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Practical and highly stereoselective method for the preparation of several chiral arylsulfinamides and arylsulfinates based on the spontaneous crystallization of diastereomerically pure *N*-benzyl-*N*-(1-phenylethyl)-arylsulfinamides

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ABSTRACT

A novel and simple process for the preparation of enantiomerically pure (S_S)-benzenesulfinamide (S_S)-**3a**, (S_S)-*p*-toluenesulfinamide (S_S)-**3b**, (S_S)-*p*-chloro-benzenesulfinamide (S_S)-**3c** and (S_S)-*p*-fluorobenzenesulfinamide (S_S)-**3d** has been developed. The treatment of arylsulfinyl chlorides with (*R*)-*N*-benzyl-1-phenylethanamine in the presence of excess triethylamine gave diastereomeric mixtures of *N*-benzyl-*N*-(1-phenylethyl)-arylsulfinamides **1**, which underwent spontaneous crystallization to furnish diastereomerically pure (*R*,S_S)-*N*-benzyl-*N*-(1-phenylethyl)-arylsulfinamides (*R*,S_S)-**1a**–**1d** in 28%, 29%, 27% and 31% yields, respectively. The diastereomerically pure compounds (*R*,S_S)-**1** were then converted into four enantiopure (R_S)-methyl arylsulfinates (R_S)-**2**, and finally into four enantiopure (S_S)-arylsulfinamides (S_S)-**3** in good yields.

1. Introduction

Chiral sulfinamides are important compounds in asymmetric synthesis; they have been extensively utilized as chiral auxiliaries for the preparation of structurally diverse optically active amines and amine-derived compounds.[1–26] Moreover, enantiopure sulfinamides and their derivatives have also been successively used as chiral ligands in many catalytic asymmetric transformations.[21,27–37]

Due to the aforementioned utilities of chiral sulfinamides, the preparation of these compounds is of considerable interest. A literature search revealed that enantiopure *p*-toluenesulfinamide served as the first widely used auxiliary for asymmetric nucleophilic addition of imines,[38,39] and that enantiopure *tert*-butylsulfinamide, which was discovered by Ellman et al. in 1997,[40] served as the second versatile auxiliary and was superior to *p*-toluenesulfinamide for some asymmetric processes.[1,24,25,40] Although the synthesis of both enantiopure *p*-toluenesulfinamide and *tert*-butylsulfinamide has been well studied, and hence some elegant methods for the preparation of these two enantiopure sulfinamides have been developed,[1,38–50] methods for the preparation of other chiral sulfinamides are relatively rare.[48–50] Herein we report our recent work regarding a novel method for the preparation of several chiral arylsulfinamides including (S_S)-benzenesulfinamide, (S_S)-*p*-toluenesulfinamide, (S_S)-*p*-chlorobenzenesulfinamide and (S_S)-*p*-fluorobenzenesulfinamide.

2. Results and discussion

As depicted in Scheme 1, arylsulfinyl chlorides were prepared in situ by exposure of arylsulfinic acid sodium salt with oxalyl chloride in toluene,[44] and then the freshly prepared arylsulfinyl chlorides (R = H, Me, Cl and F) were treated immediately with (*R*)-*N*-benzyl-1-phenylethanamine in the presence of excess triethylamine to give the corresponding diastereomeric mixtures of *N*-benzyl-*N*-(1-phenylethyl)arylsulfinamides **1a–1d** in good yields but with disappointing stereoselectivities (RR_S/RS_S = 49:51 for **1a**, 51:49 for **1b**, 53:47 for **1c** and 49:51 for **1d**). However, diastereomerically pure (de >99%) compounds (*R*,S_S)-**1a**, (*R*,S_S)-**1b**, (*R*,S_S)-**1c** and (*R*,S_S)-**1d** could be obtained in 28%, 29%, 27% and 31% respective yields via spontaneous crystallization in a mixed solvent (EtOAc/hexane = 1:9), and diastereomerically enriched compounds **1a–1d** (RR_S/RS_S = 75:25 for **1a**, 77:23 for **1b**, 79:21 for **1c** and 76:24 for **1d**) being left in the mother liquor. Although the yields of diastereomerically pure compounds (*R*,S_S)-**1a–1d** are relatively low, the aforementioned spontaneous crystallization process can be easily scaled up due to the lack of chromatography, meaning that this method is practical and might be suitable for the preparation of enantiomerically pure *N*-benzyl-*N*-(1-phenylethyl)arylsulfinamides (*R*,S_S)-**1a–1d** in large quantities. Moreover, if necessary, the diastereomerically enriched compounds **1a–1d** in the mother liquor could be further separated by chromatography to afford another batch of compounds (*R*,S_S)-**1a–1d** and their diastereomers (*R*,R_S)-**1a–1d**. It is worthy of note that use of (*R*)-*N*-benzyl-1-phenylethanamine was crucial for the spontaneous crystallization, because when other chiral amines such as (*R*)-1-phenylethanamine

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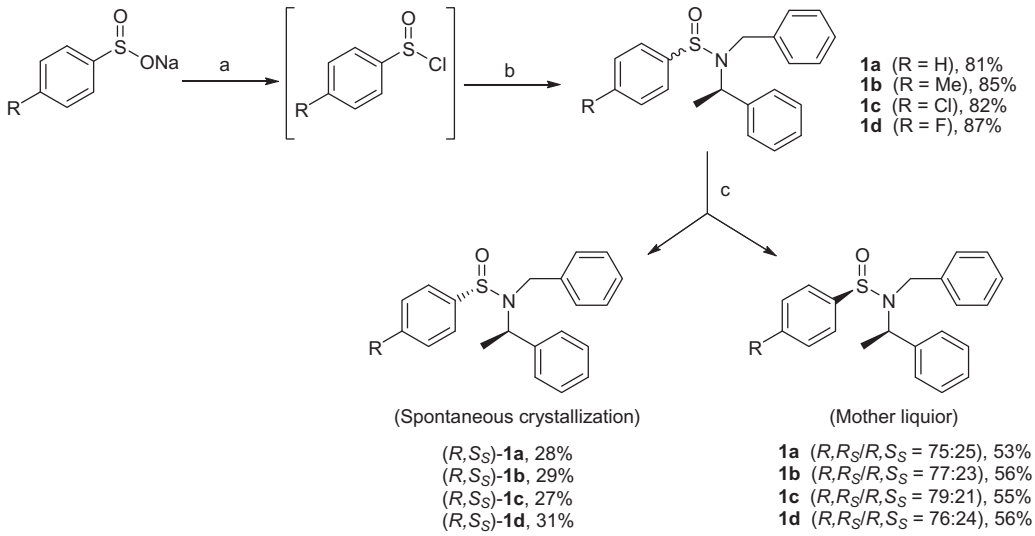


Scheme 1. Preparation of (*R*,*S*$_S$)-*N*-benzyl-*N*-(1-phenylethyl)arylsulfinamides (*R*,*S*$_S$)-1 via spontaneous crystallization. Reagents and conditions: (a) Oxalyl chloride (1.05 equiv), 0 °C for 1 h, and then rt for 2 h in toluene. (b) Et_3N (2 equiv), (*R*)-*N*-benzyl-1-phenylethanamine (1.2 equiv), 0 °C to rt for 2 h in toluene. (c) Stirring at rt for 2 h in a mixed solvent (EtOAc/Hexane = 1:9), and then standing at rt overnight.

or (*R*)-*N*-allyl-1-phenylethanamine or (*R*)-*N*-methyl-1-phenyl-ethanamine were used instead of (*R*)-*N*-benzyl-1-phenylethanamine for the reaction, no spontaneous crystallization occurred at all.

The absolute configurations of the chiral sulfur atoms of the aforementioned four diastereomerically pure *N*-benzyl-*N*-(1-phenylethyl)-arylsulfinamides (*R*,*S*$_S$)-**1a–1d** were assigned either by converting them into authentic sulfoxides or by cultivating their single crystals for X-ray analysis. When compounds (*R*,*S*$_S$)-**1a** and (*R*,*S*$_S$)-**1b** were exposed to butyllithium at −78 °C in tetrahydrofuran,[51] (*S*$_S$)-butylphenylsulfoxide[52] and (*S*$_S$)-butyl-*p*-tolylsulfoxide[53] were obtained in 75% and 78% yields, respectively, meaning that both arylsulfinamides (*R*,*S*$_S$)-**1a** and (*R*,*S*$_S$)-**1b** have an (*S*$_S$)-absolute configuration at the sulfur atom, indicating a *Waldern* type inversion and a change of preferential sequence of substituents during the conversions of sulfinamides (*R*,*S*$_S$)-**1a** and (*R*,*S*$_S$)-**1b** into sulfoxides. For the other two diastereomerically pure compounds (*R*,*S*$_S$)-**1c** and (*R*,*S*$_S$)-**1d**, the absolute configurations of the sulfur atoms were determined unequivocally by X-ray diffraction analysis of the corresponding single crystals; the ORTEP drawing of the compounds (*R*,*S*$_S$)-**1c** and (*R*,*S*$_S$)-**1d** are shown in Figures 1 and 2, respectively.

The four diastereomerically pure *N*-benzyl-*N*-(1-phenylethyl)-arylsulfinamides (*R*,*S*$_S$)-**1a**–**1d** could be used as productive intermediates for chiral arylsulfinates and arylsulfinamides. As shown in Scheme 2, we first attempted to convert them into enantiopure (*R*$_S$)-methyl benzenesulfinate (*R*$_S$)-**2a**,[54] (*R*$_S$)-methyl *p*-toluenesulfinate (*R*$_S$)-**2b**,[55] (*R*$_S$)-methyl *p*-chlorobenzenesulfinate (*R*$_S$)-**2c** and (*R*$_S$)-methyl *p*-fluorobenzenesulfinate (*R*$_S$)-**2d**. Lewis acid-catalyzed transformation of *N*-benzyl-*N*-(1-phenylethyl)arylsulfinamides (*R*,*S*$_S$)-**1** into methyl arylsulfinates (*R*$_S$)-**2** under various conditions was investigated fully, and the results are summarized in Table 1. Although high yields were obtained under all circumstances (Table 1, entries 1–20), partial racemization in some instances occurred at the sulfur atom probably due to the transesterification of the sulfinates under the acidic conditions.[56,57] Toluene was found to be the best solvent, when arylsulfinamides (*R*,*S*$_S$)-**1** were treated with 3 equiv of methanol and 1.5 equiv of $BF_3{\cdot}OEt_2$ at −5 °C in toluene, arylsulfinates (*R*$_S$)-**2** could be obtained in nearly quantitative yields without observable racemization (entries 6, 15, 19 and 20). An increase of the amount of methanol favored the transesterification of sulfinates, and thus tended to facilitate racemization (entries 1, 7 and 8). A lower temperature was crucial for the reaction, since when the conversion was performed at room temperature (20 °C), racemization would take place rapidly (entries 11 and 18).

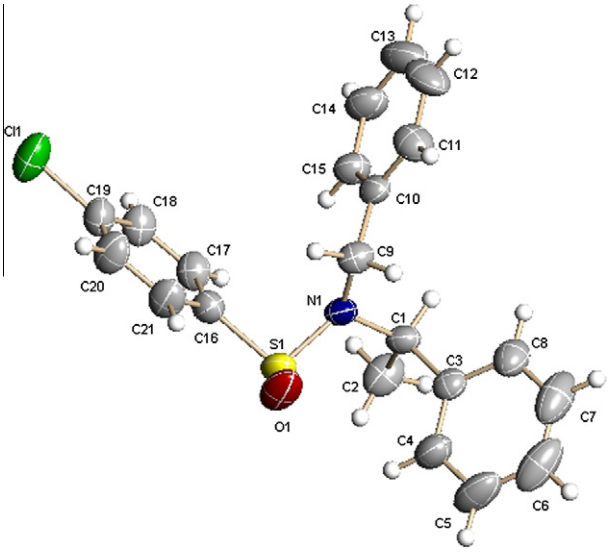


Figure 1. ORTEP drawing of (*R*,*S*$_S$)-*N*-benzyl-*N*-(1-phenylethyl)-*p*-chlorobenzenesulfinamide (*R*,*S*$_S$)-**1c**.

Finally, enantiopure sulfinamides (*S*$_S$)-**3a**,[58] (*S*$_S$)-**3b**,[59] (*S*$_S$)-**3c**[48] and (*S*$_S$)-**3d** were prepared from enantiopure sulfinates (*R*$_S$)-**2a**, (*R*$_S$)-**2b**, (*R*$_S$)-**2c** and (*R*$_S$)-**2d**, respectively. Normally, sulfinates can be converted into sulfinamides by treating them either with $LiNH_2$ in liquid ammonia[49] or with $LiN(SiMe_3)_2$ in THF.[42] Herein, enantiopure sulfinates (*R*$_S$)-**2a–2d** were treated first with $LiN(SiMe_3)_2$ and then with aqueous NH_4Cl in an one-pot procedure to afford enantiopure sulfinamides (*S*$_S$)-**3a–3d** in good yields, the (*R*$_S$)-configuration of the sulfur atoms changed into the (*S*$_S$)-configuration via a *Waldern* type inversion during the conversion.

We also attempted to prepare enantiopure sulfinamides (*S*$_S$)-**3a–3d** from diastereomerically pure *N*-benzyl-*N*-(1-phenylethyl)arylsulfinamides (*R*,*S*$_S$)-**1a**–**1d** via direct reductive removal of the benzyl groups (see also Scheme 2). However, when Pd/C, P-2 nickel,[60] Raney-Ni or PtO_2 was used as the catalyst, hydrogenation

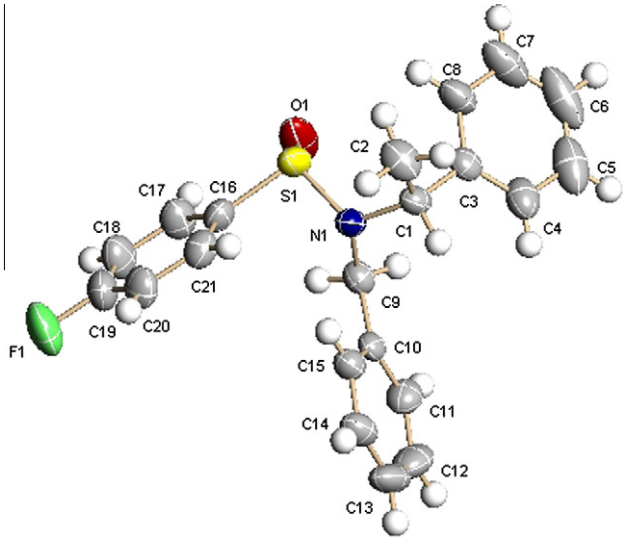
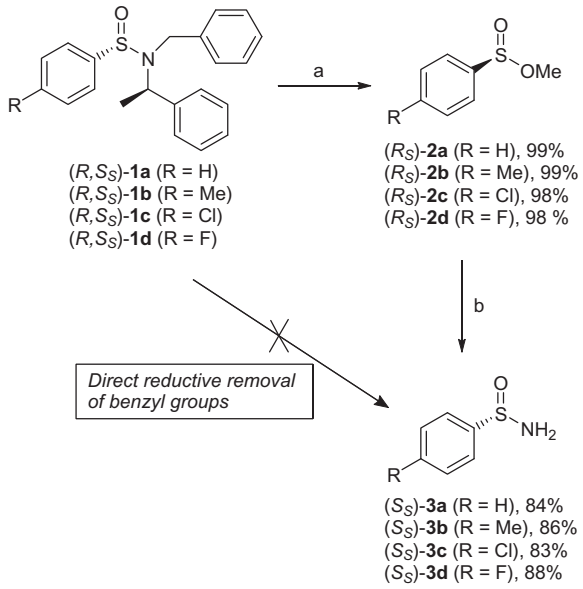


Figure 2. ORTEP drawing of (*R*,*S*$_S$)-*N*-benzyl-*N*-(1-phenylethyl)-*p*-flurobenzenesulfinamide (*R*,*S*$_S$)-**1d**.



Scheme 2. Preparation of enantiopure (*R*$_S$)-arylsulfinates (*R*$_S$)-**2** and (*S*$_S$)-arylsulfinamides (*S*$_S$)-**3** from diastereomerically pure compounds (*R*,*S*$_S$)-**1**. Reagents and conditions: (a) $BF_3{\cdot}OEt_2$ (1.5 equiv), CH_3OH (3 equiv), −5 °C for 2.5 h in toluene. (b) $LiN(SiMe_3)_2$ (1.5 equiv), −78 °C for 3 h in THF; and then aqueous NH_4Cl, −78 °C to rt for 2 h.

of *N*-benzyl-*N*-(1-phenylethyl)arylsulfinamides (*R*,*S*$_S$)-**1a–1d** in various solvents at different temperatures failed to give desired sulfinamides (*S*$_S$)-**3a–3d**. The hydrogenation of all four sulfinamides (*R*,*S*$_S$)-**1a–1d** was sluggish at room temperature, and gave a complex mixture after prolonged heating.

3. Conclusion

In conclusion, a novel, simple, highly stereoselective and practical method for the preparation of enantiomerically pure (*S*$_S$)-arylsulfinamides (*S*$_S$)-**3a–3d** is described. Enantiopure (*S*$_S$)-benzenesulfinamide (*S*$_S$)-**3a**, (*S*$_S$)-*p*-toluenesulfinamide (*S*$_S$)-**3b**, (*S*$_S$)-*p*-chlorobenzenesulfinamide (*S*$_S$)-**3c** and (*S*$_S$)-*p*-fluorobenzenesulfinamide (*S*$_S$)-**3d** were synthesized from the corresponding arylsulfinic acids sodium salts via four steps in 23.3%, 24.7%, 22.0% and 26.7% overall yields, respectively. The key point of the method was the highly stereoselective, spontaneous, crystallization of compounds (*R*,*S*$_S$)-**1a–1d** from diastereomeric mixtures of *N*-benzyl-*N*-(1-phenylethyl)-arylsulfinamides **1a–1d**. No chromatography and the easy operation over the whole process allow us to easily synthesize enantiopure arylsulfinamides (*S*$_S$)-**3a–3d** in gram quantities despite low overall yields. Moreover, four enantiomerically pure arylsulfinates (*R*$_S$)-**2a–2d** were also obtained in the synthesis, which may be useful chiral intermediates for the synthesis of chiral sulfoxides.[61,62]

In addition, it should be pointed out that when we started with (*S*)-*N*-benzyl-1-phenylethanamine instead of (*R*)-*N*-benzyl-1-phenylethanamine, we could accordingly obtain four enantiopure arylsulfinamides (*R*$_S$)-**3a–3d** as well as four enantiopure arylsulfinates (*S*$_S$)-**2a–2d** by the same method described in this paper.

4. Experimental

4.1. General methods

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were acquired on Bruker AM-500. Chemical shifts are given on the delta scale as parts per million (ppm) with tetramethylsilane (TMS) as the internal standard. IR spectra were recorded on Nicolet Magna IR-550. Mass spectra were recorded on HP5989A. Optical rotations of chiral compounds were measured on WZZ-1S automatic polarimeter at room temperature. HPLC analysis was performed with an Agilent/HP 1100 series equipped with an Alltech ELSD 2000ES detector. All chemicals were analytically pure and used as such from commercial suppliers.

4.2. (*R*)-*N*-Benzyl-1-phenylethanamine

To a solution of (*R*)-(+)-1-phenylethanamine (48.47 g, 0.40 mol) in toluene (300 mL), was added benzaldehyde (43.51 g, 0.41 mol). The resulting solution was heated at reflux. Stirring was then continued at reflux for around 3 h and water was removed by azeotropic distillation with a Dean–Stark trap during refluxing. After the reaction was complete, the solvent was removed by vacuum distillation to give a residue as pale yellow oil, which was then dissolved in anhydrous methanol (300 mL). The solution was cooled down to 0 °C with an ice bath, and the powdered $NaBH_4$ (15.52 g, 0.41 mol) was added in portions over 0.5 h. After the addition was complete, the mixture was stirred at 0 °C for a further 2 h, and the reaction was traced by TLC (EtOAc/hexane = 1:6). When the reaction was complete, methanol was removed by vacuum distillation. The solid residue was then partitioned between toluene (300 mL) and water (150 mL). Two phases were separated, and the aqueous phase was extracted twice with toluene (2 × 75 mL). The extracts were combined and dried over anhydrous $MgSO_4$. Evaporation of toluene under vacuum gave an oily residue, which was dissolved in ethanol (250 mL). Concentrated hydrochloric acid (40 mL, 12 M, 0.48 mol) was added, and the mixture was heated at reflux for 2 h. After the solution was concentrated to dryness, a residue was obtained as a pale yellow solid. A mixed solvent of ethyl acetate (100 mL) and hexane (200 mL) was added. The suspension was stirred at reflux for 2 h. After the suspension was cooled to room temperature, the off-white solid was collected on Buchner funnel by suction, and was rinsed with a mixed solvent (EtOAc/hexane = 1:3). The solid was then partitioned between ethyl acetate (400 mL) and aqueous sodium hydroxide (250 mL, 20% w/v). Two phases were separated and the aqueous phase was extracted twice with ethyl acetate (2 × 100 mL). After the combined extracts were dried over anhydrous $MgSO_4$, evaporation of the solvent under vacuum afforded (*R*)-*N*-benzyl-1-phenylethanamine (78.1 g, 0.37 mol) as colorless oil in 92% yield. $[\alpha]_D^{25} = +59.1$ (*c* 1.2, EtOH) {lit.[63] $[\alpha]_D^{25} = +56.2$ (*c* 1.1, EtOH)}. ^{1}H NMR ($CDCl_3$) δ 1.40 (d, *J* = 6.6 Hz, 3H), 3.63 (d,

Table 1
Conversion of diastereomerically pure *N*,*N*-disubstituted arylsulfinamides (*R*,*S*$_S$)-**1** into chiral methyl arylsulfinates (*R*$_S$)-**2** under various conditions

Entry	(*R*,*S*$_S$)-**1**	Solvent	CH_3OH (equiv)	$BF_3{\cdot}OEt_2$ (equiv)	*T* (°C)	*t* (h)	(*R*$_S$)-**2**	$[\alpha]_D^{25}$	Ee[a] (%)	Yield[b] (%)
1	**1a**	CH_3OH	—	1.5	−5	1	**2a**	−148.5	76	90
2	**1a**	THF	3	1.5	−5	6	**2a**	−167.4	86	88
3	**1a**	CH_2Cl_2	3	1.5	−5	2.5	**2a**	−189.2	97	95
4	**1a**	$CHCl_3$	3	1.5	−5	5	**2a**	−175.0	90	91
5	**1a**	Toluene	2	1.5	−5	4	**2a**	−194.1	>98	96
6	**1a**	Toluene	3	1.5	−5	2.5	**2a**	−195.0[c]	>98	99
7	**1a**	Toluene	5	1.5	−5	2	**2a**	−189.5	97	98
8	**1a**	Toluene	10	1.5	−5	1.5	**2a**	−181.1	93	97
9	**1a**	Toluene	3	1.5	0	2	**2a**	−193.1	98	97
10	**1a**	Toluene	3	1.5	10	1.5	**2a**	−179.2	92	97
11	**1a**	Toluene	3	1.5	20	1	**2a**	−156.9	80	94
12	**1a**	Toluene	3	2	−5	2	**2a**	−193.5	>98	98
13	**1a**	Toluene	3	3	−5	1.5	**2a**	−190.1	97	97
14	**1b**	Toluene	3	1.5	−11	4	**2b**	−210.2	>98	95
15	**1b**	Toluene	3	1.5	−5	2.5	**2b**	−210.2[d]	>98	99
16	**1b**	Toluene	3	1.5	0	2	**2b**	−209.0	98	98
17	**1b**	Toluene	3	1.5	10	1.5	**2b**	−194.4	93	96
18	**1b**	Toluene	3	1.5	20	1	**2b**	−170.3	81	93
19	**1c**	Toluene	3	1.5	−5	2.5	**2c**	−173.0[e]	>98	98
20	**1d**	Toluene	3	1.5	−5	2.5	**2d**	−171.9[f]	>98	98

[a] Ee values were estimated according to high-resolution ^1H NMR (500 MHz) using (*S*)-2,2,2-trifluoro-1-phenylethanol as the chiral shift reagent.[55]
[b] Isolated yield.
[c] For enantiopure compound (*R*$_S$)-**2a**: $[\alpha]_D^{25} = -195.0$ (*c* 1.2, EtOH) {lit.[54] $[\alpha]_{589} = -188.0$ (*c* 1.5, EtOH)}.
[d] For enantiopure compound (*R*$_S$)-**2b**: $[\alpha]_D^{25} = -210.2$ (*c* 1.4, EtOH) {lit. $[\alpha]_D^{25} = -211.7$ (*c* 4.5, EtOH), calculated from the data of $[\alpha]_D^{25} = -25.4$ (*c* 4.5, EtOH, 12% ee) in Ref. 55}.
[e] For enantiopure compound (*R*$_S$)-**2c**: $[\alpha]_D^{25} = -173.0$ (*c* 1.3, EtOH).
[f] For enantiopure compound (*R*$_S$)-**2d**: $[\alpha]_D^{25} = -171.9$ (*c* 1.3, EtOH).

J = 13.1 Hz, 1H), 3.69 (d, *J* = 13.1 Hz, 1H), 3.84 (q, *J* = 6.6 Hz, 1H), 7.24–7.40 (m, 10H). MS *m*/*z* (%) 212 (M^++1, 100), 196 (56), 91 (48).

4.3. Typical procedure for the preparation of (*R*,*S*$_S$)-*N*-benzyl-*N*-(1-phenylethyl)-arylsulfinamides (*R*,*S*$_S$)-1

To a suspension of benzenesulfinic acid sodium salt (16.42 g, 0.10 mol) in toluene (150 mL), was dropwise added oxalyl chloride (13.33 g, 0.105 mol) over 10 min at 0 °C. After the addition was finished, stirring was continued at 0 °C for one more hour and at room temperature for 2 h. The mixture obtained was then added into a cooled solution of (*R*)-*N*-benzyl-1-phenylethanamine (25.36 g, 0.12 mol) and triethylamine (20.3 g, 0.20 mol) in toluene (50 mL) over 15 min at 0 °C. After the addition was finished, the ice bath was removed, and the mixture was stirred further for around 2 h, while the temperature was allowed to gradually rise to room temperature. An aqueous solution of citric acid (150 mL, 15% w/v) was added, and the mixture was vigorously stirred for 5 min. Two phases were separated, and the aqueous phase was extracted twice with toluene (2 × 50 mL). The extracts were combined, and washed successively with saturated aqueous solution of $NaHCO_3$ (30 mL) and brine (20 mL). After the organic solution was dried over anhydrous Na_2SO_4, the solvent was removed by vacuum distillation to give a residue. A mixed solvent of ethyl acetate (20 mL) and hexane (180 mL) was added, the mixture was stirred at room temperature for 2 h, and then was allowed to stand at room temperature overnight. Finally, filtration by suction through a Buchner funnel afforded (*R*,*S*$_S$)-*N*-benzyl-*N*-(1-phenylethyl)benzenesulfinamide (*R*,*S*$_S$)-**1a** (9.40 g, 28.02 mmol) in 28% yield. The mother liquid was then concentrated under vacuum to give a residue, which was purified by chromatography (eluent: EtOAc/hexane = 1:16) to give second batch of compound (*R*,*S*$_S$)-**1a** (4.45 g, 13.26 mmol) in 13% yield and its diastereomer (*R*,*R*$_S$)-**1a** (13.33 g, 39.74 mmol) in 40% yield.

4.3.1. (*R*,*S*$_S$)-*N*-Benzyl-*N*-(1-phenylethyl)benzenesulfinamide (*R*,*S*$_S$)-1a

R_f = 0.60 (EtOAc/hexane = 1:4), mp 110–111 °C, $[\alpha]_D^{25} = +42.2$ (*c* 1.1, EtOAc). ^1H NMR (acetone-d_6) δ 1.56 (d, *J* = 7.2 Hz, 3H), 3.70 (d, *J* = 15.2 Hz, 1H), 4.07 (d, *J* = 15.2 Hz, 1H), 4.47 (q, *J* = 7.2 Hz, 1H), 7.01 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 2H), 7.15–7.24 (m, 3H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.47–7.54 (m, 3H), 7.55–7.61 (m, 2H), 7.82 (dd, J_1 = 7.1 Hz, J_2 = 1.4 Hz, 2H). ^{13}C NMR (acetone-d_6) δ 22.1, 48.3, 59.3, 127.3, 128.4, 128.6, 129.2, 129.4, 129.5, 129.6, 130.1, 132.0, 138.6, 142.2, 146.4. MS *m*/*z* (%) 335 (M^+, 2), 320 (3), 258 (1), 231 (3), 210 (85), 194 (16), 167 (3), 140 (4), 125 (17), 105 (100), 91 (82), 77 (16), 65 (7). IR (KBr film) 3063, 3021, 2979, 2926, 2905, 1600, 1584, 1495, 1453, 1436, 1084, 1053, 911, 868, 768, 753, 737, 700, 537, 500, 463 cm^{-1}. Anal. Calcd for $C_{21}H_{21}NOS$: C, 75.19; H, 6.31; N, 4.18. Found: C, 75.38; H, 6.17; N, 4.14.

4.3.2. (*R*,*R*$_S$)-*N*-Benzyl-*N*-(1-phenylethyl)benzenesulfinamide (*R*,*R*$_S$)-1a

Pale yellow oil, R_f = 0.50 (EtOAc/hexane = 1:4), $[\alpha]_D^{25} = +111.1$ (*c* 4.1, EtOAc). ^1H NMR (acetone-d_6) δ 1.74 (d, *J* = 7.0 Hz, 3H), 3.98 (d, *J* = 14.8 Hz, 1H), 4.05 (d, *J* = 14.8 Hz, 1H), 4.44 (q, *J* = 7.0 Hz, 1H), 7.16 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 2H), 7.20–7.37 (m, 8H), 7.47–7.58 (m, 3H), 7.63 (dd, J_1 = 8.1 Hz, J_2 = 1.3 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 18.3, 47.9, 57.1, 126.2, 127.5, 127.6, 127.8, 128.4, 128.5, 128.9, 129.1, 130.8, 137.2, 141.8, 144.4. MS *m*/*z* (%) 335 (M^+, 2), 320 (4), 258 (1), 231 (4), 210 (86), 194 (18), 167(3), 140 (4), 125 (18), 105 (100), 91 (75), 77 (8), 65 (5). HRMS (EI) *m*/*z* calcd for $C_{21}H_{21}NOS$ $[M]^+$: 335.1344, found 335.1350. IR (neat) 3063, 3021, 2979, 2937, 1600, 1584, 1495, 1453, 1379, 1358, 1205, 1089, 1058, 1026, 911, 868, 753, 700, 537, 505, 474 cm^{-1}.

4.3.3. (*R*,*S*$_S$)-*N*-Benzyl-*N*-(1-phenylethyl)-*p*-toluenesulfinamide (*R*,*S*$_S$)-1b

R_f = 0.62 (EtOAc/hexane = 1:4), mp 125–126 °C, $[\alpha]_D^{25} = +32.1$ (*c* 1.2, EtOAc). ^1H NMR (acetone-d_6) δ 1.55 (d, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 3.69 (d, *J* = 15.2 Hz, 1H), 4.05 (d, *J* = 15.2 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 1H), 7.02 (dd, J_1 = 7.9 Hz, J_2 = 1.9 Hz, 2H), 7.16–7.24 (m, 3H), 7.25–7.31 (m, 1H), 7.32–7.40 (m, 4H), 7.50 (dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (acetone-d_6) δ 21.6, 22.1, 48.3, 59.3, 127.4, 128.3, 128.6, 129.2, 129.4, 129.5, 129.6, 130.7, 138.7, 142.3, 142.4, 143.3. MS *m*/*z* (%) 349 (M^+, 3), 334 (4), 245 (3), 210 (100), 194 (10), 154 (7), 139 (29), 105 (50),

91 (42), 77 (6), 65 (4). IR (KBr film) 3032, 2916, 1595, 1489, 1453, 1084, 911, 868, 821, 763, 732, 700, 647, 537, 505, 453 cm^{-1}. Anal. Calcd for $C_{22}H_{23}NOS$: C, 75.61; H, 6.63; N, 4.01. Found: C, 75.83; H, 6.46; N, 3.98.

4.3.4. (*R*,*R*$_S$)-*N*-Benzyl-*N*-(1-phenylethyl)-*p*-toluenesulfinamide (*R*,*R*$_S$)-1b

Pale yellow oil, R_f = 0.50 (EtOAc/hexane = 1:4), $[\alpha]_D^{25} = +128.7$ (*c* 4.4, EtOAc). ^{1}H NMR (acetone-d_6) δ 1.73 (d, *J* = 7.0 Hz, 3H), 2.35 (s, 3H), 3.96 (d, *J* = 14.8 Hz, 1H), 4.05 (d, *J* = 14.8 Hz, 1H), 4.42 (q, *J* = 7.0 Hz, 1H), 7.18 (dd, J_1 = 8.1 Hz, J_2 = 1.6 Hz, 2H), 7.21–7.37 (m, 10H), 7.52 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 18.3, 21.4, 47.8, 57.0, 126.2, 127.4, 127.5, 127.8, 128.38, 128.42, 129.1, 129.6, 137.3, 141.1, 141.2, 141.9. HRMS (EI) *m*/*z* calcd for $C_{22}H_{23}NOS$ $[M]^+$: 349.1500, found 349.1499. IR (neat) 3021, 2979, 2916, 1600, 1495, 1453, 1379, 1089, 1063, 911, 868, 816, 753, 700, 505 cm^{-1}.

4.3.5. (*R*,*S*$_S$)-*N*-Benzyl-*N*-(1-phenylethyl)-*p*-chlorobenzenesulfinamide (*R*,*S*$_S$)-1c

R_f = 0.55 (EtOAc/hexane = 1:4), mp 155–156 °C, $[\alpha]_D^{25} = +22.7$ (*c* 1.2, EtOAc). ^{1}H NMR ($CDCl_3$) δ 1.60 (d, *J* = 7.1 Hz, 3H), 3.73 (d, *J* = 15.1 Hz, 1H), 4.05 (d, *J* = 15.1 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 1H), 6.92 (dd, J_1 = 7.1 Hz, J_2 = 2.2 Hz, 2H), 7.17–7.25 (m, 3H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 21.6, 47.5, 58.8, 127.4, 127.8, 127.9, 128.0, 128.4, 128.5, 128.7, 129.1, 137.0, 137.1, 140.5, 143.3. MS *m*/*z* (%) 369 (M^+, 1), 354 (3), 265 (2), 210 (62), 194 (10), 159 (26), 105 (100), 91 (69), 77 (13), 65 (7). HRMS (EI) *m*/*z* calcd for $C_{21}H_{20}ClNOS$ $[M]^+$: 369.0954, found 369.0946. IR (KBr film) 3086, 3029, 2943, 1494, 1470, 1453, 1379, 1103, 1076, 1066, 1051, 1009, 868, 767, 742, 702, 538 cm^{-1}.

4.3.6. (*R*,*R*$_S$)-*N*-Benzyl-*N*-(1-phenylethyl)-*p*-chlorobenzenesulfinamide (*R*,*R*$_S$)-1c

R_f = 0.45 (EtOAc/hexane = 1:4), mp 80–81 °C, $[\alpha]_D^{25} = +137.4$ (*c* 2.3, EtOAc). ^{1}H NMR ($CDCl_3$) δ 1.78 (d, *J* = 7.0 Hz, 3H), 3.97 (d, J = 14.7 Hz, 1H), 4.05 (d, J = 14.7 Hz, 1H), 4.41 (q, *J* = 7.0 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 2H), 7.22–7.30 (m, 6H), 7.34 (dd, J_1 = 7.2 Hz, J_2 = 7.6 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 18.3, 48.0, 57.3, 127.6, 127.72, 127.74, 127.8, 128.5, 128.6, 129.0, 129.1, 136.9, 137.1, 141.7, 143.0. HRMS (EI) *m*/*z* calcd for $C_{21}H_{20}ClNOS$ $[M]^+$: 369.0954, found 369.0948. IR (KBr film) 3084, 3028, 2914, 1574, 1494, 1469, 1455, 1375, 1203, 1128, 1102, 1080, 1066, 1008, 984, 913, 856, 831, 765, 743, 698 cm^{-1}.

4.3.7. (*R*,*S*$_S$)-*N*-Benzyl-*N*-(1-phenylethyl)-*p*-fluorobenzenesulfinamide (*R*,*S*$_S$)-1d

R_f = 0.52 (EtOAc/hexane = 1:4), mp 161–162 °C, $[\alpha]_D^{25} = +39.7$ (*c* 1.0, EtOAc). ^{1}H NMR ($CDCl_3$) δ 1.60 (d, *J* = 7.2 Hz, 3H), 3.71 (d, *J* = 15.1 Hz, 1H), 4.07 (d, *J* = 15.1 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 1H), 6.88–6.94 (m, 2H), 7.15–7.22 (m, 5H), 7.27–7.33 (m, 1H), 7.38 (dd, J_1 = 7.2 Hz, J_2 = 7.7 Hz, 2H), 7.45 (dd, J_1 = 7.2 Hz, J_2 = 1.5 Hz, 2H), 7.71–7.79 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 21.6, 47.3, 58.7, 115.9, 116.1, 127.4, 127.8, 128.0, 128.4, 128.5, 128.6, 128.7, 137.2, 140.28, 140.31, 140.6, 163.0, 165.5. MS *m*/*z* (%) 353 (M^+, 1), 338 (4), 249 (4), 210 (83), 194 (12), 143 (17), 105 (100), 91 (54), 77 (7), 65 (4). HRMS (EI) *m*/*z* calcd for $C_{21}H_{20}FNOS$ $[M]^+$: 353.1250, found 353.1256. IR (KBr film) 3087, 3066, 3030, 2922, 1585, 1493, 1454, 1219, 1084, 1065, 870, 768, 697 cm^{-1}.

4.3.8. (*R*,*R*$_S$)-*N*-Benzyl-*N*-(1-phenylethyl)-*p*-fluorobenzenesulfinamide (*R*,*R*$_S$)-1d

Pale yellow oil, R_f = 0.41 (EtOAc/hexane = 1:4), $[\alpha]_D^{25} = +105.8$ (*c* 1.2, EtOAc). ^{1}H NMR ($CDCl_3$) δ 1.69 (d, *J* = 7.0 Hz, 3H), 3.90 (d, *J* = 14.7 Hz, 1H), 3.96 (d, *J* = 14.7 Hz, 1H), 4.33 (q, *J* = 7.0 Hz, 1H), 7.00 (dd, J_1 = 7.9 Hz, J_2 = 1.5 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 7.12–7.22 (m, 6H), 7.25 (dd, J_1 = 6.9 Hz, J_2 = 7.7 Hz, 2H), 7.42–7.49 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 18.3, 47.8, 57.2, 115.9, 116.1, 127.6, 127.7, 127.8, 128.4, 128.49, 128.52, 129.0, 137.0, 139.94, 139.97, 141.7, 163.0, 165.5. HRMS (EI) *m*/*z* calcd for $C_{21}H_{20}FNOS$ $[M]^+$: 353.1250, found 353.1252. IR (neat) 3063, 3030, 2974, 1587, 1487, 1454, 1223, 1151, 1065, 1027, 837, 814, 751, 699 cm^{-1}.

4.4. Typical procedure for the preparation of (*R*$_S$)-methyl arylsulfinates (*R*$_S$)-2

Compound (*R*,*S*$_S$)-**1a** (3.35 g, 9.99 mmol) was dissolved in toluene (20 mL), after which methanol (0.96 g, 29.96 mmol) was added, and the mixture was cooled to −5 °C with a salt-ice bath. A solution of $BF_3{\cdot}OEt_2$ (2.13 g, 15.01 mmol) in toluene (10 mL) was added dropwise over 5 min, and the mixture was stirred at −5 °C for around 2.5 h. The reaction was monitored by TLC (EtOAc/hexane = 1:6). After the mixture was diluted with toluene (50 mL), the reaction was quenched by adding an aqueous saturated solution of $NaHCO_3$ (20 mL). The organic phase was separated, and then washed successively with an aqueous solution of citric acid (20 mL, 15% w/v) and aqueous saturated solution of $NaHCO_3$ (5 mL). The organic solution was dried over anhydrous $MgSO_4$. The solvent was removed by vacuum distillation to afford (*R*$_S$)-methyl benzenesulfinate (*R*$_S$)-**2a** (1.54 g, 9.86 mmol) as a colorless oil in 99% yield. All aqueous phases were combined and adjusted to pH ⩾ 10 by adding powdered KOH. The resulting aqueous mixture was then twice extracted with ethyl acetate (2 × 50 mL). The organic extracts were combined and dried over anhydrous $MgSO_4$. Removal of the solvent by vacuum distillation gave a pale yellow oily residue. After flash chromatography through a short column (5–8 cm) of silica gel, pure (*R*)-*N*-benzyl-1-phenylethanamine (2.07 g, 9.80 mmol) was recovered in 98% yield and could be re-used in the preparation of compounds **1**.

4.4.1. (*R*$_S$)-Methyl benzenesulfinate (*R*$_S$)-2a

$[\alpha]_D^{25} = -195.0$ (*c* 1.2, EtOH) {lit.[54] $[\alpha]_D^{25} = -188.0$ (*c* 1.5, EtOH)}. ^{1}H NMR ($CDCl_3$) δ 3.48 (s, 3H), 7.52–7.59 (m, 3H), 7.68–7.74 (m, 2H). MS *m*/*z* (%) 156 (M^+, 3), 141 (63), 125 (38), 77 (100), 65 (6), 51 (20). IR (neat) 3063, 2985, 2955, 1762, 1582, 1475, 1446, 1363, 1327, 1188, 1145, 1078, 999, 883, 788, 753, 715, 687, 595, 539, 503, 461 cm^{-1}.

4.4.2. (*R*$_S$)-Methyl *p*-toluenesulfinate (*R*$_S$)-2b

$[\alpha]_D^{25} = -210.2$ (*c* 1.4, EtOH) {lit. $[\alpha]_D^{25} = -211.7$ (*c* 4.5, EtOH), calculated from the data of $[\alpha]_D^{25} = -25.4$ (*c* 4.5, EtOH, 12% ee) in Ref. 55}. ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H), 3.47 (s, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H). MS *m*/*z* (%) 170 (M^+, 52), 155 (1), 139 (100), 124 (2), 111 (6), 107 (5), 91 (24), 77 (9), 65 (12). IR (neat) 2940, 1916, 1761, 1596, 1453, 1134, 1082, 964, 814, 713, 682, 628, 574, 447 cm^{-1}.

4.4.3. (*R*$_S$)-Methyl *p*-chlorobenzenesulfinate (*R*$_S$)-2c

$[\alpha]_D^{25} = -173.0$ (*c* 1.3, EtOH). ^{1}H NMR ($CDCl_3$) δ 3.49 (s, 3H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 49.7, 126.9, 129.4, 138.6, 142.5. HRMS (ESI) *m*/*z* calcd for $C_7H_8ClO_2S$ $[M+H]^+$: 190.9934, found 190.9922. IR (neat) 3085, 2941, 1915, 1574, 1475, 1391, 1135, 1087, 961, 826, 744, 711, 687, 592, 577, 504, 485, 429 cm^{-1}.

4.4.4. (*R*$_S$)-Methyl *p*-fluorobenzenesulfinate (*R*$_S$)-2d

$[\alpha]_D^{25} = -171.9$ (*c* 1.3, EtOH). ^{1}H NMR ($CDCl_3$) δ 3.49 (s, 3H), 7.20–7.30 (m, 2H), 7.66–7.76 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 49.6, 116.2, 116.4, 127.8, 127.9, 139.76, 139.79, 163.7, 166.3. HRMS

(EI) *m/z* calcd for $C_7H_7FO_2S$ $[M]^+$: 174.0151, found 174.0148. IR (neat) 3070, 2943, 1907, 1724, 1590, 1492, 1230, 1132, 1093, 963, 838, 717, 685, 573, 452 cm^{-1}.

4.5. Typical procedure for the preparation of (S_S)-arylsulfinamides (S_S)-3

A solution of compound (R_S)-**2**a (1.35 g, 8.64 mmol) in anhydrous THF (20 mL) was cooled to −78 °C by a dry-ice bath under an atmosphere of argon. A solution of $LiN(SiMe_3)_2$ in toluene (13 mL, 1 M, 13.00 mmol) was injected via a syringe. The mixture was stirred at −78 °C for around 3 h, and the reaction was monitored by TLC (EtOAc/hexane = 1:3). After the reaction was complete, an aqueous saturated solution of NH_4Cl (20 mL) was added, and the dry-ice bath was removed. Stirring was continued for 2 h, while the temperature was allowed to gradually to rise to room temperature. Ethyl acetate (20 mL) and water (20 mL) were added. The two phases were separated, and aqueous phase was extracted twice with ethyl acetate (2 × 20 mL). The extracts were combined, and washed successively with an aqueous saturated solution of $NaHCO_3$ (10 mL) and brine (10 mL). After the organic solution was dried over anhydrous $MgSO_4$, solvent was then removed by vacuum distillation. The crude solid product was then triturated in a mixed solvent of ether and hexane (1:1). (S_S)-benzenesulfinamide (R_S)-**3a** (1.03 g, 7.29 mmol) was obtained as white crystal in 84% yield after suction.

4.5.1. (S_S)-Benzenesulfinamide (S_S)-3a

Mp 101–102 °C (lit.[58] 102–103), $[\alpha]_D^{25} = +83.1$ (*c* 1.0, acetone) {lit.[58] $[\alpha]_D^{25} = +82.9$ (acetone)}. HPLC analysis: Column: Diacel AD; mobile phase: hexane/ethanol = 90:10; wavelength: 235 nm; flow rate: 0.5 mL/min; t_R (retention time): 22.4 min for (S_S)-isomer, 26.5 min for (S_R)-isomer; purity: 99.64% for (S_S), 0.36% for (S_R). ^1H NMR ($CDCl_3$) δ 4.50 (s, 2H), 7.47–7.54 (m, 3H), 7.72–7.78 (m, 2H). HRMS (ESI) *m/z* calcd for C_6H_7NOSNa $[M+Na]^+$: 164.0146, found 164.0126. IR (KBr film) 3442, 3282, 3162, 3075, 1629, 1475, 1443, 1401, 1087, 1017, 995, 748, 696 cm^{-1}.

4.5.2. (S_S)-*p*-Toluenesulfinamide (S_S)-3b

Mp 113–114 °C (lit.[59] 115–116 °C), $[\alpha]_D^{25} = +85.5$ (*c* 1.0, $CHCl_3$) {lit.[59] $[\alpha]_D^{25} = +84.5$ (*c* 1.0, $CHCl_3$)}. HPLC analysis: Column: Diacel AD; mobile phase: hexane/ethanol = 90:10; wavelength: 235 nm; flow rate: 0.5 mL/min; t_R (retention time): 21.2 min for (S_S)-isomer, 27.8 min for (S_R)-isomer; purity: 99.68% for (S_S), 0.32% for (S_R). ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H), 4.49 (s, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H). HRMS (ESI) *m/z* calcd for C_7H_9NOSK $[M+K]^+$: 194.0042, found 194.0038. IR (KBr film) 3215, 3106, 1399, 1089, 1051, 1023, 1013, 808, 721, 703 cm^{-1}.

4.5.3. (S_S)-*p*-Chlorobenzenesulfinamide (S_S)-3c

Mp 135–136 °C (lit.[48] 135–137 °C), $[\alpha]_D^{25} = +72.3$ (*c* 0.7, $CHCl_3$). HPLC analysis: Column: Diacel AD; mobile phase: hexane/ethanol = 90:10; wavelength: 235 nm; flow rate: 0.5 mL/min; t_R (retention time): 24.4 min for (S_S)-isomer, 43.5 min for (S_R)-isomer; purity: 99.72% for (S_S), 0.28% for (S_R). ^1H NMR ($CDCl_3$) δ 4.42 (s, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (DMSO-d_6) δ 127.4, 128.6, 135.1, 147.1. HRMS (ESI) *m/z* calcd for C_6H_7NOSCl $[M+H]^+$: 175.9937, found 175.9915. IR (KBr film) 3197, 3103, 1572, 1472, 1396, 1081, 1048, 1023, 1009, 924, 822, 743, 719, 503 cm^{-1}.

4.5.4. (S_S)-*p*-Fluorobenzenesulfinamide (S_S)-3d

Mp 155–156 °C, $[\alpha]_D^{25} = +80.0$ (*c* 0.7, $CHCl_3$). HPLC analysis: Column: Diacel AD; mobile phase: hexane/ethanol = 90:10; wavelength: 235 nm; flow rate: 0.5 mL/min; t_R (retention time): 23.2 min for (S_S)-isomer, 38.5 min for (S_R)-isomer; purity: 99.58% for (S_S), 0.42% for (S_R). ^1H NMR ($CDCl_3$) δ 4.46 (s, 2H), 7.07–7.15 (m, 2H), 7.61–7.69 (m, 2H). ^{13}C NMR (DMSO-d_6) δ 115.5, 115.7, 127.9, 128.0, 144.10, 144.13, 162.0, 164.5. HRMS (EI) *m/z* calcd for C_6H_6NOSF $[M]^+$: 159.0154, found 159.0153. IR (KBr film) 3278, 3164, 3072, 1591, 1491, 1398, 1241, 1158, 1090, 1022, 1011, 837, 816, 672, 533, 436 cm^{-1}.

4.6. Determination of the absolute configurations of (R,S_S)-*N*-benzyl-*N*-(1-phenylethyl)-arylsulfinamides (R,S_S)-1a–1d

4.6.1. Conversion of compounds (R,S_S)-1a and (R,S_S)-1b into (S_S)-butylphenylsulfoxide and (S_S)-butyl-*p*-tolylsulfoxide to determine their absolute configurations

A solution of compound (R,S_S)-**1a** (336 mg, 1.00 mmol) in anhydrous THF (5 mL) was cooled to −78 °C by a dry-ice bath under an atmosphere of argon. A solution of *n*-BuLi (1.5 mL, 1 M, 1.50 mmol) in THF was injected via syringe, and the mixture was then stirred at −78 to −50 °C for 4 h. After the reaction was complete as shown by TLC (EtOAc/hexane = 1:3), it was quenched by adding a dilute aqueous solution of HCl (2 M, 10 mL). The mixture was extracted twice with ethyl acetate (2 × 20 mL). Extracts were combined, washed with brine (10 mL), and then dried over anhydrous $MgSO_4$. Evaporation of solvent under vacuum gave an oily residue which was purified by chromatography (eluent: EtOAc/hexane = 1:4) to afford (S_S)-butyl-phenylsulfoxide (137 mg, 0.75 mmol) in 75% yield.

(S_S)-Butyl-*p*-tolylsulfoxide could be obtained in 78% yield from compound (R,S_S)-**1b** according to the same procedure.

Characterization data for (S_S)-butylphenylsulfoxide: $[\alpha]_D^{25} = -151.9$ (*c* 1.3, acetone) {lit.[52] $[\alpha]_D^{25} = -131.5$ (*c* 0.98, acetone)}. ^1H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.36–1.50 (m, 2H), 1.55–1.64 (m, 1H), 1.68–1.78 (m, 1H), 2.80 (t, *J* = 7.7 Hz, 2H), 7.46–7.54 (m, 3H), 7.60–7.65 (m, 2H). MS *m/z* (%) 182 (M^+, 17), 165 (7), 126 (100), 110 (4), 104 (7), 97 (3), 78 (41). IR (neat) 2959, 2932, 2872, 1477, 1465, 1443, 1088, 1038, 998, 750, 693 cm^{-1}.

Characterization data for (S_S)-butyl-*p*-tolylsulfoxide: $[\alpha]_D^{25} = -162.6$ (*c* 1.8, acetone) {lit.[53] $[\alpha]_D^{25} = -162.3$ (*c* 3.2, acetone)}. ^1H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.36–1.49 (m, 2H), 1.54–1.63 (m, 2H), 1.66–1.75 (m, 1H), 2.41 (s, 3H), 2.72–2.82 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H). MS *m/z* (%) 196 (M^+, 20), 179 (10), 140 (100), 124 (4), 104 (9), 92 (68). IR (neat) 2959, 2930, 2871, 1597, 1494, 1463, 1400, 1380, 1087, 1038, 813 cm^{-1}.

4.6.2. Determination of the absolute configurations of compounds (R,S_S)-1c and (R,S_S)-1d by X-ray analysis of their single crystals

A clear solution of compound (R,S_S)-**1c** (0.25 g) in ether (20 mL) was put into a flask. The flask was then sealed with a thin film of polyvinyl chloride (PVC), and allowed to stand overnight at room temperature. As the ether gradually evaporated, crystals of compound (R,S_S)-**1c** were formed on the bottom of the flask.

Crystals of compound (R,S_S)-**1d** were obtained according to the same procedure as above.

Crystal data for (R,S_S)-*N*-benzyl-*N*-(1-phenylethyl)-*p*-chlorobenzenesulfinamide (R,S_S)-**1c**: $C_{21}H_{20}ClNOS$, M_r = 369.89, orthorhombic, space group $P2_12_12_1$, *a* = 7.4740 (7), *b* = 12.7861 (12), *c* = 19.7011 (19) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *V* = 1882.7 (3) $Å^3$, *Z* = 4, D_C = 1.305 Mg/m^3, μ (Mo Kα) = 0.322 mm^{-1}, *F* (0 0 0) = 776, colorless prism, dimensions: 0.428 × 0.357 × 0.311 mm. *R* = 0.0414, *wR* = 0.0994, goodness-of-fit on F^2 = 0.988 for 3666 observed reflections with $I > 2\sigma(I)$.

Crystal data for (R,S_S)-*N*-benzyl-*N*-(1-phenylethyl)-*p*-fluorobenzenesulfinamide (R,S_S)-**1d**: $C_{21}H_{20}FNOS$, M_r = 353.44, orthorhombic, space group $P2_12_12_1$, *a* = 7.4856 (14), *b* = 12.703 (3), *c* = 19.159 (4) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *V* = 1821.9

(6) Å^3, Z = 4, D_C = 1.289 Mg/m^3, μ (Mo Kα) = 0.195 mm^{-1}, F(0 0 0) = 744, colorless prism, dimensions: 0.408 × 0.356 × 0.311 mm. R = 0.0331, wR = 0.0743, goodness-of-fit on F^2 = 0.989 for 2622 observed reflections with $I > 2\sigma(I)$.

Diffraction intensities were collected on a Bruker SMART CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The absorption was corrected empirically. The structure was solved by direct methods using SHELXS-97 and refined on F^2 by full-matrix least-squares methods using SHELXL-97. All non-H atoms were refined anisotropically and H-atoms isotropically.

Crystallographic data for the structure herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 797311 and 797312. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Tel.: +44(0) 1223 762910, fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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