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# BINOL derived $C_2$-symmetric bis-sulfinates as efficient sulfinyl transfer agents in the synthesis of *tert*-butyl sulfoxides

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ABSTRACT

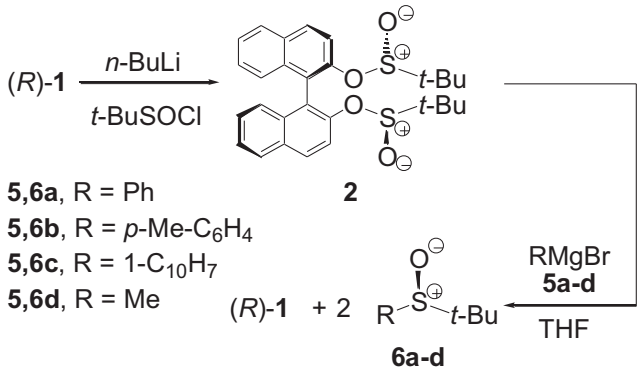
The reaction of novel $C_2$-symmetric bis-sulfinate esters derived from (*R*)-BINOL with Grignard reagents affords *tert*-butyl sulfoxides in ee up to 97%. The desired enantiomer can be generated at will by the proper selection of BINOL.



## 1. Introduction

Research in the field of synthesis of enantiomerically pure sulfoxides is continuously developing. These unremitting efforts find their justification in the broad applications of the sulfinyl moiety as chiral auxiliaries for C–C and C–O bonds forming reactions and as ligands in catalytic stereoselective reactions.[1] In particular, in the last few years *tert*-butyl sulfoxides have assumed great importance in asymmetric synthesis and numerous examples are reported of their use as chiral ligands,[2] chiral auxiliaries,[3] and Lewis base catalysts.[4] Moreover, a variety of pharmacological active compounds contains the sulfinyl functional group.[5] The major synthetic strategies to sulfoxides rely on the direct oxidation of parent sulfides[6] and the more versatile nucleophilic displacement by organometallic species at the stereogenic sulfur atom of diastereoisomerically pure sulfinylating species.[1b,c,7] Numerous diastereoisomerically pure sulfinates,[8] thiosulfinates,[9] sulfinamides,[10] cyclic sulfites,[11] oxathiazolidine-2-oxides[12] for transfer of the sulfinyl group have been developed. The success of the latter approach is based on the stereospecificity of the substitution at the sulfur atom, which proceeds with inversion of configuration.[13] In this context it is surprising that no literature report deals with the use of chiral auxiliaries having a $C_2$-symmetry axis. In fact, it is often observed that auxiliaries with a $C_2$-symmetry axis provide higher levels of stereochemical control with respect to other auxiliaries, which lack such symmetry.[14]

In the present study we report a new $C_2$-symmetric bis-sulfinate **2** derived from (*R*)-1,1′-binaphthyl-2,2′-diol (**1**) (BINOL) as a chiral sulfinyl transfer reagent, capable to react with Grignard reagents affording enantiomerically enriched *tert*-butyl sulfoxides **6** (Scheme 1).




**Scheme 1.** Synthesis of aryl *tert*-butyl sulfoxides **6a**–**d**.

## 2. Results and discussion

The reaction of (*R*)-**1** with *n*-butyllithium (*n*-BuLi) (2.2 equiv, THF, −78 °C) followed by addition of *tert*-butylsulfinyl chloride (2 equiv, THF, −78 °C) gave a mixture of three bis-sulfinate ester diastereoisomers **2**–**4** where mono-sulfinates were absent (Scheme 2).

The diastereoselectivity of the process could be determined through $^1$H NMR spectroscopic analysis of the reaction mixture. Homotopic 2,2′-*tert*-butyl groups of $C_2$-symmetric stereoisomers are singlets with a chemical shift of 0.69 and 0.61 ppm for **2** and **4**, respectively. On the other hand, each diastereotopic *tert*-butyl group of **3** is a singlet with a chemical shift of 0.75 and 0.62 ppm. Moreover, the composition of the crude material could also be

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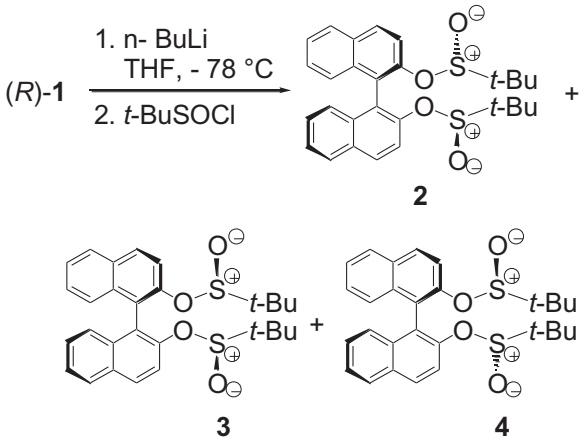



**Scheme 2.** Synthesis of bis-sulfinates **2**–**4**.

assigned by HPLC. Under the previously described reaction conditions, a mixture of **2**/**3**/**4** in 82:16:2 ratio was obtained in 95% overall yield (Table 1, entry 1). Silica gel flash chromatography provided **2**, in 77% yield with 97% diastereoisomeric excess.[15]

**Table 1**
Influence of the base on diastereoselectivity of bis-sulfinates synthesis[a]

| Entry | Base | Time (h) | Yield (%) | **2**[b] (%) | **4**[b] (%) | **3**[b] (%) |
|---|---|---|---|---|---|---|
| 1 | *n*-BuLi | 1 | 95 | 82 | 2 | 16 |
| 2 | *n*-BuLi/LiCl[c] | 1 | 90 | 84 | 2 | 14 |
| 3 | *t*-BuLi | 1 | 95 | 75 | 6 | 19 |
| 4 | NaH[d] | 3 | 81 | 68 | 7 | 25 |
| 5 | $^{i}Pr_2NEt$ | 2 | 71 | 57 | 15 | 28 |
| 6 | $LiN[Si(CH_3)_3]_2$ | 1 | 93 | 56 | 12 | 32 |
| 7 | $LiN[Si(CH_3)_3]_2$/LiCl[c] | 1 | 94 | 76 | 5 | 19 |
| 8 | DBU[e] | 2.5 | 80 | 31 | 21 | 48 |
| 9 | Pyridine[e] | 2 | 75 | 39 | 15 | 46 |

[a] Reaction conditions: the base (2.2 mmol) was added to a THF solution of (*R*)-BINOL (1 mmol) at −78 °C. After 30 min *tert*-butylsulfinyl chloride (4 mmol) was dropwise added and stirring was continued at −78 °C.
[b] Diastereoisomeric ratios were determined by $^1H$ NMR spectroscopic analysis and HPLC analysis.
[c] A 0.5 M (8 mL, 4 mmol) LiCl solution in THF was added after base addition.
[d] *T*=0–25 °C.
[e] *T*=−78/−40 °C.

In order to investigate the influence of the base on the stereochemical outcome, different bases were used in sulfinate esters synthesis (Table 1). In fact, it is well known from the literature that an achiral base could have a stereocontrolling effect on the prevailing sulfinate diastereoisomer formation.[16] Sulfinate **2** is the major diastereoisomer when *n*-butyllithium (entry 1), *tert*-butyllithium (entry 3), sodium hydride (entry 4), *N*,*N*-di-*iso*-propylethylamine (entry 5), and hexamethyldisilazane lithium salt ($LiN[Si(CH_3)_3]_2$) (entry 6) were used as bases. On the other hand, sulfinate **3** was preferentially formed when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (entry 8) and pyridine (entry 9) were employed. The best diastereoselectivity was obtained with *n*-butyllithium.

The deprotonation step to give a dianionic species is responsible for the formation of ion-pair aggregate structures, whose reactivity could be modified by LiCl addition. Therefore, the synthesis of bis-sulfinates **2**–**4** has also been carried out by addition of LiCl to the reaction mixture when *n*-BuLi and $LiN[Si(CH_3)_3]_2$ were used (Table 1, entries 2 and 7). In the case of $LiN[Si(CH_3)_3]_2$ a remarkable increase in bis-sulfinate **2** formation was observed, whereas only a slight increase was found when *n*-BuLi was used.

The mono-sulfinates were never detected in the experimental conditions of Table 1, as we verified by comparison with an authentic sample prepared by treating (*R*)-BINOL with 0.5 M equiv of anhydrous potassium carbonate and subsequent reaction with 0.5 M equiv of *tert*-butylsulfinyl chloride.[17]

In order to test the efficiency of bis-sulfinate esters as sulfinyl transfer agents, the mixture of **2**–**4** (Table 1, entry 1) was dissolved in THF and phenylmagnesium bromide (**5a**) was dropwise added at −78 °C. After complete addition, the temperature was allowed to reach −20 °C in 1 h and quenched with $NH_4Cl_{sat}$. The reaction afforded (*S*)-(-)-*tert*-butyl phenyl sulfoxide (**6a**) in 53% chemical yield and 80% ee as determined by chiral HPLC analysis (Table 2, entry 1). Moreover, enantiomerically pure (*R*)-BINOL was recovered in almost quantitative yield after flash chromatography. Assuming that the displacement step at the sulfur atom occurs with complete inversion,[13] the absolute configuration of the major bis-sulfinate **2** was determined to be $R,R_S,R_S$.

**Table 2**
Synthesis of (*S*)-*tert*-butyl sulfoxides **6a**–**e** by displacement reactions of sulfinate **2**[a]

| Entry | R | Solvent | Time (h) | Yield (%) | ee (%) |
|---|---|---|---|---|---|
| 1[b,c] | $C_6H_5$ **5a** | THF | 2 | 53 | 80 |
| 2[c,d] | $C_6H_5$ **5a** | $Et_2O$ | 1 | 66 | 79 |
| 3[c] | $C_6H_5$ **5a** | $Et_2O$ | 1 | 63 | 78 |
| 4[e] | $C_6H_5$ **5a** | THF | 2 | 69 | 85 |
| 5 | $C_6H_5$ **5a** | THF | 3 | 84 | 97 |
| 6 | $p$-$CH_3$–$C_6H_4$ **5b** | THF | 3 | 85 | 95 |
| 7 | 1-Naphthyl **5c** | THF | 4 | 71 | 94 |
| 8 | $p$-$CH_3O$–$C_6H_4$ **5d** | THF | 3 | 73 | 97 |
| 9 | $CH_3$ **5e** | THF | 3 | 77 | 87 |

[a] Reaction conditions: **2** (1 equiv), RMgBr (1.5 equiv), THF, at −78 °C.
[b] Grignard reagent (1 M equiv) was used in entry 1.
[c] Crude reaction mixture of bis-sulfinates **2**–**4**.
[d] Addition at room temperature of a bis-sulfinates **2**–**4** solution ($Et_2O$) to a solution of **5a** in $Et_2O$.
[e] After RMgBr addition the temperature was allowed to reach 25 °C.

Reaction conditions with Grignard reagent were optimized after several trials in which solvent, temperature, reagents addition order were analyzed. The best results have been obtained by the addition of 1.5 M equiv of phenylmagnesium bromide solution to the sulfinate dissolved in THF at −78 °C.

After completion of the Grignard reagent addition, the temperature was allowed to gradually increase to −20 °C in 1 h and the reaction mixture was quenched with $NH_4Cl_{sat}$. Chromatographic purification afforded (*S*)-(−)-*tert*-butylphenyl sulfoxide (**6a**) in 84% chemical yield and 97% ee (Table 2, entry 5). The ee of the sulfoxide did not change during the progress of the reaction as verified by chiral HPLC injections of several crude samples at different times.

In an effort to expand the scope of the process we compared a series of Grignard reagents (**5b**–**e**) in the displacement reaction. The results are depicted in Table 2. The corresponding sulfoxides **6b**–**e** have been isolated in good yields and ees up to 97%.

The next goal was to verify if structural modifications on the chiral auxiliary could exert an effect on the ratio of sulfinates. (*R*)-3,3′-Diphenyl-1,1′-bis-(2-naphthol) was prepared from the commercial available (*R*)-3,3′-dibromo-1,1′-bis-(2-naphthol),[18] and then converted to bis-sulfinate ester diastereoisomers by using *n*-BuLi as base. However, since the presence of phenyl groups in 3,3′ positions of the aromatic rings did not increase the diastereoselection nor simplify the purification of the crude bis-sulfinates mixture, we did not proceed with the displacement reaction with Grignard reagent.

## 3. Conclusion

In summary, we developed a new practical approach to enantiomerically enriched sulfoxides through conversion of (*R*)-BINOL **1** to bis-sulfinate **2**, followed by displacement of the latter with Grignard reagents. Direct displacement of the crude bis-sulfinates

**2**–**4** mixture afforded sulfoxide **6a** in good chemical yield but with ee in the 80% range. However, high ees of the desired sulfoxides had been obtained by using pure sulfinate **2**, recovered by standard chromatographic purification. As expected, the ee of the sulfoxides was found to be strictly correlated with the diastereoisomeric excess of the bis-sulfinate. Moreover, as determined by chiral HPLC of the crude reaction mixture at uncomplete conversions, the ee of the sulfoxide did not change during the displacement reaction.

The stereochemical outcome of the bis-sulfinate synthesis is influenced by the base employed in the BINOL deprotonation step. It is also worth noting that 2 mol of sulfoxide could be obtained per each mole of BINOL, a cheap commercially available chiral auxiliary that was recovered in almost quantitative yield.

The displacement reaction by Grignard reagents affords *tert*-butyl sulfoxides with high ee, good yields, and a predictable absolute configuration. In fact the desired sulfoxide enantiomer can be generated at will by the proper selection of the starting chiral auxiliary.

For these reasons this paper fills a gap in the use of $C_2$ chiral auxiliaries and appears to be a useful complement to existing routes to enantiopure sulfoxides.

## 4. Experimental section

### 4.1. General remarks

Melting points were determined on a BÜCHI 535. NMR spectra were recorded on Bruker AC 300 or AC 200 spectrometers, operating at 300.13 or 200.13 MHz for $^1$H NMR and 75.3 or 50 MHz for $^{13}$C NMR. Coupling constants *J* are in hertz. Chemical shifts were reported by using $CHCl_3$ as external standard (7.24 ppm for $^1$H NMR and 77.0 for $^{13}$C NMR). Column chromatography on silica gel (230–400 mesh) was performed by the flash technique. Petroleum ether (PE) refers to the fraction boiling in the range of 40–60 °C. Mass spectra were measured on an LCQ Advantage Thermo-Finnigan spectrometer. Optical rotations were measured with a Perkin–Elmer 241 polarimeter; the $[\alpha]_D^{25}$ values are reported in $10^{-1}$ deg cm$^2$ g$^{-1}$, concentration (*c*) is reported in g per 100 mL. Chiral HPLC separations were performed on an Agilent HP 1100 apparatus, equipped with a diode array detector, using mixtures of hexane/2-propanol as eluant, detection at 230 nm unless otherwise stated. The flux was set to 1 ml min$^{-1}$ and the volume of injection was 20 μL.

### 4.2. Synthesis of (*R*,*S*$_R$,*S*$_R$)-1,1′-binaphthalene-2,2′-diyl-bis-(*tert*-butylsulfinate) (2)

To a solution at −78 °C of *R*-(+)-BINOL (286 mg, 1 mmol) in dry tetrahydrofuran (5 mL) under nitrogen was added dropwise *n*-butyllithium (1.96 mL, 1.12 M in hexane, 2.2 mmol). After 30 min, *tert*-butylsulfinyl chloride (563 mg, 4 mmol) was dropwise added and stirring was continued for 80 min at −78 °C. The resulting mixture was quenched by the addition of saturated aqueous ammonium chloride (5 mL) and diluted with ethyl acetate (5 mL). The aqueous layer was extracted with ethyl acetate (3×20 mL) and the combined organic layers were dried and concentrated to a small volume. Flash chromatography of the crude material with hexane/ethyl acetate (1:10) afforded the title compound as a white solid (381 mg, 77% yield); mp 178–180 °C $[\alpha]_D^{25}$ −160 (*c* 1, $CHCl_3$); $\delta_H$ (300 MHz, $CDCl_3$) 0.69 (s, 18H, C–C*H*$_3$), 7.13 (d, 2H, *J* 8.5 Hz, ArH), 7.29 (d, 2H, *J* 7.4 Hz, ArH), 7.43 (m, 2H, ArH), 7.67 (d, 2H, *J* 8.8 Hz, ArH), 7.90 (d, 2H, *J* 8.1 Hz, ArH), 7.96 (d, 2H, *J* 8.8 Hz, ArH); $\delta_C$ (75 MHz, $CDCl_3$) 20.9 ($CH_3$), 58.6 (C), 121.0 (CH), 122.9 (C), 125.4 (CH), 126.1 (CH), 126.9 (CH), 128.0 (CH), 130.1 (CH), 131.2 (C), 133.7 (C), 150.4 (C); *m*/*z* (APCI) 495; IR (neat, cm$^{-1}$) 2951, 2922, 2853, 1589, 1563, 1458, 1335, 1204, 1127, 968, 745. Anal. Calcd for $C_{28}H_{30}O_4S_2$ (494.67): C, 67.98; H, 6.11. Found: C, 67.78; H, 6.13.

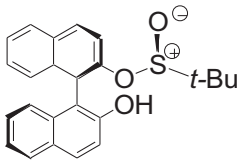
HPLC (Chiralcel OD hex/$^i$PrOH 99:1) $t_R$ 12.4 min ($t_R$ **3** 11.4 min; $t_R$ **4** 10.0 min); de 97%.

Sulfinates **3** and **4** were also recovered as a mixture:

**3**: $\delta_H$ (300 MHz, $CDCl_3$) 0.62 (s, 9H, C–C*H*$_3$), 0.75 (s, 9H, C–C*H*$_3$), 7.13 (d, 2H, *J* 8.5 Hz, ArH), 7.29 (d, 2H, *J* 7.4 Hz, ArH), 7.43 (m, 2H, ArH), 7.67 (d, 2H, *J* 8.8 Hz, ArH), 7.90 (d, 2H, *J* 8.1 Hz, ArH), 7.96 (d, 2H, *J* 8.8 Hz, ArH); HPLC (Chiralcel OD hex/$^i$PrOH 99:1) $t_R$ 11.4 min.

**4**: $\delta_H$ (300 MHz, $CDCl_3$) 0.61 (s, 18H, C–C*H*$_3$), 7.13 (d, 2H, *J* 8.5 Hz, ArH), 7.29 (d, 2H, *J* 7.4 Hz, ArH), 7.43 (m, 2H, ArH), 7.67 (d, 2H, *J* 8.8 Hz, ArH), 7.90 (d, 2H, *J* 8.1 Hz, ArH), 7.96 (d, 2H, *J* 8.8 Hz, ArH); HPLC (Chiralcel OD hex/$^i$PrOH 99:1) $t_R$ 10.0 min.

### 4.3. Synthesis of 2′-hydroxy-1,1′-binaphthyl-2-yl 2-methylpropane-2-sulfinate (7)




7

To a solution of *R*-(+)-BINOL (572 mg, 2 mmol) in acetone (2 mL) under nitrogen was added $K_2CO_3$ (346 mg, 2.5 mmol) at room temperature. After stirring for 15 min at the same temperature *tert*-butylsulfinyl chloride (281 mg, 2 mmol) was dropwise added and stirring was continued for 3 h. The resulting mixture was quenched by the addition of saturated aqueous ammonium chloride (5 mL) and diluted with ethyl acetate (5 mL). The aqueous layer was extracted with ethyl acetate (3×20 mL) and the combined organic layers were dried and concentrated to a small volume. Flash chromatography of the crude material with $Et_2O$/PE (1:3) afforded the title compound (437 mg, 56% yield) mp 160 °C, $[\alpha]_D^{25}$ +326.2 (*c*, 0.7, $CHCl_3$) $\delta_H$ (300 MHz, $CDCl_3$) 0.71 (s, 9H, C–C*H*$_3$), 7.14 (d, 1H, *J* 7.9 Hz, ArH), 7.26–7.43 (m, 5H, ArH), 7.53 (m, 1H, ArH), 7.73 (d, 1H, *J* 8.9 Hz, ArH), 7.86 (d, 1H, *J* 8.5 Hz, ArH), 7.93 (d, 1H, *J* 8.9 Hz, ArH), 8.00 (d, 1H, *J* 8.2 Hz, ArH), 8.08 (d, 1H, *J* 8.9 Hz, ArH); $\delta_C$ (75 MHz, $CDCl_3$) 20.9 ($CH_3$), 58.8 (C), 114.0 (C), 117.4 (CH), 121.2 (C), 121.7 (CH), 123.6 (CH), 124.8 (CH), 125.3 (CH), 126.0 (CH), 126.8 (CH), 127.7 (CH), 127.9 (CH), 128.4 (CH), 129.0 (C), 130.3 (CH), 131.1 (CH), 131.9 (C), 133.3 (C), 133.7 (C), 151.2 (C), 151.4 (C); IR (neat, cm$^{-1}$) 3420, 2945, 2910, 2830, 1580, 1535, 1465, 1342, 1212, 1133, 973, 725; *m*/*z* (ESI) 413 [M+Na]$^+$. Anal. Calcd for $C_{24}H_{22}O_3S$ (390.50): C, 73.82; H, 5.68. Found: C, 73.74; H, 5.76.

### 4.4. Typical procedure for the synthesis of sulfoxides 6a–e

To a solution of sulfinate ester **2** (494 mg, 1 mmol) in anhydrous THF under nitrogen at −78 °C, a solution of phenylmagnesium bromide (**5a**) (3 mmol, 3 mL of 1 M THF solution) was dropwise added over a 5 min period. The reaction mixture was stirred at −78 °C for 30 min, then was allowed to reach −20 °C, quenched by the addition of saturated aqueous ammonium chloride solution. The temperature was allowed to reach 20 °C and ethyl acetate (10 mL) was added. The aqueous layer was extracted with ethyl acetate (3×20 mL), the combined organic layers were dried and the solvent was removed in vacuo. Flash chromatography of the crude material with dichloromethane/ethyl acetate (8:2) afforded 306 mg (84% yield) of (*S*)-(−)-*tert*-butylsulfinylbenzene (**6a**) as a white solid mp 89 °C [lit.[2] (*S*)-**6a**, 90 °C]. $[\alpha]_D^{25}$ −171 (*c* 1, $CHCl_3$), [lit.[2] (*S*)-**6a** −175 ($CHCl_3$)]; HPLC Chiralcel OD hex/$^i$PrOH 99:1, $t_R$ (*S*) 26.7 min; $t_R$ (*R*) 24.7 min, ee 97%.

Sulfoxides **6b**–**d** are known compounds and have been prepared by using the same procedure described above for **6a** by using the proper Grignard reagent **5b**–**d**. Physical and spectroscopic properties of **6b**–**d** are identical to those previously reported. Optical purity has been determined by comparison of $[\alpha]_D^{25}$ with those reported in the literature.

(*S*)-(−)-1-Methyl-4-*tert*-butylsulfinylbenzene (**6b**) $[\alpha]_D^{25}$ −180 (*c* 0.8, EtOH), ee 95% [lit.[19] (*R*)-**6b** $[\alpha]_D^{25}$ +190 (EtOH)].

(*S*)-(−)-*tert*-Butylsulfinyl-1-naphthalene (**6c**) $[\alpha]_D^{25}$ −310 (*c* 1.30, $CHCl_3$) ee 94% [lit.[4] (*S*)-**6c** $[\alpha]_D^{25}$ −330 (*c* 1.39, $CHCl_3$)].

(*S*)-(−)-1-Methoxy-4-*tert*-butylsulfinylbenzene (**6d**) $[\alpha]_D^{25}$ −148 (*c* 1.35, $CHCl_3$) ee 97% [lit.[20] (*R*)-**6d** $[\alpha]_D^{25}$ +116 (*c* 0.9, $CHCl_3$) ee 76%].

(*S*)-(−)-*tert*-Butyl-methylsulfoxide (**6e**) $[\alpha]_D^{25}$ +6.8 (*c* 6.5, $CHCl_3$) ee 87% [lit.[21] (*S*)-**6e** $[\alpha]_D^{25}$ +7.8 (*c* 7, $CHCl_3$)].

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