An Asymmetric Biaryl Suzuki Cross-Coupling Reaction: Stereogenic Benzylic Carbinols as Chiral Auxiliaries

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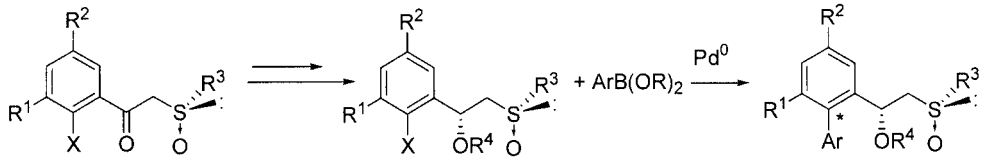
Asymmetric biaryl Suzuki coupling reactions were performed with various aryl- or naphthylhalide-bearing enantiomerically pure benzylic alcohols and aryl- or naphthylboronic acids (or esters). The stereogenic benzylic alcohol was introduced by diastereoselective reduction of the arylhalide bearing a β-keto sulfoxide. In the presence of $Pd(OAc)_2$/CsF and dppf or PPh_3 excellent yields and atropodiastereoselectivities were obtained. The absolute configurations of the biaryls were determined by X-ray crystallography and ^1H NMR NOESY experiments.

Introduction

ortho-Substituted biphenyls (or more generally biaryls)[1–4] are found in a wide variety of natural products including alkaloids, coumarins, flavonoids, lignans, etc. Compounds incorporating biaryl building blocks also find applications as chiral reagents, chiral phases for chromatography, and chiral liquid crystals. Many efficient methodologies for asymmetric coupling between the two aromatic portions have been described using either chiral ligands, stoichiometric chiral auxiliaries, or chiral starting materials.[5] Currently, a very important challenge in the synthetic usefulness of this biaryl coupling reaction is the development of a highly efficient asymmetric version.

Since its discovery in 1981 the Suzuki–Miyaura coupling[6] has become a powerful tool for the construction of a biaryl bond due to its efficiency and wide functional-group tolerance. However, efficient methodologies for an asymmetric Suzuki biaryl coupling reaction are relatively rare and have been reported only in the past few years. Three strategies have been applied for the synthesis of chiral biaryls by Suzuki coupling. The first one, described by Uemura,[5i] consists of using chiral arene(chromium)halide complexes. The second is another atropodiastereoselective method reported by Lipshutz using a stereocenter attached to a phosphane ligand as chiral auxiliary.[5e] In the third strategy, the atroposelectivity is induced by chiral catalysts. This was first illustrated in the total synthesis of Vancomycin[7] by Nicolaou, who obtained a chiral biaryl with up to 55% diastereomeric excess in the presence of a chiral ligand. Enantioselective Suzuki couplings induced by a chiral ligand have also been reported by Cammidge,[8] Buchwald,[9] Baudoin,[10] Johannsen,[11] and, very recently, by Mikami.[12] We recently communicated the use of BINAP or Tol-BINAP in the synthesis of 2,2′-dimethoxy-1,1′-dinaphthalene, and showed that the ligand-to-palladium ratio influences the sense of the enantioselection.[13]

We report here the use of benzylic carbinols as efficient stereochemical controllers in the biaryl Suzuki coupling reaction.[14] This stereogenic alcohol was introduced by the reduction of a β-keto sulfoxide[15] in the position *ortho* to the aryl halide unit (Scheme 1).



Scheme 1. Palladium-catalyzed Suzuki coupling with an aryl iodide bearing a β-hydroxysulfoxide

The presence of a chiral center such as a chiral benzylic alcohol in the *ortho* position of the aryl halide could be very useful in the total synthesis of biologically active compounds such as (–)-Steganacin,[16] Korupensamine A,[17] and the biaryl unit of Vancomycine,[18] which could arise from precursors bearing a benzylic stereocenter (Scheme 2).

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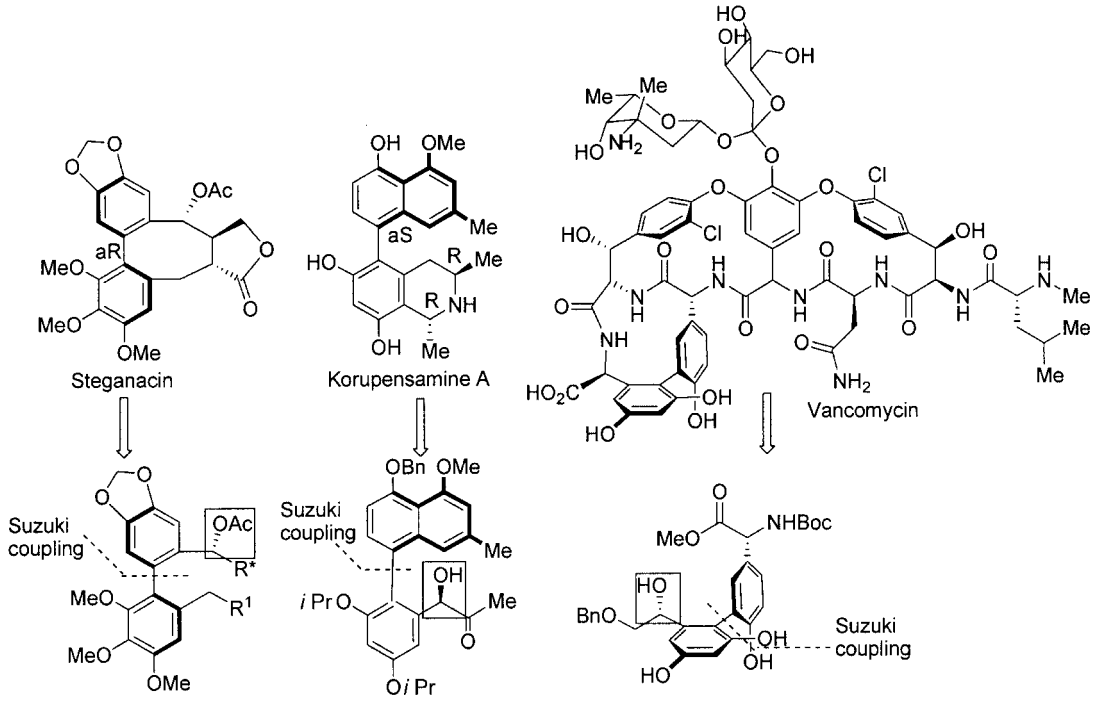
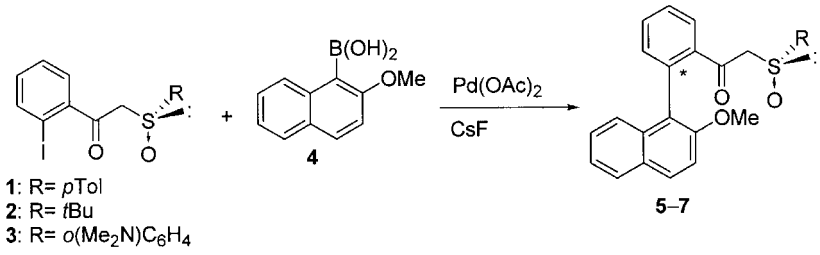


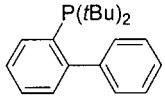
Scheme 2. Retrosynthesis of Steganacin, Korupensamine A, and Vancomycin

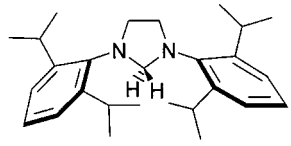
Table 1. Suzuki reactions of **1**–**3** with 2-methoxy-1-naphthylboronic acid (**4**)



1: R= *p*Tol
2: R= *t*Bu
3: R= *o*(Me_2N)C_6H_4

Entry[a]	Substrate	Solvent	Ligand	Biaryl, yield (%)[b]	*dr*[c]
1	**1**	DME	PPh_3	**5**, 28	60:40
2	**1**	DME	dppf	**5**, 38	65:35
3	**1**	DME	BINAP	**5**, 69	60:40
4	**1**	DME	(*R*)-BINAP	**5**, 58	60:40
5	**1**	dioxane	dppf	**5**, 54	70:30
6	**1**	dioxane	A	**5**, 56	60:40
7	**1**	dioxane	B	**5**, 57	60:40
8	**1**	THF	dppf	**5**, 60	70:30
9	**2**	dioxane	dppf	**6**, 33	60:40
10	**3**	DME	dppf	**7**, 15	60:40

Ligand A: 

Ligand B: 

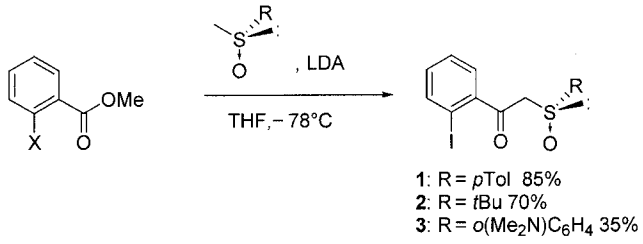
[a] Reaction conditions: **1**–**3** (1 equiv.), **4** (1.5 equiv.), $Pd(OAc)_2$ (10 mol%), ligand (15 or 30 mol%), CsF (4.5 equiv.), 50 °C, 3–5 h. [b] Yield of product isolated after chromatography. [c] Determined by ^1H NMR spectroscopy after chromatography.

Simultaneously to our first communication,[14] a diastereoselective Suzuki coupling between a chiral benzylic alcohol and sterically hindered arylboronic esters was reported in an approach to cyclooctadiene lignans.[19]

Results and Discussion

Search for the Optimal Experimental Conditions for the Suzuki Coupling Reaction with Aryl-Halides-Containing β-Keto Sulfoxides

Recently we reported an efficient Suzuki cross-coupling[13] of sterically hindered substrates inDME using cesium fluoride as a base and $Pd(OAc)_2/PPh_3$ as catalyst. In order to study the induction from the stereogenic β-keto sulfoxide to the chiral axis we first explored the Suzuki coupling reaction between 2-methoxy-1-naphthylboronic acid (**4**)[20] and the readily available enantiopure 1-[(+)-aryl or (–)-*tert*-butylsulfinyl]-2-(*o*-iodophenyl)-2-ethanone (**1**–**3**) under previously reported conditions[13] (Table 1). The preparation of compounds **1**–**3** was achieved in good yields by condensation of the lithiated anion of (+)-[(S)*R*] methyl *p*-tolyl sulfoxide,[21] (+)-[(S)*R*] (*o*-dimethylaminophenyl) methyl sulfoxide,[22] or (–)-[(S)*S*] *tert*-butyl methyl sulfoxide[23] to 2-iodo-1-methylbenzoate in THF (Scheme 3).



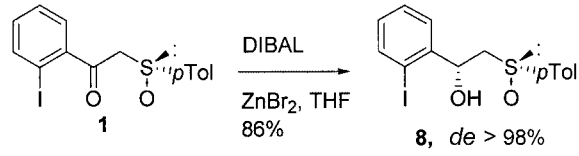
Scheme 3. Synthesis of the β-keto sulfoxide derivatives **1**–**3**

The Pd-catalyzed Suzuki cross-couplings took place with $Pd(OAc)_2$[24] in the presence of a phosphane [PPh_3, dppf, racemic BINAP, (*R*)-BINAP, 2-(di-*tert*-butylphosphanyl)biphenyl[25] (Ligand A)] or imidazolidine ligand [1,3-bis(2,6-diisopropylphenyl)imidazolidine[26] (Ligand B)] (Table 1).

In the coupling reaction with the iodophenyl-containing β-keto-*p*-tolylsulfoxide **1**, dppf was found to give the best diastereomeric ratio[27] in dioxane or THF with CsF as base (Table 1, entries 5 and 8) but no reaction occurred in the presence of Ag_2CO_3 or K_3PO_4. Changing the substitution at the sulfoxide did not improve the selectivity and decreased the yield (Table 1, entries 9 and 10).

Suzuki Coupling Reactions with Aryl-Halide-Containing β-Hydroxysulfoxides

In view ofthe modest induction with the β-keto sulfoxide auxiliaries we reduced the β-keto sulfoxide **1** in order to obtain the desired stereogenic benzylic alcohol. The reduction was performed with DIBAL in the presence of $ZnBr_2$, which is known to provide the desired [2*R*,(S)*R*]-β-hydroxysulfoxide **8** in 86% yield and excellent diastereomeric excess (>98%; Scheme 4).[28] In this case the benzyloxy group is *syn* to the bulky substituent (*p*-tolyl group) of the sulfoxide.

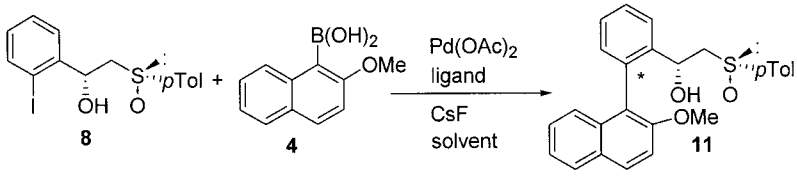


Scheme 4. Synthesis of the β-hydroxysulfoxide derivative **8**

Table 2 summarizes the results obtained in the palladium-catalyzed Suzuki coupling of 2-methoxy-1-naphthylboronic acid (**4**)[20] and the enantiopure iodophenyl-containing β-hydroxysulfoxide **8**.

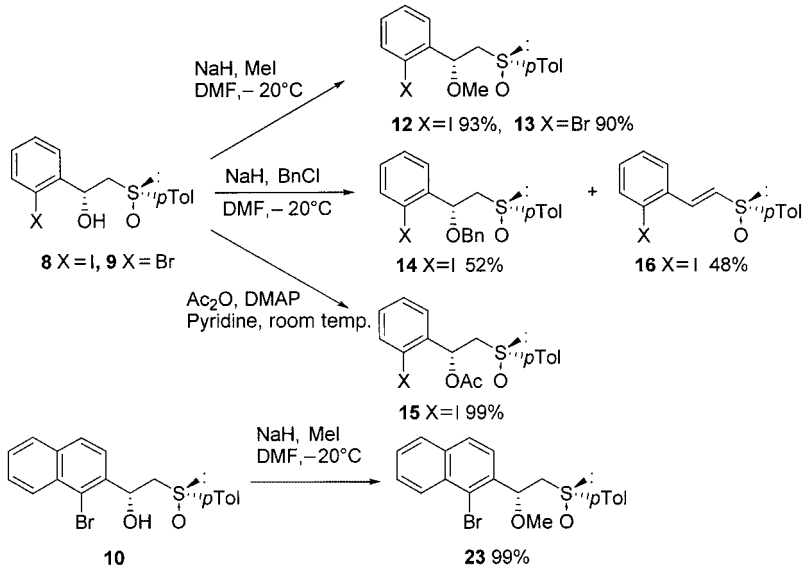
A remarkable stereocontrol (*dr* = 98:2)[29] was obtained with a combination of dppf and $Pd(OAc)_2$ in dioxane or THF, with a yield of 70% in dioxane at reflux (Table 2, entries 1 and 2). Use of racemic BINAP or 2-(di-*tert*-butylphosphanyl)biphenyl(Ligand A) did not provide any coup-

Table 2. Suzuki reactions of **8** with 2-methoxynaphthylboronic acid (**4**)



Entry[a]	Solvent	Ligand	Biaryl **11** yield (%)[c]	*dr*[b]	Starting material yield (%)	Reduction product yield (%)
1	dioxane	dppf	70	97:3	9	20
2	THF	dppf	50	98:2	33	17
3	dioxane	BINAP	0		85	<15
4	dioxane	A	0		>85	
5	dioxane	B	50	15:85	50	0

[a] Reaction conditions: **8** (1 equiv.), **4** (2 equiv.), $Pd(OAc)_2$ (10 mol%), bidentate ligand (15 mol%), monodentate ligand (30 mol%), CsF (4 equiv.), 70 °C, 3–5 h. [b] Determined by ^1H NMR spectroscopy of the crude mixtures. [c] Yield of product isolated after chromatography.

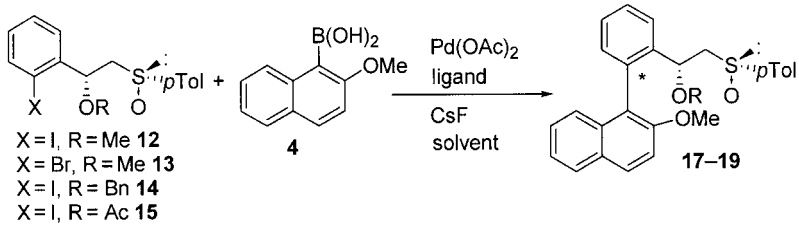


Scheme 5. Synthesis of the protected β-hydroxysulfoxide derivatives **11, 12, 13, 15**, and **23**

ling product. Surprisingly, 1,3-bis(2,6-diisopropylphenyl) imidazolidine(Ligand B) gave the coupling product with opposite axial chirality (*dr* = 15:85; Table 2, entry 5). However, we also observed the hydrodehalogenation of the aryl iodide (20% in the case of the coupling reaction performed in dioxane). Either the free hydroxy group or the acidic protons of the boronic acid might be responsible for the reduction of the aryl halide. Thus, we first protected the hydroxy group of the β-hydroxysulfoxide derivatives as a methoxy by treatment with NaH and methyl iodide in DMF at –20 °C to give **12** in 93% yield starting from the iodide, and **13** in 90% yield and **23** in 99% yield starting from the corresponding bromides. We also protected the hydroxy group as a benzyloxy by treatment with benzyl chloride under the same conditions to give **14** in 52% yield (in this case a side-product of elimination **16** was obtained in 48% yield). Compound **15**, with an acetoxy group, was obtained in 99% yield upon treatment with Ac_2O and DMAP in pyridine (Scheme 5).

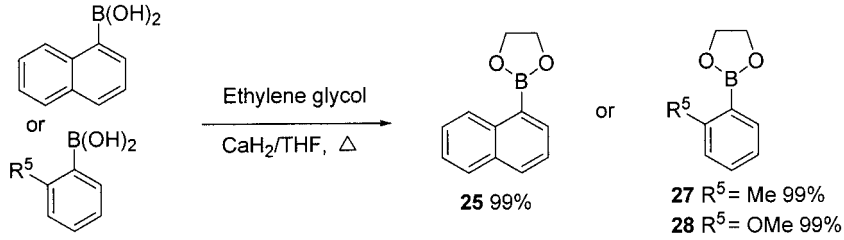
Table 3 summarizes the results obtained in the palladium-catalyzed Suzuki coupling of 2-methoxy-1-naphthylboronic acid (**4**)[20]and the protected aryl iodides **12**–**15**. With methoxy, benzyloxy, and acetoxy derivatives, excellent yields and diastereomeric excess were obtained in only one hour (Table 3, entries 1, 3, 4). No trace of the other diastereomer was detected by ^1H and ^{13}C NMR spectroscopy. Starting from the bromide **13** instead of the iodide, the results were also excellent (Table 3, entry 2). Changing the ligand from dppf to PPh_3 afforded the coupling product in a slightly lower yield (93%) but still with excellent diastereo-

Table 3. Suzuki reactions of phenyl-halide-containing protected β-hydroxy derivatives **12**–**15** with 2-methoxynaphthylboronic acid (**4**)



Entry[a]	Halide	$Pd(OAc)_2$ (mol%)	Ligand	Biaryl, yield (%)	*dr*[b] (%)
1	**12**	10	dppf	**17**, 99	>99:1
2	**13**	10	dppf	**17**, 98	>99:1
3	**14**	10	dppf	**18**, 97	>99:1
4	**15**	10	dppf	**19**, 99	>99:1
5	**12**	10	PPh_3	**17**, 93	>99:1
6	**12**	3	PPh_3	**17**, 93	>99:1
7	**12**	2	PPh_3	**17**, 68	>99:1
8	**12**	1	PPh_3	**17**, 0	–

[a] Reaction conditions: **12**–**15** (1 equiv.), **4** (2 equiv.), $Pd(OAc)_2$ (*x* mol%), bidentate ligand (1.5*x* mol%), monodentate ligand (3*x* mol%), CsF (4 equiv.), 110 °C, 1 h. [b] Determined by ^1H NMR spectroscopy of the crude mixtures.



Scheme 6. Synthesis of the boronic esters **25, 27**, and **28**

selectivity (Table 3, entry 5). We also tried to decrease the amount of catalyst; 3 mol% $Pd(OAc)_2$ with 9 mol% $PPh_3$was sufficient to obtain the same yield and selectivity. With smaller quantities the yield of coupling product decreased, and with 1 mol% $Pd(OAc)_2$ and 3 mol% PPh_3 no reaction occurred (Table 3, entries 6–8).

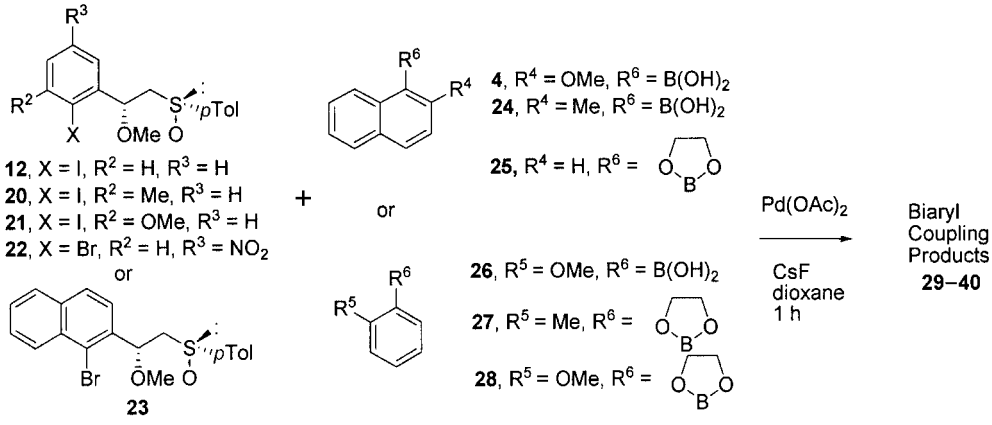
To investigate the scope of this method, and in order to avoid the reductive hydrodehalogenation, we synthesized, in good yields, the boronic esters **25**, **27**, and **28** by condensation of ethylene glycol with the corresponding boronic acids in the presence of CaH_2 in refluxing THF[30] (Scheme 6).

Scope of the Palladium-Catalyzed Suzuki Coupling Reaction with Aryl-Halide-Containing Protected β-Hydroxysulfoxides

Table 4 summarizes the results obtained in the palladium-catalyzed Suzuki coupling of various boronic acids[31] (**4**, **24**, and **26**) or esters[32] (**25**, **27**, and **28**) with β-methoxysulfoxide derivatives **12** and **20**–**23**.

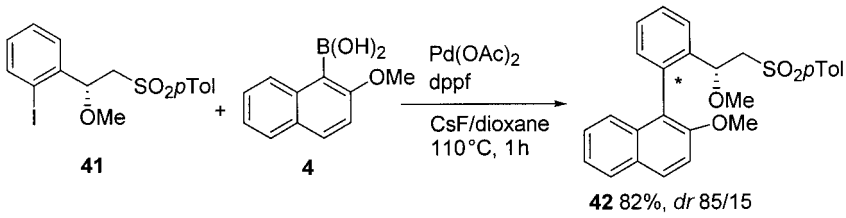
The coupling reaction of **12** with 2-methyl-1-naphthylboronic acid (**24**) occurred with excellent yield and diastereoselectivity (Table 4, entry 1). Starting from the bromide **22**,

Table 4. Suzuki coupling reactions between β-methoxysulfoxide derivatives **12** and **20**–**23** and boronic acids **4**, **24**, and **26** or boronic esters **25**, **27**, and **28**

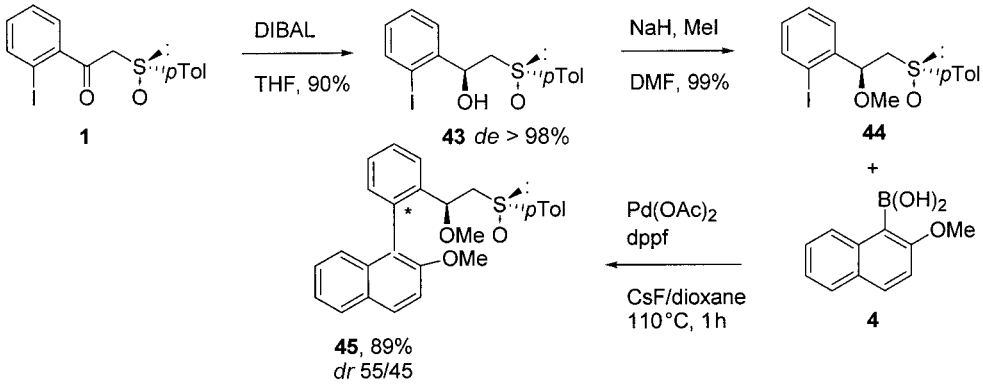


Entry[a]	Halide	Boronic derivative	Ligand	Biaryl, yield[b] (%)	*dr*[c]
1	**12**	**24**	dppf[d]	**29** 99	>99:1
2	**20**	**25**	PPh_3[e]	**30** 88	90:10
3	**20**	**27**	PPh_3[e]	**31** 82	75:25
4	**20**	**28**	PPh_3[e]	**32** 89	80:20
5	**21**	**25**	PPh_3[e]	**33** 86	95:5
6	**21**	**27**	PPh_3[e]	**34** 86	90:10
7[f]	**21**	**26**	dppf[d]	**35** 80	85:15
8[f]	**21**	**28**	dppf[d]	**35** 95	85:15
9	**23**	**25**	dppf[d]	**36** 88	85:15
10	**23**	**27**	PPh_3[e]	**37** 75	75:25
11	**23**	**28**	PPh_3[e]	**38** 75	80:20
12	**22**	**4**	PPh_3[e]	**39** 93	>99:1
13	**22**	**24**	PPh_3[e]	**40** 84	>99:1

[a] Reaction conditions: **12**, **20**–**23** (1 equiv.), **4**, **24**–**28** (2 equiv.), CsF (4 equiv.), reflux dioxane, 1 h. [b] Isolated product after chromatography. [c] Determined by ^1H NMR spectroscopy on the crude mixture. [d] $Pd(OAc)_2$ (10 mol%), dppf (15 mol%). [e] $Pd(OAc)_2$ (3 mol%), PPh_3 (9 mol%). [f] 70 °C.



Scheme 7. Suzuki coupling between the sulfone **41** and 2-methoxy-1-naphthylboronic acid (**4**)



Scheme 8. Suzuki coupling between **44** and **4**

with a nitro group in the *para* position, and 2-methoxy-1-naphthylboronic acid (**4**) or 2-methyl-1-naphthylboronic acid (**24**), the coupling products were obtained very efficiently (Table 4, entries 12, 13). β-Methoxysulfoxide **23**, bearing a naphthyl moiety,gave good yields in the Suzuki coupling with the boronic esters **25**, **27**, and **28** but control of the axial chirality was slightly lower (up to 85:15 *dr*) (Table 4, entries 9–11). The coupling reaction between aryl iodides bearing a methoxy group in the *ortho* position (**21)** or a methyl group in the *ortho* position (**20)** and phenyl- or naphthylboronic acids or estersafforded the coupling products in very good yields and selectivities of up to 95:5 *dr* (Table 4, entries 2–8).

In order to determine the relative contribution of both stereogenic centers to the asymmetric induction of the coupling reaction, we oxidized the sulfoxide into the corresponding sulfone **41**. The coupling reaction of sulfone derivative **41** with 2-methoxy-1-naphthylboronic acid (**4**) afforded the corresponding coupling product **42** in 82% yield and an 85:15 diastereomeric ratio (Scheme 7). Thus, oxidation of the coupling product **17**,[33] obtained as a single atropodiastereomer, was performed and, as expected, we obtained exactly the same ^{1}H NMR spectra as the ^{1}H NMR spectra of the major atropoisomer **42**. This result indicates that the diastereoselectivity of the coupling reaction is mainly controlled by the stereogenic benzylic carbon atom, which is closer to the biaryl C–C bond.

We also synthesized the [2*S*,(S)*R*]-β-hydroxysulfoxide **43**, the epimer of **8** at the stereogenic carbon atom, by diastereoselective reduction of the β-keto sulfoxide **1** with DIBAL only. Here, the hydroxy group is *anti* to the bulky substituent of the sulfoxide. After protection of the hydroxy group as methoxy (**44**), we performed the coupling reaction of **44** with 2-methoxy-1-naphthylboronic acid (**4**). The coupling product **45** was obtained in 89% yield but only a 55:45 diastereomeric ratio (Scheme 8). Reduction of **17** and **45** with Raney nickel[34] gave two different diastereomers, thus indicating that the two coupling products have the same configuration of the chiral axis (a pair of enantiomeric biaryls would otherwise have been obtained).

At the moment we are performing a number of experiments on specific substrates in order to understand this high atropodiastereoselectivity and to investigate the sense of the chiral induction. The results will be reported in due course.

The absolute structures of the compounds **38** and **11** were determined by X-ray crystallographic analysis.[35] In the case of the coupling reaction between **23** and **28**, the absolute configuration of the major diastereomer of **38** is [a*S*,2*R*,(S)*R*] with the aromatic methoxy in front (Figure 1). NOESY correlations were in agreement with the solid-state structure experiment, with a correlation between the aromatic methoxy and the aromatic hydrogen from the *p*-tolyl,

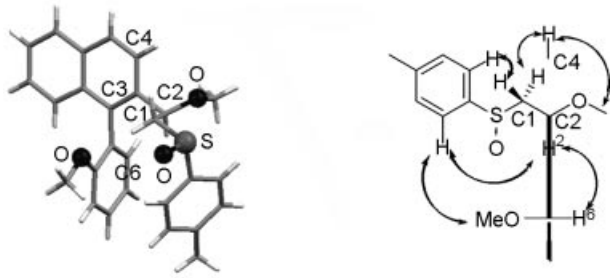


Figure 1. X-ray crystal structure (left) and NOESY experiment correlations (right) of biaryl [a*S*,1*R*,(S)*R*]-**38**

and a correlation between H^2 and the *ortho* aromatic hydrogen of the phenyl moiety.

In the case of the coupling reaction between **8** and **4** in the presence of ligand B, single crystals of the major diastereomer **11** revealed that the chiral axis was a*S* with the naphthylic methoxy in front (Figure 2). NOESY experiments confirmed this configuration, with a correlation between the H^2 and the rear-facing naphthyl hydrogen, as well as a correlation between the OH and the naphthyl hydrogen H^8. Thus, using dppf or PPh_3 in this coupling reaction gave the coupling product with an a*R* chiral axis and the naphthylic methoxy at the back. The agreement between the NOESY correlations and the solid-state structure allowed us to deduce the absolute configuration of all the major biaryl products formed from NOESY experiments (see Supporting Information and Scheme 9).

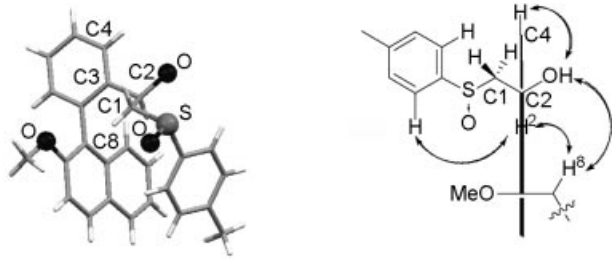
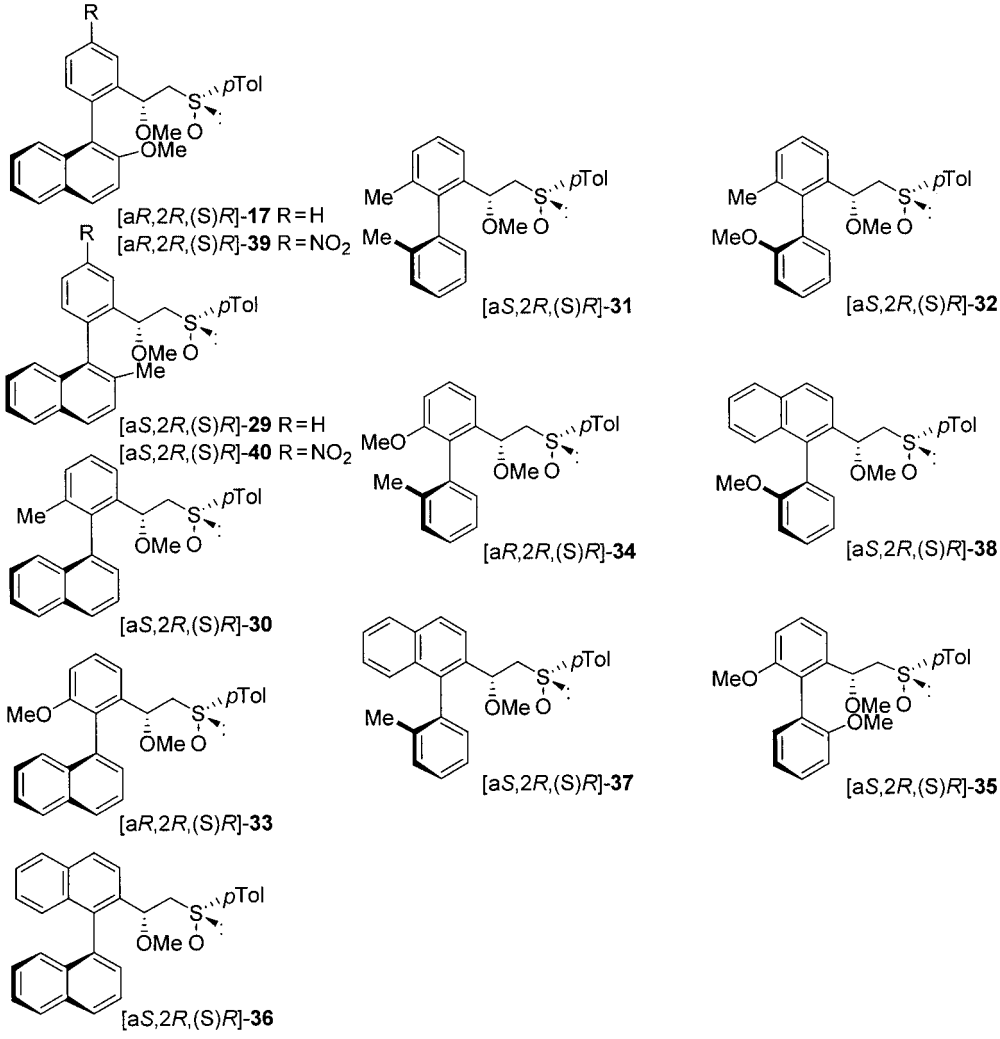


Figure 2. X-ray crystal structure (left) and NOESY experiment correlations (right) of biaryl [a*S*,1*R*,(S)*R*]-**11**

Conclusions

We have performed a new atropodiastereoselective Suzuki coupling reaction that allows the synthesis of biphenyl, binaphthyl, and phenylnaphthyl derivatives with an excellent control of the axial chirality and excellent yield. A 1,3-chirality induction from a stereogenic benzyloxy group to the chiral axis is mainly responsible for the atropodiastereoselectivity. This methodology provides an efficient catalytic access to axially chiral biaryls bearing a benzylic stereocenter. The synthesis of the biaryl part of Vancomycin as well as the synthesis of Steganacin using this methodology will be reported in due course.



Scheme 9. Absolute configuration of the major biaryl compounds obtained in the presence of PPh_3 or dppf

Experimental Section

General Remarks: Unless otherwise specified, materials were purchased from commercial suppliers and used without further purification. THF, diethyl ether, and dioxane were distilled from sodium/benzophenone immediately before use. Triethylamine and diisopropylamine were distilled from calcium hydride and stored over potassium hydroxide. Moisture-sensitive reactions were conducted in oven- or flame-dried glassware under an argon atmosphere. All reactions were stirred magnetically and monitored by thin-layer chromatography using precoated silica gel (60 F 254) plates. Column chromatography was performed with the indicated solvents using silica gel-60. NMR spectra were recorded at room temperature using $CDCl_3$ (δ = 7.26 ppm) as the reference (Bruker AC-200, Bruker Avance 300 and Bruker Avance 400, ^1H at 200, 300 and 400 MHz and ^{13}C at 50, 75 and 100 MHz, respectively). Chemical shifts are expressed in ppm and coupling constants (J) in hertz. Optical rotations were determined with a Perkin–Elmer 241 MC polarimeter operating at the sodium D line at 20 °C. IR were recorded with a Perkin–Elmer Spectum One spectrophotometer; $\tilde{\nu}$ values are quoted in cm^{-1}. X-ray diffraction data collection was carried out with a Kappa CCD diffractometer equipped with an Oxford liquid N_2 device, using graphite-monochromatised Mo-K_α radiation. Diffraction data were corrected for absorption and analysed using the OpenMolEn package.[36] All non-H atoms were refined anisotropically.

General Procedure for the Preparation of Aryl Halides Bearing a β-Keto Sulfoxide (1–3): A solution of *n*BuLi (1.6 M in hexane, 8.0 mmol, 2 equiv.) was added at –15 °C to a solution of diisopropylamine (8.0 mmol, 2 equiv.) in anhydrous THF (20 mL). After 30 min at –15 °C the reaction mixture was warmed to 0 °C and a solution of sulfoxide (8.0 mmol, 2 equiv.) in THF (20 mL) was added. After 30 min the lithiated anion was added dropwise by cannula at 0 °C to a solution of 2-iodo-1-methyl benzoate (4.0 mmol, 1 equiv.) in THF (20 mL). The resulting mixture was warmed to room temp. and after 4 h was hydrolyzed at 0 °C by addition of a saturated solution of NH_4Cl and acidified to pH 2 with 5% H_2SO_4. The aqueous layer was extracted with EtOAc. The combined organic layers were then washed with brine, dried with $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by flash chromatography over silica gel.

(+)-[(S)*R*]-1-(2-Iodophenyl)-2-(*p*-tolylsulfinyl)ethanone (1): Yellow solid (82% yield). R_f = 0.55 (EtOAc). M.p. 65–68 °C. $[\alpha]_D^{20}$ = +133.1 (c = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3463, 3053, 2920, 1682, 1595, 1579, 1493, 1462, 1426, 1398, 1378, 1284, 1254, 1191, 1117, 1084, 1056, 1016, 984, 812, 757. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.4 (s, 3 H, CH_3), 4.46 (AB, $J_{A,B}$ = 13.9 Hz, $\Delta\nu$ = 58 Hz, 2 H, CH_2), 7.14 (ddd, J = 7.9, 6.1, 2.9 Hz, 1 H, H_{ar}), 7.37–7.44 (m, 2 H, H_{ar}), 7.45 (A_2B, $J_{A,B}$ = 8 Hz, $\Delta\nu$ = 82 Hz, 4 H, H_{ar}), 7.91 (br. d, J = 7.9 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.4 (CH_3), 68.0 (CH_2), 91.6 (C_{ar}), 124.4 (CH_{ar}), 128.2 (CH_{ar}), 129.6 (CH_{ar}), 130.1 (CH_{ar}), 132.7 (CH_{ar}), 139.9 (C_{ar}), 140.9 (CH_{ar}), 142.3 (C_{ar}), 142.3 (C_{ar}), 194.7 (CO) ppm.

(–)-[(S)*S*]-2-(*tert*-Butylsulfinyl)-1-(2-iodophenyl)ethanone (2): Yellow oil (66% yield). R_f = 0.32 (EtOAc/hexanes, 9:1). $[\alpha]_D^{20}$ = –140.2 (c = 0.94, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2963, 2868, 1693, 1581, 1560, 1462, 1429, 1392, 1362, 1288, 1246, 1189, 1134, 1039, 987, 885, 789, 749. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.32 (s, 9 H, *t*Bu), 4.07 (s, 2 H, CH_2), 7.17 (td, J = 7.8, 1.6 Hz, 1 H, H_{ar}), 7.47 (td, J = 7.8, 1.7 Hz, 1 H, H_{ar}), 7.63 (dd, J = 7.8, 1.7 Hz, 1 H, H_{ar}), 7.95 (br. d, J = 7.8 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 22.8 (*t*Bu), 54.7 (*C*CH_3), 58.3 (CH_2), 91.4 (C_{ar}), 128.4 (CH_{ar}), 129.6 (CH_{ar}), 132.6 (CH_{ar}), 140.8 (CH_{ar}), 142.8 (C_{ar}), 196.4 (CO) ppm.

(+)-[(S)*R*]-2-[2-(Dimethylamino)phenylsulfinyl]-1-(2-iodophenyl)-ethanone (3): Orange oil (24% yield). R_f = 0.53 (EtOAc/hexanes, 1:1). $[\alpha]_D^{20}$ = +252 (c = 1, $CHCl_3$). ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.68 (s, 6 H, NMe_2), 4.53 (AB, $J_{A,B}$ = 13.4 Hz, $\Delta\nu$ = 75 Hz, 2 H, CH_2), 7.06–7.16 (m, 2 H, H_{ar}), 7.22–7.52 (m, 4 H, H_{ar}), 7.82–7.93 (m, 2 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 44.6 (NMe_2), 64.1 (CH_2), 91.6 (CH_{ar}), 119.8 (CH_{ar}), 124.6 (CH_{ar}), 125.2 (CH_{ar}), 128.1 (CH_{ar}), 129.7 (CH_{ar}), 131.9 (CH_{ar}), 132.3 (CH_{ar}), 136.7 (C_{ar}), 140.7 (C_{ar}), 142.5 (C_{ar}), 150.5 (C_{ar}), 194.7 (CO) ppm.

General Procedure for the Synthesis of Aryl Halides Bearing a β-Hydroxysulfoxide: A solution of the corresponding β-keto sulfoxide (15.6 mmol, 1 equiv.) and dry zinc bromide in THF (5 mL) was stirred at room temp. for 15 min and then cooled to –78 °C. DIBALH (1 M in toluene) (31.23 mmol, 2 equiv.) was added dropwise, the resulting mixture was stirred at –78 °C for 5 h, and then quenched by addition of a saturated solution of sodium tartrate. The resulting mixture was vigorously stirred until the phases were easily separated. The aqueous layer was then extracted with EtOAc and the combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified by flash chromatography.

(–)-[1*R*,(S)*R*]-1-(2-Iodophenyl)-2-(*p*-tolylsulfinyl)ethanol (8): White solid (86% yield; 5.2 g, 13.4 mmol; *de* > 98%); R_f = 0.3 (EtOAc/hexanes, 1:1). M.p. 169–173 °C. $[\alpha]_D^{20}$ = –76 (c = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3308, 2919, 1583, 1596, 1563, 1493, 1459, 1437, 1399, 1338, 1309, 1221, 1195, 1111, 1071, 1083, 1024, 1010, 987, 910, 835, 808, 760, 735. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.41 (s, 3 H, CH_3), 3.02 (AB part of an ABX system, $J_{A,B}$ = 13.2, $J_{A,X}$ = 10.1, $J_{B,X}$ = 1.6 Hz, $\Delta\nu$ = 70 Hz, 2 H, CH_2), 4.64 (br. s, 1 H, OH), 5.57 [X part of an ABX system (br. d), $J_{A,X}$ = 10.1 Hz, 1 H, C*H*(OH)], 6.97 (td, J = 7.8, 1.7 Hz, 1 H, H_{ar}), 7.37 (br. t, J = 7.8 Hz, 1 H, H_{ar}), 7.49 (A_2B_2, $J_{A,B}$ = 7.9 Hz, $\Delta\nu$ = 73 Hz, 4 H, H_{ar}), 7.61 (dd, J = 7.8, 1.7 Hz, 1 H, H_{ar}), 7.78 (dd, 1 H, J = 7.8 Hz, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.4 (CH_3), 62.4 (CH_2), 75.1 [CH(OH)], 96.4 (C_{ar}), 123.9 (CH_{ar}), 127.5 (CH_{ar}), 128.8 (CH_{ar}), 129.7 (CH_{ar}), 130.2 (CH_{ar}), 139.3 (CH_{ar}), 140.4 (C_{ar}), 142.2 (C_{ar}), 143.5 (C_{ar}) ppm. $C_{15}H_{15}IO_2S$ (386.25): calcd. C 46.64, H 3.91, S 8.3; found C 46.66, H 3.98, S 8.4.

(+)-[1*S*,(S)*R*]-1-(2-Iodophenyl)-2-(*p*-tolylsulfinyl)ethanol (43): White solid (90% yield; *de* > 98%); R_f = 0.47 (EtOAc/hexanes, 1:2). M.p. 127–128 °C. $[\alpha]_D^{20}$ = +173.1 (c = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3264, 1596, 1584, 1563, 1492, 1459, 1436, 1315, 1197, 1110, 1084, 1068, 1028, 1009, 808, 756. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.45 (s, 3 H, CH_3), 3.00 (AB part of an ABX system, $J_{A,B}$ = 13.9, $J_{A,X}$ = 1.9, $J_{B,X}$ = 9.8 Hz, $\Delta\nu$ = 126 Hz, 2 H, CH_2), 5.10 (d, J = 1.9 Hz, 1 H, OH), 5.33 [X part of an ABX system (br. dt), $J_{A,X}$ = 1.9, $J_{B,X}$ = 9.8 Hz, 1 H, C*H*(OH)], 6.96 (td, J = 7.8, 1.8 Hz, 1 H, H_{ar}), 7.39 (m, 1 H, H_{ar}), 7.51 (A_2B_2, $J_{A,B}$ = 8.4 Hz, $\Delta\nu$ = 69 Hz, 4 H, H_{ar}), 7.69 (br. dd, J = 7.8, 1.4 Hz, 2 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 57.2 (CH_2), 73.4 [CH(OH)], 95.8 (C_{ar}), 124.7 (CH_{ar}), 128.1 (CH_{ar}), 128.8 (CH_{ar}), 129.6 (CH_{ar}), 130.2 (CH_{ar}), 137.9 (C_{ar}), 139.3 (CH_{ar}), 142 (C_{ar}), 143.5 (C_{ar}) ppm. $C_{15}H_{15}IO_2S$ (386.25): calcd. C 46.64, H 3.91, S 8.3; found C 46.8, H 3.89, S 8.36.

General Procedure for the Synthesis of Aryl Halides Bearing a β-Methoxysulfoxide: NaH (60%; 6 mmol, 1.2 equiv.) was washed with hexane. A solution of the β-hydroxysulfoxide (5 mmol, 1 equiv.) in DMF (3 mL) was added at –20 °C to a suspension of NaH in DMF (2 mL). After 30 min, methyl iodide (2 mmol, 2 equiv.) was added. The resulting mixture was stirred for 1 h at –20 °C, quenched by addition of a saturated solution of NH_4Cl, and extracted with Et_2O. The combined organic layers were then dried with $MgSO_4$,

filtered, and the solvents evaporated. The crude product was purified by flash chromatography over silica gel.

(–)-[1*R*,(S)*R*]-1-Iodo-2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]benzene (12): Colorless gum (98.4% yield). R_f = 0.32 (EtOAc/hexanes, 1:1). $[\alpha]_D^{20}$ = –13.7 (*c* = 1, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.44 (s, 3 H, CH_3), 3.12 (2 H, AB part of an ABX system, $J_{A,B}$ = 13, $J_{A,X}$ = 3.2, $J_{B,X}$ = 10.2 Hz, $\Delta\nu$ = 86 Hz, CH_2), 3.14 (s, 3 H, OCH_3), 4.34 (1 H, X part of an ABX system, $J_{A,X}$ = 3.2, $J_{B,X}$ = 10.2 Hz, C*H*(OMe)], 6.99 (br. t, 1 Hd, *J* = 7.35, 2.07 Hz, H_{ar}), 7.4 (m, 1 H, H_{ar}), 7.43 (dd, *J* = 7.9, 2.0 Hz, 1 H7 Hz, H_{ar}), 7.51 (4 H, A_2B_2, $J_{A,B}$ = 8.3 Hz, $\Delta\nu$ = 90 Hz, H_{ar}), 7.71 (dd, *J* = 7.9, 0.8 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.4 (CH_3), 56.7 (OCH_3), 63.5 (CH_2), 82.1 [CH(OMe)], 97.6 (C_{ar}), 124.8 (CH_{ar}), 127.1 (CH_{ar}), 128.8 (CH_{ar}), 129.8 (CH_{ar}), 129.8 (CH_{ar}), 139.5 (CH_{ar}), 140.0 (C_{ar}), 140.7 (C_{ar}), 141.8 (C_{ar}) ppm. $C_{16}H_{17}IO_2S$ (400.27): calcd. C 48.01, H 4.28, S 8.01; found C 48.11, H 4.34, S 8.05.

(–)-[1*R*,(S)*R*]-1-Bromo-2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]benzene (13): Colorless oil (89.2% yield). R_f = 0.49 (Et_2O). $[\alpha]_D^{20}$ = –3 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2926, 1595, 1493, 1464, 1436, 1399, 1230, 1207, 1117, 1104, 1086, 1047, 981, 808, 761. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.44 (s, 3 H, CH_3), 3.16 (s, 3 H, CH_2), 3.18 (AB part of an ABX system, $J_{A,B}$ = 13.1, $J_{A,X}$ = 3.2, $J_{B,X}$ = 9.9 Hz, $\Delta\nu$ = 81 Hz, 2 H, CH_2), 3.16 (s, 3 H, OCH_3), 4.53 [X part of an ABX system, $J_{A,X}$ = 3.2, $J_{B,X}$ = 9.9 Hz, 1 H, C*H*(OMe)], 7.15 (dt, *J* = 7.7, 1.6 Hz, 1 H, H_{ar}), 7.35 (m, 1 H, H_{ar}), 7.47 (dd, *J* = 7.7, 1.6 Hz, 1 H, H_{ar}), 7.47 (dd, *J* = 8.0, 1.3 Hz, 1 H, H_{ar}), 7.5 (A_2B_2, $J_{A,B}$ = 8.3 Hz, $\Delta\nu$ = 86 Hz, 4 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 56.94 (OCH_3), 63.48 (CH_2), 77.79 [CH(OMe)], 122.51 (C_{ar}), 124.89 (CH_{ar}), 127.52 (CH_{ar}), 128.12 (CH_{ar}), 129.62 (CH_{ar}), 129.94 (CH_{ar}), 133.04 (CH_{ar}), 138.18 (C_{ar}), 140.32 (C_{ar}), 141.99 (C_{ar}) ppm. $C_{16}H_{17}BrO_2S$ (353.27): calcd. C 54.4, H 4.85, S 9.08; found C 54.2, H 4.9, S 8.93.

(–)-[1*R*,(S)*R*]-1-Iodo-2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]-6-methylbenzene (20): White solid (97% yield). R_f = 0.4 (Et_2O). M.p. 101–105 °C. $[\alpha]_D^{20}$ = –35.1 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2920, 1571, 1493, 1443, 1399, 1243, 1204, 1100, 1081, 1032, 1005, 980, 820, 795, 778. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.34 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 3.07 (AB part of an ABX system, $J_{A,B}$ = 13, $J_{A,X}$ = 3, $J_{B,X}$ = 10.2 Hz, $\Delta\nu$ = 66 Hz, 2 H, CH_2), 3.07 (s, 3 H, OCH_3), 4.42 [X part of an ABX system, $J_{A,X}$ = 3, $J_{B,X}$ = 10.2 Hz, 1 H, C*H*(OMe)], 7,08–7,22 (m, 3 H, H_{ar}), 7.44 (A_2B_2, $J_{A,B}$ = 8.1 Hz, $\Delta\nu$ = 92 Hz, 4 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 29.5 (CH_3), 56.8 (OCH_3), 63.6 (CH_2), 83.1 [CH(OMe)], 105.1 (C_{ar}), 124.5 (CH_{ar}), 125.0 (CH_{ar}), 128.6 (CH_{ar}), 129.7 (CH_{ar}), 129.9 (CH_{ar}), 140.3 (C_{ar}), 141.6 (C_{ar}), 141.9 (C_{ar}), 142.5 (C_{ar}) ppm. $C_{17}H_{19}IO_2S$ (414.30): calcd. C 49.28, H 4.62, S 7.74; found C 49.31, H 4.68, S 7.8.

(–)-[1*R*,(S)*R*]-1-Iodo-6-methoxy-2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]benzene (21): White solid (97% yield). R_f = 0.2 (Et_2O). M.p. 74–75 °C. $[\alpha]_D^{20}$ = –22 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2935, 1651, 1596, 1585, 1567, 1493, 1463, 1427, 1398, 1286, 1264, 1108, 1084, 1040, 1014, 985, 808, 775. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.44 (s, 3 H, CH_3), 3.15 (s, 3 H, OCH_3), 3.15 (AB part of an ABX system, $J_{A,B}$ = 13.2, $J_{A,X}$ = 3, $J_{B,X}$ = 10.2 Hz, $\Delta\nu$ = 74 Hz, 2 H, CH_2), 3.86 (s, 3 H, OCH_3), 4.49 [X part of an ABX system, $J_{A,X}$ = 3, $J_{B,X}$ = 10.2 Hz, 1 H, C*H*(OMe)], 6.75 (dd, *J* = 8.3, 1.3 Hz, 1 H, H_{ar}), 7.07 (dd, *J* = 7.7, 1.3 Hz, 1 H, H_{ar}), 7.33 (br. t, 1 H, *J* = 8 Hz, H_{ar}), 7.52 (A_2B_2, $J_{A,B}$ = 8.1 Hz, $\Delta\nu$ = 91 Hz, 4 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 56.5 (OCH_3), 56.8 (OCH_3), 63.5 (CH_2), 82.6 [CH(OMe)], 90.3 (C_{ar}), 110.6 (CH_{ar}), 119.5 (CH_{ar}), 125.1 (CH_{ar}), 129.9 (CH_{ar}), 129.9 (CH_{ar}), 140.3 (C_{ar}), 142.0 (C_{ar}), 142.9 (C_{ar}), 158.0 (C_{ar}) ppm. $C_{17}H_{19}IO_3S$ (430.3): calcd. C 47.45, H 4.45, S 7.45; found C 47.52, H 4.5, S 7.56.

(+)-[1*R*,(S)*R*]-1-Bromo-2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]-4-nitrobenzene (22): Colorless gum (93% yield). R_f = 0.29 (Et_2O). $[\alpha]_D^{20}$ = +17.6 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3093, 2928, 1606, 1573, 1525, 1455, 1346, 1106, 1086, 1046, 1031, 982, 813, 741. ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.44 (s, 3 H, CH_3), 3.18 (AB part of an ABX system, $J_{A,B}$ = 13.3, $J_{A,X}$ = 3.2, $J_{B,X}$ = 9.3 Hz, $\Delta\nu$ = 60 Hz, 2 H, CH_2), 3.19 (s, 3 H, OMe), 3.65 [X part of an ABX system, $J_{A,X}$ = 3.2, $J_{B,X}$ = 9.2 Hz, 1 H, C*H*(OMe)], 7.5 (A_2B_2, $J_{A,B}$ = 8.5 Hz, $\Delta\nu$ = 77 Hz, 4 H, H_{ar}), 7.7 (d, *J* = 8.8 Hz, 1 H, H_{ar}), 8.01 (dd, *J* = 8.8, 2.7 Hz, 1 H, H_{ar}), 8.34 (d, *J* = 2.7 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.5 (CH_3), 57.4 (CH_2), 62.3 [CH(OMe)], 122.7 (CH_{ar}), 124.1 (CH_{ar}), 124.7 (CH_{ar}), 129.2 (C_{ar}), 130.0 (CH_{ar}), 134.2 (CH_{ar}), 140.0 (C_{ar}), 140.9 (C_{ar}), 142.1 (C_{ar}), 148.0 (C_{ar}) ppm.

(+)-[1*R*,(S)*R*]-1-Bromo-2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]naphthalene (23): White solid (99% yield). M.p. 79–81 °C; R_f = 0.26 (EtOAc/hexanes, 1:1). $[\alpha]_D^{20}$ = +1.1 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3054, 2985, 2927, 1596, 1494, 1455, 1399, 1328, 1303, 1258, 1232, 1107, 1086, 1046, 997, 961, 821, 810, 749. ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.46 (s, 3 H, CH_3), 3.18 (s, 3 H, OCH_3), 3.25 (AB part of an ABX system, $J_{A,B}$ = 13, $J_{A,X}$ = 3.2, $J_{B,X}$ = 9.9 Hz, $\Delta\nu$ = 106 Hz, 2 H, CH_2), 4.87 [X part of an ABX system, $J_{A,X}$ = 3.2, $J_{B,X}$ = 9.9 Hz, 1 H, C*H*(OMe)], 7.54 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1 H, H_{ar}), 7.56 (A_2B_2, $J_{A,B}$ = 9.04 Hz, $\Delta\nu$ = 88 Hz, 4 H, H_{ar}), 7.58 (d, *J* = 8.7 Hz, 1 H, H_{ar}), 7.59 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1 H, H_{ar}), 7.82 (ddd, 1 H, *J* = 8.3, 1.5 Hz, H_{ar}), 7.85 (d, *J* = 8.7 Hz, 1 H, H_{ar}), 8.24 (br. d, *J* = 8.5 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.5 (CH_3), 57.0 (OCH_3), 63.4 (CH_2), 78.5 [CH(OMe)], 122.9 (C_{ar}), 123.8 (CH_{ar}), 124.9 (CH_{ar}), 127.0 (CH_{ar}), 127.2 (CH_{ar}), 127.7 (CH_{ar}), 128.2 (CH_{ar}), 128.7 (CH_{ar}), 129.9 (CH_{ar}), 132.2 (C_{ar}), 134.4 (C_{ar}), 136.3 (C_{ar}), 140.4 (C_{ar}), 142.0 (C_{ar}) ppm. $C_{20}H_{19}BrO_2S$ (403.33): calcd. C 59.56, H 4.75, S 7.95; found C 59.51, H 7.79, S 7.94.

(–)-[1*R*,(S)*R*]-2-[1-Benzyloxy-2-(*p*-tolylsulfinyl)ethyl]-1-iodobenzene (14): Prepared by the same procedure as for the formation of aryl halides bearing a β-methoxysulfoxide, with BnCl in place of MeI. Colorless oil (52% yield; 190 mg, 0.4 mmol); R_f = 0.13 (EtOAc/*n*-hexane, 2:1). $[\alpha]_D^{20}$ = –42.5 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3056, 3030, 2920, 2868, 1596, 1584, 1563, 1493, 1455, 1435, 1396, 1346, 1208, 1110, 1084, 1045, 1012, 808, 749, 737, 698. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.39 (s, 3 H, CH_3), 3.18 (AB part of an ABX system, $J_{A,B}$ = 13, $J_{A,X}$ = 2.9, $J_{B,X}$ = 10.2 Hz, $\Delta\nu$ = 100 Hz, 2 H, CH_2), 4.28 (AB, $J_{A,B}$ = 11.87 Hz, $\Delta\nu$ = 93 Hz, 2 H, O*C*H_2Ph), 4.54 [X part of an ABX system, $J_{A,X}$ = 2.9, $J_{B,X}$ = 10.17 Hz, 1 H, C*H*(OBn)], 7.00 (td, *J* = 7.7, 1.7 Hz, 1 H, H_{ar}), 7.22–7.46 (m, 10 H, H_{ar}), 7.53 (dd, *J* = 7.7, 1.7 Hz, 1 H, H_{ar}), 7.76 (dd, *J* = 7.9, 1.1 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 64.0 (CH_2), 70.7 (O*C*H_2Ph), 79.4 [CH(OBn)], 97.5 (C_{ar}), 125.0 (CH_{ar}), 127.7 (CH_{ar}), 128.0 (CH_{ar}), 128.2 (CH_{ar}), 128.5 (CH_{ar}), 129.1 (CH_{ar}), 130.0 (CH_{ar}), 130.1 (CH_{ar}), 137.2 (C_{ar}), 139.7 (CH_{ar}), 140.4 (C_{ar}), 141.1 (C_{ar}), 141.8 (C_{ar}) ppm.

(+)-[(S)*R*]-1-Iodo-2-[2-(*p*-tolylsulfinyl)vinyl]benzene (16): Colorless gum (48% yield; *E*/*Z*: > 99:1); R_f = 0.5 (EtOAc). $[\alpha]_D^{20}$ = +94 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3051, 2920, 1595, 1580, 1492, 1458, 1432, 1303, 1178, 1083, 1050, 1013, 958, 806. ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.39 (s, 3 H, CH_3), 6.71 (d, *J* = 15.3 Hz, 1 H, CH=CH), 6.98 (t, *J* = 7.9 Hz, 1 H, H_{ar}), 7.27 (t, *J* = 7.9 Hz, 1 H, H_{ar}), 7.39 (d, *J* = 7.9 Hz, 1 H, H_{ar}), 7.44 (A_2B_2, $J_{A,B}$ = 8 Hz, $\Delta\nu$ = 78 Hz, 4 H, H_{ar}), 7.56 (d, *J* = 15.3 Hz, 1 H, CH=CH), 7.84 (d, *J* = 7.9 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.4 (CH_3), 100.2 (C_{ar}), 124.8 (CH_{ar}), 127.4 (CH_{ar}), 128.4 (CH_{ar}), 130.1

(CH_{ar}), 130.7 (CH_{ar}), 136.7 (CH_{ar}), 137.2 (C_{ar}), 139.4 (*CH*=*C*H), 139.9 (CH=CH), 140.4 (C_{ar}), 141.7 (C_{ar}) ppm.

(+)-[1*R*,(S)*R*]-1-(2-Bromophenyl)-2-(*p*-tolylsulfinyl)ethyl Acetate (15): Acetic anhydride (50 μL, 0,57 mmol, 1.1 equiv.) was added dropwise to a solution of β-hydroxysulfoxide **8** (200 mg, 0,52 mmol, 1 equiv.) and DMAP (catalytic amount) in pyridine (7 mL). The resulting mixture was stirred for 2 h at room temp. and then quenched by addition of a saturated solution of NH_4Cl. The aqueous phase was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and the solvents evaporated. The crude product was purified by flash chromatography over silica gel (Et_2O). Colorless oil (99% yield; 225 mg, 0.53 mmol); R_f = 0.32 (Et_2O). $[\alpha]_D^{20}$ = +58.8 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3054, 2922, 1747, 1494, 1435, 1372, 1233, 1085, 1041, 1013, 977, 933, 880, 761, 731. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.108 [s, 3 H, OC(=O)*CH*$_3$], 2.42 (s, 3 H, CH_3), 3.26 (AB part of an ABX system, $J_{A,B}$ = 13.4, $J_{A,X}$ = 3, $J_{B,X}$ = 10.2 Hz, Δν = 47 Hz, 2 H, CH_2), 6.08 [X part of an ABX system, $J_{A,X}$ = 3, $J_{B,X}$ = 10.2 Hz, 1 H, C*H*(OAc)], 6.98 (ddd, *J* = 7.9, 6.6, 2.5 Hz, 1 H, H_{ar}), 7.30–7.40 (m, 2 H, H_{ar}), 7.49 (A_2B_2, $J_{A,B}$ = 8.5 Hz, Δν = 82 Hz, 4 H, H_{ar}), 7.76 (br. dd, *J* = 7.9, 1.5 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.8 [OC(=O)*C*H$_3$], 21.4 (CH_3), 62.5 (CH_2), 74.0 [CH(OAc)], 96.3 (C_{ar}), 124.6 (CH_{ar}), 126.9 (CH_{ar}), 128.8 (CH_{ar}), 130.1 (CH_{ar}), 130.1 (CH_{ar}), 139.8 (CH_{ar}), 140.3 (C_{ar}), 140.7 (C_{ar}), 142.1 (C_{ar}), 169.3 [OC(=O)CH$_3$] ppm.

(–)-[1*R*,(S)*R*]-1-Iodo-2-[1-methoxy-2-(*p*-tolylsulfonyl)ethyl]benzene (41): A solution of *m*CPBA (285 mg, 0.8 mmol, 2.2 equiv.) was added to a solution of the β-methoxysulfoxide **12** (300 mg, 0.75 mmol, 1 equiv.) in CH_2Cl_2 (15 mL). The resulting mixture was stirred at room temp. for 6 h and then quenched by addition of a 1 M solution of NaOH (15 mL); the aqueous phase was then extracted with CH_2Cl_2. The organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography over silica gel (EtOAc/*n*-hexane, 1:4). Colorless oil (99% yield; 380 mg; 0.94 mmol). R_f = 0.22 (EtOAc/hexanes, 1:2). $[\alpha]_D^{20}$ = –80.1 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3060, 2984, 2929, 2827, 1733, 1597, 1461, 1434, 1301, 1243, 1159, 1140, 1115, 1103, 1013, 987, 818. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.46 (s, 3 H, CH_3), 3.17 (s, 3 H, OCH_3), 3.36 [AB part of an ABX system (m), 2 H, CH_2], 4.94 [X part of an ABX system, $J_{A,X}$ = 5.6, $J_{B,X}$ = 6.8 Hz, 1 H, C*H*(OMe)], 6.99 (ddd, *J* = 7.9, 5.6, 3.8 Hz, 1 H, H_{ar}), 7.30–7.38 (m, 2 H, H_{ar}), 7.6 (A_2B_2, $J_{A,B}$ = 8.3 Hz, Δν = 157 Hz, 4 H, H_{ar}), 7.8 (br. d, *J* = 7.9 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.6 (CH_3), 57.1 (OCH_3), 62.0 (CH_2), 81.7 [CH(OMe)], 97.6 (C_{ar}), 127.3 (CH_{ar}), 128.3 (CH_{ar}), 128.9 (CH_{ar}), 129.6 (CH_{ar}), 130.1 (CH_{ar}), 137.6 (CH_{ar}), 139.8 (C_{ar}), 140.6 (C_{ar}), 144.4 (C_{ar}) ppm.

(+)-[1*S*,(S)*R*]-1-Iodo-2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]benzene (44): White solid (99% yield). R_f = 0.35 (Et_2O). M.p. 79–82 °C. $[\alpha]_D^{20}$ = +26.1 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3016, 1561, 1494, 1110, 1098, 1038, 1030, 1018, 1009, 981, 801, 751. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.38 (s, 3 H, CH_3), 2.92 (AB part of an ABX system, $J_{A,B}$ = 13.2, $J_{A,X}$ = 10.9, $J_{B,X}$ = 2.4 Hz, Δν = 101 Hz, C2 H, H_2), 3.39 (s, 3 H, OCH_3), 5.05 [X part of an ABX system, $J_{A,X}$ = 10.9, $J_{B,X}$ = 2.4 Hz, 1 H, C*H*(OMe)], 6.98 (td, *J* = 7.7, 1.8 Hz, 1 H, H_{ar}), 7.36 (td, *J* = 7.7, 1.1 Hz, 1 H, H_{ar}), 7.44 (dd, *J* = 7.7, 1.8 Hz, 1 H, H_{ar}), 7.43 (A_2B_2, $J_{A,B}$ = 8.1 Hz, Δν = 85 Hz, 4 H, H_{ar}), 7.8 (dd, *J* = 7.7, 1.1 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.3 (CH_3), 57.4 (OCH_3), 64.8 (CH_2), 80.7 [CH(OMe)], 97.7 (C_{ar}), 123.9 (CH_{ar}), 127.2 (CH_{ar}), 128.8 (CH_{ar}), 129.9 (CH_{ar}), 129.9 (CH_{ar}), 139.9 (CH_{ar}), 141.1 (C_{ar}), 141.4 (C_{ar}), 141.6 (C_{ar}) ppm. $C_{16}H_{17}IO_2S$ (400.27): calcd. C 48.01, H 4.28, S 8.01; found C 48.17, H 4.36, S 8.14.

General Procedure for the Synthesis of 1,3,2-Dioxaborolane: A suspension of the boronic acid (5 mmol, 1 equiv.), ethylene glycol (5 mmol, 1 equiv.), and CaH_2 (10 mmol, 2 equiv.) in THF (10 mL) was refluxed for 2 h. The reaction mixture was then cooled to room temp., filtered through a pad of celite, and washed with EtOAc. The crude product was used without any further purification.

2-(Naphthalen-1-yl)-1,3,2-dioxaborolane (25): White solid (99% yield). M.p. 36–39 °C. IR (neat): $\tilde{\nu}$ = 2911, 1572, 1507, 1396, 1315, 1255, 1200, 1135, 1050, 1030, 1015, 938, 803, 779, 747. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.48 (s, 4 H, CH_2), 7,48–7,56 (m, 3 H, H_{ar}), 7.86 (dd, *J* = 7.7, 1.5 Hz, 1 H, H_{ar}), 7.97 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 8.12 (d, *J* = 6.8 Hz, 1 H, H_{ar}), 8.75 (d, *J* = 8.3 Hz, 1 H, H_{ar}) ppm. ^{11}B NMR ($CDCl_3$, 128.38 MHz): δ = 35.17 ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 65.9 (CH_2), 125.0 (CH_{ar}), 125.5 (CH_{ar}), 126.4 (CH_{ar}), 128.2 (CH_{ar}), 128.4 (CH_{ar}), 132.0 (CH_{ar}), 133.2 (C_{ar}), 136.1 (CH_{ar}), 136.8 (C_{ar}) ppm.

2-*o*-Tolyl-1,3,2-dioxaborolane (27): Colorless oil (99% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.55 (s, 3 H, CH_3), 4.37 [s, 4 H, $(OCH_2)_2$], 7,15–7,21 (m, 2 H, H_{ar}), 7.34 (td, *J* = 7.5, 1.7 Hz, 1 H, H_{ar}), 7.81 (dd, *J* = 7.9, 1.7 Hz, 1 H, H_{ar}) ppm. ^{11}B ($CDCl_3$, 128.38 MHz): δ = 34.96 ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 22.3 (CH_3), 65.8 [$(OCH_2)_2$], 124.8 (CH_{ar}), 129.9 (CH_{ar}), 131.1 (CH_{ar}), 136.3 (CH_{ar}), 145 (C_{ar}) ppm.

2-(2-Methoxyphenyl)-1,3,2-dioxaborolane (28): White solid (99% yield). M.p. 29–33 °C. IR (neat): $\tilde{\nu}$ = 2968, 1597, 1574, 1489, 1457, 1435, 1385, 1330, 1272, 1244, 1210, 1074, 1022, 943, 767. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.88 (s, 3 H, OCH_3), 4.38 (s, 4 H, CH_2), 6.9 (br. d, 8.3 H, H_{ar}), 6.97 (td, *J* = 0.8 Hz, 7.4 H, H_{ar}), 7.44 (ddd, *J* = 7.4, 1.9 Hz, 8.3 H, H_{ar}), 7.76 (dd, *J* = 1.7 Hz, 7.2 H, H_{ar}) ppm. ^{11}B NMR ($CDCl_3$, 128.38 MHz): δ = 34.55 ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 55.58 (O*C*H$_3$), 65.85 (CH_2), 110.21 (CH_{ar}), 120.31 (CH_{ar}), 133.07 (CH_{ar}), 127.43 (CH_{ar}), 164.3 (C_{ar}) ppm.

General Procedure for the Suzuki Coupling Reaction: CsF (151.8 mg, 1.0 mmol, 4 equiv.) was fused under vacuum in a two-necked, round-bottomed flask. After cooling to room temperature, the boronic acid **4** (100.9 mg, 0.5 mmol, 2 equiv.) and dry dioxane (2.5 mL) were added under argon. The aromatic halide **12** (100 mg, 0.25 mmol, 1 equiv.), palladium acetate (1.68 mg, 0.007 mmol, 3 mol%), dppf (6.23 mg, 0.011, 4.5 mol%), and dry dioxane (5 mL) were placed in a second round-bottomed flask under argon. This second reaction mixture was stirred at room temperature for 30 min and then added to the boronic acid **4** by cannula. This mixture was stirred under argon at 80 °C for 1 h. It was then cooled to room temperature, diluted with water (20 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The organic layer was dried ($MgSO_4$) and the solvents evaporated. The residue was purified by chromatography over silica gel.

(–)-[a*R*,1*R*,(S)*R*]-1-[2-(2-Methoxynaphthalen-1-yl)phenyl]-2-(*p*-tolylsulfinyl)ethanol (a*R*-11): Orange solid (64% yield). R_f = 0.15 (EtOAc/hexanes, 1:1). M.p. 60–64 °C. $[\alpha]_D^{20}$ = –101.6 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3244, 1621, 1593, 1509, 1462, 1254, 1062, 1019, 1010, 802, 759, 746, 729. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.33 (s, 3 H, CH_3), 2.71 (AB part of an ABX system, $J_{A,B}$ = 13.2, $J_{A,X}$ = 10.5, $J_{B,X}$ = 1.9 Hz, Δν = 191 Hz, 2 H, CH_2), 3.61 (br. s, 1 H, OH), 3.81 (s, 3 H, OMe), 4.82 [X part of an ABX system, $J_{A,X}$ = 10.5, $J_{B,X}$ = 1.9 Hz, 1 H, C*H*(OH)], 6.88 (A_2B_2, $J_{A,B}$ = 8.3 Hz, Δν = 35 Hz, 4 H, H_{ar}), 7.09 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.14 (dd, *J* = 7.5, 1.3 Hz, 1 H, H_{ar}), 7.27 (ddd, *J* = 8.3, 5.6, 1.3 Hz, 1 H, H_{ar}), 7.33 (d, *J* = 9 Hz, 1 H, H_{ar}), 7.39 (td, *J* = 8.3, 1.1 Hz, 1 H, H_{ar}), 7.4 (td, *J* = 7.5, 1.3 Hz, 1 H, H_{ar}), 7.48 (td, *J* = 7.7, 1.1 Hz, 1 H, H_{ar}), 7.79 (br. d, *J* = 7.8 Hz, 1 H, H_{ar}), 7.88 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.92 (d, *J* = 9 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$,

50 MHz): δ = 21.3 (CH_3), 56.4 (OMe), 64.3 (CH_2), 68.3 [CH(OH)], 113.2 (CH_{ar}), 122.1 (C_{ar}), 123.3 (CH_{ar}), 123.5 (CH_{ar}), 124.4 (CH_{ar}), 125.4 (CH_{ar}), 126.7 (CH_{ar}), 127.7 (CH_{ar}), 128.0 (CH_{ar}), 128.2 (CH_{ar}), 128.9 (C_{ar}), 129.4 (CH_{ar}), 129.5 (CH_{ar}), 130.9 (CH_{ar}), 133.4 (C_{ar}), 133.7 (C_{ar}), 139.5 (C_{ar}), 141.1 (C_{ar}), 141.5 (C_{ar}), 153.0 (C_{ar}) ppm. $C_{26}H_{24}O_3S$ (416.53): calcd. C 74.97, H 5.81, S 7.7; found C 74.73, H 5.79, S 7.77.

(–)-[a*S*,1*R*,(S)*R*]-1-[2-(2-Methoxynaphthalen-1-yl)phenyl]-2-(*p*-tolylsulfinyl)ethanol (a*S*-11): White cristals; R_f = 0.15 (EtOAc/hexanes, 1:1). M.p. 211–213 °C. $[\alpha]_D^{20}$ = –3.8 (*c* = 1, $CHCl_3$). ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.39 (s, 3 H, CH_3), 3.03 (AB part of an ABX system, $J_{A,B}$ = 13.1, $J_{A,X}$ = 9.8, $J_{B,X}$ = 2.3 Hz, Δν = 37 Hz, 2 H, CH_2), 3.77 (s, 3 H, OMe), 3.78 (d, *J* = 1.9 Hz, 1 H, OH), 4.84 [X part of an ABX system (br. d), $J_{A,X}$ = 9.8 Hz, 1 H, C*H*(OH)], 7.1–7.54 (m, 11 H, H_{ar}), 7.76–7.96 (m, 3 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.4 (CH_3), 56.2 (OMe), 63.9 (CH_2), 68.8 [CH(OH)], 112.8 (CH_{ar}), 122.5 (C_{ar}), 123.5 (CH_{ar}), 123.9 (CH_{ar}), 124.7 (CH_{ar}), 126.0 (CH_{ar}), 127.0 (CH_{ar}), 127.8 (CH_{ar}), 127.9 (CH_{ar}), 128.4 (CH_{ar}), 128.9 (C_{ar}), 129.8 (CH_{ar}), 129.9 (CH_{ar}), 131.0 (CH_{ar}), 133.3 (C_{ar}), 133.7 (C_{ar}), 140.4 (C_{ar}), 141.3 (C_{ar}), 141.6 (C_{ar}), 153.5 (C_{ar}) ppm.

(–)-[a*R*,1*R*,(S)*R*]-2-Methoxy-1-{2-[1-methoxy-2-(*p*-tolylsulfinyl)-ethyl]phenyl}naphthalene (a*R*-17): White solid (99% yield). R_f = 0.2 (Et_2O). M.p. 43–46 °C. $[\alpha]_D^{20}$ = –138 (*c* = 1, $CHCl_3$). IR (neat): ṽ = 2934, 1593, 1508, 1463, 1266, 1254, 1085, 1041, 807, 761, 750. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.35 (X part of an ABX system, $J_{A,X}$ = 12.2, $J_{B,X}$ = 2.4 Hz, 1 H, CH_2), 2.37 (s, 3 H, CH_3), 3.11 [s, 3 H, CH(OCH_3)], 3.48 [AB part of an ABX system, $J_{A,B}$ = 11.3, $J_{A,X}$ = 12.2, $J_{B,X}$ = 2.4 Hz, Δν = 78 Hz, 2 H, CH_2, C*H*(OMe)], 3.63 (s, 3 H, OCH_3), 6.82 (A_2B_2, $J_{A,B}$ = 8.1 Hz, Δν = 24 Hz, 4 H, H_{ar}), 7.02 (br. d, *J* = 8.2 Hz, 1 H, H_{ar}), 7.06 (dd, *J* = 7.5, 1.2 Hz, 1 H, H_{ar}), 7.09 (d, *J* = 8.9 Hz, 1 H, H_{ar}), 7.3 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1 H, H_{ar}), 7.37 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1 H, H_{ar}), 7.38 (td, *J* = 7.4, 1.4 Hz, 1 H, H_{ar}), 7.48 (td, *J* = 7.5, 1.4 Hz, 1 H, H_{ar}), 7.66 (dd, *J* = 7.8, 1.4 Hz, 1 H, H_{ar}), 7.82 (d, *J* = 8.9 Hz, 1 H, H_{ar}), 7.84 (br. d, *J* = 8.2 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.4 (CH_3), 55.6 [CH(OCH_3)], 56.2 (OCH_3), 64.4 (CH_2), 76.1 [CH(OMe)], 112.1 (CH_{ar}), 121.4 (C_{ar}), 123.6 (CH_{ar}), 123.8 (CH_{ar}), 124.3 (CH_{ar}), 125.4 (CH_{ar}), 126.9 (CH_{ar}), 127.8 (CH_{ar}), 127.9 (CH_{ar}), 128.2 (CH_{ar}), 128.8 (C_{ar}), 129.3 (CH_{ar}), 129.3 (CH_{ar}), 131.1 (CH_{ar}), 133.5 (C_{ar}), 135.2 (C_{ar}), 138.6 (C_{ar}), 139.2 (C_{ar}), 140.8 (C_{ar}), 152.2 (C_{ar}) ppm. $C_{27}H_{26}O_3S$ (430.56): calcd. C 75.32, H 6.09, S 8.34; found C 75.55, H 6.18, S 8.09.

(–)-[a*S*,1*R*,(S*)R*]-2-Methoxy-1-{2-[1-methoxy-2-(*p*-tolylsulfinyl)-ethyl]phenyl}naphthalene (a*S*-17): White gum; R_f = 0.17 (EtOAc/hexanes, 2:1). $[\alpha]_D^{20}$ = –8.6 (*c* = 1, $CHCl_3$). IR (neat): ṽ = 2927, 1621, 1594, 1509, 1464, 1332, 1255, 1266, 1176, 1111, 1067, 1021, 975, 921, 869, 811, 763. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.31 (s, 3 H, CH_3), 2.76–2.85 [X part of an ABX system (m), 1 H, CH_2], 2.87 [s, 3 H, CH(OCH_3)], 3.44–3.53 [AB part of an ABX system (m), 2 H, C*H*(OMe) + CH_2], 3.72 (s, 3 H, OCH_3), 7.03 (A_2B_2, $J_{A,B}$ = 7.9 Hz, Δν = 57 Hz, 4 H, H_{ar}), 7.03 (br. d, *J* = 8.4 Hz, 1 H, H_{ar}), 7.08 (dd, *J* = 7.4, 1.4 Hz, 1 H, H_{ar}), 7.17 (d, *J* = 9 Hz, 1 H, H_{ar}), 7.21 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1 H, H_{ar}), 7.3 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1 H, H_{ar}), 7.39 (td, *J* = 7.4, 1.4 Hz, 1 H, H_{ar}), 7.5 (td, *J* = 7.4, 1.4 Hz, 1 H, H_{ar}), 7.66 (dd, *J* = 7.6, 1.4 Hz, 1 H, H_{ar}), 7.78 (d, *J* = 8.1 Hz, 1 H, H_{ar}), 7.83 (d, *J* = 9 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.4 (CH_3), 56.0 [CH(OCH_3)], 56.2 (OCH_3), 64.3 (CH_2), 75.9 [CH(OMe)], 112.8 (CH_{ar}), 121.6 (C_{ar}), 123.4 (CH_{ar}), 123.9 (CH_{ar}), 124.3 (CH_{ar}), 125.7 (CH_{ar}), 126.3 (CH_{ar}), 127.8 (CH_{ar}), 128.0 (CH_{ar}), 128.4 (CH_{ar}), 128.6 (C_{ar}), 129.2 (CH_{ar}), 129.4 (CH_{ar}), 131.2 (CH_{ar}), 132.7 (C_{ar}), 135.4 (C_{ar}), 138.2 (C_{ar}), 139.3 (C_{ar}), 141.1 (C_{ar}), 153.8 (C_{ar}) ppm.

(–)-[a*R*,1*R*,(S)*R*]-1-{2-[1-Benzyloxy-2-(*p*-tolylsulfinyl)ethyl]phenyl}-2-methoxynaphthalene (a*R*-18): Orange solid (97% yield; *dr* > 99:1); R_f = 0.25 (Et_2O). M.p. 47–49 °C. $[\alpha]_D^{20}$ = –94 (*c* = 1, $CHCl_3$). IR (neat): ṽ = 2922, 1621, 1593, 1508, 1454, 1380, 1332, 1265, 1253, 1068, 1040, 806, 747, 697. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.39 (s, 3 H, CH_3), 2.46 (X part of an ABX system, $J_{A,X}$ = 12.8, $J_{B,X}$ = 2.4 Hz, 1 H, CH_2), 3.68 [AB part of an ABX system, $J_{A,B}$ = 11.2, $J_{A,X}$ = 12.8, $J_{B,X}$ = 2.4 Hz, Δν = 134 Hz, 2 H, C*H*(OBn) + CH_2], 3.7 (s, 3 H, OMe), 4.25 (AB, $J_{A,B}$ = 11.8 Hz, Δν = 135 Hz, 2 H, CH_2Ph), 6.76 (A_2B_2, $J_{A,B}$ = 8.2 Hz, Δν = 33 Hz, 4 H, H_{ar}), 7.04 (br. d, *J* = 8.1 Hz, 1 H, H_{ar}), 7.11 (dd, *J* = 7.4, 1.5 Hz, 1 H, H_{ar}), 7.12 (d, *J* = 9 Hz, 1 H, H_{ar}), 7.33 (m, 1 H, H_{ar}), 7.33–7.43 (m, 5 H, H_{ar}), 7.4 (m, 1 H, H_{ar}), 7.44 (td, *J* = 7.4, 1.5 Hz, 1 H, H_{ar}), 7.53 (td, *J* = 7.4, 1.5 Hz, 1 H, H_{ar}), 7.79 (dd, 1 H, *J* = 7.8 Hz, H_{ar}), 8.84 (d, *J* = 9 Hz, 1 H, H_{ar}), 8.85 (br. d, *J* = 7.4 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 55.8 (CH), 70.5 (CH_2), 74.9 (CH_2), 112.2 (CH_{ar}), 121.6 (C_{ar}), 123.8 (CH_{ar}), 124.0 (CH_{ar}), 124.5 (CH_{ar}), 125.7 (CH_{ar}), 127.1 (CH_{ar}), 127.3 (CH_{ar}), 127.6 (CH_{ar}), 127.9 (CH_{ar}), 128.1 (CH_{ar}), 128.4 (CH_{ar}), 128.5 (CH_{ar}), 128.9 (C_{ar}), 129.4 (CH_{ar}), 129.5 (CH_{ar}), 131.2 (CH_{ar}), 133.6 (C_{ar}), 135.2 (C_{ar}), 138.2 (C_{ar}), 138.9 (C_{ar}), 140.9 (C_{ar}), 152.3 (C_{ar}) ppm.

(–)-[a*R*,2*R*,(S)*R*]-1-[2-(2-Methoxynaphthalen-1-yl)phenyl]-2-(*p*-tolylsulfinyl)ethyl Acetate (a*R*-19): White solid (99% yield; *dr* > 99:1); R_f = 0.32 (EtOAc/hexanes, 2:1). M.p. 45–48 °C. $[\alpha]_D^{20}$ = –58.4 (*c* = 1, $CHCl_3$). IR (neat): ṽ = 2935, 1620, 1593, 1508, 1370, 1257, 1224, 1034, 1020, 806. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.08 (s, 3 H, CH_3), 2.36 (s, 3 H, OAc), 2.92 (AB part of an ABX system, $J_{A,B}$ = 13.4, $J_{A,X}$ = 11.1, $J_{B,X}$ = 2.07 Hz, Δν = 180 Hz, 2 H, CH_2), 3.79 (s, 3 H, OMe_{ar}), 5.83 [X part of an ABX system, $J_{A,X}$ = 11.1, $J_{B,X}$ = 2.07 Hz, 1 H, C*H*(OAc)], 6.87 (A_2B_2, $J_{A,B}$ = 8.2 Hz, Δν = 26 Hz, 4 H, H_{ar}), 6.99 (br. d, *J* = 8.4 Hz, 1 H, H_{ar}), 7.11 (dd, *J* = 7.4, 1.6 Hz, 1 H, H_{ar}), 7.23 (d, *J* = 9 Hz, 1 H, H_{ar}), 7.24 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1 H, H_{ar}), 7.33 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1 H, H_{ar}), 7.4 (td, *J* = 7.4, 1.5 Hz, 1 H, H_{ar}), 7.46 (td, *J* = 7.4, 1.5 Hz, 1 H, H_{ar}), 7.64 (dd, *J* = 7.7, 1.6 Hz, 1 H, H_{ar}), 7.8 (br. d, *J* = 8.1 Hz, 1 H, H_{ar}), 7.82 (d, *J* = 9 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.9 (CH_3), 21.4 (OCOCH_3), 56 (OMe), 64 (CH_2), 68.1 [CH(OAc)], 112.6 (CH_{ar}), 120.8 (C_{ar}), 123.3 (CH_{ar}), 123.4 (CH_{ar}), 124 (CH_{ar}), 125.5 (CH_{ar}), 126.7 (CH_{ar}), 127.9 (CH_{ar}), 128.1 (CH_{ar}), 128.2 (CH_{ar}), 128.6 (C_{ar}), 129.4 (CH_{ar}), 129.6 (CH_{ar}), 131.5 (CH_{ar}), 133.3 (C_{ar}), 134.1 (C_{ar}), 138.1 (C_{ar}), 139.5 (C_{ar}), 140.9 (C_{ar}), 153.1 (C_{ar}), 169.2 (O*C*OMe) ppm. $C_{28}H_{26}O_4S$ (428.28): calcd. C 73.34, H 5.71, S 6.99; found C 73.29, H 5.77, S 6.89.

(–)-[a*S*,1*R*,(S)*R*]-1-{2-[1-Methoxy-2-(*p*-tolylsulfinyl)ethyl]phenyl}-2-methylnaphthalene (a*S*-29): White solid (99% yield; *dr* > 99:1); R_f = 0.28 (Et_2O). M.p. = 123–126 °C. $[\alpha]_D^{20}$ = –27.4 (*c* = 1, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.02 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.47 (X part of an ABX system, $J_{A,X}$ = 12.4, $J_{B,X}$ = 1.9 Hz, 1 H, CH_2), 3.06 (s, 3 H, OCH_3), 3.39 [AB part of an ABX system, $J_{A,B}$ = 11.1, $J_{A,X}$ = 12.3, $J_{B,X}$ = 1.9 Hz, Δν = 36 Hz, CH_2, 2 H, C*H*(OMe)], 6.78 (A_2B_2, $J_{A,B}$ = 8.2 Hz, Δν = 44 Hz, 4 H, H_{ar}), 6.96 (br. d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.07 (dd, *J* = 7.5, 1.4 Hz, 1 H, H_{ar}), 7.22 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.3 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1 H, H_{ar}), 7.4 (td, *J* = 7.3, 1.4 Hz, 1 H, H_{ar}), 7.45 (ddd, 1 H, *J* = 8.1, 6.9, 1 Hz, H_{ar}), 7.51 (td, *J* = 7.5, 1.4 Hz, 1 H, H_{ar}), 7.68 (dd, *J* = 7.3, 1.3 Hz, 1 H, H_{ar}), 7.71 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.86 (d, *J* = 8.1 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.2 (CH_3), 21.3 (CH_3), 56.3 (OCH_3), 64.5 (CH_2), 76.1 [CH(OMe)], 123.6 (CH_{ar}), 125.0 (CH_{ar}), 125.5 (CH_{ar}), 125.8 (CH_{ar}), 126.3 (CH_{ar}), 127.4 (CH_{ar}), 127.9 (CH_{ar}), 127.9 (CH_{ar}), 128.2 (CH_{ar}), 128.4 (CH_{ar}), 129.4 (CH_{ar}), 130.5 (CH_{ar}), 131.8 (C_{ar}), 132.2 (C_{ar}), 132.6 (C_{ar}), 134.6 (C_{ar}), 137.7 (C_{ar}), 138.2 (C_{ar}), 138.9 (C_{ar}), 140.8

(C_{ar}) ppm. $C_{27}H_{26}O_2S$ (414.56): calcd. C 78.23, H 6.32, S 7.73; found C 78.13, H 6.37, S 7.62.

[1*R*,(S)*R*]-1-{2-[1-Methoxy-2-(*p*-tolylsulfinyl)ethyl]-6-methylphenyl}naphthalene (30): Orange solid (88% yield; *dr* 90:10); R_f = 0.24 (Et_2O). $C_{27}H_{26}O_2S$: calcd. C 78.23, H 6.32, S 7.73; found C 78.11, H 6.46, S 7.67.

[a*S*,1*R*,(S)*R*]-30: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.81 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.4 (X part of an ABX system, $J_{A,X}$ = 12.3, $J_{B,X}$ = 1.9 Hz, 1 H, CH_2), 3.03 (s, 3 H, OMe), 3.47 [AB part of an ABX system, $J_{A,B}$ = 11.3, $J_{A,X}$ = 12.3, $J_{B,X}$ = 1.9 Hz, $\Delta\nu$ = 34 Hz, 2 H, CH_2, C*H*(OMe)], 6.79 (A_2B_2, $J_{A,B}$ = 8.3 Hz, $\Delta\nu$ = 21 Hz, 4 H, H_{ar}), 6.99 (dd, *J* = 6.8, 1 Hz, 1 H, H_{ar}), 7.08 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.26 (br. d, *J* = 6.8 Hz, 1 H, H_{ar}), 7.35 (dd, *J* = 8.3, 6.8 Hz, 1 H, H_{ar}), 7.36 (ddd, *J* = 8.0, 6.8, 1.3 Hz, 1 H, H_{ar}), 7.42 (t, *J* = 7.5 Hz, 1 H, H_{ar}), 7.51 (br. d, *J* = 7.5 Hz, 1 H, H_{ar}), 7.53 (ddd, *J* = 8.0, 6.8, 1 Hz, 1 H, H_{ar}), 7.57 (br. d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.92 (br. d, *J* = 8 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.9 (CH_3), 21.4 (CH_{3ar}), 30.2 (OMe), 56.0 (CH_2), 64.8 (CH), 75.6 (CH_{ar}), 123.4 (CH_{ar}), 123.7 (CH_{ar}), 125.0 (CH_{ar}), 125.1 (CH_{ar}), 125.7 (CH_{ar}), 125.8 (CH_{ar}), 126.0 (CH_{ar}), 126.1 (CH_{ar}), 126.5 (CH_{ar}), 127.4 (CH_{ar}), 128.3 (CH_{ar}), 129.5 (C_{ar}), 131.8 (C_{ar}), 133.5 (C_{ar}), 136.2 (C_{ar}), 137.2 (C_{ar}), 137.5 (C_{ar}), 138.8 (C_{ar}), 140.8 (C_{ar}) ppm.

[a*R*,1*R*,(S)*R*]-30: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.83 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 2.4 [A part of an ABX system (m), 1 H, CH_2], 2.72 (B part of an ABX system, *J* = 12.8 Hz, 1 H, CH_2), 2.85 (s, 3 H, OMe), 3.23 [X part of an ABX system, $J_{A,X}$ = 10.8, $J_{B,X}$ = 3 Hz, 1 H, CH(OMe)], 6.75–7.92 (m, 14 H, H_{ar}) ppm.

[1*R*,(S)*R*]-6-[1-Methoxy-2-(*p*-tolylsulfinyl)ethyl]-2,2′-dimethylbiphenteyl (31): Orange gum (82% yield; *dr*: 75:25); R_f = 0.27 (Et_2O). $C_{24}H_{26}O_2S$: calcd. C 76.15, H 6.92, S 8.47; found C 75.79, H 6.88, S 8.23.

[a*S*,1*R*,(S)*R*]-31: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18 (s, 3 H, CH_3), 1.86 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 2.52 (X part of an ABX system, 1 H, CH_2), 2.99 (s, 3 H, OMe), 3.57 [AB part of an ABX system, $J_{A,B}$ = 10.9, $J_{A,X}$ = 2.69, $J_{B,X}$ = 12.5 Hz, $\Delta\nu$ = 66 Hz, 2 H, C*H*(OMe), CH_2], 6.73 (br. d, *J* = 7.5 Hz, 1 H, H_{ar}), 7.04 (br. t, *J* = 7.5 Hz, 1 H, H_{ar}), 7.09 (br. t, *J* = 7.5 Hz, 1 H, H_{ar}), 7.18 (m, 1 H, H_{ar}), 7.19 (A_2B_2, $J_{A,B}$ = 8.3 Hz, $\Delta\nu$ = 51 Hz, 4 H, H_{ar}), 7.19 (m, 1 H, H_{ar}), 7.31 (t, *J* = 7.7 Hz, 1 H, H_{ar}), 7.4 (d, *J* = 7.7 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.3 (CH_3'), 19.9 (CH_3), 21.5 (CH_3), 56.0 (OMe), 64.5 (CH_2), 75.2 (CH), 123.5 (CH_{ar}), 124.2 (CH), 125.7 (C_{ar}), 127.1 (CH_{ar}), 128.0 (CH_{ar}), 128.4 (CH_{ar}), 129.5 (CH_{ar}), 129.7 (CH_{ar}), 129.8 (CH_{ar}), 130.3 (CH_{ar}), 135.7 (C_{ar}), 136.3 (C_{ar}), 136.4 (C_{ar}), 137.7 (C_{ar}), 140.3 (C_{ar}), 141.5 (C_{ar}) ppm.

[a*R*,1*R*,(S)*R*]-31: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.8 (s, 3 H, CH_3), 1.84 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 2.75 (m, 1 H, CH_2), 3 (s, 3 H, OMe), 3.4 [m, 2 H, C*H*(OMe), CH_2], 6.72–7.41 (m, 11 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.2 (CH_3), 20.0 (CH_3), 21.4 (CH_3), 56.3 (OMe), 64.5 (CH_2), 76.5 (CH), 122.9 (CH_{ar}), 124.5 (CH), 124.4 (C_{ar}), 126.2 (CH_{ar}), 127.4 (CH_{ar}), 127.9 (CH_{ar}), 129.4 (CH_{ar}), 129.5 (CH_{ar}), 129.9 (CH_{ar}), 134.5 (CH_{ar}), 136.5 (C_{ar}), 136.6 (C_{ar}), 139.3 (C_{ar}), 139.5 (C_{ar}), 139.8 (C_{ar}), 141.3 (C_{ar}) ppm.

(+)-[a*S*,1*R*,(S)*R*]-2′-Methoxy-6-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]-2-methylbiphenyl (a*S*-32): Yellow solid (70% yield). R_f = 0.18 (Et_2O). M.p. 148–150 °C. $[\alpha]_D^{20}$ = +1.8 (*c* = 0.6, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2919, 1596, 1496, 1465, 1436, 1295, 1265, 1243, 1228, 1187, 1101, 1040, 1027, 799, 782. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.9 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 2.71 (X part of an ABX system, $J_{A,X}$ = 2.9, $J_{B,X}$ = 10.9 Hz, 1 H, CH_2), 3 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 3.6 [AB part of an ABX system, $J_{A,B}$ = 13.1, $J_{A,X}$ = 2.9, $J_{B,X}$ = 10.9 Hz, $\Delta\nu$ = 150 Hz, 2 H, C*H*(OMe), CH_2], 6.76 (br. d, *J* = 8.3 Hz, 1 H, H_{ar}), 6.76 (dd, *J* = 7.5, 1.8 Hz, 1 H, H_{ar}), 6.85 (td, *J* = 7.5, 1 Hz, 1 H, H_{ar}), 7.19 (br. d, $J_{A,B}$ = 7.5 Hz, $\Delta\nu$ = 63 Hz, 1 H, H_{ar}), 7.22 (A_2B_2, *J* = 7.8 Hz, 4 H, H_{ar}), 7.27 (ddd, *J* = 8.3, 7.5, 1.8 Hz, 1 H, H_{ar}), 7.32 (td, 1 H, *J* = 7.5 Hz, H_{ar}), 7.39 (br. d, *J* = 7.5 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.1 (CH_3), 21.5 (CH_3), 55.0 (OMe), 56.0 (OMe), 65.0 (CH_2), 75.8 (CH), 110.8 (CH_{ar}), 120.54 (CH_{ar}), 123.02 (CH_{ar}), 124.24 (CH_{ar}), 127.09 (C_{ar}), 128.04 (CH_{ar}), 128.63 (CH_{ar}), 129.2 (CH_{ar}), 129.7 (CH_{ar}), 129.8 (CH_{ar}), 137.0 (C_{ar}), 137.1 (C_{ar}), 137.5 (C_{ar}), 139.9 (C_{ar}), 141.2 (C_{ar}), 156.4 (C_{ar}) ppm. $C_{24}H_{26}O_3S$ (394.53): calcd. C 73.06, H 6.64, S 8.13; found C 72.9, H 6.75, S 7.95.

(–)-[a*R*,1*R*,(S)*R*]-2′-Methoxy-6-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]-2-methylbiphenyl (a*R*-32): Yellow solid (19% yield). R_f = 0.25 (Et_2O). M.p. 133–135 °C. $[\alpha]_D^{20}$ = –19.4 (*c* = 0.5, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2929, 1594, 1581, 1500, 1459, 1301, 1263, 1242, 1108, 1042, 1023, 1010, 976, 813, 772. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.9 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 2.62 (X part of an ABX system, $J_{A,X}$ = 2.8, $J_{B,X}$ = 12.4 Hz, 1 H, CH_2), 3 (s, 3 H, OMe), 3.48 [AB part of an ABX system, $J_{A,B}$ = 10.9, $J_{A,X}$ = 2.8, $J_{B,X}$ = 12.4 Hz, $\Delta\nu$ = 42 Hz, 2 H, C*H*(OMe), CH_2], 3.52 (s, 3 H, OMe), 6.73 (br. d, 1 H, *J* = 8.2, 0.9 Hz, H_{ar}), 6.79 (dd, *J* = 7.4, 1.7 Hz, 1 H, H_{ar}), 6.92 (td, *J* = 7.4, 1.1 Hz, 1 H, H_{ar}), 7.19 (A_2B_2, $J_{A,B}$ = 7.9 Hz, $\Delta\nu$ = 36 Hz, 4 H, H_{ar}), 7.19 (br. d, *J* = 7.3 Hz, 1 H, H_{ar}), 7.3 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1 H, H_{ar}), 7.31 (t, *J* = 7.3 Hz, 1 H, H_{ar}), 7.39 (br. d, *J* = 7.3 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.26 (CH_3), 21.51 (CH_3), 54.82 (OMe), 56.12 (OMe), 64.37 (CH_2), 76.45 (CH), 110.48 (CH_{ar}), 121.01 (CH_{ar}), 122.7 (CH_{ar}), 124.63 (CH_{ar}), 126.85 (C_{ar}), 128.01 (CH_{ar}), 128.83 (CH_{ar}), 129.47 (CH_{ar}), 129.74 (CH_{ar}), 131.09 (CH_{ar}), 136.9 (C_{ar}), 137.16 (C_{ar}), 137.52 (C_{ar}), 139.52 (C_{ar}), 141.17 (C_{ar}), 155.15 (C_{ar}) ppm.

[1*R*,(S)*R*]-1-{2-Methoxy-6-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]-phenyl}naphthalene (33): White solid (86.1% yield; *dr* 95:5); R_f = 0.28 (Et_2O). $C_{27}H_{26}O_3S$: calcd. C 75.32, H 6.09, S 7.45; found C 74.84, H 6.12, S 7.54.

[a*R*,1*R*,(S)*R*]-33: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.36 (s, 3 H, CH_3), 2.37 (X part of an ABX system, 1 H, CH_2), 3.04 (s, 3 H, OMe), 3.46 [AB part of an ABX system, $J_{A,B}$ = 11, $J_{A,X}$ = 2.3, $J_{B,X}$ = 12.5 Hz, $\Delta\nu$ = 55 Hz, 2 H, C*H*(OMe), CH_2], 3.57 (s, 3 H, OMe), 6.78 (A_2B_2, $J_{A,B}$ = 8.3 Hz, $\Delta\nu$ = 28 Hz, 4 H, H), 6.95 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.01 (dd, *J* = 7, 1.3 Hz, 1 H, H_{ar}), 7.11 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.27 (dd, *J* = 7.8, 1 Hz, 1 H, H_{ar}), 7.33 (dd, *J* = 8.3, 7 Hz, 1 H, H_{ar}), 7.34 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1 H, H_{ar}), 7.49 (t, *J* = 8.3 Hz, 1 H, H_{ar}), 7.52 (m, 1 H, H_{ar}), 7.76 (br. d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.9 (br. d, *J* = 8 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 55.8 (OMe), 56.2 (OMe), 64.5 (CH_2), 75.4 (CH), 110.3 (CH_{ar}), 118.1 (CH_{ar}), 123.8 (CH_{ar}), 125.0 (CH_{ar}), 125.3 (CH_{ar}), 126.0 (CH_{ar}), 126.3 (CH_{ar}), 126.4 (CH_{ar}), 127.6 (CH_{ar}), 128.3 (CH_{ar}), 128.5 (C_{ar}), 129.5 (CH_{ar}), 129.6 (CH_{ar}), 132.5 (C_{ar}), 133.5 (C_{ar}), 133.6 (C_{ar}), 138.9 (C_{ar}), 139.3 (C_{ar}), 141.0 (C_{ar}), 157.4 (C_{ar}) ppm.

[a*S*,1*R*,(S)*R*]-33: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.3 (s, 3 H, CH_3), 2.7 (AB part of an ABX system, $J_{A,B}$ = 12.5, $J_{A,X}$ = 3.1, $J_{B,X}$ = 10 Hz, $\Delta\nu$ = 115 Hz, 2 H, CH_2), 2.84 (s, 3 H, OMe), 3.25 (X part of an ABX system, $J_{A,X}$ = 3.1, $J_{B,X}$ = 10 Hz, 1 H, CH), 3.59 (s, 3 H, OMe), 6.50–7.90 (m, 14 H, H_{ar}) ppm.

[2*R*,(S)*R*]-2-Methoxy-6-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]-2′-methylbiphenyl (34): Light-yellow solid (86% yield; *dr* 90:10); R_f = 0.41 (Et_2O/CH_2Cl_2, 2:1).

[a*R*,1*R*,(S)*R*]-34: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.87 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 2.98 (AB part of an ABX system, $J_{A,B}$

= 12.6, $J_{A,X}$ = 10.9, $J_{B,X}$ = 2.8 Hz, Δν = 293 Hz, 2 H, CH_2), 3.09 (s, 3 H, OMe), 3.68 (s, 3 H, OMe), 3.75 (X part of an ABX system, $J_{A,X}$ = 10.9, $J_{B,X}$ = 2.8 Hz, 1 H, CH), 6.76 (d, J = 7.5 Hz, 1 H, H_{ar}), 6.89 (d, J = 7.9 Hz, 1 H, H_{ar}), 7.04 (t, J = 7.5 Hz, 1 H, H_{ar}), 7.14 (m, 1 H, H_{ar}), 7.2 (A_2B_2, J = 8.1 Hz, 4 H, H_{ar}), 7.2 (m, 1 H, H_{ar}), 7.21 (m, 1 H, H_{ar}), 7.41 (t, $J_{A,B}$ = 8.1 Hz, Δν = 36 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.4 (CH_3), 21.4 (CH_3), 55.5 (OMe), 56.1 (OMe), 64.2 (CH_2), 75.9 (CH), 109.9 (CH_{ar}), 117.8 (CH_{ar}), 124.3 (CH_{ar}), 125.3 (CH_{ar}), 127.2 (CH_{ar}), 128.9 (CH_{ar}), 129.1 (CH_{ar}), 129.5 (C_{ar}), 129.8 (CH_{ar}), 129.8 (CH_{ar}), 134.7 (C_{ar}), 136.8 (C_{ar}), 138 (C_{ar}), 139.3 (C_{ar}), 141.4 (C_{ar}), 156.5 (C_{ar}) ppm. **[a*S*,1*R*,(S)*R*]-34:** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.88 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 2.81 (m, 1 H, CH_2), 2.99 (s, 3 H, OMe), 3.44–3.49 [m, 2 H, CH_2, C*H*(OMe)], 3.68 (s, 3 H, OMe), 6.76–7.44 (m, 11 H, H_{ar}) ppm.

(–)-[a*S*,1*R*,(S)*R*]-2,2′-Dimethoxy-6-[1-methoxy-2-(*p*-tolylsulfinyl-ethyl]biphenyl (a*S*-35): White solid (70% yield). R_f = 0.23 (Et_2O). M.p. 118–120 °C. $[\alpha]_D^{20}$ = –74.7 (c = 1.1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2941, 2922, 1594, 1581, 1466, 1436, 1293, 1266, 1231, 1250, 1231, 1106, 1070, 1043, 1030, 986, 910, 806, 758, 750. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.43 (s, 3 H, CH_3), 2.59 (AB part of an ABX system, $J_{A,B}$ = 12.6, $J_{A,X}$ = 10.9, $J_{B,X}$ = 2.8 Hz, Δν = 246 Hz, 2 H, CH_2), 3.04 (s, 3 H, OMe), 3.5 (s, 3 H, $OMe_{ar'}$), 3.58 (X part of an ABX system, $J_{A,X}$ = 10.9, $J_{B,X}$ = 2.8 Hz, 1 H, CH), 3.66 (s, 3 H, OMe_{ar}), 6.71 (dd, J = 8.3, 0.9 Hz, 1 H, H_{ar}), 6.85 (dd, J = 7.2, 1.8 Hz, 1 H, H_{ar}), 6.89 (dd, J = 8.1, 0.9 Hz, 1 H, H_{ar}), 6.93 (td, J = 7.2, 1.1 Hz, 1 H, H_{ar}), 7.17 (dd, J = 8, 0.8 Hz, 1 H, H_{ar}), 7.19 (A_2B_2, $J_{A,B}$ = 7.9 Hz, Δν = 31 Hz, 4 H, H_{ar}), 7.3 (ddd, J = 8.3, 7.2, 1.8 Hz, 1 H, H_{ar}), 7.38 (t, J = 8 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 54.9 (OMe), 55.8 (OMe), 56.2 (OMe), 64.1 (CH_2), 76.2 (CH), 110.5 (CH_{ar}), 110.6 (CH_{ar}), 117.3 (CH_{ar}), 120.8 (CH_{ar}), 123.8 (C_{ar}), 124.6 (CH_{ar}), 126.4 (C_{ar}), 128.8 (CH_{ar}), 129.1 (CH_{ar}), 129.8 (CH_{ar}), 132 (CH_{ar}), 139.2 (C_{ar}), 139.5 (C_{ar}), 141.2 (C_{ar}), 155.4 (C_{ar}), 157 (C_{ar}) ppm. $C_{24}H_{26}O_4S$ (394.53): calcd. C 70.22, H 6.38, S 7.81; found C 70.11, H 6.5, S 7.46.

(+)-[a*R*,1*R*,(S)*R*]-2,2′-Dimethoxy-6-[1-methoxy-2-(*p*-tolylsulfinyl)-ethyl]biphenyl (a*R*-35): Light-yellow solid (10% yield). R_f = 0.13 (Et_2O). M.p. 134–137 °C. $[\alpha]_D^{20}$ = +35.5 (c = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2921, 1596, 1582, 1496, 1466, 1438, 1292, 1254, 1102, 1068, 1037, 1027, 986, 910, 808, 801, 758, 738. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.41 (s, 3 H, CH_3), 2.98 (s, 3 H, OMe), 3.04 (AB part of an ABX system, $J_{A,B}$ = 13, $J_{A,X}$ = 10.9, $J_{B,X}$ = 2.8 Hz, Δν = 219 Hz, 2 H, CH_2), 3.58 (s, 3 H, OMe), 3.66 (s, 3 H, OMe_{ar}), 3.77 (X part of an ABX system, $J_{A,X}$ = 10.9, $J_{B,X}$ = 2.8 Hz, 1 H, CH), 6.74 (br. d, J = 8.3 Hz, 1 H, H_{ar}), 6.81 (dd, J = 7.3, 2.3 Hz, 1 H, H_{ar}), 6.85 (td, J = 7.3, 0.9 Hz, 1 H, H_{ar}), 6.89 (dd, J = 8.3, 0.9 Hz, 1 H, H_{ar}), 7.17 (dd, J = 8.3, 0.9 Hz, 1 H, H_{ar}), 7.23 (A_2B_2, $J_{A,B}$ = 7.7 Hz, Δν = 48 Hz, 1 H, H_{ar}), 7.26 (td, J = 7.3, 2.3 Hz, 1 H, H_{ar}), 7.39 (t, J = 8.3 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.47 ($CH_{3ar(pTol)}$), 55.2 (OMe), 55.9 (OMe), 56.0 (OMe), 64.2 (CH_2), 75.4 (CH), 110.3 (CH_{ar}), 110.9 (CH_{ar}), 117.8 (CH_{ar}), 120.3 (CH_{ar}), 124.3 ($CH_{ar[pTol)}$), 124.3 (C_{ar}), 127.2 (C_{ar}), 128.7 (CH_{ar}), 129.1 (CH_{ar}), 129.7 (CH_{ar}), 130.5 (CH_{ar}), 138.7 (C_{ar}), 139.9 (C_{ar}), 141.3 (C_{ar}), 157.0 (C_{ar}), 157.0 (C_{ar}) ppm.

[1*R*,(S)*R*]-2-[1-Methoxy-2-(*p*-tolylsulfinyl)ethyl]-1,1′-binaphthalenyl (36): White solid (88% yield; *dr* 85:15); R_f = 0.25 (Et_2O/EtOAc, 4:1).
[a*S*,1*R*,(S)*R*]-36: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.38 (s, 3 H, CH_3), 2.49 [X part of an ABX system (m), 1 H, CH_2], 3.04 (s, 3 H, OMe), 3.58–3.68 [AB part of an ABX system (m), 2 H, C*H*(OMe), CH_2], 6.83 (s, 4 H, H_{ar}), 6.94 (d, J = 8.3 Hz, 1 H, H_{ar}), 7.01 (d, J = 8.3 Hz, 1 H, H_{ar}), 7.12 (dd, J = 7, 1.1 Hz, 1 H, H_{ar}), 7.22 (ddd, J = 8.3, 6.8, 1.2 Hz, 1 H, H_{ar}), 7.27 (ddd, J = 8.3, 6.8, 1.2 Hz, 1 H, H_{ar}), 7.42 (dd, J = 8.3, 7 Hz, 1 H, H_{ar}), 7.46 (ddd, J = 8.3, 6.8, 1.2 Hz, 1 H, H_{ar}), 7.53 (ddd, J = 8.3, 6.8, 1.2 Hz, 1 H, H_{ar}), 7.78 (d, J = 8.7 Hz, 1 H, H_{ar}), 7.86 (d, J = 8.3 Hz, 1 H, H_{ar}), 7.91 (d, J = 8.3 Hz, 1 H, H_{ar}), 7.96 (d, J = 8.3 Hz, 1 H, H_{ar}), 8.03 (d, J = 8.7 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 56.1 (OMe), 64.2 (CH_2), 75.8 (CH), 123.0 (CH_{ar}), 123.8 (CH_{ar}), 125.0 (CH_{ar}), 125.7 (CH_{ar}), 126.1 (CH_{ar}), 126.2 (CH_{ar}), 126.4 (CH_{ar}), 126.6 (CH_{ar}), 126.7 (CH_{ar}), 126.9 (CH_{ar}), 127.8 (CH_{ar}), 127.9 (CH_{ar}), 128.3 (CH_{ar}), 129.1 (CH_{ar}), 129.4 (CH_{ar}), 132.7 (C_{ar}), 132.9 (C_{ar}), 133.0 (C_{ar}), 133.5 (C_{ar}), 134.5 (C_{ar}), 135.0 (C_{ar}), 136.7 (C_{ar}), 138.8 (C_{ar}), 141.0 (C_{ar}) ppm.
[a*S*,1*R*,(S)*R*]-36: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.33 (s, 3 H, CH_3), 2.78 (X part of an ABX system, $J_{A,X}$ = 12.6, $J_{B,X}$ = 3 Hz, 1 H, CH_2), 3.04 (s, 3 H, OMe), 3.46 (B part of an ABX system, J = 10.9, 12.6, 3 Hz, 1 H, CH_2), 3.58–3.64 [A part of an ABX system (m), 1 H, C*H*(OMe)], 6.81–8.82 (m, 17 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 30.3 (CH_3), 56.5 (OMe), 64.4 (CH_2), 76.3 (CH), 122.7 (CH_{ar}), 124.1 (CH_{ar}), 125.3 (CH_{ar}), 125.4 (CH_{ar}), 125.4 (CH_{ar}), 125.9 (CH_{ar}), 126 (CH_{ar}), 126.4 (CH_{ar}), 127.7 (CH_{ar}), 127.8 (CH_{ar}), 128 (CH_{ar}), 128.1 (CH_{ar}), 128.4 (CH_{ar}), 129.1 (CH_{ar}), 129.5 (CH_{ar}), 131.7 (C_{ar}), 133.1 (C_{ar}), 133.1 (C_{ar}), 133.5 (C_{ar}), 134.6 (C_{ar}), 134.9 (C_{ar}), 136.3 (C_{ar}), 138.9 (C_{ar}), 141.2 (C_{ar}) ppm.

[1*R*,(S)*R*]-2-[1-Methoxy-2-(*p*-tolylsulfinyl)ethyl]-1-(*o*-tolyl)naphthalene (37): Orange solid (75% yield; *dr* 75:25); R_f = 0.29 (Et_2O).
[a*S*,1*R*,(S)*R*]-37: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.7 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 2.59 (X part of an ABX system, $J_{A,X}$ = 2.6, $J_{B,X}$ = 12.6 Hz, 1 H, CH_2), 3.04 (s, 3 H, OMe), 3.77 [AB part of an ABX system, $J_{A,B}$ = 11, $J_{A,X}$ = 2.6, $J_{B,X}$ = 12.6 Hz, Δν = 71 Hz, 2 H, C*H*(OMe), CH_2], 6.87 (dd, J = 7.3, 1.3 Hz, 1 H, H_{ar}), 7.1 (m, 1 H, H_{ar}), 7.13 (m, 1 H, H_{ar}), 7.14 (m, 1 H, H_{ar}), 7.24 (A_2B_2, $J_{A,B}$ = 8.2 Hz, Δν = 45 Hz, 4 H, H_{ar}), 7.29 (m, 1 H, H_{ar}), 7.34 (m, 1 H, H_{ar}), 7.46 (ddd, J = 8.2, 6.9, 1.3 Hz, 1 H, H_{ar}), 7.68 (d, J = 8.7 Hz, 1 H, H_{ar}), 7.86 (d, J = 8.1 Hz, 1 H, H_{ar}), 7.93 (d, J = 8.7 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 19.6 (Me), 21.5 (CH_3), 56.1 (OMe), 64.2 (CH_2), 75.3 (CH), 123.1 (H_{ar}), 124.3 (CH_{ar}), 125.7 (H_{ar}), 126.2 (H_{ar}), 126.2 (H_{ar}), 126.4 (H_{ar}), 127.5 (H_{ar}), 128.0 (H_{ar}), 128.7 (H_{ar}), 129.4 (H_{ar}), 129.7 (CH_{ar}), 129.8 (H_{ar}), 130.3 (C_{ar}), 132.0 (C_{ar}), 133.1 (C_{ar}), 133.3 (C_{ar}), 136.4 (C_{ar}), 136.9 (C_{ar}), 138.1 (C_{ar}), 141.6 (C_{ar}) ppm.
[a*S*,1*R*,(S)*R*]-37: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.78 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 2.82 (X part of an ABX system, $J_{A,X}$ = 2.6, $J_{B,X}$ = 10.8 Hz, 1 H, CH_2), 3.02 (s, 3 H, OMe), 3.63 (AB part of an ABX system, J = 10.8, 2.6, 10.8 Hz, 2 H, C*H*(OMe), CH_2), 6.83–7.95 (m, 14 H, H_{ar}) ppm.

(+)-[a*S*,1*R*,(S)*R*]-1-(2-Methoxyphenyl)-2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]naphthalene (a*S*-38): White solid (60% yield). R_f = 0.2 (Et_2O). M.p. 131–133 °C. $[\alpha]_D^{20}$ = +28.4 (c = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2922, 1597, 1492, 1448, 1431, 1248, 1231, 1103, 1084, 1044, 1028, 992, 965, 835, 812, 780, 762, 752. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.43 (s, 3 H, CH_3), 2.99 (s, 3 H, OMe), 3.22 (AB part of an ABX system, $J_{A,B}$ = 12.8, $J_{A,X}$ = 11.1, $J_{B,X}$ = 2.8 Hz, Δν = 244 Hz, 2 H, CH_2), 3.52 (s, 3 H, OMe), 3.95 (X part of an ABX system, $J_{A,X}$ = 11.1, $J_{B,X}$ = 2.8 Hz, 1 H, CH), 6.8 (d, J = 8.5 Hz, 1 H, H_{ar}), 6.9 (dd, J = 7.4, 2.2 Hz, 1 H, H_{ar}), 6.94 (td, J = 7.4, 1 Hz, 1 H, H_{ar}), 7.2 (br. d, J = 6.8 Hz, 1 H, H_{ar}), 7.27 (A_2B_2, $J_{A,B}$ = 7.9 Hz, Δν = 58 Hz, 4 H, H_{ar}), 7.31 (ddd, J = 8.1, 6.8, 1.3 Hz, 1 H, H_{ar}), 7.33 (m, 1 H, H_{ar}), 7.45 (ddd, J = 8.1, 6.8, 1.2 Hz, 1 H, H_{ar}), 7.67 (d, J = 8.7 Hz, 1 H, H_{ar}), 7.85 (br. d, J = 8.1 Hz, 1 H, H_{ar}), 7.93 (d, J = 8.7 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 55.1 (OMe), 55.9 (OMe), 64.1 (CH_2), 75.8 (CH), 110.9 (CH_{ar}), 120.4 (CH_{ar}), 123.0 (CH_{ar}), 124.3 (CH_{ar}), 125.8 (C_{ar}), 126.0 (CH_{ar}), 126.1 (CH_{ar}), 126.3 (CH_{ar}), 127.9 (CH_{ar}),

128.7 (CH_{ar}), 129 (CH_{ar}), 129.7 (CH_{ar}), 130.8 (CH_{ar}), 132.6 (C_{ar}), 133.1 (C_{ar}), 133.9 (C_{ar}), 135.3 (C_{ar}), 139.9 (C_{ar}), 141.4 (C_{ar}), 157.3 (C_{ar}) ppm.

[a*R*,1*R*,(S)*R*]-1-(2-Methoxyphenyl)-2-[1-methoxy-2-(*p*-tolylsulfinyl)-ethyl]naphthalene (a*R*-38): Yellow solid (15% yield). R_f = 0.3 (Et_2O). M.p. 162–165 °C. $[\alpha]_D^{20}$ = –28.1 (*c* = 0.21, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2922, 1597, 1492, 1448, 1431, 1248, 1231, 1103, 1084, 1044, 1028, 992, 965, 835, 812, 780, 762, 752. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.44 (s, 3 H, CH_3), 2.67 (X part of an ABX system, $J_{A,X}$ = 3.2, $J_{B,X}$ = 12.6 Hz, 1 H, CH_2), 3.03 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.66 [AB part of an ABX system, $J_{A,B}$ = 10.9, $J_{A,X}$ = 3.2, $J_{B,X}$ = 12.6 Hz, $\Delta\nu$ = 67 Hz, 2 H, CH_2, C*H*(OMe)], 6.81 (d, *J* = 8.5 Hz, 1 H, H_{ar}), 6.89 (dd, *J* = 7.3, 1.9 Hz, 1 H, H_{ar}), 6.98 (td, *J* = 7.5, 1.1 Hz, 1 H, H_{ar}), 7.22 (br. d, *J* = 8.5 Hz, 1 H, H_{ar}), 7.23 (A_2B_2, $J_{A,B}$ = 8.5 Hz, $\Delta\nu$ = 43 Hz, 4 H, H_{ar}), 7.3 (ddd, *J* = 8.3, 6.8, 1.5 Hz, 1 H, H_{ar}), 7.39 (ddd, *J* = 8.3, 7.5, 1.9 Hz, 1 H, H_{ar}), 7.44 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1 H, H_{ar}), 7.68 (d, *J* = 8.7 Hz, 1 H, H_{ar}), 7.85 (br. d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.92 (d, *J* = 8.7 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 54.9 (OMe), 56.2 (OMe), 64.1 (CH_2), 76.5 (CH), 110.6 (CH_{ar}), 120.9 (CH_{ar}), 122.5 (CH_{ar}), 124.6 (CH), 125.5 (C_{ar}), 125.9 (CH_{ar}), 126.0 (CH_{ar}), 126.1 (CH_{ar}), 127.9 (CH_{ar}), 128.6 (CH_{ar}), 129.2 (CH_{ar}), 129.8 (CH_{ar}), 132.1 (CH_{ar}), 132.7 (C_{ar}), 133.2 (C_{ar}), 134.5 (C_{ar}), 134.8 (C_{ar}), 139.5 (C_{ar}), 141.3 (C_{ar}), 155.8 (C_{ar}) ppm.

(–)-[a*R*,1*R*,(S)*R*]-2-Methoxy-1-{2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]-4-nitrophenyl}naphthalene (a*R*-39): Light-yellow solid (93% yield). R_f = 0.13 (Et_2O). M.p. 72–75 °C. $[\alpha]_D^{20}$ = –80.3 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 1740, 1730, 1604, 1522, 1455, 1435, 1344, 1304, 1248, 1125, 1086, 1031, 897, 811, 738. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.39 (s, 3 H, CH_3), 2.79 (AB part of an ABX system, $J_{A,B}$ = 12.9, $J_{A,X}$ = 11, $J_{B,X}$ = 2.4 Hz, $\Delta\nu$ = 296 Hz, 2 H, CH_2), 3.15 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.73 (X part of an ABX system, $J_{A,X}$ = 11, $J_{B,X}$ = 2.4 Hz, 1 H, CH), 6.85 (A_2B_2, $J_{A,B}$ = 8.1 Hz, $\Delta\nu$ = 35 Hz, 4 H, H_{ar}), 6.95 (br. d, *J* = 8.7 Hz, 1 H, H_{ar}), 7.12 (d, *J* = 9 Hz, 1 H, H_{ar}), 7.27 (d, *J* = 8.7 Hz, 1 H, H_{ar}), 7.35 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1 H, H_{ar}), 7.43 (ddd, *J* = 8.3, 6.9, 1.5 Hz, 1 H, H_{ar}), 7.88 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.9 (d, *J* = 9 Hz, 1 H, H_{ar}), 8.24 (dd, *J* = 8.3, 2.5 Hz, 1 H, H_{ar}), 8.54 (d, *J* = 2.5 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.5 (CH_3), 55.6 [CH(O*C*H$_3$)], 56.8 (O*C*H$_3$), 63.9 (CH_2), 75.9 (CH), 111.9 (CH_{ar}), 119.2 (C_{ar}), 121.0 (CH_{ar}), 123.0 (CH_{ar}), 123.5 (CH_{ar}), 123.9 (CH_{ar}), 124.2 (CH_{ar}), 127.7 (CH_{ar}), 128.3 (CH_{ar}), 128.9 (C_{ar}), 129.6 (CH_{ar}), 130.5 (CH_{ar}), 132.7 (C_{ar}), 132.7 (CH_{ar}), 139.3 (C_{ar}), 141.2 (C_{ar}), 141.7 (C_{ar}), 142.4 (C_{ar}), 148.4 (C_{ar}), 152.0 (C_{ar}) ppm. $C_{27}H_{25}NO_5S$ (475.56): calcd. C 68.19, H 5.3, N 2.95, S 6.74; found C 67.87, H 5.53, N 3, S 6.47.

(–)-[a*S*,1*R*,(S)*R*]-1-{2-[1-Methoxy-2-(*p*-tolylsulfinyl)ethyl]-4-nitrophenyl}-2-methylnaphthalene (a*S*-40): Light-orange solid (84% yield). R_f = 0.23 (Et_2O). M.p. 187–189 °C. $[\alpha]_D^{20}$ = –16 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2948, 1596, 1510, 1342, 1213, 1097, 1083, 1043, 979, 912, 916, 747. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.02 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.83 (AB part of an ABX system, $J_{A,B}$ = 12.8, $J_{A,X}$ = 10.7, $J_{B,X}$ = 2.5 Hz, $\Delta\nu$ = 259 Hz, 2 H, CH_2), 3.13 (s, 3 H, OMe), 3.58 [X part of an ABX system, $J_{A,X}$ = 10.7, $J_{B,X}$ = 2.5 Hz, 1 H, C*H*(OMe)], 6.82 (A_2B_2, $J_{A,B}$ = 8.2 Hz, $\Delta\nu$ = 52 Hz, 4 H, H_{ar}), 6.88 (br. d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.25 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.3 (d, *J* = 8.3 Hz, 1 H, H_{ar}), 7.36 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1 H, H_{ar}), 7.5 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1 H, H_{ar}), 7.78 (d, *J* = 8.4 Hz, 1 H, H_{ar}), 7.9 (d, *J* = 8 Hz, 1 H, H_{ar}), 8.27 (d, *J* = 8.3 Hz, 1 H, 2.5 Hz, H_{ar}), 8.58 (dd, 1 H, *J* = 2.5 Hz, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.2 (CH_3), 21.5 (CH_3), 57.0 (O*C*H$_3$), 64.0 (CH_2), 75.9 (CH), 121.5 (CH_{ar}), 123.2 (CH_{ar}), 123.7 (CH_{ar}), 124.8 (CH_{ar}), 125.7 (CH_{ar}), 127.1 (CH_{ar}), 128.1 (CH_{ar}), 128.3 (CH_{ar}), 128.6 (CH_{ar}), 129.6 (CH_{ar}), 131.9 (C_{ar}), 132.0 (C_{ar}), 132.0 (C_{ar}), 132.1 (CH_{ar}), 132.6 (C_{ar}), 139.1 (C_{ar}), 140.8 (C_{ar}), 141.2 (C_{ar}), 145.3 (C_{ar}), 148.5 (C_{ar}) ppm. $C_{27}H_{25}NO_4S$ (459.56): calcd. C 70.57, H 5.48, N 3.05, S 6.98; found C 70.49, H 5.61, N 3.22, S 6.98.

(+)-[a*R*,1*S*]-2-Methoxy-1-{2-[1-methoxy-2-(*p*-tolylsulfonyl)ethyl]-4-nitrophenyl}naphthalene (a*R*-42). Major Atropodiastereomer: Brown solid (70% yield). R_f = 0.25 (EtOAc/hexanes, 1:1). M.p. 159–162 °C. $[\alpha]_D^{20}$ = +4.5 (*c* = 1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 1594, 1510, 1462, 1301, 1311, 1255, 1247, 1134, 1112, 1084, 1062, 818, 811, 168, 743. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.36 (s, 3 H, CH_3), 2.77 (s, 3 H, CH[OC*H*$_3$)), 3.46 (AB part of an ABX system, $J_{A,B}$ = 14.7, $J_{A,X}$ = 9.7, $J_{B,X}$ = 2.2 Hz, $\Delta\nu$ = 29 Hz, 2 H, CH_2), 3.89 (s, 3 H, OCH_3), 4.21 [X part of an ABX system, $J_{A,X}$ = 9.7, $J_{B,X}$ = 2.2 Hz, 1 H, C*H*(OMe)], 7.13–7.21 (m, 2 H, H_{ar}), 7.27 (ddd, *J* = 8.2, 6.7, 1.5 Hz, 1 H, H_{ar}), 7.34 (ddd, *J* = 8.1, 6.7, 1.5 Hz, 1 H, H_{ar}), 7.35 (A_2B_2, $J_{A,B}$ = 8.3 Hz, $\Delta\nu$ = 107 Hz, 4 H, H_{ar}), 7.41 (d, *J* = 8.9 Hz, 1 H, H_{ar}), 7.42 (td, *J* = 7.3, 1.8 Hz, 1 H, H_{ar}), 7.47 (td, *J* = 7.3, 1.5 Hz, 1 H, H_{ar}), 7.55 (m, *J* = 8.1 Hz, 1.5 Hz, 1 H, H_{ar}), 7.86 (dd, 1 H, *J* = 8.9 Hz, H_{ar}), 7.98 (d, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.5 (CH_3), 55.9 [CH(O*C*H$_3$)], 56.2 (O*C*H$_3$), 63.0 (CH_2), 75.3 [CH(OMe)], 112.8 (CH_{ar}), 121.3 (C_{ar}), 123.4 (CH_{ar}), 124.3 (CH_{ar}), 125.6 (CH_{ar}), 126.4 (CH_{ar}), 127.9 (CH_{ar}), 128.0 (CH_{ar}), 128.1 (CH_{ar}), 128.3 (CH_{ar}), 128.9 (C_{ar}), 129.2 (CH_{ar}), 130.0 (CH_{ar}), 131.3 (CH_{ar}), 133.1 (C_{ar}), 135.4 (C_{ar}), 137.2 (C_{ar}), 138.5 (C_{ar}), 143.8 (C_{ar}), 153.9 (C_{ar}) ppm. $C_{27}H_{26}O_4S$ (446.56): calcd. C 72.62, H 5.87, S 7.18; found C 72.81, H 5.94, S 7.21.

(–)-[a*S*,1*R*]-2-Methoxy-1-{2-[1-methoxy-2-(*p*-tolylsulfonyl)ethyl]-4-nitrophenyl}naphthalene (a*S*-42). Minor Atropodiastereomer: Brown gum (12% yield). R_f = 0.13 (EtOAc/hexanes, 1:1). $[\alpha]_D^{20}$ = –64.4 (*c* = 0.22, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2925, 2849, 1621, 1594, 1508, 1448, 1315, 1301, 1256, 1137, 1085, 1067, 1020, 986, 810, 746. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.04 (s, 3 H, CH_3), 2.38 [s, 3 H, CH(OC*H*$_3$)], 3.97 (AB part of an ABX system, $J_{A,B}$ = 14.4, $J_{A,X}$ = 10.7, $J_{B,X}$ = 1.6 Hz, $\Delta\nu$ = 168 Hz, 2 H, CH_2), 3.23 (s, 3 H, OCH_3), 4.37 [X part of an ABX system, $J_{A,X}$ = 10.7, $J_{B,X}$ = 1.6 Hz, 1 H, C*H*(OMe)], 7.13–7.99 (m, 14 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.55 (CH_3), 55.87 [CH(O*C*H$_3$)], 56.78 (O*C*H$_3$), 62.48 (CH_2), 74.95 [CH(OMe)], 112.71 (CH_{ar}), 121.32 (C_{ar}), 123.62 (CH_{ar}), 123.97 (CH_{ar}), 125.48 (CH_{ar}), 127 (CH_{ar}), 127.47 (CH_{ar}), 128.09 (CH_{ar}), 128.29 (CH_{ar}), 128.32 (CH_{ar}), 129.1 (C_{ar}), 129.26 (CH_{ar}), 129.89 (CH_{ar}), 131.36 (CH_{ar}), 133.54 (C_{ar}), 135.09 (C_{ar}), 136.65 (C_{ar}), 138.84 (C_{ar}), 143.57 (C_{ar}), 152.78 (C_{ar}) ppm.

(+)-[a*R*,1*S*,(S)*R*]-2-Methoxy-1-{2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]phenyl}naphthalene (a*R*-45). Major Atropodiastereomer: White solid (49% yield). R_f = 0.3 (EtOAc/hexanes, 1:1). M.p. 155–158 °C. $[\alpha]_D^{20}$ = +214.4 (*c* = 1.2, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2923, 1622, 1594, 1510, 1461, 1356, 1333, 1257, 1105, 1067, 1031, 1016, 801, 764, 745. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.38 (s, 3 H, CH_3), 3 [s, 3 H, CH(OC*H*$_3$)], 3.01 (AB part of an ABX system, $J_{A,B}$ = 13.3, $J_{A,X}$ = 10.7, $J_{B,X}$ = 2.1 Hz, $\Delta\nu$ = 50 Hz, 2 H, CH_2), 3.85 (s, 3 H, OCH_3), 4.42 [X part of an ABX system, $J_{A,X}$ = 10.7, $J_{B,X}$ = 2.1 Hz, 1 H, C*H*(OMe), CH_2], 7.18–7.51 (m, 11 H, H_{ar}), 7.62 (dd, *J* = 7.6, 1.4 Hz, 1 H, H_{ar}), 7.85 (dd, *J* = 8.2, 2.2 Hz, 1 H, H_{ar}), 7.97 (d, *J* = 8.9 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.3 (CH_3), 55.8 [CH(O*C*H$_3$)], 56.6 (O*C*H$_3$), 66.3 (CH_2), 74 [CH(OMe)], 121.7 (CH_{ar}), 121.3 (C_{ar}), 123.4 (CH_{ar}), 123.7 (CH_{ar}), 124.5 (CH_{ar}), 125.9 (CH_{ar}), 126.4 (CH_{ar}), 128 (CH_{ar}), 128.1 (CH_{ar}), 128.2 (CH_{ar}), 129 (C_{ar}), 129.7 (CH_{ar}), 130 (CH_{ar}), 131.3 (CH_{ar}), 133.4 (C_{ar}), 135.9 (C_{ar}), 139.1 (C_{ar}), 140.9 (C_{ar}), 142.1 (C_{ar}), 154 (C_{ar}) ppm. $C_{27}H_{26}O_3S$ (430.56): calcd. C 75.32, H 6.09, S 7.45; found C 75.09, H 6.35, S 7.37.

(+)-[a*S*,1*S*,(S)*R*]-2-Methoxy-1-{2-[1-methoxy-2-(*p*-tolylsulfinyl)ethyl]phenyl}naphthalene (a*S*-45). Minor Atropodiastereomer: White solid (40% yield). R_f = 0.1 (EtOAc/hexanes, 1:1). M.p. 41–43 °C. $[\alpha]_D^{20}$ = +257.8 (c = 1.9, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2934, 1620, 1593, 1508, 1463, 1380, 1333, 1265, 1253, 1105, 1086, 1047, 1017, 806, 760, 749. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.32 (s, 3 H, CH_3), 2.49 (AB part of an ABX system, $J_{A,B}$ = 13.3, $J_{A,X}$ = 10.7, $J_{B,X}$ = 2.4 Hz, $\Delta\nu$ = 61 Hz, 2 H, CH_2), 2.37 [s, 3 H, CH(OCH_3)], 2.88 (s, 3 H, OCH_3), 4.56 [X part of an ABX system, $J_{A,X}$ = 10.7, $J_{B,X}$ = 2.4 Hz, 1 H, CH(OCH_3)], 6.93 (A_2B_2, $J_{A,B}$ = 8.1 Hz, $\Delta\nu$ = 69 Hz, 4 H, H_{ar}), 7.01–7.04 (m, 1 H, H_{ar}), 7.19–7.25 (m, 2 H, H_{ar}), 7.32–7.50 (m, 4 H, H_{ar}), 6.68 (dd, J = 7.6, 1.6 Hz, 1 H, H_{ar}), 7.92 (d, J = 8.2 Hz, 1 H, H_{ar}), 8 (d, J = 8.9 Hz, 1 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.3 (CH_3), 55.9 [CH(OCH_3)], 57 (OCH_3), 64.6 (CH_2), 74.2 [CH(OMe)], 112.9 (CH_{ar}), 121.4 (C_{ar}), 123.3 (CH_{ar}), 123.9 (CH_{ar}), 124.3 (CH_{ar}), 125.5 (CH_{ar}), 126.5 (CH_{ar}), 127.8 (CH_{ar}), 128.1 (CH_{ar}), 128.4 (CH_{ar}), 129.2 (C_{ar}), 129.5 (CH_{ar}), 130 (CH_{ar}), 131.4 (CH_{ar}), 133.8 (C_{ar}), 135.4 (C_{ar}), 139.4 (C_{ar}), 141 (C_{ar}), 141.7 (C_{ar}), 153 (C_{ar}) ppm.

X-ray Analysis of (–)-[a*S*,1*R*,(S)*R*]-(11): $C_{26}H_{24}O_3S$, M = 415.54 g mol^{-1}, orthorhombic, space group = $P2_12_12_1$, a = 11.1954(3) Å, b = 11.6368(3) Å, c = 16.6489(4) Å, V = 2169.00(9) Å^3, Z = 4, colorless crystal 0.12 × 0.08 × 0.06 mm^3, $D_{calcd.}$ = 1.27 g cm^{-3}, F_{000} = 876, μ(Mo-K_α) = 0.174 cm^{-1}, θ_{max} = 173 K. A total of 6311 reflections were collected. The final cycle of the full-matrix least-squares refinement was based on 3256 observed reflections [$I > 3\sigma(I)$] and 275 variable parameters and converged with unweighted and weighted agreement factors of R = 0.046 and R_w = 0.059, respectively (GOF = 1.025). The maximum peak in the final difference Fourier map corresponded to 0.678 e Å^{-3}.

X-ray Analysis of (+)-[a*S*,1*R*,(S)*R*]-(38): $C_{27}H_{26}O_3S$, M = 430.57 g mol^{-1}, hexagonal, space group = $P3_1$, a = 9.3783(2) Å, b = 9.3783(2) Å, c = 22.7193(8) Å, α = 90°, β = 90°, γ = 120°, V = 1730.49(8) Å^3, Z = 3, colorless crystal 0.20 × 0.20 × 0.04, $D_{calcd.}$ = 1.24 g cm^{-3}, F_{000} = 684, μ(Mo-K_α) = 0.166 cm^{-1}, θ_{max} = 173 K. A total of 5120 reflections were collected. The final cycle of the full-matrix least-squares refinement was based on 3540 observed reflections [$I > 3\sigma(I)$] and 279 variable parameters and converged with unweighted and weighted agreement factors of R = 0.045 and R_w = 0.060, respectively (GOF = 1.058). The maximum peak in the final difference Fourier map corresponded to 0.241 e Å^{-3}.

CCDC-223158 and CCDC-249442 for **(–)-[a*S*,1*R*,(S)*R*]-(11)** and **(+)-[a*S*,1*R*,(S)*R*]-(38)**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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