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Synthesis of chiral *ortho*-(*p*-tolylsulfinyl) benzyl ketones

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Dedicated to the late Dr. Martina Vicente for her valuable contribution to asymmetric organic synthesis

Abstract—(*S*)-*ortho*-(*p*-Tolylsulfinyl)benzyl alkyl (and aryl) ketones **1a–e** were prepared in good yields by reaction of esters or nitriles with the lithium benzyl carbanion derived from 2-(*p*-tolylsulfinyl) methylbenzene. α-Methylbenzyl ketones **2** were prepared as ca. 1:1 diastereoisomeric mixtures by methylation of the unsubstituted ketones **1** with NaH/MeI. The use of the ethylbenzene derivative as the starting material afforded complex mixtures. The obtention of pure (*S*,(S)*S*)-**2** diastereoisomers could be attained in good yields by oxidation with PCC of the alcohols (epimeric mixtures at the hydroxylic carbon) obtained from reactions of aldehydes with the lithium carbanion derived from 2-(*p*-tolylsulfinyl)ethylbenzene.
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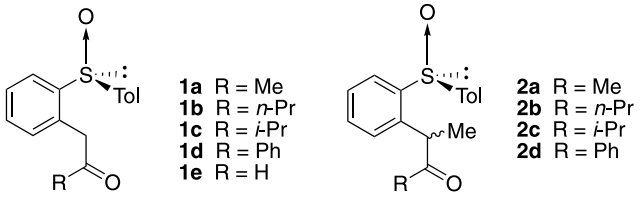
1. Introduction

The use of the sulfinyl group as a diastereo- and enantiocontrolling element in asymmetric synthesis has been profusely developed since 1980.[1] For reactions taking place on electrophilic or nucleophilic centers close to the chiral sulfur (1,2[2]- or 1,3-related[3–6]), numerous highly stereoselective methods have been reported. Much smaller is the number of reports concerning induction processes promoted by the sulfinyl group at remote positions (1,*n*-stereocontrol, with $n>3$). 1,4-Asymmetric induction on electrophilic centers are involved in the reductions[7] and other nucleophilic additions[8] to γ-ketosulfoxides. Recently we have demonstrated that the sulfinyl groups are also able to control the stereoselectivity of the additions of *ortho*-sulfinyl benzyllithium carbanions to different electrophiles.[9] These good results prompted us to evaluate the ability of the sulfinyl group to control 1,5-asymmetric induction processes, that, to our knowledge, lack of precedents in the literature. In this paper we describe different approaches to the synthesis of the optically pure *ortho*-(*p*-tolylsulfinyl)-benzyl alkyl (and aryl) ketones **1a–1d**, the *ortho*-(*p*-tolylsulfinyl)phenylacetaldehyde (**1e**), and their corresponding α-methyl derivatives (**2**) (Scheme 1). The use of these compounds as chiral electrophiles will be reported in due course.



Scheme 1.

2. Results and discussion

The synthesis of ketones **1a–d** was performed from (*S*)-2-methyl-1-(*p*-tolylsulfinyl)benzene (**3**)[9c,10] by deprotonation at −78 °C with lithium diisopropylamide (LDA) followed by reaction with different electrophiles. The use of 10 equiv of nitriles (method A, Table 1), allowed us to obtain good yields of ketones **1a** and **1d**. However the results obtained with *n*-Pr-CN and *i*-Pr-CN were unsuccessful (starting material was recovered). We tried to improve these results by using 1:1 mixtures of R-CN:$BF_3\cdot OEt_2$ as the electrophiles (method B, Table 1). Compounds **1b** (41%) and **1c** (31%) could be so obtained with 1.5 equiv of R-CN:$BF_3\cdot OEt_2$. A higher number of equivalents scarcely improved the yields.

Surprisingly, the reactions performed with esters as the electrophiles were more successful (method C, Table 1).

Keywords: Stereoselective ketone synthesis; Chiral benzyl ketones; Chiral benzyllithium.
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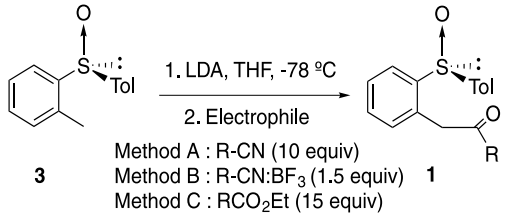
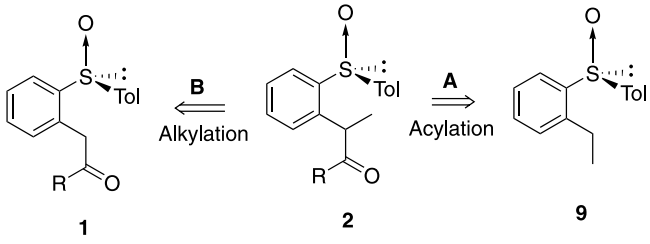
Table 1. Synthesis of *ortho*-(*p*-Tolylsulfinyl)benzyl ketones **1**



R	Compound	Isolated yield (%)		
		A	**B**	**C**
Me	**1a**	75	—	81
n-Pr	**1b**	0	41	81
i-Pr	**1c**	0	31	80
Ph	**1d**	87	—	—
H	**1e**	—	—	14

However, good yields could be obtained in all cases only by using a large excess of ester (15 equiv).

The synthesis of the aldehyde **1e** from ethyl formate (method C) was troublesome, mainly due to its unstability as well as its reactivity (it reacted with a second equivalent of the benzyl carbanion yielding a secondary alcohol). When the reaction was performed by addition of a highly diluted solution of the benzylic anion on a large excess of the ethyl formiate (40 equiv), the ^{1}H NMR spectrum of the reaction crude showed the formation of **1e** as the main product, but only a 14% yield could be isolated after chromatographic purification. By using DMF as the electrophile[11] the isolated yield of **1e** slightly increased (25%). Other formylation agents such as *N*-formylpiperidine,[12] or paraformaldehyde followed by oxidation,[13] were not successful. We prepared enantiomerically pure compound **1e** from *o*-bromobenzaldehyde **4**, following a Wittig based strategy (Scheme 2). The reaction of **4** with (methoxy)triphenylphosphoranylidenemethane yields **5** which evolves into the corresponding 2-*o*-bromophenylacetaldehyde dimethylacetal (**6**)[14] by reaction with methanol and *p*-toluenesulfonic acid. This compound could be easily transformed into the sulfinyl acetal **7** upon treatment with butyllithium and further

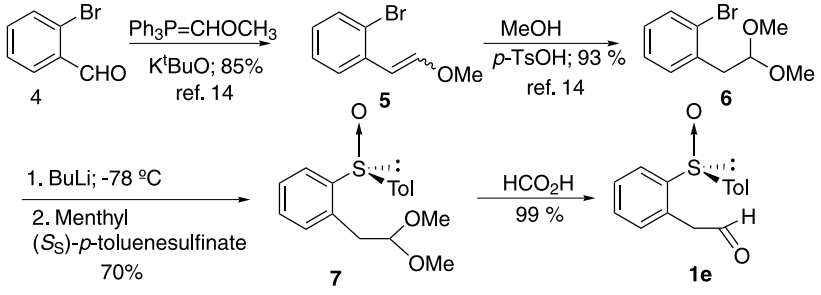


Scheme 3.

reaction with menthyl [(S)*S*]-*p*-toluenesulfinate. Hydrolysis of **7** with formic acid afforded the aldehyde **1e** in quantitative yield. Enantiomeric purity of **1e** (ee≥99%) was determined by chiral HPLC with a Chiralcel AD column.[†]

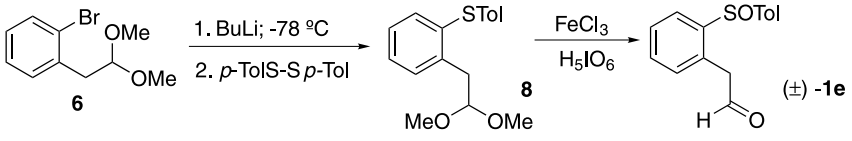
The synthesis of the sulfinylketones **2**, bearing a methyl group at the benzylic position, was tried by the two routes shown in Scheme 3, involving the acylation of 2-(*p*-tolylsulfinyl)ethylbenzene **9** (route A) and the alkylation of the ketones **1** previously obtained (route B), respectively.

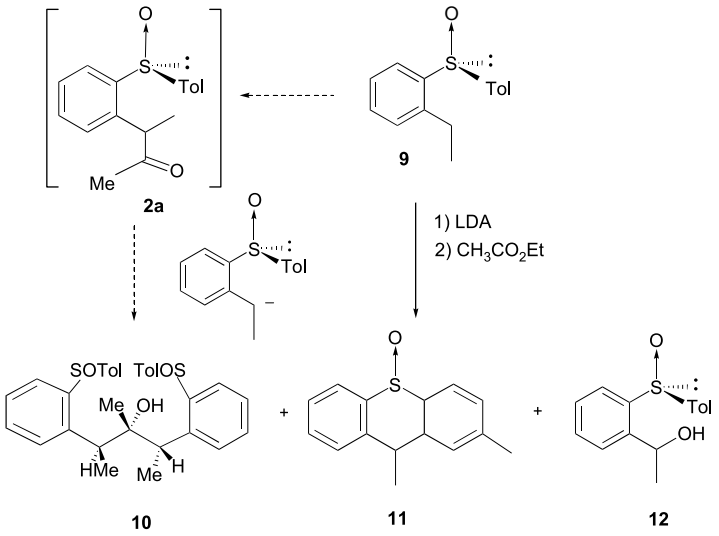
The reaction of compound **9** with LDA and subsequent addition of R-CO_2Et (R=Me, *n*-Pr, *i*-Pr, Ph) or R-CN (R=Me, COMe, Ph) did not afford the expected ketones **2** in good yields. A detailed study of the reaction with ethyl acetate was performed. Initially, we observed the formation of not easily reproducible complex mixtures, compounds **10**, **11** and **12** being their three main components (Scheme 4), in a ratio which was strongly dependent upon the experimental conditions. Significant amounts of the starting material **9**, and the desired ketone **2a** in a very low proportion, were also obtained in most of cases. After exhaustive experimental research we found out that compound **10**, resulting from a double addition of the anion to the ester, could be obtained in 68% yield, when neat ethyl acetate was quickly added into the preformed anion at −78 °C. It indicates that the difference of reactivity between **2a** and ethyl acetate is so large that it cannot be compensated with the excess of the latter. Remarkably, only one diastereoisomer was formed in these reactions, which



Scheme 2.

[†] Racemic **1e** was prepared by sulfenylation of lithium derivative obtained from **6**.





Scheme 4.

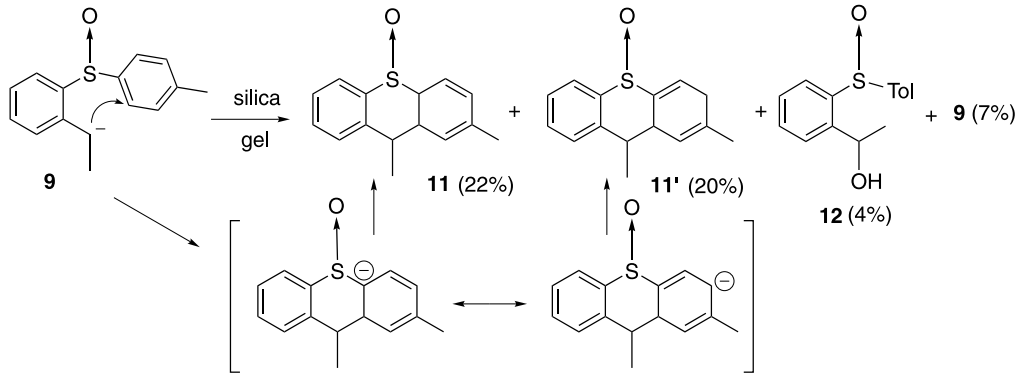
suggests that the anion derived from **9** reacts with both ethyl acetate and **2a** in a completely diastereoselective manner.[‡] On the other hand, the slow addition of the electrophile (solved in THF) into the lithium derivative gave mainly the unaltered starting material. It is worth mentioning the surprising change produced by the inverse addition of the reagents. In fact, when the anion derived from **9** was added into a solution containing ethyl acetate, compound **12** was the major component of the mixture (tertiary alcohol **10** was not detected), traces of compound **11**[¶] being also observed. However, the proportion of both compounds was not coincident in the different experiences which were performed and the reactions were not reproducible in our hands. It is worth mentioning that the alcohol **12** was always obtained as a sole diastereoisomer, and in some cases with a 62% isolated yield.

Then we tried to obtain the ketones **2** by alkylation of **1** (method B, Scheme 3). NaH was chosen as the base[§] because it had been reported to give the best results in the α-alkylation of β-ketosulfoxides.[3c] Deprotonation of ketosulfoxides **1** with NaH followed by reaction with MeI afforded ketosulfoxides **2** as an almost equimolecular mixture of epimers at the benzylic carbon (**A** and **B**, Table 2). In those experiences yielding a significant amount of dimethylderivative (entry 3) the A/B ratio became 1:3, thus suggesting that the second alkylation was easier for isomer **A** than for isomer **B**. The best conditions, optimized from ketosulfoxide **1a**, were achieved by using 1.7 equiv of base and 3.6 equiv of the electrophile at −40 °C (entry 2). Smaller amounts of the hydride (<1.4 equiv) gave low conversions (≤55%, entry 1), whereas more than 2 equiv of both reagents yielded a significant proportion of the bismethylated ketone (entry 3, Table 2).

Chromatographic separation of diastereoisomers **A** and **B**, obtained from the methylation with methyl iodide, is not an easy task. It was unsuccessful in our hands except for the

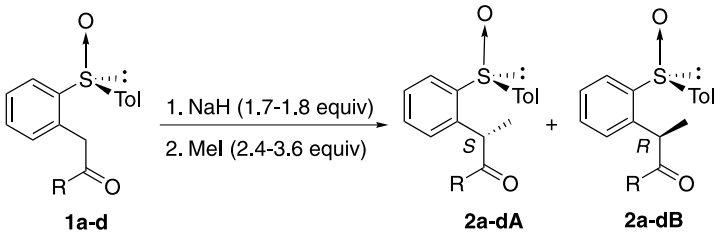
[‡] The fact that reactions from compound **3**, under similar conditions, only evolved into ketones **1** instead of producing alcohols such as **10**, could be due to the immediate enolization of **1**, once formed from **3**. The lower stability of the enolates derived from **2**, containing a tetrasubstituted double bond, could account for their more difficult enolization.

[¶] The formation of compound **11** can be explained by the intramolecular attack of the benzylic carbanion to the sulfinylated ring and subsequent protonation of the resulting anion. The electronic transfer from the carbanion to produce an anion-radical on the tolyl ring cannot be discarded. With the aim of verifying that the formation of compound **11** does not require the electrophile participation, we directly dropped the lithium derivative of **9** (formed, as usually, with LDA at –78 °C during 1 h) over a preparative TLC of silica gel, and left to dry overnight. Under these conditions a mixture of compounds **11** and **11′** were obtained as the major products.



[§] The use of LDA did not improve the results.

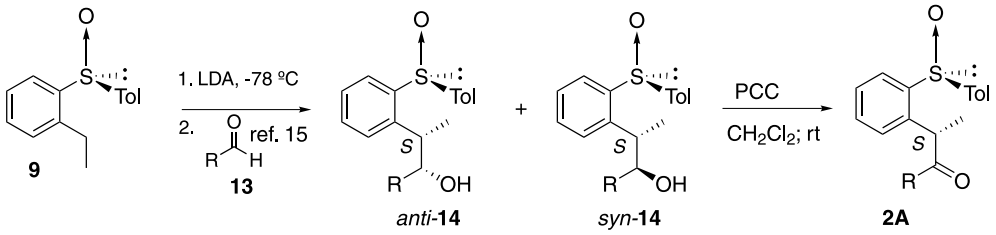
Table 2. Synthesis of γ-methyl δ-ketosulfoxide **2a–d** by alkylation of **1**



Entry	NaH (equiv)/CH_3I (equiv)	Ketone (R)	A:B ratio[a]	Conversion (yield %)
1	1.4/2.4	**2a** (CH_3)	46:54	55
2	1.7/3.6	**2a** (CH_3)	47:53	100 (78)
3	2.2/2.4	**2a** (CH_3)	29:71	100 (37)[b]
4	1.8/2.4	**2b** (*n*-Pr)	47:53	100 (67)
5	1.8/3.6	**2c** (*i*-Pr)	44:56	100 (87)
6	1.8/3.6	**2d** (Ph)	59:41	100 (77)

[a] Established from the ^1H NMR spectra of the reaction crudes.
[b] α,α′-Dimethyl ketone was obtained as the major product (53%).

Table 3. Synthesis of γ-methyl δ-ketosulfoxide **2A** by PCC oxidation of *syn*+*anti* mixtures of γ-methyl δ-hydroxysulfoxides **14**



Entry	Aldehyde (R)	*anti*-**14**: *syn*-**14**[a]	PCC (equiv)	Time (h)	Ketone (yield %)
1	**13d** (Ph)	85:15	1.5	5	**2dA** (65)
2	**13f** (*n*-Bu)	37:63	2.0	21	**2fA** (74)
3	**13g** (*t*-Bu)	24:76	2.0	21	**2gA** (73)
4	**13h** (*p*-$OMeC_6H_4$)	84:16	1.5	6	**2hA** (74)
5	**13i** (2,6-diMeC_6H_3)	67:33	1.5	7	**2iA** (71)

[a] Data taken from Ref. 15.

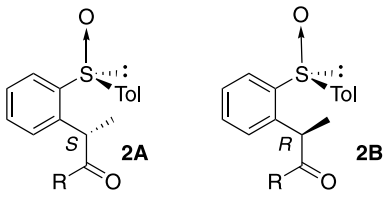
epimers **2aA** and **2aB** (R=Me), that were obtained diastereomerically pure by using a hexane:ethyl acetate 2:1 mixture as the eluent, **2aA** being the isomer with higher R_f. Configurational assignment of the epimers **A** and **B** based on of their NMR parameters proved to be difficult.

Taking into account the above-mentioned difficulties to obtain diastereomerically pure compounds **2b–d**, we decided to exploit the reported high stereoselectivity at the benzylic position of the reactions of the lithium carbanion derived from **9** with aldehydes.[15] As these reactions afforded alcohols **14** as epimeric mixtures at the hydroxylic carbon, both with the same *S* configuration at the benzylic carbon, the oxidation of their hydroxylic groups would yield enantiomerically pure ketones **2** of known configuration. As expected, the use of pyridinium chlorochromate (PCC) at room temperature in dichloromethane afforded the desired diastereomerically pure ketones **2** in excellent yields (Table 3).

The resulting ketones exhibit the *S* configuration at the benzylic carbon.[15]In the case of **2d**, its spectroscopic ^1H NMR parameters are those corresponding to the diastereoisomers denoted as **A** in the mixture obtained by methylation of **1d**, which differ significantly from those of the epimer **B** only in the chemical shift of the methyl group (see Table 4). On this base, the configurational assignments

Table 4. Significant ^1H NMR parameters for the configurational assignment of γ-methyl δ-ketosulfoxides **2**

Compound	R	δ (H_2)	δ (CH_3)
2aA	CH_3	4.25	1.11
2aB	CH_3	4.14	0.94
2bA	*n*-Pr	4.13	1.13
2bB	*n*-Pr	4.13	0.94
2cA	*i*-Pr	4.37	1.10
2cB	*i*-Pr	4.29	0.90
2dA	Ph	5.14	1.41
2dB	Ph	5.05	1.07
2fA	*n*-Bu	4.21	1.21
2gA	*t*-Bu	4.84	1.22
2hA	(*p*-OMe)C_6H_4	5.08	1.37
2iA	(2,6-diMe)C_6H_3	5.16	1.64



Scheme 5.

of the compounds **2aA**, **2aB**; **2bA**, **2bB** and **2cA**, **2cB** (as a mixture) could be made unambiguously (Scheme 5).

In summary we have described the synthesis of the δ-ketosulfoxides **1** and **2** in optically pure form, as well as the problems related to some of the involved reactions. The use of these compounds as chiral electrophiles and nucleophiles under different conditions will be reported at a later date.

3. Experimental

3.1. General

NMR spectra were obtained in a Bruker spectrometer (300 and 75 MHz for ^{1}H and ^{13}C, respectively) in $CDCl_3$ solutions. Melting points were measured using a Gallemkamp apparatus in open capillary tubes. Mass spectra (MS) were determined by FAB$^+$, APCI or EI (70 eV). Specific rotations were measured in a Perkin–Elmer 241 MC polarimeter. De's were evaluated by integration of well-separated signals of the NMR spectra. All reactions were carried out in anhydrous solvents under argon atmosfere. THF and diethyl ether were distilled from sodium-benzofenone under argon. CH_2Cl_2 was distilled from P_2O_5. Flash column chromatography was perfomed using silica gel Merck-60 (230–400 mesh).

3.2. Synthesis of δ-ketosulfoxides

Method A. By reaction of (S)-1-methyl-2-(p-tolylsulfinyl)-benzene with RCN. A solution of *n*-BuLi (5.19 mmol, 2.5 M in hexanes) was added into a solution of *i*-Pr_2NH (7.70 mmol) in THF (26.0 mL) at 0 °C. After stirring for 30 min, the mixture was cooled at −78 °C and a solution of the sulfoxide **3** (4.34 mmol) in THF (17.3 mL) was then added. The mixture was stirred at the same temperature for 1 h, before adding the corresponding nitrile (43.40 mmol) at −78 °C. The reaction mixture was stirred for 30 min, quenched (5% aqueous HCl solution, 30 mL) and stirred for 12 h. The crude product was extracted with CH_2Cl_2 (3× 40 mL), dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by flash chromatography (the eluent was indicated in each case).

Method B. By reaction of (S)-1-methyl-2-(p-tolylsulfinyl)-benzene with RCN-BF_3. A solution of *n*-BuLi (5.19 mmol, 2.5 M in hexanes) was added into a solution of *i*-Pr_2NH (7.70 mmol) in THF (26.0 mL) at 0 °C. After stirring for 30 min, the mixture was cooled at −78 °C and a solution of the sulfoxide **3** (4.34 mmol) in THF (17.3 mL) was then added. The reaction mixture was stirred at the same temperature for 1 h, before adding a mixture, previously stirred (1 h) at −78 °C, of the corresponding nitrile (12.90 mmol) and boron trifluoride etherate (13.00 mmol) in CH_2Cl_2 over the carbanion. The reaction mixture was stirred for 30 min. The work up to extract the crude was performed as in method A.

Method C. By reaction of (S)-1-methyl-2-(p-tolylsulfinyl)-benzene with RCO_2Et. A solution of *n*-BuLi (5.19 mmol, 2.5 M in hexane) was added into a solution of *i*-Pr_2NH (7.70 mmol) in THF (26.0 mL) at 0 °C. After stirring for 30 min, the mixture was cooled at −78 °C. A solution of the sulfoxide **3** (4.34 mmol) in THF (17.3 mL) was then added. The reaction flask was stirred at the same temperature for 1 h, before adding the corresponding carbanion over the ester (65.1 mmol) at −78 °C. The reaction flask was maintained 30 min under stirring before quenching with saturated aqueous NH_4Cl. The crude ketone was extracted with CH_2Cl_2 (3×40 mL), the extracts dried ($MgSO_4$), and the solvent evaporated. The residue was purified by flash chromatography (the eluent was indicated in each case).

3.2.1. (*S*)-1-[2-(*p*-Tolylsulfinyl)phenyl)propan-2-one (1a). It was prepared following method C. Eluent: hexane–ethyl acetate 1:1. Yield: 81%; white solid; mp: 77–79 °C (diethyl ether); $[\alpha]_D^{20}=-9.6$ (*c* 1.1, $CHCl_3$); IR (NaCl): 2922, 1722, 1473, 1034 cm^{-1}; ^{1}H NMR: δ 7.77 (m, 1H), 7.55–7.40 (m, 5H), 7.24 (d, $J=8.0$ Hz, 1H), 7.15 (m, 1H), 4.04 and 3.89 (AB system, $J=17.3$ Hz, 2H), 2.34 (s, 3H), 2.11 (s, 3H); ^{13}C NMR: δ 204.5, 143.8, 141.5, 140.9, 133.2, 131.7, 131.5, 130.0, 128.5, 126.7, 125.7, 46.5, 29.6, 21.3; MS (EI$^+$) *m/z*: 273 (M$^+$); HRMS [M$^+$]: calcd for $C_{16}H_{16}O_2S$: 273.0871; found, 273.0949.

3.2.2. (*S*)-1-[2-(*p*-Tolylsulfinyl)phenyl]pentan-2-one (1b). It was prepared following method C. Eluent: hexane–ethyl acetate 2:1. Yield: 81%; white solid; mp: 40–41 °C; $[\alpha]_D^{20}=-97.6$ (*c* 0.5, $CHCl_3$); IR (KBr): 2969, 1703, 1409, 1034 cm^{-1}; ^{1}H NMR: δ 7.78–7.69 (m, 1H), 7.47–7.33 (m, 4H), 7.25–7.10 (m, 3H), 3.97 and 3.84 (AB system, $J=17.2$ Hz, 1H), 2.35–2.26 (m, 2H), 2.31 (s, 3H), 1.52 (s, $J=7.5$ Hz, 2H), 0.82 (t, $J=7.5$ Hz, 3H); ^{13}C NMR: δ 206.4, 143.6, 141.3, 140.8, 133.1, 131.4, 131.2, 129.7, 128.2, 126.3, 125.5, 45.5, 44.1, 21.1, 16.8, 13.4; MS (FAB) *m/z*: 301 [M+1]$^+$; HRMS [M+1]$^+$: calcd for $C_{18}H_{21}O_2S$: 301.1184; found, 301.1255. Anal. calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71; S, 10.67. Found: C, 71.73; H, 6.69; S, 10.51.

3.2.3. (*S*)-3-Methyl-1-[2-(*p*-tolylsulfinyl)phenyl]butan-2-one (1c). It was prepared following method C. Eluent: hexane–ethyl acetate 2:1. Yield: 80%; white solid; mp: 46–47 °C; $[\alpha]_D^{20}=-98.3$ (*c* 1.0, $CHCl_3$); IR (NaCl): 2962, 1715, 1083, 1035 cm^{-1}; ^{1}H NMR: δ 7.70–7.67 (m, 1H), 7.48–7.37 (m, 4H), 7.24–7.21 (m, 2H), 7.40–7.11 (m, 1H), 4.11 and 3.94 (AB system, $J=17.3$ Hz, 1H), 2.66 (sp, $J=$ 6.8 Hz, 1H), 2.33 (s, 3H), 1.09 (d, 6H); ^{13}C NMR: δ 210.2, 143.8, 141.2, 140.8, 133.5, 131.4, 131.3, 129.7, 128.3, 126.5, 125.5, 43.4, 40.6, 21.2, 18.2, 18.1; MS (FAB) *m/z*: 301 (M+1)$^+$; HRMS (M+1)$^+$: calcd for $C_{18}H_{21}O_2S$: 301.1184; found, 301.1274. Anal. calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71; S, 10.67. Found: C, 71.82; H, 6.68; S, 10.65.

3.2.4. (*S*)-1-Phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]ethan-1-one (1d). It was prepared following method A. Eluent: hexane–ethyl acetate 2:1. Yield: 87%; white solid; mp:

106–108 °C; $[\alpha]_D^{20}=-120.2$ (*c* 1.0, $CHCl_3$); IR (KBr): 3424, 1686, 1323, 1077 cm^{-1}; ^1H NMR: δ 7.91–7.88 (m, 2H), 7.82–7.29 (m, 1H), 7.57–7.53 (m, 1H), 7.45–7.38 (m, 6H), 7.20–7.11 (m, 3H), 4.58 and 4.48 (AB system, $J=16.9$ Hz, 2H), 2.29 (s, 3H); ^{13}C NMR: δ 195.7, 143.6, 141.1, 140.6, 135.9, 133.5, 133.2, 131.6, 131.2, 129.7, 128.4, 128.2, 128.0, 126.5, 125.5, 41.3, 21.1; MS (FAB) *m/z*: 335 $[M+1]^+$; HRMS $[M+1]^+$: calcd for $C_{21}H_{19}O_2S$: 335.1027; found, 335.1103. Anal. calcd for $C_{21}H_{18}O_2S$: C, 75.42; H, 5.42; S, 9.59. Found: C, 75.29; H, 5.49; S, 9.47.

3.3. Synthesis of sulfinyl aldehyde 1e

3.3.1. (*S*)-1-(2,2-Dimethoxyethyl)-2-(*p*-tolylsulfinyl)benzene (7). A solution of bromide **6** (0.40 mmol) in THF (0.4 mL) at −78 °C was added into a solution of *n*-BuLi (0.40 mmol, 2.5 M in hexane), and the reaction flask was stirred for 45 min at the same temperature before the addition over a solution of (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (0.34 mmol) in THF (0.2 mL) at −78 °C. The reaction mixture was stirred for 6 h at −78 °C until completion, and then it was hydrolyzed with a saturated aqueous NH_4Cl solution (0.5 mL), extracted with CH_2Cl_2 (3×0.5 mL), dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by flash chromatography with hexane–ethyl acetate 1:1 as the eluent. Yield: 70%; yellow oil; $[\alpha]_D^{20}=-31.8$ (*c* 3.2, $CHCl_3$); IR (NaCl): 2956, 2934, 1439, 1118 cm^{-1}; ^1H NMR: δ 7.82–7.79 (m, 1H), 7.44–7.15 (m, 7H), 4.34–4.30 (m, 1H), 3.24 (s, 3H), 3.20 (s, 3H), 3.08–2.95 (m, 2H), 2.27 (s, 3H); ^{13}C NMR: δ 143.6, 141.5, 141.2, 134.9, 130.8, 130.7, 129.6, 127.6, 125.6, 125.0, 104.1, 53.7, 53.3, 35.3, 21.0; MS (FAB) *m/z*: 273 $[(M+1)-MeOH]^+$.

3.3.2. (*S*)-2-[2-(*p*-Tolylsulfinyl)phenyl]acetaldehyde (1e). A solution of the acetal **7** (0.83 mmol) in formic acid (41.57 mmol) was stirred for 1 h at room temperature. Then, the mixture was diluted with dichloromethane, washed ($NaHCO_3$ saturated aqueous solution) and the solvents evaporated under reduced pressure. The residue was purified by flash chromatography using as the eluent hexane–ethyl acetate 2:1. Enantiomeric purity (ee≥99%) was determined by HPLC (Chiralcel AD column) with 70:30 hexane–isopropanol as the eluent (1 mL min^{-1}, 35 °C; (*S*): $t_R=6.1$; (*R*): $t_R=6.8$(. Yield: 99%; yellow oil; $[\alpha]_D^{20}=-21.0$ (*c* 0.5, $CHCl_3$); IR (NaCl): 3331, 2924, 1723 cm^{-1}; ^1H NMR: δ 9.46 (t, $J=1.6$ Hz, 1H), 7.88–7.83 (m, 1H), 7.47–7.39 (m, 4H), 7.22–7.13 (m, 3H), 3.91 (dd, $J=17.3$ Hz, 1.6 Hz, 1H) 3.82 (dd, 1H). 2.30 (s, 3H); ^{13}C NMR: δ 197.2, 143.6, 141.6, 140.4, 131.7, 131.4, 130.9, 129.9, 128.5, 126.3, 125.5, 46.0, 21.1; MS (FAB) *m/z*: 259 $(M+1)^+$; HRMS $(M+1)^+$: calcd for $C_{15}H_{15}O_2S$: 259.0715; found, 259.0802.

3.4. Protocol for obtaining dimeric sulfoxide 10

3.4.1. ((S)*S*,2*S*,4*S*)-2,4-Bis-[2-(*p*-tolylsufinyl)phenyl]-3-methylpentan-3-ol (10). To a solution of *n*-BuLi (5.19 mmol, 2.5 M in hexane) was added *i*-Pr_2NH (7.70 mmol) in THF (5.0 mL) at 0 °C. After stirring for 30 min, the mixture was cooled at −78 °C. A solution of the sulfoxide **9** (4.34 mmol) in THF (5.0 mL) was then added, and the mixture was stirred for 1 h. Ethyl acetate (65.1 mmol) was added quickly at −78 °C over the purple lithium derivative of compound **9**. The reaction flask was stirred for 30 min. The reaction was quenched (saturated NH_4Cl), extracted with diethyl ether (3×20 mL), dried ($MgSO_4$), and the solvent was evaporated to yield a crude mixture of compounds **10** and **2aA** (^1H NMR). The residue was purified by flash chromatography (hexane–ethyl acetate 1:3) to afford pure compound **10**. Yield: 68%; colorless oil; $[\alpha]_D^{20}=+31.9$ (*c* 0.2, CH_3COCH_3); IR (NaCl): 3329, 1592, 1492, 810 cm^{-1}; ^1H NMR: δ 8.02 (dd, $J=7.9$, 1.4 Hz, 1H), 7.73 (dd, $J=7.6$, 1.4 Hz, 2H), 7.51 (m, 13H), 5.18 (bs, 1H), 3.72 (q, $J=7.1$ Hz, 1H), 3.52 (q, $J=7.1$ Hz, 1H), 2.40 (s, 6H), 1.19 (d, $J=7.1$ Hz, 3H), 0.77 (d, $J=7.1$ Hz, 3H), 0.47 (s, 3H); ^{13}C NMR: δ 145.7, 145.5, 142.4, 142.1, 141.6, 141.3, 141.2, 140.5, 132.2, 132.1, 131.4, 130.8, 130.4, 129.8, 126.9, 126.4, 126.3, 126.2, 125.4, 124.3, 75.9, 40.1, 39.7, 21.4, 21.2, 19.9, 16.5, 15.9. Anal. calcd for $C_{32}H_{34}O_3S_2$: C, 72.42; H, 6.46; S, 12.08. Found: C, 72.48; H, 6.50; S, 12.10.

3.5. Protocols for the synthesis of ketones 2

Method A. General procedure for methylation of ketones **1**. A solution (0.26 M in THF) of δ-ketosulfoxides **1a–d** was added into a stirred suspension of NaH (1.7 or 1.8 equiv, free of paraffin) in THF (2 mL) at room temperature. After stirring for 1 h, the mixture was cooled at −40 °C and methyl iodide (3.6 or 2.4 equiv) was injected under stirring at the same temperature (see Table 2 in the text for proportions). Then, an aqueous saturated solution of NH_4Cl was added, and the mixture was left under stirring to reach room temperature. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined extracts were dried ($MgSO_4$) and the solvent evaporated. The residue was purified by flash chromatography (the eluent was indicated in each case).

Method B. General procedure for oxidation of alcohols **14**. The epimeric mixture of alcohols **14**, obtained following the previously described procedure,[15] was solved in dry CH_2Cl_2 and PCC was added (1.5 or 2.0 equiv for aromatic or aliphatic derivatives, respectively). The mixture was stirred at room temperature (see reaction times in Table 3) and then the solvent was partially evaporated and the residue was chromatographied.

3.5.1. [3*S*,(S)*S*] and [3*R*,(S)*S*]-3-[2-(*p*-Tolylsulfinyl)-phenyl]butan-2-one (2aA) and (2aB). They were obtained as a 47:53 epimeric mixture by methylation of ketone **1a** and separated by flash chromatography (hexane–ethyl acetate 3:1).

Compound [3*S*,(S)*S*]-(**2aA**). It was obtained as a white solid. Yield: 26%; mp: 87–90 °C; $[\alpha]_D^{20}=+103$ (*c* 0.8, $CHCl_3$); ^1H NMR: δ 7.90 (m, 1H), 7.45–7.37 (AA'BB' system, 4H), 7.19 (m, 2H), 7.05 (m, 1H), 4.25 (q, 1H, $J=6.9$ Hz, CH_3CH), 2.31 (s, 3H, CH_3Ar), 1.63 (s, 3H, CH_3CO), 1.12 (d, $J=6.9$ Hz, 3H, CH_3CH); ^{13}C NMR: δ 207.5, 142.7, 142.1, 141.3, 139.6, 131.9, 130.1, 128.5, 128.1, 126.9, 126.1, 47.6, 28.4, 21.3, 17.5; MS (APCI$^+$) *m/z*: 287.1 $[M+1]^+$; HRMS: calcd for $C_{17}H_{19}O_2S$: 287.1100. Found: 287.1114.

Compound [3*R*,(S)*S*]-(**2aB**). It was obtained as a colorless oil. Yield: 53%; $[\alpha]_D^{20}=-248$ (*c* 3.9, $CHCl_3$); ^1H NMR: δ 7.95 (dd, $J=7.7$, 1.6 Hz, 1H), 7.45–7.35 (m, 4H), 7.19 (d, $J=7.7$ Hz, 2H), 7.06–7.02 (m, 1H), 4.14 (q, 1H, $J=6.7$ Hz, CH_3CH), 2.30 (s, 3H, CH_3Ar), 1.92 (s, 3H, CH_3CO), 0.94 (d, 3H, $J=6.7$ Hz, CH_3CH); ^{13}C NMR: δ 206.7, 142.6, 141.9, 141.2, 138.7, 131.6, 130.0, 128.2, 127.8, 126.0, 125.6, 47.4, 28.3, 21.2, 16.5; MS ($APCI^+$) *m/z*: 287.1 $[M+1]^+$. Anal. calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34; S, 11.20. Found: C, 71.38; H, 6.35; S, 10.70.

3.5.2. [2*S*,(S)*S*] and [2*R*,(S)*S*]-2-[2-(*p*-Tolylsulfinyl)-phenyl]hexan-3-one (2bA) and (2bB). They were obtained as a 47:53 epimeric mixture by methylation from ketone **1b**. Chromatographic purification (hexane–ethyl acetate 3:1) afforded the mixture of **2bA** and **2bB** as a yellow oil. Overall yield: 67%; ^1H NMR: δ 7.97–7.92 (m, 2H), 7.43–7.33 (m, 8H), 7.21–7.18 (m, 4H),7.06–7.03 (m, 2H), 4.13 (q, $J=6.8$ Hz, 2H, CH_3CH), 2.29 (s, 6H, CH_3Ar), 2.19–2.16 (m, 2H, CH_2–CO), 1.73–1.67 (m, 2H, CH_2CO), 1.47–1.33 (m, 2H, CH_2CH_2CO), 1.29–1.18 (m, 2H, CH_2CH_2CO), 1.13 (d, $J=6.9$ Hz, 3H, CH_3CHCO, **A**), 0.94 (d, $J=6.7$ Hz, 3H, CH_3CHCO, **B**), 0.69 (t, $J=7.5$ Hz, 3H, CH_3CH_2, **B**), 0.55 (t, $J=7.3$ Hz, 3H, CH_3CH_2, **A**); ^{13}C NMR: δ 209.5, 209.0, 142.2, 142.0, 141.9, 141.5, 141.4, 139.5, 138.9, 131.7, 131.6, 130.1, 130.0, 128.3, 128.2, 128.0, 127.9, 126.4, 126.3, 126.0, 125.6, 46.8, 43.3, 42.9, 21.3, 17.7, 17.1, 16.9, 16.8, 13.4, 13.3; MS ($APCI^+$) *m/z*: 315.1 $[M+1]^+$. Anal. calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05; S, 10.20. Found: C, 72.07; H, 7.03; S, 10.04.

3.5.3. [4*S*,(S)*S*] and [4*R*,(S)*S*]-2-Methyl-4-[2-(*p*-tolylsulfinyl)phenyl]pentan-3-one (2cA) and (2cB). They were obtained as a 44:56 epimeric mixture by methylation of ketone **1c**. Chromatographic purification (hexane–ethyl acetate 2:1) afforded a mixture of **2cA** and **2cB** as a yellow oil. Overall yield: 87%; ^1H NMR: δ 7.97–7.86 (m, 2H), 7.44–7.34 (m, 8H), 7.22–7.19 (m, 4H), 7.08–7.03 (m, 2H), 4.37 (q, 1H, $J=6.7$ Hz, CH_3CH, **A**), 4.29 (q, $J=6.9$ Hz, 1H, CH_3CH, **B**), 2.51 (s, $J=7.1$ Hz, 1H, $CH(CH_3)_2$, **B**), 2.31 (s, 3H, CH_3Ar, A), 2.30 (s, 3H, CH_3Ar, B), 2.07 (s, $J=7.1$ Hz, 1H, $CH(CH_3)_2$, A), 1.10 (d, $J=6.7$ Hz, 3H, CH_3CH, **A**), 1.03 (d, $J=7.1$ Hz, 3H, $(CH_3)_2CH$, **A**), 0.90 (d, $J=6.9$ Hz, 3H, CH_3CH, **B**), 0.81 (d, $J=7.1$ Hz, 3H, $(CH_3)_2CH$, **A**), 0.76 (d, $J=7.1$ Hz, 3H, $(CH_3)_2CH$, **B**), 0.69 (d, $J=7.1$ Hz, 3H, $(CH_3)_2CH$, **B**); ^{13}C NMR: δ 209.6, 209.1, 142.3, 142.1, 141.9, 141.5, 139.6, 138.9, 131.8, 131.6, 130.1, 128.4, 128.2, 128.1, 127.9, 125.7, 46.9, 43.4, 42.9, 21.4, 21.3, 17.8, 17.2, 16.9, 16.8, 13.5, 13.4; MS ($APCI^+$) *m/z*: 315.1 $[M+1]^+$; HRMS $[M+1]^+$: calcd for $C_{19}H_{23}O_2S$: 315.1413. Found: 315.1419.

3.5.4. [2*S*,(S)*S*] and [2*R*,(S)*S*]-1-Phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]propan-1-one (2dA) and (2dB). They were obtained as a 59:41 epimeric mixture by methylation of ketone **1d**. Chromatographic purification (hexane–ethyl acetate 1:1) afforded a mixture of **2dA** and **2dB** as a colorless oil. Overall yield: 77%.

Compound [2*S*,(S)*S*]-(**2dA**). Obtained by oxidation from a 85:15 mixture of *anti*- and *syn*-**14d**. Reaction time: 5 h. Eluent for chromatography: hexane–ethyl acetate 1:1. Yield: 65%. $[\alpha]_D^{20}$: +236.1 (*c* 1, $CHCl_3$); IR: 3058, 2979, 1683, 1499, 1180, 1083, 1032 cm^{-1}; ^1H NMR: δ 7.94 (m, 1H), 7.58 (m, 2H), 7.46–7.34 (m, 5H), 7.21–7.16 (m, 5H), 5.14 (q, $J=6.9$ Hz, 1H, CH_3CH), 2.35 (s, 3H, CH_3Ar), 1.41 (d, $J=6.9$ Hz, 3H, CH_3CH); ^{13}C NMR: δ 199.6, 141.8, 141.5, 140.8, 140.1, 135.8, 132.8, 131.8, 130.0, 128.7, 128.5, 128.3, 127.9, 126.5, 126.4, 42.6, 21.3, 18.9. MS (EI^+) *m/z*: 348 (M^+, 16), 243 (43), 225 (76), 135 (39), 105 (100), 91 (36), 77 (93); HRMS: calcd for $C_{22}H_{20}O_2S$: 348.1184. Found: 348.1184.

Compound [2*R*,(S)*S*]-(**2dB**) *from a mixture of* **A**+**B**, *obtained following method A*; ^1H NMR: δ 8.03 (dd, $J=7.7$, 1.6 Hz, 1H), 7.60–7.33 (m, 8H), 7.27–7.17 (m, 5H), 5.05, (q, $J=6.6$ Hz, 1H, CH_3CH), 2.34 (s, 3H, CH_3Ar), 1.07 (d, $J=6.6$ Hz, 3H, CH_3CH); ^{13}C NMR: δ 189.9, 142.3, 141.9, 141.2, 139.4, 135.7, 133.1, 131.6, 130.9, 130.2, 128.2, 128.1, 126.6, 126.2, 125.6, 42.4, 21.4, 18.4; MS ($APCI^+$) *m/z*: 349.0 $[M+1]^+$. Anal. calcd for $C_{22}H_{20}O_2S$: C, 75.83; H, 5.79; S, 9.20. Found: C, 75.54; H, 5.96; S, 8.95.

3.5.5. [2*S*,(S)*S*]-2-[2-(*p*-Tolylsulfinyl)phenyl]heptan-3-one (2fA). Obtained by oxidation of a 37:63 mixture of *anti*- and *syn*-**14f**. Reaction time: 21 h. Eluent for chromatography: hexane–ethyl acetate 3:2. Yield: 74%. $[\alpha]_D^{20}$: +152.5 (*c* 1, $CHCl_3$); IR: 2930, 1714, 1468, 1083, 1033 cm^{-1}; ^1H NMR: δ 8.00 (m, 1H), 7.51–7.42 (m, 2H), 7.47 and 7.27 (AA'BB' system, 4H), 7.12 (m, 1H), 4.21 (q, $J=6.9$ Hz, 1H, CH_3CH), 2.37 (s, 3H, CH_3Ar), 1.80 (m, 2H, $COCH_2$), 1.33–1.18 (m, 2H, $CH_2CH_2CH_2$), 1.21 (d, $J=6.9$ Hz, 3H, CH_3CH), 1.06–0.93 (m, 2H, CH_2CH_3), 0.72 (t, $J=7.3$ Hz, 3H, CH_3CH_2); ^{13}C NMR: δ 209.6, 142.2, 142.0, 141.5, 139.5, 131.7, 130.1, 128.3, 127.9, 126.4, 126.3, 46.9, 40.7, 25.5, 21.9, 21.3, 17.8, 13.6; MS (EI^+) *m/z*: 328 (M^+, 15), 243 (33), 225 (100), 211 (52), 151 (44), 135 (94), 91 (54), 77 (27); HRMS: calcd for $C_{20}H_{24}O_2S$: 328.1496. Found: 328.1497.

3.5.6. [4*S*,(S)*S*]-2,2′-Dimethyl-4-[2-(*p*-tolylsulfinyl)-phenyl]pentan-3-one (2gA). Obtained by oxidation from a 24:76 mixture of *anti*- and *syn*-**14g**. Reaction time: 21 h. Eluent for chromatography: hexane–ethyl acetate 3:2. Yield: 73%. $[\alpha]_D^{20}$: +75.1 (*c* 1, $CHCl_3$); IR: 2970, 1703, 1470, 1084, 1054 cm^{-1}; ^1H NMR: δ 7.83 (m, 1H), 7.52 (m, 2H), 7.45–7.30 (m, 5H), 4.84 (q, $J=6.9$ Hz, 1H, CH_3CH), 2.41 (s, 3H, CH_3Ar), 1.22 (d, $J=6.9$ Hz, 3H, CH_3CH), 0.93 (s, 9H, $(CH_3)_3$); ^{13}C NMR: δ 215.8, 141.8, 141.3, 140.7, 140.6, 131.8, 130.0, 128.0, 127.7, 127.3, 126.1, 45.0, 40.6, 26.2, 21.3, 20.5; MS (EI^+) *m/z*: 328 (M^+, 10), 243 (31), 225 (100), 211 (31), 151 (23), 135 (69), 91 (44), 77 (22); HRMS: calcd for $C_{20}H_{24}O_2S$: 328.1500. Found: 328.1497.

3.5.7. [1*S*,(S)*S*]-1-(*p*-Methoxyphenyl)-2-[2-(*p*-tolylsulfinyl)phenyl)]propanone (2hA). It was obtained by oxidation of a 84:16 mixture of *anti*- and *syn*-**14h**. Reaction time: 6 h. Eluent for chromatography: hexane–ethyl acetate 1:1. Yield: 74%; mp: 139–140 °C (diethyl ether–hexane). $[\alpha]_D^{20}$: +183.2 (*c* 1, $CHCl_3$); IR: 1674, 1600, 1510, 1263, 1084, 1030 cm^{-1}; ^1H NMR: δ 7.94 (m, 1H), 7.57 and 7.45 (AA'BB' system, 4H), 7.38 (m, 2H), 7.22 and 6.57 (part of AA'BB' system, 4H), 7.19 (m, 1H), 5.08 (q, $J=6.9$ Hz, 1H, CH_3CH), 3.77 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3Ar), 1.37 (d, 3H, CH_3CH); ^{13}C NMR: δ 198.1, 163.2, 141.8, 141.3, 140.8, 140.5, 131.8, 130.9, 130.1, 128.7, 127.8, 126.5,

126.4, 113.5, 53.3, 42.3, 21.3, 19.0. Anal. calcd for $C_{23}H_{22}O_3S$: C, 72.99; H, 5.86; S, 8.47. Found: C, 73.05; H, 5.37; S, 8.00; MS (EI^+) *m/z*: 378 (M^+, 2), 243 (22), 225 (21), 135 (100), 91 (9), 77 (17); HRMS: calcd for $C_{23}H_{22}O_3S$: 378.1290. Found: 378.1295.

3.5.8. (2*S*,(S)*S*)-1-(2,6-Dimethylphenyl)-2-[2-(*p*-tolysulfinyl)phenyl)]propanone (2iA).[15] It was obtained by oxidation of a 67:33 mixture of *anti*- and *syn*-**14i**. Reaction time: 7 h. Eluent for chromatography: hexane–ethyl acetate 1:1. Yield: 71%; mp: 106–107 °C (diethyl ether–hexane). $[\alpha]_D^{20}$: −48.2 (*c* 0.75, $CHCl_3$); IR: 1698, 1466, 1085, 1033 cm^{-1}; ^1H NMR: δ 7.57–7.51 (m, 2H), 7.47 (dt, J= 1.6, 8.1 Hz, 1H), 7.35 (dt, J=1.6, 8.1 Hz, 1H), 7.15 (t, J= 7.7 Hz, 1H), 7.03 and 6.92 (AA'BB' system, 4H), 6.84 (d, J=8.1 Hz, 2H), 5.16 (q, J=6.9 Hz, 1H, CH_3CH–), 2.32 (s, 3H, CH_3Ar), 2.00 (s, 6H, 2 CH_3Ar), 1.64 (d, J=6.9 Hz, 3H, CH_3–CH–); ^{13}C NMR: δ 208.2, 144.7, 141.4, 140.9, 140.6, 138.1, 133.4, 131.6, 129.7, 128.9, 128.6, 128.0, 127.3, 124.7, 48.1, 21.3, 19.5, 18.5. Anal. calcd for $C_{24}H_{24}O_2S$: C, 76.56; H, 6.42; S, 8.52. Found: C, 76.73; H, 6.27; S, 8.06; MS (EI^+) *m/z*: 376 (M^+, 5), 243 (10), 225 (24), 133 (100), 105 (36), 91 (10), 77 (13); HRMS: calcd for $C_{24}H_{24}O_2S$: 376.1497. Found: 376.1491.

3.6. Protocol for obtaining compounds 11 and 11′

To a solution of *n*-BuLi (0.86 mmol, 2.5 M in hexane) was added *i*-Pr_2NH (1.28 mmol) in THF (5.1 mL) at 0 °C. After stirring for 30 min, the mixture was cooled at −78 °C and a solution of the sulfoxide **9** (0.71 mmol) in THF (2.5 mL) was added. After stirring for 40 min the purple carbanion **9** was added slowly with a syringe to a preparative TLC plate of silica gel. After 12 h the mixture was extracted with ethyl acetate, and filtered. The solvent was evaporated and the residue was separated by flash chromatography (ethyl acetate–hexane 2:1) to afford pure compounds **11** and **11′**.

3.6.1. Compound 11. It was obtained as a colorless oil. Yield: 22%; ^1H NMR: δ 7.70 (dd, J=7.6, 1.6 Hz, 1H), 7.40–7.20 (m, 3H), 6.01 (dd, J=9.6, 4.7 Hz, 1H, CH=CH–C–CH_3), 5.84 (d, J=9.6 Hz, 1H, CH=CH–C–CH_3), 5.09 (m, 1H, CH=C–CH_3), 3.83 (ddd, J=12.3, 4.7, 1.7 Hz, 1H, CHSO), 3.47 (dq, J=7.2, 2.9 Hz, 1H, $CHCH_3$), 3.26 (m, 1H, CH–CH–CH_3), 1.61 (m, 3H, CH=C–CH_3), 1.29 (d, J= 7.2 Hz, 3H, $CHCH_3$); ^{13}C NMR: δ 141.8, 141.7, 130.9, 130.4, 126.9, 126.8, 126.6, 120.6, 120.5, 64.9, 38.4, 36.7, 21.3, 16.9.

3.6.2. Compound 11′. It was obtained as a white solid. Yield: 20%; $[\alpha]_D^{20}$ = −129 (*c* 0.54, $CHCl_3$); ^1H NMR: δ 7.77 (dd, J=7.3, 1.5 Hz, 1H), 7.55–7.25 (m, 3H), 6.91 (t, J= 9.6 Hz, 1H, CH=C–S), 5.46 (m, 1H, CH=C–CH_3), 3.91 (m, 1H, CH_3–CH–CH), 3.10 (dq, J=7.1, 4.1 Hz, 1H, CH–CH_3), 2.85 (m, 2H, CH_2–CH–CH_3), 1.78 (s, 3H, CH= C–CH_3), 0.96 (d, J=7.1 Hz, 3H, CH–CH_3); ^{13}C NMR: δ 142.2, 137.8, 131.7, 131.4, 131.2, 130.1, 129.9, 127.8, 120.7, 40.0, 32.7, 32.3, 22.7, 18.7; MS ($APCI^+$) *m/z*: 245.1 $[M+1]^+$. Anal. calcd for $C_{15}H_{16}OS$ C, 73.73; H, 6.60; S, 13.12. Found: C, 72.92; H, 6.60; S, 12.64; HRMS: calcd for $C_{15}H_{16}OS$: 244.0922. Found: 244.0917.

3.7. Protocol for the synthesis of alcohol 12

3.7.1. Compound [1*S*,(S)*S*]-1-[2-(*p*-tolylsulfinyl)phenyl]-ethanol (12).[7f] To a solution of *n*-BuLi (0.33 mmol, 2.5 M in hexanes) was added *i*-Pr_2NH (0.49 mmol) in THF (1.7 mL) at 0 °C. After stirring for 30 min, the mixture was cooled at −78 °C and a solution of the sulfoxide **9** (0.27 mmol) in THF (1.1 mL) was added. After stirring for 1 h the purple carbanion **9** was slowly added, into a solution of ethyl acetate (10.9 mmol) in THF (1.1 mL) at −78 °C. The reaction was stirred for 30 min and quenched with saturated NH_4Cl, extracted with CH_2Cl_2 (3×20 mL), dried ($MgSO_4$) and the solvent evaporated. The residue was purified by flash chromatography (ethyl acetate–hexane 6:4) to afford alcohol **12** as a colorless oil. Yield: 62%. $[\alpha]_D^{20}$= −37 (*c* 9.1, $CHCl_3$); ^1H NMR: δ 7.86 (d, J=7.7 Hz, 1H), 7.59–7.23 (m, 7H), 5.26 (dq, J=6.5, 3.6 Hz, 1H, CH–CH_3), 2.99 (d, J=3.6 Hz, 1H, OH), 2.36 (s, 6H, CH_3Ar), 1.46 (d, J=6.5 Hz, 3H, $CHCH_3$); ^{13}C NMR: δ 144.1, 142.0, 141.3, 131.9, 129.9, 128.4, 126.5, 126.4, 126.3, 125.3, 65.1, 23.2, 21.3; MS (FAB^+) *m/z*: 261 $[M+1]^+$, 260 (4), 243 (100), 242 (88). Anal. calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19; S, 12.32. Found: C, 69.22; H, 6.47; S, 11.75.

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