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# $\gamma$ -Chiral $\beta$ -ketosulfones in asymmetric synthesis: a unified synthetic strategy for enantiopure $\gamma$ -amino and $\gamma$ -hydroxy vinyl sulfones

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## Abstract

Enantiopure  $\gamma$ -hydroxy and  $\gamma$ -amino vinyl sulfones have been prepared in a short synthetic sequence from the chiral pool derived  $\gamma$ -acetoxy/amino  $\beta$ -ketosulfones. © 1998 Elsevier Science Ltd. All rights reserved.

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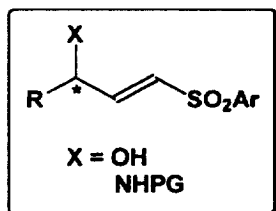
## 1. Introduction

In recent years,  $\gamma$ -chiral vinyl sulfones have evolved as useful chiral probes.<sup>1</sup>  $\gamma$ -Hydroxy vinyl sulfones have been extensively studied in this regard and through the pioneering works of Isobe<sup>1c</sup> and Fuchs<sup>1d</sup> and of late, by Carretero and others,<sup>2,3</sup> these synthons have shown impressive degrees of diastereoselection (1,2-asymmetric induction) in conjugate additions of organometallic and other heteroatomic nucleophiles to their enesulfone moiety. Such diastereoselective features have also found elegant use in several natural product syntheses.  $\gamma$ -Amino vinyl sulfones, the rational congeners, are equally interesting chiral probes and by analogy with vinylogous amino acid esters,<sup>4</sup> promise rich dividends in asymmetric synthesis. However, while  $\gamma$ -amino vinyl sulfones are altogether unknown,<sup>5</sup> synthetic studies with  $\gamma$ -hydroxy vinyl sulfones are restricted only to the racemic series due to the lack of a convenient and general synthetic repertoire for their enantiopure synthesis. Only recently, have a few enantiopure syntheses of  $\gamma$ -hydroxy vinyl sulfones appeared in the literature *viz.* lipase mediated resolution of racemic  $\gamma$ -hydroxy vinyl sulfones,<sup>6a</sup> regioselective dehydration of homochiral  $\beta,\gamma$ -dihydroxy sulfones<sup>6b</sup> and Peterson-olefination of enantiopure  $\alpha$ -alkoxy aldehydes<sup>3a</sup> which however suffer from lengthy sequences and/or are specific for a few substrate types. In order to enhance the overall appeal of  $\gamma$ -chiral vinyl sulfones in EPC synthesis, new synthetic methodologies need to be developed which would not only broaden the repertoire for enantiopure  $\gamma$ -hydroxy vinyl sulfones but would also provide access to a wide variety

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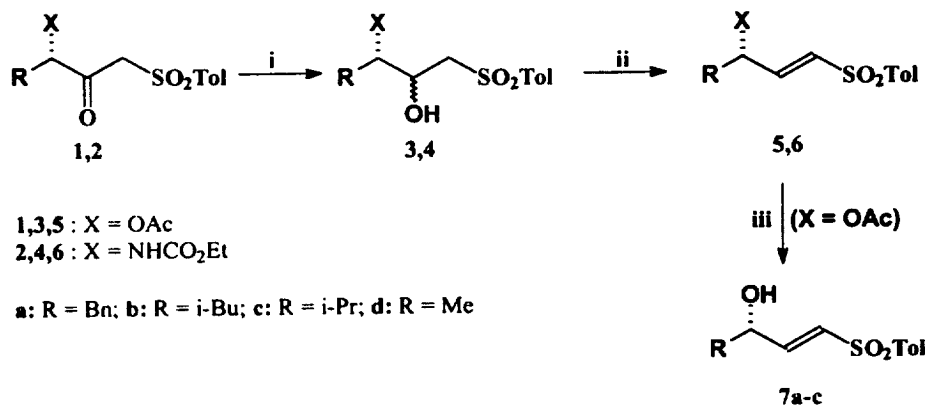
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of enantiopure  $\gamma$ -amino vinyl sulfones. In a program directed towards synthetic utilities of enantiopure  $\gamma$ -chiral- $\beta$ -ketosulfones,<sup>7</sup> we had the opportunity to address these propositions and present herein an unified chiral-pool strategy that leads to the enantiopure synthesis of both  $\gamma$ -hydroxy and  $\gamma$ -amino vinyl sulfones.



## 2. Results and discussion

Our synthetic strategy was designed according to the Julia-protocol<sup>8</sup> in which enantiopure  $\gamma$ -acetoxy and  $\gamma$ -amino- $\beta$ -ketosulfones upon reduction followed by dehydration, were envisaged to produce the respective  $\gamma$ -chiral vinyl sulfones in a short synthetic sequence. In the event, we started from the  $\gamma$ -acetoxy and  $\gamma$ -amino- $\beta$ -ketosulfones **1** and **2** which were readily prepared in high yields starting from the chiral pool derived enantiopure  $\alpha$ -acetoxy and  $\alpha$ -amino diazoketones, respectively, *via* sequential treatment with 47% HBr and NaSO<sub>2</sub>Tol, according to our recently published procedure.<sup>7a</sup> Alternatively, the  $\gamma$ -amino- $\beta$ -ketosulfones **2** could also be prepared through low temperature condensation of N-CO<sub>2</sub>Et protected amino acid esters with  $\alpha,\alpha$ -dilithio methyl tolyl sulfone.<sup>9</sup> Borohydride reduction of **1** and **2** was found to be *anti*-selective, as expected for chelation controlled reductions and produced the respective  $\beta$ -hydroxy sulfones **3** and **4** as diastereomeric mixtures (*anti:syn*  $\geq 75:35$ ) which, without further purification, were subjected to dehydration with excess MsCl in pyridine to give the  $\gamma$ -acetoxy and  $\gamma$ -amino vinyl sulfones **5** and **6** in good overall yields (Scheme 1, Table 1). For reasons not clear to us, dehydrations in the  $\gamma$ -acetoxy series were found to be much slower (*ca.* 36 h) and required a larger excess of MsCl than that needed in the  $\gamma$ -amino series. Moreover, in both cases, the putative mesylate intermediate could not be isolated or observed in TLC-monitoring of these reactions. The  $\gamma$ -acetoxy vinyl sulfones **5a–c** were subsequently hydrolyzed with LiOH in THF–H<sub>2</sub>O at room temperature (preferred over KOH in MeOH) to give the corresponding  $\gamma$ -hydroxy vinyl sulfones **7a–c** in high yields (Table 1).



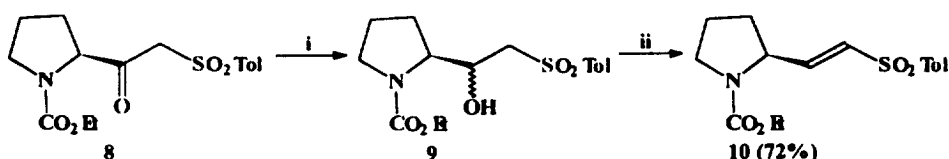
Scheme 1. (i) NaBH<sub>4</sub>, THF–MeOH, 0°C; (ii) MsCl, Py, RT; (iii) LiOH·2H<sub>2</sub>O, THF–H<sub>2</sub>O, RT

Table 1  
Synthesis of enantiopure  $\gamma$ -hydroxy and  $\gamma$ -amino vinyl sulfones (Scheme 1)

R	X	5 (yield%)	X	7 (yield%)	X	6 (yield%)
Bn	OAc	5a (63) (95) <sup>a</sup>	OH	7a (81)	NHCO <sub>2</sub> Et	6a (61)
i-Bu	"	5b (70) (87) <sup>a</sup>	"	7b (74)	"	6b (71)
i-Pr	"	5c (60) (72) <sup>a</sup>	"	7c (77)	"	6c (61)
Me	--	--	--	--	"	6d (66)

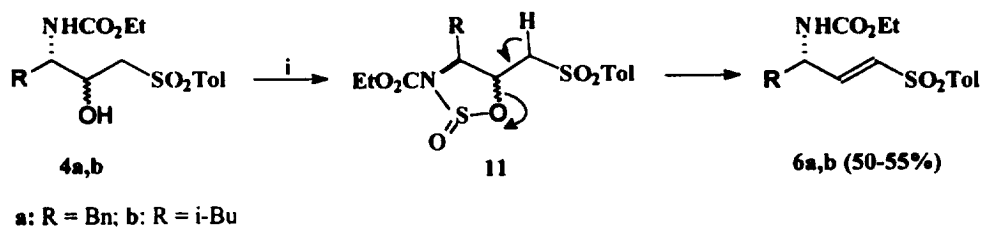
<sup>a</sup> based on recovered  $\beta$ -hydroxy sulfone

Similarly, the N-CO<sub>2</sub>Et-(*S*)-proline derived  $\beta$ -ketosulfone **8**<sup>7a</sup> upon borohydride reduction (to **9**) followed by dehydration with MsCl in pyridine smoothly gave rise to the prolyl vinyl sulfone **10** in 72% overall yield (Scheme 2).



Scheme 2. Reaction conditions (i) and (ii) are the same as in Scheme 1

Interestingly, the  $\gamma$ -amino- $\beta$ -hydroxy sulfones **4** could also be converted to the corresponding vinyl sulfones *via* treatment with SOCl<sub>2</sub>/Et<sub>3</sub>N in CH<sub>2</sub>Cl<sub>2</sub>. As shown for **4a,b**, dehydration by this latter method produced the  $\gamma$ -amino vinyl sulfones **6a,b** in 50–55% yields (Scheme 3), presumably, *via* initial *in situ* formation of the cyclic sulfamidites **11**<sup>10</sup> followed by Et<sub>3</sub>N induced  $\beta$ -elimination. These seminal examples of dehydrations of 1,2-amino alcohols *via* cyclic sulfamidites bear close analogy to the SOCl<sub>2</sub>/Et<sub>3</sub>N induced dehydrations of 1,2-diols *via* cyclic sulfite formations<sup>6b,11</sup> and promise much broader synthetic ramifications. Indirect support for this hypothesis also comes from the fact that dehydrations of  $\gamma$ -acetoxy- $\beta$ -hydroxy sulfones **3** could not be achieved with SOCl<sub>2</sub>/Et<sub>3</sub>N since these substrates cannot form any cyclic sulfite intermediates. This also rules out the formation of any  $\beta$ -chloro sulfone intermediate during dehydrations of **4a,b** with thionyl chloride.



Scheme 3. (i) SOCl<sub>2</sub>, Et<sub>3</sub>N (5 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, RT

In summary, we have developed a facile new chiral-pool synthesis of enantiopure  $\gamma$ -hydroxy and  $\gamma$ -amino vinyl sulfones. The methodology is comparable, if not superior, to the existing repertoire and is attractive on several counts: it involves a short synthetic sequence, is operationally simple and produces uniformly good overall yields. Moreover, the unified strategy described here which caters to the enantiopure synthesis of both the  $\gamma$ -hydroxy and  $\gamma$ -amino congeners is expected to greatly enhance their prospects in EPC synthesis.

### 3. Experimental

All melting points are uncorrected. IR spectra were taken on a Perkin–Elmer R-297 spectrometer.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  on JEOL FX-100 (100 MHz), Bruker DPX-200 (200 MHz) and DPX-300 (300 MHz) instruments. Optical rotations were measured in  $\text{CHCl}_3$  at  $25^\circ\text{C}$  on a JASCO DIP-360 polarimeter. The  $\gamma$ -acetoxy and  $\gamma$ -amino- $\beta$ -ketosulfones **1a–c** and **2a–d** were prepared according to reported procedures.<sup>7a,9</sup>

#### 3.1. General procedure for the preparation of $\gamma$ -acetoxy and $\gamma$ -amino vinyl sulfones **5**, **6** and **10**

$\text{NaBH}_4$  (1.0 mmol) was added to a solution of the  $\beta$ -ketosulfones **1**, **2** or **8** (0.5 mmol) in  $\text{MeOH}:\text{THF}$  (1:3) (5 ml) at  $0^\circ\text{C}$ . After 30 min at  $25^\circ\text{C}$ , the reaction was quenched with a few drops of  $\text{HOAc}$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with water, dried and the solvent removed under reduced pressure to give the corresponding  $\beta$ -hydroxy sulfones **3**, **4** or **9**. The latter was dissolved in pyridine (8 ml) and was treated with  $\text{MsCl}$  (3.0–5.0 mmol for **3a–c**, 1.5–2.0 mmol for **4a–d** and **9**) and a catalytic amount of DMAP at  $0^\circ\text{C}$ . Stirring was continued at  $25^\circ\text{C}$  till completion of reaction (36 h for **3a–c**, 4 h for **4a–d** and **9**) after which it was diluted with  $\text{CH}_2\text{Cl}_2$  (15 ml), washed successively with dil.  $\text{HCl}$  and water and dried. Removal of solvent at reduced pressure followed by chromatography over silica gel (30–40%  $\text{EtOAc}$  in *pet.* ether) gave the respective vinyl sulfones **5a–c**, **6a–d** and **10** (Table 1).

##### 3.1.1. (S)-(E)-3-Acetoxy-4-phenyl-1-(p-tolylsulfonyl)but-1-ene (**5a**)

Mp  $63\text{--}65^\circ\text{C}$  (*pet.* ether– $\text{EtOAc}$ );  $[\alpha]_{\text{D}} -1.7$  (*c* 1.7); IR (Nujol): 1730, 1640, 1450, 1370, 1280  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 2.0 (s, 3H), 2.40 (s, 3H), 2.97 (m, 2H), 5.66 (m, 1H), 6.40 (dd, 1H,  $J=1.7$ , 16 Hz), 6.90 (dd, 1H,  $J=4$ , 16 Hz), 7.26 (m, 7H), 7.72 (d, 2H,  $J=8$  Hz); found: C, 66.16; H, 6.06;  $\text{C}_{19}\text{H}_{20}\text{O}_4\text{S}$  requires C, 66.28 and H, 5.80%.

##### 3.1.2. (S)-(E)-3-Acetoxy-5-methyl-1-(p-tolylsulfonyl)hex-1-ene (**5b**)

Oil;  $[\alpha]_{\text{D}} -26.6$  (*c* 3.0); IR (Nujol): 1730, 1625, 1590, 1450, 1365  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 0.91 (d, 3H,  $J=5$  Hz), 0.92 (d, 3H,  $J=5$  Hz), 1.60 (m, 3H), 2.06 (s, 3H), 2.44 (s, 3H), 5.52 (m, 1H), 6.44 (dd, 1H,  $J=1.6$ , 15 Hz), 6.92 (dd, 1H,  $J=4$ , 15 Hz), 7.36 (d, 2H,  $J=8$  Hz), 7.78 (d, 2H,  $J=8$  Hz); found: C, 60.24; H, 6.63;  $\text{C}_{16}\text{H}_{22}\text{O}_4\text{S}$  requires C, 61.9 and H, 7.09%.

##### 3.1.3. (S)-(E)-3-Acetoxy-4-methyl-1-(p-tolylsulfonyl)pent-1-ene (**5c**)

Oil;  $[\alpha]_{\text{D}} -14.6$  (*c* 2.7); IR (neat): 1735, 1630, 1590, 1450, 1370  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 0.94 (d, 3H,  $J=6$  Hz), 0.98 (d, 3H,  $J=6$  Hz), 1.85 (m, 1H), 2.06 (s, 3H), 2.47 (s, 3H), 5.29 (m, 1H), 6.36 (dd, 1H,  $J=1.8$ , 15 Hz), 6.86 (dd, 1H,  $J=3.9$ , 15 Hz), 7.33 (d, 2H,  $J=8$  Hz), 7.73 (d, 2H,  $J=8$  Hz); found: C, 60.70; H, 6.75;  $\text{C}_{15}\text{H}_{20}\text{O}_4\text{S}$  requires C, 60.81 and H, 6.76%.

##### 3.1.4. (S)-(E)-3-(Ethoxycarbonyl amino)-4-phenyl-1-(p-tolylsulfonyl)but-1-ene (**6a**)

Mp  $105\text{--}106^\circ\text{C}$  (*pet.* ether– $\text{EtOAc}$ );  $[\alpha]_{\text{D}} -4.0$  (*c* 1.5); IR (Nujol): 3340, 1680, 1280, 1140  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 1.17 (t, 3H,  $J=7$  Hz), 2.44 (s, 3H), 2.93 (m, 2H), 4.07 (q, 2H,  $J=7$  Hz), 4.48–4.96 (br m, 2H), 6.33 (dd, 1H,  $J=1.8$ , 16 Hz), 6.94 (dd, 1H,  $J=4$ , 16 Hz), 7.08–7.30 (m, 7H), 7.73 (d, 2H,  $J=8$  Hz); found: C, 64.19; H, 6.09; N, 3.70;  $\text{C}_{20}\text{H}_{23}\text{NO}_4\text{S}$  requires C, 64.34; H, 6.17 and N, 3.75%.

**3.1.5. (S)-(E)-3-(Ethoxycarbonyl amino)-5-methyl-1-(p-tolylsulfonyl)hex-1-ene (6b)**

Mp 73–74°C (pet. ether–EtOAc);  $[\alpha]_D -22.6$  (c 1); IR (Nujol): 3200, 1685, 1260, 1150  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 0.94 (d, 6H,  $J=5$  Hz); 1.19 (t, 3H,  $J=7$  Hz), 1.3–1.96 (m, 3H), 2.44 (s, 3H), 4.07 (q, 2H,  $J=7$  Hz), 4.24–5.00 (br m, 2H), 6.40 (dd, 1H,  $J=1.8, 16$  Hz), 6.86 (dd, 1H,  $J=4, 16$  Hz), 7.32 (d, 2H,  $J=8$  Hz), 7.76 (d, 2H,  $J=8$  Hz); found: C, 60.15; H, 7.30; N, 4.12;  $\text{C}_{17}\text{H}_{25}\text{NO}_4\text{S}$  requires C, 60.18; H, 7.37 and N, 4.13%.

**3.1.6. (S)-(E)-3-(Ethoxycarbonyl amino)-4-methyl-1-(p-tolylsulfonyl)pent-1-ene (6c)**

Oil;  $[\alpha]_D -10.4$  (c 0.5); IR (neat): 3350, 1680, 1250, 1140  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 0.88 (d, 3H,  $J=5$  Hz), 0.94 (d, 3H,  $J=5$  Hz), 1.18 (t, 3H,  $J=6$  Hz), 1.52–2.16 (m, 1H), 2.44 (s, 3H), 4.09 (q, 2H,  $J=6$  Hz), 4.24–4.48 (m, 1H), 4.68 (br d, 1H), 6.44 (dd, 1H,  $J=1.8, 16$  Hz), 6.92 (dd, 1H,  $J=4, 16$  Hz), 7.36 (d, 2H,  $J=8$  Hz), 7.78 (d, 2H,  $J=8$  Hz); found: C, 59.01; H, 7.03; N, 4.21;  $\text{C}_{16}\text{H}_{23}\text{NO}_4\text{S}$  requires C, 59.08; H, 7.08 and N, 4.31%.

**3.1.7. (S)-(E)-3-(Ethoxycarbonyl amino)-1-(p-tolylsulfonyl)but-1-ene (6d)**

Oil;  $[\alpha]_D -21.4$  (c 2.5); IR (neat): 3345, 1730, 1230, 1140  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 1.14 (d, 3H,  $J=7$  Hz), 1.24 (t, 3H,  $J=7$  Hz), 2.41 (s, 3H), 4.07 (q, 2H,  $J=7$  Hz), 4.32–4.80 (br m, 2H), 6.38 (dd, 1H,  $J=1.8, 16$  Hz), 6.88 (dd, 1H,  $J=4, 15$  Hz), 7.32 (d, 2H,  $J=8$  Hz), 7.76 (d, 2H,  $J=8$  Hz); found: C, 56.43; H, 6.29; N, 6.60;  $\text{C}_{14}\text{H}_{19}\text{NO}_4\text{S}$  requires C, 56.56; H, 6.39 and N, 4.71%.

**3.1.8. (S)-(E)-2-[(N-Ethoxycarbonyl) pyrrolidin-2-yl]-1-(p-tolylsulfonyl)ethylene (10)**

Mp 70–72°C;  $[\alpha]_D -37.0$  (c 1.0); IR (KBr): 1700, 1260, 1140  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 1.22 (t, 3H,  $J=7$  Hz), 1.68–2.24 (m, 4H), 2.40 (s, 3H), 4.01 (q, 2H,  $J=7$  Hz), 4.28–4.76 (br m, 1H), 6.28 (dd, 1H,  $J=1.6, 16$  Hz), 6.82 (dd, 1H,  $J=4, 16$  Hz), 7.30 (d, 2H,  $J=8$  Hz), 7.74 (d, 2H,  $J=8$  Hz); found: C, 59.41; H, 6.43; N, 4.32;  $\text{C}_{16}\text{H}_{21}\text{NO}_4\text{S}$  requires C, 59.44; H, 6.50 and N, 4.33%.

**3.2. General procedure for the hydrolysis of  $\gamma$ -acetoxo vinyl sulfones 5a–c**

$\text{LiOH}\cdot\text{H}_2\text{O}$  (1.5 mmol) was added to a solution of **5a–c** (1 mmol) in  $\text{THF}:\text{H}_2\text{O}$  (3:1) (15 ml) and was stirred at RT for 36 h. The reaction mixture was then neutralized with dil. HCl and the solvent removed under reduced pressure. The residue was partitioned between brine and  $\text{CH}_2\text{Cl}_2$ , the organic layer separated, dried and removed in vacuo. The crude  $\gamma$ -hydroxy vinyl sulfones **7a–c** thus obtained were further purified by chromatography over silica gel (30% EtOAc in pet. ether) or through recrystallization (Table 1).

**3.2.1. (S)-(E)-4-Phenyl-1-(p-tolylsulfonyl)but-1-ene-3-ol (7a)**

Mp 174–176°C (pet. ether–EtOAc);  $[\alpha]_D +13.3$  (c 0.9); IR (KBr): 3460, 1620, 1490, 1450, 1390, 1280  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 1.82 (d, 1H,  $J=4$  Hz), 2.44 (s, 3H), 2.92 (m, 2H), 4.60 (m, 1H), 6.60 (dd, 1H,  $J=1.8, 15$  Hz), 7.04 (dd, 1H,  $J=4, 15$  Hz), 7.28 (m, 7H), 7.78 (d, 2H,  $J=8$  Hz); found: C, 67.23, H, 6.11;  $\text{C}_{17}\text{H}_{18}\text{O}_3\text{S}$  requires C, 67.55 and H, 5.96%.

**3.2.2. (S)-(E)-5-Methyl-1-(p-tolylsulfonyl)hex-1-ene-3-ol (7b)**

Mp 102–103°C (pet. ether–EtOAc);  $[\alpha]_D +30.5$  (c 0.7); IR (Nujol): 3490, 1615, 1590, 1450, 1365, 1270  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 0.92 (d, 6H,  $J=7$  Hz), 1.40 (m, 2H), 1.80 (br m, 2H), 2.44 (s, 3H), 4.40 (m, 1H), 6.56 (dd, 1H,  $J=1.2, 15$  Hz), 6.96 (dd, 1H,  $J=4, 15$  Hz), 7.32 (d, 2H,  $J=8$  Hz), 7.76 (d, 2H,  $J=8$  Hz); found: C, 62.39; H, 7.38;  $\text{C}_{14}\text{H}_{20}\text{O}_3\text{S}$  requires C, 62.68 and H, 7.46%.

### 3.2.3. (S)-(E)-4-Methyl-1-(p-tolylsulfonyl)pent-1-ene-3-ol (7c)

Mp 50–52°C (pet. ether–EtOAc);  $[\alpha]_D^{25} +36.8$  (c 1.3); IR (KBr): 3510, 1620, 1590, 1450, 1400, 1300  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR: 0.91 (d, 3H,  $J=7$  Hz), 0.94 (d, 3H,  $J=7$  Hz), 1.85 (m, 2H), 2.44 (s, 3H), 4.19 (m, 1H), 6.59 (dd, 1H,  $J=1.8, 15$  Hz), 6.97 (dd, 1H,  $J=4, 15$  Hz), 7.33 (d, 2H,  $J=8$  Hz), 7.76 (d, 2H,  $J=8$  Hz); found: C, 61.13; H, 7.23;  $\text{C}_{13}\text{H}_{18}\text{O}_3\text{S}$  requires C, 61.41 and H, 7.08%.

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