Facile Intramolecular Acylation Reactions of γ- and δ-(Acyloxy)Sulfones: Synthesis of Substituted Chiral Dihydrofurans and Dihydropyrans[1]

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The acylation of (*S*)-4-(*p*-tolylsulfonyl)-2-butanol and (*S*)-(*p*-tolylsulfonyl)-3-pentanol, chirons that are available in high optical purities, with a variety of acid chlorides gave the corresponding derivatives **9–16**. Deprotonation of these substrates with LHMDS in THF at −78 °C led to the selective formation of the α-sulfonyl carbanions. These carbanions cyclized readily to give in good yields an equilibrium mixture of the expected lactols with the open chain hydroxy ketones. This ring closure/acyl transfer reaction was facile and found to be compatible with functionalities such as halides and esters in the acyl side chain. The mixture of lactols with the open chain hydroxy ketones obtained from this reaction could be dehydrated in good yields using mild acid conditions to give the corresponding chiral nonracemic dihydrofurans or dihydropyrans. Alternatively, this equilibrium mixture could be trapped as the open-chain (*tert*-butyldimethylsilyl)oxy ketosulfone derivatives **32–35** and subsequently desulfonylated.

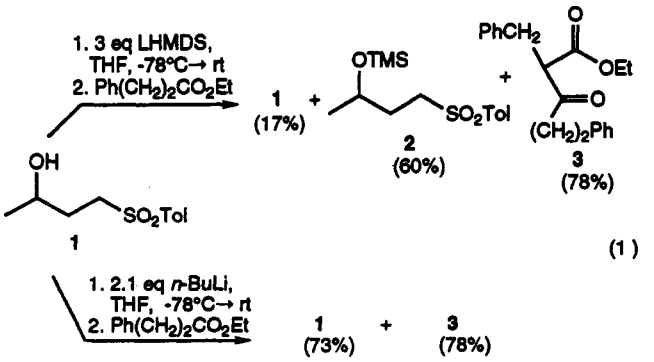
Introduction

Recently, there has been much interest in the preparation of chiral hydroxy sulfones and their applications to asymmetric synthesis.[2,3] The bakers' yeast reduction of γ- and δ-keto sulfones has been used to prepare some chiral hydroxy sulfones in high enantiomeric purities.[4] Also, the resolution of racemic hydroxy sulfones by lipase catalyzed transesterification has been successfully achieved by a number of groups.[5] As part of a program designed to enhance the synthetic utility of chiral γ- and δ-hydroxy sulfones, we have investigated the acyl-transfer reactions of both γ- and δ-(acyloxy) sulfones and their applications to the synthesis of chiral substituted dihydrofurans and dihydropyrans.

Reactions involving α-sulfonyl anions are synthetically most useful when the alkylating or acylating agents are relatively simple and incapable of participating in side reactions due to the presence of additional functionalities. In particular, the alkylation of sulfones with bifunctional alkylating agents can be complex and can lead to the formation of other products from the initially formed intermediates.[6] The acylation of α sulfonyl carbanions with bifunctional reagents can also lead to undesired competing reactions.[7] For example, when ethyl bromoacetate is reacted with a sulfonyl carbanion, products of both acylation and alkylation can result.[7a] Hence, the ability to effect the selective acylation of sulfones with acid derivatives having other potentially reactive substituents would be a desirable synthetic transformation.

Results and Discussion

Our attempts to acylate the dianion of the hydroxy sulfone **1**[6b] with some esters led predominantly to recovered starting material. These results led us to examine this reaction in closer detail (eq 1). The hydroxy sulfone **1** was



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(3) For some recent uses of hydroxy sulfones in synthesis see: (a) Ichikawa, Y.; Isobe, M.; Masaki, H.; Kawai, T.; Goto, T. *Tetrahedron* **1987**, *43*, 4759. (b) Brimble, M. A.; Officer, D. L.; Williams, G. M. *Tetrahedron Lett.* **1988**, *29*, 3609. (c) Alzerreca, A.; Aviles, M.; Collazo, L.; Prieto, A. *J. Heterocycl. Chem.* **1990**, *27*, 1729. (d) Robin, S.; Huet, F. *Tetrahedron Lett.* **1993**, *34*, 2945. (e) Kozikowski, A. P; Mugrage, B. B.; Lu, C. S., Felder, L. *Tetrahedron Lett.* **1986**, *27*, 4817. (f) Tanikaga, R.; Hosoya, K.; Kaji, A. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1799. (g) Sato, T.; Okumura, Y.; Itai, J.; Fujisawa, T. *Chem. Lett.* **1988**, 1537. (h) Tanikaga, R.; Hosoya, K.; Hamamura, K.; Kaji, A. *Tetrahedron Lett.* **1987**, *28*, 3705. (i) Solladié, G.; Frechou, C.; Demailly, G.; Greck, C. *J. Org. Chem.* **1986**, *51*, 1912. (j) Yamamoto, K.; Shimizu, M.; Yamada, S.; Iwata, S.; Hoshino, O. *J. Org. Chem.* **1992**, *57*, 33. (k) Solladié, G.; Lohse, O. *J. Org. Chem.* **1993**, *58*, 4555. (l) Keck, G. E.; Kachensky, D. F.; Enholm, E. J. *J. Org. Chem.* **1985**, *50*, 4317. (m) Williams, D. R.; Moore, J. L.; Yamada, M. *J. Org. Chem.* **1986**, *51*, 3916.

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(7) (a) Julia, M.; Badet, B. *Bull. Soc. Chim. Fr.* **1976**, 525. (b) Mussatto, M. C.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1980**, *45*, 4002. (c) Mussatto, M. C.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 260.

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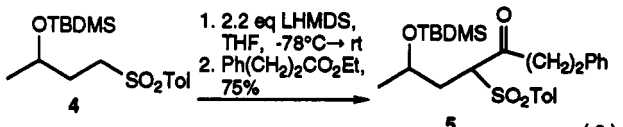
first deprotonated with 3 equiv of lithium (hexamethyldisilyl)amide (LHMDS) and then treated with ethyl 3-phenylpropionate at −78 °C and the reaction subsequently allowed to warm to room temperature. The product from this reaction was then purified. The desired product from acylation of the α-sulfonyl carbanion was not isolated. Instead, the unreacted hydroxy sulfone **1** and its trimethylsilylated derivative[8] **2** were isolated in 17% and 60% yields, respectively. In addition, the Claisen condensation product **3** was obtained in 78% yield (from ethyl 3-phenylpropionate). The results were similar when 2.2 equiv of LHMDS was used to achieve the deprotonation of sulfone **1**. When *n*-BuLi (2.1 equiv) was used as the base in this reaction, **1** was recovered in 73% yield along with ester **3** (78% yield). This clearly suggests that rapid proton exchange had occurred between the sulfone and ethyl 3-phenylpropionate under the reaction conditions. In contrast, the TBDMS-protected hydroxy sulfone **4**, could be readily acylated with ethyl 3-phenylpropionate to give the desired product **5**, in 75% yield (eq 2). These

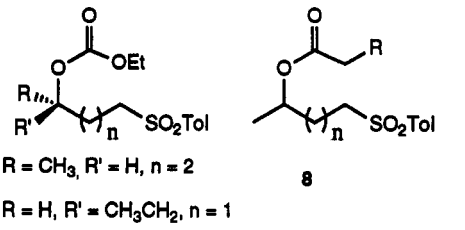


(2)

results led us to examine the intramolecular acylation reactions of hydroxy sulfones as an alternate strategy for their functionalization.

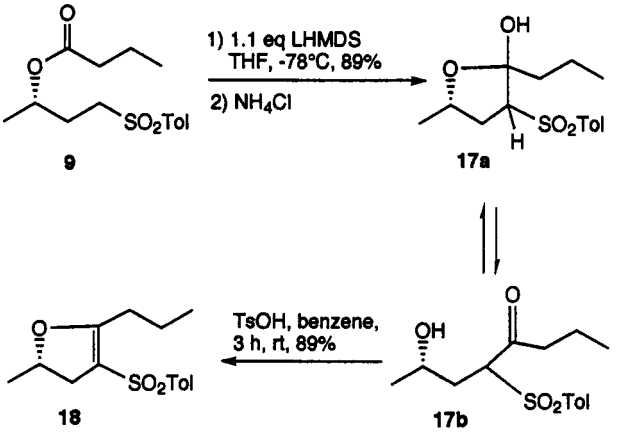
The deprotonation of the mixed carbonates **6** and **7** with LHMDS at −78 °C in THF has been reported to give the corresponding sulfonyl carbanions that undergo ring closure to give some chiral lactones.[5a] In contrast, the intramolecular acylation reactions of sulfones of the type **8** are expected to be more complex. pK_a data indicate that the protons adjacent to the ester and the sulfone are of comparable acidity, and hence, selective deprotonation α to the sulfone could be problematic.[9] If the sulfonyl carbanion does form preferentially, its potential equilibration to give an ester enolate could adversely effect the desired transformation. There have been only a few reports on the successful intramolecular acylations of simple sulfones with esters, anhydrides, and amides.[10] Hence, it was difficult to predict whether selective anion formation adjacent to the sulfonyl moiety followed by intramolecular acyl transfer could be achieved efficiently in substrates such as **8** in a synthetically useful manner. Here, we would like to present the results of our study on the preparation and intramolecular acyl transfer reactions of a number of acyloxy sulfones. The ready availability of some chiral nonracemic hydroxy sulfones in high optical purities (≥98%) has allowed us to also demonstrate the value of this methodology to asymmetric synthesis.

The esterification of (*S*)-**1** and (*S*)-(*p*-tolylsulfonyl)-3-pentanol[4a] with various acid chlorides in the presence of



triethylamine in ether proceeded cleanly to give the desired derivatives in high yields (Table 1). The deprotonation of the sulfone **9** was accomplished by addition of 1.1 equiv of LHMDS to a solution of the substrate in THF at −78 °C. The reaction was stirred at −78 °C for 2 h and then quenched with saturated ammonium chloride at −78 °C. The crude product upon purification gave a mixture of the lactol **17a** and the open chain hydroxy ketone **17b** in good yields (Scheme 1). The diastereomeric mixture **17** was dehydrated with TsOH in benzene to the chiral dihydrofuran **18**. The dehydration of the lactol was extremely facile and could be achieved under a variety of mildly acidic conditions.

Scheme 1. Intramolecular Acylation of 9



The intramolecular acylation reactions of substrates **10**–**16** have also been examined using a procedure similar to that used for **9**. In the case of substrates **10**–**15**, the products obtained were once again an equilibrium mixture of the expected lactol and the corresponding open chain hydroxy ketone as clearly supported by ^1H NMR and IR spectroscopy (Table 2).[11] This mixture was usually obtained as the major product of the reaction along with some residual starting material. Our studies show that this reaction is extremely facile and is compatible with the presence of a variety of sensitive functionality in the acyl side chain. The ring closure to give 5- or 6-membered ring lactols appears to be faster than other potentially competing reactions. Even for the diester **12**, where alternate cyclization pathways are available, intramolecular acylation occurred to give the 5-membered ring lactol **21** exclusively. It is of interest to mention that the carbamate **16** gave the open chain hydroxy amide **25** as expected. This is in contrast to the cyclization of the carbonates **6** and **7** to give lactones.

The major product from the intramolecular acylation reaction was an inseparable equilibrium mixture of lactol and hydroxy ketone which could be purified by chromatography. However, the ^1H NMR of these products were rather complex due to the fact that they are diastereomeric

(8) Silylation of alcohols with HMDS has been reported; see: Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991, pp 68–73.

(9) (a) Bordwell, F. G.; Harrelson, J. A., Jr.; Zhang, X. *J. Org. Chem.* **1991**, *56*, 4448. (b) Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978, pp 36–85.

(10) For examples of intramolecular acylation reaction of sulfones see: (a) Reutrakul, V.; Tuchinda, P.; Kusamran, K. *Chem. Lett.* **1979**, 1055. (b) Babudri, F.; Florio, S.; Vitrani, A.; Di Nunno, L. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1899. (c) Gaoni, Y. *Tetrahedron Lett.* **1976**, 503. (d) Grimm, E. L.; Coutu, M. L.; Trimble, L. A. *Tetrahedron Lett.* **1993**, *34*, 7017. (e) Yang, Y.-L.; Manna, S.; Falck, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 3811. (f) Date, M.; Watanabe, M.; Furukawa, S. *Chem. Pharm. Bull.* **1990**, *38*, 902.

(11) Alvarez, E.; Cuvigny, T.; du Penhoat, H.; Julia, M. *Tetrahedron* **1988**, *44*, 119.

Table 1. Preparation of Acyloxy Sulfones

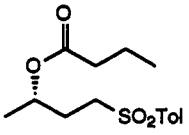
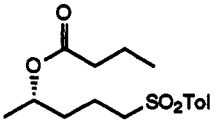
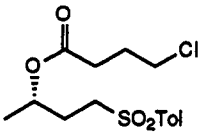
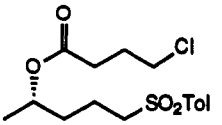
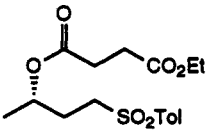
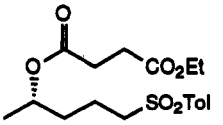
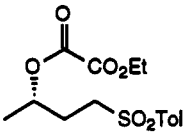
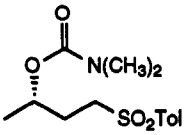
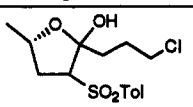
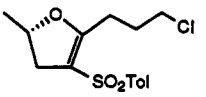
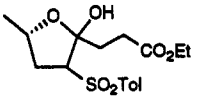
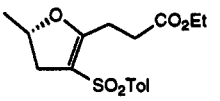
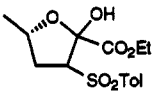
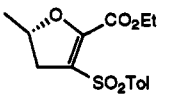
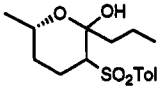
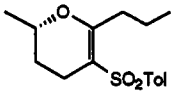
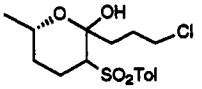
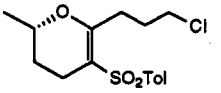
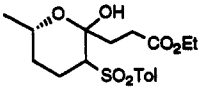
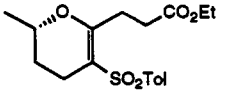
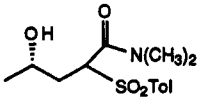
entry	ester	no.	yield (%)	entry	ester	no.	yield (%)
1		9	84	5		13	89
2		10	84	6		14	88
3		11	75	7		15	68
4		12	86	8		16	47

Table 2. Results of the Intramolecular Acylation of Substrates 10–16

entry	substrate	product	no.	yield (%)	dihydrofuran/dihydropyran	no.	yield (%)
1	10		19	52[a]		26	90[b]
2	11		20	56[a]		27	52[c]
3	12		21	75[a]		28	48[d]
4	13		22	75[a]		29	92[b]
5	14		23	56[a]		30	92[b]
6	15		24	70[a]		31	66[c]
7	16		25	60			

[a] Equilibrium mixture of lactols with corresponding hydroxy ketones. [b] Benzene, TsOH, 3 h. [c] 10% HCl/EtOH, 5 h. [d] Benzene, TsOH, reflux, 8 h.

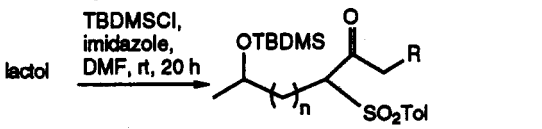
mixtures. Also, in a few cases, some dehydration of the lactols was observed during the chromatographic purification. The transformation of these intermediates to chiral nonracemic dihydrofurans and dihydropyrans[12] could be readily achieved using mild acid catalysts in good yields (Table 2). These products were more stable and could be readily purified to homogeneity and completely characterized.

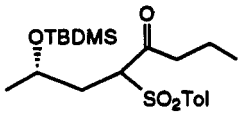
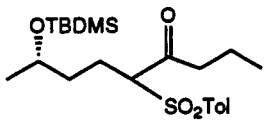
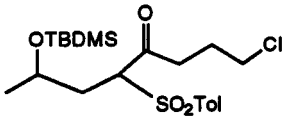
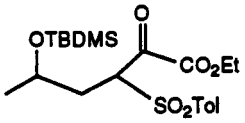
The trapping of the equilibrium mixture of lactols and hydroxy ketones as the open chain (*tert*-butyldimethylsilyl)oxy keto sulfones has also been investigated. TBDMS was chosen as the protecting group because it is expected to be stable to the reaction conditions of the subsequent desulfonylation. Further, it can be easily introduced under the near neutral conditions essential to avoid dehydration of these lactols to the dihydrofurans. Treatment of the diastereomeric mixture, for example, **17**, with *tert*-butyldimethylsilyl chloride in the presence of imidazole in DMF gave the protected ketosulfone as a mixture of diastereomers (1:1 by ^{1}H NMR) in good yields (Table 3).[11,13]

(12) For some reports on the preparation of dihydrofurans/dihydropyrans using sulfone chemistry see: (a) McCombie, S. W.; Shankar, B. B.; Ganguly, A. K. *Tetrahedron Lett.* **1987**, *28*, 4123. (b) McCombie, S. W.; Shankar, B. B.; Ganguly, A. K. *Tetrahedron Lett.* **1989**, *30*, 7029. (c) Lee, J. W.; Oh, D. Y. *Heterocycles* **1990**, *31*, 1417. (d) Pelter, A.; Ward, R. S.; Little, G. M. *J. Chem. Soc., Perkin Trans.* 1 **1990**, 2775. (e) Weichert, A.; Hoffmann, H. M. R. *J. Org. Chem.* **1991**, *56*, 4098.

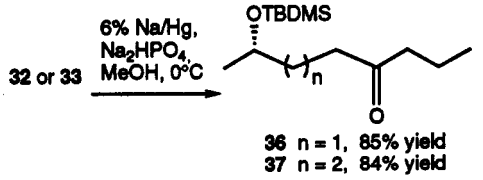
(13) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

Table 3. *tert*-Butyldimethylsilylation of Some Lactols



entry	lactol	TBDMS ether	no.	yield (%)
1	17		32	85
2	23		33	80
3	19		34	52
4	21		35	78

Lactols **19** and **21** prepared from racemic **10** and **12** could also be protected using this procedure in 52% and 78% yields, respectively. It was also possible to cleave the sulfonyl group of these protected keto sulfones using sodium mercury amalgam[14] to obtain TBDMS-protected hydroxy ketones (eq 3).



(3)

In conclusion, the intramolecular acyl-transfer reaction of acyl derivatives of γ- and δ-hydroxy sulfones has been shown to be an attractive route for the preparation of potentially valuable synthetic intermediates. The preparation of a number of chiral nonracemic dihydrofurans and dihydropyrans having varying substituents could be achieved in good yields from a readily available chiral hydroxy sulfone in three steps. The intermediate lactols from this study could also be protected as their open chain (*tert*-butyldimethylsilyl)oxy keto sulfones. Further extensions of this methodology and some applications to the synthesis of natural products are currently under investigation.

Experimental Section

General Procedures. Melting points were obtained on a Fisher Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Series 1600 spectrophotometer. ^{1}H NMR spectra were obtained on a Varian XL 200-MHz and ^{13}C spectra on a Varian Unity 400-MHz spectrometer in $CDCl_3$ using TMS as an internal standard unless otherwise noted. Optical rotations were measured using a Perkin-Elmer 241 polarimeter. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Mass spectroscopic analyses were obtained on a Hewlett-Packard (HP) 5995A GC/MS operating at 70 eV using a direct insertion probe (DIP).

(14) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

Column chromatography was performed on silica gel 60 (70–230 mesh) obtained from EM Science. For analytical and preparative thin-layer chromatography silica 60/F254 plastic- or glass-backed plates (EM Science) were used. Some of the compounds were purified using a Chromatotron (Harrison Scientific) on silica gel 60 plates as indicated. All solvents for chromatography were HPLC grade and were obtained from either Fisher Scientific Co. or VWR Scientific Co.

THF was freshly distilled from sodium/benzophenone. Reagents obtained from Aldrich Chemical Co. were used without purification unless otherwise noted. Lithium bis(trimethylsilyl)-amide (LHMDS) was obtained from Aldrich as a 1.0 M solution in hexane. The (*S*)-(*p*-tolylsulfonyl)-3-pentanol and (*S*)-4-(*p*-tolylsulfonyl)-2-butanol needed for this study were prepared in ≥98% ee by bakers' yeast reduction of the corresponding keto sulfone.[4a]

Acylation of Hydroxy Sulfones. Representative Procedure. (*S*)-1-Methyl-3-(*p*-tolylsulfonyl)propyl Butanoate (9). To a solution of (*S*)-**1**[4a] (0.528 g, 2.32 mmol) in ether (3 mL) at 0 °C under N_2 was added butyryl chloride (1.2 mL, 11.6 mmol, previously dried with CaH_2) and triethylamine (0.64 mL, 4.6 mmol) and the mixture stirred at room temperature for 6 h. The mixture was diluted with ether (50 mL) and washed with 2 N HCl (40 mL), saturated $NaHCO_3$ (40 mL), and NaCl (40 mL). The organic layer was dried ($MgSO_4$) and filtered and the solvent removed *in vacuo* to give the crude ester (0.795 g). The crude product was purified by silica gel chromatography (10% ethyl acetate/hexane) to give **9** (0.579 g, 84.0%) as a colorless oil: $[\alpha]_D$ −1.6° (*c* 1.8, $CHCl_3$); IR (neat) 2967, 2991, 2876, 1732, 1598 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.79 and 7.38 (AB q, *J* = 8.4 Hz, 4 H), 5.01–4.85 (m, 1 H), 3.17–3.04 (m, 2 H), 2.47 (s, 3 H), 2.22 (t, *J* = 7.3 Hz, 2 H), 1.90 (m, 2 H), 1.69–1.50 (m, 2 H), 1.58 (d, *J* = 6.3 Hz, 3 H), 0.92 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 172.9, 144.8, 136.0, 130.0, 128.1, 68.5, 52.8, 36.3, 29.0, 21.6, 19.9, 18.4, 13.6. Anal. Calcd for $C_{15}H_{22}O_4S$: C, 60.37; H, 7.43. Found: C, 60.65; H, 7.71.

(*S*)-1-Methyl-3-(*p*-tolylsulfonyl)propyl 4-Chlorobutanoate (10). A procedure similar to that used to prepare **9** was followed. The product **10** was isolated as an oil in 83.6% yield after chromatographic purification: $[\alpha]_D$ −3.1° (*c* 6.6, MeOH); IR (neat) 2982, 2931, 1732, 1598 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.80 and 7.38 (AB q, *J* = 8.3 Hz, 4 H), 5.06–4.90 (m, 1 H), 3.57 (t, *J* = 6.2 Hz, 2 H), 3.18–3.07 (m, 2 H), 2.46 (s, 3 H), 2.44 (t, *J* = 7.3 Hz, 2 H), 2.14–1.91 (m, 4 H), 1.22 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 172.0, 144.9, 135.9, 130.0, 128.1, 69.0, 52.7, 44.0, 31.3, 28.9, 27.5, 21.7, 19.8. Anal. Calcd for $C_{15}H_{21}ClO_4S$: C, 54.13; H, 6.36. Found: C, 53.97; H, 6.33.

(*S*)-Ethyl 1-Methyl-3-(*p*-tolylsulfonyl)propyl Succinate (11). A procedure similar to that used to prepare **9** was followed. The product **11** was isolated as an oil in 74.8% yield after chromatographic purification: $[\alpha]_D$ −7.5° (*c* 2.6, $CHCl_3$); IR (neat) 2984, 2931, 1732, 1598 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.80 and 7.38 (AB q, *J* = 8.2 Hz, 4 H), 5.03–4.90 (m, 1 H), 4.12 (q, *J* = 7.1 Hz, 2 H), 3.29–3.00 (m, 2 H), 2.57 (s, 4 H), 2.47 (s, 3 H), 2.19–1.91 (m, 2 H), 1.25 (t, *J* = 7.3 Hz, 3 H), 1.22 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 172.2, 171.7, 144.8, 136.0, 130.0, 128.1, 69.2, 60.7, 52.7, 29.3, 29.1, 29.0, 21.6, 19.9, 14.2. Anal. Calcd for $C_{17}H_{24}O_6S$: C, 57.28; H, 6.79. Found: C, 57.21; H, 6.82.

Ethyl (*S*)-1-Methyl-3-(*p*-tolylsulfonyl)propyl Oxalate (12). A procedure similar to that used to prepare **9** was followed. The product **12** was isolated as an oil in 85.9% yield after chromatographic purification: $[\alpha]_D$ +4.3° (*c* 2.1, MeOH); IR (neat) 2985, 2938, 1766, 1745, 1598 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.80 and 7.38 (AB q, *J* = 8.0 Hz, 4 H), 5.21–5.04 (m, 1 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 3.39–3.04 (m, 2 H), 2.47 (s, 3 H), 2.18–2.03 (m, 2 H), 1.37 (t, *J* = 7.1 Hz, 3 H), 1.34 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.6, 157.2, 145.0, 135.8, 130.1, 128.1, 72.4, 63.2, 52.4, 28.8, 21.6, 19.5, 13.9. Anal. Calcd for $C_{15}H_{20}O_6S$: C, 54.86; H, 6.14. Found: C, 54.63; H, 6.23.

(*S*)-1-Methyl-4-(*p*-tolylsulfonyl)butyl Butanoate (13). A procedure similar to that used to prepare **9** was followed starting with (*S*)-(*p*-tolylsulfonyl)-3-pentanol.[4a] The crystalline product **13** was isolated in 89.1% yield after chromatographic purification: $[\alpha]_D$ +9.8° (*c* 2.4, $CHCl_3$); mp 39–39.5 °C; IR (KBr) 2966, 2875, 1729, 1597, 1457 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.78 and 7.37 (AB q, *J* = 8.3 Hz, 4 H), 4.97–4.82 (m, 1 H), 3.08 (t, 3

H), 2.46 (s, 3 H), 2.21 (t, J = 7.2 Hz, 2 H), 1.88–1.53 (m, 6 H), 1.80 (d, J = 6.4 Hz, 3 H), 0.92 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 173.2, 144.7, 136.1, 129.9, 128.1, 69.4, 55.9, 36.4, 34.3, 21.6, 19.9, 18.9, 18.5, 13.6. Anal. Calcd for $C_{16}H_{24}O_4S$: C, 61.51; H, 7.74. Found: C, 61.59; H, 7.56.

(*S*)-1-Methyl-4-(*p*-tolylsulfonyl)butyl 4-Chlorobutanoate (14). A procedure similar to that used to prepare **9** was followed starting with (*S*)-(*p*-tolylsulfonyl)-3-pentanol.[4a] The product **14** was isolated as an oil in 88.0% yield after chromatographic purification: $[\alpha]^{20}_D$ +10.0° (c = 3.2, $CHCl_3$); IR (neat) 2976, 2907, 1728, 1596 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.78 and 7.37 (AB q, J = 8.4 Hz, 4 H), 4.91–4.83 (m, 1 H), 3.57 (t, J = 6.4 Hz, 2 H), 3.14–3.01 (m, 2 H), 2.46 (s, 3 H), 2.43 (t, J = 7.6 Hz, 2H), 2.09–1.98 (m, 2 H), 1.83–1.57 (m, 4 H), 1.20 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 172.1, 144.7, 136.2, 129.9, 128.0, 70.0, 55.9, 44.0, 34.3, 31.5, 27.6, 21.6, 19.8, 18.9. Anal. Calcd for $C_{16}H_{23}ClO_4S$: C, 55.40; H, 6.68. Found: C, 55.68; H, 6.62.

(*S*) Ethyl 1-Methyl-4-(*p*-tolylsulfonyl)butyl Succinate (15). A procedure similar to that used to prepare **9** was followed starting with (*S*)-(*p*-tolylsulfonyl)-3-pentanol.[4a] The product **15** was isolated as an oil in 68.2% yield after chromatographic purification: $[\alpha]^{20}_D$ +5.38° (c = 2.8, $CHCl_3$); IR (neat) 2980, 2927, 1732, 1597 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 and 7.36 (AB q, J = 8.4 Hz, 4 H), 4.92–4.82 (m, 1 H), 4.14 (q, J = 7.2 Hz, 2 H), 3.13–3.01 (m, 2 H), 2.59–2.54 (dt, 4 H), 2.46 (s, 3 H), 1.82–1.53 (m, 4 H), 1.26 (t, J = 7.2 Hz, 3 H), 1.19 (d, J =6.4Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 172.2, 171.8, 144.7, 136.3, 129.9, 128.1, 70.2, 60.7, 55.9, 34.3, 29.4, 29.2, 21.6, 19.8, 18.9, 14.2. Anal. Calcd for $C_{18}H_{26}O_6S$: C, 58.36; H, 7.07. Found: C, 58.14; H, 7.04.

(*S*)-1-Methyl-3-(*p*-tolylsulfonyl)propyl-*N*,*N*-Dimethylcarbamate (16). A procedure similar to that used to prepare **9** was followed except the reaction mixture was refluxed for 72 h. The product **16** was isolated as an oil in 46.8% yield after chromatographic purification: $[\alpha]_D$ +24.2° (c 2.3, $CHCl_3$); IR (neat) 2932, 1699, 1597 cm^{-1}; ^{1}H NMR (400 NHz, $CDCl_3$) δ 7.78 and 7.36 (AB q, J = 7.9 Hz, 4 H), 4.84–4.78 (m, 1 H), 3.21–3.09 (m, 2 H), 2.87 (s, 3 H), 2.84 (s, 3 H), 2.46 (s, 3 H), 1.99–1.92 (m, 2 H), 1.22 (d, J = 6.7 Hz, 3 H);^{13}C NMR (400 MHz, $CDCl_3$) δ 155.8, 144.8, 136.0, 129.9, 128.0, 69.6, 53.0, 36.4, 35.8, 29.3, 21.6, 20.4. Anal. Calcd for $C_{14}H_{21}NO_4S$: C, 56.17; H, 7.07; N, 4.68. Found: C, 56.00; H, 6.90; N, 4.55.

Representative Procedure for Intramolecular Acylation Reactions. Preparation of Lactol 17 from 9. To a solution of the sulfone **9** (0.292 g, 0.980 mmol) in freshly distilled THF (27 mL) at −78 °C under N_2 was added LHMDS (1.07 mL, 1.07 mmol). The solution was stirred at −78 °C for 2 h and then quenched at −78 °C in saturated NH_4Cl (30 mL). The product was extracted into ethyl acetate (2 × 30 mL), washed with saturated NaCl (30 mL), dried ($MgSO_4$), and filtered and the solvent removed *in vacuo* to give an oil (0.304 g, 104%). Purification by silica gel chromatography on the Chromatotron (33%–50% ethyl acetate/hexane) gave as an oil the product **17** which was a mixture of the lactol and hydroxy ketone (0.259 g, 88.7%): IR (neat) 3509, 2967, 2992, 2875, 1716, 1597, 1455 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_4S$: C, 60.37; H, 7.43. Found: C, 60.57; H, 7.49. The identity of product **17** was further confirmed by its conversion to the corresponding dihydrofuran **18** which was completely characterized.

Preparation of Lactol 19 from 10. A procedure similar to that used to prepare **17** was followed. The product **19** was isolated as a mixture of the lactol and the hydroxy ketone in 47.3% yield after chromatographic purification: IR (neat) 3511, 2969, 2928, 1721, 1598 cm^{-1}. The identity of product **19** was confirmed by its conversion to the corresponding dihydrofuran **26** which was completely characterized.

Preparation of Lactol 20 from 11. A procedure similar to that used to prepare **17** was followed except 2 equiv of LHMDS was used to effect deprotonation. The product **20** was isolated as a mixture of the lactol and the hydroxy ketone in 56.3% yield after chromatographic purification: IR (neat) 3506, 2979, 2931, 1732 br, 1598 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_6S$: C, 57.28; H, 6.79. Found: C, 57.40; H, 6.94. The identity of product **20** was further confirmed by its conversion to the corresponding dihydrofuran **27** which was completely characterized.

Preparation of Lactol 21 from 12. A procedure similar to that used to prepare **17** was followed. The product **21** was isolated as a mixture of the lactol and the hydroxy ketone in 74.5% yield after chromatographic purification: IR (neat) 3453, 2980, 2932, 1747, 1597 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_6S$: C, 54.86; H, 6.14. Found: C, 54.54; H, 6.29. The identity of product **21** was further confirmed by its conversion to the corresponding dihydrofuran **28** which was completely characterized.

Preparation of Lactol 22 from 13. A procedure similar to that used to prepare **17** was followed. The product **22** was isolated as a mixture of the lactol and the hydroxy ketone in 74.8% yield after chromatographic purification: IR (neat) 3526, 3049, 2966, 2933, 2876, 1716, 1597 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_4S$: C, 61.51; H, 7.74. Found: C, 61.43; H, 7.86. The identity of product **22** was further confirmed by its conversion to the corresponding dihydropyran **29** which was completely characterized.

Preparation of Lactol 23 from 14. A procedure similar to that used to prepare **17** was followed. The product **23** was isolated as a mixture of lactol and the hydroxy ketone in 56.2% yield after chromatographic purification: IR (neat) 3515, 2967, 1721, 1597 cm^{-1}. The identity of product **23** was confirmed by its conversion to the corresponding dihydropyran **30** which was completely characterized.

Preparation of Lactol 24 from 15. A procedure similar to that used to prepare **17** was followed except 2 equiv of LHMDS was used to effect deprotonation. The product **24** was isolated as a mixture of the lactol and the hydroxy ketone in 69.7% yield after chromatographic purification: IR (neat) 3514, 2971, 2892, 1723 br, 1597cm^{-1}. The identity of product **24** was confirmed by its conversion to the corresponding dihydropyran **31** which was completely characterized.

Preparation of Hydroxyamide 25 from 16. A procedure similar to that used to prepare **17** was followed. The product **25** was isolated as an inseparable mixture of hydroxyamide diastereomers in 60.3% yield: IR (KBr) 3457, 2971, 1738, 1651, 1597 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 and 7.70 (AB q, J = 3.0, 4 H), 4.78–4.71 (m, 1 H), 4.57–4.50 (m, 1 H), 3.92–3.83 (m, 1 H), 3.62–3.52 (m, 1 H), 3.15 (s, 3 H), 3.14, (s, 3 H), 2.98 (s, 3 H), 2.95 (s, 3 H), 2.44 (s, 3 H), 2.17–1.83 (m, 2 H), 1.17 (d, J = 6.1 Hz, 3 H), 1.14 (d, J = 6.4 Hz, 3 H). Anal. Calcd for $C_{14}H_{21}NO_4S$: C, 56.17; H, 7.07; N, 4.68. Found: C, 55.90; H, 7.05: N, 4.53.

Elimination of lactols to dihydrofurans and dihydropyrans. Representative procedure. (5*S*)-Methyl-2-propyl-3-(*p*-tolylsulfonyl)-4,5-dihydrofuran (18). To a solution of the lactol/hydroxy ketone mixture **17** (54.5 mg, 0.183 mmol) in benzene (1 mL) was added a catalytic amount of TsOH and the reaction mixture stirred at room temperature for 3 h. Anhydrous Na_2SO_4 and K_2CO_3 were added and the mixture stirred for 15 min. The mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a short silica gel column to give as an oil the dihydrofuran **18** (45.7 mg, 89.2%) which was homogeneous by TLC: $[\alpha]_D$ -43.6° (c 1.6, $CHCl_3$); IR (neat) 2965, 2930, 2872, 1632, 1598 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75 and 7.32 (AB q, J = 7.9 Hz, 4 H), 4.84–4.64 (m, 1 H), 3.03–2.89 (m, 1 H), 2.65 (t, J = 7.1 Hz, 2 H), 2.52 (m, 1 H), 2.43 (s, 3 H), 1.72–1.53 (m, 2 H), 1.30 (d, J = 6.3 Hz, 3 H), 0.97 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 168.4, 143.4, 139.4, 129.7, 126.8, 108.2, 78.4, 37.3, 28.7, 21.6, 21.5, 20.3, 13.8. Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.25; H, 7.19. Found: C, 63.91; H, 7.11.

(*S*)-2-(3-Chloropropyl)-5-methyl-3-(*p*-tolylsulfonyl)-4,5-dihydrofuran (26). A procedure similar to that used to prepare **18** was followed. The product **26** was prepared from **19** and isolated as an oil in 90.0% yield after chromatographic purification: $[\alpha]_D$ -31.2° (c 1.4, $CHCl_3$); IR (neat) 2975, 2927, 2869, 1633, 1598 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75 and 7.33 (AB q, J = 8.0 Hz, 4 H), 4.85–4.46 (m, 1 H), 3.58 (t, J = 6.7 Hz, 2 H), 3.14–2.78 (complex, 3 H), 2.54–2.38 (m, 1 H), 2.44 (s, 3 H), 2.17–1.99 (m, 2 H), 1.31 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 166.8, 143.6, 139.4, 129.8, 126.8, 109.1, 78.8, 44.1, 37.2, 29.9, 24.6, 21.6. Anal. Calcd for $C_{15}H_{19}ClO_3S$: C, 57.23; H, 6.08. Found: C, 57.43; H, 6.09.

(*S*)-2-[2-(Ethoxycarbonyl)ethyl]-5-methyl-3-(*p*-tolylsulfonyl)-4,5-dihydrofuran (27). A solution of the lactol/hydroxy ketone mixture **20** (0.0546 g, 0.153 mmol) in 10% ethanolic HCl (2 mL) was stirred for 5 h at room temperature. The solvent was then removed *in vacuo* and the remaining residue redissolved in CH_2Cl_2 (2 mL). Solid K_2CO_3 and Na_2SO_4 were then added, and

the mixture was stirred for 15 min. The mixture was then filtered through a short silica gel column (CH_2Cl_2). The solvent was removed *in vacuo* and the crude reaction mixture purified by preparative thin-layer chromatography (50% ethyl acetate/hexane) to give the dihydrofuran **27** (0.0267 g, 51.5%) as an oil: $[\alpha]_D$ −30.5° (*c* 1.1, $CHCl_3$); IR (neat) 2980, 2917, 1733, 1634, 1601 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.77 and 7.33 (AB q, *J* = 8.2 Hz, 4 H), 4.81–4.62 (m, 1 H), 4.14 (q, *J* = 7.0 Hz, 2 H), 3.15–2.84 (complex, 3 H), 2.58 (t, *J* = 7.6 Hz, 2 H), 2.44 (s, 3 H), 2.48–2.37 (m, 1 H), 1.28 (d, *J* = 6.4 Hz, 3 H), 1.26 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 172.1, 166.2, 143.6, 139.5, 129.7, 126.9, 109.1, 78.8, 60.6, 37.2, 31.0, 22.6, 21.6, 21.5, 14.2; MS *m/z* (relative intensity) 338 (3), 182 (100). Anal. Calcd for $C_{17}H_{22}O_5S \cdot 0.5\ H_2O$: C, 58.82; H, 6.67. Found: C, 58.84; H, 6.70.

(*S*)-2-(Ethoxycarbonyl)-5-methyl-3-(*p*-tolylsulfonyl)-4,5-dihydrofuran (28). To a solution of the lactol/hydroxy ketone mixture **21** (68.9 mg, 0.210 mmol) in benzene (3 mL) at reflux was added a catalytic amount of TsOH and the solution heated at reflux for 8 h. The reaction was cooled, K_2CO_3 and Na_2SO_4 were added, and the resulting mixture was stirred for 15 min. The mixture was then filtered through a short silica gel column (CH_2Cl_2). The solvent was removed *in vacuo*. The crude product was purified by preparative thin layer chromatography (50% ethyl acetate/hexane) to give the dihydrofuran **28** (31.2 mg, 47.9%) as an oil: $[\alpha]_D$ −32.5° (*c* 1.0, $CHCl_3$); IR (neat) 2981, 2932, 1747, 1636, 1598 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.88 and 7.35 (AB q, *J* = 8.4 Hz, 4 H), 5.10–4.89 (m, 1 H), 4.39 (q, *J* = 7.1 Hz, 2 H), 3.21–3.06 (m, 1 H), 2.70–2.59 (m, 1 H), 2.45 (s, 3 H), 1.41 (d, *J* = 6.2 Hz, 3 H), 1.39 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 159.5, 153.5, 144.3, 138.3, 129.7, 127.6, 116.2, 81.9, 62.8, 37.3, 21.6, 21.4, 13.9. Anal. Calcd for $C_{15}H_{18}O_5S$: C, 58.05; H, 5.85. Found: C, 57.86; H, 5.78.

(6*S*)-Methyl-2-propyl-3-(*p*-tolylsulfonyl)-5,6-dihydropyran (29). A procedure similar to that used for **18** was followed. The product **29** was prepared from **22** and was isolated as an oil in 92.1% yield after chromatographic purification: $[\alpha]_D$ −113.3° (*c* 2.4, $CHCl_3$); IR (neat) 2962, 2932, 2873, 1615 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.76–7.27 (m, 4 H), 4.04–3.88 (m, 1 H), 2.81–2.52 (m, 2 H), 2.42 (s, 3 H), 2.40–2.30 (m, 2 H), 1.82–1.98 (m, 1 H), 1.39–1.66 (m, 3 H), 1.26 (d, *J* = 6.3 Hz, 3 H), 0.91 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 165.7, 143.2, 139.9, 129.5, 126.8, 110.2, 72.7, 33.9, 28.4, 22.1, 21.5, 21.1, 20.3, 13.9. Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.27; H, 7.53. Found: C, 65.49; H, 7.73.

(*S*)-2-(3-Chloropropyl)-6-methyl-3-(*p*-tolylsulfonyl)-5,6-dihydropyran (30). A procedure similar to that used for **18** was followed. The crystalline product **30** was prepared from **23** in 91.9% yield after chromatographic purification: $[\alpha]^{20}_D$ −106.1° (*c* = 2.1, $CHCl_3$); mp 98.5–99°; IR (KBr) 2974, 2920, 1618 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 and 7.30 (AB q, *J* = 8.0 Hz, 4 H), 4.00–3.93 (m, 1 H), 3.56 (t, *J* = 6.8 Hz, 2 H), 2.94–2.72 (m, 2 H), 2.43 (s, 3 H), 2.31–2.25 (m, 2 H), 2.11–1.97 (m, 2 H), 1.93–1.83 (m, 1 H), 1.52–1.42 (m, 1 H), 1.27 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 164.0, 143.4, 139.7, 129.6, 126.8, 111.1, 73.0, 44.5, 30.8, 29.9, 28.3, 22.1, 21.5, 20.3. Anal. Calcd for $C_{16}H_{21}O_3SCl$: C, 58.44; H, 6.44. Found: C, 58.60; H, 6.24.

(*S*)-2-[2-(Ethoxycarbonyl)ethyl]-6-methyl-3-(*p*-tolylsulfonyl)-5,6-dihydropyran (31). A procedure similar to that used to prepare **27** was followed. The product **31** was prepared from **25** and isolated as an oil in 65.9% yield after chromatographic purification: $[\alpha]^{20}_D$ −100.4° (*c* = 1.3, $CHCl_3$); IR (neat) 2980, 2935, 1732, 1621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 and 7.30 (AB q, *J* = 8.0 Hz, 4 H), 4.13 (q, *J* = 7.2 Hz, 2 H), 3.97–3.91 (m, 1 H), 3.18–2.93 (m, 2 H), 2.57–2.48 (m, 2 H), 2.42 (s, 3 H), 2.38–2.30 (m, 2 H), 1.92–1.83 (m, 1 H), 1.57–1.41 (m, 1 H), 1.26 (t, *J* = 7.6 Hz, 3 H), 1.26 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 172.6, 163.3, 143.4, 139.5, 129.6, 126.8, 111.0, 73.1, 60.4, 31.9, 28.3, 27.6, 22.1, 21.5, 20.2, 14.2. Anal. Calcd for $C_{18}H_{24}O_5S$: C, 61.34; H, 6.86. Found: C, 61.17; H, 6.77.

***tert*-Butyldimethylsilylation of Lactols. Representative procedure. 7(*S*)-[(*tert*-Butyldimethylsilyl)oxy]-5-(*p*-tolylsulfonyl)-4-octanone (32).** To a solution of the lactol/hydroxy ketone mixture **17** (0.102 g, 0.342 mmol) in DMF (1.5 mL) under N_2 was added imidazole (58.2 mg, 0.855 mmol) followed by *tert*-butyldimethylsilyl chloride (77.3 mg, 0.513 mmol) and the solution stirred for 20 h. The reaction was diluted with CH_2Cl_2 (30 mL), washed with water (2 × 40 mL), dried ($MgSO_4$), and filtered and the solvent removed *in vacuo*. The crude product was purified by silica gel chromatography on a Chromatotron (33%–50% ethyl acetate/hexane) to give as an oil a diastereomeric mixture of the keto sulfone **32** (120 mg, 85.1%) which was inseparable by silica gel chromatography: IR (neat) 2957, 2931, 2857, 1722, 1601 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.62 and 7.33 (AB q, *J* = 8.3 Hz, 4 H), 4.46–4.37 (m, 1 H), 4.06–4.68 (m, 1 H), 3.09–2.52 (m, 2 H), 2.43 (s, 3 H), 2.22–1.57 (m, 4 H), 1.08 and 1.01 (d, *J* = 6.1 Hz, 3 H), 0.90 (t, *J* = 7.3 Hz, 3 H), 0.83 and 0.81 (s, 9 H), 0.06 and 0.03 (s, 6 H). Anal. Calcd for $C_{21}H_{36}O_4SSi$: C, 61.12; H, 8.79. Found: C, 60.96; H, 8.50.

(8*S*)-[(*tert*-Butyldimethylsilyl)oxy]-5-(*p*-tolylsulfonyl)-4-nonanone (33). The *tert*-butyldimethylsilylation of **22** was carried out using a procedure similar to that used for **17**. After chromatographic purification, the product **33** was obtained in 79.6% yield as an inseparable mixture of diastereomers: IR (neat) 2930, 2877, 1720, 1598 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.65 and 7.34 (AB q, *J* = 7.9 Hz, 4 H), 4.16–4.04 (m, 1 H), 3.83–3.77 (m, 1 H), 3.01–2.80 (m, 1 H), 2.70–2.54 (m, 1 H), 2.45 (s, 3 H), 2.09–1.57 (m, 4 H), 1.40–1.18 (m, 2 H), 1.05 (d, *J* = 6.2 Hz, 3 H), 0.93 (t, 7.2 Hz, 3 H), 0.85 and 0.82 (s, 9 H), 0.03 (s, 6 H). Anal. Calcd for $C_{22}H_{38}O_4SSi$: C, 61.93; H, 8.98. Found: C, 62.13; H, 8.83.

7-[(*tert*-Butyldimethylsilyl)oxy]-1-chloro-5-(*p*-tolylsulfonyl)-4-octanone (34). The *tert*-butyldimethylsilylation of racemic **19** was carried out using a procedure similar to that used for **17**. After chromatographic purification, the product **34** was obtained in 52.4% yield as an inseparable mixture of diastereomers: IR (neat) 2957, 2930, 2857, 1722, 1598 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.58 and 7.29 (AB q, *J* = 8.3 Hz, 4 H), 4.49–4.27 (m, 1 H), 4.05–3.70 (m, 1 H), 3.48 (t, *J* = 5.7 Hz, 2 H), 3.29–2.74 (m, 2 H), 2.39 (s, 3 H), 2.25–1.84 (m, 4 H), 1.04 and 0.96 (d, *J* = 6.1 Hz, 3 H), 0.77 and 0.75 (s, 9 H), 0.04 and 0.02 (s, 6 H). Anal. Calcd for $C_{21}H_{35}ClO_4Si$: C, 56.41; H, 7.89. Found: C, 56.47; H, 7.53.

Ethyl 5-[(*tert*-butyldimethylsilyl)oxy]-2-oxo-3-(*p*-tolylsulfonyl)hexanoate (35). The *tert*-butyldimethylsilylation of racemic **21** was carried out using a procedure similar to that used for **17**. After chromatographic purification, the product **35** was obtained in 78.1% yield as an inseparable mixture of diastereomers: IR (neat) 2956, 2930, 2858, 1761, 1734, 1597 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.73 and 7.41 (AB q, *J* = 8.2 Hz, 4 H), 5.63–5.45 (m, 1 H), 4.36 (q, *J* = 7.2 Hz, 2 H), 4.12–3.88 (m, 1 H), 2.51 (s, 3 H), 2.43–2.10 (m, 2 H), 1.41 (t, *J* = 7.2 Hz, 3 H), 1.21 and 1.10 (d, *J* = 6.1 Hz, 3 H), 0.86 and 0.83 (s, 9 H), 0.08 and 0.03 (s, 6 H). Anal. Calcd for $C_{21}H_{34}O_6SSi$: C, 56.98; H, 7.74. Found: C, 57.27; H, 7.79.

7(*S*)-[(*tert*-Butyldimethylsilyl)oxy]-4-octanone (36). To a solution of the sulfone **32** (0.103 g, 0.250 mmol) in methanol (13 mL, 0.02 M) under N_2 at 0 °C were added Na_2HPO_4 (0.142 g, 1.00 mmol) and 6% sodium/mercury amalgam (1.25 g, 3.26 mmol), and the mixture was stirred at 0 °C for 3.5 h. The mixture was vacuum filtered through a silica gel column using ethyl acetate (50 mL) and the solvent removed *in vacuo*. The remaining residue was suspended in CH_2Cl_2 (20 mL) and filtered through a short silica gel column. The solvent was removed *in vacuo* to give **36** (55.1 mg, 85.3%) as a colorless oil: $[\alpha]_D$ +19.3° (*c* 1.5, $CHCl_3$); IR (neat) 2930, 2838, 1716 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.90–3.73 (m, 1 H), 2.51–2.33 (m, 4 H), 1.81–1.48 (m, 4 H), 1.09 (d, *J* = 6.0 Hz, 3 H), 0.88 (t, *J* = 7.3 Hz, 3 H), 0.85 (s, 9 H), 0.02 (s, 6 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 211.2, 67.6, 44.8, 38.7, 33.2, 25.9, 23.7, 18.1, 17.4, 13.8, −4.4, −4.8. Anal. Calcd for $C_{14}H_{30}SiO_2$: C, 65.06; H, 11.70. Found: C, 65.25; H, 11.99.

(*S*)-8-[(*tert*-Butyldimethylsilyl)oxy]-4-nonanone (37). Using a procedure similar to that used for **36**, the product **37** was prepared from **33** in 84.4% yield after chromatographic purification: $[\alpha]_D$ +12.6° (*c* 1.7, $CHCl_3$); IR (neat) 2958, 2930, 2857, 1716 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.88–3.73 (m, 1 H), 2.46–2.33 (m, 4 H), 1.72–1.32 (m, 6 H), 1.07 (d, *J* = 6.0 Hz, 3 H), 0.86 (t, *J* = 7.7 Hz, 3 H), 0.84 (s, 9 H), 0.04 (s, 6 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 211.7, 68.4, 44.7, 42.9, 39.1, 25.9, 23.7, 20.2, 18.1, 17.3, 13.8, −4.4, −4.7. Anal. Calcd for $C_{15}H_{32}O_2Si$: C, 66.11; H, 11.84. Found: C, 66.39; H, 12.04.