ 0.83 (3H, t, J = 7.2 Hz), 1.24, 1.42, 1.65 and 1.93 (4H, m), 2.43 (3H, br.s), 2.84 (2H, m), 2.95 (1H, d, J = 4.5 Hz), 5.55 (1H, t, J = 54.0 Hz), 7.35 and 7.55 (4H, m); 19F NMR (CDCl₃) δ -125.57 and -124.70 (br.dd, J = 290.0 and 54.0 Hz).

 $(1'R, 2S, R_S)$ -2-difluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]butyloxirane (12b): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 3, Table 1; yield 16.6%; $R_f 0.46$; ¹H NMR (CDCl₃) $\delta 0.85$ (3H, t, J = 7.0 Hz), 1.0-2.0 (4H, m), 2.44 (3H, br.s), 3.02 (1H, d, J = 4.5 Hz), 3.11 (1H, dd, J = 8.5 and 4.5 Hz), 3.27 (1H, dt, J = 4.5 and 1.8 Hz) 5.68 (1H, t, J = 55.0 Hz), 7.36 and 7.57 (4H, m); ¹⁹F NMR (CDCl₃) $\delta -131.57$ (br.d, J = 55.0 Hz).

 $(1'S, 2R, R_S)$ -2-difluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]butyloxirane (13b): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 3, Table 1; yield 10.6%; R_f 0.50; ¹H NMR (CDCl₃) δ 0.75 (3H, t, J = 7.0 Hz), 0.9-2.4 (4H, m), 2.44 (3H, br.s), 2.95 (1H, dd, J = 9.0 and 2.5 Hz), 3.02 (1H, d, J = 4.5 Hz), 3.17 (1H, dt, J = 4.5 and 1.8 Hz), 5.67 (1H, t, J = 55.0 Hz), 7.35 and 7.47 (4H, m); ¹⁹F NMR (CDCl₃) δ -126.53 and -124.84 (br.dd, J = 295.0 and 55.0 Hz).

Apart from oxiranes $(1'S, 2S, R_S)$ -11b $(1'R, 2S, R_S)$ -12b $(1'S, 2R, R_S)$ -13b, the corresponding enol ethers 14b were isolated. $(E,Z),(R_S)$ -1,1-difluoro-2-methoxy-3-[(4-methylphenyl)sulfinyl]hex-2-ene: first isomer; 4.9% yield; $R_f 0.50$; ¹⁹F NMR (CDCl₃) δ -115.30 and -120.40 (br.dd, J = 317.0 and 53.0 Hz). Second isomer; 12.4% yield; $R_f 0.48$; ¹⁹F NMR (CDCl₃) δ -116.80 and -122.20 (br.dd, J = 316.0 and 53.0 Hz).

(1'S,2S,Rg)-2-trifluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]ethyloxirane (11c): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 5, Table 1; 56.4% yield; R_f 0.45; yellowish oil; $[\alpha]_D^{20} = +168.0 (c \ 1.9, CHCl_3)$; ¹H NMR (CDCl_3) δ 1.28 (3H, dq, J = 6.8 and 1.1 Hz), 2.41 (3H, br.s), 3.02 (1H, q, J = 6.8 Hz), 3.11 (1H, br.d, J = 4.4 Hz), 3.16 (1H, dq, J =4.4 and 1.7 Hz), 7.33 and 7.46 (4H, m); ¹⁹F NMR (CDCl_3) δ -76.15 (br.s). Anal. calcd for C₁₂H₁₃F₃O₂S: C, 51.81; H, 4.71; F, 20.47. Found: C, 51.76; H, 4.73; F, 20.49.

 $(1'R, 2S, R_S)$ -2-trifluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]ethyloxirane (12c): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 5, Table 1; 19.1% yield; R_f 0.40; yellowish oil; $[\alpha]_D^{20} = +140.0$ (c 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 1.06 (3H, d, J = 7.2 Hz), 2.44 (3H, br.s), 3.20 (1H, br.d, J = 4.2 Hz), 3.25 (1H, dq, J = 4.2 and 1.7 Hz), 3.44 (1H, q, J = 7.2 Hz), 7.36 and 7.56 (4H, m); ¹⁹F NMR (CDCl₃) δ -76.78 (br.s). Anal. calcd for C₁₂H₁₃F₃O₂S: C, 51.81; H, 4.71; F, 20.47. Found: C, 51.83; H, 4.73; F, 20.44.

(1'S,2R,R_S)-2-trifluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]ethyloxirane (13c): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 5, Table 1; 7.5% yield; R_f 0.55; mp 68-70 °C (di-*i*-propyl ether); $[\alpha]_D^{20} = +150.0$ (c 1.1, CHCl₃); ¹H NMR (CDCl₃) δ 0.95 (3H, t, J = 7.2 Hz), 2.44 (3H, br.s), 3.13 (1H, q, J = 7.2 Hz), 3.24 (1H, br.d, J = 4.4 Hz), 3.37 (1H, dq, J = 4.5 and 1.8 Hz), 7.36 and 7.45 (4H, m); ¹⁹F NMR (CDCl₃) δ -76.73 (br.s). Anal. calcd for C₁₂H₁₃F₃O₂S: C, 51.81; H, 4.71; F, 20.47. Found: C, 51.78; H, 4.72; F, 20.45.

Apart from oxiranes $(1'S, 2S, R_S)$ -11c, $(1'R, 2S, R_S)$ -12c and $(1'S, 2R, R_S)$ -13c, the corresponding enol ethers 14c were isolated.

 $(E,Z),(R_S)$ -1,1,1-trifluoro-2-methoxy-3-[(4-methylphenyl)sulfinyl]but-2-ene: first isomer; yield 4.0%; R_f 0.60; yellowish oil; $[\alpha]_D^{20} = -358.0 (c \ 1.2, CHCl_3)$; ¹H NMR (CDCl_3) δ 1.85 (3H, q, J = 2.8 Hz), 2.41 (3H, br.s), 3.89 (3H, q, J = 1.2 Hz), 7.31 and 7.52 (4H, m); ¹⁹F NMR (CDCl_3) δ -64.57 (br.s). Anal. calcd for C₁₂H₁₃F₃O₂S: C, 51.81; H, 4.71; F, 20.47. Found: C, 51.80; H, 4.0; F, 20.50. Second isomer; yield 5.3%; R_f 0.55; yellowish oil; $[\alpha]_D^{20} = -38.4 (c \ 1.2, CHCl_3)$; ¹H NMR (CDCl_3) δ 1.79 (3H, q, J = 2.1 Hz), 2.40 (3H, br.s), 3.74 (3H, br.s), 7.32 and 7.46 (4H, m); ¹⁹F NMR (CDCl_3) δ -60.52 (br.s). Anal. calcd for C₁₂H₁₃F₃O₂S: C, 51.81; H, 4.71; F, 20.47. Found: C, 51.78; H, 4.70; F, 20.51.

(1'S,2S,R_S)-2-trifluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]butyloxirane (11d): isolated by FC (chloroform/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 11, Table 1; yield 51.3%; R_f 0.54; yellowish oil; $[\alpha]_D^{20} = +149.8$ (c 1.3, CHCl₃); ¹H NMR (CDCl₃) δ 0.82 (3H, t, J = 7.2 Hz), 1.06, 1.37, 1.64 and 2.01 (4H, m), 2.43 (3H, br.s), 2.84 (1H, dq, J = 4.4 and 1.8 Hz), 2.86 (1H, dd, J = 8.5 and 4.8 Hz), 3.08 (1H, d, J = 4.4 Hz), 7.34 and 7.52 (4H, m); ¹⁹F NMR (CDCl₃) δ -75.85 (br.s). Anal. calcd for C₁₄H₁₇F₃O₂S: C, 54.89; H, 5.59; F, 18.60. Found: C, 54.85; H, 5.58; F, 18.63.

 $(1'S, 2R, R_S)$ -2-trifluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]butyloxirane (13d): isolated by FC (chloroform/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 11, Table 1; yield 19.1%; $R_f 0.50$; $[\alpha]_D D^{20} = +112.5$ (c 0.3, CHCl₃); ¹H NMR (CDCl₃) δ 0.73 (3H, t, J = 6.9 Hz), 0.8-2.2 (4H, m), 2.43 (3H, br.s), 2.89 (1H, dd, J = 9.8 and 2.9 Hz), 3.26 (1H, d, J = 4.6 Hz), 3.42 (1H, dq, J = 4.6 and 1.9 Hz), 7.36 and 7.46 (4H, m); ¹⁹F NMR (CDCl₃) δ -77.22 (br.s). Anal. calcd for C₁₄H₁₇F₃O₂S: C, 54.89; H, 5.59; F, 18.61. Found: C, 54.87; H, 5.60; F, 18.60.

 $(1'R, 2S, R_S)$ -2-trifluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]butyloxirane (12d): isolated by FC (chloroform/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 11, Table 1; yield 15.7%; R_f 0.48; ¹H NMR (CDCl₃) δ 0.85 (3H, t, J = 7.0 Hz), 0.9-2.1 (4H, m), 2.43 (3H, br.s), 3.12 (1H, d, J = 4.6 Hz), 3.18 (1H, dd, J = 9.0 and 4.8 Hz), 3.55 (1H, dq, J = 4.6 and 1.8 Hz), 7.34 and 7.51 (4H, m); ¹⁹F NMR (CDCl₃) δ -77.81 (br.s).

Apart from oxiranes $(1'S, 2S, R_S)$ -11d, $(1'R, 2S, R_S)$ -12d and $(1'S, 2R, R_S)$ -13d, the corresponding enol ethers 14d were isolated.

 $(Z, E), (R_S)-1, 1, 1$ -trifluoro-2-methoxy-3-[(4-methylphenyl)sulfinyl]hex-2-ene: first isomer; 13.9% yield; $R_f 0.38$ (chloroform/ethyl acetate 4:1); yellowish oil; $[\alpha]_D^{20} = -90.5$ (c 0.9, CHCl₃); ¹H NMR (CDCl₃) δ 0.77 (3H, t, J = 6.8 Hz), 1.10, 1.37, 2.02 and 2.30 (4H, m), 2.39 (3H, br.s), 3.86 (3H, q, J = 1.0Hz), 7.31 and 7.55 (4H, m); ¹⁹F NMR (CDCl₃) δ -64.96 (br.s). Anal. calcd for C₁₂H₁₃F₃O₂S: C, 51.81; H, 4.71; F, 20.47. Found: C, 51.80; H, 4.68; F, 20.50. Second isomer; 5.2% yield; $R_f 0.35$ (chloroform/ethyl acetate 4:1); ¹H NMR (CDCl₃) δ 0.82 (3H, t, J = 7.2 Hz), 0.82, 1.37, 2.02 and 2.30 (4H, m), 2.40 (3H, br.s), 3.77 (3H, q, J = 1.0 Hz), 7.31 and 7.48 (4H, m); ¹⁹F NMR (CDCl₃) δ -59.07 (br.s).

(1'S,2S,RS)-2-chlorodifluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]but-2'-enyloxirane

(11e): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 13, Table 1; yield 63.6%; R_f 0.35; yellowish oil; $[\alpha]_D^{20} = +123.3$ (*c* 0.8, CHCl₃); ¹H NMR (CDCl₃) δ 2.43 (3H, br.s), 2.44 and 2.62 (2H, m), 3.19 (1H, ddd, J = 4.3, 2.6 and 1.1 Hz), 3.24 (1H, dd, J = 7.9 and 5.2 Hz), 3.31 (1H, d, J = 4.3 Hz), 4.98 and 5.00 (2H, m), 5.49 (1H, m), 7.34 and 7.53 (4H, m); ¹⁹F NMR (CDCl₃) δ -65.10 and -62.22 (br.d, J = 167.0 Hz). Anal. calcd for C₁₄H₁₅ClF₂O₂S: C, 52.42; H, 4.71; F, 11.84. Found: C, 52.40; H, 4.73; F, 11.83.

(1'R,2S,R_S)-2-chlorodifluoromethyl-2-1'-[(4-methylphenyl)sulfinyl]but-2'-enyloxirane

(12e): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 13, Table 1; yield 10.3%; R_f 0.40; ¹H NMR (CDCl₃) δ 2.06 and 2.20 (2H, m), 2.44 (3H, br.s), 3.09 (1H, dd, J = 9.6 and 3.6 Hz), 3.37 (1H, d, J = 4.6 Hz), 3.57 (1H, ddd, J = 4.6, 2,6 and 1.1 Hz), 4.87 and 4.93 (2H, m), 5.60 (1H, m), 7.37 and 7.48 (4H, m); ¹⁹F NMR (CDCl₃) δ -63.71 and -65.10 (br.d, J = 166 Hz).

Apart from oxiranes $(1'S, 2S, R_S)$ -11e and $(1'R, 2S, R_S)$ -12e, the corresponding enol ethers 14e were isolated.

 $(E,Z),(R_S)$ -1-chloro-1,1-difluoro-2-methoxy-3-[(4-methylphenyl)sulfinyl]hexa-2,5diene: first isomer; 2.6% yield; R_f 0.40; ¹H NMR (CDCl₃) δ 2.39 (3H, br.s), 2.94 and 3.07 (2H, m), 3.83 (3H, t, J = 1.2 Hz), 4.82 and 4.84 (2H, m), 5.32 (1H, m), 7.30 and 7.50 (4H, m); ¹⁹F NMR (CDCl₃) δ -51.87 and -43.57 (br.d, J = 168.0 Hz). Anal. calcd for C₁₄H₁₅ClF₂O₂S: C, 52.42; H, 4.71; F, 11.85. Found: C, 52.43; H, 4.73; F, 11.80. Second isomer; 4.3% yield; R_f 0.38; ¹H NMR (CDCl₃) δ 2.41 (3H, br.s), 3.10 and 3.25 (2H,m), 3.96 (3H, br.s), 4.85 and 4.91 (2H, m), 5.41 (1H, m), 7.28 and 7.54 (4H, m); ¹⁹F NMR (CDCl₃) δ -55.90, -52.09 (br.d, J = 170.0 Hz).

(1'S,2S,R_S)-2-difluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]benzyloxirane (11g):

isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 17, Table 1; yield 8.2%; $R_f 0.40$; ¹H NMR (CDCl₃) δ 2.31 (3H, br.s), 3.02 (1H, d, J = 4.5 Hz), 3.92 (1H, dt, J = 1.8 Hz), 3.99 (1H, br.s), 5.66 (1H, t, J = 55.0 Hz), 7.0-7.4 (9H, m); ¹⁹F NMR (CDCl₃) δ -131.17 (1F, br.dd, J = 290.0 and 55.0 Hz), -125.87 (1F, br.dd, J = 290.0 and 55.0 Hz).

 $(1'R, 2S, R_S)$ -2-difluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]benzyloxirane (12g): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 16, Table 1; yield 62%; R_f 0.33; yellowish oil; $[\alpha]_D^{20} = -216.6 (c \ 1.0, CHCl_3)$; ¹H NMR (CDCl_3) δ 2.31 (3H, br.s), 3.29 (1H, d, J = 4.5 Hz), 4.00 (1H, dt, J = 4.5 and 1.7 Hz), 4.26 (1H, br.d, J = 1.3 Hz), 5.60 (1H, dd, J = 56.0 and 55.0 Hz), 6.9-7.4 (9H, m); ¹⁹F NMR (CDCl_3) δ -133.09 (1F, br.dd, J = 291.0 and 56.0 Hz), -127.09 (1F, br.dd, J = 291.0 and 55.0 Hz); Anal. calcd for C₁₇H₁₆F₂O₂S: C, 63.34; H, 5.00; F, 11.79. Found: C, 63.30; H, 5.04; F, 11.80.

Apart from oxiranes $(1'S, 2S, R_S)$ -11g and $(1'R, 2S, R_S)$ -12g, the corresponding enol ethers 14g were isolated.

 $(E,Z),(R_S)$ -1,1-difluoro-2-methoxy-3-[(4-methylphenyl)sulfinyl]-3-phenylprop-2-ene: first isomer; 4.1% yield; R_f 0.40; ¹H NMR (CDCl₃) δ 2.41 (3H, br.s), 4.28 (3H, q, J = 2.0 Hz), 5.52 (1H, t, J = 54.0 Hz), 6.8-7.5 (9H, m); ¹⁹F NMR (CDCl₃) δ -122.22 and -118.35 (br.dd, J = 316.0 and 54.0 Hz). Second isomer; 23% yield; R_f 0.38; ¹H NMR (CDCl₃) δ 2.38 (3H, br.s), 4.08 (3H, q, J = 2.0 Hz), 5.85 (1H, t, J = 52.5 Hz), 6.8-7.5 (9H, m); ¹⁹F NMR (CDCl₃) δ -121.30 and -116.95 (br.dd, J = 316.0 and 52.5 Hz).

(1'S,2S,R_S)-2-trifluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]benzyloxirane (11h): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 19, Table 1; 16.6% yield; $R_f 0.45$; ¹H NMR (CDCl₃) δ 2.35 (3H, br.s), 3.35 (1H, dd, J = 4.6 and 1.0 Hz), 3.98 (1H, br.s), 4.03 (1H, dq, J = 4.6 and 1.7 Hz), 6.8-7.5 (9H, m); ¹⁹F NMR (CDCl₃) δ -75.51 (br.s).

 $(1'R, 2S, R_S)$ -2-trifluoromethyl-2-[1'-(4-methylphenyl)sulfinyl]benzyloxirane (12h): isolated by FC (hexane/ethyl acetate 4:1) of the reaction mixture obtained under the conditions specified in entry 18, Table 1; yield 53.7%; R_f 0.39; yellowish oil; $[\alpha]_D^{20} = -136.0 (c \ 1.1, CHCl_3)$; ¹H NMR (CDCl_3) δ 2.30 (3H, br.s), 3.45 (1H, d, J = 4.0 Hz), 4.12 (1H, dq, J = 4.0 and 1.9 Hz), 4.23 (1H, br.s), 6.9-7.3 (9H, m); ¹⁹F NMR (CDCl_3) δ -75.04 (br.s); Anal. calcd for C₁₇H₁₅F₃O₂S: C, 59.99; H, 4.44; F, 16.74. Found: C, 60.03; H, 4.40; F, 16.70.

Apart from oxiranes $(1'S, 2S, R_S)$ -11h and $(1'R, 2S, R_S)$ -12h, the corresponding enol ethers 14h were isolated (entry 19).

 $(E,Z),(R_S)$ -1,1,1-trifluoro-2-methoxy-3-[(4-methylphenyl)sulfinyl]-3-phenylprop-2-ene: first isomer; 3.9% yield; R_f 0.45; ¹H NMR (CDCl₃) δ 2.43 (3H, br.s), 3.50 (3H, q, J = 1.5 Hz), 7.0-7.6 (9H, m); ¹⁹F NMR (CDCl₃) δ -60.75 (br.s). Second isomer; 26% yield; R_f 0.43; ¹H NMR (CDCl₃) δ 2.40 (3H, br.s), 4.04 (3H, q, J = 1.5 Hz), 7.0-7.6 (9H, m); ¹⁹F NMR (CDCl₃) δ -63.42 (br.s). **Ring-opening reactions of oxiranes with water.** Synthesis of 1,2-diols. General procedure. To a solution of the corresponding oxirane (2.0 mmol) in a 1:1 mixture of THF/H₂O (12 mL), perchloric acid (70%, 0.1 mmol) was added. After 5 d at rt, pH of the reaction medium was adjusted to 7 by adding a diluted (0.1 N) solution of NaHCO₃, then the solvent was evaporated *in vacuo* to dryness and the residue was purified by FC.

 $(2S,3S,R_S)$ -2-trifluoromethyl-3-[(4-methylphenyl)sulfinyl]butan-1,2-diol (15). Starting from (1'S,2S,R_S)-11c diol (2S,3S,R_S)-15 was obtained in 89% yield; R_f 0.38 (chloroform/ethyl acetate 1:1); mp 116.0-118.5 °C (di-*i*-propyl ether); $[\alpha]_D^{20} = +147.3$ (c 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 1.10 (3H, d, J =7.1 Hz), 2.39 (3H, br.s), 3.02 (1H, q, J = 7.1 Hz), 3.93 and 4.14 (2H, br.d, J = 12.2 Hz), 4.97 (1H, br.m) 5.66 (1H, br.s), 7.32 and 7.46 (4H, m); ¹⁹F NMR (CDCl₃) δ -77.68 (br.s); Anal. calcd for C₁₂H₁₅F₃O₃S: C, 48.66; H, 5.10; F, 19.23. Found: C, 48.60; H, 5.13; F, 19.24.

(2S,3R,RS)-2-chlorodifluoromethyl-3-[(4-methylphenyl)sulfinyl]hex-5-en-1,2-diol (16). Starting from (1'R,2S,RS)-12e diol (2S,3R,RS)-16 was obtained in 80% yield: R_f 0.30 (hexane/ethyl acetate 4:1); $[\alpha]D^{20}$ +106.5 (c 1.0, CHCl3); ¹H NMR (CDCl3), δ : 2.08 and 2.52 (2H, m), 2.44 (3H, br.s), 2.85 (1H,br.m), 3.57 (1H, dd, J = 6.0 and 5.2 Hz), 3.80 and 3.85 (2H, m), 4.78 and 4.79 (2H, m), 5.17 (1H, m), 7.30 (1H, br.m), 7.36 and 7.72 (1H, br.m); ¹⁹F NMR (CDCl3), δ -58.79 (br.s).

(2S,3R)-2-Trifluoromethyl-3-[(4-methylphenyl)sulfenyl]butan-1,2-diol (27). From (1'*R*,2*S*)-25 the corresponding diol (2*S*,3*R*)-27 was obtained in 97% yield; R_f 0.27; yellowish oil; $[\alpha]_D^{20} = -42.7$ (c 1.3, CHCl₃); ¹H NMR (CDCl₃) δ 1.44 (3H, dq, J = 7.3 and 1.2 Hz), 2.32 (3H, br.s), 2.66 (1H, t, J = 6.5 Hz), 3.52 (1H, q, J = 7.3 Hz), 3.91 (2H, m), 4.03 (1H, br.s), 7.12 and 7.38 (4H, m); ¹⁹F NMR (CDCl₃) δ -76.00 (br.s); Anal. calcd for C₁₂H₁₅F₃O₂S: C, 51.42; H, 5.39; F, 20.33. Found: C, 51.47; H, 5.42; F, 20.34.

Ring-opening reactions of oxiranes with mono- or dibenzylamine. Synthesis of 1,2aminoalcohols. General procedure. Mono- or dibenzylamine (10.0 mmol) was added at rt to the corresponding oxirane (1.0 mmol) and the reaction was stirred at rt for one or three days, respectively. The resultant mixture was evaporated *in vacuo* and the residue was purified by flash chromatography (hexane/ethyl acetate 4:1).

(2S,3S,R_S)-1-(N-Benzyl)amino-2-trifluoromethyl-3-[(4-methylphenyl)sulfinyl]butan-2ol (17). From (1'S,2S,R_S)-11c amino-alcohol (2S,3S,R_S)-17 was obtained in 91.0% yield; R_f 0.35; mp 103.0-104.5 °C (di-*i*-propyl ether); [α]_D²⁰ = +77.7 (c 1.0, CHCl₃); ¹H NMR (CDCl₃ + drop D₂O) δ 1.02 (3H, d, J = 7.2 Hz), 2.41 (3H, br.s), 2.95 (1H, q, J = 7.2 Hz), 2.95 and 3.33 (2H, br.d, J = 14.0 Hz), 3.91 (2H, br.s), 7.2-7.5 (9H, m); ¹⁹F NMR (CDCl₃) δ -78.85 (br.s); Anal. calcd for C₁₉H₂₂F₃NO₂S: C, 59.21; H, 5.75; F, 14.79. Found: C, 59.25; H, 5.72; F, 14.75.

 $(2S,3S,R_S)$ -1-(N,N-Dibenzyl)amino-2-trifluoromethyl-3-[(4-methylphenyl)sulfinyl]hexan-2-ol (18). From (1'S,2S,R_S)-11d, by the reaction with dibenzylamine the corresponding compound $(2S,3S,R_S)$ -18 was obtained in 55% yield: R_f 0.25 (hexane/diethyl ether 4:1); yellowish oil; $[\alpha]_D^{20} = +31.0$ (c 0.8, CHCl₃); ¹H NMR (CDCl₃) δ 0.62 (3H, m), 0.65, 1.02, 1.98, and 2.03 (4H, m), 2.37 (3H, br.s), 2.94 (1H, dd, J = 8.0 and 6.4 Hz), 3.01 and 3.51 (2H, d, J = 15.4 Hz), 3.77 and 3.89 (4H, br.d, J = 13.9 Hz), 6.30 $(1H, br.s), 7.2-7.5 (14H, m); {}^{19}F NMR (CDCl_3) \delta -77.88 (br.s); Anal. calcd for C_{28}H_{32}F_3NO_2S: C, 66.78; H, 6.40; F, 11.32. Found: C, 66.73; H, 6.40; F, 11.36.$

(2R,3S,RS)-1-(N-Benzyl)amino-2-trifluoromethyl-3-[(4-methylphenyl)sulfinyl]butan-2-ol (19). From $(1'S,2R,R_S)$ -13c compound $(2R,3S,R_S)$ -19 was obtained in 90.0% yield: R_f 0.35; mp 112-113 °C (di-*i*-propyl ether); $[\alpha]_D^{20} = +98.1$ (c 1.1, CHCl₃); ¹H NMR (CDCl₃ + drop D₂O) δ 1.06 (3H, d, J = 7.0 Hz), 2.39 (3H, br.s), 2.96 (1H, q, J = 7.0 Hz), 3.06 and 3.35 (2H, br.d, J = 14.0 Hz), 3.83 and 3.91 (2H, br.d, J = 13.1 Hz), 7.2-7.4 (9H, m); ¹⁹F NMR (CDCl₃) δ -77.71 (br.s); Anal. calcd for C₁₉H₂₂F₃NO₂S: C, 59.21; H, 5.75; F, 14.79. Found: C, 59.23; H, 5.70; F, 14.76.

(2S,3R,RS)-1-(N-Benzyl)amino-2-trifluoromethyl-3-[(4-methylphenyl)sulfinyl]butan-2ol (20). From $(1'R,2S,R_S)$ -12c amino derivative $(2S,3R,R_S)$ -20, was obtained in 90.0% yield; ¹H NMR (CDCl₃ + drop D₂O) δ 0.88 (3H, br.d, J = 7.2 Hz), 2.46 (3H, br.s), 2.88 and 2.97 (2H, br.d, J = 13.0 Hz), 3.56 (1H, br.q, J = 7.2 Hz), 3.74 and 3.90 (2H, d, J = 13.2 Hz), 7.2-7.7 (9H, m); ¹⁹F NMR (CDCl₃) δ -75.68 (br.s).

 $(2S,3S,R_S)$ -1-(N-Benzyl)amino-2-trifluoromethyl-3-phenyl-3-[(4-methylphenyl)sulfinyl]propan-2-ol (21). From (1'S,2S, R_S)-11h amino compound (2S,3S, R_S)-21 was obtained in 83% yield: R_f 0.31; yellowish oil; $[\alpha]_D^{20} = -62.8$ (c 0.8, CHCl₃); ¹H NMR (CDCl₃ + drop D₂O) δ 2.30 (3H, br.s), 2.99 and 3.35 (2H, br.d, J = 13.0 Hz), 3.86 and 3.89 (2H, br.d, J = 13.3 Hz), 4.21 (1H, br.s), 7.0-7.4 (14H, m); ¹⁹F NMR (CDCl₃) δ -76.10 (br.s); Anal. calcd for C₂₄H₂₄F₃NO₂S: C, 64.41; H, 5.41; N, 3.13. Found: C, 64.43; H, 5.40; N, 3.15.

(2S,3S,RS)-1-(*N*-Benzyl)amino-2-difluoromethyl-3-[(4-methylphenyl)sulfinyl]hexan-2ol (22). From (1'S,2S,RS)-11b amino derivative (2S,3S,RS)-22 was obtained in 60% yield: R_f 0.27; yellowish oil; $[\alpha]_D^{20} = -70.2$ (*c* 1.1, CHCl₃); ¹H NMR (CDCl₃ + drop D₂O) δ 0.52, 0.93, 1.24 and 1.91 (4H, m), 0.57 (3H, br.t, J = 6.9 Hz), 2.40 (3H, br.s), 2.75 (1H, dd, J = 5.8 and 3.2 Hz), 2.82 and 3.12 (2H, br.d, J = 13.2 Hz), 3.88 (2H, br.s), 5.71 (1H, t, J = 55.5 Hz), 7.2-7.5 (9H, m); ¹⁹F NMR (CDCl₃) δ -131.69 and -129.84 (br.dd, J = 284.0 and 55.5 Hz); Anal. calcd for C₂₁H₂₇F₂NO₂S: C, C, 63.77; H, 6.88; N, 3.54. Found: C, 63.75; H, 6.87; N, 3.52.

(2S,3S,RS)-1-(N-Benzyl)amino-2-difluoromethyl-3-phenyl-3-[(4-methylphenyl)-

sulfinyl]propan-2-ol (23). From (1'S,2S,R_S)-11g derivative (2S,3S,R_S)-23 was obtained in 70% yield: R_f 0.32; yellowish oil; $[\alpha]_D^{20} = -96.2$ (c 1.1, CHCl₃); ¹H NMR (CDCl₃ + drop D₂O) δ 2.29 (3H, br.s), 3.10 and 3.56 (2H, br.d, J = 12.8 Hz), 3.85 (1H, d, J = 3.0 Hz), 3.93 (2H, br.s), 5.35 (1H, dd, J = 57.5 and 54.5 Hz), and 7.0-7.4 (14H, m); ¹⁹F NMR (CDCl₃) δ -136.98 (1F, br.dd, J = 284.0 and 57.5 Hz) and -132.80 (1F, br.dd, J = 284.0 and 54.5 Hz); Anal. calcd for C₂₄H₂₅F₂NO₂S: C, 67.11; H, 5.87; N, 3.26. Found: C, 67.13; H, 5.90; N, 3.24.

Reduction of sulfoxide into sulfide group. General procedure. NaI (2.0 mmol) and the substrates (1.0 mmol) were suspended in acetone (10 mL) under N₂ atmosphere and stirred at -20 °C for 10 min. Then a solution of (CF₃CO)₂O (3.0 mmol) in the same solvent (5 mL) was added dropwise and stirring was continued at the same temperature for 20 min. Saturated solutions of Na₂SO₃ and NaHCO₃ (1:1 vol) were added and the organic layers were extracted with ethyl ether, dried over Na₂SO₄, filtered and evaporated *in vacuo* to dryness. The targeted products were purified by FC.

(1'S,2S)-2-Trifluoromethyl-2-[1'-(4-methylphenyl)sulfenyl]ethyloxirane (24). From (1'S,2S, $R_{\rm S}$)-11c sulfenyl derivative (1'S,2S)-24 was obtained in 92% yield; R_f 0.28 (hexane/diethyl ether 9:1); yellowish oil; [α]_D²⁰ = +24.6 (c 1.5, CHCl₃); ¹H NMR (CDCl₃) δ 1.36 (3H, br.d, J = 7.2 Hz), 2.33 (3H, br.s), 3.02 (1H, dq, J = 4.8 and 1.7 Hz), 3.05 (1H, d, J = 4.8 Hz), 3.68 (1H, q, J = 7.2 Hz), 7.12 and 7.31 (4H, m); ¹⁹F NMR (CDCl₃) δ -75.00 (br.s); Anal. calcd for C₁₂H₁₃F₃OS: C, 54.95; H, 5.00; F, 21.73. Found: C, 54.93; H, 5.00; F, 21.76.

(1'*R*,2*S*)-2-Trifluoromethyl-2-[1'-(4-methylphenyl)sulfenyl]ethyloxirane (25): From (1'*R*,2*S*,*R*_S)-12c sulfenyl derivative (1'*R*,2*S*)-25 was obtained in 90% yield; *R*_f 0.35 (hexane/diethyl ether 9:1); yellowish oil; $[\alpha]_D^{20} = -7.7$ (*c* 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 1.49 (3H, dq, *J* = 7.2 and 1.2 Hz), 2.33 (3H, br.s), 2.75 (1H, dq, *J* = 4.7 and 1.8 Hz), 3.00 (1H, br.d, *J* = 4.7 Hz), 3.39 (1H, q, *J* = 7.2 Hz), 7.12 and 7.37 (4H, m); ¹⁹F NMR (CDCl₃) δ -72.78 (br.s); Anal. calcd for C₁₂H₁₃F₃OS: C, 54.95; H, 5.00; F, 21.73. Found: C, 54.95; H, 4.96; F, 21.70.

(2S,3S)-2-Trifluoromethyl-3-[(4-methylphenyl)sulfenyl]butan-1,2-diol (26). From $(2S,3S,R_S)$ -15 sulfenyl derivative (2S,3S)-26 was obtained in 95% yield; R_f 0.25; yellowish oil; $[\alpha]_D^{20} = +52.6$ (c 1.2, CHCl₃); ¹H NMR (CDCl₃) δ 1.51 (3H, dq, J = 7.4 and 1.7 Hz), 2.31 (3H, br.s), 2.87 (1H, dd, J = 8.9 and 5.0 Hz), 3.56 (1H, q, J = 7.4 Hz), 3.79 (1H, dd, J = 11.9 and 8.9 Hz), 3.93 (1H, dd, J = 11.9 and 5.0 Hz), 4.27 (1H, br.s), 7.12 and 7.36 (4H, m); ¹⁹F NMR (CDCl₃) δ -75.29 (br.s); Anal. calcd for C₁₂H₁₅F₃O₂S: C, 51.42; H, 5.39; F, 20.33. Found: C, 51.45; H, 5.36; F, 20.30.

(2S,3S)-1-(N-Benzyl-N-trifluoroacetyl)amino-2-trifluoromethyl-3-[(4-methylphenyl)sulfenyl]butan-2-ol (28). From (2S,3S,R_S)-17 sulfenyl derivative (2S,3S)-28 was obtained in 91% yield; R_f 0.28 (hexane/diethyl ether 9:1); yellowish oil; $[\alpha]_D^{20} = -15.3$ (c 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 1.39 (3H, dq, J = 7.3 and 1.3 Hz), 2.33 (3H, br.s), 3.44 (1H, q, J = 7.3 Hz), 3.66 and 3.98 (2H, d, J = 15.2 Hz), 4.62 and 5.06 (2H, br.d, J = 16.4 Hz), 4.88 (1H, br.m), 7.0-7.5 (9H, m); ¹⁹F NMR (CDCl₃) δ -75.16 (3F, br.s), -69.31 (3F, s); Anal. calcd for C₂₁H₂₁NF₆O₂S: C, 54.18; H, 4.55; N,3.01. Found: C, 54.17; H, 4.52; N, 3.02.

(2S,3R)-1-(N-Benzyl-N-trifluoroacetyl)amino-2-trifluoromethyl-3-[(4-

methylphenyl)sulfenyl]butan-2-ol (29). From $(2S,3R,R_S)$ -20 sulfenyl derivative (2S,3R)-29 was obtained in 95% yield; R_f 0.39 (*n*-hexane/diethyl ether 9:1); yellowish oil; $[\alpha]_D^{20} = -70.3$ (*c* 0.7, CHCl₃); for ¹H and ¹⁹F NMR data of (2S,3R)-32 see those described below for its enantiomer (2R,3S)-33. Anal. calcd for $C_{21}H_{21}NF_6O_2S$: C, 54.19; H, 4.55; N, 3.01. Found: C, 54.12; H, 4.56; N, 3.03.

(2S,3S)-1-O-Benzoyl-2-trifluoromethyl-3-[(4-methylphenyl)sulfenyl]butan-1,2-diol (31). Benzoylation reaction. Benzoic acid (183 mg, 1.5 mmol) and DCC (226 mg, 1.1 mmol) were added to a solution of (2S,3S, R_S)-15 (296 mg, 1.0 mmol) in dichloromethane (10.0 mL), stirred at rt. After 5 min, DMAP (12.2 mg, 0.1 mmol) was added: immediately the solution became white and precipitates formed. After 2 h, the reaction mixture was filtered and the filtrate was evaporated *in vacuo* to dryness to give a residue that was purified by FC (hexane/ethyl acetate 7:3). O-Benzoyl derivative (2S,3S, R_S)-30 was isolated in 81% yield; R_f 0.35; mp 146-148 °C (di-*i*-propyl ether); $[\alpha]_D^{20} = +64.3$ (c 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 1.17 (3H, d, J = 7.2 Hz), 2.42 (3H, br.s), 2.99 (1H, q, J = 7.2 Hz), 4.71 and 4.86 (2H, br.d, J = 12.7 Hz), 4.98 (1H, br.m), 7.34, 7.46, 7.48, 7.62 and 8.05 (9H, m); ¹⁹F NMR (CDCl₃) δ -76.02 (br.s); Anal. calcd for C₁₉H₁₉F₃O₄S: C, 56.99; H, 4.78; F, 14.23. Found: C, 56.92; H, 4.76; F, 14.20. *O*-Benzoyl derivative (2*S*,3*S*,*R*_S)-**30** was reduced under the conditions described above to afford (2*S*,3*S*)-**31** in 80% yield; R_f 0.35; mp 68.5-69.5 °C (di-*i*-propyl ether); $[\alpha]_D^{20} = +34.2$ (*c* 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 1.58 (3H, br.d, J = 7.3 Hz), 2.28 (3H, br.s), 3.62 (1H, q, J = 7.2 Hz), 3.70 (1H, br.m), 4.61 and 4.70 (2H, br.d, J = 12.0 Hz), 7.05, 7.36, 7.43, 7.60 and 7.97 (9H, m); ¹⁹F NMR (CDCl₃) δ -74.86 (br.s); Anal. calcd for C₁₉H₁₉F₃O₃S: C, 59.37; H, 4.98; F, 14.83. Found: C, 59.35; H, 4.96; F, 14.83.

(2R,3S)-1-(N-Benzyl-N-trifluoroacetyl)amino-2-trifluoromethyl-3-[(4-methylphenyl)-sulfenyl]butan-2-ol (33). From $(2R,3S,R_S)$ -19 sulfenyl derivative (2R,3S)-33 was obtained in 98% yield; R_f 0.39 (hexane/diethyl ether 9:1); yellowish oil; $[\alpha]_D^{20} = +70.8$ (c 0.6, CHCl₃); ¹H NMR (CDCl₃) δ 1.58 (3H, dq, J = 7.3 and 1.9 Hz), 2.34 (3H, br.s), 3.30 (1H, br.q, J = 7.3 Hz), 3.38 and 4.16 (2H, d, J = 14.7 Hz), 4.80 and 5.02 (2H, br.d, J = 16.4 Hz), 4.83 (1H, br.m), 7.0-7.5 (9H, m); ¹⁹F NMR (CDCl₃) δ -75.95 (3F, br.s), -69.14 (3F, s); Anal. calcd for C₂₁H₂₁NF₆O₂S: C, 54.19; H, 4.55; N, 3.01. Found: C, 54.20; H, 4.58; N, 3.00.

Hydrogenolytic removal of the sulfenyl group. General procedure. The corresponding sulfenyl derivative (1.0 mmol) was dissolved in ethanol (5 mL) and *Raney*-Ni was added (three times wt.). The mixture was stirred at reflux under H₂ atm, then the black powder was removed by filtration. The filtrate was concentrated *in vacuo* and the residual product was purified by FC. Initially, the column was packed in pentane or hexane, then eluted with a gradient solvent system indicated for each case.

(S)-2-Trifluoromethyl-1-(O-benzoyl)butan-1,2-diol (32). Starting from (2S,3S)-31 product (S)-32 was obtained in 72% yield; R_f 0.35 (chloroform/ethyl acetate 97:3); yellowish oil; $[\alpha]_{365}^{20} = -1.5$ (c 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 1.08 (3H, t, J = 7.6 Hz), 1.85 (2H, br.q, J = 7.6 Hz), 2.95 (1H, br.m), 4.48 and 4.53 (2H, br.d, J = 12.3 Hz), 7.48, 7.58 and 8.02 (5H, m); ¹⁹F NMR (CDCl₃) δ -80.22 (br.s); Anal. calcd for C₁₂H₁₃F₃O₃: C, 54.96; H, 5.00; F, 21.73. Found: C, 54.98; H, 4.98; F, 21.71.

(S)-1-(N-Benzyl-N-trifluoroacetyl)amino-2-trifluoromethylbutan-2-ol (34). Starting from (2R,3S)-33 compound (R)-34 was obtained in 65% yield; R_f 0.35 (hexane/ethyl acetate 9:1); yellowish oil; $[\alpha]_D^{20} = +40.3$ (c 1.3, CHCl₃); $[\alpha]_{365}^{20} = +125.8$ (c 1.3, CHCl₃); ¹H NMR (CDCl₃) δ 0.99 (3H, br.t, J = 7.5 Hz), 1.64 and 1.78 (2H, br.dq, J = 14.5 and 7.5 Hz), 3.37 and 3.82 (2H, br.d, J = 15.2 Hz), 4.51 (1H, br.m), 4.61 and 4.95 (2H, br.d, J = 16.6 Hz), 7.1-7.5 (5H, m); ¹⁹F NMR (CDCl₃) δ -79.70 (3F, br.s), -69.40 (3F, s); Anal. calcd for C₁₄H₁₅F₆NO₂: C, 48.99; H, 4.40; N, 4.08. Found: C, 48.98; H, 4.37; N, 4.06.

(S)-1-(*N*-Benzyl)amino-2-trifluoromethylbutan-2-ol (35). A 1 *N* solution of NaOH in a 1.1 mixture of water and methanol (1.0 mL) was added at rt to a solution of (*R*)-34 (1.0 mmol, 272 mg) in methanol (10.0 mL) and the stirring was continued at rt for 5 min. Then 1.0 mL of water was added and the organic layers were extracted with ethyl acetate (3 x 1.0 mL). The combined organic extracts were dried over anhydrous sodium sulfate and, after filtration, the solvent was evaporated *in vacuo* to dryness to give a residue that was purified by FC (hexane/ethyl acetate 4:1). (*R*)-35 was obtained in 87% yield; R_f 0.35; yellowish oil; $[\alpha]_D^{20} = -10.7$ (*c* 1.2, CHCl₃); $[\alpha]_{365}^{20} = -39.2$ (*c* 1.2, CHCl₃); ¹H NMR (CDCl₃) δ 0.91 (3H, br.t, J = 7.6 Hz), 1.54 and 1.78 (2H, br.dq, J = 14.4 and 7.6 Hz), 2.52 and 3.06 (2H, br.d, J = 13.4 Hz), 3.00 (2H, br.m), 3.83 and 3.87 (2H, br.d, J = 13.4 Hz), 7.2-7.4 (5H, m); ¹⁹F NMR (CDCl₃) δ -80.86 (br.s); Anal. calcd for C₁₂H₁₆F₃NO: C, 58.29; H, 6.52; N, 5.66. Found: C, 58.30; H, 6.55; N, 5.67.

Thermal syn-elimination of sulfoxide group. General procedure. A solution of substrate (1.0 mmol) in *p*-xylene (20 mL) was heated at 150 °C under N₂ atmosphere for 10 min. Then the solution was concentrated *in vacuo* and the residue was purified by FC. Initially, the column was packed in pentane or hexane, then eluted with a gradient solvent system indicated for each case.

(S)-3-Trifluoromethyl-4-(O-benzoyl)but-1-en-3,4-diol (36). Starting from $(2S,3S,R_S)$ -30 olefinic derivative (S)-36 was obtained in 78% yield; R_f 0.35 (pentane/diethyl ether 9:1); yellowish oil; $[\alpha]_D^{20} = -3.8$ (c 0.6, CHCl₃); $[\alpha]_{365}^{20} = -15.2$ (c 0.6, CHCl₃); ¹H NMR (CDCl₃) δ 3.41 (1H, br.s), 4.51 and 4.60 (2H, br.d, J = 11.9 Hz), 5.56 and 5.78 (2H, m), 5.98 (1H, dd, J = 16.8 and 10.5 Hz), and 7.48, 7.61 and 8.02 (5H, m); ¹⁹F NMR (CDCl₃) δ -80.30 (br.s); Anal. calcd for C₁₂H₁₁F₃O₃: C, 55.39; H, 4.26; F, 21.90. Found: C, 55.41; H, 4.28; F, 21.93.

(S)-4-(N-Benzyl)amino-3-trifluoromethylbut-1-en-3-ol (37). Starting from $(2S,3S,R_S)$ -17 olefinic derivative (S)-37 was obtained in 82% yield; R_f 0.35 (pentane/diethyl ether 9:1); yellowish oil; $[\alpha]_D^{20} = -7.8$ (c 1.2, CHCl₃); $[\alpha]_{365}^{20} = -28.8$ (c 1.2, CHCl₃); ¹H NMR (CDCl₃) δ 2.69 and 3.10 (2H, br.d, J = 12.8 Hz), 3.10 (2H, br.m), 3.83 (2H, br.s), 5.41 and 5.69 (2H, m), 5.84 (1H, dd, J = 16.6 and 10.2 Hz), 7.2-7.4 (5H, m); ¹⁹F NMR (CDCl₃) δ -80.95 (br.s); Anal. calcd for C₁₂H₁₄NF₃O: C, 58.77; H, 5.75; N, 5.71. Found: C, 58.78; H, 5.71; N, 5.70.

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