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Enantioselective Synthesis of Benzyl *tert*-Butyl Sulfoxides

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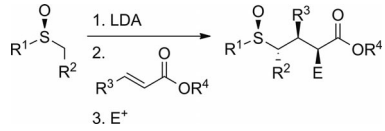
Enantiomerically pure benzyl sulfoxides are effective tools for the formation of new C–C bonds with control of configuration at new stereogenic centres. The reaction of enantioenriched *tert*-butyl *tert*-butanethiosulfinate with benzyllithium derivatives, obtained by deprotonation of the corresponding toluene derivatives, gave a wide variety of benzyl *tert*-butyl sulfoxides with complete inversion of configuration. The benzyl sulfoxides were deprotonated in situ, and addition of the electrophiles gave α-substituted products with good diastereoselectivity.

Introduction

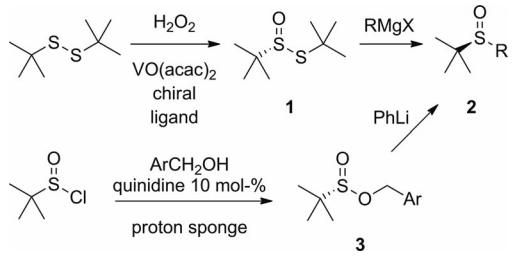
Enantiopure sulfoxides are widely used as intermediates in asymmetric synthesis [1,2] and are attracting growing interest as chiral catalysts and ligands.[3,4] A large number also show biological activity, and some are important drugs.[1,5] Many of their applications in asymmetric synthesis stem from the fact that sulfoxides readily undergo α-deprotonation, and the resulting anions can be treated with a wide range of electrophiles to give products with high stereoselectivity at the newly created stereogenic centers.[1,2,6] There are several synthetically useful methods to remove the sulfinyl group subsequent to the α-substitution,[7–9] and therefore, it may be regarded as a chiral auxiliary for carbanions. Earlier, we showed that sulfoxide-stabilized carbanions undergo efficient regioselective conjugate addition to α,β-unsaturated esters and ketones, generally resulting in excellent diastereoselectivity (Scheme 1).[10,11] As expected, the nonacidic group on the sulfoxide, referred to as the "spectator group" (R^1 in Scheme 1), has a pronounced effect on the yield and diastereoselectivity in these reactions.[1,2,6,10–12] Reactions of benzyl sulfoxides with a *tert*-butyl spectator group yielded particularly good results, and the potential of this methodology was showcased in a very short formal total synthesis of (±)-podophyllotoxin.[13]



Scheme 1. Diastereoselective conjugate additions of sulfoxides.

Having developed this strategy using racemic sulfoxides, we needed to find an efficient method for the enantioselective synthesis of benzyl *tert*-butyl sulfoxides. The preparation of this class of sulfoxides through the asymmetric oxidation of sulfides has been studied, and very good results have been obtained using chiral reagents,[14] but catalytic asymmetric oxidation resulted in modest enantioselectivity.[15] We briefly investigated asymmetric oxidation using vanadium[16] and titanium[17] catalysis, but the results were not promising and therefore were not pursued.

The second major method for asymmetric synthesis of sulfoxides is by the reaction of organometals with enantioenriched sulfinic acid derivatives.[1,3] Benzyl *tert*-butyl sulfoxide has been made with excellent enantioselectivity from sulfinates derived from chiral auxiliaries,[18,19] but we favored a catalytic approach. In Ellman's highly influential work in this area, a simple and efficient method was reported for the catalytic asymmetric oxidation of *tert*-butyl disulfide to form a highly enantioenriched thiosulfinate ester **1** [20] which was then used as an intermediate for the asymmetric synthesis of *tert*-butyl sulfoxides **2** (Scheme 2).[21]



Scheme 2. Enantioselective synthesis of sulfoxides **2** through thiosulfinate **1**[21] and sulfinate **3**.[22]

The Ellman group also showed that highly enantioenriched *tert*-butanesulfinate esters **3** are readily obtained by reaction of *tert*-butanesulfinyl chloride with benzyl alcohols in the presence of chiral sulfinyl transfer catalysts.[22] Similar results were also reported by Shibata.[23] However, we could find no reference to the reaction of these sulfinate

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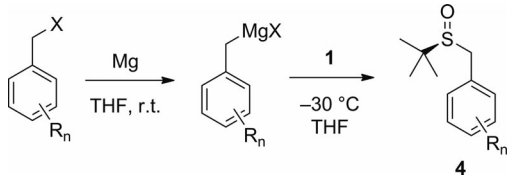
or thiosulfinate esters with benzylmagnesium halides, apart from a mention in a footnote.[24] We now report that the reaction of benzylmagnesium halides with thiosulfinate **1** can give sulfoxides, though it is limited in scope. However, the reaction of benzyllithium derivatives with the thiosulfinate can generate a wide array of benzyl *tert*-butyl sulfoxides with good yields and high enantioselectivities.

Results and Discussion

The enantioselective synthesis of sulfoxides by treating enantioenriched sulfinic acid derivatives with Grignard reagents is a long-established reaction,[1] therefore, we investigated it as a possible strategy for the preparation of benzyl *tert*-butyl sulfoxides. The formation of benzylmagnesium halides is often accompanied by Wurtz coupling, so we used an excess amount of activated magnesium, prepared by Brown's method,[25] to minimize this side reaction. By carefully choosing the reaction conditions, three benzylic Grignard reagents were obtained relatively cleanly, but the attempted preparation of [(4-bromophenyl)methyl]magnesium bromide predominantly resulted in the coupled product under all the conditions studied. Addition of (*R*)-thiosulfinate[20] to the Grignard reagents in THF (tetrahydrofuran) at –30 °C gave sulfoxides **4** with essentially complete inversion of configuration (Table 1). Substantial reduction in the enantiopurity was found when higher temperatures were used and when the order of addition was reversed. This indicates that the racemization of (*R*)-thiosulfinate **1**, by the thiolate byproduct produced in the reaction, can become competitive with sulfoxide formation if the conditions are not carefully controlled.

Table 1. Reaction of thiosulfinate **1** with benzylmagnesium halides.

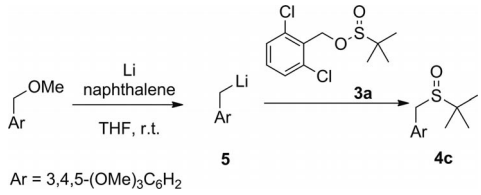


Product	R_n	X	% *ee* (*R*)-**1**[a]	% Yield	% *ee* **4**[a,b]
4a	3,4-OCH_2O	Br	96	50	94 (*S*)
4b	H	Br	92	60	92 (*S*)
4c	3,4,5-$(OMe)_3$	Cl	90	0	–

[a] Measured by HPLC using a CHIRALPAK AS-H column. [b] The configurations of sulfoxides **4** were determined as described in Table 2.

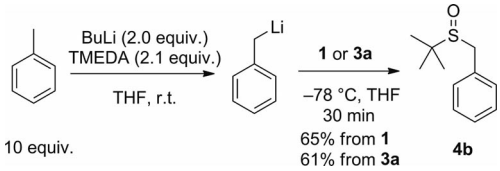
Although the unsubstituted Grignard reagent and the 3,4-methylenedioxy-substituted analog gave moderate yields of sulfoxide by this method, the 3,4,5-trimethoxy derivative did not react with the thiosulfinate, even at room temperature (Table 1). This preliminary study showed that the reaction of benzylic Grignard reagents with the thiosulfinate is a viable and convenient method for the enantioselective synthesis of sulfoxides, and no doubt it could be extended to the preparation of many additional examples. However, it failed in some cases, therefore, we attempted to find an alternative that might be more successful for the preparation of heavily oxygenated benzylic sulfoxides.

We investigated using the more reactive benzyllithium derivatives. As in the case of benzylmagnesium compounds, the generation of benzyllithium derivatives is often complicated by competing Wurtz coupling, but preparation has been accomplished by the reductive lithiation of benzyl methyl ethers.[26,27] At first, we applied Azzena's method to obtain (3,4,5-trimethoxybenzyl)lithium (**5**)[28] through the reductive cleavage of 3,4,5-trimethoxybenzyl methyl ether with Li metal and catalytic naphthalene (Scheme 3). However, addition of sulfinate ester **3a** to the reaction mixture gave only small amounts of the substituted benzyl *tert*-butyl sulfoxide **4c**, possibly because of the instability of sulfinate ester **3a** under the strongly reducing environment of this reaction.



Scheme 3. Attempted formation of sulfoxide using benzyllithium formed by reductive lithiation.

In contrast, we found that benzyllithium, generated by treating toluene with butyllithium and TMEDA (*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine) at 20 °C,[29] reacted smoothly with racemic sulfinate ester **3a** and with racemic thiosulfinate ester **1** at low temperature to form benzyl *tert*-butyl sulfoxide **4b** (Scheme 4). Initially, 1.3 equiv. of BuLi was used, but the yield of sulfoxide **4b** was low and a substantial amount of sulfinate ester **3a** was recovered. It seemed likely that the benzyllithium was being consumed by the deprotonation of **4b** under the strongly basic conditions. This hypothesis was confirmed by the addition of benzaldehyde to the reaction mixture which resulted in the formation of an adduct in good yield by trapping the lithiated benzyl sulfoxide (see Table 3). When a twofold excess amount of benzyllithium was employed, reasonable yields of sulfoxide **4b** were obtained. As thiosulfinate ester **1** gave slightly better yields and cleaner reaction mixtures, and it was easier to prepare by catalytic asymmetric oxidation of *tert*-butyl disulfide,[20] we focused on it instead of sulfinate ester **3a**.



Scheme 4. Formation of sulfoxide using benzyllithium formed by deprotonation.

Although this method worked well for the preparation of the unsubstituted benzyl sulfoxide **4b**, the literature sug-

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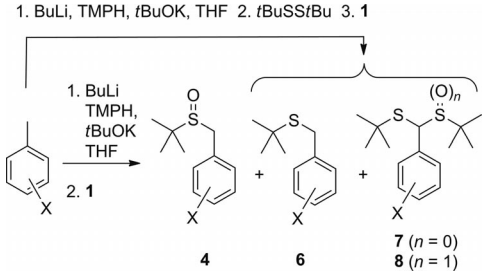
gested that it could not be used for a wide range of substituted toluene derivatives. Superbasic mixtures of organolithium derivatives and/or lithium dialkylamides together with alkali metal alkoxides can be used for the α-lithiation of a broad range of toluene derivatives.[30] Recently, O'Shea and co-workers used a superbasic mixture formed from BuLi, *t*BuOK, and 2,2,6,6-tetramethylpiperidine (TMPH),[31] and we adopted a similar procedure. We found that the benzyllithium derivatives generated in this way do react with the thiosulfinate **1**, but attack occurs at both sulfur atoms (Scheme 5). Reaction at the expected sulfur(IV) site gave the desired sulfoxides **4** in moderate yields, but the competing reaction at the sulfur(II) atom gave benzyl *tert*-butyl sulfides **6**. Significant amounts of dithioacetals **7** and dithioacetal monosulfoxides **8** were also formed. When the unsubstituted benzyl sulfide **6** was formed, by reaction of di-*tert*-butyl disulfide with excess benzyllithium, formed from toluene as shown in Scheme 5, and sulfinate **1** was added, side products **7** and **8** were formed. However, deprotonation of sulfoxide **4b** using benzyllithium followed by reaction with either di-*tert*-butyl disulfide or thiosulfinate **1** only resulted in unchanged sulfoxide. These control experiments demonstrate that dithioacetals **7** and **8** were formed in situ by deprotonation of sulfides **6** at the benzylic position and subsequent reaction with the thiosulfinate ester **1**.

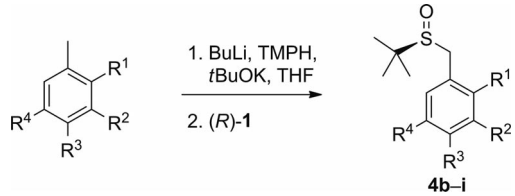


Scheme 5. Reaction of thiosulfinate **1** with benzyllithium derivatives.

Optimization revealed that conducting the reactions at low concentration (approximately 0.1 M) gave homogeneous mixtures and resulted in higher yields of sulfoxides **4** with less side-product formation. It should be noted that the desired sulfoxides are easily separated from the side products by chromatography.

The reaction of the benzyllithium derivatives, prepared from the corresponding toluene derivatives using this optimized method, with enantioenriched thiosulfinate ester (*R*)-**1**, obtained using Ellman's procedure,[20] gave a range of enantioenriched sulfoxides **4b**–**i** (Table 2). The thiosulfinate precursor **1** was obtained in 86% *ee*, and recrystallization at low temperature gave samples with up to 99% *ee*.[20] The substitution reactions occurred with complete inversion of configuration at the sulfur atom and gave moderate to good yields of the benzyl *tert*-butyl sulfoxides bearing a range of substituents. Table 2 shows that one, two, or three alkoxy substituents, needed for application to lignan syntheses, were tolerated. The yields for the *ortho*- and *meta*-substituted compounds are very similar to those found by O'Shea using different electrophiles,[31] and in addition, these results show that acceptable yields can be obtained with an alkoxy group in the *para* position. It is not surprising that the presence of electron-withdrawing substituents facilitated the deprotonation and resulted in good yields of sulfoxides **4h** and **4i**. For 4-cyanotoluene, the deprotonation was carried out using preformed LTMP and *t*BuOK to avoid the competing addition of BuLi to the nitrile.

Table 2. Enantioselective synthesis of benzyl *tert*-butyl sulfoxides.



Product	R^1	R^2	R^3	R^4	% *ee* **1**[a]	% Yield	% *ee* **4**[a,b]
4b	H	H	H	H	>98	60	>98 (*S*)
4c	H	OMe	OMe	OMe	92	47	91 (*S*)
4d	H	OMe	OMe	H	97	52	97 (*S*)
4e	OMe	H	H	H	>98	75	>98 (*S*)
4f	H	OMe	H	H	92	70	92 (*S*)
4g	H	H	OMe	H	92	33	91 (*S*)
4h	H	F	H	H	97	76	96 (*S*)
4i	H	H	CN	H	90	80 [c]	88 (*S*)

[a] Measured by HPLC using a CHIRALPAK AS-H column. [b] The configuration of sulfoxide **4b** was determined by comparison of the specific rotation with the literature value (ref.[15]). The configurations of the other sulfoxides were assigned by analogy, supported by the observation that the minor enantiomer eluted first from the CHIRALPAK® AS-H column in every case, except for sulfoxide **4i**. [c] Preformed LTMP (lithium 2,2,6,6-tetramethylpiperidide) was used for lithiation.

Attempts to form the 3,4-methylenedioxy derivative by this method failed, as selective deprotonation of the toluene could not be achieved.[32,33] Numerous experiments using a variety of bases gave complex mixtures, indicating that deprotonation occurred mostly at the acetal carbon to give products suggestive of carbenoid intermediates.[34] Because methylenedioxyphenyl groups are common in lignan structures, we decided to persevere, but instead to pursue the formation of the requisite benzyllithium derivative by tin–lithium exchange.[35] The benzyltributylstannane **9** was formed in a standard way,[36] and tin–lithium exchange, followed by addition of the thiosulfinate **1** (>98% *ee*), successfully furnished the sulfoxide **4a** (57%, >98% *ee*) (Scheme 6). To the best of our knowledge, this is the first report of the efficient formation of a methylenedioxy-substituted benzyllithium derivative.

As described earlier, the in situ deprotonation of the benzyl sulfoxides by a second equivalent of benzyllithium occurs under the reaction conditions, and this suggests the possibility of the one-pot formation for α-substituted products with one or two additional stereocenters. Initially, using methyl cinnamate as the electrophile, we found that 2.4 equiv. of BuLi and 2.6 equiv. of *t*BuOK were necessary to generate an excess of benzyllithium and provide a good yield of conjugate adduct, but as a mixture of two dia-

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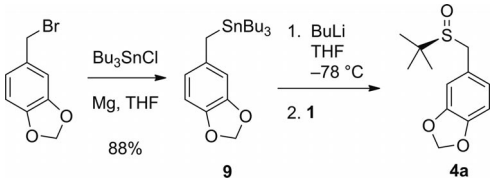
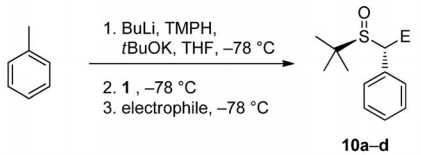


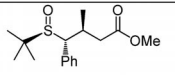
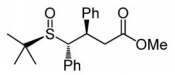
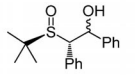
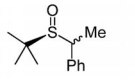
Scheme 6. Enantioselective synthesis of methylenedioxy-substituted benzyl *tert*-butyl sulfoxide.

stereomers. In the case of methyl crotonate, the product of two consecutive conjugate additions was obtained, even after short reaction times. These results are in striking contrast to the efficient stereoselective conjugate additions observed using lithiated sulfoxides generated by deprotonation with LDA (lithium diisopropylamide)[11] and again highlight the marked effect of the potassium alkoxide additive. Optimization of the reaction conditions revealed that reducing the amount of *t*BuOK to 0.8 equiv. gave much better results (Table 3). Clean conjugate addition with high diastereoselectivity (no more than traces of products that might have been diastereomers were evident in the ^{1}H NMR spectra of the crude mixtures) was observed with methyl crotonate and methyl cinnamate, but at the expense of slightly lower yields, possibly because of the less efficient generation of the benzyllithium derivative. Conjugate adduct **10a** was obtained in high *ee* (90%, >98% after recrystallization), thus proving that highly enantioenriched α-substituted sulfoxides could be formed in this way, and the remaining one-pot reactions were carried out using the racemic thiosulfinate. When benzaldehyde was used as electrophile, the two diastereomeric adducts **10c** and **10c′** were obtained in a 3.5:1 ratio.[37] In the case of iodomethane,[38]

Table 3. One-pot formation of α-substituted benzyl sulfoxides **10**.



10a–d

Electrophile	Product		Yield (%)
Methyl crotonate		**10a**	50[a]
Methyl cinnamate		**10b**	41
PhCHO		β-OH **10c**[b], α-OH **10c'**	42, 12
CH_3I[c]		β-Me **10d**[d], α-Me **10d'**	50, 15

[a] The *ee* of thiosulfinate used was 96%, and the *ee* of the product **10a** was 90% (analysis by HPLC using a CHIRALPAK AS-H column). [b] Stereochemistry assigned according to ref.[37] [c] The reaction mixture was warmed to –20 °C after addition of electrophile. [d] Stereochemistry assigned according to ref.[38]

the isolated yield of the major diastereomer of methylated product **10d** was highest employing the original method of 2.6 equiv. of *t*BuOK. The results for these one-pot reactions compare favorably with those obtained by formation of the sulfoxide followed by a separate reaction with the electrophiles.[10,11,38,39] In contrast to these results, we found that when benzylic sulfoxides are formed using Grignard reagents under the conditions described earlier, in situ deprotonation does not occur. Thus, the ability to form highly enantioenriched α-substituted sulfoxides in a one-pot procedure is a new and unique feature of the benzyllithium method. As far as we are aware, this is the first report of a method that allows formation and α-substitution of enantioenriched sulfoxides in one operation.

Conclusions

These results show that a wide variety of benzyl *tert*-butyl sulfoxides can be obtained with high enantioselectivity by deprotonation of toluene derivatives using superbasic conditions and the in situ reaction of the benzyllithium derivatives with *tert*-butyl *tert*-butanethiosulfinate. A unique aspect of this method is that complex α-substituted sulfoxides can be formed with high stereoselectivity in a one-pot procedure by addition of electrophiles to the reaction mixtures. Using benzylmagnesium halides also gives sulfoxides, but this method, although very convenient, is more limited in scope. These new methods should prove useful for the asymmetric synthesis of natural products, especially lignans, and work in this area is well advanced.

Experimental Section

General: All reagents were purchased from commercial suppliers and used as obtained, unless otherwise stated. All reactions were carried out under a nitrogen atmosphere in oven- or flame-dried glassware, and all moisture-sensitive liquids and solutions were transferred through a syringe or cannula. Methyl crotonate and benzaldehyde were used after distillation. TMEDA and 2,2,6,6-tetramethylpiperidine (TMPH) were distilled from CaH_2 prior to use. (*R*)-(+)-thiosulfinate ester **1**[20] and racemic sulfinate ester **3**[22] were prepared by reported methods. Magnesium turnings were mechanically activated for 3–4 d in a Schlenk tube using Brown's method.[25] The concentration of the butyllithium solution in hexane was determined by titration with diphenylacetic acid in THF before use.[39] Flash column chromatography was performed using silica 60 (40–63 microns). Assignments of the signals in the ^{1}H NMR spectra were supported by gCOSY (gradient COSY) and HSQCAD (heteronuclear single bond coherence adiabatic) spectra. For HPLC analyses, a CHIRALPAK AS-H column was used, and detection was achieved with UV analysis at 3 wavelengths, 210.8, 230.8, and 254.8 nm. Mass spectrometry data were obtained using electrospray ionization (ESI), and high resolution mass spectra were collected with a TOF (time-of-flight) spectrometer.

General Procedure A. Enantioselective Synthesis of Benzyl Sulfoxides Using Grignard Reagents: To a flask (25 mL) containing activated magnesium turnings (74 mg, 3.08 mmol, 4 equiv.) was added a solution of benzylic halide (1.69 mmol, 2.2 equiv.) in THF (5 mL). The reaction mixture was stirred vigorously at room tem-

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perature for 2 h before it was filtered through a syringe into another flask (25 mL) and cooled to –30 °C. A solution of (*R*)-(+)-thiosulfinate ester **1** (150 mg, 0.77 mmol) in dry THF (5 mL) was added very slowly through a cannula, and the mixture was stirred for 50 min. The reaction was quenched with water (7 mL), and the mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried with $MgSO_4$ and concentrated to dryness. Purification by silica gel chromatography afforded the pure benzyl sulfoxide.

(*S*)-*tert*-Butyl (1,3-Benzodioxol-5-yl)methyl Sulfoxide (4a): Applying general procedure A and using 5-bromomethyl-1,3-benzodioxole (363 mg, 1.69 mmol) as the substrate yielded sulfoxide **4a** (93 mg, 50%) as a white solid after chromatography (pentane/EtOAc, 1:1); m.p. 141–143 °C (heptane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 [s, 9 H, C(CH_3)$_3$], 3.53 (d, J = 12.8 Hz, 1 H, CH_2Ar), 3.75 (d, J = 12.8 Hz, 1 H, CH_2Ar), 5.95 (s, 2 H, O-CH_2-O), 6.79 (apparent s, 2 H, Ar), 6.83 (apparent s, 1 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.0 (CH_3), 52.7 (CH_2), 53.5 (C), 101.1 (CH_2), 108.5 (CH), 110.1 (CH), 123.4 (CH), 125.4 (C), 147.5 (C), 147.9 (C) ppm. IR (KBr): $\tilde{\nu}$ = 827, 1028, 1249, 2980 cm^{-1}. MS (ESI): m/z = 241.1 [M + H]$^+$. HRMS: calcd. for $C_{12}H_{17}O_3S$ [M + H]$^+$ 241.0898; found 241.0895. HPLC (CHIRALPAK AS-H column; heptane/EtOH, 90:10; 1.0 mL/min): t_R (minor enantiomer) = 18.86 min, t_R (major enantiomer) = 22.86 min, 94% *ee*. $C_{12}H_{16}O_3S$ (240.32): calcd. C 59.97, H 6.71; found C 59.76, H 6.57.

(*S*)-Benzyl *tert*-Butyl Sulfoxide (4b): Applying general procedure A and using benzyl bromide (289 mg, 1.69 mmol) as the substrate yielded sulfoxide **4b** (92 mg, 60%) as a white solid after chromatography (pentane/EtOAc, 3:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 [s, 9 H, C(CH_3)$_3$], 3.63 (d, J = 12.9 Hz, 1 H, CH_2Ar), 3.83 (d, J = 12.9 Hz, 1 H, CH_2Ar), 7.29–7.39 (m, 5 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.2 (CH_3), 53.1 (CH_2), 53.8 (C), 128.1 (CH), 129.1 (CH), 130.1 (CH), 132.1 (C) ppm. MS (ESI): m/z = 197.3 [M + H]$^+$. HRMS: calcd. for $C_{11}H_{17}OS$ [M + H]$^+$ 197.1000; found 197.0999. HPLC (CHIRALPAK AS-H column; heptane/EtOH, 90:10; 1.0 mL/min): t_R (minor enantiomer) = 8.43 min, t_R (major enantiomer) = 12.64 min, 92% *ee*.

Synthesis of (±)-Benzyl *tert*-Butyl Sulfoxide (4b) Using Benzyllithium Obtained from an Organolithium Amine Complex: A solution of BuLi (2.5 M in hexane, 0.85 mL, 2.14 mmol, 2.0 equiv.) was added to tetramethylethylenediamine (0.33 mL, 2.24 mmol, 2.1 equiv.) at room temperature under nitrogen, and the mixture was stirred for 10 min before dry toluene (1.14 mL, 10.7 mmol, 10 equiv.) was added. After 30 min, the mixture was transferred through a syringe to a solution of racemic sulfinate ester **3a** (300 mg, 1.07 mmol, 1 equiv.) in dry THF (7 mL) at –78 °C. The reaction mixture was stirred for 30 min before the addition of saturated $NaHCO_3$ (5 mL), and it was then allowed to warm to room temp. Water (5 mL) was added, and the product was extracted into EtOAc (3 × 15 mL). The combined organic extracts were dried with magnesium sulfate and concentrated to dryness. Purification by silica gel chromatography (pentane/EtOAc, 3:2) afforded pure benzyl sulfoxide **4b** (127 mg, 61%) as a white solid. Applying the same procedure using racemic thiosulfinate ester **1** (207 mg, 1.07 mmol) as the electrophile yielded sulfoxide **4b** (136 mg, 65%) as a white solid.

General Procedure B. Enantioselective Synthesis of Benzyl Sulfoxides Using Benzyllithium Derivatives Generated from a Superbasic Mixture: To a stirred solution of the toluene (2.68 mmol, 2.60 equiv.) at –78 °C in THF (26 mL) was added dropwise a solution of BuLi (2.0 M in hexane, 1.2 mL, 2.47 mmol, 2.4 equiv.), and the mixture was stirred for 5 min. A solution of *t*BuOK (1.0 M in THF, 2.68 mL, 2.68 mmol, 2.60 equiv.) was added dropwise followed by the addition of 2,2,6,6-tetramethylpiperidine (0.43 mL, 2.52 mmol, 2.45 equiv.). After 35 min, a solution of (*R*)-(+)-thiosulfinate ester **1** (200 mg, 1.03 mmol) in THF (3 mL) was added over a period of 5 to 8 min. The reaction mixture was stirred for another 35 min before quenching with the addition of saturated $NaHCO_3$ (5 mL). The mixture was then allowed to warm to room temp. Water (7 mL) was added, and the product was extracted with EtOAc (3 × 15 mL). The combined extracts were dried with magnesium sulfate and concentrated to dryness. Purification by silica gel chromatography afforded pure benzyl sulfoxides **4b**–**4h**.

(*S*)-Benzyl *tert*-Butyl Sulfoxide (4b): Applying general procedure B and using toluene (0.28 mL) as the substrate yielded sulfoxide **4b** (122 mg, 60%) as a white solid after chromatography (pentane/EtOAc 3:2). $[\alpha]_D$ = –191.1 (c = 1, $CHCl_3$), ref.[15] $[\alpha]_D$ = –128 (c = 0.6, $CHCl_3$). HPLC (CHIRALPAK AS-H column; heptane/EtOH, 90:10; 1.0 mL/min), t_R (minor enantiomer) = 8.46 min, t_R (major enantiomer) = 13.31 min, >98% *ee*.

(*S*)-*tert*-Butyl (3,4,5-Trimethoxyphenyl)methyl Sulfoxide (4c): Applying general procedure B and using 3,4,5-trimethoxytoluene (0.44 mL) as the substrate yielded sulfoxide **4c** (138 mg, 47%) as a white solid after chromatography (pentane/EtOAc, 3:7); m.p. 101–103 °C (heptane). $[\alpha]_D$ = –242.7 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 [s, 9 H, C(CH_3)$_3$], 3.56 (d, J = 12.8 Hz, 1 H, CH_2Ar), 3.74 (d, J = 12.8 Hz, 1 H, CH_2Ar), 3.84 (s, 3 H, O*Me*), 3.87 (s, 6 H, 2 O*Me*), 6.57 (s, 2 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.1 (CH_3), 53.1 (CH_2), 53.6 (C), 56.1 (CH_3), 60.8 (CH_3), 106.9 (CH), 127.4 (C), 137.8 (C), 153.4 (C) ppm. IR (KBr): $\tilde{\nu}$ = 780, 1039, 1122, 2835, 2998 cm^{-1}. MS (ESI): m/z = 287.4 [M + H]$^+$. HRMS: calcd. for $C_{14}H_{23}O_4S$ [M + H]$^+$ 287.1317; found 287.1315. HPLC (CHIRALPAK AS-H column; heptane/EtOH, 90:10; 1.0 mL/min): t_R (minor enantiomer) = 10.47 min, t_R (major enantiomer) = 13.95 min, 91% *ee*. $C_{14}H_{22}O_4S$ (286.39): calcd. C 58.71, H 7.74; found C 58.68, H 7.76.

(*S*)-*tert*-Butyl (3,4-Dimethoxyphenyl)methyl Sulfoxide (4d): Applying general procedure B and using 3,4-dimethoxytoluene (0.38 mL) as the substrate yielded sulfoxide **4d** (138 mg, 52%) as a white solid after chromatography (pentane/EtOAc, 3:7); m.p. 136–139 °C (heptane). $[\alpha]_D$ = –209.9 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 [s, 9 H, C(CH_3)$_3$], 3.58 (d, J = 12.9 Hz, 1 H, CH_2Ar), 3.78 (d, J = 12.9 Hz, 1 H, CH_2Ar), 3.88 (s, 3 H, O*Me*), 3.90 (s, 3 H, O*Me*), 6.80–6.94 (m, 3 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.1 (CH_3), 52.5 (CH_2), 53.5 (C), 55.91 (CH_3), 55.93 (CH_3), 111.3 (CH), 112.8 (CH), 122.2 (CH), 124.3 (C), 148.9 (C), 149.1 (C) ppm. IR (KBr): $\tilde{\nu}$ = 766, 1037, 1261, 1518, 2961 cm^{-1}. MS (ESI): m/z = 257.4 [M + H]$^+$. HRMS: calcd. for $C_{13}H_{21}O_3S$ [M + H]$^+$ 257.1211; found 257.1199. HPLC (CHIRALPAK AS-H column; heptane/EtOH, 90:10; 1.0 mL/min): t_R (minor enantiomer) = 13.72 min, t_R (major enantiomer) = 15.89 min, 97% *ee*. $C_{13}H_{20}O_3S$ (256.36): calcd. C 60.91, H 7.86; found C 60.50, H 7.78.

(*S*)-*tert*-Butyl (2-Methoxyphenyl)methyl Sulfoxide (4e): Applying general procedure B and using 2-methoxytoluene (0.33 mL) as the substrate yielded sulfoxide **4e** (175 mg, 75%) as a white solid after chromatography (pentane/EtOAc, 1:1); m.p. 80–82 °C (heptane). $[\alpha]_D$ = –259.2 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 [s, 9 H, C(CH_3)$_3$], 3.30 (d, J = 12.5 Hz, 1 H, CH_2Ar), 4.13 (d, J = 12.5 Hz, 1 H, CH_2Ar), 3.75 (s, 3 H, O*Me*), 6.77–6.90 (m, 2 H, Ar), 7.18–7.29 (m, 2 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 22.8 (CH_3), 48.3 (CH_2), 53.5 (C), 55.4 (CH_3), 110.4 (CH), 120.6 (C), 120.7 (CH), 129.3 (CH), 131.8 (CH), 157.3 (C) ppm. IR (KBr): $\tilde{\nu}$ = 750, 1099, 1250, 2959, 3063 cm^{-1}. MS (ESI): m/z = 227.4 [M + H]$^+$. HRMS: calcd. for $C_{12}H_{19}O_2S$ [M + H]$^+$ 227.1106; found

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227.1112. HPLC (CHIRALPAK AS-H column; heptane/EtOH, 90:10; 1.0 mL/min): t_R (minor enantiomer) = 8.71 min, t_R (major enantiomer) = 9.73 min, >98% *ee*. $C_{12}H_{18}O_2S$ (226.33): calcd. C 63.68, H 8.02; found C 63.63, H 8.01.

(*S*)-*tert*-Butyl (3-Methoxyphenyl)methyl Sulfoxide (4f): Applying general procedure B and using 3-methoxytoluene (0.33 mL) as the substrate yielded sulfoxide **4f** (164 mg, 70%) as a white solid after chromatography (pentane/EtOAc, 1:1); m.p. 93–95 °C (heptane). $[\alpha]_D$ = –192.7 (*c* = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 [s, 9 H, C(CH_3)$_3$], 3.60 (d, *J* = 12.8 Hz, 1 H, CH_2Ar), 3.80 (d, *J* = 12.8 Hz, 1 H, CH_2Ar), 3.81 (s, 3 H, O*Me*), 6.83–6.95 (m, 3 H, Ar), 7.24–7.29 (m, 1 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 22.0 (CH_3), 52.0 (CH_2), 52.7 (C), 54.2 (CH_3), 112.8 (CH), 114.2 (CH), 121.2 (CH), 128.8 (CH), 132.4 (C), 158.8 (C) ppm. IR (KBr): $\tilde{\nu}$ = 794, 1049, 1154, 1267, 2961 cm^{-1}. MS (ESI): *m*/*z* = 227.4 [M + H]$^+$. HRMS: calcd. for $C_{12}H_{19}O_2S$ [M + H]$^+$ 227.1106; found 227.1108. HPLC (CHIRALPAK AS-H column; heptane/EtOH, 85:15; 1.0 mL/min): t_R (minor enantiomer) = 8.77 min, t_R (major enantiomer) = 11.78 min, 92% *ee*. $C_{12}H_{18}O_2S$ (226.33): calcd. C 63.68, H 8.02; found C 63.84, H 8.06.

(*S*)-*tert*-Butyl (4-Methoxyphenyl)methyl Sulfoxide (4g): Applying general procedure B and using 4-methoxytoluene (0.33 mL) as the substrate yielded sulfoxide **4g** (70 mg, 33%) as a white solid after chromatography (pentane/EtOAc, 1:1); m.p. 124–126 °C (heptane). $[\alpha]_D$ = –232.5 (*c* = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 [s, 9 H, C(CH_3)$_3$], 3.58 (d, *J* = 12.9 Hz, 1 H, CH_2Ar), 3.79 (d, *J* = 12.9 Hz, 1 H, CH_2Ar), 3.80 (s, 3 H, O*Me*), 6.86–6.92 (m, 2 H, Ar), 7.22–7.29 (m, 2 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.0 (CH_3), 52.1 (CH_2), 53.4 (C), 55.2 (CH_3), 114.3 (CH), 123.7 (C), 131.1 (CH), 159.4 (C) ppm. IR (KBr): $\tilde{\nu}$ = 794, 1049, 1267, 1582, 2961 cm^{-1}. MS (ESI): *m*/*z* = 227.4 [M + H]$^+$. HRMS: calcd. for $C_{12}H_{19}O_2S$ [M + H]$^+$ 227.1106; found 227.1106. HPLC (CHIRALPAK AS-H column; heptane/EtOH, 90:10; 1.0 mL/min): t_R (minor enantiomer) = 12.46 min, t_R (major enantiomer) = 15.78 min, 91% *ee*. $C_{12}H_{18}O_2S$ (226.33): calcd. C 63.68, H 8.02; found C 63.38, H 8.03.

(*S*)-*tert*-Butyl (3-Fluorophenyl)methyl Sulfoxide (4h): Applying general procedure B and using 3-fluorotoluene (0.28 mL) as the substrate yielded sulfoxide **4h** (168 mg, 76%) as a white solid after chromatography (pentane/EtOAc, 1:1); m.p. 69–71 °C (heptane). $[\alpha]_D$ = –287.2 (*c* = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 [s, 9 H, C(CH_3)$_3$], 3.59 (d, *J* = 12.8 Hz, 1 H, CH_2Ar), 3.80 (d, *J* = 12.8 Hz, 1 H, CH_2Ar), 6.97–7.16 (m, 3 H, Ar), 7.27–7.36 (m, 1 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 22.9 (CH_3), 52.4 (d, *J* = 2 Hz, CH_2), 53.8 (C), 114.8 (d, *J* = 21 Hz, CH), 116.9 (d, *J* = 21 Hz, CH), 125.7 (d, *J* = 3 Hz, CH), 130.2 (d, *J* = 8.3 Hz, CH), 134.4 (d, *J* = 7.8 Hz, C), 162.8 (d, *J* = 246.8 Hz, C) ppm. IR (KBr): $\tilde{\nu}$ = 786, 1034, 1258, 2976, 3056 cm^{-1}. MS (ESI): *m*/*z* = 215.3 [M + H]$^+$. HRMS: calcd. for $C_{11}H_{16}FOS$ [M + H]$^+$ 215.0906; found 215.0907. HPLC (CHIRALPAK AS-H column; heptane/EtOH, 85:15; 1.0 mL/min): t_R (minor enantiomer) = 6.62 min, t_R (major enantiomer) = 11.57 min, 96% *ee*.

(*S*)-*tert*-Butyl (4-Cyanophenyl)methyl Sulfoxide (4i): To a stirred solution of 2,2,6,6-tetramethylpiperidine (0.43 mL, 2.52 mmol, 2.45 equiv.) in THF (20 mL) at –78 °C was added dropwise a solution of BuLi (2.0 M in hexane, 1.2 mL, 2.47 mmol, 2.4 equiv.) followed by the addition of a solution of *t*BuOK (1.0 M in THF, 2.68 mL, 2.68 mmol, 2.60 equiv.). After 5 min, a solution of 4-methylbenzonitrile (0.31 g, 2.68 mmol, 2.60 equiv.) in THF (5 mL) was added dropwise, and the mixture was stirred for 35 min. A solution of thiosulfinate ester **1** (200 mg, 1.03 mmol) in THF (3 mL) was added over a period of 8 min. The reaction mixture was stirred for 35 min and then quenched by the addition of saturated $NaHCO_3$ (5 mL). The mixture was warmed to room temp. Water (7 mL) was added, and the product was extracted with EtOAc (3 × 15 mL). The combined extracts were dried with magnesium sulfate and concentrated to dryness. Purification by silica gel chromatography afforded the pure benzyl sulfoxide **4i** (183 mg, 80%) as a white solid after chromatography (pentane/EtOAc, 3:2); m.p. 109–111 °C (heptane). $[\alpha]_D$ = –257.1 (*c* = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 [s, 9 H, C(CH_3)$_3$], 3.65 (d, *J* = 12.6 Hz, 1 H, CH_2Ar), 3.83 (d, *J* = 12.6 Hz, 1 H, CH_2Ar), 7.44–7.50 (m, 2 H, Ar), 7.63–7.69 (m, 2 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 22.9 (CH_3), 52.4 (CH_2), 54.2 (C), 111.9 (C), 118.5 (C), 130.8 (CH), 132.4 (CH), 137.7 (C) ppm. IR (KBr): $\tilde{\nu}$ = 540, 1034, 2229, 2963, 3035 cm^{-1}. MS (ESI): *m*/*z* = 222.1 [M + H]$^+$. HRMS: calcd. for $C_{12}H_{16}NOS$ [M + H]$^+$ 222.0953; found 222.0949. HPLC (CHIRALPAK AS-H column; heptane/EtOH, 90:10; 1.0 mL/min): t_R (major enantiomer) = 24.62 min, t_R (minor enantiomer) = 29.38 min, 88% *ee*.

(*tert*-Butylsulfinyl)(*tert*-butylthio)methylbenzene (8): To a stirred solution of toluene (0.26 mol, 2.46 mmol, 2.2 equiv.) at –78 °C in THF (8 mL) was added dropwise a solution of BuLi (2.0 M in hexane, 1.0 mL, 2.24 mmol, 2.0 equiv.), and the mixture was stirred for 5 min. A solution of *t*BuOK (1.0 M in THF, 2.24 mL, 2.24 mmol, 2.0 equiv.) was added dropwise followed by the addition of 2,2,6,6-tetramethylpiperidine (0.37 mL, 2.24 mmol, 2.0 equiv.). After 30 min, a solution of *tert*-butyl disulfide (200 mg, 1.12 mmol) in THF (3 mL) was added dropwise. After 35 min, a solution of racemic thiosulfinate ester **1** (217 mg, 1.12 mmol) in THF (3 mL) was added over a period of 6 min. The reaction mixture was stirred for 35 min followed by the addition of saturated $NaHCO_3$ (5 mL), and the mixture was allowed warm to room temperature. Water (5 mL) was added, and the product was extracted with EtOAc (3 × 15 mL). The combined extracts were dried with magnesium sulfate and concentrated to dryness. Purification by silica gel chromatography (pentane/EtOAc, 3:1) afforded the following: (i) an inseparable mixture of (*tert*-butylthio)methylbenzene and bis(*tert*-butylthio)-methylbenzene[40] and (ii) a mixture of diastereomeric dithioacetal monosulfoxides **8** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 [s, 9 H, C(CH_3)$_3$], 1.20 [s, 9 H, C(CH_3)$_3$], 1.31 [s, 9 H, C(CH_3)$_3$], 1.36 [s, 9 H, C(CH_3)$_3$], 4.83 (s, 1 H, C*H*Ar), 4.88 (s, 1 H, C*H*Ar), 7.26–7.44 (m, 10 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.9 (CH_3), 24.0 (CH_3), 31.2 (CH_3), 31.9 (CH_3), 46.0 (C), 46.1 (C), 56.6 (C), 56.8 (C), 61.4 (CH), 65.5 (CH), 109.9 (C), 128.2 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.9 (CH), 129.7 (CH), 138.4 (C) ppm. IR (KBr): $\tilde{\nu}$ = 702, 1039, 1156, 1367, 1455, 2956, 3029 cm^{-1}. HRMS: calcd. for $C_{15}H_{24}OS_2$ [M + H]$^+$ 307.1166; found 307.1154.

(1,3-Benzodioxo-5-ylmethyl)tributylstannane (9): To a two-necked flask (25 mL) containing magnesium turnings (210 mg, 8.36 mmol) was added a solution of tributyltin chloride (0.98 mL, 3.60 mmol) in THF (5 mL), and the mixture was heated to 60 °C. After 10 min, a solution of 3,4-methylenedioxybenzyl bromide (500 mg, 2.34 mmol) in THF (5 mL) was added dropwise through a syringe. The reaction mixture was stirred for an additional 3 h, and then it was cooled in an ice bath and quenched with water (8 mL). The mixture was extracted with Et_2O (3 × 15 mL). The combined extracts were washed with 5% HCl, water, and brine and then dried with anhydrous Na_2SO_4. The resulting mixture was concentrated in vacuo to complete dryness. Purification by silica gel chromatography (pentane/Et_2O, 9.8:0.2) afforded (1,3-benzodioxo-5-ylmethyl)tributylstannane (**9**[41], 877 mg, 88%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77–0.90 (m, 15 H, CH_3-CH_2), 1.20–1.31 (m, 6 H, CH_2), 1.36–1.47 (m, 6 H, CH_2), 2.23 (s, 2 H, CH_2Ar),

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5.86 (s, 2 H, O-CH_2-O), 6.42 (dd, J = 1.6, 7.9 Hz, 1 H, Ar), 6.49 (d, J = 1.4 Hz, 1 H, Ar), 6.63 (d, J = 7.9 Hz, 1 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 9.2 (CH_2), 13.6 (CH_3), 17.7 (CH_2), 27.2 (CH_2), 29.0 (CH_2), 100.3 (CH_2), 107.6 (CH), 108.1 (CH), 119.1 (CH), 137.4 (C), 143.4 (C), 147.4 (C) ppm.

Enantioselective Synthesis of (*S*)-*tert*-Butyl (1,3-Benzodioxol-5-yl)-methyl Sulfoxide (4a) Using Benzyllithium Obtained by Tin–Lithium Exchange: To a stirred solution of the benzyltributylstannane **9** (0.56 g, 1.33 mmol, 2.60 equiv.) in THF (15 mL) at –78 °C was added dropwise a solution of BuLi (2.0 M in hexane, 0.59 mL, 1.18 mmol, 2.3 equiv.). After 35 min, a solution of (*R*)-(+)-thiosulfinate ester **1** (100 mg, 0.51 mmol) in THF (4 mL) was added over a period of 8 min. The reaction mixture was stirred for another 35 min followed by the addition of saturated $NaHCO_3$ (5 mL). The reaction mixture was then warmed to room temp. Water (5 mL) was added, and the product was extracted with EtOAc (3 × 15 mL). The combined organic extracts were dried with magnesium sulfate and concentrated to dryness. Purification by silica gel chromatography (1:1 pentane/EtOAc) afforded sulfoxide **4a** (69 mg, 57%) as a white solid. $[\alpha]_D$ = –230.1 (c = 1, $CHCl_3$). HPLC (CHIRALPAK AS-H column; heptane/EtOH, 90:10; 1.0 mL/min): t_R (major enantiomer) = 23.21 min, >98% *ee*.

General Procedure C. Formation of α-Substituted Benzyl Sulfoxides (10a–10c): To a stirred solution of toluene (0.46 mL, 4.31 mmol, 2.8 equiv.) at –78 °C in THF (40 mL) was added dropwise a solution of BuLi (2.0 M in hexane, 1.8 mL, 3.69 mmol, 2.4 equiv.), and the mixture was stirred for 5 min. A solution of *t*BuOK (1.0 M in THF, 1.22 mL, 1.22 mmol, 0.8 equiv.) was added dropwise followed by the addition of 2,2,6,6-tetramethylpiperidine (0.63 mL, 3.77 mmol, 2.45 equiv.). After 60 min, a solution of thiosulfinate ester **1** (300 mg, 1.54 mmol) in THF (3 mL) was added over a period of 5 to 8 min. The reaction mixture was stirred for an additional 45 min, and then the electrophile (1.38 mmol, 0.9 equiv.) was added. After 15 min, the reaction was quenched by the addition of saturated $NaHCO_3$ (7 mL), and the mixture was warmed to room temp. Water (10 mL) was added, and the product was extracted with EtOAc (3 × 20 mL). The combined extracts were dried with magnesium sulfate and concentrated to dryness. Purification by silica gel chromatography afforded α-substituted benzyl sulfoxides **10a**–**10c**.

Methyl (*S*$_S$,3*S*,4*R*)-4-(*tert*-Butylsulfinyl)-3-methyl-4-phenylbutanoate (10a): Applying general procedure C and using (*R*)-(+)-thiosulfinate ester (96% *ee*) with methyl crotonate (0.14 mL, 1.38 mmol, 0.9 equiv.) as the electrophile yielded conjugate adduct **10a** (230 mg, 50%) as a clear oil after silica gel chromatography (pentane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03–1.07 (obscured d, 3 H, CH_3), 1.06 [s, 9 H, C(CH_3)$_3$], 2.02 (dd, J = 4.2, 15.0 Hz, 1 H, H^2), 2.91 (dd, J = 3.5, 15.0 Hz, 1 H, H^2), 2.94–3.09 (m, 1 H, H^3), 3.65 (s, 3 H, COOCH_3), 3.85 (d, J = 4.0 Hz, 1 H, H^4), 7.19–7.39 (m, 5 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 17.9 (CH_3), 23.6 (CH_3), 30.7 (CH), 36.9 (CH_2), 51.5 (CH_3), 55.6 (C), 65.3 (CH), 128.0 (CH), 128.6 (CH), 129.8 (CH), 134.5 (C), 172.6 (C) ppm. MS (ESI): m/z = 297.2 [M + H]$^+$. HRMS: calcd. for $C_{16}H_{25}O_3S$ [M + H]$^+$ 297.1524; found 297.1539. HPLC (CHIRALPAK AS-H column; heptane/EtOH, 90:10; 1.0 mL/min): t_R (minor enantiomer) = 5.63 min, t_R (major enantiomer) = 7.77 min, 90% *ee*.

***rac*-Methyl (*S*$_S$,3*R*,4*R*)-4-(*tert*-Butylsulfinyl)-3,4-diphenylbutanoate (10b):** Applying general procedure C and using methyl cinnamate (224 mg, 1.38 mmol, 0.9 equiv.) as the electrophile yielded conjugate adduct **10b** (230 mg, 41%) as a clear oil after silica gel chromatography (pentane/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 [s, 9 H, C(CH_3)$_3$], 2.71 (dd, J = 11.6, 15.6 Hz, 1 H, H^2), 3.19 (dd, J = 4.2, 15.6 Hz, 1 H, H^2), 3.49 (s, 3 H, COOCH_3), 3.99 (d, J = 3.4 Hz, 1 H, H^4), 4.15–4.26 (m, 1 H, H^3) 6.82–7.32 (m, 10 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.6 (CH_3), 34.7 (CH_2), 41.5 (CH), 51.5 (CH_3), 56.0 (C), 66.0 (CH), 126.9 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.6 (CH), 130.3 (CH), 133.8 (C), 140.0 (C), 171.7 (C) ppm. MS (ESI): m/z = 359.1 [M + H]$^+$. HRMS: calcd. for $C_{21}H_{27}O_3S$ [M + H]$^+$ 359.1681; found 359.1677.

***rac*-(*S*$_S$,1*S*,2*S*)-2-(*tert*-Butylsulfinyl)-1,2-diphenylethanol (10c) and *rac*-(*S*$_S$,1*R*,2*S*)-2-(*tert*-Butylsulfinyl)-1,2-diphenylethanol (10c′):** Applying general procedure C and using benzaldehyde (0.14 mL, 1.38 mmol, 0.9 equiv.) as the electrophile yielded α-substituted product **10c** (200 mg, 42%) and **10c′** (60 mg, 12%) as white solids after chromatography (pentane/EtOAc, 1:1). Data for **10c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 [s, 9 H, C(CH_3)$_3$], 4.09 [d, J = 9.4 Hz, 1 H, CHS(O)], 5.38 [d, J = 9.4 Hz, 1 H, PhCH(OH)], 6.14 (br. s, 1 H, OH), 6.92–7.20 (m, 10 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.3 (CH_3), 56.6 (C), 66.7 (CH), 77.7 (CH), 127.0 (CH), 127.5 (CH), 127.7 (CH), 128.5 (CH), 129.5 (CH), 134.3 (C), 140.1 (C) ppm. IR (KBr): $\tilde{\nu}$ = 706, 985, 1047, 3033, 3324 cm^{-1}. MS (ESI): m/z = 303.4 [M + H]$^+$. HRMS: calcd. for $C_{18}H_{23}O_2S$ [M + H]$^+$ 303.1419; found 303.1432. Data for **10c′**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 [s, 9 H, C(CH_3)$_3$], 3.98 [d, J = 2.5 Hz, 1 H, CHS(O)], 4.53 (d, J = 5.2 Hz, 0.5 H, OH), 4.55 (d, J = 5.2 Hz, 0.5 H, OH), 5.67 [br. dd, J = 2.5, 5.2 Hz, 1 H, PhCH(OH)], 6.97–7.27 (m, 10 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 23.5 (CH_3), 55.4 (C), 67.7 (CH), 72.3 (CH), 126.5 (CH), 127.2 (CH), 127.7 (CH), 127.9 (CH), 128.0 (CH), 130.7 (CH), 132.7 (C), 140.5 (C) ppm. IR (KBr): $\tilde{\nu}$ = 703, 1017, 1056, 2956, 3304 cm^{-1}. MS (ESI): m/z = 303.4 [M + H]$^+$. HRMS: calcd. for $C_{18}H_{23}O_2S$ [M + H]$^+$ 303.1419; found 303.1412.

***rac*-(*S*$_S$,1*R*)-*tert*-Butyl 1-Phenylethyl Sulfoxide (10d) and *rac*-(*S*$_S$,1*S*)-*tert*-Butyl 1-Phenylethyl Sulfoxide (10d′):** To a stirred solution of toluene (0.46 mL, 4.31 mmol, 2.8 equiv.) in THF (40 mL) at –78 °C was added dropwise a solution of BuLi (2.0 M in hexane, 1.8 mL, 3.69 mmol, 2.4 equiv.), and the mixture was stirred for 5 min. A solution of *t*BuOK (1.0 M in THF, 4.0 mL, 4.0 mmol, 2.6 equiv.) was added dropwise followed by the addition of 2,2,6,6-tetramethylpiperidine (0.63 mL, 3.77 mmol, 2.45 equiv.). After 35 min, racemic thiosulfinate ester **1** (300 mg, 1.54 mmol) in THF (3 mL) was added over a period of 6 min. The reaction mixture was stirred for 35 min. Iodomethane (0.1 mL, 1.84 mmol, 1.2 equiv.) was added, and the reaction mixture was warmed to –25 °C. After 1 h, saturated $NaHCO_3$ (7 mL) was added, and the reaction mixture was warmed to room temp. Water (10 mL) was added, and the product was extracted with EtOAc (3 × 20 mL). The combined organic extracts were dried with magnesium sulfate and concentrated to dryness. Purification by silica gel chromatography (pentane/EtOAc, 1:1) afforded α-methylbenzyl sulfoxide **10d** (160 mg, 50%) and **10d′** (50 mg, 15%) as white solids. Data for **10d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 [s, 9 H, C(CH_3)$_3$], 1.64 (d, J = 7.2 Hz, 3 H), 3.89 (q, J = 7.2 Hz, 1 H), 7.25–7.37 (m, 5 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 17.8 (CH_3), 23.6 (CH_3), 55.1 (C), 56.9 (CH), 127.7 (CH), 128.0 (CH), 128.9 (CH), 139.8 (C) ppm. HRMS: calcd. for $C_{12}H_{19}OS$ [M + H]$^+$ 211.1157; found 211.1163. Data for **10d′**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 [s, 9 H, C(CH_3)$_3$], 1.73 (d, J = 7.3 Hz, 3 H), 3.84 (q, J = 7.3 Hz, 1 H), 7.27–7.39 (m, 5 H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 19.5 (CH_3), 23.5 (CH_3), 54.8 (C), 55.1 (CH), 127.8 (CH), 128.3 (CH), 129.0 (CH), 137.3 (C) ppm.

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