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The Sulfinyl Group as a Remote Chiral Auxiliary in Stereoselective Conjugate Additions of Alkyl Groups to α-Methylidene Carbonyl Compounds Initiated by Et_3B/O_2

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Dedicated to the memory of our colleague and friend Christian G. Claessens

Keywords: Radical reactions / Conjugate addition / Diastereoselectivity / Chiral auxiliaries / Allylation / Sulfoxides

Reactions of α-[2-(*p*-tolylsulfinyl)phenyl] α-methylidene carbonyl compounds **1** and **2** with alkyl radicals generated from Et_3B/O_2 and RI give, after protonation, β-alkyl derivatives with a high degree of control of the configuration at the α carbon. In the case of aldehyde **2**, when further combined with allylation of the carbonyl group, a one-pot radical-addition/protonation/allylation sequence provides a highly stereoselective synthesis of compounds bearing two adjacent chiral centres. The stereochemical course of the reaction is controlled by the sulfinyl group acting as a remote chiral auxiliary, and this group can be easily removed with *t*BuLi.

Introduction

The sulfinyl group has been widely used in asymmetric synthesis as a chiral auxiliary in many types of ionic and concerted reactions.[1] However, its use as a stereocontrolling group in radical processes is much more limited.[2] Vinyl sulfoxides undergo facile inter- and intramolecular radical conjugate additions with a variety of radicals.[3] For some of these reactions to proceed with a good diastereoselectivity, the presence within the substrate of an additional Lewis base (e.g., a keto or alkoxy group) is required. This can form a chelation complex with the Lewis acids used as catalysts, and so provide sterically differentiated diastereotopic faces.[3d,4] However, for 2-arylsulfinyl enones,[5,6] dipolar repulsion of the C=O and S–O bonds can control the stereoselectivity in the absence of Lewis acids.[7] The main problem with these reactions derives from the fact that one of the chiral centres formed in the reaction is attached to the sulfinyl group, and is eliminated upon removal of the chiral auxiliary. Thus, the use of a sulfinyl group as a remote chiral auxiliary that could be removed without affecting the chiral elements of the product molecules, could be very interesting. With this idea in mind, we initiated a program to investigate whether a remote sulfinyl group could efficiently control the stereoselectivity of ionic reactions. Most of these studies concerned 1,4- and 1,5-asymmetric induction processes using lithium 2-*p*-tolylsulfinylbenzyl carbanions as nucleophiles,[8] but excellent results were also obtained in reactions in which the sulfinyl moiety was incorporated into the electrophile.[9]

With the aim of widening the scope of the remote asymmetric induction mediated by sulfoxides, we decided to explore their efficiency in radical reactions. This paper is our first contribution to this field. We focussed our attention on intermolecular 1,4-radical additions to enantiomerically pure β-unsubstituted, α,β-unsaturated ketones bearing a 2-(*p*-tolylsulfinyl)phenyl group[10] (Scheme 1) at the α-position. We wanted to study the ability of the sulfoxide moiety to act as a remote chiral auxiliary in these radical processes, as it is well known that it can act in that capacity in similar ionic reactions.[11] Moreover, the almost neutral conditions used in these radical processes could provide enantiomerically pure α-alkyl benzylketones, which are not easily obtained using ionic reactions due to their facile epimerization. In this paper, we describe the reactions of alkyl radicals with enones **1A**–**1E** and enal **2** (Scheme 1) to evaluate the role of the sulfinyl group on the stereoselectivity. The scope of these reactions for generating benzylic chiral centres is also explored. Moreover, for compound **2**, the one-pot radical-addition/protonation/allylation (with allyltributyltin) process, involving the simultaneous creation of two chiral centres, is also reported.

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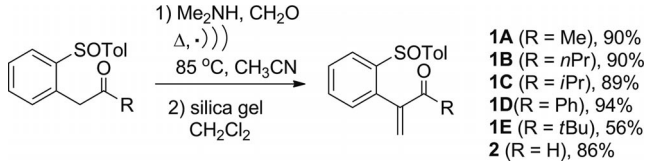
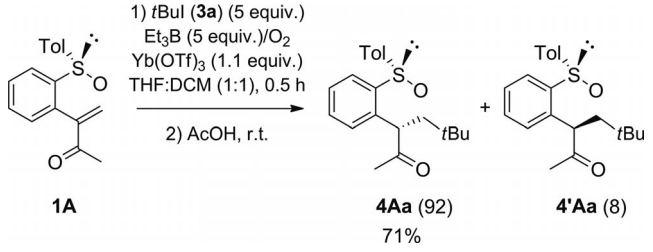


Scheme 1. Synthesis of the starting materials.

Results and Discussion

The synthesis of unsaturated ketones **1A**–**1E** has been reported previously, starting from appropriate (*S*)-2-(*p*-tolylsulfinyl)benzyl ketones.[12] The starting ketones were treated with Me_2NH and formaldehyde in a modified Mannich reaction under ultrasound irradiation to give the corresponding adducts. These adducts were subsequently treated with silica gel to eliminate the dimethylamino group (Scheme 1).[9] The synthesis of (*S*)-2-[2-(*p*-tolylsulfinyl)-phenyl]propenal (**2**) was performed using the same procedure (Scheme 1).

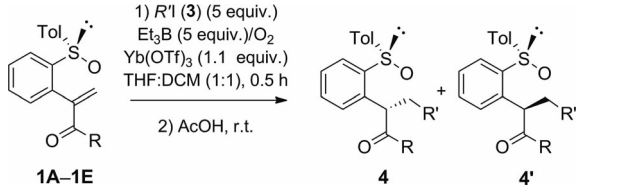
We first studied the reaction of **1A** with *tert*-butyl radical, generated using Et_3B/O_2 as the initiator system[13] and *t*BuI (**3a**) as the radical source.[14] The initial trials, performed in the presence of Bu_3SnH (acting as chain-carrier and H-atom donor[15]), gave low yields and poor stereoselectivities.[16] Thus, we decided to remove the Bu_3SnH, which meant that Et_3B would act both as radical initiator (providing the ethyl radicals required to generate *tert*-butyl radicals from *t*BuI) and chain-carrier[17] (see Scheme 8). Therefore, it would be necessary to use a protonation agent to obtain compound **4Aa**. After optimization of the reaction conditions[18] (solvent, Lewis acid, protonation agent, and reaction temperature, see SI for details), the best yields and stereoselectivities were observed by using a 1:1 mixture of THF and CH_2Cl_2 as solvent, $Yb(OTf)_3$ as Lewis acid, and AcOH as proton source. The protonation temperature is the main factor controlling the stereoselectivity, with the highest *de* value being obtained at room temp. As we can see in Scheme 2, an easily separable 92:8 mixture of **4Aa** and **4′Aa** was obtained under these conditions, with the major product being isolated in diastereomerically pure form in 71% yield.



Scheme 2. Optimal conditions for the conjugate addition of the *tert*-butyl radical to ketone **1A**.

We then evaluated the scope of the reaction, considering the nature of the radical precursor as well as the substituent on the carbonyl group. Regarding the radical precursor, we found that the addition of tertiary radicals derived from **3a** and **3b**, gave the expected products exclusively and in good yields (Table 1). The stereoselectivity was dependent on the size of the R group at the starting ketone. Thus, reactions of **1A** with **3a** (Table 1, entry 1) and **3b** (Table 1, entry 2) gave diastereomeric mixtures of **4Aa** (*dr* 92:8) and **4Ab** (*dr* 90:10), respectively. Similar results were obtained in the reactions of **1B** (R = *n*Pr) with **3a** and **3b** (Table 1, entries 4 and 5), which afforded compounds **4Ba** (*dr* 92:8) and **4Bb** (*dr* 90:10) exclusively. Reactions with *t*BuI (**3a**) were also studied with **1C** (Table 1, entry 7) and **1D** (Table 1, entry 8), which gave diastereoisomeric mixtures of **4Ca** (*dr* 68:32) and **4Da** (*dr* 80:20), respectively. Finally, **1E** did not react with **3a** (Table 1, entry 9).

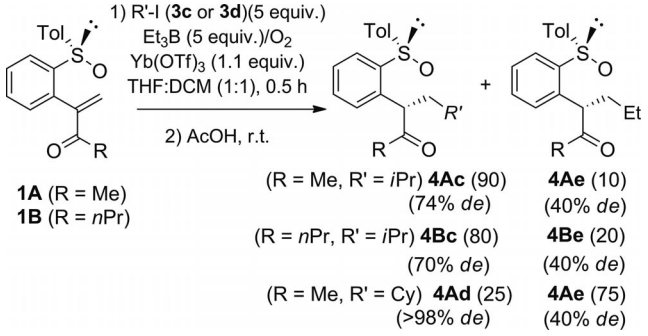
Table 1. Reactions of enones **1A**–**1E** with alkyl radicals.



Entry[a]	1 (R)	**3** (R′)	**4**:**4′** (*dr*) [b]	Yield [%][c]
1	**1A** (Me)	**3a** (*t*Bu)	**4Aa**:**4′Aa** (92:8)	71 (**4Aa**)
2	**1A** (Me)	**3b**[d]	**4Ab**:**4′Ab** (90:10)	78 (**4Ab**)
3	**1A** (Me)	–	**4Ae**:**4′Ae** (70:30)	65 (**4Ae**)
4	**1B** (*n*Pr)	**3a** (*t*Bu)	**4Ba**:**4′Ba** (92:8)	80 (**4Ba**)
5	**1B** (*n*Pr)	**3b**[d]	**4Bb**:**4′Bb** (90:10)	79 (**4Bb**)
6	**1B** (*n*Pr)	–	**4Be**:**4′Be** (70:30)	78 (**4Be + 4′Be**)
7	**1C** (*i*Pr)	**3a** (*t*Bu)	**4Ca**:**4′Ca** (68:32)	61 (**4Ca + 4′Ca**)
8	**1D** (Ph)	**3a** (*t*Bu)	**4Da**:**4′Da** (80:20)	65 (**4Da + 4′Da**)
9	**1E** (*t*Bu)	**3a** (*t*Bu)	–	–

[a] For experimental details, see Supporting Information. [b] Determined by ^1H NMR spectroscopy. [c] Isolated yield. [d] R′ = $Cl(CH_2)_3(CH_3)_2C$–.

The behaviour of the secondary radicals was different (Scheme 3). The reaction of **1A** with *i*PrI (**3c**) gave a 90:10 mixture of the expected adduct **4Ac** (*dr* 87:13) and compound **4Ae** (*dr* 70:30), resulting in the addition of the ethyl radical to the starting enone **1A** (Scheme 3). A similar situation was observed in the reaction of **1B** with **3c**, which gave an 80:20 mixture of **4Bc** (*dr* 85:15) and **4Be** (*dr* 70:30). Significant differences were observed in the reaction of **1A** with cyclohexyl iodide (**3d**), which also gave a 25:75 mixture of **4Ad** (*dr* > 98:2) and **4Ae** (*dr* 70:30), but with the expected cylohexyl adduct **4Ad** as the minor component in the reac-

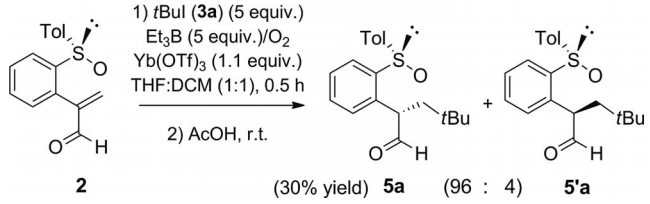


Scheme 3. Reactions of enones **1A** and **1B** with secondary radicals.

tion mixture (Scheme 3). We could not improve this result by changing the ratio of **3d** to Et_3B (see SI for details).[19] These results indicate that ethyl radicals (generated from Et_3B and O_2) compete with secondary radicals for the substrate **1A**.

The absence of adducts formed from ethyl radicals in the reactions reported in Table 1 suggests that the ethyl radicals are consumed in the very fast formation of tertiary radicals, which are the only species that go on to attack the substrate. This means that the rate of formation of tertiary radicals is much higher than the rate of attack of the ethyl radicals on the substrate. In contrast, the presumably slower formation of the secondary radicals (by the reaction of ethyl radicals with secondary halides) would determine that the two rates (i.e., the rate of formation of secondary radicals and the rate of reaction of ethyl radicals with the substrate) become similar, and ethyl and secondary radicals would be present simultaneously, competing for the substrate, and so forming mixtures of reaction products. According to this explanation, the presumably very slow formation of primary radicals (by reaction of the appropriate R–I with the ethyl radical), compared to the rate of attack of ethyl radical on the substrate, suggests that the almost exclusive formation of ethyl radical adducts would be expected. We have confirmed this suggestion in the reactions of **1A** or **1B** with several primary alkyl iodides (*n*-butyl, ethoxycarbonylmethyl, benzyl, methoxymethyl, allyl, etc).[20] In all these cases, compounds **4Ae** or **4Be** were obtained exclusively. As expected, these products were also formed from enones **1A** and **1B** with Et_3B/O_2 in the absence of alkyl iodides (Table 1, entries 3 and 6).

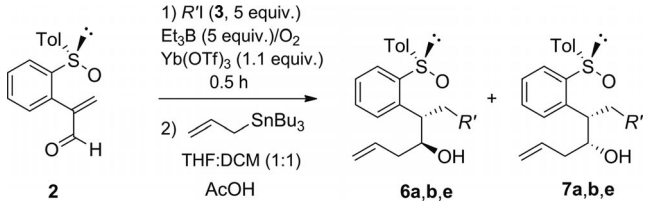
We then studied reactions of aldehyde **2** with **3a** (Scheme 4), which took place with complete chemoselectivity (compound **5e**, obtained from the reaction of ethyl radical with **2** was not observed). Regioselectivity (only 1,4-radical addition products were formed) and stereoselectivity were also very high, and a 96:4 mixture of **5a** and **5′a** was obtained. However, despite the fact that the reaction was very clean, and conversion to the product was quantitative, as judged from the NMR spectra of the crude reaction product, the isolated yield for **5a** was rather modest (30%). As this result can be attributed to the instability of the resulting aldehyde under the purification conditions, we decided to attempt the in situ transformation of the aldehyde group in **5** to obtain a more easily isolable compound.



Scheme 4. Reaction of aldehyde **2** with **3a**.

The usually good results obtained in reactions of allylmetal reagents with carbonyl compounds, especially those catalysed by $Yb(OTf)_3$ and a carboxylic acid,[21] suggested to us that allyltributyltin[22,23] would be an appropriate reagent to trap the crude aldehyde formed in the reaction of **2** with *tert*-butyl iodide (**3a**), in which both of these catalytic species would already be present. The results are given in Table 2. Under these conditions, it was possible to obtain diastereomerically pure **6a** in good yield (60%) from the 96:4 diastereomeric mixture of **6a** and **7a** (Table 2, entry 1). A similar reaction with the tertiary radical generated from **3b** gave a 90:10 mixture of **6b** and **7b**, from which **6b** was isolated in 61% yield (Table 2, entry 2). Finally, the reaction of **2** with EtI (**3e**) followed by treatment with the tin derivative, gave an 85:15 mixture of alcohols **6e** and **7e** (Table 2, entry 3), from which pure **6e** was obtained in 58% yield. We also performed reactions with *i*PrI and CyI (Cy = cyclohexyl), but in both cases, 85:15 mixtures of **6e** and **7e** were formed exclusively. Enones **1A**–**1E** did not react under the conditions of the addition/protonation/allylation process.

Table 2. Results obtained from **2** in the conjugate-addition/protonation/allylation process.



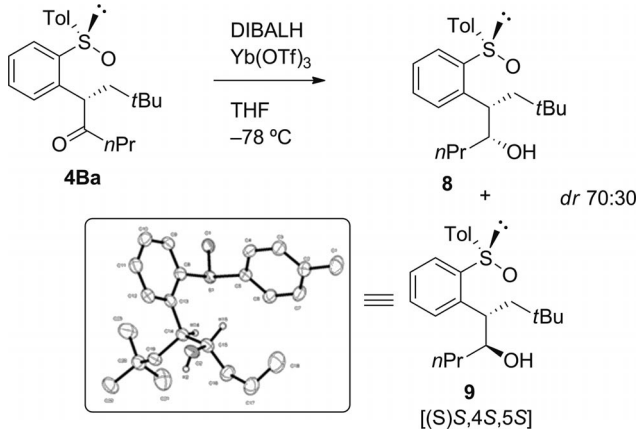
Entry[a]	**3** (R′)	*dr* (**6**:**7**)[b]	Yield [%][c]
1	**3a** (*t*Bu)	96:4	60 (**6a**)
2	**3b** [$Cl(CH_2)_3(CH_3)_2C$–]	90:10	61 (**6b**)
3	**3c** (*i*Pr)	–[d]	–
4	**3d** (Cy)	–[d]	–
5	**3e** (Et)	85:15	58 (**6e**)

[a] For experimental details, see Supporting Information. [b] Determined by ^1H NMR spectroscopy. [c] Isolated yield. [d] An 85:15 mixture of ethyl adducts **6e:7e** was obtained.

Configurational Assignments

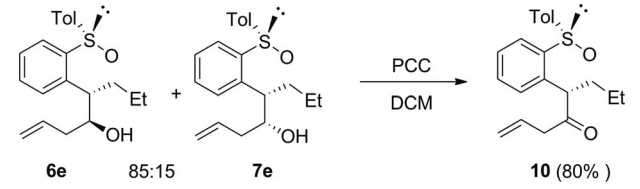
The configurational assignment of the compounds in Table 1 was unequivocally established as follows: compound **4Ba**, obtained as the major product in Table 1, entry 4, was reduced with DIBALH (diisobutylaluminium hydride) and $Yb(OTf)_3$ to give a 70:30 mixture of two alcohols (**8** and **9**), which were epimeric at the hydroxylic carbon (Scheme 5). After their chromatographic separation, the minor product (i.e., **9**) was analysed by X-ray diffraction,[24] which allowed us to assign it the [(S)*S*,4*S*,5*S*] configuration (Scheme 5). Then, the starting material (i.e., **4Ba**) should be assigned as [(S)*S*,*S*]. We assigned the same configuration to all the major products **4** shown in Table 1.

The configuration of compound **6a** (Table 2) was unequivocally established to be [(S)*S*,4*S*,5*S*] by X-ray diffraction studies.[25] The same configuration was assigned to major diastereoisomers **6b** and **6e** shown in Table 2. The minor diastereoisomers (i.e., **7**) were assigned as [(S)*S*,4*R*,5*S*] based on the fact that the PCC oxidation of a diastereomeric mixture of **6e** + **7e** gave diastereomerically



Scheme 5. Configurational assignment of compound **4Ba**.

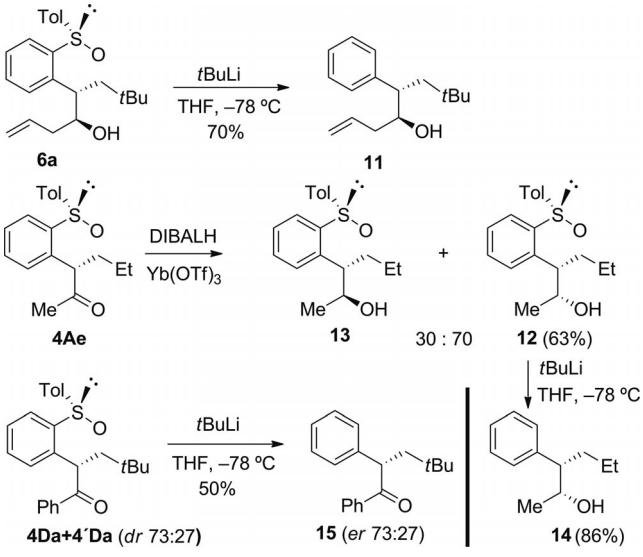
pure ketone **10** (Scheme 6), which indicates that **6e** and **7e** were epimers at the hydroxylic carbon.



Scheme 6. PCC oxidation of an 85:15 mixture of **6e** and **7e**.

Desulfinylation Reactions

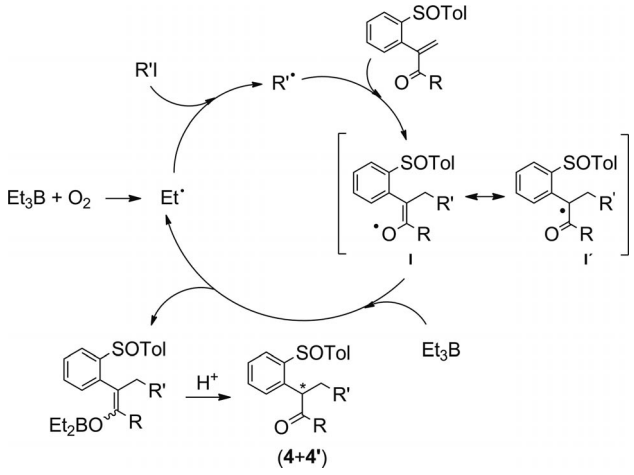
The carbinols shown in Table 2 can be easily desulfinylated with *t*BuLi,[26] as we have demonstrated for compound **6a**. Under the reaction conditions used, the configurational integrity of the two chiral centres was not affected, and compound **11** was obtained in diastereomerically pure form (> 98% *de*) in high yield (Scheme 7). In a similar way, carbinol **12**, obtained as the major diastereoisomer in the DIBALH reduction of **4Ae**, could also be desulfinylated to give **14** without erosion of its configurational integrity (Scheme 7). It is remarkable that desulfinylation with *t*BuLi can be applied to ketones **4** without producing epimerization, despite the high acidity of their benzylic protons. Thus, starting from the inseparable 73:27 diastereomeric mixture of **4Da** + **4′Da**, we obtained desulfinylated compound **15** as a 73:27 enantiomeric mixture (measured by chiral HPLC), which suggested that none of the initial diastereoisomers had suffered epimerization.



Scheme 7. Desulfinylation reactions.

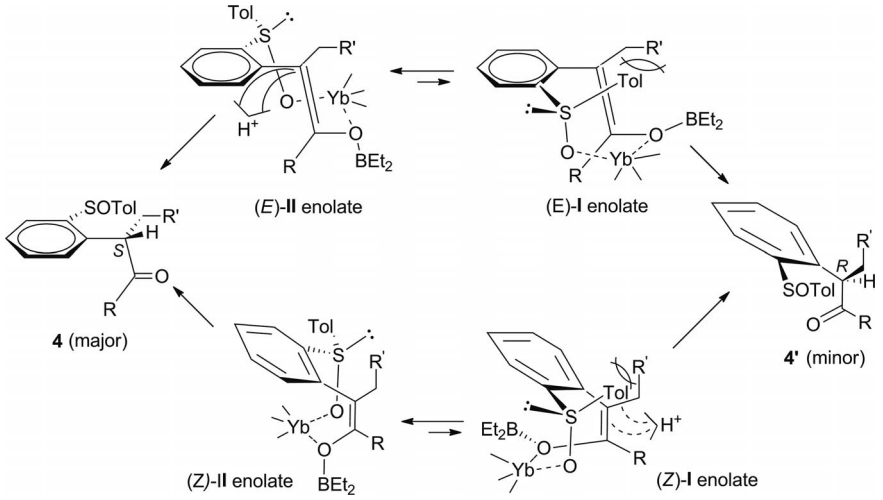
Mechanistic Proposal

From the results obtained, we can conclude that protonation is the most important step in the control of stereoselectivity. Moreover, the diastereomeric excesses are higher when the size of the attacking radical increases (tertiary > secondary > primary). According to the literature, Et_3B acts as chain initiator and chain carrier in the absence of Bu_3SnH,[17] capturing the enoyl radical and generating a boron enolate[27] and an ethyl radical to carry the chain (Scheme 8). Finally, compounds **4** and **4′** are the result of protonation of the boron enolates.



Scheme 8. Mechanism proposed for the reactions with Et_3B in the absence of Bu_3SnH.[27]

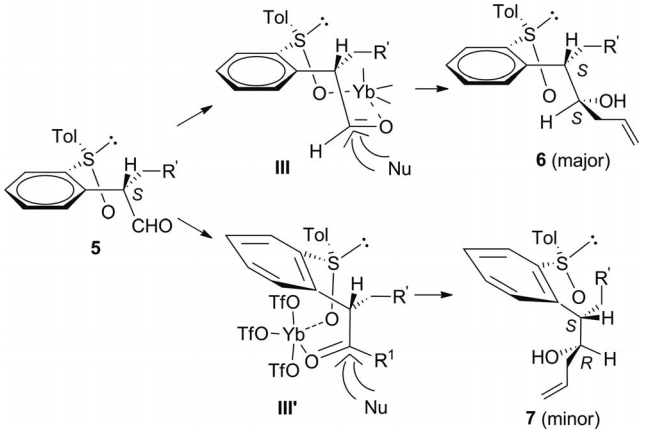
Taking into account that the results indicated in Schemes 2, 3, 4, and Table 1 were obtained in the presence of $Yb(OTf)_3$, the (*E*) and (*Z*) enolates will presumably form chelated species that can adopt two main conformations, **I** and **II**, where the sulfinyl groups are respectively located on the *re* and *si* faces of the enolates (Scheme 9). All of these species have only one face accessible to the approach of the proton (the opposite face to that occupied by the sulfinyl group), which will result in the formation of isomers **4** and **4′** according to the mechanism shown in Scheme 9. As the protonation rate must be similar for the different boron enolates, the observed ratio of **4**:**4′** should depend on the relative stability of the starting enolates. Conformations **II** will be favoured, in both (*E*) and (*Z*) isomers, because the (pTol/CH_2R′) interaction destabilizes conformations **I** (Scheme 9), and this preference is higher when the R group



Scheme 9. Chelated species formed by (*E*) and (*Z*) boron enolates with $Yb(OTf)_3$.

becomes larger (*t*Bu > *i*Pr > Et). The predominance of isomers **4** in all the reaction mixtures can be explained as being the result of the protonation of species (*E*)-**II** and (*Z*)-**II**, which must be favoured in the equilibrium shown in Scheme 9. The dependence of the stereoselectivity on the protonation temperature, with a maximum stereoselectivity being observed at room temp., can be rationalized by assuming a slow equilibration at lower temperatures.

Finally, the stereochemical results obtained in the one-pot radical-addition/protonation/allylation of aldehyde **2** (Table 2) can be explained by assuming that allylation takes place after protonation of the boron enolate formed from the radical adduct. According to Scheme 4, protonation of this enolate will mainly generate compounds **5**, with an *S* configuration at the benzylic carbon. It could form two chelated species, **III** and **III′** (Scheme 10), neither of which have an interaction between the Tol and the CH_2R' groups, but with **III′** being unfavoured due to the interactions of the Lewis acid with the aromatic ring. The approach of the allylic reagent to the only accessible face of **III** would explain the formation of [(S)*S*,*S*,*S*]-**6** as the major carbinol in these reactions.



Scheme 10. Reaction of the aldehyde adduct **5**.

Conclusions

The results described in this paper indicate that the sulfinyl group can act as an efficient remote chiral auxiliary in conjugate additions to 3-arylenones **1** conducted with Et_3B/O_2 and alkyl iodides. This efficiency is related to the ability of the sulfinyl group and the boron enolate formed in the initial radical step to form chelated species with $Yb(OTf)_3$ that have sterically well-differentiated diastereotopic faces. The one-pot radical conjugate-addition/protonation/carbonyl allylation of aldehyde **2**, allows the simultaneous creation of two chiral centres in a highly stereoselective manner.

Experimental Section

General Methods: NMR spectra were acquired with a Bruker AC-300 instrument at 300 and 75.5 MHz for ^1H and ^{13}C NMR, respectively. Chemical shifts (δ) are reported in parts per million relative to TMS, using residual solvent signals as references ($CHCl_3$: 7.26 ppm for ^1H, 77.0 ppm for ^{13}C). ^{13}C NMR spectra were acquired in broadband decoupled mode. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. Mass spectra (MS) were determined by FAB and ESI, as indicated in each case. High resolution mass spectra (HRMS) were performed using a magnetic-sector mass analyser (for FAB ionization mode) or time-of-flight (TOF) mass analyser (for ESI ionization modes), as indicated for each compound. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or phosphomolybdic acid dip. Flash column chromatography was performed using silica gel (230–400 mesh). All reactions were carried out in anhydrous solvents. THF and CH_2Cl_2 were dried with molecular sieves. Commercially available starting materials were used without purification. Alkyl iodides **3a** and **3c**–**3e** were purchased from Aldrich, and **3b**[28] was synthesized.

General Procedure for Radical Conjugate Addition: A solution of the corresponding α,β-unsaturated carbonyl compound (0.1 mmol) and $Yb(OTf)_3$ (0.11 mmol) in THF/CH_2Cl_2 (1:1, 0.05 M) was

stirred at room temp. for 30 min under an argon atmosphere. Then the alkyl iodide (0.5 mmol), triethylborane (1 M in hexane, 0.6 mmol), and O_2 (5 mL, by syringe) were added in that order at the same temperature. When the reaction had finished (as monitored by TLC), the mixture was treated with AcOH (1 mmol). Then, after stirring for 10 min, water (5 mL) was added. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The organic extracts were washed with brine (2 × 5 mL) and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography. The eluent is indicated in each case.

(*S*)-5,5-Dimethyl-3-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}hexan-2-one (4Aa): Compound **4Aa** was obtained as the major diastereomer from enone **1A** (29 mg, 0.1 mmol) and *tert*-butyl iodide (**3a**). Chromatography: *n*-hexane/EtOAc, 2:1, yield 71%; colourless oil. $[a]_D^{20}$ = +34.7 (*c* = 1.9, $CHCl_3$). ^{1}H NMR: δ = 8.09–8.06 (m, 1 H), 7.54–7.42 (m, 4 H), 7.30–7.22 (m, 3 H), 4.11 (dd, *J* = 7.8, 4.0 Hz, 1 H), 2.37 (s, 3 H), 2.23 (dd, *J* = 14.0, 7.9 Hz, 1 H), 1.50 (s, 3 H), 1.42 (dd, *J* = 14.1, 4.0 Hz, 1 H), 0.88 (s, 9 H) ppm. ^{13}C NMR: δ = 205.5, 141.6, 140.7, 140.6, 137.2, 130.4, 129.4, 127.5, 127.1, 126.2, 124.6, 48.9, 45.8, 30.2, 28.9, 28.0, 20.4 ppm. MS (ESI): *m*/*z* (%) = 362 (21) $[M + Na]^+$, 343 (100) $[M + 1]^+$. HRMS calcd. for $C_{21}H_{27}O_2S$ $[M + 1]^+$ 343.1732; found 343.1725.

(*S*)-8-Chloro-5,5-dimethyl-3-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}octan-2-one (4Ab): Compound **4Ab** was obtained as the major diastereomer from enone **1A** (29 mg, 0.1 mmol) and 1-chloro-4-iodo-4-methylpentane (**3b**). Chromatography: *n*-hexane/EtOAc, 3:1, yield 78%; colourless oil. $[a]_D^{20}$ = +24.6 (*c* = 1.4, $CHCl_3$). ^{1}H NMR: δ = 8.09–8.06 (m, 1 H), 7.55–7.42 (m, 4 H), 7.30–7.22 (m, 3 H), 4.11 (dd, *J* = 4.0, 7.6 Hz, 1 H), 3.45 (t, *J* = 6.7 Hz, 2 H), 2.38 (s, 3 H), 2.28 (dd, *J* = 7.8, 14.3 Hz, 1 H), 1.77–1.64 (m, 2 H), 1.47 (s, 3 H), 1.38–1.21 (m, 3 H), 0.87 (s, 3 H), 0.83 (s, 3 H) ppm. ^{13}C NMR: δ = 206.4, 142.7, 141.8, 141.6, 138.2, 131.5, 130.4, 128.5, 128.5, 127.2, 125.7, 49.4, 45.8, 44.8, 39.7, 33.5, 29.0, 27.5, 27.4, 27.3, 21.5 ppm. MS (ESI): *m*/*z* (%) = 405 (100) $[M + 1]^+$, 315 (41). HRMS: calcd. for $C_{23}H_{30}ClO_2S$ [M + 1] + 405.1649; found 405.1634.

(*S*)-5-Methyl-3-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}hexan-2-one (4Ac): Compound **4Ac** was obtained as a 90:10 mixture of (**4Ac** + **4′Ac**, 74% *de*) and (**4Ae** + **4′Ae**, 40% *de*) from enone **1A** (29 mg, 0.1 mmol) and isopropyl iodide (**3c**). Compound **4Ac** was characterized from a 90:10 inseparable mixture of **4Ac** and **4Ae**. Chromatography: *n*-hexane/EtOAc, 2:1, total yield 74%; colourless oil. ^{1}H NMR: δ = 8.07–8.04 (m, 1 H), 7.52–7.45 (m, 4 H), 7.29–7.19 (m, 3 H), 4.15 (t, *J* = 7.7 Hz, 1 H), 2.37 (s, 3 H), 1.99–1.86 (m, 2 H), 1.55 (s, 3 H), 1.49–1.37 (m, 1 H), 0.90 (d, *J* = 6.5 Hz, 3 H), 0.84 (d, *J* = 6.4 Hz, 3 H) ppm. ^{13}C NMR: δ = 206.5, 142.3, 142.1, 141.6, 137.2, 131.1, 129.7, 127.9, 127.6, 125.8, 125.3, 50.9, 41.9, 28.6, 25.5, 22.2, 22.1, 20.9 ppm. MS (ESI): *m*/*z* (%) = 351 (37) $[M + Na]^+$, 329 (100) $[M + 1]^+$. HRMS calcd. for $C_{20}H_{25}O_2S$ $[M + 1]^+$ 329.1569; found 329.1566.

(*S*)-4-Cyclohexyl-3-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}butan-2-one (4Ad): Diastereomerically pure **4Ad** was isolated from a 25:75 mixture of (**4Ad** + **4′Ad**, 98% *de*) and (**4Ae** + **4′Ae**, 40% *de*) obtained from enone **1A** (29 mg, 0.1 mmol) and cyclohexyl iodide (**3d**). Chromatography: *n*-hexane/EtOAc, 3:1, yield 19%; colourless oil. $[a]_D^{20}$ = +6.9 (*c* = 0.75, $CHCl_3$). ^{1}H NMR: δ = 8.06–8.03 (m, 1 H), 7.53–7.44 (m, 4 H), 7.29–7.19 (m, 3 H), 4.19 (t, *J* = 7.0 Hz, 1 H), 2.37 (s, 3 H), 1.93 (dt, *J* = 7.4, 13.8 Hz, 1 H), 1.74–1.60 (m, 4 H), 1.58 (s, 3 H), 1.39 (dt, *J* = 13.8, 6.5 Hz, 1 H), 1.17–1.06 (m, 4 H), 0.89–0.83 (m, 3 H) ppm. ^{13}C NMR: δ = 206.2, 141.5, 141.3, 140.8, 136.9, 130.6, 129.3, 127.5, 127.1, 125.7, 125.0, 49.7, 39.9, 34.4, 32.5, 32.4, 28.1, 25.4, 25.1, 25.0, 20.4 ppm. MS (ESI): *m*/*z* (%) = 391 (12) $[M + Na]^+$, 369 (100) $[M + 1]^+$. HRMS calcd. for $C_{30}H_{29}O_2S$ $[M + 1]^+$ 369.1882; found 369.1886.

(*S*)-3-{2-[(*S*)-*p*-Tolylsulfinyl]phenyl}hexan-2-one (4Ae): Compound **4Ae** was obtained as the major diastereomer from enone **1A** (29 mg, 0.1 mmol). Chromatography: *n*-hexane/EtOAc, 3:1, yield 65%; colourless oil. $[a]_D^{20}$ = +51.6 (*c* = 0.7, $CHCl_3$). ^{1}H NMR: δ = 8.04–8.01 (m, 1 H), 7.53–7.43 (m, 4 H), 7.29–7.25 (m, 2 H), 7.21–7.17 (m, 1 H), 4.15 (t, *J* = 7.1 Hz, 1 H), 2.37 (s, 3 H), 1.99–1.89 (m, 1 H), 1.61 (s, 3 H), 1.42–1.20 (m, 2 H), 1.13–1.01 (m, 1 H), 0.83 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR: δ = 207.2, 142.9, 142.1, 141.7, 138.0, 131.8, 130.2, 128.5, 128.1, 126.8, 126.5, 53.1, 35.3, 29.2, 21.4, 20.8, 14.0 ppm. MS (ESI): *m*/*z* (%) = 337 (33) $[M + Na]^+$, 315 (100) $[M + 1]^+$. HRMS calcd. for $C_{19}H_{23}O_2S$ $[M + 1]^+$ 315.1413; found 315.1399.

(*S*)-7,7-Dimethyl-5-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}octan-4-one (4Ba): Compound **4Ba** was obtained as the major diastereomer from enone **1B** (31 mg, 0.1 mmol) and *tert*-butyl iodide (**3a**). Chromatography: *n*-hexane/EtOAc, 2:1, yield 80%; colourless oil. $[a]_D^{20}$ = +28.4 (*c* = 1.4, $CHCl_3$). ^{1}H NMR: δ = 8.12–8.09 (m, 1 H), 7.54–7.40 (m, 4 H), 7.30–7.20 (m, 3 H), 3.99 (dd, *J* = 8.3, 3.5 Hz, 1 H), 2.37 (s, 3 H), 2.98 (dd, *J* = 14.1, 8.3 Hz, 1 H), 1.70–1.60 (m, 2 H), 1.44–1.38 (m, 1 H), 1.27–1.12 (m, 2 H), 0.87 (s, 9 H), 0.54 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR: δ = 208.5, 142.7, 141.8, 141.4, 138.3, 131.3, 130.4, 128.5, 128.0, 127.6, 125.4, 49.3, 47.0, 43.9, 31.2, 29.9, 21.4, 16.7, 13.2 ppm. MS (ESI): *m*/*z* (%) = 393 (16) $[M + Na]^+$, 371 (100) $[M + 1]^+$. HRMS calcd. for $C_{23}H_{31}O_2S$ $[M + 1]^+$ 371.2039; found 371.2023.

(*S*)-10-Chloro-7,7-dimethyl-5-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}decan-4-one (4Bb): Compound **4Bb** was obtained as the major diastereomer from enone **1B** (31 mg, 0.1 mmol) and 1-chloro-4-iodo-4-methylpentane (**3b**). Chromatography: *n*-hexane/EtOAc, 3:1, yield 79%; colourless oil. $[a]_D^{20}$ = +44.0 (*c* = 0.85, $CHCl_3$). ^{1}H NMR: δ = 8.12–8.09 (m, 1 H), 7.56–7.41 (m, 4 H), 7.31–7.21 (m, 3 H), 4.02 (dd, *J* = 3.7, 8.1 Hz, 1 H), 3.49–3.44 (m, 2 H), 2.38 (s, 3 H), 2.30 (dd, *J* = 14.1, 8.1 Hz, 1 H), 1.75–1.60 (m, 2 H), 1.45–1.18 (m, 7 H), 0.87 (s, 3 H), 0.83 (s, 3 H), 0.55 (t, *J* = 7.4 Hz, 3 H) ppm. ^{13}C NMR: δ = 208.4, 142.8, 141.7, 141.5, 138.2, 131.4, 130.4, 128.5, 128.1, 127.6, 125.5, 48.8, 45.9, 45.1, 43.9, 39.8, 33.5, 27.5, 27.3, 21.4, 16.7, 13.3 ppm. MS (ESI): *m*/*z* (%) = 451 (19) $[M + Na]^+$, 433 (100) $[M + 1]^+$. HRMS calcd. for $C_{25}H_{34}ClO_2S$ $[M + 1]^+$ 433.1962; found 433.1908.

(*S*)- and (*R*)-7-Methyl-5-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}octan-4-one (4Bc + 4′Bc): Compounds **4Bc** and **4′Bc** were obtained as an 80:20 mixture of (**4Bc** + **4′Bc**, 74% *de*) and (**4Be** + **4′Be**, 40% *de*) from enone **1B** (31 mg, 0.1 mmol) and isopropyl iodide (**3c**). Compounds **4Bc** + **4′Bc** were characterized from an 80:20 inseparable mixture of **4Bc** + **4′Bc** and **4Be** + **4′Be**. Chromatography: *n*-hexane/EtOAc, 3:1, total yield 60%; colourless oil. ^{1}H NMR: δ = 8.09–8.07 (m, 1 H, **4**), 7.88–7.85 (m, 1 H, **4′**), 7.51–7.43 (m, 4 H), 7.28–7.19 (m, 3 H), 4.33 (dd, *J* = 5.0, 9.4 Hz, 1 H, **4′**), 4.06 (t, *J* = 7.0 Hz, 1 H, **4**), 2.38 (s, 3 H), 2.35 (m, 1 H), 2.08–1.87 (m, 1 H), 1.74–1.14 (m, 6 H), 0.90 (d, *J* = 6.4 Hz, 3 H, **4**), 0.85 (d, *J* = 6.4 Hz, 3 H, **4**), 0.77 (t, *J* = 7.4 Hz, 3 H, **4′**), 0.76 (d, *J* = 6.6 Hz, 3 H, **4′**), 0.71 (d, *J* = 6.6 Hz, 3 H, **4′**), 0.58 (t, *J* = 7.5 Hz, 3 H, **4**) ppm. ^{13}C NMR: δ = 208.4, 208.3, 143.2, 142.9, 142.8, 142.6, 142.3, 142.1, 141.8, 141.5, 138.8, 138.2, 138.0, 132.1, 131.9, 131.8, 130.6, 128.9, 128.8, 128.6, 128.4, 127.5, 126.9, 126.8, 126.7, 125.9, 51.1, 51.0, 43.0, 41.8, 26.7, 26.4, 23.4, 23.2, 22.9, 22.5, 17.4, 17.1, 14.4, 13.7 ppm. MS (ESI): *m*/*z* (%) = 379 (6) $[M + Na]^+$, 357 (100) $[M + 1]^+$. HRMS calcd. for $C_{22}H_{29}O_2S$ $[M + 1]^+$ 357.1882; found 357.1831.

(*S*)- and (*R*)-5-{2-[(*S*)-*p*-Tolylsulfinyl]phenyl}octan-4-one (4Be + 4′Be): Compounds **4Be** and **4′Be** were obtained as a 70:30

diastereoisomeric mixture from enone **1B** (31 mg, 0.1 mmol). Chromatography: *n*-hexane/EtOAc, 3:1, total yield 78%; colourless oil. ^{1}H NMR: δ = 8.07–8.04 (m, 1 H, **4**), 7.98–7.95 (m, 1 H, **4′**), 7.51–7.43 (m, 4 H), 7.28–7.19 (m, 3 H), 4.14 (dd, J = 9.0, 4.8 Hz, 1 H, **4′**), 4.06 (t, J = 7.0 Hz, 1 H, **4**), 2.38 (s, 3 H), 2.34–2.23 (m, 1 H), 1.99–1.86 (m, 1 H), 1.7–1.63 (m, 1 H), 1.50–1.02 (m, 5 H), 0.84 (t, J = 7.2 Hz, 3 H, **4**), 0.78 (t, J = 7.3 Hz, 3 H, **4′**), 0.70 (t, J = 7.1 Hz, 3 H, **4′**), 0.60 (t, J = 7.4 Hz, 3 H, **4**) ppm. ^{13}C NMR: δ = 209.2, 209.0, 142.8, 142.7, 142.2, 141.8, 137.9, 131.6, 131.6, 130.2, 130.1, 128.5, 128.2, 128.0, 126.8, 126.5, 126.0, 125.9, 52.5, 52.4, 44.7, 43.9, 35.6, 34.6, 21.4, 21.1, 20.8, 17.1, 16.8, 14.0, 13.5, 13.5 ppm. MS (ESI): m/z (%) = 365 (22) [M + Na]$^+$, 343 (100) [M + 1]$^+$. HRMS calcd. for $C_{21}H_{27}O_2S$ [M + 1]$^+$ 343.1726; found 343.1698.

(*S*)- and (*R*)-2,6,6-Trimethyl-4-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}heptan-3-one (4Ca + 4′Ca): Compounds **4Ca** and **4′Ca** were obtained as a 68:32 diastereoisomeric mixture from enone **1C** (31 mg, 0.1 mmol) and *tert*-butyl iodide (**3a**). Chromatography: *n*-hexane/EtOAc, 3:1, total yield 61%; colourless oil. ^{1}H NMR: δ = 8.08–8.06 (m, 1 H, **4**), 7.72–7.69 (m, 1 H, **4′**), 7.56–7.37 (m, 5 H), 7.31–7.28 (m, 2 H, **4**), 7.14–7.12 (m, 2 H, **4′**), 4.66 (dd, J = 9.5, 2.5 Hz, 1 H, **4**), 4.21 (dd, J = 9.0, 3.1 Hz, 1 H, **4**), 2.85–2.76 (m, 1 H, **4′**), 2.49 (dd, J = 14.0, 9.5 Hz, 1 H, **4′**), 2.40 (s, 3 H), 2.32 (dd, J = 14.0, 8.9 Hz, 1 H, **4**), 1.77–1.62 (m, 1 H, **4**), 1.39 (dd, J = 14.0, 2.9 Hz, 1 H, **4**), 126–1.20 (m, 1 H, **4′**), 1.17 (d, J = 7.0 Hz, 3 H, **4′**), 0.89 (s, 9 H, **4**), 0.86 (d, J = 6.7 Hz, 3 H, **4′**), 0.76 (d, J = 6.6 Hz, 3 H, **4**), 0.75 (s, 9 H, **4′**), 0.55 (d, J = 6.7 Hz, 3 H, **4**) ppm. ^{13}C NMR: δ = 212.5, 212.4, 142.5, 141.8, 141.6, 138.8, 131.8, 131.6, 130.2, 130.0, 128.6, 128.3, 128.1, 127.1, 126.2, 125.9, 48.4, 46.9, 45.9, 40.7, 40.4, 31.2, 30.0, 29.8, 21.4, 21.3, 19.4, 19.2, 18.6, 18.4 ppm. MS (ESI): m/z (%) = 393 (28) [M + Na]$^+$, 371 (100) [M + 1]$^+$. HRMS calcd. for $C_{23}H_{31}O_2S$ [M + 1]$^+$ 371.2039; found 371.2029.

(*S*)- and (*R*)-4,4-Dimethyl-1-phenyl-2-{2-[(*S*)-*p*-tolylsulfinyl]-phenyl}pentan-1-one (4Da + 4′Da): Compounds **4Da** and **4′Da** were obtained as an 80:20 diastereoisomeric mixture from enone **1D** (35 mg, 0.1 mmol) and *tert*-butyl iodide (**3a**). Chromatography: *n*-hexane/EtOAc, 3:1, total yield 65%; colourless oil. ^{1}H NMR: δ = 8.01–7.98 (m, 1 H, **4**), 7.85–7.82 (m, 1 H, **4**), 7.65–7.62 (m, 1 H, **4′**), 7.48–7.02 (m, 11 H), 5.37 (dd, J = 2.9, 9.6 Hz, 1 H, **4′**), 5.08 (dd, J = 4.4, 8.1 Hz, 1 H, **4**), 2.51 (dd, J = 9.6, 14.0 Hz, 1 H, **4′**), 2.36 (dd, J = 8.0, 14.0 Hz, 1 H, **4**), 2.35 (s, 3 H), 1.70 (dd, J = 4.4, 14.0 Hz, 1 H, **4**), 1.28 (dd, J = 2.9, 14.0 Hz, 1 H, **4′**), 0.87 (s, 9 H, **4**), 0.71 (s, 9 H, **4′**) ppm. ^{13}C NMR: δ = 199.2, 142.0, 141.7, 141.5, 141.2, 141.0, 141.0, 139.9, 138.8, 136.5, 133.3, 132.9, 131.9, 131.5, 130.1, 130.0, 129.1, 128.9, 128.8, 128.7, 128.4, 128.3, 128.3, 128.2, 127.4, 127.0, 126.3, 126.2, 48.0, 47.6, 44.6, 43.8, 31.9, 31.6, 30.2, 30.0, 21.4, 21.3 ppm. MS (FAB): m/z (%) = 405 (100) [M + 1]$^+$. HRMS calcd. for $C_{26}H_{29}O_2S$ [M + 1]$^+$ 405.1888; found 405.1890.

(*S*)-4,4-Dimethyl-2-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}pentanal (5a): Compound **5a** was obtained as the major diastereomer from aldehyde **2** (27 mg, 0.1 mmol) and *tert*-butyl iodide (**3a**). Compound **5a** could not be isolated as pure compound. Chromatography: *n*-hexane/EtOAc, 4:1, yield 30%; colourless oil; ^{1}H NMR: δ = 9.01 (d, J = 1.5 Hz, 1 H), 8.08–8.03 (m, 1 H), 7.52–7.43 (m, 4 H), 7.24–7.15 (m, 3 H), 4.19–4.11 (m, 1 H), 2.36 (s, 3 H), 2.24 (dd, J = 14.2, 5.9 Hz, 1 H), 1.67–1.57 (m, 1 H), 0.89 (s, 9 H) ppm.

General Procedure for Conjugate Radical Addition and Aldehyde Allylation of (*S*)-2-[2-(*p*-Tolylsulfinyl)phenyl]propenal: A solution of aldehyde **2** (0.15 mmol) and Yb(OTf)$_3$ (0.16 mmol) in THF/CH_2Cl_2 (1:1, 0.05 M) was stirred at room temp. for 30 min under an argon atmosphere. The mixture was cooled to 0 °C, and then the alkyl iodide (0.75 mmol), triethylborane (0.9 mmol, 1 M in hexane), and O_2 (5 mL, by syringe) were added. After 30 min, allyltributyltin (0.12 mmol) and then AcOH (1.5 mmol) were added. After stirring for 10 min, water (5 mL) was added, the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The organic extracts were washed with brine (2 × 5 mL) and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography. The eluent is indicated in each case.

(4*S*,5*S*)-7,7-Dimethyl-5-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}oct-1-en-4-ol (6a): Compound **6a** was obtained as the major diastereomer from aldehyde **2** (41 mg, 0.15 mmol) and *tert*-butyl iodide (**3a**). Chromatography: *n*-hexane/EtOAc, 3:1, yield 60%; colourless oil. $[\alpha]_D^{20}$ = –37.8 (c = 1.4, $CHCl_3$). ^{1}H NMR: δ = 8.05–8.02 (m, 1 H), 7.52–7.44 (m, 4 H), 7.25–7.23 (m, 3 H), 5.48–5.34 (m, 1 H), 5.01–4.88 (m, 2 H), 3.19–3.16 (m, 1 H), 2.91 (br. s, 1 H), 2.37 (s, 3 H), 1.81–1.73 (m, 4 H), 0.79 (s, 9 H) ppm. ^{13}C NMR: δ = 143.4, 142.3, 142.1, 141.7, 135.0, 130.8, 130.1, 128.7, 127.4, 127.2, 125.4, 117.9, 73.9, 43.9, 41.4, 39.4, 31.1, 30.1, 21.4 ppm. MS (ESI): m/z (%) = 371 (100) [M + 1]$^+$, 353 (28). HRMS calcd. for $C_{23}H_{31}O_2S$ [M + 1]$^+$ 371.2045; found 371.2047.

(4*S*,5*S*)-10-Chloro-7,7-dimethyl-5-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}-dec-1-en-4-ol (6b): Compound **6b** was obtained as the major diastereomer from aldehyde **2** (41 mg, 0.15 mmol) and 1-chloro-4-iodo-4-methylpentane (**3b**). Chromatography: *n*-hexane/EtOAc, 3:1, yield 61%; colourless oil. $[\alpha]_D^{20}$ = –46.8 (c = 0.5, $CHCl_3$). ^{1}H NMR: δ = 8.04–8.03 (m, 1 H), 7.53 (m, 5 H), 7.25–7.23 (m, 2 H), 5.47–5.34 (m, 1 H), 5.02–4.87 (m, 2 H), 3.28–3.24 (m, 2 H), 3.18 (br. s, 1 H), 2.95 (br. s, 1 H), 2.37 (s, 3 H), 1.83–1.67 (m, 5 H), 1.34–1.17 (m, 3 H), 0.79 (s, 3 H), 0.77 (s, 3 H) ppm. ^{13}C NMR: δ = 143.2, 142.3, 142.3, 141.6, 135.0, 130.9, 130.9, 128.7, 127.5, 127.2, 125.4, 118.1, 73.8, 45.7, 41.8, 40.9, 39.5, 39.4, 33.4, 27.9, 27.8, 27.7, 21.4 ppm. MS (ESI): m/z (%) = 433 (100) [M + 1]$^+$, 415 (22). HRMS calcd. for $C_{25}H_{34}O_2SCl$ [M + 1]$^+$ 433.1968; found 433.1962.

(4*S*,5*S*)-5-{2-[(*S*)-*p*-Tolylsulfinyl]phenyl}oct-1-en-4-ol (6e): Compound **6e** was obtained as the major diastereomer from aldehyde **2** (41 mg, 0.15 mmol) and ethyl iodide (**3e**). Chromatography: *n*-hexane/EtOAc, 3:1, yield 58%; colourless oil. $[\alpha]_D^{20}$ = –50.3 (c = 1.25, $CHCl_3$). ^{1}H NMR: δ = 8.00–7.07 (m, 1 H), 7.49–7.43 (m, 4 H), 7.37–7.34 (m, 1 H), 7.25–7.22 (m, 2 H), 5.62–5.48 (m, 1 H), 5.02–4.87 (m, 2 H), 3.43 (br. s, 1 H), 3.19–3.12 (m, 1 H), 2.36 (s, 3 H), 2.27 (d, J = 3.2 Hz, 1 H), 1.86–1.75 (m, 2 H), 1.36–1.42 (m, 2 H), 1.03–0.95 (m, 2 H), 0.79 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR: δ = 143.5, 142.0, 141.8, 141.7, 135.4, 131.4, 130.0, 128.4, 127.3, 126.7, 126.1, 117.8, 73.2, 45.4, 38.9, 33.7, 21.3, 20.3, 14.3 ppm. MS (ESI): m/z (%) = 343 (100) [M + 1]$^+$, 325 (39). HRMS calcd. for $C_{21}H_{27}O_2S$ [M + 1]$^+$ 343.1732; found 343.1731.

General Procedure for Reduction: A solution of the ketone (0.14 mmol) and Yb(OTf)$_3$ (0.15 mmol) in THF/CH_2Cl_2 (1:1, 0.05 M) was stirred at room temp. for 30 min under an argon atmosphere. The mixture was cooled to –78 °C, and then a solution of DIBALH (0.2 mmol, 1 M in heptane) was added. After 6 h and three more additions of DIBALH (3 × 0.20 mmol), the reaction was quenched with HCl (10% aqueous). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (2 × 10 mL) and dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography. The eluent is indicated in each case.

(4*S*,5*S*)-7,7-Dimethyl-5-{2-[(*S*)-*p*-tolylsulfinyl]phenyl}octan-4-ol (9): Compound **9** was obtained as the minor diastereomer from **4Ba** (52 mg, 0.14 mmol). Chromatography: *n*-hexane/EtOAc, 4:1, yield

28%; white solid. $[\alpha]_D^{20}$ = –31.4 (*c* = 0.5, $CHCl_3$). ^1H NMR: δ = 8.05–8.03 (m, 1 H), 7.51–7.42 (m, 5 H), 7.25–7.22 (m, 2 H), 3.15–3.12 (m, 1 H), 2.86 (m, 1 H), 2.36 (s, 3 H), 1.83–1.65 (m, 2 H), 1.18–1.01 (m, 2 H), 1.00–0.80 (m, 2 H), 0.79 (s, 9 H), 0.73 (t, *J* = 7.3 Hz, 3 H) ppm. ^{13}C NMR: δ = 143.9, 142.1, 141.7, 130.8, 130.1, 128.5, 127.3, 127.2, 125.6, 75.3, 43.7, 42.0, 37.0, 31.1, 30.1, 21.4, 19.7, 13.8 ppm.

(2*R*,3*S*)-3-{2-[(*S*)-*p*-Tolylsulfinyl]phenyl}hexan-2-ol (12): Compound **12** was obtained as the major diastereomer from **4Ae** (44 mg, 0.14 mmol). Chromatography: *n*-hexane/EtOAc, 2:1, yield 63%; colourless oil; ^1H NMR: δ = 7.84–7.81 (m, 1 H), 7.52–7.47 (m, 3 H), 7.43–7.35 (m, 2 H), 7.25–7.23 (m, 2 H), 3.77–3.66 (m, 1 H), 3.29–3.21 (m, 1 H), 2.36 (s, 3 H), 2.14 (br. s, 1 H), 1.65–1.43 (m, 2 H), 1.19 (d, *J* = 6.2 Hz, 3 H), 0.89–0.76 (m, 2 H), 0.75–0.69 (m, 3 H) ppm. ^{13}C NMR: δ = 144.5, 143.4, 141.7, 141.1, 132.0, 129.8, 127.7, 127.3, 127.2, 125.5, 71.7, 47.8, 34.9, 21.9, 21.3, 20.2, 14.3 ppm.

(S_S,5*S*)-5-[2-(*p*-Tolylsulfinyl)phenyl]oct-1-en-4-one (10): PCC (31 mg, 0.142 mmol) was added to a solution of a diastereoisomeric mixture of **6e** and **7e** (34 mg, 0.1 mmol) in CH_2Cl_2 (2 mL). After 3 h, the solvent was evaporated under reduced pressure. Compound **10** was obtained as a single diastereoisomer. Chromatography: *n*-hexane/EtOAc, 4:1, yield 80%; colourless oil; ^1H NMR: δ = 8.01 (dd, *J* = 7.1, 2.1 Hz, 1 H), 7.48–7.45 (m, 4 H), 7.29–7.20 (m, 3 H), 5.68–5.62 (m, 1 H), 4.99 (d, *J* = 10.2 Hz, 1 H), 4.76 (d, *J* = 17.2 Hz, 1 H), 4.16 (t, *J* = 7.0 Hz, 1 H), 2.59 (d, *J* = 6.8 Hz, 2 H), 2.37 (s, 3 H), 1.99–1.88 (m, 1 H), 1.36–1.20 (m, 2 H), 1.09–1.01 (m, 1 H), 0.81 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR: δ = 207.0, 142.7, 142.2, 141.6, 137.7, 131.8, 130.2, 130.2, 128.8, 128.1, 126.6, 126.5, 118.3, 52.2, 46.4, 35.5, 21.4, 20.8, 14.0 ppm.

General Desulfinylation Procedure: *tert*-BuLi (1.7 M in pentane, 0.4 mmol) was added dropwise to a solution of the corresponding sulfoxide (0.12 mmol) in dry THF (2 mL) at –78 °C. When the reaction was complete (30 min), the mixture was quenched with H_2O (1 mL), and then extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (10 mL) and dried ($MgSO_4$), and the solvent was removed under reduced pressure.

(2*S*,3*S*)-7,7-Dimethyl-5-phenyloct-1-en-4-ol (11): Compound **11** was obtained as a single diastereomer from sulfoxide **6a** (44 mg, 0.12 mmol). Chromatography: *n*-hexane/EtOAc, 2:1, yield 70%; colourless oil. $[\alpha]_D^{20}$ = +2.2 (*c* = 1.1, $CHCl_3$). ^1H NMR: δ = 7.33–7.27 (m, 2 H), 7.23–7.18 (m, 3 H), 5.85–5.70 (m, 1 H), 5.13–5.03 (m, 2 H), 3.65–3.55 (m, 1 H), 2.76–2.68 (m, 1 H), 2.15–2.09 (m, 1 H), 1.97–1.85 (m, 2 H), 1.77–1.68 (m, 1 H), 0.76 (s, 9 H) ppm. ^{13}C NMR: δ = 144.1, 135.3, 128.8, 128.2, 126.3, 118.2, 75.1, 48.6, 44.5, 39.3, 31.1, 30.1 ppm. MS (ESI): *m*/*z* (%) = 255 (60) $[M + Na]^+$, 173 (100). HRMS calcd. for $C_{16}H_{24}ONa$ $[M + Na]^+$ 255.1719; found 255.1726.

(2*R*,3*S*)-3-Phenylhexan-2-ol (14): Compound **14** was obtained as a single diastereomer from sulfoxide **12** (38 mg, 0.12 mmol). Chromatography: *n*-hexane/EtOAc, 2:1, yield 86%; colourless oil. $[\alpha]_D^{20}$ = +9.6 (*c* = 0.5, $CHCl_3$). ^1H NMR: δ = 7.36–7.31 (m, 2 H), 7.24–7.20 (m, 3 H), 3.95–3.86 (m, 1 H), 2.55–2.48 (m, 1 H), 1.71–1.60 (m, 2 H), 1.20 (d, *J* = 6.25 Hz, 3 H), 1.17–1.08 (m, 2 H), 0.85 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR: δ = 141.6, 128.9, 128.5, 126.7, 71.3, 53.9, 34.1, 21.2, 20.7, 14.1 ppm. MS (ESI): *m*/*z* (%) = 201 (34) $[M + Na]^+$, 161 (30), 149 (49), 105 (100). HRMS calcd. for $C_{12}H_{18}ONa$ $[M + Na]^+$ 201.1249; found 201.1240.

4,4-Dimethyl-1,2-diphenylpentan-1-one (15): Compound **15** was obtained from a 73:27 mixture of **4Da** + **4′Da** (50 mg, 0.12 mmol). Chromatography: *n*-hexane/EtOAc, 25:1. ColourYield: 50%; 46% *ee* [HPLC analysis of the product: Daicel CHIRALPAK AD column; solvent system: 1% *i*PrOH in hexanes; 1.0 mL/min; retention times: 22.9 min (major), 29.8 min (minor)]; colourless oil. $[\alpha]_D^{20}$ = –36.7 (*c* = 0.5, $CHCl_3$). ^1H NMR: δ = 7.41–7.22 (m, 10 H), 3.70 (dd, *J* = 8.7, 3.9 Hz, 1 H), 2.01 (dd, *J* = 14.1, 4.0 Hz, 1 H), 1.60 (dd, *J* = 14.1, 8.7 Hz, 1 H), 1.02 (s, 9 H) ppm.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra for all new starting materials and final products.

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