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# Symmetric Diarylsulfoxides as Asymmetric Sulfinylating Reagents for Dialkylmagnesium Compounds

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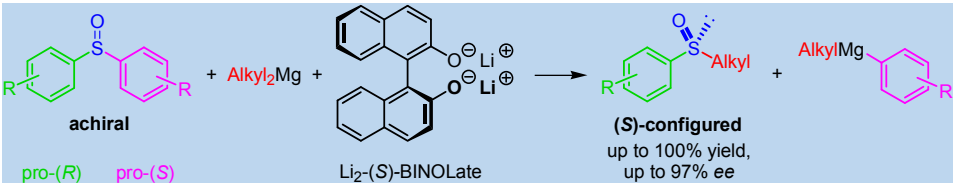



**ABSTRACT:** At −78°C primary dialkylmagnesium compounds reacted with diaryl sulfoxides when 1.5 equiv. of the dilithium salt of (*S*)-BINOL were added as a promotor. Alkyl aryl sulfoxides resulted in up to quantitative yield and with up to 97% *ee*. This demonstrates the feasibility of asymmetric sulfinylations by achiral sulfinylating agents (from the perspective of $Alkyl_2Mg$) as well as the feasibility of asymmetric sulfoxide-magnesium exchanges (from the perspective of $Ar_2SO$).

## INTRODUCTION

Non-racemic, i. e. enantioenriched or enantiomerically pure sulfoxides[1] occur widely in asymmetric synthesis[2] – either stoichiometrically as carriers of chiral information[3] or catalytically as ligands for transition metals[4] – and natural product synthesis.[5] Non-racemic sulfoxides[6] are prepared, inter alia, by the asymmetric oxidation of sulfides[7] (the enantioselective oxidation leading to esomperazole – one of the top-selling drugs for gastric diseases – is a prominent example[8]), by the functionalization of organometallics with enantiomerically pure sulfinylating agents (e. g. ref.[9,11-21]), and by the asymmetric alkylation (or arylation) of sulfenate anions by alkyl (or aryl) halides.[10] Grignard reagents have provided non-racemic sulfoxides upon functionalization by enantiomerically pure sulfinic acid derivatives – e. g. by menthyl (*S*)-*para*-toluenesulfinate,[11] (4*S*)-4-benzyl-*N*-[(*S*)-*para*-toluenesulfinyl]oxazolidinone,[12] and *tert*-butyl [(*R*)-*tert*-butylsulfinyl] sulfide[13] – or by enantiomerically pure sulfoxides (**1**,[14] **2**,[15] **3**,[16] **7**,[17] **8**,[18] (*S*)-**9**,[18] **12**,[19,20] **13**,[20] **14**[21] or **15**,[21] Figure 1; ref. [22]). When one of the mentioned sulfinic acid derivatives sulfinylates a Grignard reagent, the leaving group is a magnesium alkoxide, a magnesium carbamate or a magnesium sulfide. When such sulfinylations are

carried out with one of the sulfoxides **1**-**3**, **7**-(*S*)-**9** or **12**-**15** the leaving group is a(nother) Grignard reagent. That feature makes the latter processes sulfoxide-magnesium exchange reactions.[23]

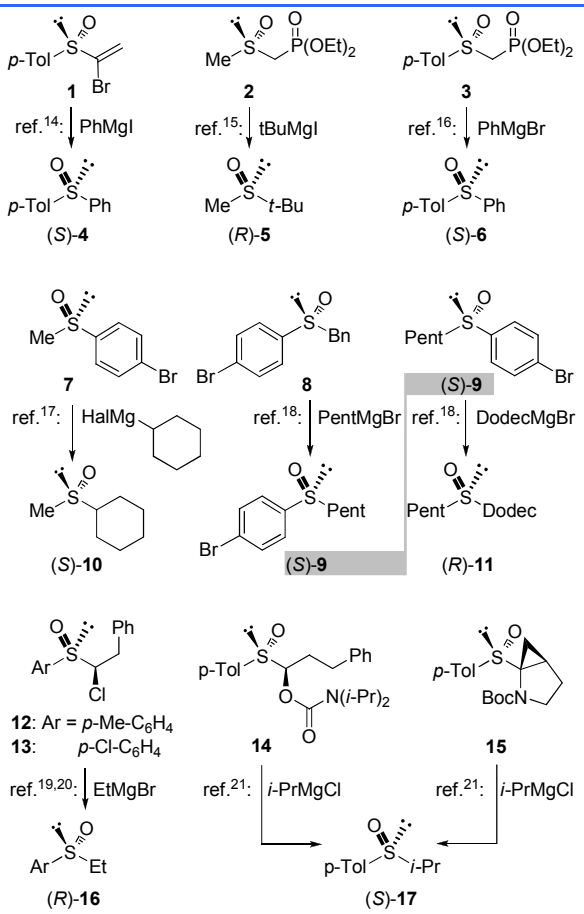
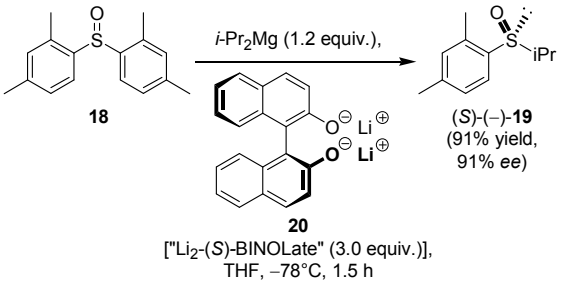



**Figure 1.** Enantiomerically pure sulfinylating agent, which convert Grignard reagents into non-racemic sulfoxides while expelling another Grignard compound as a leaving group.

In 2012 we reported that *non-racemic* isopropyl aryl sulfoxides are accessible by sulfinylating *i*-$Pr_2Mg$[24] by *symmetric* (achiral!) diarylsulfoxides.[25] The best-working sulfinylating agent of the latter kind was the diaryl sulfoxide **18** (Scheme 1). One of its enantiotopic 2,4-dimethylphenyl groups was replaced by the isopropyl group with a 95.5:4.5 preference over the other – i. e., with 91% *ee*. The underlying enantiocontrol was exerted by 3.0 equiv. of the dilithium salt "$Li_2$-(*S*)-BINOLate" (**20**) of (*S*)-BINOL. **20** forms a 1:1 complex with $Et_2Mg$ in the solid state.[26] An analogous interaction between **20** and *i*-$Pr_2Mg$ was expected to arise upon mixing "THF"[27] solutions of the two components at −78°C.

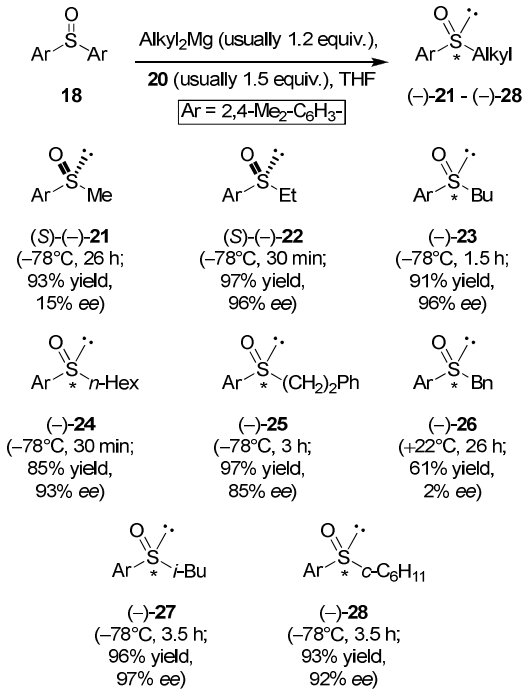
**Scheme 1. Asymmetric Sulfinylation of a Secondary Dialkylmagnesium Compound by the Symmetric Diaryl Sulfoxide 18 in the Presence of an Excess of the Dilithium Salt "$Li_2$-(*S*)-BINOLate" (20) of (*S*)-BINOL (ref.[25])**




## RESULTS AND DISCUSSION

The present study demonstrates that symmetric diaryl sulfoxides sulfinylate *primary* dialkylmagnesium compounds in good yields,[28] too, and even with up to 97% *ee* (Schemes 2-6). This required fulfilling three prerequisites: (1) In the preparatory phase of the reaction the dialkylmagnesium reagent had to be separated from the Schlenk equilibrium of the initially prepared Grignard reagent by precipitating the accompanying $MgBr_2$ with diglyme (0.39 equiv.) and 1,4-dioxane (0.60 equiv.). (2) The resulting dialkylmagnesium reagent (1.2 equiv.) had to be complexed by "$Li_2$-(*S*)-BINOLate" (**20**; 1.5 equiv.) prior to adding the sulfoxide. (3) The duration of the sulfinylation had to be monitored carefully. At −78°C[29] the optima ranged from 10 s to 26 h. Even moderately longer reaction times could decrease the yield and/or the enantioselectivity when we used $Et_2Mg$ or $Bu_2Mg$. As previously,[25] the inducing ligand was recoverable as (*S*)-BINOL in almost quantitative yield by flash chromatography on silica gel;[30] it elutes prior to no matter which sulfoxide.

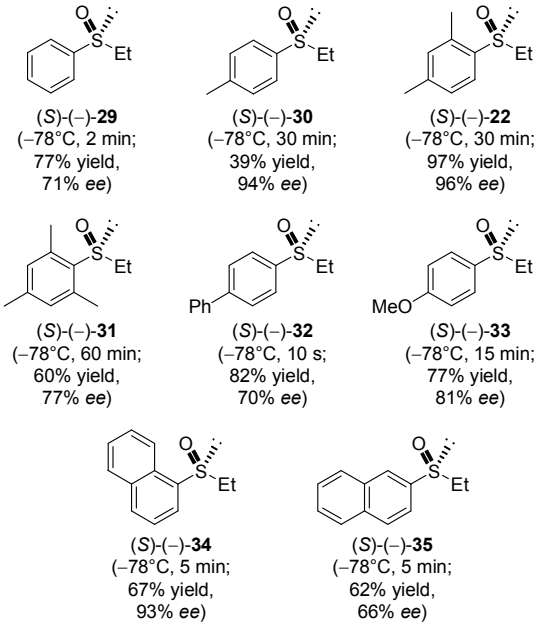
**Scheme 2. Li2-(*S*)-BINOLate (20)-Promoted Asymmetric Sulfinylations of Primary Dialkylmagnesium Compounds and of Dicyclohexylmagnesium by the Symmetric Diaryl Sulfoxide 18 (Configurational Assignments: Ref.[32])[a]**




[a] The sulfoxides **21** and **28** were obtained from differently composed reactant mixtures than the other sulfoxides, using the sulfoxide **18** and more of the exchange-inducing reagents $Me_2Mg$ (2.4 equiv), $Bn_2Mg$ (2.4 equiv.), and **20** (3.0 equiv.). Under the "usual" conditions lower yields were obtained.

Scheme 2 shows $Li_2$-(*S*)-BINOLate (**20**)-induced sulfinylations of $Me_2Mg$, $Bn_2Mg$,[31] five other examples of $(R_{prim})_2Mg$, and $(c\text{-}C_6H_{11})_2Mg$ with the symmetric diaryl sulfoxide **18**. They proceeded with 15% *ee*, 2% *ee*,[31] 85-97% *ee*, and 92% *ee*, respectively. In most cases the yield surpassed 90%. The preferentially formed sulfoxide enantiomer was levorotatory without an exception;[32] the products, whose absolute configurations we clarified [(–)-**21**, (–)-**22**] were (*S*)-configured.[32] According to the survey of Scheme 2 $Et_2Mg$, $Bu_2Mg$, and $i\text{-}Bu_2Mg$ were sulfinylated by a mixture of sulfoxide **18** and $Li_2$-(*S*)-BINOLate (**20**) with the highest enantiomeric excesses, namely with 96%, 96%, and 97%, respectively. This led us to explore how the same organometallics are sulfinylated by mixtures of $Li_2$-(*S*)-BINOLate (**20**; 1.25 equiv.) and symmetric diaryl sulfoxides (0.83 equiv.) other than **18** (Schemes 3-6).

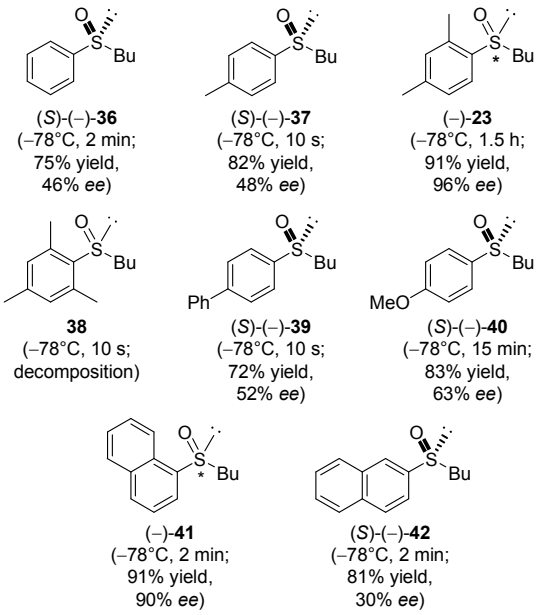
**Scheme 3. Nonracemic Sulfoxides [(*S*)-Configurations: Ref.[32]] From $Li_2$-(*S*)-BINOLate (20)-Promoted Asymmetric Sulfinylations of $Et_2Mg$ by Symmetric Diaryl Sulfoxides[a,33]**




[a] The aryl ethyl sulfoxide depicted here were prepared from a symmetric diarylsulfoxide and the exchange-inducing reagents $Et_2Mg$ (1.2 equiv) and **20** (1.5 equiv.), i. e., under the "usual" conditions of Scheme 2.

The $Li_2$-(*S*)-BINOLate (**20**)-induced asymmetric sulfinylations of $Et_2Mg$ (Scheme 3) reached completion at −78°C between as little as 10 s [→ (*S*)-(−)-**32**] and 1 h at maximum [→ (*S*)-(−)-**31**].[33] The ethyl aryl sulfoxides **22** and **29**-**35** resulted in an average yield of 70%. They were uniformly levorotatory and (*S*)-configured.[32] The highest enantiocontrol resulted from (2,4-dimethylphenyl)sulfinyl transfer [→ 97% (*S*)-(−)-**22**, 96% *ee*]. The runners-up were *para*-tolylsulfinyl transfer (94% *ee*) and α-naphthylsulfinyl transfer (93% *ee*).

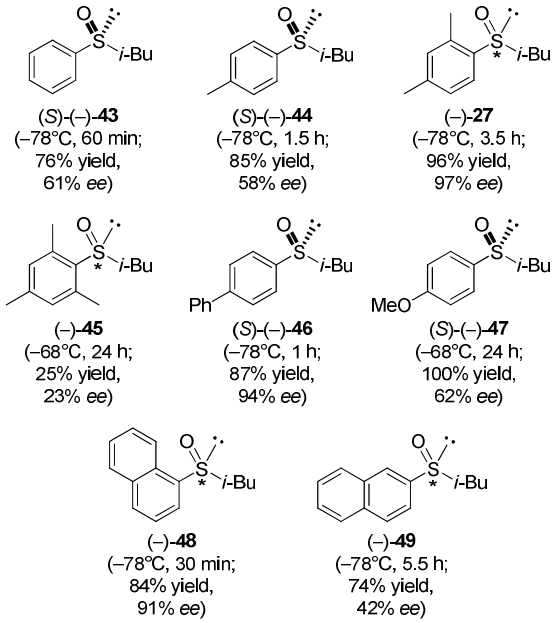
**Scheme 4. Nonracemic Sulfoxides (Configurational Assignments: Ref.[32]) From $Li_2$-(*S*)-BINOLate (20)-Promoted Asymmetric Sulfinylations of $Bu_2Mg$ by Achiral Diaryl Sulfoxides[a]**




[a] The aryl butyl sulfoxide depicted here were prepared from a symmetric diarylsulfoxide and the exchange-inducing reagents $Bu_2Mg$ (1.2 equiv) and **20** (1.5 equiv.), i. e., under the "usual" conditions of Scheme 2.

The $Li_2$-(*S*)-BINOLate (**20**)-induced asymmetric sulfinylations of $Bu_2Mg$ (Scheme 4) were even faster than the analogous sulfinylations of $Et_2Mg$ (cf. above). This rendered the non-racemic sulfoxides **23**, **36**-**37**, and **39**-**42** in 62-91% yield. In contrast, butyl 2,4,6-trimethylphenyl sulfoxide (**38**) did not form because of an almost instantaneous decomposition of a mixture of its precursors. The sulfoxides of Scheme 4 were consistently levorotatory and the five sulfoxides, whose 3D structure we clarified, were (*S*)-configured.[32] The highest *ee* value in this series of (96%) was observed for the (2,4-dimethylphenyl)sulfinylation [→ 91% (–)-**23**].

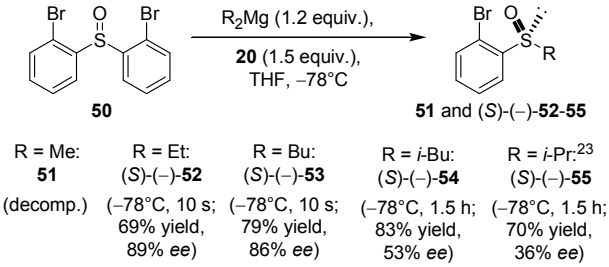
**Scheme 5. Nonracemic Sulfoxides (Configurational Assignments: Ref.[32]) From $Li_2$-(*S*)-BINOLate (20)-Promoted Asymmetric Sulfinylations of *i*-$Bu_2Mg$ by Achiral Diarylsulfoxides[a]**




[a] The aryl isobutyl sulfoxides depicted here were prepared from a symmetric diarylsulfoxide and the exchange-inducing reagents *i*-$Bu_2Mg$ (1.2 equiv) and **20** (1.5 equiv.), i. e., under the "usual" conditions of Scheme 2.

The third dialkyl magnesium reagent, which was sulfinylated asymmetrically in the presence of $Li_2$-(*S*)-BINOLate (**20**) by a variety of symmetric diaryl sulfoxides was *i*-$Bu_2Mg$ (Scheme 5). It was less reactive than $Et_2Mg$ and $Bu_2Mg$ so that full conversions required 0.5-24 h and possibly a slightly elevated temperature (–68°C instead of –78°C). The newly formed sulfoxides were levorotatory, and those, whose absolute configurations we clarified (**43**, **44**, **46**, and **47**), were (*S*)-configured.[32] Enantiocontrol was best when the (2,4-dimethylphenyl)sulfinyl group was transferred [→ 96% (*S*)-(–)-**27**, 97% *ee*] or the (4-phenylphenyl)sulfinyl group [→ 87% (*S*)-(–)-**46**, 94% *ee*].

**Scheme 6. Nonracemic (2-Bromophenyl) Sulfoxides [(*S*)-Configurations: Ref.[32]] From $Li_2$-(*S*)-BINOLate (20)-Promoted Asymmetric Sulfinylations by the Symmetric Bis(2-bromophenyl) Sulfoxide 50**



In the presence of $Li_2$-(*S*)-BINOLate (**20**) bis(2-bromophenyl) sulfoxide (**50**) had been a capricious sulfinylating agent for *i*-$Pr_2Mg$:[25] 3.9 equiv. of this additive were required for accelerating the sulfinylation proper [→ 70% (*S*)-**55**] at the expense of an ensuing Br→Mg exchange; the latter interfered unavoidably under standard conditions.[25] No Br→Mg exchanges occurred when mixtures of bis(2-bromophenyl) sulfoxide (**50**) and $Li_2$-(*S*)-BINOLate (**20**) sulfinylated $Et_2Mg$, $Bu_2Mg$, and *i*-$Bu_2Mg$ – yet not $Me_2Mg$ – asymmetrically (Scheme 6). The corresponding brominated sulfoxides (*S*)-**52** - (*S*)-**54**[32] resulted in 69-83% yield and with 53-89% *ee*.

## CONCLUSION

In summary, we have shown that symmetric diaryl sulfoxides transfer arylsulfinyl groups on di(*prim*-alkyl) magnesium compounds *asymmetrically* when 1.5 equiv. of $Li_2$-(*S*)-BINOLate (**20**) are present. This transformation is a novel entry into the synthesis of non-racemic alkyl aryl sulfoxides.

Ethyl, butyl, and isobutyl aryl sulfoxides arose with up to 97% *ee*. Hexyl and phenylethyl 2,4-dimethylphenyl sulfoxide resulted with 93 and 87% *ee*, respectively. In stark contrast, methyl 2,4-dimethylphenyl sulfoxide resulted with little enantiocontrol (15% *ee*) and benzyl 2,4-dimethylphenyl sulfoxide virtually without (2% *ee*). We are at a loss interpreting these substituent dependencies. Hence it remains unclear to which extent – and in the affirmative case: where – steric effects and/or electronic effects and/or other effects are operative the *ee*-determining or the yield-determining step. This is not least because the sulfoxide/magnesium exchange – let alone our asymmetric variant thereof – is only poorly understood mechanistically.

The strategy, which underlies our present synthesis of alkyl aryl sulfoxides would become more generally useful if enantiomerically pure additives like $Li_2$-(*S*)-BINOLate (**20**) allowed to sulfinylate organometallics asymmetrically also by other symmetric sulfoxides than diaryl sulfoxides. At least there are many kinds of (admittedly: unsymmetric) sulfoxides, which sulfinylate Grignard reagents while expelling a magnesium-containing leaving group (examples: Figure 1). The latter may be stable,[34] β-eliminate,[35] α-eliminate/rearrange[36] or undergo a semipinacol rearrangement.[37] If a *pair* of progenitors of any such leaving group binds to a –S(=O)– linchpin a symmetric sulfoxide candidate for effecting another asymmetric sulfinylation like contemplated above would be defined. Such a sulfoxide might act not just on $R_2Mg$ but also on RMgHal, $RMgOX(=O)_nR'$, $R_3MgLi$ or other organometallics.[38,39]

## EXPERIMENTAL SECTION

### General

**Working technique:** All reactions were carried out under an atmosphere of $N_2$. Prior to use reaction flasks were dried in vacuo with a heat gun. Liquids were added with a syringe through a septum. Prior to use THF, $Et_2O$, and diglyme were distilled over sodium or potassium under an atmosphere of $N_2$. *i*-$Pr_2NH$ was distilled over $CaH_2$ similarly. Other solvents and reagents were employed as obtained commercially, i. e. without further purification. **Flash chromatography on silica gel:** Purification by flash chromatography was conducted on silica gel 60 (230-400 mesh). All eluents were distilled prior to use. Chromatography conditions are documented in a shorthand form like, e. g. "(*c*-$C_6H_{12}$:EtOAc a:b, F. 10-20)", which means we eluted with an a:b mixture (v:v) of *c*-$C_6H_{12}$ and EtOAc and that the product was isolated from fractions 10-20. Fraction and column size were chosen in accordance to the parameters described by Still *et al.*[40] **Nuclear magnetic resonance spectra:** NMR spectra were registered with 300 MHz and 400 MHz spectrometers ($^1$H NMR) and with a 100 MHz spectrometer ($^{13}$C NMR); referenced internally to the $^1$H- and $^{13}$C-NMR signals of the solvent [$CDCl_3$: 7.26 ppm ($^1$H) and 77.10 ppm ($^{13}$C)]. $^1$H-NMR data are reported as follows: chemical shift (δ in ppm), multiplicity (s for singlet; d for doublet; t for triplet; q for quartet; m for multiplet; $m_c$ for symmetric multiplet; br for broad signal), coupling constant(s) (Hz), integral, assignment. $^{13}$C-NMR data are reported in terms of chemical shift and assignment. Assignments of $^1$H-NMR and $^{13}$C-NMR resonances refer to the IUPAC nomenclature except within substituents (where primed numbers are used) or where explicitly indicated otherwise. NMR assignments were supported by a combination of 1D and 2D techniques (DQF-COSY and ed-HSQC). **High-resolution mass spectra** were obtained employing a CI/$NH_3$ (110 eV) mode and using an orbitrap analyzer. **Elemental analyses** were obtained with a CHNS analyzer. **Melting points** are uncorrected and were determined using open glass capillaries. **IR spectra** were measured with an FT-IR spectrometer irradiating sample films spread on a NaCl plate. The *ee* values were determined by **chiral HPLC**. **Optical rotations** were measured at 365, 436, 546, 578, and 589 nm at 20°C and were calculated by the Drude equation {$[\alpha] = (\alpha_{exp} \times 100)/(c \times d)$}; rotational values are the average of five measurements of $\alpha_{exp}$ in a given solution of the respective sample.

### Preparation of Reactants

#### Preparation of $Alkyl_2Mg$ solutions in $Et_2O$ (Alkyl = Et, Bu, *n*-Hex, $(CH_2)_2Ph$, Bn, *i*-Bu and *c*-$C_6H_{11}$)[41]

At room temperature the appropriate alkyl bromide (128 mmol) was added dropwise to a suspension of Mg turnings (3.14 g, 129 mmol, 1.0 equiv.) in $Et_2O$ (60 mL) within 1.5 h. The dark grey suspension was heated under reflux for 4 h. After cooling to 0°C, diglyme (7.20 mL, 6.75 g, 50.3 mmol, 0.39 equiv.) in $Et_2O$ (9 mL) and thereafter dioxane (6.60 mL, 6.80 g, 77.2 mmol, 0.60 equiv.) in $Et_2O$ (6 mL) were added dropwise with a syringe pump within 75 and 50 min, respectively. The white suspension was stirred at –10°C for 16 h and then filtered with suction an atmosphere of nitrogen. The clear and colorless filtrate was concentrated to about half its volume by a stream of nitrogen. Usually a small amount of a white precipitate formed concomitantly; it remained in the solution without decreasing its activity. The resulting solution of $Alkyl_2Mg$ could be stored at 4°C for several weeks. Its concentration was determined by titration with salicylic aldehyde phenylhydrazone.[42]

#### Preparation of $Me_2Mg$ and $Hex_2Mg$ solutions in $Et_2O$[43]

At room temperature MeLi or HexLi (solutions in THF, 12.0 mmol, 1.0 equiv.) was added dropwise to a solution of the corresponding AlkylMgCl (solution in THF, 12.0 mmol, 1.0 equiv.). After 5 min the solvent was removed by applying high vacuo (~ 0.4 mbar). The residue

was extracted with $Et_2O$ (3 × 10 mL) from precipitated LiCl. The concentration of the resulting clear and colorless solution was determined by titration with salicylic aldehyde phenylhydrazone.[42] At 4°C such solutions could be stored for several weeks.

**Preparation of the Symmetric Diaryl Sulfoxides**

The symmetric diaryl sulfoxides used in this work were materials from our previous study.[25]

**Preparation of Alkyl Aryl Sulfoxides**:

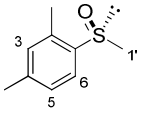
**General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides**[44]

$Alkyl_2Mg$ (0.38-0.80 M solutions in $Et_2O$, 0.55-1.2 equiv.) was added to a solution of the appropriate diaryl sulfoxide (0.148-0.494 mmol, 1.0 equiv.) in THF (1 mL) at room temperature (for further details and deviations from this procedure: cf. individual descriptions). After complete conversion, the reaction was quenched by the addition of MeOH (1 mL) and a saturated aqueous solution of $NH_4Cl$ (1 mL). The layers were separated. The aqueous layer was extracted with *t*-BuOMe (3 × 2 mL). The combined organic layers were dried over $MgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel[40] (further details: cf. individual descriptions).

**Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides**

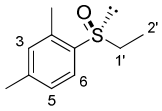
At 0°C *n*-BuLi [2.05-2.27 M solution in hexane, 3.0 equiv.] was added to a precooled solution of (*S*)-BINOL (1.5 equiv.) in THF (2 mL). After 10 min stirring was continued at room temperature for another 10 min. Subsequently, a solution of $Alkyl_2Mg$ (0.38-0.80 m solution in $Et_2O$, 1.2 equiv.) was added dropwise. After 10 min the reaction mixture was cooled to −78°C and a solution of the appropriate diaryl sulfoxide (0.174-0.786 mmol, 1.0 equiv.) in THF (1.5 mL) was added during 10 min. If $Alkyl_2Mg$ was $Et_2Mg$ or $Bu_2Mg$, the solution of the appropriate diaryl sulfoxide had to be (1) precooled to −78°C and (2) added to the $Li_2$-(*S*)-BINOLate/$Alkyl_2Mg$ mixture very fast. After full conversion was achieved (10 s to 24 h) the reaction was quenched by the addition of MeOH (2 mL). The resulting mixture was warmed to room temperature and diluted with *t*-BuOMe (5 mL). A saturated, aqueous solution of $NH_4Cl$ (3 mL) was added. The layers were separated. The aqueous layer was extracted with *t*-BuOMe (3 × 2 mL). The combined organic layers were dried over $mgSO_4$ and evaporated. The crude product was purified by flash chromatography on silica gel[40] (details: cf. individual descriptions) to yield the title compound.

**(2,4-Dimethylphenyl) Methyl Sulfoxide (21): (*S*)-(–)-Enantiomer and Racemic**[45]



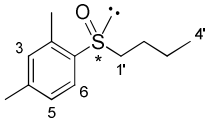

The **racemic synthesis**[44] did not follow the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides*): At 0°C *n*-BuLi (2.1 M in hexane, 0.56 mL, 1.2 mmol, 6.1 equiv.) was added to a solution of *rac*-BINOL (169 mg, 0.591 mmol, 3.0 equiv.) in THF (1 mL). After 10 min $Me_2Mg$ (0.40 M in $Et_2O$, 1.18 mL, 0.472 mmol, 2.4 equiv.) was added. After another 10 min a solution of bis(2,4-dimethylphenyl) sulfoxide (50.9 mg, 0.197 mmol) in THF (0.75 mL) was added. After stirring at room temperature for 9 h the reaction was quenched and the resulting mixture was worked up. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 55:45, F. 30-42) delivered *rac*-**21** (26.2 mg, 79%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (101 mg, 0.391 mmol), (*S*)-BINOL (3.0 equiv.) and $Me_2Mg$ (2.4 equiv.). After 72 h this delivered (*S*)-(–)-**21** (61.4 mg, 93%; 15% *ee*) as a colorless oil. $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, Ar-$CH_3$), 2.37 (s, 3 H, Ar-$CH_3$), 2.66 (s, 3 H, 1'-$H_3$), 7.01 (br. s, 1 H, 3-H), 7.25 (d, low-field branch superimposed by the singlet of $CHCl_3$, $J_{5,6}$ = 7.9 Hz, 1 H, 5-H), 7.83 ppm (d, $J_{6,5}$ = 8.1, 1 H, 6-H). The preceding data are consistent with those reported in the literature.[46] The *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(R)$ = 16.83 min, $t_r(S)$ = 22.21 min. $[\alpha]_{365}^{20}$ = –163.1, $[\alpha]_{436}^{20}$ = –81.2, $[\alpha]_{546}^{20}$ = –40.2, $[\alpha]_{578}^{20}$ = –34.6, $[\alpha]_{589}^{20}$ = –32.1 (*c* = 2.00 in EtOH; the respective sample had 15% *ee*); Lit.[47]: $[\alpha]_{589}^{20}$ = –87.8 [*c* = 1.3 in acetone, a sample of the (*S*)-enantiomer with 73% *ee*]. The absolute configuration was determined by comparing the sense of the optical rotation with literature data.[47]

**(2,4-Dimethylphenyl) Ethyl Sulfoxide (22): (*S*)-(–)-Enantiomer and Racemic**[45]



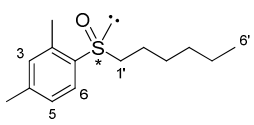
The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (100 mg, 0.387 mmol) with $Et_2Mg$ (0.52 M in $Et_2O$, 0.91 mL, 0.47 mmol, 1.2 equiv.) within 30 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 60:40, F. 24-38) delivered *rac*-**22** (34.3 mg, 49%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* (cf. Section 3.2) using bis(2,4-dimethylphenyl) sulfoxide (200 mg, 0.774 mmol). After 30 min this delivered (*S*)-(–)-**22** (137 mg, 97%; 96% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.23 (dd, $J_{2',1'\text{-A}} = J_{2',1'\text{-B}}$ = 7.3 Hz, 3 H, 2'-$H_3$), 2.34 (s, 3 H, Ar-$CH_3$), 2.36 (s, 3 H, Ar-$CH_3$), AB signal ($\delta_A$ = 2.71, $\delta_B$ = 2.86, $J_{A,B}$ = 13.6 Hz, A part additionally split by q, $J_{1'\text{-A},2'}$ = 8.0 Hz, 1'-$H_A$; B part additionally split by q, $J_{1'\text{-B},2'}$ = 6.9 Hz, 1'-$H_B$), 7.01 ($m_c$, 1 H, 3-H), 7.22 ($m_c$[49], $J_{5,6}$ = 7.9 Hz, 1 H, 5-H), 7.75 ppm (d, $J_{6',5'}$ = 8.1 Hz, 1 H, 6-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 6.4 (C-2'), 18.3 (Ar-$CH_3$), 21.3 (Ar-$CH_3$), 48.5 (C-1'), 124.4 (C-6), 127.9 (C-5), 131.5 (C-3), 134.5, 138.6, 141.2 ppm (C-1, C-2, and C-4). The preceding data are consistent with those reported in the literature.[46] The *ee* was determined by chiral HPLC (Chiralcel OD-3, *n*-heptane/*i*-PrOH 96:4, 22°C, 1 mL/min, $\lambda_{detector}$ = 204 nm): $t_r(R)$ = 9.06 min, $t_r(S)$ = 13.49 min. $[\alpha]_{365}^{20}$ = –1247.6, $[\alpha]_{436}^{20}$ = –614.3, $[\alpha]_{546}^{20}$ = –305.5, $[\alpha]_{578}^{20}$ = –261.8, $[\alpha]_{589}^{20}$ = –248.7 (*c* = 1.64 in EtOH; the respective sample had 96% *ee*). The absolute configuration was assigned by chemical correlation (cf. Supporting Information).

**Butyl (2,4-Dimethylphenyl) Sulfoxide (23): (–)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (95.7 mg, 0.370 mmol) with $Bu_2Mg$ (0.69 M in $Et_2O$, 0.65 mL, 0.45 mmol, 1.2 equiv.) within 1.5 h at 0°C. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 24-40) delivered *rac*-**23** (60.0 mg, 77%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (102 mg, 0.393 mmol). After 1.5 h this delivered (–)-**23** (75.3 mg, 91%; 96% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 0.93 (t, $J_{4',3'}$ = 7.6 Hz, 3 H, 4'-$H_3$), 1.35-1.56 (m, 2 H, 3'-$H_2$), 1.59-1.83 (m, 2 H, 2'-$H_2$), 2.33 (s, 3 H, Ar-$CH_3$), 2.36 (s, 3 H, Ar-$CH_3$), AB signal ($\delta_A$ = 2.70, $\delta_B$ = 2.75, $J_{A,B}$ = 13.3 Hz, A part additionally split by dd, $J_{1'\text{-A},2'\text{-A}}$ = 9.4, $J_{1'\text{-A},2'\text{-B}}$ = 5.2 Hz, 1-$H_A$; B part additionally split by dd, $J_{1'\text{-B},2'\text{-B}}$ = 9.4 Hz, $J_{1'\text{-B},2'\text{-A}}$ = 5.7 Hz, 1-$H_B$), 7.01 (d, $J_{3,5}$ = 0.7 Hz, 1 H, 3-H), 7.22 (dd, $J_{5,6}$ = 8.1 Hz, $J_{5,3}$ = 0.8 Hz, 1 H, 5-H), 7.77 ppm (d, $J_{6,5}$ = 8.4 Hz, 1 H, 6-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 13.9 (C-4'), 18.3 (Ar-$CH_3$), 21.3 (Ar-$CH_3$), 22.0 (C-3'), 24.5 (C-2'), 55.5 (C-1'), 124.2 and 128.2 (C-5, and C-6'), 131.7 (C-3), 134.3, 139.4, and 141.3 ppm (C-1, C-2, and C-4). IR ($CDCl_3$): $\tilde{\nu}$ = 3900, 3450, 3530, 3225, 3030, 2960, 2930, 2870, 2735, 2615, 2295, 2280, 2260, 2055, 1920, 1635, 1605, 1575, 1455, 1400, 1380, 1345, 1280, 1230, 1185, 1155, 1070, 1035, 970, 915, 880, 820, 730 $cm^{-1}$. HRMS (CI, $NH_4Cl$): $C_{12}H_{19}SO$ ($M + H^+$), calculated: 211.11566, found: 211.11560 (Δ = –0.3 ppm). Elemental analysis: calculated (%) for $C_{12}H_{18}SO$ (210.3 g/mol): C 68.52, H 8.63, S 15.24; found: C 68.53, H 8.74, S 15.26. The *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(1)$ = 8.02 min, $t_r(2)$ = 9.05 min. $[\alpha]_{365}^{20}$ = –1273.5, $[\alpha]_{436}^{20}$ = –634.2, $[\alpha]_{546}^{20}$ = –391.3, $[\alpha]_{578}^{20}$ = –273.6, $[\alpha]_{589}^{20}$ = –253.9 (*c* = 1.74 in EtOH; the respective sample had 96% *ee*).

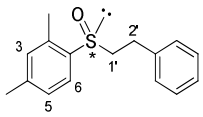
**Hexyl (2,4-Dimethylphenyl) Sulfoxide (24): (–)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (38.0 mg, 0.147 mmol) with $Hexyl_2Mg$ (1.4 M in $Et_2O$, 0.13 mL, 0.18 mmol, 1.2 equiv.) within 15 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 85:15, F. 27-36) delivered *rac*-**24** (17.0 mg, 48%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (50.0 mg, 0.193 mmol). After 30 min this delivered (–)-**24** (39.1 mg, 85%; 93% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$, sample contained 10% of the starting material): δ = 0.86-0.89 (m, 3 H, 6'-$H_3$), 1.26-1.51 (m, 6 H, 3'-, 4'-, and 5'-$H_2$), 1.61-1.84 (m, 2 H, 2'-$H_2$), 2.34 (s, Ar-$CH_3$), 2.36 (s, Ar-

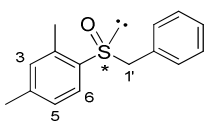
$CH_3$), AB signal ($\delta_A$ =2.70, $\delta_B$ = 2.75, $J_{A,B}$ = 13.1 Hz, A part additionally split by dd, $J_{1'\text{-}A,2'\text{-}A}$ = 7.2 Hz, $J_{1'\text{-}A,2'\text{-}B}$ = 5.5 Hz, 1'-$H_A$; B part additionally split by dd, $J_{1'\text{-}B,2\text{-}A}$ = 9.3 Hz, $J_{1'\text{-}B,2'\text{-}B}$ = 6.7 Hz, 1'-$H_B$), 7.01 ($m_c$, 1 H, 3-H), 7.22 ($m_c$, 1 H, 5-H), 7.77 ppm (d, $J_{6,5}$ = 7.9 Hz, 1 H, 6-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 14.0 (C-1'), 18.2 (Ar-$CH_3$), 21.3 (Ar-$CH_3$), 22.49, 22.55, 28.5, 31.5, 55.9 (C-1'), 124.1 (C-6), 128.0 (C-5), 131.5 (C-3), 134.4, 139.5, 140.7 ppm (C-1, C-2, and C-4). IR ($CDCl_3$): $\tilde{\nu}$ = 3470, 2955, 2930, 2860, 1605, 1570, 1480, 1465, 1455, 1400, 1380, 1275, 1230, 1160, 1060, 1035, 920, 820, 725 $cm^{-1}$. HRMS (CI, $NH_4Cl$): $C_{14}H_{23}SO$ ($M + H^+$), calculated: 239.14696, found: 239.14660 (Δ = –1.5 ppm). The *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, $\lambda_{detector}$ = 209 nm): $t_r(1)$ = 7.35 min, $t_r(2)$ = 9.76 min. $[\alpha]_{365}^{20}$ = –1098.5, $[\alpha]_{436}^{20}$ = –550.5, $[\alpha]_{546}^{20}$ = –282.0, $[\alpha]_{578}^{20}$ = –224.0, $[\alpha]_{589}^{20}$ = –225.5 (*c* = 0.20 in EtOH; the respective sample had 93% *ee*).

**(2,4-Dimethylphenyl) (2-Phenylethyl) Sulfoxide (25): (–)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (91.8 mg, 0.355 mmol) with 2-Phenylethyl$_2$Mg (0.98 M in $Et_2O$, 0.40 mL, 0.39 mmol, 1.1 equiv.) within 30 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 21-36) delivered *rac*-**25** (31.6 mg, 34%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (600 mg, 2.32 mmol).[48] After 3 h this delivered (–)-**25** (581 mg, 97%; 85% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, Ar-$CH_3$), 2.36 (s, 3 H, Ar-$CH_3$), 2.90-3.15 (m, 4 H, 1'- and 2'-$H_2$), 7.01 ($m_c$, 1 H, 1 × Ar-H), 7.17-7.25 (m, 4 H, 4 × Ar-H), 7.26-7.30 (m, 2 H, 2 × Ar-H), 7.80 ppm (d, $^3J_{6,5}$ = 8.0 Hz, 1 H, 6-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 18.1 (Ar-$CH_3$), 21.3 (Ar-$CH_3$), 28.6 (C-2'), 56.6 (C-1'), 124.2 (C-6), 126.7, 128.0, 128.6, 128.8, 131.6, 134.3, 138.9, 139.1, 141.2 ppm. IR ($CDCl_3$): $\tilde{\nu}$ = 3455, 3060, 3030, 2965, 2920, 2865, 2095, 1640, 1605, 1495, 1480, 1455, 1400, 1380, 1325, 1275, 1232, 1155, 1060, 1030, 965, 920, 875, 820, 750, 700 $cm^{-1}$. HRMS (CI, $NH_4Cl$): $C_{16}H_{19}SO$ ($M + H^+$), calculated: 259.11566, found: 259.11580 (Δ = +0.5 ppm). Elemental analysis: calculated (%) for $C_{16}H_{18}SO$ (258.4 g/mol): C 74.38, H 7.02, S 12.41; found: C 74.05, H 6.94, S 12.02. The *ee* was determined by chiral HPLC **(**Chiralpak AD-3, *n*-heptane/*i*-PrOH 95:5, 1 mL/min, $\lambda_{detector}$ = 206 nm): $t_r(1)$ = 8.17 min, $t_r(2)$ = 15.73 min. $[\alpha]_{365}^{20}$ = –885.7, $[\alpha]_{436}^{20}$ = –432.8, $[\alpha]_{546}^{20}$ = –216.2, $[\alpha]_{578}^{20}$ = –185.6, $[\alpha]_{589}^{20}$ = –175.0 (*c* = 0.90 in EtOH; the respective sample had 85% *ee*).

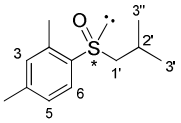
**Benzyl (2,4-Dimethylphenyl) Sulfoxide (26): (–)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] did not follow the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides*: At 0°C *n*-BuLi (2.1 M in hexane, 0.56 mL, 1.2 mmol, 6.1 equiv.) was added to a solution of *rac*-BINOL (167 mg, 0.583 mmol, 3.0 equiv.) in THF (1 mL). After 10 min $Bn_2Mg$ (0.40 M in $Et_2O$, 1.18 mL, 0.473 mmol, 2.4 equiv.) was added. After another 10 min a solution of bis(2,4-dimethylphenyl) sulfoxide (50.9 mg, 0.197 mmol) in THF (0.75 mL) was added. After stirring for 9 h at room temperature the reaction was quenched and the resulting mixture was worked up. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 30-42) delivered *rac*-**26** (38.0 mg, 79%) as a colorless solid (mp. = 65-66°C). The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis (2,4-dimethylphenyl) Sulfoxide (101 mg, 0.391 mmol), (S)-BINOL (3.0 equiv.), and $Bn_2Mg$ (2.4 equiv.). After 72 h this delivered 72 h (–)-**26** (58.3 mg, 61%; 2% *ee*) as a colorless solid (mp. = 65-66°C). $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 2.01 (s, 3 H, Ar-$CH_3$), 2.35 (s, 3 H, Ar-$CH_3$), AB signal ($\delta_A$ = 3.98, $\delta_B$ = 4.09, $J_{A,B}$ = 12.4 Hz, 2 H, 1'-H), 6.91 (d, $J_{3,5}$ = 0.6 Hz, 1 H, 3-H), 6.98-7.01 (m, 2 H, 2 × Ar-H), 7.15 (dd, $J_{5,6}$ = 6.3 Hz, $J_{5,3}$ = 0.6 Hz, 1 H, 5-H), 7.21-7.30 (m, 3 H, 3 × Ar-H superimposed by the singlet of $CHCl_3$), 7.61 ppm (d, $J_{6,5}$ = 7.0 Hz, 1 H, 6-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 18.0 (Ar-$CH_3$), 21.4 (Ar-$CH_3$), 62.7 (C-1'), 124.4 (C-6), 128.0 (C-5), 128.3, 128.5, 129.6, 130.5, 131.0 (C-3), 135.6, 138.4, 141.3 ppm. IR ($CDCl_3$): $\tilde{\nu}$ = 3895, 3545, 3255, 3030,2920, 2860, 2610, 2260, 1650, 1795, 1775, 1675, 1625, 1600, 1600, 1565, 1550, 1515, 1490, 1450, 1400, 1380, 1340, 1235, 1155, 1060, 1035, 925, 820, 765, 700 $cm^{-1}$. HRMS (CI, $NH_4Cl$): $C_{15}H_{17}SO$ ($M + H^+$), calculated: 245.10000, found: 245.10001 (Δ = ±0.0 ppm). Elemental analysis: calculated (%) for $C_{15}H_{16}SO$ (244.4 g/mol): C 73.73, H 6.60, S 13.12; found: C 73.52, H 6.64, S 12.82. The *ee* was determined by chi-

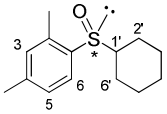
ral HPLC (Chiralcel OD-H, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(1)$ = 14.85 min, $t_r(2)$ = 20.81 min. $[\alpha]^{20}_{365}$ = –18.8, $[\alpha]^{20}_{436}$ = –9.0, $[\alpha]^{20}_{546}$ = –5.6, $[\alpha]^{20}_{578}$ = –6.5, $[\alpha]^{20}_{589}$ = –6.3 (*c* = 0.53 in EtOH; the respective sample had 2% *ee*).

**(2,4-Dimethylphenyl) Isobutyl Sulfoxide (27): (–)-Enantiomer and Racemic**[45]



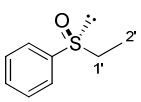
The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (100 mg, 0.387 mmol) with *i*-$Bu_2Mg$ (0.80 M in $Et_2O$, 0.59 mL, 0.47 mmol, 1.2 equiv.) within 5 h at 0°C. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 75:25, F. 12-20) delivered *rac*-**27** (54.2 mg, 67%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (601 mg, 2.33 mmol) and delivered after 3.5 h (–)-**27** (470 mg, 96%; 97% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.05 (d, $J_{3',2'}$ = 6.8 Hz, 3 H, 3'-$H_3$), 1.17 (d, $J_{3'',2'}$ = 6.5 Hz, 3 H, 3''-$H_3$), 2.25-2.35 (m, 1 H, 2'-H superimposed by the singlet of Ar-$CH_3$ at 2.33 ppm), 2.33 (s, 3 H, Ar-$CH_3$), 2.36 (s, 3 H, Ar-$CH_3$), AB signal ($\delta_A$ = 2.67, $\delta_B$ = 2.46, $J_{A,B}$ = 13.1 Hz, A part additionally split by d, $J_{1'-A,2'}$ = 9.7 Hz, 1'-$H_A$; B part additionally split by dd, $J_{1'-B,2'-A}$ = 4.3 Hz, $J_{1'-B,2'-B}$ = 0.4 Hz, 1'-$H_B$), 7.01 ($m_c$, 1 H, 3-H), 7.23 ($m_c$[49], $J_{5,6}$ = 7.9 Hz, 1 H, 5-H), 7.79 ppm (d, $J_{6',5'}$ = 8.0 Hz, 1 H, 6-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 18.1 (Ar-$CH_3$), 21.3 (Ar-$CH_3$) 23.0 (C-3'), 24.4 (C-3''), 66.3(C-1'), 123.8 (C-6), 128.2 (C-5), 131.5 (C-3), 134.1, 140.0, 140.9 ppm (C-1, C-2, and C-4). IR ($CDCl_3$): $\tilde{\nu}$ = 2910, 2510, 2960, 2925, 2870, 2735, 2195, 1775, 1605, 1460, 1380, 1330, 1230, 1170, 1075, 1030, 820, 695 $cm^{-1}$. HRMS (CI, $NH_4Cl$): $C_{12}H_{19}SO$ ($M + H^+$), calculated: 211.11566, found: 211.11570 (Δ = +0.2 ppm). The *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, $\lambda_{detector}$ = 209 nm): $t_r(1)$ = 6.95 min, $t_r(2)$ = 8.96 min. $[\alpha]^{20}_{365}$ = –1425.9, $[\alpha]^{20}_{436}$ = –720.6, $[\alpha]^{20}_{546}$ = –366.2, $[\alpha]^{20}_{578}$ = –314.5, $[\alpha]^{20}_{589}$ = –299.1 (*c* = 1.90 in EtOH; the respective sample had 97% *ee*).

**Cyclohexyl (2,4-Dimethylphenyl) Sulfoxide (28): (–)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (100 mg, 0.387 mmol) with (*c*-$C_6H_{11})_2Mg$ (0.38 M in $Et_2O$, 1.24 mL, 0.472 mmol, 1.2 equiv.) within 6 h at 0°C. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 70:30, F. 12-21) delivered *rac*-**28** (86.3 mg, 94%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2,4-dimethylphenyl) sulfoxide (100 mg, 0.387 mmol). After 3.5 h this delivered (–)-**28** (84.9 mg, 93%; 92% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.16-1.31 (m, 3 H), 1.43-1.57 (m, 2 H), 1.61-1.67 (m, 1 H), 1.76-1.88 (m, 4 H), 2.35 (s, 3 H, Ar-$CH_3$), 2.36 (s, 3 H, Ar-$CH_3$), 2.57 (dddd, $J_{1',2'-ax}$ = $J_{1',6'-ax}$ = 11.7 Hz, $J_{1',2'-eq}$ = $J_{1',6'-eq}$ = 3.4 Hz, 1 H, 1'-H), 7.01 ($m_c$, 1 H, 3-H), 7.20 ($m_c$[49], $J_{5,6}$ = 8.1 Hz, 1 H, 5-H), 7.70 ppm (d, $J_{6,5}$ = 8.1 Hz, 1 H, 6-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 18.7 (Ar-$CH_3$), 21.4 (Ar-$CH_3$), 24.0, 25.47, 25.57, 25.9, 26.8, 62.1 (C-1), 125.3 (C-6), 127.8 (C-5), 131.4 (C-3), 135.7, 137.7, 141.0 ppm (C-1, C-2, and C-4). IR ($CDCl_3$): $\tilde{\nu}$ = 3935, 3760, 3525, 3280, 3030, 3005, 2930, 2855, 2735, 2655, 2615, 2360, 2295, 2240, 2055, 1920, 1720, 1635, 1605, 1475, 1450, 1380, 1340, 1270, 1230, 1180, 1155, 1120, 1060, 1035, 920, 890, 820, 745, 710 $cm^{-1}$. HRMS (CI, $NH_4Cl$): $C_{14}H_{21}SO$ ($M + H^+$), calculated: 237.13131, found: 237.13150 (Δ = +0.8 ppm). The *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-heptane/*i*-PrOH 96:4, 1 mL/min, $\lambda_{detector}$ = 254 nm): $t_r(1)$ = 6.84 min, $t_r(2)$ = 9.98 min. $[\alpha]^{20}_{365}$ = –1168.7, $[\alpha]^{20}_{436}$ = –564.0, $[\alpha]^{20}_{546}$ = –275.7, $[\alpha]^{20}_{578}$ = –237.9, $[\alpha]^{20}_{589}$ = –226.2 (*c* = 1.10 in EtOH; the respective sample had 92% *ee*).

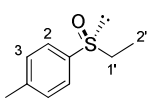
**Ethyl Phenyl Sulfoxide (29): (*S*)-(–)-Enantiomer**[33] **and Racemic**[45]



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using diphenyl sulfoxide (39.8 mg, 0.197 mmol) with $Et_2Mg$ (0.33 M in $Et_2O$, 0.33 mL, 0.11 mmol, 0.55 equiv.) within 30 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 55:45, F. 32-46) delivered *rac*-**29** (25.1 mg, 83%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using diphenyl sulfoxide (39.8 mg, 0.197 mmol). After 2 min this delivered (*S*)-(–)-**29** (23.3 mg, 77%; 71% *ee*) as a col-

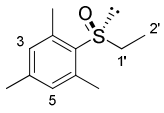
orless oil. After 30 min (*S*)-(−)-**29** was obtained in a lower yield with a lower *ee* (34%; 31% *ee*). $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 1.20 (dd, $J_{2',1'\text{-A}} = J_{2',1'\text{-B}}$ = 7.5 Hz, 3 H, 2'-$H_3$), AB signal ($\delta_A$ = 2.76, $\delta_B$ = 2.90, $J_{A,B}$ = 13.4 Hz, A part additionally split by q, $J_{1'\text{-A},2'}$ = 7.5 Hz, 1'-$H_A$; B part additionally split by q, $J_{1'\text{-B},2'}$ = 7.4 Hz, 1'-$H_B$), 7.46-7.55 (m, 3 H, 3 × Ar-H), 7.59-7.64 ppm (m, 2 H, 2 × Ar-H). The preceding data are consistent with those reported in the literature.[50] The *ee* was determined by chiral HPLC (Chiralcel OJ-H, *n*-heptane/EtOH 95:5, 1 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(R)$ = 11.86 min, $t_r(S)$ = 12.76 min. $[\alpha]_{365}^{20}$ = –354.0, $[\alpha]_{436}^{20}$ = –179.5, $[\alpha]_{546}^{20}$ = –92.5, $[\alpha]_{578}^{20}$ = –78.0, $[\alpha]_{589}^{20}$ = –73.5 (*c* = 0.20 in EtOH; the respective sample had 31% *ee*); Lit.[51]: $[\alpha]_{589}^{20}$ = –219.6 [*c* = 1.4 in EtOH, a sample of the (*S*)-enantiomer with 99% *ee*]. The absolute configuration was determined by comparing the sense of the optical rotation with literature data.[51]

**Ethyl (*p*-Tolyl) Sulfoxide (30): (*S*)-(−)-Enantiomer[33] and Racemic[45]**



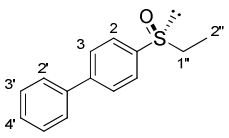
The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(*p*-tolyl) sulfoxide (45.4 mg, 0.197 mmol) with $Et_2Mg$ (0.16 M in $Et_2O$, 1.35 ml, 0.216 mmol, 1.1 equiv.) within 1.25 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 50:50, F. 27-40) delivered *rac*-**30** (7.0 mg, 21%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(*p*-tolyl) sulfoxide (45.3 mg, 0.197 mmol). After 10 s this delivered (*S*)-(−)-**30** (29.8 mg, 90%; 69% *ee*) as a colorless oil. After 30 min (*S*)-(−)-**30** was obtained in a lower yield with a higher *ee* (39%; 94% *ee*). $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 1.19 (dd, $J_{2',1'\text{-A}} = J_{2',1'\text{-B}}$ = 7.4 Hz, 3 H, 2'-$H_3$), AB signal ($\delta_A$ = 2.75, $\delta_B$ = 2.87, $J_{A,B}$ = 14.8 Hz, A part additionally split by q, $J_{1'\text{-A},2'}$ = 7.3 Hz, 1'-$H_A$; B part additionally split by q, $J_{1'\text{-B},2'}$ = 7.4 Hz, 1'-$H_B$), AA'BB' signal with signal centers at $\delta_A$ = 7.32 and $\delta_B$ = 7.50 ppm (4 H, 2 × 2-H and 2 × 3-H). The preceding data are consistent with those reported in the literature.[50] The *ee* was determined by chiral HPLC (Chiralcel OJ-H, *n*-heptane/EtOH 98:2, 1 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(R)$ = 17.63 min, $t_r(S)$ = 20.92 min. $[\alpha]_{365}^{20}$ = –723.5, $[\alpha]_{436}^{20}$ = –361.6, $[\alpha]_{546}^{20}$ = –183.6, $[\alpha]_{578}^{20}$ = –157.3, $[\alpha]_{589}^{20}$ = –148.5 (*c* = 0.55 in EtOH; the respective sample had 69% *ee* was used); Lit.[50]: $[\alpha]_{589}^{20}$ = –247 [*c* = 2.60 in $CHCl_3$; the respective sample had 94% *ee*]. The absolute configuration was determined by comparing the sense of the optical rotation with literature data.[50]

**Ethyl (2,4,5-Trimethylphenyl) Sulfoxide (31): (*S*)-(−)-Enantiomer and Racemic[45]**



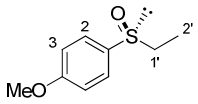
The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(2,4,6-trimethylphenyl) sulfoxide (56.5 mg, 0.197 mmol) with $Et_2Mg$ (0.42 M in $Et_2O$, 0.52 mL, 0.22 mmol, 1.1 equiv.) within 2 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 60:40, F. 24-30) delivered *rac*-**31** (16.2 mg, 42%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2,4,6-trimethylphenyl) sulfoxide (56.4 mg, 0.197 mmol). After 1 h this delivered (*S*)-(−)-**31** (23.2 mg, 60%; 77% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$, the sample contained a small amount of inseparateable impurity with signals at 1.23, 2.26, 2.68-2.75, 2.80-2.87, 6.97 and 7.60 ppm): δ = 1.28 (dd, $J_{2',1'\text{-A}} = J_{2',1\text{-B}}$ = 7.5 Hz, 3 H, 2'-$H_3$), 2.28 (s, 3 H, Ar-$CH_3$), 2.54 (s, 6 H, 2 × Ar-$CH_3$), AB signal ($\delta_A$ = 2.95, $\delta_B$ = 3.21, $J_{A,B}$ = 12.9 Hz, A part additionally split by q, $J_{1'\text{-A},2'}$ = 7.6 Hz, 1'-$H_A$; B part additionally split by q, $J_{1'\text{-B},2'}$ = 7.5 Hz, 1'-$H_B$), 6.86 ppm (s, 2 H, 2 × Ar-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 8.6 (C-1'), 19.5 (2 × Ar-$CH_3$), 21.2 (Ar-$CH_3$), 46.2 (C-2'), 131.0 (C-3 and C-5), 134.5, 138.6, 141.1 ppm (C-1, C-2, C-4, and C-6). IR ($CDCl_3$): $\tilde{\nu}$ = 3290, 2970, 2925, 2855, 2450, 2045, 1600, 1570, 1455, 1380, 1295, 1250, 1070, 1045, 1015, 965, 850, 775, 715, 665 $cm^{-1}$. HRMS (CI, $NH_4Cl$): $C_{11}H_{17}SO$ ($M + H^+$), calculated: 197.10001, found: 197.10020 (Δ = +1.0 ppm). The *ee* was determined by chiral HPLC (Chiralcel OD-3, *n*-heptane/*i*-PrOH 98:2, 1.0 mL/min, $\lambda_{detector}$ = 205 nm): $t_r(R)$ = 11.91 min, $t_r(S)$ = 20.69 min. $[\alpha]_{365}^{20}$ = –1256.8, $[\alpha]_{436}^{20}$ = –552.7, $[\alpha]_{546}^{20}$ = –255.5 $[\alpha]_{578}^{20}$ = –219.5, $[\alpha]_{589}^{20}$ = –210.0 (*c* = 0.22 in EtOH; the respective sample had 77% *ee*). The absolute configuration was assigned by chemical correlation (cf. Supporting Information).

**Ethyl (4-Phenylphenyl) Sulfoxide (32): (*S*)-(−)-Enantiomer[33] and Racemic[45]**



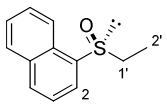
The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(4-phenylphenyl) sulfoxide (74.1 mg, 0.209 mmol) with $Et_2Mg$ (0.33 M in $Et_2O$, 0.35 mL, 0.116 mmol, 0.55 equiv.) within 30 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 52:48, F. 26-42) delivered *rac*-**32** (37.3 mg, 77%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(4-phenylphenyl) sulfoxide (69.8 mg, 0.197 mmol). After 10 s this delivered (*S*)-(−)-**32** (37.4 mg, 82%; 70% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.24 (dd, $J_{2'',1''\text{-A}} = J_{2'',1''\text{-B}}$ = 7.5 Hz, 3 H, 2''-$H_3$), AB signal ($\delta_A$ = 2.82, $\delta_B$ = 2.94, $J_{A,B}$ = 13.3 Hz, A part additionally split by q, $J_{1''\text{-A},2''}$ = 7.3 Hz, 1''-$H_A$; B part additionally split by q, $J_{1''\text{-B},2''}$ = 7.5 Hz, 1''-$H_B$), 7.37-7.42 (m, 1 H, 4'-H), 7.45-7.49 (m, 2 H, 2 × 2'-H*), 7.59-7.62 (m, 2 H, 2 × 3'-H*), AA'BB' signal with signal centers at $\delta_A$ = 7.67 and $\delta_B$ = 7.74 ppm (4 H, 2 × 2-H and 2 × 3-H); *assignments interchangeable. $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 6.2 (C-2''), 50.5 (C-1''), 124.8 (C-2), 127.3 (C-2'*), 127.9 (C-3), 128.2 (C-4'), 129.1 (C-3'*), 139.9, 142.2, 144.1 ppm (C-1, C-4, and C-1'); *assignments interchangeable. IR ($CDCl_3$): $\tilde{\nu}$ = 3520, 3055, 3030, 3000, 2920, 2850, 2455, 2065, 1660, 1595, 1560, 1480, 1390, 1265, 1110, 1090, 1045, 1025, 965, 915, 935, 835, 760, 720, 695, 655 cm$^{-1}$. HRMS (CI, $NH_4Cl$): $C_{14}H_{15}SO$ ($M + H^+$), calculated: 231.08436, found: 231.08460 (Δ = +1.0 ppm). Elemental analysis: calculated (%) for $C_{14}H_{14}SO$ (230.3 g/mol): C 73.01, H 6.13, S 13.92; found: C 72.74, H 6.08, S 13.73. The *ee* was determined by chiral HPLC (Chiralcel OJ-H, *n*-heptane/EtOH 95:5, 1.0 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(R)$ = 27.54 min, $t_r(S)$ = 29.81 min. $[\alpha]^{20}_{365}$ = –834.0, $[\alpha]^{20}_{436}$ = –374.6, $[\alpha]^{20}_{546}$ = –178.7, $[\alpha]^{20}_{578}$ = –153.0, $[\alpha]^{20}_{589}$ = –145.4 (*c* = 1.4 in EtOH; the respective sample had 70% *ee*). The absolute configuration was assigned by chemical correlation (cf. Supporting Information).

**Ethyl (4-Methoxyphenyl) Sulfoxide (33): (*S*)-(−)-Enantiomer and Racemic[45]**



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(4-methoxyphenyl) sulfoxide (51.8 mg, 0.197 mmol) with $Et_2Mg$ (0.16 M in $Et_2O$, 1.35 mL, 0.216 mmol, 1.1 equiv.) within 1.25 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 40:60, F. 21-36) delivered *rac*-**33** (11.5 mg, 32%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(4-methoxyphenyl) sulfoxide (51.7 mg, 0.196 mmol). After 15 min this delivered (*S*)-(−)-**33** (28.0 mg, 77%; 81% *ee*) as a colorless oil. $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 1.18 (dd, $J_{2',1'\text{-A}} = J_{2',1'\text{-B}}$ = 7.5 Hz, 3 H, 2'-$H_3$), AB signal ($\delta_A$ = 2.84, $\delta_B$ = 2.77, $J_{A,B}$ = 13.1 Hz, A part additionally split q, $J_{1'\text{-A},2'}$ = 7.4 Hz, 1'-$H_A$; B part additionally split by q, $J_{1'\text{-B},2'}$ = 7.5 Hz, 1'-$H_B$), 3.86 (s, 3 H, O-$CH_3$), AA'BB' signal with signal centers at $\delta_A$ = 7.03 and $\delta_B$ = 7.55 ppm (4 H, 2 × 2-H and 2 × 3-H). The preceding data are consistent with those reported in the literature.[52] The *ee* was determined by chiral HPLC (Chiralcel OD-3, *n*-heptane/*i*-PrOH 98:2, 1.0 mL/min, $\lambda_{detector}$ = 230 nm): $t_r(R)$ = 20.03 min, $t_r(S)$ = 22.32 min. $[\alpha]^{20}_{365}$ = –819.1, $[\alpha]^{20}_{436}$ = –396.6, $[\alpha]^{20}_{546}$ = –196.0, $[\alpha]^{20}_{578}$ = –167.6, $[\alpha]^{20}_{589}$ = –161.8 (*c* = 0.82 in EtOH; the respective sample had 81% *ee*); Lit.[52]: $[\alpha]^{20}_{589}$ = +130.0 [*c* = 1.4 in MeOH for a sample of the (*R*)-enantiomer. The *ee* of this sample is not stated in ref. 52]. The absolute configuration was determined by comparing the sense of the optical rotation with literature data.[52]

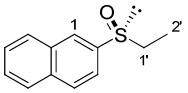
**Ethyl (1-Naphthyl) Sulfoxide (34): (*S*)-(−)-Enantiomer and Racemic[45]**



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using di(1-naphthyl) sulfoxide (59.8 mg, 0.198 mmol) with $Et_2Mg$ (0.33 M in $Et_2O$, 0.33 mL, 0.109 mmol, 0.55 equiv.) within 1.5 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 55:45, F. 14-24) delivered *rac*-**34** (17.0 mg, 42%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using di(1-naphthyl) sulfoxide (59.6 mg, 0.197 mmol). After 5 min this delivered (*S*)-(−)-**34** (27.0 mg, 67%; 93% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.22 (dd, $J_{2',1'\text{-A}} = J_{2',1'\text{-B}}$ = 7.3 Hz, 3 H, 2'-$H_3$), AB signal ($\delta_A$ = 2.85, $\delta_B$ = 3.12, $J_{A,B}$ = 13.6 Hz, A part additionally split q, $J_{1'\text{-A},2'}$ = 7.5 Hz, 1'-$H_A$; B part additionally split by q, $J_{1'\text{-B},2'}$ = 7.6 Hz, 1'-$H_B$), 7.55-

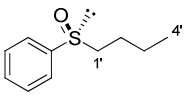
7.61 (m, 2 H, 2 × Ar-H), 7.67 (dd, $^3J$ = 8.2 Hz, $^3J$ = 7.0 Hz, 1 H, 1 × Ar-H), 7.93-7.99 (m, 3 H, 3 × Ar-H), 8.11 ppm (dd, $^3J$ = 7.2 Hz, $^4J$ = 1.2 Hz, 1 H, 1 × Ar-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 6.2 (C-2‘), 48.8 (C-1‘), 121.7, 123.6, 125.6, 126.7, 127.3, 129.1, 129.2, 131.2, 133.6, 139.1 ppm. IR ($CDCl_3$): $\tilde{\nu}$ = 3470, 3055, 2955, 2925, 2870, 2850, 2425, 2045, 1645, 1590, 1505, 1455, 1405, 1370, 1345, 1260, 1190, 1140, 1065, 1055, 1045, 1020, 965, 920, 865, 805, 775, 740, 665 cm$^{-1}$. HRMS (CI, $NH_4Cl$): $C_{12}H_{13}SO$ ($M + H^+$), calculated: 205.06871, found: 205.06860 (Δ = –0.5 ppm). The *ee* was determined by chiral HPLC (Chiralcel OJ-H, *n*-heptane/*i*-PrOH 80:20, 0.8 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(R)$ = 9.17 min, $t_r(S)$ = 10.45 min. $[\alpha]^{20}_{365}$ = –1098.4, $[\alpha]^{20}_{436}$ = –512.3, $[\alpha]^{20}_{546}$ = –277.6, $[\alpha]^{20}_{578}$ = –221.8, $[\alpha]^{20}_{589}$ = –248.7 (*c* = 1.40 in EtOH; the respective sample had 93% *ee*). The absolute configuration was assigned by chemical correlation (cf. Supporting Information).

**Ethyl (2-Naphthyl) Sulfoxide (35): (*S*)-(–)-Enantiomer and Racemic**[45]



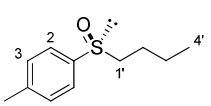

The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using di(2-naphthyl) sulfoxide (59.6 mg, 0.197 mmol) with $Et_2Mg$ (0.33 M in $Et_2O$, 0.33 mL, 0.109 mmol, 0.55 equiv.) within 1.5 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 55:45, F. 42-50) delivered *rac*-**35** (30.0 mg, 75%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using di(2-naphthyl) sulfoxide (59.6 mg, 0.197 mmol). After 5 min this delivered (*S*)-(–)-**35** (25.1 mg, 62%; 66% *ee*) as a colorless oil. $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 1.22 (dd, $J_{2',1'\text{-A}} = J_{2',1'\text{-B}}$ = 7.4 Hz, 3 H, 2‘-$H_3$), AB signal ($\delta_A$ = 2.99, $\delta_B$ = 2.84, $J_{A,B}$ = 13.4 Hz, A part additionally split by q, $J_{1'\text{-A},2'}$ = 7.3 Hz, 1‘-$H_A$; B part additionally split by q, $J_{1'\text{-B},2'}$ = 7.4 Hz, 1‘-$H_B$), 7.55-7.62 (m, 3 H, 3 × Ar-H), 7.90-7.99 (m, 3 H, 3 × Ar-H), 8.18x ppm (br. s, 1 H, 1-H). The preceding data are consistent with those reported in the literature.[53] The *ee* was determined by chiral **HPLC** (Chiralcel OJ-H, *n*-heptane/EtOH 95:5, 1 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(R)$ = 17.24 min, $t_r(S)$ = 18.35 min. $[\alpha]^{20}_{365}$ = –501.0, $[\alpha]^{20}_{436}$ = –244.7, $[\alpha]^{20}_{546}$ = –123.9, $[\alpha]^{20}_{578}$ = –106.3, $[\alpha]^{20}_{589}$ = –99.8 (*c* = 0.49 in EtOH; the respective sample had 66% *ee*); Lit.[51]: $[\alpha]^{20}_{589}$ = –180.5 [*c* = 1.3 in acetone; the respective sample of the (*S*)-enantiomer had >99% *ee*]; The absolute configuration was determined by comparing the sense of the optical rotation with literature data.[51]

**Butyl Phenyl Sulfoxide (36): (*S*)-(–)-Enantiomer and Racemic**[45]




The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using diphenyl sulfoxide (39.8 mg, 0.197 mmol) with $Bu_2Mg$ (0.75 M in $Et_2O$, 0.14 mL, 0.105 mmol, 0.53 equiv.) within 30 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, 28-40) delivered *rac*-**36** (24.1 mg, 67%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using diphenyl sulfoxide (39.7 mg, 0.196 mmol). After 2 min this delivered (*S*)-(–)-**36** (27.0 mg, 75%; 46% *ee*) as a colorless oil. $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 0.92 (t, $J_{4',3'}$ = 7.2 Hz, 3 H, 4‘-$H_3$), 1.35-1.82 (m, 4 H, 2‘- and 3‘-$H_2$), AB signal ($\delta_A$ = 2.79, $\delta_B$ = 2.80, $J_{A,B}$ = 7.1 Hz, 2 H, 1’-$H_A$ and 1‘-$H_B$), 7.48-7.55 (m, 3 H, 3 × Ar-H), 7.60-7.64 ppm (m, 2 H, 2 × Ar-H). The preceding data are consistent with those reported in the literature.[53] The *ee* was determined by chiral HPLC (Chiralcel OJ-H, *n*-heptane/EtOH 98:2, 1 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(R)$ = 11.72 min, $t_r(S)$ = 12.45 min. $[\alpha]^{20}_{365}$ = –498.7, $[\alpha]^{20}_{436}$ = –254.5, $[\alpha]^{20}_{546}$ = –131.6, $[\alpha]^{20}_{578}$ = –113.9, $[\alpha]^{20}_{589}$ = –107.2 (*c* = 0.86 in EtOH; the respective sample had 46% *ee*); Lit.[53]: $[\alpha]^{20}_{589}$ = +150 [*c* = 0.1 in $CH_2Cl_2$, a sample of the (*R*)-enantiomer with 75% *ee*]. The absolute configuration was determined by comparing the sense of the optical rotation with literature data.[53]

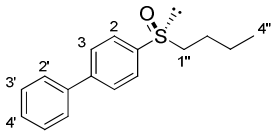
**Butyl (*p*-Tolyl) Sulfoxide (37): (*S*)-(–)-Enantiomer and Racemic**[45]




The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(*p*-tolyl) sulfoxide (45.6 mg, 0.198 mmol) with $Bu_2Mg$ (0.75 M in $Et_2O$, 0.14 mL, 0.105 mmol, 0.53 equiv.) within 30 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 60:40, F. 12-18) delivered *rac*-**37** (23.8 mg, 62%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagne-*

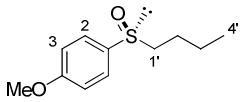
*sium Compounds by Symmetric Diaryl Sulfoxides* using bis(*p*-tolyl) sulfoxide (45.5 mg, 0.198 mmol). After 10 s this delivered (*S*)-(−)-**37** (31.8 mg, 82%; 48% *ee*) as a colorless oil. $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 0.92 (t, $J_{4',3'}$ = 7.2 Hz, 3 H, 4'-$H_3$), 1.34-1.51 (m, 2 H, 3'-$H_2$), 1.52-1.74 (m, 2 H, 2'-$H_2$), 2.42 (s, 3 H, Ar-$CH_3$), 2.70-2.86 (m , 2 H, 1'-$H_2$), AA'BB' signal with signal centers at $\delta_A$ = 7.32 and $\delta_B$ = 7.51 ppm (2 × 2-H and 2 × 3-H). The preceding data are consistent with those reported in the literature.[54] The *ee* was determined by chiral HPLC (Chiralcel OD-3, *n*-heptane/*i*-PrOH 98:2, 1 mL/min, $\lambda_{detector}$ = 205 nm): $t_r(R)$ = 12.21 min, $t_r(S)$ = 15.35 min. $[\alpha]^{20}_{365}$ = –507.6, $[\alpha]^{20}_{436}$ = –257.8, $[\alpha]^{20}_{546}$ = –131.6, $[\alpha]^{20}_{578}$ = –113.5, $[\alpha]^{20}_{589}$ = –108.1 (*c* = 0.37 in EtOH; the respective sample had 48% *ee*); Lit.[55]: $[\alpha]^{20}_{589}$ = –162.3 (*c* = 3.2 in acetone, a sample of the (*S*)-enantiomer with 91% *ee*); The absolute configuration was determined by comparing the sense of the optical rotation with literature data.[55]

**Butyl (4-Phenylphenyl) Sulfoxide (39): (*S*)-(–)-Enantiomer and Racemic**[45]



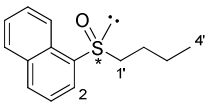

The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(4-phenylphenyl) sulfoxide (69.9 mg, 0.197 mmol) with $Bu_2Mg$ (0.75 M in $Et_2O$, 0.14 mL, 0.11 mmol, 0.55 equiv.) within 30 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 27-44) delivered *rac*-**39** (27.3 mg, 54%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(4-phenylphenyl) sulfoxide (83.1 mg, 0.234 mmol). After 10 s this delivered (*S*)-(−)-**39** (43.5 mg, 72%; 52% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 0.94 (t, $J_{4'',3''}$ = 7.3 Hz, 3 H, 4''-$H_3$), 1.37-1.56 (m, 2 H, 3''-$H_2$), 1.58-1.72 (m, 1 H, 2''-$H_A$), 1.73-1.80 (m, 1 H, 2''-$H_B$), 2.78-2.89 (m, 2 H, 1''-$H_2$), 7.37-7.42 (m, 1 H, 4'-H), 7.45-7.49 (m, 2 H, 2 × 2'-H*), 7.59-7.62 (m, 2 H, 2 × 3'-H*), AA'BB' signal with signal centers at $\delta_A$ = 7.68 and $\delta_B$ = 7.74 ppm (4 H, 2 × 2-H and 2 × 3-H); *assignments interchangeable. $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 13.8 (C-4''), 22.0 (C-3''), 24.3 (C-2''), 57.2 (C-1''), 124.7 (C-2), 127.3 (C-2'*), 128.0 (C-3), 128.2 (C-4'), 129.1 (C-3'*), 139.9, 142.9, 144.1 ppm (C-1, C-4, and C-1'); *assignments interchangeable. IR ($CDCl_3$): $\tilde{\nu}$ = 3650, 3240, 3055, 2955, 2930, 2870, 2395, 1950, 1560, 1480, 1465, 1450, 1395, 1165, 1095, 1075, 1030, 1015, 105, 915, 835, 750, 715, 690, 655 $cm^{-1}$. HRMS (CI, $NH_4Cl$): $C_{16}H_{19}SO$ ($M + H^+$), calculated: 259.11566, found: 259.11590 (Δ = +0.9 ppm). Elemental analysis: calculated (%) for $C_{16}H_{18}SO$ (258.4 g/mol): C 73.38, H 7.02, S 12.41; found: C 74.23, H 6.93, S 12.49. The *ee* was determined by chiral HPLC (Chiralcel OD-3, *n*-heptane/*i*-PrOH 96:4, 1.0 mL/min, $\lambda_{detector}$ = 206 nm): $t_r(R)$ = 12.47 min, $t_r(S)$ = 13.65 min. $[\alpha]^{20}_{365}$ = –561.3, $[\alpha]^{20}_{436}$ = –255.5, $[\alpha]^{20}_{546}$ = –124.7, $[\alpha]^{20}_{578}$ = –106.6, $[\alpha]^{20}_{589}$ = –100.9 (*c* = 0.47 in EtOH; the respective sample had 52% *ee*). The absolute configuration was assigned by chemical correlation (cf. Supporting Information).

**Butyl (4-Methoxyphenyl) Sulfoxide (40): (*S*)-(–)-Enantiomer and Racemic**[45]



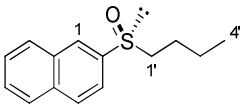

The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(4-methoxyphenyl) sulfoxide (51.6 mg, 0.196 mmol) with $Bu_2Mg$ (0.75 M in $Et_2O$, 0.29 mL, 0.22 mmol, 1.1 equiv.) within 1 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 55:45, F. 24-34) delivered *rac*-**40** (15.6 mg, 37%) as a colorless oil. The asymmetric synthesis followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(4-methoxyphenyl) sulfoxide (51.8 mg, 0.197 mmol). After 15 min this delivered (*S*)-(−)-**40** (34.6 mg, 83%; 63% *ee*) as a colorless oil. $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 0.92 (t, $J_{4',3'}$ = 7.2 Hz, 3 H, 4'-$H_3$), 1.34-1.50 (m, 2 H, 3'-$H_2$), 1.51-1.75 (m, 2 H, 2'-$H_2$), 2.69-2.86 (m, 1 H, 1'-$H_2$), 3.86 (s, 3 H, O-$CH_3$), AA'BB' signal with signal centers at $\delta_A$ = 7.02 and $\delta_B$ = 7.56 ppm (4 H, 2 × 2-H and 2 × 3-H). The preceding data are consistent with those reported in the literature.[56] The *ee* was determined by chiral HPLC (Chiralcel OJ-H, *n*-heptane/EtOH 98:2, 1 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(S)$ = 19.94 min, $t_r(R)$ = 21.38 min. $[\alpha]^{20}_{365}$ = –468.4, $[\alpha]^{20}_{436}$ = –238.9, $[\alpha]^{20}_{546}$ = –126.6, $[\alpha]^{20}_{578}$ = –117.7, $[\alpha]^{20}_{589}$ = –114.7 (*c* = 0.64 in EtOH; the respective sample had 63% *ee*). The absolute configuration was assigned by chemical correlation (cf. Supporting Information).

**Butyl (1-Naphthyl) Sulfoxide (41): (–)-Enantiomer and Racemic**[45]



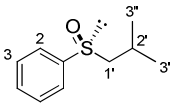
The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using di(1-naphthyl) sulfoxide (57.9 mg, 0.192 mmol) with $Bu_2Mg$ (0.75 M in $Et_2O$, 0.14 mL, 0.11 mmol, 0.57 equiv.) within 35 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 20-30) delivered *rac*-**41** (25.5 mg, 56%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using di(1-naphthyl) sulfoxide (59.4 mg, 0.197 mmol). After 2 min this delivered (−)-**41** (41.5 mg, 91%; 90% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 0.91 (t, $J_{4',3'}$ = 7.3 Hz, 3 H, 4'-$H_3$), 1.34-1.56 (m, 2 H, 3'-$H_2$), 1.59-1.69 (m, 1 H, 2'-$H_A$), 1.81-1.91 (m, 1 H, 2'-$H_B$), AB signal ($\delta_A$ = 2.83, $\delta_B$ = 3.03, $J_{A,B}$ = 13.2 Hz, A part additionally split by dd, $J_{1'-A,2'-B}$ = 9.5 Hz, $J_{1'-A,2'-A}$ = 4.9 Hz, 1'-$H_A$; B part additionally split by dd, $J_{1'-B,2'-B}$ = 10.2 Hz, $J_{1'-B,2'-A}$ = 6.8 Hz, 1'-$H_B$), 7.55-7.61 (m, 2 H, 2 × Ar-H), 7.67 (dd, $^3J$ = 6.9 Hz, $^3J$ = 5.9 Hz, 1 H, 1 × Ar-H), 7.94-7.98 (m, 3 H, 3 × Ar-H), 8.13 ppm (dd, $^3J$ = 7.2 Hz, $^4J$ = 1.2 Hz, 1 H, 1 × Ar-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 13.8 (C-4'), 22.0 (C-3'), 24.6 (C-2'), 55.9 (C-1'), 121.6, 123.2, 125.7, 126.7, 127.2, 129.0, 129.2, 131.1, 133.6, 139.9 ppm. IR ($CDCl_3$): $\tilde{\nu}$ = 3535, 3055, 2930, 2925, 2870, 2405, 2045, 1645, 1590, 1505, 1465, 1400, 1380, 1345, 1260, 1215, 1190, 1140, 1100, 1070, 1040, 965, 800, 770, 740, 665 cm$^{-1}$. HRMS (CI, $NH_4Cl$): $C_{14}H_{17}SO$ ($M + H^+$), calculated: 233.10001, found: 233.10000 (Δ = –0.1 ppm). Elemental analysis: calculated (%) for $C_{14}H_{16}SO$ (232.3 g/mol): C 72.37, H 6.94, S 13.80; found: C 72.00, H 6.90, S 13.83. The *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-heptane/*i*-PrOH 95:5, 1 mL/min, $\lambda_{detector}$ = 209 nm): $t_r(1)$ = 17.39 min, $t_r(2)$ = 24.68 min. $[\alpha]^{20}_{365}$ = –2378.2, $[\alpha]^{20}_{436}$ = –1147.8, $[\alpha]^{20}_{546}$ = –573.0, $[\alpha]^{20}_{578}$ = –491.5, $[\alpha]^{20}_{589}$ = –466.8 (*c* = 1.28 in EtOH; the respective sample had 90% *ee*).

**Butyl (2-Naphthyl) Sulfoxide (42): (*S*)-(−)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using di(2-naphthyl) sulfoxide (61.0 mg, 0.202 mmol) with $Bu_2Mg$ (0.75 M in $Et_2O$, 0.15 mL, 0.11 mmol, 0.55 equiv.) within 35 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 24-37) delivered *rac*-**42** (20.1 mg, 47%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using di(2-naphthyl) sulfoxide (59.6 mg, 0.197 mmol). After 2 min this delivered (*S*)-(−)-**42** (37.2 mg, 81%; 30% *ee*) as a colorless oil**.** $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 0.92 (t, $J_{4',3'}$ = 7.1 Hz, 3 H, 4'-$H_3$), 1.36-1.55 (m, 2 H, 3'-$H_2$), 1.57-1.67 (m, 1 H, 2'-$H_A$), 1.71-1.86 (m, 1 H, 2'-$H_B$), 2.85-2.91 (m, 2 H, 1'-$H_2$), 7.56-7.62 (m, 3 H, 3 × Ar-H), 7.89-7.99 (m, 3 H, 3 × Ar-H), 8.19 ppm (br. s, 1 H, 1-H). The preceding data are consistent with those reported in the literature.[53] The *ee* was determined by chiral HPLC (Chiralcel OD-3, *n*-heptane/*i*-PrOH 98:2, 1 mL/min, $\lambda_{detector}$ = 224 nm): $t_r(R)$ = 13.40 min, $t_r(S)$ = 15.81 min. $[\alpha]^{20}_{365}$ = –288.0, $[\alpha]^{20}_{436}$ = –139.8, $[\alpha]^{20}_{546}$ = –71.5, $[\alpha]^{20}_{578}$ = –61.3, $[\alpha]^{20}_{589}$ = –58.0 (*c* = 0.61 in EtOH; the respective sample had 30% *ee*); Lit.[53]: $[\alpha]^{20}_{589}$ = +188 [*c* = 0.12 in $CH_2Cl_2$, a sample of the (*R*)-enantiomer with 67% *ee*]. The absolute configuration was determined by comparing the sense of the optical rotation with literature data.[53]

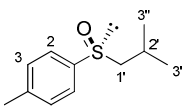
**Isobutyl Phenyl Sulfoxide (43): (*S*)-(−)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using diphenyl sulfoxide (70.0 mg, 0.346 mmol) with *i*-$Bu_2Mg$ (0.80 M in $Et_2O$, 0.24 mL, 0.19 mmol, 0.55 equiv.) within 1.5 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 27-39) delivered *rac*-**43** (46.6 mg, 74%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using diphenyl sulfoxide (80.5 mg, 0.393 mmol). After 1 h this delivered (*S*)-(−)-**43** (54.7 mg, 76%; 61% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.06 (d, $J_{3',2'}$ = 6.8 Hz, 3 H, 3'-$H_3$), 1.16 (d, $J_{3'',2'}$ = 6.5 Hz, 3 H, 3''-$CH_3$), 2.24 ($m_c$, 1 H, 2'-H), 2.47 (dd, $J_{1'-A,1'-B}$ = 13.0 Hz, $J_{1'-A,2'}$ = 9.2 Hz, 1 H, 1'-$H_A$), 2.81 (dd, $J_{1'-B,1'-A}$ = 13.0 Hz, $J_{1'-B,2'}$ = 5.0 Hz, 1 H, 1'-$H_B$), 7.45-7.54 (m, 3 H, 3 × Ar-H), 7.61-7.65 ppm (m, 2 H, 2 × Ar-H). The preceding data are consistent with those reported in the literature.[57] The *ee* was determined by chiral HPLC (Chiralcel OD-3, *n*-heptane/*i*-PrOH 95:5, 1 mL/min, $\lambda_{detector}$ = 209 nm): $t_r(R)$ = 6.57 min, $t_r(S)$ = 8.23 min. $[\alpha]^{20}_{365}$ = –721.2, $[\alpha]^{20}_{436}$ = –374.3, $[\alpha]^{20}_{546}$ = –194.2, $[\alpha]^{20}_{578}$ = –167.2, $[\alpha]^{20}_{589}$ = –159.8 (*c* = 1.45 in EtOH; the respective sample had 61% *ee*);

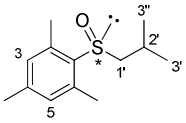
Lit.[57]: $[\alpha]_{589}^{20}$ = +129.0 [*c* = 1.0 in $CHCl_3$, a sample of the (*R*)-enantiomer with 48% *ee*]. The absolute configuration was determined by comparing the sense of the optical rotation with literature data.[57]

**Isobutyl (*p*-Tolyl) Sulfoxide (44): (*S*)-(–)-Enantiomer and Racemic**[45]



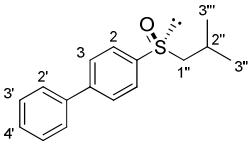
The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(*p*-tolyl) sulfoxide (101 mg, 0.439 mmol) with *i*-$Bu_2Mg$ (0.80 M in $Et_2O$, 0.61 mL, 0.49 mmol, 1.1 equiv.) within 1.5 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 37-49) delivered *rac*-**44** (74.3 mg, 86%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(*p*-tolyl) sulfoxide (45.3 mg, 0.197 mmol). After 1 h this delivered (*S*)-(–)-**44** (32.9 mg, 85%; 58% *ee*) as a colorless oil. $^1$H-NMR (300.1 MHz, $CDCl_3$): δ = 1.05 (d, $J_{3',2'}$ = 5.9 Hz, 3 H, 3'-$H_3$), 1.14 (d, $J_{3'',2'}$ = 6.3 Hz, 3 H, 3''-$H_3$), 2.13-2.27 (m, 1 H, 2'-H), 2.41 (s, 3 H, Ar-$CH_3$ superimposed by AB signal), AB signal ($\delta_A$ = 2.44, $\delta_B$ = 2.45, $J_{A,B}$ = 8.4 Hz, 2 H, 1'-$CH_2$), AA'BB' signal with signal centers at $\delta_A$ = 7.31 and $\delta_B$ = 7.52 ppm (2 × 2-H and 2 × 3-H). The preceding data are consistent with those reported in the literature.[50] The *ee* was determined by chiral HPLC (Chiralcel OD-3, *n*-heptane/*i*-PrOH 150:1, 1 mL/min, $\lambda_{detector}$ = 249 nm): $t_r$(*R*) = 17.66 min, $t_r$(*S*) = 20.84 min. $[\alpha]_{365}^{20}$ = –657.2, $[\alpha]_{436}^{20}$ = –334.5, $[\alpha]_{546}^{20}$ = –172.0, $[\alpha]_{578}^{20}$ = –148.3, $[\alpha]_{589}^{20}$ = –139.9 (*c* = 1.27 in EtOH; the respective sample had 58% *ee*); Lit.[57]: $[\alpha]_{589}^{20}$ = –150 [*c* = 0.75 in $CHCl_3$, a sample of the (*S*)-enantiomer with 71% *ee*]. The absolute configuration was determined by comparing the sense of the optical rotation with literature data.[50]

**Isobutyl (2,4,6-Trimethylphenyl) Sulfoxide (45): (–)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] did not follow the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* : At 0°C *n*-BuLi (2.1 M in hexane, 0.56 mL, 1.2 mmol, 3.0 equiv.) was added to a solution of *rac*-BINOL (167 mg, 0.584 mmol, 1.5 equiv.) in THF (1 mL). After 10 min *i*-$Bu_2Mg$ (0.80 M in $Et_2O$, 0.59 mL, 0.47 mmol, 1.2 equiv.) was added. After another 10 min a solution of bis(2,4,6-trimethylphenyl) sulfoxide (113 mg, 0.395 mmol) in THF (1.5 mL) was added. After stirring for 24 h at room temperature the reaction was quenched and the resulting mixture was worked up. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 18-24) delivered *rac*-**45** (45.9 mg, 52%) as a colourless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2,4,6-trimethylphenyl) sulfoxide (56.4 mg, 0.197 mmol). After 24 h at –68°C this delivered (–)-**45** (11.0 mg, 25%; 23% *ee*) as a colorless oil. $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 1.11 (d, $J_{3',2'}$ = 5.4 Hz, 3 H, 3'-$H_3$), 1.13 (d, $J_{3'',2'}$ = 5.7 Hz, 3 H, 3''-$H_3$), 2.17-2.27 (m, 1 H, 2'-H superimposed by singlet of 4-$CH_3$), 2.27 (s, 3 H, 4-$CH_3$), 2.50 (dd, $J_{1'-A,1'-B}$ = 13.0 Hz, $J_{1'-A,2'}$ = 8.8 Hz, 1 H, 1'-$H_A$ superimposed by singlet of 2- and 6-$CH_3$), 2.54 (s, 6 H, 2- and 6-$CH_3$), 3.27 (dd, $J_{1'-B,1'-A}$ = 13.4 Hz, $J_{1'-B,2'}$ = 5.0 Hz, 1 H, 1'-$H_B$), 6.85 ppm (s, 2 H, 3- and 5-H). The preceding data are consistent with those reported in the literature.[58] The *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-heptane/*i*-PrOH 97:3, 1 mL/min, $\lambda_{detector}$ = 265 nm): $t_r$(1) = 11.33 min, $t_r$(2) = 12.61 min. $[\alpha]_{365}^{20}$ = –107.3, $[\alpha]_{436}^{20}$ = –73.5, $[\alpha]_{546}^{20}$ = –32.9, $[\alpha]_{578}^{20}$ = –26.7, $[\alpha]_{589}^{20}$ = –22.2 (*c* = 0.80 in EtOH; the respective sample had 23% *ee*).

**Isobutyl (4-Phenylphenyl) Sulfoxide (46): (*S*)-(–)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(4-phenylphenyl) sulfoxide (101 mg, 0.286 mmol) with *i*-$Bu_2Mg$ (0.80 M in $Et_2O$, 0.20 mL, 0.16 mmol, 0.55 equiv.) within 1 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 27-48) delivered *rac*-**46** (64.3 mg, 87%) as a colorless solid (mp. = 56-57°C). The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(4-phenylphenyl) sulfoxide (139.3 mg, 0.393 mmol). After 1 h this delivered (*S*)-(–)-**46** (87.8 mg, 87%; 94% *ee*) as a colorless solid (mp. = 56-57°C). $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.09 (d, $J_{3'',2''}$ = 6.9, 3 H, 3''-$H_3$), 1.18 (d, $J_{3''',2''}$ = 6.5 Hz, 3 H, 3'''-$H_3$), 2.27 ($m_c$, 1 H, 2''-H), 2.52 (dd, $J_{1''-A,1''-B}$ = 12.9 Hz, $J_{1''-A,2''}$ = 9.2 Hz, 1 H, 1''-$H_A$), 2.87 (dd, $J_{1''-B,1''-A}$ = 13.0 Hz, $J_{1''-B,2''}$ = 5.0 Hz, 1 H, 1''-$H_B$), 7.37-7.42

(m, 1 H, 4‘-H), 7.44-7.49 (m, 2 H, 2 × 2‘-H), 7.59-7.62 (m, 2 H, 2 × 3‘-H), AA’BB‘ signal with signal centers at $\delta_A$ = 7.70 and $\delta_B$ = 7.74 ppm (4 H, 2 × 2-H und 2 × 3-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 21.8 (C-3‘‘‘), 22.9 (C-3‘‘), 24.3 (C-2‘‘), 67.7 (C-1‘‘), 124.5 (C-2), 127.3 (C-2‘*), 128.1 (C-3), 128.2 (C-4‘), 129.1 (C-3‘*), 140.0, 143.6, 144.1 ppm (C-1, C-4, and C-1’); *assignments interchangeable. IR ($CDCl_3$): $\tilde{\nu}$ = 3280, 3055, 3030, 2955, 2925, 2855, 2410, 2045, 1665, 1595, 1480, 1465, 1385, 1370, 1240, 1090, 1040, 1005, 840, 810, 760, 720 700, 655 cm$^{-1}$. HRMS (CI, $NH_4Cl$): $C_{16}H_{19}SO$ ($M + H^+$), calculated: 259.11566, found: 259.11550 (Δ = –0.6 ppm). Elemental analysis: calculated (%) for $C_{16}H_{18}SO$ (258.4 g/mol): C 74.38, H 7.02, S 12.41; found: C 74.23, H 6.77, S 12.06. The *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22°C, $\lambda_{detector}$ = 204 nm): $t_r(S)$ = 12.90 min, $t_r(R)$ = 16.83 min. $[\alpha]^{20}_{365}$ = –1512.3, $[\alpha]^{20}_{436}$ = –819.5, $[\alpha]^{20}_{546}$ = –410.7, $[\alpha]^{20}_{578}$ = –352.5, $[\alpha]^{20}_{589}$ = –334.7 (*c* = 1.16 in EtOH; the respective sample had 94% *ee*). The absolute configuration of the title compound was elucidated by X-ray crystal structure analysis (Figure 1). Detailed information are given in Section 2 of the “Supporting Information – Spectra and HPLC Traces. X-Ray Details”.

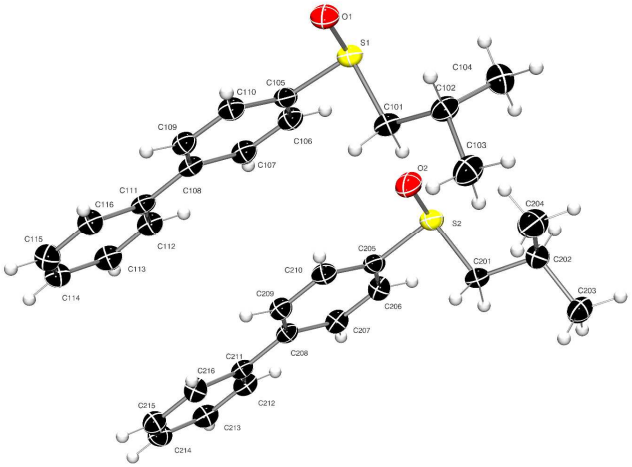
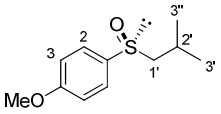


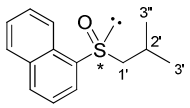

**Figure 2**: ORTEP plot of the crystal structure of sulfoxide (–)-**46** (at 100 K).[59] The unit cell contains two crystallographically independent molecules.

**Isobutyl (4-Methoxyphenyl) Sulfoxide (47): (*S*)-(–)-Enantiomer and Racemic**[45]



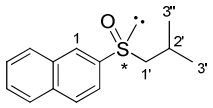

The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(4-methoxyphenyl) sulfoxide (130 mg, 0.496 mmol) with *i*-$Bu_2Mg$ (0.80 M in $Et_2O$, 0.68 mL, 0.54 mmol, 1.1 equiv.) within 2 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 55:45, F. 17-35) delivered *rac*-**47** (70.8 mg, 67%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(4-methoxyphenyl) sulfoxide (51.7 mg, 0.198 mmol). After 24 h at –68°C this delivered (*S*)-(–)-**47** (41.8 mg, 100%; 62% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.06 (d, $J_{3‘,2‘}$ = 6.7 Hz, 3 H, 3‘-$H_3$), 1.13 (d, $J_{3‘‘,2‘}$ = 6.5 Hz, 3 H, 3‘‘-$H_3$), 2.17 ($m_c$, 1 H, 2‘-H), 2.44 (dd, $J_{1‘\text{-}A,1‘\text{-}B}$ = 13.3 Hz, $J_{1‘\text{-}A,2‘}$ = 9.0 Hz, 1 H, 1‘-$H_A$), 2.82 (dd, $J_{1‘\text{-}B,1‘\text{-}A}$ = 12.8 Hz, $J_{1‘\text{-}B,2‘}$ = 5.5 Hz, 1 H, 1‘-$H_B$), 3.85 (s, 3 H, O-C$H_3$), AA’BB‘ signal with signal centers at $\delta_A$ = 7.02 and $\delta_A$ = 7.57 ppm (2 × 2-H and 2 × 3-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 21.9 (C-3‘‘), 22.9 (C-3‘), 24.4 (C-2‘), 55.8 (O-$CH_3$), 67.8 (C-1‘), 114.9 (C-2), 126.1 (C-3), 135.8, 162.1 ppm (C-1 and C-4). IR ($CDCl_3$): $\tilde{\nu}$ = 3460, 3070, 2960, 2870, 2840, 2425, 2045, 1645, 1595, 1580, 1495, 1465, 1445, 1405, 1385, 1370, 1305, 1251, 1170, 1110, 1090, 1070, 1030, 1005, 830, 810, 795 cm$^{-1}$. HRMS (CI, $NH_4Cl$): $C_{11}H_{17}SO_2$ ($M + H^+$), calculated: 213.09493, found: 213.09510 (Δ = +0.8 ppm). Elemental analysis: calculated (%) for $C_{11}H_{16}SO_2$ (212.3 g/mol): C 62.23, H 7.60, S 15.10; found: C 62.11, H 7.55, S 14.94. The *ee* was determined by chiral HPLC (Chiralpak AD-H, *n*-heptane/*i*-PrOH 95:5, 1 mL/min, 22°C, $\lambda_{detector}$ = 204 nm): $t_r(R)$ = 21.00 min, $t_r(S)$ = 24.79 min. $[\alpha]^{20}_{365}$ = –576.0, $[\alpha]^{20}_{436}$ = –284.0, $[\alpha]^{20}_{546}$ = –142.5, $[\alpha]^{20}_{578}$ = –122.8, $[\alpha]^{20}_{589}$ = –117.0 (*c* = 1.0 in EtOH; the respective sample had 62% *ee*). The absolute configuration was assigned by chemical correlation (cf. Supporting Information).

**Isobutyl (1-Naphthyl) Sulfoxide (48): (–)-Enantiomer and Racemic**[45]



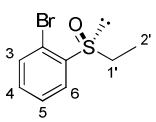
The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using di(1-naphthyl) sulfoxide (50.1 mg, 0.166 mmol) with *i*-$Bu_2Mg$ (0.80 M in $Et_2O$, 0.11 mL, 0.088 mmol, 0.53 equiv.) within 2 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 18-25) delivered *rac*-**48** (27.8 mg, 72%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using di(1-naphthyl) sulfoxide (57.5 mg, 0.190 mmol). After 30 Min this delivered (–)-**48** (37.0 mg, 84%; 91% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.06 (d, $J_{3',2'}$ = 6.8 Hz, 3 H, 3'-$H_3$), 1.27 (d, $J_{3'',2'}$ = 6.6 Hz, 3 H, 3''-$H_3$), 2.36-2.46 (m, 1 H, 2'-H), 2.72-2.80 (m, 2 H, 1'-$H_2$), 7.55-7.61 (m, 2 H, 2 × Ar-H), 7.65-7.68 (dd, $^3J$ = 8.2 Hz, $^3J$ = 7.3 Hz, 1 H, 1 × Ar-H), 7.91-7.97 (m, 3 H, 3 × Ar-H), 8.15 ppm (dd, $^3J$ = 7.3 Hz, $^4J$ = 1.2 Hz, 1 H, 1 × Ar-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 21.6 (C-3'), 22.9 (C-3''), 24.6 (C-2'), 66.7 (C-1'), 121.5, 122.8, 125.9, 126.7, 127.3, 128.9, 129.2, 131.1, 133.6, 140.8 ppm. IR ($CDCl_3$): $\tilde{\nu}$ = 3055, 2960, 2870, 1590, 1505, 1465, 1400, 1380, 1345, 1260, 1170, 1140, 1040, 965, 860, 800, 770, 740, 665, 560 cm$^{-1}$. HRMS (CI, $NH_4Cl$): $C_{14}H_{17}SO$ ($M + H^+$), calculated: 233.10001, found: 233.10000 (Δ = –0.1 ppm) and $C_{14}H_{20}SNO$ ($M + NH_4^+$), calculated: 250.12656, found: 250.12660 (Δ = +0.2 ppm). The *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, $\lambda_{detector}$ = 209 nm): $t_r(1)$ = 5.29 min, $t_r(2)$ = 24.19 min. $[\alpha]_{365}^{20}$ = –1512.3, $[\alpha]_{436}^{20}$ = –819.5, $[\alpha]_{546}^{20}$ = –410.8, $[\alpha]_{578}^{20}$ = –352.5, $[\alpha]_{589}^{20}$ = –334.7 (*c* = 1.10 in EtOH; the respective sample had 91% *ee*).

**Isobutyl (2-Naphthyl) Sulfoxide (49): (–)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using di(2-naphthyl) sulfoxide (101 mg, 0.333 mmol) with *i*-$Bu_2Mg$ (0.8 M in $Et_2O$, 0.23 mL, 0.18 mmol, 0.55 equiv.) within 3 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 21-34) delivered *rac*-**49** (52.1 mg, 67%) as a colorless solid (mp. = 59-60°C). The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using di(2-naphthyl) sulfoxide (58.1 mg, 0.192 mmol). After 5.5 h this delivered (–)-**49** (32.8 mg, 74%; 42% *ee*) as a colorless solid (mp. = 59-60°C). $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.09 (d, $J_{3',2'}$ = 6.9 Hz, 3 H, 3'-$H_3$), 1.19 (d, $J_{3'',2'}$ = 6.9 Hz, 3 H, 3''-$H_3$), 2.23-2.33 (m, 1 H, 2'-H), 2.57 (dd, $J_{1'-A,1'-B}$ = 13.1 Hz, $J_{1'-A,2'}$ = 8.4 Hz, 1 H, 1'-$H_A$), 2.88 (dd, $J_{1'-B,1'-A}$ = 13.1 Hz, $J_{1'-B,2'}$ = 4.7 Hz, 1 H, 1'-$H_B$), 7.58-7.61 (m, 3 H, 3 × Ar-H), 7.89-7.99 (m, 3 H, 3 × Ar-H), 8.20 ppm (br. s, 1 H, 1-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 21.9 (C-3'), 23.0 (C-3''), 24.4 (C-2'), 67.5 (C-1'), 120.0, 124.6 (C-1), 127.4, 127.8, 128.2, 128.6, 129.6, 133.0, 134.6, 142.0 ppm (C-2). IR ($CDCl_3$): $\tilde{\nu}$ = 3470, 3055, 2960, 2930, 2900, 2870, 1430, 2035, 1625, 1590, 1505, 1465, 1390, 1385, 1370, 1345, 1265, 1235, 1195, 1170, 1135, 1110, 1080, 1035, 945, 905, 860, 810, 765, 750 cm$^{-1}$. HRMS (CI, $NH_4Cl$): $C_{14}H_{17}SO$ ($M + H^+$), calculated: 233.10001, found: 233.10000 (Δ = –0.1 ppm). Elemental analysis: calculated (%) for $C_{14}H_{16}SO$ (232.3 g/mol): C 72.37, H 6.94, S 13.80; found: C 72.24, H 6.79, S 13.63. The *ee* was determined by chiral HPLC (Chiralcel OD-3, *n*-heptane/EtOH 97:3, 1 mL/min, $\lambda_{detector}$ = 209 nm): $t_r(1)$ = 7.97 min, $t_r(2)$ = 8.64 min. $[\alpha]_{365}^{20}$ = –344.3, $[\alpha]_{436}^{20}$ = –204.1, $[\alpha]_{546}^{20}$ = –103.5, $[\alpha]_{578}^{20}$ = –89.3, $[\alpha]_{589}^{20}$ = –73.7 (*c* = 1.78 in EtOH; the respective sample had 42% *ee*).

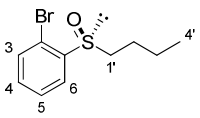
**(2-Bromophenyl) Ethyl Sulfoxide (52): (*S*)-(–)-Enantiomer and Racemic**[45]



The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(2-bromophenyl) sulfoxide (53.2 mg, 0.148 mmol) with $Et_2Mg$ (0.16 M in $Et_2O$, 0.51 mL, 0.081 mmol, 0.55 equiv.) within 1.25 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 18-27) delivered *rac*-**52** (17.0 mg, 49%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2-bromophenyl) sulfoxide (70.9 mg, 0.197 mmol). After 10 s this delivered (*S*)-(–)-**52** (31.9 mg, 69%; 89% *ee*) as a colorless oil. $^1$H NMR (300.1 MHz, $CDCl_3$): δ = 1.25 (dd, $J_{2',1'-A} = J_{2',1'-B}$ = 7.3 Hz, 3 H, 3'-$H_3$), AB signal ($\delta_A$ = 2.85, $\delta_B$ = 3.13, $J_{A,B}$ = 13.6 Hz, A part additionally split by q, $J_{1'-A,2'}$ = 7.4 Hz, 1'-$H_A$; B part additionally split by q, $J_{1'-B,2'}$ = 7.4 Hz, 1'-$H_B$), 7.36 (ddd, $^3J$ = 8.8 Hz, $^3J$ = 7.7 Hz, $^4J$ = 1.7 Hz, 4- or 5-H), 7.53-7.58 (m, 2 H, 2 × Ar-H), 7.86 ppm (dd, $^3J$ = 8.1

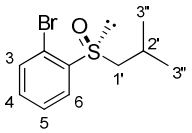
Hz, $^4J$ = 1.8 Hz, 3- or 6-H). The preceding data are consistent with those reported in the literature.[60] The *ee* was determined by chiral HPLC (Chiralcel OJ-H, *n*-heptane/EtOH 300:1, 1.0 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(S)$ = 29.23 min, $t_r(R)$ = 33.41 min. $[\alpha]^{20}_{365}$ = –1090.0, $[\alpha]^{20}_{436}$ = –562.9, $[\alpha]^{20}_{546}$ = –290.6, $[\alpha]^{20}_{578}$ = –250.8, $[\alpha]^{20}_{589}$ = –239.5 (*c* = 0.62 in EtOH; the respective sample had 89% *ee*). The absolute configuration was determined by chemical correlation (cf. Supporting Information).

**(2-Bromophenyl) Butyl Sulfoxide (53): (*S*)-(–)-Enantiomer and Racemic**[45]




The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(2-bromophenyl) sulfoxide (70.9 mg, 0.197 mmol) with $Bu_2Mg$ (0.69 M in $Et_2O$, 0.14 mL, 0.10 mmol, 0.51 equiv.) within 30 min. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 13-20) delivered *rac*-**53** (25.5 mg, 50%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2-bromophenyl) sulfoxide (70.8 mg, 0.197 mmol). After 10 s this delivered 10 s (*S*)-(–)-**53** (40.4 mg, 79%; 86% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 0.95 (t, $J_{4',3'}$ = 7.3 Hz, 3 H, 4'-$H_3$), 1.39-1.50 (m, 2 H, 3'-$H_2$), 1.51-1.67 (m, 1 H, 2'-$H_A$), 1.85-1.91 (m, 1 H, 2'-$H_B$), AB signal ($\delta_A$ = 2.76, $\delta_B$ = 3.09, $J_{A,B}$ = 14.5 Hz, A part additionally split by dd, $J_{1'-A,2'-A}$ = 9.5 Hz, $J_{1'-A,2'-B}$ = 5.0 Hz, 1'-$H_A$; B part additionally split by dd, $J_{1'-B,2'-A}$ = 9.6 Hz, $J_{1'-B,2'-B}$ = 6.7 Hz, 1'-$H_B$), 7.36 (ddd, $^3J$ = 7.8 Hz, $^3J$ = 7.5 Hz, $^4J$ = 1.8 Hz, 1 H, 4-or 5-H), 7.54-7.58 (m, 2 H, 2 × Ar-H), 7.88 ppm (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.8 Hz, 1 H, 3- or 6-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 13.8 (C-4'), 21.9 (C-3'), 24.3 (C-2'), 54.7 (C-1'), 118.7 (C-2*), 126.7 (C-3 or C-6), 128.5, 132.2 (C-4 or C-5), 133.0, 143.9 ppm (C-1*); *assignments interchangeable. IR ($CDCl_3$): $\tilde{\nu}$ = 3555, 3060, 2960, 2930, 2870, 2385, 1965, 1565, 1445, 1430, 1380, 1245, 1160, 1095, 1045, 1015, 755, 715 cm$^{-1}$. HRMS (CI, $NH_4Cl$): $C_{10}H_{14}SOBr$ ($M + H^+$), calculated: 260.99487, found: 260.99480 (Δ = –0.3 ppm). The *ee* was determined by chiral HPLC (Chiralcel OJ-H, *n*-heptane/EtOH 98:2, 1 mL/min, $\lambda_{detector}$ = 250 nm): $t_r(S)$ = 7.96 min, $t_r(R)$ = 9.00 min. $[\alpha]^{20}_{365}$ = –1207.1, $[\alpha]^{20}_{436}$ = –632.3, $[\alpha]^{20}_{546}$ = –330.6, $[\alpha]^{20}_{578}$ = –284.5, $[\alpha]^{20}_{589}$ = –270.0 (*c* = 0.31 in EtOH; the respective sample had 86% *ee*). The absolute configuration was assigned by chemical correlation (cf. Supporting Information).

**(2-Bromophenyl) Isobutyl Sulfoxide (54): (*S*)-(–)-Enantiomer and Racemic**[45]




The **racemic synthesis**[44] followed the *General Procedure for the Preparation of Racemic Alkyl Aryl Sulfoxides* using bis(2-bromophenyl) sulfoxide (100 mg, 0.278 mmol) with *i*-$Bu_2Mg$ (0.80 M in $Et_2O$, 0.19 mL, 0.15 mmol, 0.55 equiv.) within 2 h. Flash chromatography on silica gel[40] (*c*-$C_6H_{12}$:EtOAc 80:20, F. 10-15) delivered *rac*-**54** (58.9 mg, 81%) as a colorless oil. The **asymmetric synthesis** followed the *Procedure for the Asymmetric Sulfinylations of Dialkylmagnesium Compounds by Symmetric Diaryl Sulfoxides* using bis(2-bromophenyl) sulfoxide (70.9 mg, 0.197 mmol). After 1 h this delivered (*S*)-(–)-**54** (42.9 mg, 83%; 53% *ee*) as a colorless oil. $^1$H NMR (400.1 MHz, $CDCl_3$): δ = 1.07 (d, $J_{3',2'}$ = 7.3 Hz, 3 H, 3'-$H_3$), 1.23 (d, $J_{3'',2'}$ = 8.0 Hz, 3 H, 3''-$H_3$), 2.39 ($m_c$, 1 H, 2'-H), 2.60 (dd, $J_{1'-A,1'-B}$ = 12.8 Hz, $J_{1'-A,2'}$ = 4.2 Hz, 1 H, 1'-$H_A$), 2.91 (dd, $J_{1'-B,1'-A}$ = 12.9 Hz, $J_{1'-B,2'}$ = 10.4 Hz, 1 H, 1'-$H_B$), 7.35 (ddd, $^3J$ = 9.6 Hz, $^3J$ = 7.4 Hz, $^4J$ = 1.6 Hz, 1 H, 4- or 5-H), 7.54-7.58 (m, 2 H, 2 × Ar-H), 7.91 ppm (dd, $^3J$ = 7.6 Hz, $^4J$ = 1.8 Hz, 1 H, 3- or 6-H). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ = 21.4 (C-3''), 23.0 (C-3'), 24.5 (C-2'), 65.6 (C-1'), 118.6 (C-2*), 126.3 (C-3 or C-6), 128.7, 132.2 (C-4 or C-6), 133.0, 144.7 ppm (C-1*); *assignments interchangeable. IR ($CDCl_3$): $\tilde{\nu}$ = 3665, 3260, 2960, 2925, 2870, 2405, 195, 1565, 1465, 1445, 1400, 1385, 1370, 1145, 1095, 1070, 1050, 1015, 755, 715 cm$^{-1}$. HRMS (CI, $NH_4Cl$): $C_{10}H_{14}SOBr$ ($M + H^+$), calculated: 260.99487, found: 260.99490 (Δ = +0.1 ppm). The *ee* was determined by chiral HPLC (Chiralcel OD-H, *n*-heptane/EtOH 97:3, 1 mL/min, $\lambda_{detector}$ = 210 nm): $t_r(R)$ = 8.32 min, $t_r(S)$ = 9.49 min. $[\alpha]^{20}_{365}$ = –888.8, $[\alpha]^{20}_{436}$ = –466.2, $[\alpha]^{20}_{546}$ = –243.8, $[\alpha]^{20}_{578}$ = –210.5, $[\alpha]^{20}_{589}$ = –200.1 (*c* = 1.06 in EtOH; the respective sample had 53% *ee*). The absolute configuration was assigned by chemical correlation (cf. Supporting Information).

## ASSOCIATED CONTENT

Supporting Information

Detailed procedures for the configurational assignments, copies of NMR spectra, copies of HPLC traces, and X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org

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(1) In this manuscript, sulfoxides are depicted with an S=O double bond. When this S=O bond starts from the sulfur atom of a *symmetric* disulfoxide, this representation needs no refinement. When the S=O bond starts from a sulfur atom of a chiral sulfoxide, we depict it with two heavy lines if the O atom is above the drawing plane; for reinforcing the 3D impression, we attach a hatched bond to the sulfur atom of such a sulfoxide for indicating that there is a lone pair below the drawing plane. When the S=O bond of an *asymmetric* disulfoxide is oppositely configured, we depict the S=O bond by one a bond and a parallel hatched bond for making clear that the O atom lies below the drawing plane; for reinforcing the 3D impression, we attach a wedged bond to such a sulfur atom for emphasizing that there is a lone pair above the drawing plane..

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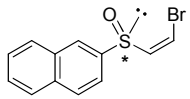
(22)  **56** (80% *ee*) Complete chirality transfer was described for the sulfinylation of methyl- and propylmagnesium halide by sulfoxide **56**: ref.[14].

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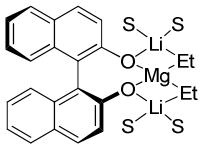
(26)  **57** ("S" = THF or DME) NOYORI *et al.* elucidated the structure of the $Li_2$-(*S*)-BINOLate complex **57** of $Et_2Mg$ in THF or in DME: Noyori, R., Suga, S., Kawai, K., Okada, S., Kitamura, M. *Pure Appl. Chem.* **1988**, *60*, 1597-1606. Since our reagents consisted of $Li_2$-(*S*)-BINOLate and $R_2Mg$ (including $Et_2Mg$) we consider "$Li_2$-(*S*)-BINOLate · $R_2Mg$" as plausible active reagents in our sulfinylation reactions.
(27) The quotation marks shall indicate that we used a solvent mixture, in which THF was the major but not the only ingredient. This is because *n*-BuLi was used as a solution in hexane and the dialkylmagnesiums were used as solutions in $Et_2O$.
(28) To the best of our knowledge, these are the first sulfoxide/magnesium exchange reactions in diaryl sulfoxides, which work with organomagensium reagents containing *primary alkyl* groups. All previous sulfoxide/magnesium exchange reactions in diaryl sulfoxides, of which we are aware, were effected with PhMgBr [(a) N. Furukawa, T. Shibutani, K. Matsumura, H. Fujihara, S. Oae, *Tetrahedron Lett.* **1986**, *27*, 3899-3902; (b) T. Satoh, Y. Kitoh, K. Onda, K. Yamakawa, *Tetrahedron Lett.* **1993**, *34*, 2331-2334], with iPr–MgCl • LiCl [(c) C. B. Rauhut, L. Melzig, P. Knochel, *Org. Lett.* **2008**, *10*, 3891-3894; (d) L. Melzig, C. B. Rauhut, P. Knochel, *Synthesis* **2009**, 1041-1048; (e) L. Melzig, C. B. Rauhut, P. Knochel, *Chem. Comm.* **2009**, *24*, 3536-3538; (f) L. Melzig, C. B. Rauhut, N. Naredi-Rainer, P. Knochel, *Chemistry* **2011**, *17*, 5362-5372] or with $iPr_2Mg$ (ref.[25]).
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(30) The yield and *ee* of the 2,4-dimethylphenyl isopropyl sulfoxide (*S*)-(−)-**19** shown in Scheme 1 did not change when that compound was kept under the reaction conditions unnecessarily long.[25] This means that (*S*)-(−)-**19** sulfinylated neither residual *i*-$Pr_2Mg$ nor the stoichiometric by-product 2,4-dimethylphenyl isopropyl magnesium.
(31) The sulfinylation of $Bn_2Mg$ had to be carried out at +22°C in order to achieve any conversion at all.
(32) The 32 non-racemic sulfoxides, which emerged from the asymmetric sulfinylations of the present study are levorotatory. This consistency is paralleled by the consistency of attributing an (*S*)-configuration to 21 of these sulfoxides by independent evidence. Details: Supporting Information.
(33) When we sulfinylated *i*-$Pr_2Mg$ asymmetrically under almost exactly the conditions specified in Scheme 1 the *ee* of the sulfoxide (*S*)-(−)-**19** did not change and the yield did not change more than marginally when we varied the reaction time between 10 min and 3 h.[25] In contrast some sulfinylations of our present study revealed *ee* and yield variations with time, e. g.: • The sulfinylation of $Et_2Mg$ delivering the sulfoxide (*S*)-(−)-**29** rendered 71% *ee* and 77% yield after 2 min (= experiment reported in Scheme 3) but 31% *ee* and 34% yield after 30 min (not mentioned elsewhere in this manuscript); the follow-up reaction, which occurred in between, thus consumed (*S*)-(−)-**29** faster than its (*R*)-enantiomer. • The sulfinylation of $Et_2Mg$ delivering the sulfoxide (*S*)-(−)-**30** rendered 90% yield and 69% *ee* after 10 s (not mentioned elsewhere in this manuscript) and 39% yield and 94% *ee* after 30 min (= experiment reported in Scheme 3); the follow-up reaction, which occurred in between, thus consumed (*S*)-(−)-**30** more slowly than its (*R*)-enantiomer. • The sulfinylation of $Et_2Mg$ delivering the sulfoxide (*S*)-(−)-**32** rendered 82% yield and 70% *ee* after 10 s (= experiment reported in Scheme 3) and 11% yield and 89% *ee* after 30 min (not mentioned elsewhere in this manuscript); the follow-up reaction, which occurred in between, thus consumed (*S*)-(−)-**32** more slowly than its (*R*)-enantiomer.
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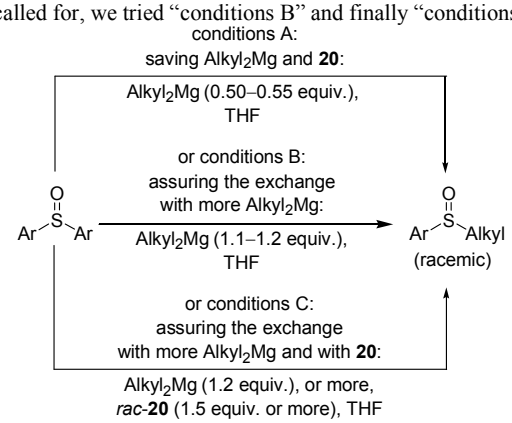


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