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Remote Stereocontrol Mediated by a Sulfinyl Group: Synthesis of Allylic Alcohols via Chemoselective and Diastereoselective Reduction of γ-Methylene δ-Ketosulfoxides

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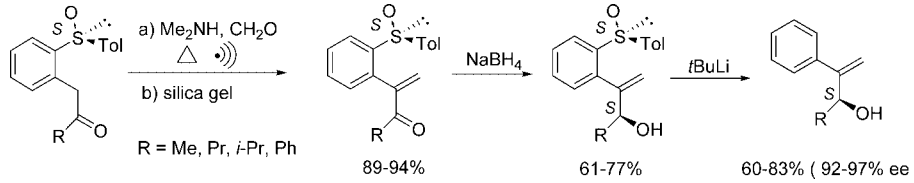

The efficiency of the sulfinyl group as a remote controller of the chemoselectivity and diastereoselectivity of the reduction of α,β-unsaturated α-[2-(*p*-tolylsulfinyl)phenyl] substituted ketones **1** has been demonstrated in reactions carried out under $NaBH_4$ in the presence of $Yb(OTf)_3$ as the chelating agent. The starting unsaturated ketones have been prepared from the corresponding 2-(*p*-tolylsulfinyl) benzyl alkyl (and aryl) ketones **2** by insertion of the methylidene group under modified Mannich conditions, exploiting ultrasound irradiation to obtain the aminomethylation adducts and silica gel treatment to produce its complete elimination. Desulfinylation of the reduction products yielded the corresponding vinyl carbinols with high enantiomeric purity.

Introduction

Chiral allylic alcohols are highly interesting targets[1] because of the stereocontrol exerted by the hydroxyl group in the functionalization of the double bond,[2] as well as their numerous synthetic applications.[3] As a consequence, many efficient methodologies for preparing optically pure allylic alcohols have been developed in the past decades. Among them, included as the most important ones are kinetic resolution methods[4] and mainly chemoselective reduction of α,β-unsaturated ketones. Enantioselective processes have been reported with chiral catalysts, including both asymmetric hydrogenation[5] and enzymatic[6] procedures. In regard to reagents, boron hydrides have been the most frequently used,[7] and a number of synthetic applications have appeared using this strategy as a key step.[8] Despite the large attention devoted to these types of compounds, the number of reports concerning the synthesis of β-unsubstituted-α,β-unsaturated allylic alcohols is rather limited. [3e,4d,7c,h] It is mainly due to the larger tendency of these compounds to

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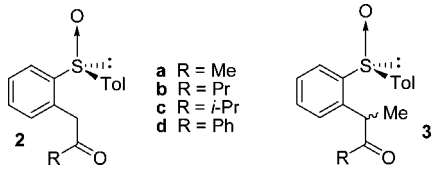
SCHEME 1



suffer other side reactions decreasing the yield (polymerization, or 1,4-addition) and the usually lower stereoselectivity observed for compounds lacking substituents at the β-position.[3e] Additionally, kinetic resolution (enzymatic,[9] chemoenzymatic,[10] or chemical[11]) of these nonencumbered allylic alcohols proceeds with poor enantiodiscrimination and sometimes provokes their isomerization to saturated ketones during the racemisation step (promoted by transition metals).[10]

In the course of our studies on asymmetric induction using remote chiral sulfoxides,[12] we reported the reduction of ketones **2a**−**d** and both epimers of **3a** (Scheme 1) with DIBAL and L-Selectride[13] and their hydrocyanation with diethylaluminum cyanide.[14] In most of the cases, the presence of stoichiometric quantities of the Lewis acid $Yb(OTf)_3$ proved to be essential to attain high yields and selectivities, as a result of the formation of stable chelated species with the metal joined to the sulfinyl and carbonyl oxygens,[12,15] which are highly reactive and provide a strong facial discrimination toward the attack of nucleophiles. The excellent results obtained under catalyzed conditions prompted us to extend the scope of these 1,5-induction processes to substrates containing additional functionalities, compounds **1**, with the double bond conjugated with the carbonyl moiety, being one of the most interesting ones because they would give access to the corresponding enantiomerically pure α-phenyl-substituted allylic carbinols depicted in Figure 1.

The comparison of the results obtained in reduction of compounds **1** with those previously reported for compounds **2**[13,14] would make it possible to evaluate how the structural modification involving the change of the benzyl carbon from tetrahedral to trigonal would influence the reduction of δ-ketosulfoxides. It would also be interesting to check whether the formation of chelated species with Lewis acids has any influence on the reactivity of the 1,4-additions to the enonic system, as much as it affects the conjugation.

We report herein our results concerning the preparation of 1-alkyl (or phenyl) 2-(2-*p*-tolylsulfinyl)phenyl prop-2-en-1-ones **1a**−**d** and their chemoselective and stereoselective carbonyl group reduction using modified Luche[7a,b] conditions to obtain enantiomerically pure 2-aryl-2-methylenecarbinols.

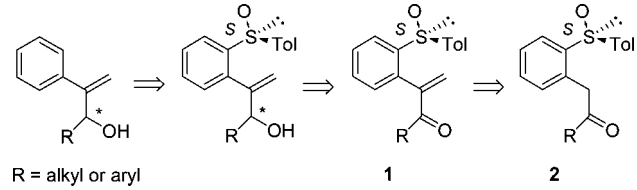


FIGURE 1. Retrosynthetic pathway of enantiomerically pure allylic carbinols.

Results and Discussion

As the starting compounds for preparing sulfinyl enones **1a**−**d** we have used 1-alkyl (or phenyl) 2-(2-*p*-tolylsulfinyl)phenyl ethanones, **2a**−**d**, whose synthesis has been reported recently.[16] We first investigated their reactions with formaldehyde (1.2 equiv) and dimethylamine (1.2 equiv) in refluxing acetonitrile. After several hours of heating (17−24 h), the reactions afforded, along with the expected α-methyleneketones **1a**−**d**, the 1:1 diastereoisomeric mixtures of the corresponding ketoamines **4a**−**d**, which presumably acted as the precursors of **1a**−**d**. Conversion was high**,** but not complete (90−95%). In order to improve the conversion and decrease the reaction times, we explored different conditions and found that the best ones involved the use of a large excess of the reagents and heating of the mixture under ultrasonic radiation.[17] These conditions were used to obtain the results indicated in Table 1. As we can see, the ratio of compounds **1**:**4** ranged between 1 and 9, mainly depending on the concentration of the starting product and the reaction time (see Table 1), which could be explained by assuming the formation of methyleneketones **1** from aminoketones **4** in the last step of the process. Initially, this ratio was really important because lower yields of methyleneketones **1a**−**d** were obtained for larger proportions of aminoketones **4a**−**d**, which are not recovered after chromatographic purification. However, when the crude reaction mixtures were stirred for 12 h with silica gel in dichloromethane at room temperature, we observed the complete disappearance of **4a**−**d** and the exclusive formation of **1a**−**d**, which could be isolated in very high yields (89−94%). Significantly, after this treatment, the yields of the unsaturated ketones **1a**−**d** were identical regardless of the composition of the starting mixtures (Table 1, entries 8−10).[18]

Once the procedure for preparing unsaturated ketones **1** was optimized, we studied their reduction into the corresponding allylic alcohols. Initially we studied the reduction of ketosulfoxide **1a** with several reagents (DIBAL, $LiAlH_4$, L-Selectride, $NaBH_4$, and $NaBH_3CN$) in THF or methanol as the solvents (Table 2).

Reaction with DIBAL resulted in moderate conversion, even with a large excess of the reagent. It did not afford allylic alcohol **5a** but ketone **6a**, resulting from the 1,4-conjugate reduction, as the major product (entry 1). A significant amount of compound **7a** resulting from the double addition was also obtained. The presence of $Yb(OTf)_3$ did not improve this result,

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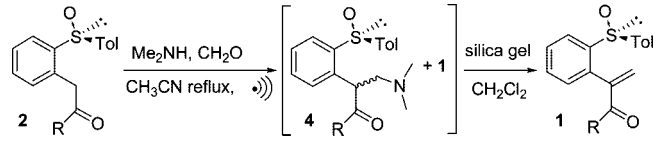
(18) Dienones resulting from a double Mannich reaction of the starting ketosulfoxides **2a** and **2b**, through their two active methylenes, can be obtained in good yield by increasing the reaction times (up to 6 days) and using 4.8 equiv of Me_2NH and 4.4 equiv of H_2CO.

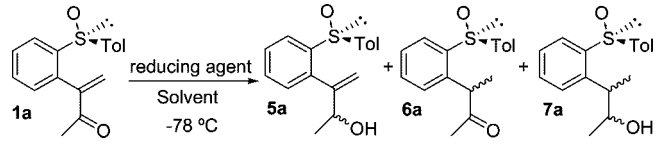
TABLE 1. Methylenation of (*S*)-1-[2-(*p*-Tolylsulfinyl)phenyl]alkan-2-ones



entry	substrate	Me_2NH/CH_2O equiv	ultrasound radiation (h)[a]	concn[b]	crude ratio[c] **1**:**4**	optimized yield of **1**[d]
1	**2a** (Me)	2.4/2.2	3	0.08	90:10	90
2	**2a** (Me)	2.4/2.2	3	0.2	70:30	
3	**2b** (Pr)	2.4/2.2	3	0.07	90:10	90
4	**2b** (Pr)	2.4/2.2	3	0.15	47:53	
5	**2c** (*i*-Pr)	2.4/2.2	4.5	0.07	80:20[e]	
6	**2c** (*i*-Pr)	4.8/4.4	6	0.07	90:10	89
7	**2c** (*i*-Pr)	4.8/4.4	6	0.17	55:45	
8	**2d** (Ph)	2.4/2.2	4.5	0.15	80:20	94
9	**2d** (Ph)	2.4/2.2	6	0.07	88:12	92
10	**2d** (Ph)	4.8/4.4	6	0.07	88:12	94

[a] Ultrasound radiation was applied at 1.5 h periods, with 10 min without radiation between periods. [b] Millimoles of **2a**−**d**/mL of acetonitrile. [c] Measured by ^{1}H NMR of the reaction crude. [d] Obtained by stirring the reaction crude with silica gel in CH_2Cl_2 for 12 h at rt. [e] 85% conversion.

TABLE 2. Reaction of (*S*)-3-[2-(*p*-Tolylsulfinyl)phenyl]but-3-en-2-one 1a with Hydrides



						ratio[b]		
entry	reagent	equiv	Lewis acid	solvent	conv (%)[b]	**5a** (**A/B**)[c]	**6a** (**A/B**)[c]	**7a**[d]
1	DIBAL[a]	8		THF	40		60 (50/50)	40
2	DIBAL	4	$Yb(OTf)_3$	THF	40		100 (70/30)	
3	$NaBH_3CN$	1.2	$Yb(OTf)_3$	MeOH	80		60 (60/40)	40
4	$NaBH_3CN$	1.2	$CeCl_3$	MeOH	60		60 (60/40)	40
5	$LiAlH_4$	1.2		THF	100	40 (80/20)	50 (50/50)	10
6	$LiAlH_4$	1.2	$Yb(OTf)_3$	THF	50	10 (50/50)	90 (55/45)	
7	L-Selectride	2		THF	100		90 (60/40)	10
8	L-Selectride	2	$Yb(OTf)_3$	THF	100		85 (70/30)	15
9	$NaBH_4$	1.2		MeOH	100	10 (50/50)	40 (80/20)	50
10	$NaBH_4$	1.2	$Yb(OTf)_3$	MeOH	100	90 (98/2)	10 (70/30)	
11	$NaBH_4$	1.2	$CeCl_3$	MeOH	100	90 (60/40)	10 (70/30)	

[a] Room temperature. [b] Measured by ^{1}H NMR of the reaction crude. [c] Diastereoisomeric ratio (by ^{1}H NMR). [d] Diastereoisomeric ratio has not been evaluated.

though conjugate reduction epimers were exclusively obtained in a poor diastereoisomeric ratio (entry 2). This behavior contrasts with that observed in reactions of DIBAL with ketosulfoxides **2a**−**d**, which evolved in a highly stereoselective way, especially in the presence of $Yb(OTf)_3$.[13] Similar results were obtained with $NaBH_3CN$ and Lewis acids such as $Yb(OTf)_3$ or $CeCl_3$ (entries 3 and 4). Total conversion was observed with $LiAlH_4$, but the major product was **6a** and the desired **5a** was obtained as a 80:20 mixture of diastereoisomers (entry 5). The addition of $Yb(OTf)_3$ (entry 6) reduced the proportion of **6a** in the reaction mixture and limited the conversion to 50%. Complete conversion was observed with L-Selectride, but the allylic alcohol was not detected (entries 7 and 8). Finally, we obtained the best results by using $NaBH_4$ in methanol as the reagent (entries 9−11). In the absence of Lewis acids, 1,4-conjugate addition is faster and compound **7a** was the major product (entry 9). However, the addition of $Yb(OTf)_3$ (entry 10) inverted the relative reactivity, and the reduction of the carbonyl was faster than the conjugate reduction, thus yielding the desired **5a** as the major product (**5a**:**6a** = 9:1) with an almost complete control of the stereoselectivity (dr 98:2), which allowed us to obtain **5a** in 54% isolated yield, which was significantly increased to 71% when the reaction was carried out in THF as the solvent. The use of $NaBH_4$ in the presence of $CeCl_3$[19] (entry 11) provided a similar chemoselectivity but very low diastereoselectivity (dr 60:40).

Once the best conditions to transform **1a** into allylic alcohol **5a** were found, ketosulfoxides **1b**−**d** were reduced with $NaBH_4$ in the presence of $Yb(OTf)_3$ at −78 °C. THF, acetonitrile, acetonitrile−methanol mixtures, and isopropanol were tested as the solvents, with the temperature ranging between −45 to −78 °C (depending on the solvent). The best results were obtained with methanol or THF, which provided a complete conversion at −78 °C in short reaction times (20−30 min) with high stereoselectivity and chemoselectivity favoring allylic alcohols **5a**−**d**.[20] Under these conditions, the major diastere-

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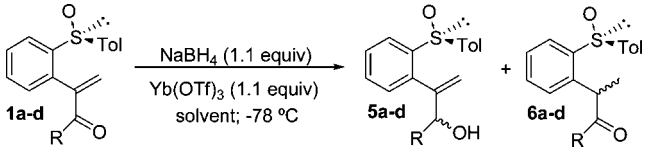
(20) It is worth of mentioning the appearance of the 1,4-adduct of methanol in the reaction mixture when the chelation time of the α-methyleneketone **1a** with the Lewis acid in methanol solution was increased up to 40 min prior to the addition of the reducing agent.

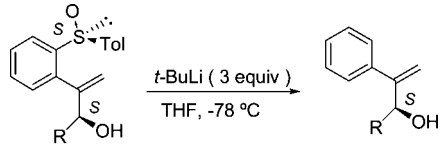
TABLE 3. Reduction of 1-Methylene-1-[2-(*p*-tolylsulfinyl)-phenyl]alkan-2-ones 1



			ratio[a]		
entry	compound	solvent	**5** (**A**/**B**)[b]	**6**[c]	yield **5A** (%)
1	**1a** (Me)	MeOH	90 (98/2)	10	54
2	**1a** (Me)	THF	90 (95/5)	10	71
3	**1b** (Pr)	MeOH	85 (95/5)	15	77
4	**1b** (Pr)	THF	90 (97/3)	10	72
5	**1c** (*i*-Pr)	MeOH	80 (88/12)	20	
6	**1c** (*i*-Pr)	THF	90 (90/10)	10	61
7	**1d** (Ph)	MeOH	90 (100/0)	10	62
8	**1d** (Ph)	THF	100 (98/2)	0	60

[a] Measured by ^{1}H NMR of the reaction crude. [b] Diastereoisomeric ratio (by ^{1}H NMR). [c] Diastereoisomeric ratio not determined.

TABLE 4. Synthesis of Allyllic Alcohols 8a−d by Desulfinylation of 5(a−d)A



entry	compound	R	ee (%)	yield (%)
1	**8a**	Me	92[a]	72
2	**8b**	Pr	96[b]	60
3	**8c**	*i*-Pr	97[a]	65
4	**8d**	Ph	97[a]	83

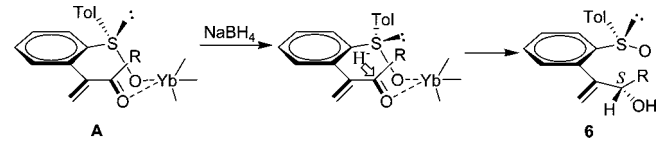
[a] Determined by HPLC Chiralcel OD, 1 mL/min, 5% isopropanol/hexane. λ = 254 nm. [b] Determined by HPLC Chiralcel AD, 0.6 mL/min, 2% isopropanol/hexane. λ = 254 nm.

oisomer of the allylic alcohols **5a−d** could be chromatographically purified and isolated in the yields indicated in Table 3.

Removal of the chiral auxiliary from **5(a−d)A** allowed us to obtain enantiomerically pure allylic alcohols **8a−d** and to establish their absolute configuration by chemical correlation. Reaction of **5dA** with 3 equiv of *t*-BuLi (Table 4, entry 4) afforded the desired allylcarbinol **8d** in 83% yield after chromatographic separation from the sulfur-containing byproduct, which was identified as racemic *tert*-butyl *p*-tolyl sulfoxide.[13,21] With less than 3 equiv of *t*-BuLi only partial desulfinylation was observed. These optimized conditions were applied to remove the chiral auxiliary from compounds **5(a−c)A** thus obtaining the allylic alcohols **8a-c** in good yields (Table 4, entries 1−3).

The enantiomeric excesses (ee's) of the desulfinylated carbinols **8a−d**, as well as their absolute configurations, were unequivocally established by HPLC with a chiral stationary phase (Table 4 and Supporting Information). Preparation of the required racemic allylic alcohols (±)-**8a−d** was performed by $NaBH_4$ reduction of the corresponding methyleneketones, which

SCHEME 2



in turn were obtained from benzyl alkyl (or phenyl) ketones under the same conditions indicated in Table 1 for sulfinyl ketones **2a−d**.

Retention times for each enantiomer of compounds **8a** and **8d**, determined by using Chiralcel OD as a chiral column (see Supporting Information), were compared with those previously reported for these compounds.[11,22] As in both cases the lowest retention times correspond to the *S* enantiomers, we assume the same behavior for compounds **8b** and **8c**. Taking into account that enantiomers **8a−d** obtained by desulfinylation of compounds **5(a−d)A** (Table 4) are those exhibiting the lowest retention time, we have assigned them the *S* configuration, which means that precursors **5(a−d)A** must be (*S*,*S*). It is noteworthy that this is also the configuration of the major isomers obtained in DIBAL reductions of ketosulfoxides **2a−d** in the presence of the $Yb(OTf)_3$,[13] which suggests a similar stereochemical course.

Results indicated in Table 3 can be explained by assuming the formation of a chelated species **A** (Scheme 2), with the metal at the catalyst joined to the sulfinyl and carbonyl oxygens, as a previous step of the reduction. These chelates maintain the conjugation of the double bond with the aromatic ring but distort the planarity of the enonic system, which would explain the fact that the formation of the conjugate 1,4-addition product **6a**, observed in reaction of **1a** with $NaBH_4$ (Table 2, entry 9), was substantially diminished when the reaction was performed in the presence of $Yb(OTf)_3$ (Table 2, entry 10). The intermolecular attack of the hydride to the less hindered face of conformation **A**[23] also accounts for the (*S*,*S*) configuration of the major products obtained in these reactions (Scheme 2).[24]

As a conclusion, we have proved the efficiency of the sulfinyl group as a remote chiral inducer in the reduction of α-aryl, α-methylene ketones with $NaBH_4$ in the presence of $Yb(OTf)_3$, according to a 1,5-asymmetric induction process. These reductions also take place with high chemoselectivity, affording the sulfinylated allylic alcohols in good yields. The synthesis of the starting α-methylene ketones evolves in excellent yield by a Mannich reaction mediated by ultrasound radiation and a silica gel treatment, essential to produce complete elimination of the aminomethylation intermediates. Removal of the chiral auxiliary by reaction with *t*-BuLi provides an excellent route to prepare optically pure α-styryl alkyl (or aryl) allylic alcohols.

Experimental Section

Methylenation of (*S*)-1-[2-(*p*-Tolylsulfinyl)phenyl]alkan-2-one (1a−d). General Procedure. A sealed tube containing mixture of a 40% solution of Me_2NH (2.4−4.8 equiv) in H_2O and a 37% aqueous solution of HCHO (2.2−4.4 equiv) in acetonitrile

(21) For a similar behavior of other diaryl sulfoxides, see: (a) Arroyo, Y.; Meana, A.; Rodríguez, J. F.; Santos, M.; Sanz-Tejedor, M. A.; García Ruano, J. L. *J. Org. Chem.* **2005**, *70*, 3914. (b) Arroyo, Y.; Rodríguez, J. F.; Santos, M.; Sanz-Tejedor, M. A.; García Ruano, J. L. *J. Org. Chem.* **2007**, *72*, 1035. (c) Furukawa, N.; Ogawa, S.; Matsumura, K.; Fujihara, H. *J. Org. Chem.* **1991**, *56*, 6341. (d) Clayden, J.; Mitjans, D.; Youssef, L. H. *J. Am. Chem. Soc.* **2002**, *124*, 5266.

(22) Chai, Z.; Liu, X.-Y.; Zhang, J.-K.; Zhao, G. *Tetrahedron: Asymmetry* **2007**, *18*, 724.

(23) The approach of the borohydride to the opposite face, which would yield compounds **6(a−d)B**, is hindered by the substituents at Yb.

(24) The Posner model has been invoked to explain the stereoselectivity of the reduction of α-alkylidene-β-ketosulfoxides: (a) Posner, G. H.; Mallamo, J. P.; Hulce, M.; Frye, L. L. *J. Am. Chem. Soc.* **1982**, *104*, 4180. (b) Posner, G. H.; Mallamo, J. P.; Miura, K. *J. Am. Chem. Soc.* **1981**, *103*, 2886.

(0.07−0.08 M) was partially submerged to the solvent level in the ultrasound unit at room temperature for 5 min. A solution of the corresponding (*S*)-1-[2-(*p*-tolylsulfinyl)phenyl]alkan-2-one **2a**−**d** in acetonitrile was added, and the mixture was sonicated and heated at 85 °C in periods of 1.5 h (the number of periods of sonication, number of equivalents, and concentration are indicated in each case). The reaction was quenched with water, the organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic extracts were dried with anhydrous $MgSO_4$, and the solvent was evaporated. The crude mixture was stirred at room temperature with silica gel and CH_2Cl_2 for 12 h, and the solvent was removed and purified by flash column chromatography, eluting with hexane/EtOAc (2:1).

(*S*)-2-[2-(*p*-Tolylsulfinyl)phenyl]but-3-en-2-one (1a). Compound **1a** was obtained from compound **2a** (0.37 mmol, 100 mg), following the general procedure for methylenation (2.4 equiv of Me_2NH and 2.2 equiv of CH_2O, 0.08 M in acetonitrile) with two periods of sonication (3 h). Yield: 90%. $[\alpha]^{20}_D = -89$ (*c* 1.0, $CHCl_3$). IR (film): 2996, 1683, 1035, 749 cm^{-1}. ^1H NMR: 7.80 (dd, $J = 7.5$ Hz, $J = 1.5$ Hz, 1H), 7.55−7.40 (m, 4H), 7.22 (d, $J = 8.3$ Hz, 2H), 7.15 (dd, $J = 7.5$ Hz, $J = 1.5$ Hz, 1H), 6.44 (s, 1H), 5.94 (s, 1H), 2.36 (s, 3H), 2.32 (s, 3H). ^{13}C NMR: 197.9, 146.6, 144.3, 141.5, 141.0, 136.9, 131.1, 130.3, 130.1, 129.8, 129.6, 125.9, 125.6, 26.3, 21.4. MS (FAB^+) *m*/*z* 285 $[M + 1]^+$ (100), 241 (13), 91 (23). HRMS $[M + 1]^+$: calcd for $C_{17}H_{17}O_2S$ 285,0949; found 285,0936.

Reduction with $NaBH_4$/Yb(OTf)$_3$. General Procedure. A solution of sulfoxide **1a**−**d** (0.7 mmol) (0.14 M in THF or 0.08 M in MeOH, indicated in each case) and Yb(OTf)$_3$ (0.77 mmol, 1.1 equiv) was stirred at room temperature for 30 min. Then $NaBH_4$ (0.77 mmol, 1.1 equiv) was added slowly to the cooled solution at −78 °C. The resulting mixture was stirred for 30 min at this temperature, quenched with saturated aqueous NH_4Cl solution, extracted with CH_2Cl_2 (3 × 5 mL), and dried over anhyd $MgSO_4$. The solvent was evaporated and the product purified by flash column chromatography.

[2*S*,(*S*)]-3-[2-(*p*-Tolylsulfinyl)phenyl]but-3-en-2-ol (5aA). Compound **5aA** was obtained from compound **1a**, following the general procedure for reduction in THF. It was isolated diastereoisomerically pure, as a colorless oil, by flash column chromatography, eluting with hexane/EtOAc (2:1). Yield: 71%. $[\alpha]^{20}_D = -52.1$ (*c* 2.0, $CHCl_3$). IR (film): 3386 (br), 2927, 1640, 755 cm^{-1}. ^1H NMR: 7.80 (m, 1H), 7.55−7.40 (m, 4H), 7.22 (d, $J = 8.3$ Hz, 2H), 7.15 (m, 1H), 5.53 (s,1H), 4.87 (s, 1H), 4.65 (q, $J = 6.5$ Hz, 1H), 2.65 (br s, 1H, OH), 2.37 (s, 3H), 1.22 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR: 150.5, 143.3, 141.5, 141.4, 139.7, 131.0, 130.3, 129.8, 128.5, 125.8, 125.7, 116.5, 70.7, 22.3, 21.4. MS (FAB^+) *m*/*z* 287 $[M + 1]^+$ (100), 286 (24). HRMS $[M + 1]^+$: calcd for $C_{17}H_{19}O_2S$ 287.1106; found 287,1104.

C−S Bond Cleavage. General Procedure. To a solution of the corresponding hydroxysulfoxide **5(a−d)A** (0.237 mmol, 1 equiv) in THF (1.5 mL) under argon at −78 °C was added a solution 1.7 M in heptane of *tert*-butyllithium (0.713 mmol, 3 equiv). The reaction was stirred for 20 min and then hydrolyzed with a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with CH_2Cl_2 (3 × 2 mL). The organic layers were combined and dried over $MgSO_4$, the solvent was evaporated, and the crude mixture purified by flash column chromatography, eluting with hexane/AcOEt 10:1.

(*S*)-3-Phenylbut-3-en-2-ol (8a).[9b] Compound **8a** was obtained from compound **6a,** following the general procedure for C−S bond cleavage. It was isolated by flash column chromatography as a colorless oil. Yield: 72%. The ee was determined by HPLC[11] (Chiralcel OD, 1 mL/min, 5% *i*-PrOH/hexane, $\lambda = 254$ nm, $t_R =$ (*S*) 8.7 min, (*R*) 11.3 min), 92% ee. lit.[9b] [95% ee, $[\alpha]^{20}_D = 34.2$ (*c* 1.77, $CHCl_3$)]. IR (film): 3386 (br), 2978, 1216, 755 cm^{-1}. ^1H NMR: 7.42−7.27 (m, 5H), 5.36 (s, 1H), 5.28 (s, 1H), 4.82 (m, 1H), 1.68 (br s, 1H, OH), 1.33 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR: 153.1, 139.9, 128.4, 127.6, 126.8, 111.6, 69.5, 22.6. MS (EI) *m*/*z*: 148 (35), 130 (84), 115 (88).

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Supporting Information Available: Experimental data of compounds **1b**−**d**, **5(b−d)A**, and **8b**−**d**, HPLC parameters of racemic allylic alcohols (±)-**8a**−**d**, ^1H and ^{13}C NMR spectra of compounds **1a**−**d**, **5(a−d)A** and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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