Nucleophilic Attack on 4,5-Dihydro-4-alkyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]thiepinium Salts. A Convenient Approach to New 2,2′-Bidentate 1,1′-Binaphthalene Ligands with Sulfur Donor Atoms†

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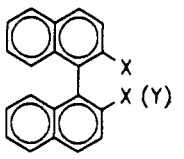
The title dihydrothiepinium salts **6** react with a wide range of N-, S-, Se-, O-, and C-nucleophiles to afford dihydrothiepin **5** and/or the corresponding bidentate ligands **7**. The dual course of the reaction can be controlled by a judicious choice of the substrate counterion. In most instances, an iodide counterion aids formation of dihydrothiepins **5**, whereas perchlorate, tetraphenyl borate, or tetrafluoroborate counterions favor formation of bidentate ligands **7**. An explanation based on a competition between the counterion and the external nucleophile is provided. Dihydrothiepinium salts **6** are easily accessible from dibromide (*R*,*S*)-**4** *via* dihydrothiepin (*R*,*S*)-**5**. Individual enantiomers (*R*)- and (*S*)-**5** have been obtained by resolution on a preparative triacetylcellulose (TAC) column and assigned absolute configuration on the basis of CD spectra and chemical correlation.

Introduction

2,2′-Disubstituted 1,1′-binaphthalene ligands **1**, which have donor atoms attached directly to the aromatic rings, have been amply investigated, and some have proved to be highly potent chiral auxiliaries in enantioselective metal-ion catalysis.[1] In contrast, homologous derivatives **2**, in which the donor sites are insulated from the aromatic moiety by a methylene unit, have received only sparse attention[2,3] in spite of the higher donating ability of the heteroatoms and a better induced fit to bonding requirements of the metal ions.[4]

Most of the attention so far has been focused on dissymmetric binaphthyl ligands **1** and **2**, which bear *identical* donor sites at the 2- and 2′-positions[5] (the C_2 symmetry group). However, there has also been increasing interest in the corresponding asymmetric ligands possessing *different* groups at the 2- and 2′-positions[7] (the C_1 symmetry group). According to recent reports,[8] ligands with C_1 symmetry afford superior optical yields in some reactions.

In most instances, binaphthyl ligands bearing the O-, N-, and P-atoms (or combinations thereof) have been investigated. Binaphthyls bearing chalcogen atoms have thus far remained virtually unexplored,[9–11] notwithstanding the catalytic potential of sulfur ligands.[11–13]



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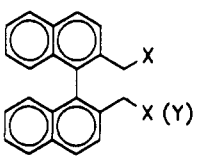

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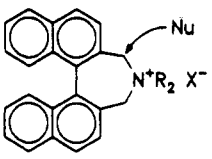

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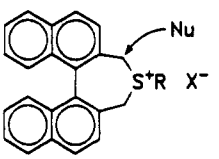

6

In this paper we report a convenient synthesis of new 2,2′-bidentate 1,1′-binaphthalene ligands of type **2** containing one or two sulfur donor atoms. Encouraged by the recent observation[7c,d] that nucleophiles preferentially attack the benzylic carbon atom in dihydroazepinium salts **3**, we have now examined an analogous cleavage of dihydrothiepinium salts **6**.

Results and Discussion

Synthesis of Racemic 4,5-Dihydro-3*H*-dinaphtho-[2,1-*c*:1′,2′-*e*]thiepin (5) and Its Resolution into

† Dedicated to Dr. Vladimír Hanuš on the occasion of his 70th birthday.

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(1) For a recent review on binaphthyl derivatives as chiral auxiliaries, see: (a) Rosini, C.; Francini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503. (b) Blaser, H.-U. *Chem. Rev.* **1992**, *92*, 935.

(2) To our knowledge, 2,2′-bis((diphenylphosphino)methyl)-1,1′-binaphthyl (NAPHOS) is the sole ligand of type **2** (X = Y = PPh_2) that has been screened in enantioselective catalysis (ref 3).

(3) Tamao, K.; Yamamoto, H.; Matsumoto, H.; Miyake, N.; Hayashi, T.; Kumada, M. *Tetrahedron Lett.* **1977**, 1389.

(4) Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gawney, J. A., Jr.; Powell, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5535.

(5) The prevailing preference for the dissymmetric binaphthyl ligands over the asymmetric ones in enantioselective catalysis probably stems from the assumption (ref 6) that reduction of the number of transition states can increase enantiomeric excess in the reaction.

(6) Kagan, H. B.; Dang, T. *J. Am. Chem. Soc.* **1972**, *94*, 6429.

(7) (a) Smrčina, M.; Lorenc, M.; Hanuš, V.; Kočovský, P. *Synlett* **1991**, 231. (b) Smrčina, M.; Lorenc, M.; Hanuš, V.; Sedmera, P.; Kočovský, P. *J. Org. Chem.* **1992**, *57*, 1917. (c) Stará, I. G.; Starý, I.; Závada, J. *J. Org. Chem.* **1992**, *57*, 6966. (d) Stará, I. G.; Starý, I.; Závada, J. *Tetrahedron Asymm.* **1992**, *3*, 1365. (e) Uozumi, Y.; Takahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945.

(8) (a) Hayashi, T. *Pure Appl. Chem.* **1988**, *60*, 7. (b) Reiser, O. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 547. (c) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566.

(9) In the course of preparation of this manuscript, the synthesis of the sulfur-bearing ligands **1** was reported (see ref 10).

(10) Fabbri, D.; Delogu, G.; De Lucchi, O. *J. Org. Chem.* **1993**, *58*, 1748.

(11) The bad reputation of sulfur compounds as catalyst poisons may be the reason for the limited use of sulfur ligands in enantioselective catalysis. For recent successful applications, see refs 12 and 13.

(12) (a) Griffin, J. H.; Kellogg, R. M. *J. Org. Chem.* **1985**, *50*, 3261. (b) Lemaire, M.; Vriesema, B. K.; Kellogg, R. M. *Tetrahedron Lett.* **1985**, *26*, 3499. (c) Vriesema, B. K.; Kellogg, R. M. *Tetrahedron Lett.* **1986**, *27*, 2049. (d) Vriesema, B. K.; Lemaire, M.; Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1986**, *51*, 5169. (e) Kellogg, R. M. *Pure Appl. Chem.* **1992**, *64*, 413.

(13) (a) Leyendecker, F.; Laucher, D. *Nouv. J. Chim.* **1985**, *9*, 13. (b) Honeychuck, R. V.; Okoroafor, M. O.; Shen, L.-H.; Brubaker, C. H., Jr. *Organometallics* **1986**, *5*, 482. (c) Okoroafor, M. O.; Ward, D. L.; Brubaker, C. H., Jr. *Organometallics* **1988**, *7*, 1504. (d) Frost, C. G.; Williams, J. M. J. *Tetrahedron Lett.* **1993**, *34*, 2015.

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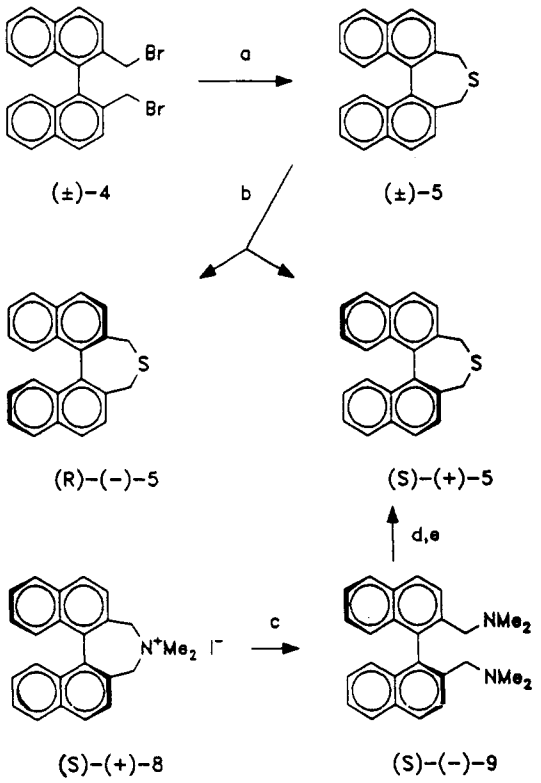
Scheme 1. Preparation of Optically Pure Sulfides (*S*)-(+)-5 and (*R*)-(−)-5[a]



[a] Key: (a) $Na_2S·9H_2O$, DMF, 100 °C (99%); (b) preparative chromatography on TAC, eluent *t*-BuOMe (100% o.p. (*S*)-(+)-5, >97% o.p. (*R*)-(−)-5); (c) 40% aqueous Me_2NH, sealed tube, 130 °C (87%); (d) MeI, CH_3CN, 35 °C; (e) $Na_2S·9H_2O$, DMF, 125 °C (35% from (*S*)-(+)-9, 100% o.p. determined by chromatography on a TAC column).

Enantiomers. Easily accessible racemic[14] 2,2'-bis(bromomethyl)-1,1'-binaphthyl (4) was used as the starting material. On reaction with sodium sulfide in DMF, dibromide 4 afforded dihydrothiepin 5 in quantitative yield (Scheme 1). In order to obtain the individual enantiomers, we resolved racemic sulfide 5 by liquid chromatography on triacetylcellulose on a preparative scale (Figure 1), thus circumventing the preparation of enantiomeric dibromides[15] (*R*)- and (*S*)-4.

The absolute configuration (*S*) was assigned to the dextrorotatory enantiomer of sulfide 5 (the isomer that eluted first from the TAC column) on the basis of comparison of its circular dichroism spectrum with those of (*S*)-(+)-4,5-dihydro-4-methyl-3*H*-dinaphth[2,1-*c*:1',2'-*e*]azepine (10) (ref 7d) and 2,2'-dimethyl-1,1'-binaphthyl (11) (ref 14) of known absolute configuration (Figure 2). In an alternative approach, a chemical correlation between quaternary ammonium iodide (*S*)-(+)-8 (ref 7d) and the dextrorotatory enantiomer of sulfide 5 (Scheme 1) allowed an independent assignment.

(14) Maigrot, N.; Mazaleyrat, J. P. *Synthesis* **1985**, 317.

(15) There are in principle two possible synthetic routes to enantiomerically pure dibromides 4: (1) the elegant but expensive Hayashi approach (ref 16) involving enantioselective cross-coupling of two naphthalene blocks catalyzed by a complex of nickel(II) and PPFOMe (one of the most expensive commercially available chiral ligands) or (2) the relatively cheap but very laborious Mazaleyrat approach (ref 14) consisting of a three-step resolution of racemic dibromide 4 *via* diastereoisomeric quaternary ephedrinium salts with an overall preparative yield of 33–42%.

(16) Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153.

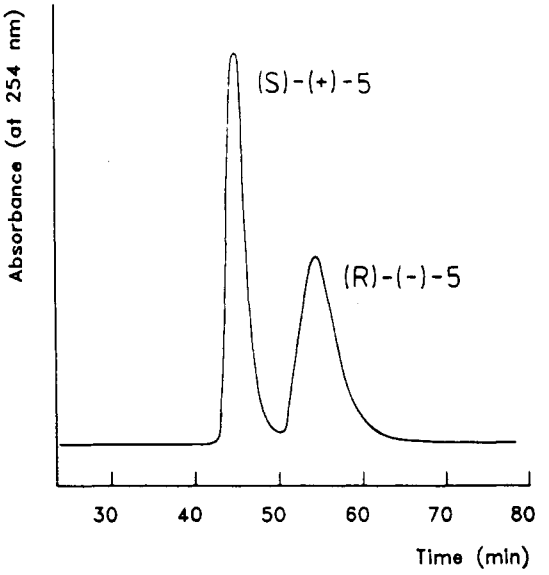


Figure 1. Resolution of the racemic sulfide 5 into enantiomers *via* chromatography on a TAC column (*tert*-butyl methyl ether as eluent, 200 g of TAC, injection 70 mg of *rac*-5 in 10 mL of eluent, flow rate 3.0 mL/min, rt).

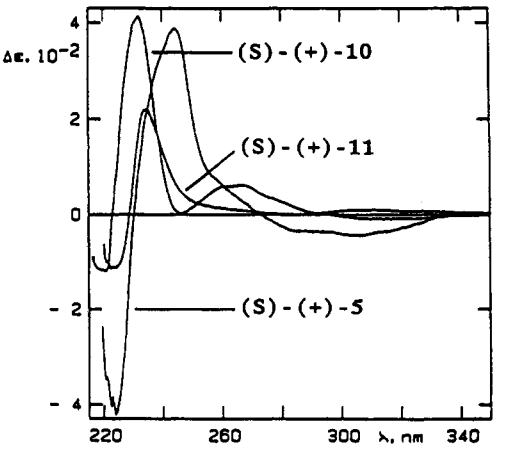
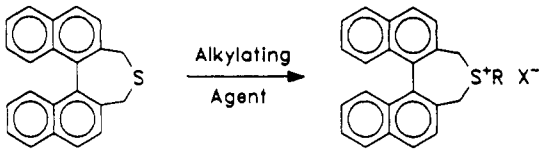


Figure 2. CD spectra of sulfide (*S*)-(+)-5 (3.717 10^{-4} mol·L^{-1}), (*S*)-(+)-4,5-dihydro-4-methyl-3*H*-dinaphth[2,1-*c*:1',2'-*e*]-azepine (10) (4.401 10^{-4} mol·L^{-1}), and (*S*)-(+)-2,2'-dimethyl-1,1'-binaphthyl (11) (4.255 10^{-4} mol·L^{-1}) in chloroform.

Preparation of Sulfonium Salts 6a–d. That the alkylation of racemic sulfide 5 with methyl iodide is a reversible process is evidenced by the very large excess of methyl iodide (about 50-fold) required to approach complete methylation (Table 1). This difficulty can be overcome by using a nonnucleophilic counterion[17] such as BPh_4^-, ClO_4^-, or BF_4^- in the reaction (Table 1). Thus, alkylation with equimolar methyl perchlorate (generated *in situ* from methyl iodide and silver perchlorate) or with the "hot" Meerwein's salt $Et_3O^+BF_4^-$ provided sulfonium salts **6c,d** in nearly quantitative yields. Sulfonium salts **6b** and **6c** could be obtained in moderate yields, although less conveniently, by ion exchange with tetraphenylborate anion following the methyl iodide alkylation and by addition of $Mg(ClO_4)_2$ (cf. footnote *f* in Table 1) to the reaction mixture, respectively. Individual sulfonium salts **6b–d** are stable for several months when stored in the

(17) A referee suggested methyl tosylate as an alternative methylating agent with nonnucleophilic leaving group. Unfortunately, the alkylation was found to be too sluggish for synthetic use, even under harsh conditions.

Table 1. Preparation of Sulfonium Salts 6a–d[a]



5 6a–d

	R	X
6a	Me	I
6b	Me	BPh_4
6c	Me	ClO_4
6d	Et	BF_4

alkylating agent	additive salt	product	yield (%)
MeI		**6a**	100[b]
MeI	$NaBPh_4$	**6b**	61[c,d]
MeI	$Mg(ClO_4)_2$	**6c**	ca. 80[e,f]
$MeClO_4$[g]		**6c**	94[c]
$MeClO_4$[g]		(*S*)-(+)-**6c**	97[c]
$Et_3O^+BF_4^-$		**6d**	100[c]

[a] For more details, see the Experimental Section. [b] Starting sulfide **5** was completely alkylated with excess MeI (50 equiv). [c] Isolated yield. [d] $NaBPh_4$ added after MeI alkylation. [e] Yield based upon 20% recovery of starting sulfide **5**. [f] Reaction conditions: $Mg(ClO_4)_2 \cdot 1.5H_2O$ (4 equiv), MeI (4 equiv), benzene–acetonitrile (1:1), 48 h, rt. [g] Generated *in situ* from MeI and $AgClO_4$.

dark at room temperature. In contrast, iodide **6a** gradually decomposes to starting sulfide **5**.

Cleavage of Sulfonium Salts 6a–d with Nucleophiles. As Table 2 shows, a great variety of N-, S-, Se-, O-, and C-nucleophiles react with sulfonium salts **6a–d** under remarkably mild conditions. In most instances (except for the reactions with sodium acetate, entries 13–15) the cleavage occurs upon mixing at room temperature. The dual course of the nucleophilic cleavage, arising from the competing S_N2 attack on the benzyl and methyl carbon atoms and leading to products **7** and **5**, respectively, is the key feature in the reaction. As seen from the product data in Table 2, the outcome depends strongly on the external nucleophile (Nu) as well as on the sulfonium salt counterion (X) and the alkyl group (R). The very pronounced effect of the nucleophile is evidenced by the wide range of **7**:**5** product ratios in the reactions of sulfonium iodide **6a**; the ratios range from 90:10 (entry 4) to 0:100 (entry 13). The effect of nucleophile is much weaker in the analogous reactions of the corresponding *tetraphenylborate*, *perchlorate*, and *tetrafluoroborate* salts, **6b–d**, which afford in most instances only the products of benzylic attack (**7a,c–e,g–j**; entries 2, 5–9, 11, 14, 15, and 18); a considerable proportion (ca. 25%) of product **5** was obtained from a single reaction (entry 17). These results suggest that in some way the substrate counterion can augment or attenuate the effect of the nucleophile in the reaction.

A plausible explanation for the experimental findings is suggested in Scheme 2. It is assumed that the nonnucleophilic counterions (X = ClO_4, BPh_4, and BF_4) of sulfonium salts **6b–d** do not compete with the external nucleophile (Nu). This assumption greatly simplifies the overall scheme, and the selectively of the external nucleophiles can be drawn immediately from the product distribution data in Table 2. The majority of the nucleophiles (entries 2, 5, 8, 11, and 14) greatly prefer the benzylic attack (**6** → **7**) (selectivity factor >100); the propensity of the cyanide nucleophile to participate in the dealkylation (**6** → **5**) is the sole exception (entry 17).

In the case of sulfonium iodide **6a**, the situation is more complicated because the nucleophilic counterion (X = I) also participates in the reaction. The attack of iodide on the benzylic carbon in **6a** affords elusive iodo derivative **12** (X = I), which is presumably in rapid equilibrium with starting salt **6a**. The attack of iodide on the alkyl carbon atom (**6** → **5**) also represents a reversible reaction. In a control experiment, sulfonium iodide **6a** yields only product **5**, which may explain the variable counterion effects observed in the reaction. A large effect is observed when the external nucleophile is less reactive than the iodide counterion ($k_{Nu} < k_I$), as is evidently the case for the acetate anion (entries 13–15). As the relative reactivity of the external nucleophile increases, the magnitude of the counterion effect gradually diminishes, as seen in the reactions with azide, thiophenoxide, and morpholine (entries 1, 2, 4–6, 10, and 11). The absence of a counterion effect in the reactions with the cyanide anion (entries 16–18) suggests that the less efficient iodide counterion has been ousted from the nucleophilic competition ($k_{Nu} > k_I$). Qualitative rate data, acquired from TLC monitoring of the individual reactions, lend full support to this suggestion.

In addition to the external nucleophile and the salt counterion, the alkyl substituent R can also take part in control of the product distribution, as evidenced by the replacement of the methyl group in **6a–c** with a sterically more demanding ethyl group (**6d**). The replacement of the methyl group suppresses the undesirable dealkylation (**6** → **5**) (Table 2, entries 17 *vs* 18).

Scheme 2. Mechanism of Nucleophilic Cleavage of Sulfonium Salts 6

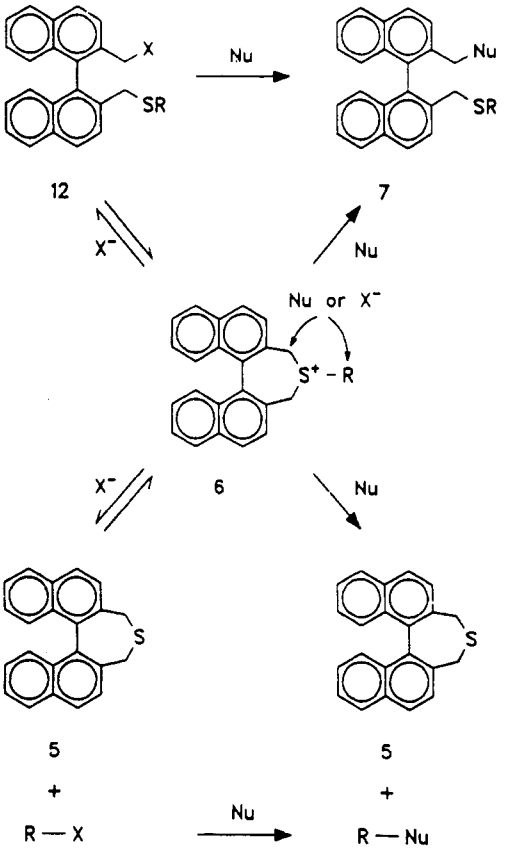
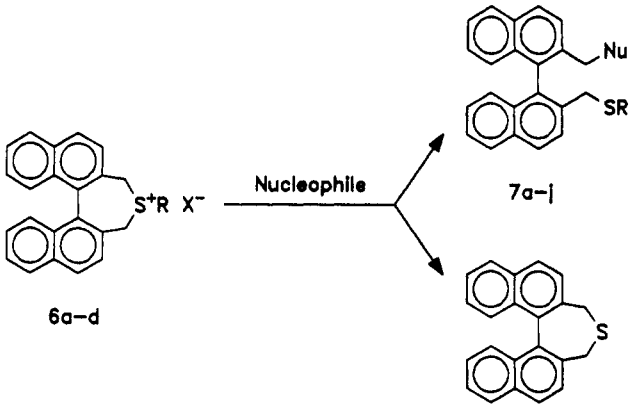


Table 2. Cleavage of Sulfonium Salts 6a–d with Nucleophiles[a]



	Nu	R
7a	N_3	Me
7b	NMe_2	Me
7c	4-morpholinyl	Me
7d	SMe	Me
7e	SPh	Me
7f	SePh	Me
7g	OAc	Me
7h	OAc	Et
7i	CN	Me
7j	CN	Et

5

entry	educt (X)	nucleophile	cond[b]	products (total yield, %)[c]	ratio[d] 7:5
1	**6a** (I)	NaN_3	A	**7a** + **5** (68)	75:25
2	**6c** (ClO_4)	NaN_3	B	**7a** (96)	100:0
3	**6a** (I)	Me_2NH	C	**7b** + **5** (63)	81:19
4	**6a** (I)	morpholine	D	**7c** + **5** (95)	90:10
5	**6b** (BPh_4)	morpholine	D	**7c** (97)	100:0
6	**6c** (ClO_4)	morpholine	D	**7c** (91)	100:0
7	(*S*)-**6c** (ClO_4)[e]	morpholine	D	(*S*)-**7c** (85)[f]	100:0
8	**6c** (ClO_4)	NaSMe	E	**7d** (86)	100:0
9	(*S*)-**6c** (ClO_4)[e]	NaSMe	E	(*S*)-**7d** (92)[g]	100:0
10	**6a** (I)	KSPh	C	**7e** + **5** (95)	82:18
11	**6c** (ClO_4)	KSPh	C	**7e** (98)	100:0
12	**6a** (I)	NaSePh	F	**7f** + **5** (97)	82:18
13	**6a** (I)	NaOAc	G	**5** (53)[h]	0:100
14	**6c** (ClO_4)	NaOAc	H	**7g** (89)[i]	100:0
15	**6d** (BF_4)	NaOAc	H	**7h** (91)[j]	100:0
16	**6a** (I)	NaCN	A	**7i** + **5** (90)	75:25
17	**6c** (ClO_4)	NaCN	A	**7i** + **5** (95)	74:26
18	**6d** (BF_4)	NaCN	A	**7j** (89)	100:0

[a] For more details, see the Experimental Section. [b] A, DMF, 1.5 h, rt; B, DMF, 30 min, rt; C, THF, 10 min, rt; D, excess of morpholine, 10 min, rt; E, ethanol, 10 min, rt; F, THF–ethanol, 10 min, rt; G, DMF, 4 days, rt; H, DMF, 6 h, 50 °C. [c] Isolated. [d] Calculated from ^{1}H NMR spectrum of crude reaction mixture. [e] Prepared from the optically pure sulfide (*S*)-(+)-**5**. [f] 100% o.p., determined by ^{1}H NMR spectroscopy using (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol in $CDCl_3$. [g] $[\alpha]^{23}_{589}$ −140° (*c* 0.32, $CHCl_3$), attempts to determine o.p. both by ^{1}H NMR spectroscopy using commercially available chiral shift reagents and by chromatography on a TAC column failed. [h] No other products except sulfide **5** and unchanged sulfonium salt **6a** were detected by TLC. [i] Yield 49% for the reaction at rt for 5 days (no sulfide **5** detected by TLC). [j] Yield 42% for the reaction at rt for 5 days (no sulfide **5** detected by TLC).

Scheme 2 can also be used to explain the possible roles of kinetic and thermodynamic control in the reaction. In the absence of the iodide counterion, both competing pathways (**6** → **7** and **6** → **5**) are irreversible, and the product distribution from reaction of the nonnucleophilic salts is thus kinetically controlled. However, if the iodide counterion is involved in the reaction, the equilibria **6** ⇌ **12** and **6** ⇌ **5** may also be involved in the product formation. Depending on the relative reactivities of the competing nucleophilic species Nu and X^-, either kinetic ($k_{Nu} > k_{X^-}$; Nu = *e.g.* CN^-) or thermodynamic ($k_{Nu} < k_{X^-}$; Nu = *e.g.* AcO^-) control may thus prevail in the reaction.

Conclusion

The proposed synthetic methodology increases the availability of optically pure axially asymmetric and/or dissymmetric binaphthyl ligands bearing a sulfur donor atom. It provides a new, convenient approach that is complementary to the cleavage of the dihydroazepinium quaternary salts we have recently reported.[7c,d] The novel methodology brings several advantages: (1) both optically pure enantiomers of starting sulfide **5** can be easily obtained from the racemate by means of a simple chiral chromatography; (2) because of the high reactivity of the sulfonium salts, a great variety of donor groups can be incorporated into the binaphthyl moiety; (3) the methodology avoids the difficulties involved in the earlier synthesis of unsymmetrical 2,2′-substituted binaphthyl ligands from ditopic symmetric precursors by means of consecutive reactions with two different nucleophiles[18] or electrophiles;[21] and (4) no configurational scrambling has been observed either in the alkylation of enantiomeric sulfides (*S*)- and (*R*)-**5** or in the nucleophilic cleavage of the chiral sulfonium salt.

Experimental Section

General. All chemicals were reagent grade. THF was distilled from $LiAlH_4$ before use, DMF from P_2O_5 or calcium hydride.

(18) 2,2′-Bis(bromomethyl)-1,1′-binaphthyl (**4**), on reaction with 1 equiv of nucleophile, affords in most instances a mixture of mono- and disubstituted products (ref 19), and this reaction is often complicated by an intramolecular cyclization (refs 7c,d and 20).

(19) Starý, I. G.; Starý, I.; Závada, J. Unpublished work.

(20) (a) Mazaleyrat, J. P.; Cram, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 4585. (b) Cottineau, F.; Maigrot, N.; Mazaleyrat, J. P. *Tetrahedron Lett.* **1985**, 421. (c) Maigrot, N.; Mazaleyrat, J. P.; Welvart, T. *J. J. Org. Chem.* **1985**, *50*, 3916. (d) Hawkins, J. M.; Fu, G. C. *J. Org. Chem.* **1986**, *51*, 2820.

(21) As an alternative to the S_N2 exchange, Chong *et al.* (ref 22) recently proposed an "umpolung" (S_E) approach based on metalation of dibromide **4** and subsequent treatment of 2,2′-bis(metalomethyl) derivative **2** (X = Y = Li) with an appropriate electrophilic reagent. However, the range of the bidentate ligands **2** available by this procedure is rather limited.

(22) Chong, J. M.; MacDonald, G. K.; Park, S. B.; Wilkinson, S. H. *J. Org. Chem.* **1993**, *58*, 1266.

Ethanol was dried using sodium. "Peroxide-free ether" means redistilled ether stored over sodium. Melting points were taken on a Kofler block and are uncorrected. Optical rotations were measured in chloroform with an accuracy of 0.2%. ^{1}H NMR spectra (200.06 MHz, FT mode) were recorded in $CDCl_3$, benzene-d_6, acetone-d_6, or DMSO-d_6 with TMS, C_6H_6, acetone, or DMSO as an internal reference, respectively. EI mass spectra were obtained at 70 eV; FAB spectra were measured in a 2-hydroxyethyl disulfide or 3-nitrobenzyl alcohol matrix in $CHCl_3$ as solvent. Flash chromatography was performed with silica gel Silpearl (5–40 μm, Kavalier Votice, Czech Republic).

Preparation of Racemic 4,5-Dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]thiepin (5). A mixture of dibromide **4** (10 g, 22.72 mmol), $Na_2S{\cdot}9H_2O$ (7.1 g, 29.56 mmol), and DMF (60 mL) was heated at 100 °C for 20 min. After cooling, the mixture was poured into water (100 mL), and the precipitate was filtered and washed with water (2 × 30 mL). The precipitate was taken up in $CHCl_3$ (150 mL), the solution was dried over Na_2SO_4, and the solvent was evaporated in vacuo. The crude material (7.03 g, 99%) was crystallized from acetone, yielding 6.25 g (88%) of title compound **5**: mp 216–218 °C (benzene), 212–213 °C (acetone), sublimation above 190 °C; ^{1}H NMR ($CDCl_3$) δ 3.43 (s, 4 H), 7.20–8.02 (m, 12 H); (C_6D_6) δ 3.14 and 3.41 (AB system, 2 × d, J = 12.7 Hz, 4 H), 6.92–8.04 (m, 12 H); (DMSO-d_6) δ 3.15 and 3.64 (AB system, 2 × d, J = 12.6 Hz, 4 H), 7.05–8.16 (m, 12 H); IR (KBr) 2918, 2831, 676, 656, 649 cm^{-1}; EI MS m/z (rel intensity) 312 (M^+, 100), 297 (9), 279 ($C_{22}H_{15}$, 57), 266 (32), 265 ($C_{21}H_{13}$, 25), 252 ($C_{20}H_{12}$, 5). Anal. Calcd for $C_{22}H_{16}S$: C, 84.58; H, 5.16; S, 10.26. Found: C, 84.53; H, 5.25; S, 10.19.

Resolution of (*R*)-(−)- and (*S*)-(+)-4,5-Dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]thiepins ((*R*)-(−)-5 and (*S*)-(+)-5). Racemic sulfide **5** was resolved into its enantiomers by chromatography on TAC (200 g) at rt using *tert*-butyl methyl ether as eluent (repeated 10-mL injections; 70 mg/10 mL). Resolution of 1.1 g of the racemate gave 456 mg of (*S*)-(+)-**5** (83%, 100% ee, eluted first) and 513 mg of (*R*)-(−)-**5** (90%, 97% ee).

(S)-(+)-5: mp 177–178 °C (benzene–ether 1:3), sublimes; $[\alpha]^{23}_{589}$ +279°, $[\alpha]^{23}_{578}$ +288°, $[\alpha]^{23}_{546}$ +318°, $[\alpha]^{23}_{436}$ +338°, $[\alpha]^{23}_{365}$ −1172° (*c* 0.20, $CHCl_3$); CD (*c*, 0.3717 mmol·L^{-1}, $CHCl_3$) $\Delta\epsilon_{306.0}$ −43.4, $\Delta\epsilon_{244.5}$ +389.1, $\Delta\epsilon_{224.0}$ −421.9 L·mol^{-1}·cm^{-1}.

(R)-(−)-5: mp 174–176 °C (benzene), sublimes; $[\alpha]^{25}_{589}$ −276°, $[\alpha]^{25}_{578}$ −286°, $[\alpha]^{25}_{546}$ −315°, $[\alpha]^{25}_{436}$ −331° (*c* 1.02, $CHCl_3$).

Chemical Correlation between Quaternary Ammonium Iodide (*S*)-(+)-8 and Sulfide (*S*)-(+)-5. A mixture of salt (*S*)-(+)-**8** (400 mg, 0.886 mmol) and 40% aqueous dimethylamine (2 mL) was heated in a sealed tube at 135 °C for 6 h. After being poured into water (10 mL), the mixture was extracted with benzene (3 × 30 mL), and the extract was dried over Na_2SO_4. Removal of the solvent gave 322 mg of crude levorotatory (*S*)-(−)-2,2′-bis[(*N*,*N*-dimethylamino)methyl]-1,1′-binaphthyl ((*S*)-(−)-**9**) together with (*S*)-(+)-4,5-dihydro-4-methyl-3*H*-dinaphth-[2,1-*c*:1′,2′-*e*]azepine ((*S*)-(+)-**10**) (ref 7d) (87:13 according to GC). ^{1}H NMR of crude (*S*)-(−)-**9** ($CDCl_3$, in a mixture with the compound (*S*)-(+)-**10**) δ 2.04 (s, 12 H), 2.93 and 3.23 (AB system, 2 × d, J = 14.0 Hz, 4 H), 6.96–8.01 (m, 12 H). A mixture of crude diamine (*S*)-(−)-**9** (154 mg), methyl iodide (0.5 mL), and acetonitrile (5 mL) was warmed at 35 °C for 4.5 h. The reaction mixture was evaporated to dryness in vacuo. The residue was heated with $Na_2S{\cdot}9H_2O$ (100 mg) in DMF (3 mL) at 120 °C for 40 min and then poured into water (10 mL). The precipitate was filtered, dissolved in benzene (20 mL), and dried over Na_2SO_4, and the solvent was evaporated. Flash chromatography in pentane–ether–acetone (80:10:10) afforded 28 mg (35%) of sulfide (*S*)-(+)-**5**; further elution with pentane–ether–acetone (50:20:30) gave 23 mg of (*S*)-(−)-2-[(*N*,*N*-dimethylamino)methyl]-2′-[(methylthio)methyl]-1,1′-binaphthyl ((*S*)-(−)-**7b**) as an oil.

(S)-(+)-5: $[\alpha]^{23}_{589}$ +269° (*c* 0.19, $CHCl_3$), 100% ee (chromatography on TAC).

(S)-(−)-7b: $[\alpha]^{28}_{589}$ −76°, $[\alpha]^{28}_{578}$ −81°, $[\alpha]^{28}_{546}$ −95°, $[\alpha]^{28}_{436}$ −190° (*c* 0.19, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 3 H), 2.07 (s, 6 H), 2.95 and 3.36 (AB system, 2 × d, J = 14.0 Hz, 2 H), 3.38 and 3.46 (AB system, 2 × d, J = 14.0 Hz, 2 H), 6.98–8.07 (m, 12 H); IR (CCl_4) 2974, 2944, 2917, 2856, 2818, 2771, 701, 669 cm^{-1}; EI MS m/z (rel intensity) 371 (M^+, 49), 356 ($(M - CH_3)^+$, 6), 325 ($C_{24}H_{23}N$, 10), 279 ($C_{22}H_{15}$, 100), 266 (16), 265 ($C_{21}H_{13}$, 24), 252 ($C_{20}H_{12}$, 4). Anal. Calcd for $C_{25}H_{25}NS$: C, 80.82; H, 6.78; N, 3.77; S, 8.63. Found: C, 80.78; H, 6.81; N, 3.65; S, 8.76.

Preparation of Sulfonium Salts. 4,5-Dihydro-4-methyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]thiepinium Iodide (6a). A mixture of sulfide **5** (1.5 g, 4.80 mmol), methyl iodide (15 mL, 241 mmol), benzene (25 mL), and methanol (25 mL) was kept in the dark at rt for 36 h. According to TLC, the starting sulfide had reacted completely. The solution obtained was stored in a refrigerator for 1 month without signs of decomposition. ^{1}H NMR (a sample of the stock solution was rapidly evaporated in vacuo at rt, and the dry residue was immediately dissolved in $CDCl_3$ and measured): δ 3.27 (s, 3 H), 3.42 (AB system, d, J = 11.6 Hz, 1 H), 4.00 (AB system, d, J = 14.3 Hz, 1 H), 5.20 (AB system, d, J = 14.3 Hz, 1 H), 5.61 (AB system, d, J = 11.6 Hz, 1 H), 6.94–8.22 (m, 12 H).

4,5-Dihydro-4-methyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]thiepinium Tetraphenylborate (6b). The stock solution of sulfonium salt **6a** (0.074 M, 10 mL) obtained in the preceding experiment was evaporated to dryness in vacuo at rt. The residue was dissolved in dry THF (3 mL), sodium tetraphenyl borate (330 mg, 0.964 mmol) was added, and the mixture was set aside at rt for 1 h. After evaporation of the solvent at rt in vacuo, the residue was suspended in dry ether, collected, and washed with ether (4 × 5 mL). The residue was then suspended in water (5 mL), filtered again, washed with water (2 × 3 mL), and dried over P_2O_5 in vacuo to yield 292 mg (61%) of sulfonium salt **6b**: mp 205–208 °C dec (acetone). Product **6b** may be stored for several months at rt in the dark; at elevated temperatures it decomposes rapidly to give sulfide **5**: ^{1}H NMR (acetone-d_6) δ 2.85 (s, 3 H), 3.72 (AB system, d, J = 12.2 Hz, 1 H), 4.30 (AB system, d, J = 14.0 Hz, 1 H), 4.47 (AB system, d, J = 14.0 Hz, 1 H), 4.63 (AB system, d, J = 12.2 Hz, 1 H), 6.69–8.32 (m, 32 H); IR (KBr) 2998, 2989, 2971, 2930, 1579, 1479, 668 cm^{-1}; FAB MS in 2-hydroxyethyl disulfide matrix, m/z (rel intensity) 327 ($(M - BPh_4)^+$, 100), 281 (44), 279 (26), 266 (16), 265 (17), 252 (6). Anal. Calcd for $C_{47}H_{39}BS$: C, 87.29; H, 6.08; S, 4.96. Found: C, 87.48; H, 6.24; S, 4.90.

4,5-Dihydro-4-methyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]thiepinium Perchlorate (6c). A mixture of sulfide **5** (1.0 g, 3.20 mmol) and methyl iodide (300 μL, 4.82 mmol) in dry CH_2Cl_2 was added to a suspension of anhyd $AgClO_4$ (700 mg, 3.37 mmol) in nitromethane (10 mL). After the mixture stirred under argon in the dark at rt overnight, the precipitate was collected and washed with a CH_2Cl_2–nitromethane mixture (1:1; 2 × 5 mL). The filtrate was concentrated at rt to about 2 mL, and dry ether (15 mL) was added dropwise with stirring. The crystals that separated were collected, washed with dry ether (3 × 5 mL), and dried over P_2O_5 in vacuo at rt to yield 1.28 g (94%) of perchlorate **6c**: mp 260–262 °C dec (nitromethane–ether 1:8); ^{1}H NMR (acetone-d_6) δ 3.16 (s, 3 H), 4.06 (AB system, d, J = 11.9 Hz, 1 H), 4.51 (AB system, d, J = 14.5 Hz, 1 H), 4.78 (AB system, d, J = 14.5 Hz, 1 H), 5.14 (AB system, d, J = 11.9 Hz, 1 H), 7.24–8.38 (m, 12 H); IR (KBr) 2993, 2947, 2932, 1095, 930, 702, 668, 624 cm^{-1}; FAB MS in 3-nitrobenzyl alcohol, m/z (rel intensity) 327 ($(M - ClO_4)^+$, 100), 281 (41), 279 (27), 266 (17), 265 (18), 252 (18). Anal. Calcd for $C_{23}H_{19}ClO_4S$: C, 64.71; H, 4.49; Cl, 8.30; S, 7.51. Found: C, 64.50; H, 4.69; Cl, 8.11; S, 7.55.

(*S*)-(+)-4,5-Dihydro-4-methyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]-thiepinium Perchlorate ((*S*)-(+)-6c). Alkylation of sulfide (*S*)-(+)-**5** (125 mg, 0.40 mmol) with methyl iodide in the presence of $AgClO_4$ as described for racemic sulfide **5** yielded 166 mg (97%) of **6c**. Crystallization from a mixture of acetone (1 mL), pentane (0.1 mL), and dry ether (0.2 mL) afforded 107 mg of pure (*S*)-(+)-**6c**: mp 172–175 °C (pentane–ether–acetone 1:2:10); $[\alpha]^{24}_{589}$ +133°, $[\alpha]^{24}_{578}$ +136°, $[\alpha]^{24}_{546}$ +145°, $[\alpha]^{24}_{436}$ +40°, $[\alpha]^{24}_{365}$ −1826° (*c* 0.30, acetone); CD (*c* 0.2488 mmol·L^{-1}, $CHCl_3$) $\Delta\epsilon_{334}$ −32.9, $\Delta\epsilon_{309}$ −46.2, $\Delta\epsilon_{251}$ +271.0, $\Delta\epsilon_{227}$ −259.0 L·mol^{-1}·cm^{-1}.

4,5-Dihydro-4-ethyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]thiepinium Tetrafluoroborate (6d). A CH_2Cl_2 solution of triethyloxonium tetrafluoroborate (1 M, 6.2 mL) was added dropwise at rt under argon to a stirred solution of sulfide **5** (1.5 g, 4.80 mmol) in CH_2Cl_2 (25 mL), and the mixture was kept for 30 min at rt. Removal of the solvent in vacuo gave a foamy residue, which was triturated with dry ether (3 × 10 mL) and dried in vacuo over P_2O_5 to yield 2.04 g (99%) of title compound **6e**: ^{1}H NMR ($CDCl_3$) δ 1.51 (t, J = 7.3 Hz, 3 H), 3.09 (qd, J = 12.8, 7.3 Hz, 1 H), 3.27 (qd, J = 12.8, 7.3 Hz, 1 H), 3.36 (AB system, d, J = 11.6 Hz, 1

H), 3.88 (AB system, d, J = 14.7 Hz, 1 H), 4.46 (AB system, d, J = 14.7 Hz, 1 H), 4.86 (AB system, d, J = 11.6 Hz, 1 H), 7.14–8.14 (m, 12 H); IR (KBr), 2983, 2943, 2879, 1121, 1083, 1063, 1031, 778, 519 cm^{-1}; FAB MS in 2-hydroxyethyl disulfide matrix, m/z (rel intensity) 769 ((M + $C_{24}H_{21}S$)$^+$, 4), 341 ((M − BF_4)$^+$, 100), 311 (5), 281 (97), 279 (35), 266 (28), 265 (29), 252 (9). Anal. Calcd for $C_{24}H_{21}BF_4S$: C, 67.30; H, 4.94; F, 17.74; S, 7.49. Found: C, 67.42; H, 4.99; F, 17.50; S, 7.38.

Cleavage of Sulfonium Salts. 2-(Azidomethyl)-2′-[(methylthio)methyl]-1,1′-binaphthyl (7a). Method A. A stock solution (0.074 M, 5.5 mL, 0.407 mmol) of sulfonium iodide **6a** was rapidly evaporated in vacuo at rt. The residue was dissolved in dry DMF (1 mL) and stirred with sodium azide (27 mg, 0.415 mmol) at rt for 1.5 h. The mixture was poured into water (10 mL) and extracted with ether (4 × 10 mL, peroxide-free). The combined extracts were washed with water (2 × 10 mL), dried over Na_2SO_4, and concentrated in vacuo at rt. Flash chromatography in light petroleum ether–ether–acetone (98:1:1) afforded 22 mg (17%) of sulfide **5** and 77 mg (51%) of oily azide **7a**.

Method B. A mixture of sulfonium perchlorate **6c** (100 mg, 0.234 mmol), sodium azide (16 mg, 0.246 mmol), and dry DMF (2 mL) was stirred at rt for 30 min. The mixture was poured into water (10 mL) and extracted with ether (4 × 10 mL, peroxide-free). The combined extracts were washed with water (5 × 10 mL) and dried over Na_2SO_4, and the solvent was evaporated in vacuo at rt to give 83 mg (96%) of azide **7a** as an oil: ^{1}H NMR ($CDCl_3$) δ 1.88 (s, 3 H), 3.36 and 3.44 (AB system, 2 × d, J = 13.0 Hz, 2 H), 4.06 and 4.21 (AB system, 2 × d, J = 14.0 Hz, 2 H), 6.98–8.09 (m, 12 H); IR (CCl_4) 2959, 2917, 2857, 2099, 701, 675 cm^{-1}; EI MS m/z (rel intensity) 341 ((M − N_2)$^+$, 4), 294 ($C_{22}H_{16}N$, 74), 280 ($C_{21}H_{14}N$, 100), 279 ($C_{22}H_{15}$, 47), 266 (44), 265 ($C_{21}H_{13}$, 56), 252 ($C_{20}H_{12}$, 18). Anal. Calcd for $C_{23}H_{19}N_3S$: C, 74.77; H, 5.18; N, 11.37; S, 8.68. Found: C, 74.75; H, 5.32; N, 11.17; S, 8.71.

2-[(*N*,*N*-Dimethylamino)methyl]-2′-[(methylthio)methyl]-1,1′-binaphthyl (7b). A stock solution of sulfonium iodide **6a** (0.074 M, 7 mL, 0.517 mmol) was rapidly evaporated at rt in vacuo. THF (3 mL, peroxide-free) and 40% aqueous dimethylamine (200 μL, 1.59 mmol) were added, and after the reaction mixture stood for 10 min, the solvent was evaporated in vacuo at rt. Water (5 mL) was added, and the product was taken up in $CHCl_3$ (3 × 5 mL); the combined extracts were washed with water (3 × 5 mL), dried over Na_2SO_4, and evaporated in vacuo at rt. Flash chromatography in light petroleum ether–ether–acetone (98:1:1) afforded 19 mg of sulfide **5** (12%). Subsequent elution with light petroleum ether–ether–acetone (80:10:10) gave 98 mg (51%) of oily product **7b**. For ^{1}H NMR, IR, and EI mass spectra, see preparation of (*S*)-(−)-**7b**.

2-[(Methylthio)methyl]-2′-(4-morpholinylmethyl)-1,1′-binaphthyl (7c). Method A. A stock solution of sulfonium iodide **6a** (5 mL, 0.074 M, 0.370 mmol) was rapidly evaporated at rt in vacuo, and the residue was mixed with morpholine (1 mL). After standing at rt for 10 min, the mixture was poured into water (10 mL) and extracted with $CHCl_3$ (4 × 5 mL), the combined extracts were washed with water (3 × 5 mL) and dried over Na_2SO_4, and the solvent was evaporated at rt in vacuo. Flash chromatography in light petroleum ether–ether–acetone (96:2:2) afforded 11 mg (10%) of sulfide **5**; elution with light petroleum ether–ether–acetone (80:10:10) gave 130 mg (85%) of oily morpholinyl derivative **7c**.

Method B. A solution of tetraphenylborate **6b** (100 mg, 0.155 mmol) or perchlorate **6c** (100 mg, 0.234 mmol) in morpholine (1 mL) was set aside for 10 min at rt. The mixture was diluted with water (10 mL) and extracted with $CHCl_3$ (4 × 5 mL). The combined extracts were washed with water (4 × 5 mL) and dried over Na_2SO_4, and the solvent was evaporated at rt in vacuo to give oily **7c** (62 mg, 97% from **6b**, or 88 mg, 91% from **6c**): ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 3 H), 2.10–2.30 (m, 4 H), 3.07 and 3.33 (AB system, 2 × d, J = 14.0 Hz, 2 H), 3.38 and 3.48 (AB system, 2 × d, J = 14.0 Hz, 2 H), 3.56 (t, J = 4.6 Hz, 4 H), 6.95–8.04 (m, 12 H); IR (CCl_4) 2962, 2933, 2916, 1119, 701, 676 cm^{-1}; EI MS m/z (rel intensity) 413 (M$^+$, 37), 398 (6), 367 ($C_{26}H_{25}NO$, 10), 279 ($C_{22}H_{15}$, 100), 266 (24), 265 ($C_{21}H_{13}$, 34) 252 ($C_{20}H_{12}$, 10). Anal. Calcd for $C_{27}H_{27}NOS$: C, 78.41; H, 6.58; N, 3.39; S, 7.75. Found: C, 78.55; H, 6.63; N, 3.30; S, 7.95.

(*S*)-(−)-2-[(Methylthio)methyl]-2′-(4-morpholinylmethyl)-1,1′-binaphthyl ((*S*)-(−)-7c). Perchlorate (*S*)-(+)-**6c** (80 mg, 0.187 mmol) was allowed to react with morpholine as described for racemic compound **7c**. Flash chromatography in pentane–ether–acetone (80:10:10) afforded 66 mg (85%) of oily product (*S*)-(−)-**7c**: $[\alpha]^{26}_{589}$ −76°, $[\alpha]^{26}_{578}$ −84°, $[\alpha]^{26}_{546}$ −94°, $[\alpha]^{26}_{436}$ −175°, $[\alpha]^{26}_{365}$ −356° (*c* 0.20, $CHCl_3$).

2,2′-Bis[(methylthio)methyl]-1,1′-binaphthyl (7d). A mixture of sodium borohydride (25 mg, 0.661 mmol), absolute ethanol (4 mL), and dimethyl disulfide (60 μL, 0.666 mmol) was stirred at 70 °C for 2 h under argon. After the mixture cooled to rt, sulfonium perchlorate **6c** (100 mg, 0.234 mmol) was added, and the mixture was set aside for 10 min at rt. The precipitate was filtered and washed with absolute ethanol (2 × 2 mL), and the filtrate was concentrated at rt in vacuo. A solution of the dry residue in benzene was applied to an alumina column (5 × 2 cm), and elution of the product with pentane yielded 75 mg (86%) of oily compound **7d**: ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 6 H), 3.39 and 3.51 (AB system, 2 × d, J = 13.7 Hz, 4 H), 7.02–8.02 (m, 12 H); IR (CCl_4) 2974, 2962, 2916, 2856, 700, 667 cm^{-1}; EI MS m/z (rel intensity) 374 (M$^+$, 18), 327 ($C_{23}H_{19}S$, 4), 312 (2), 279 ($C_{22}H_{15}$, 100), 266 (12), 265 ($C_{21}H_{13}$, 17), 252 ($C_{20}H_{12}$, 3). Anal. Calcd for $C_{24}H_{22}S_2$: C, 76.96; H, 5.92; S, 17.12. Found: C, 76.90; H, 5.98; S, 17.07.

(*S*)-(−)-2,2′-Bis[(methylthio)methyl]-1,1′-binaphthyl ((*S*)-(−)-7d). Perchlorate (*S*)-(+)-**6c** (80 mg, 0.187 mmol) was allowed to react with sodium methanethiolate as described above for racemic **7d**. Chromatography on an alumina column (5 × 2 cm) in pentane afforded 65 mg (92%) of oily product (*S*)-(−)-**7d**: $[\alpha]^{23}_{589}$ −140°, $[\alpha]^{23}_{578}$ −145°, $[\alpha]^{23}_{546}$ −170°, $[\alpha]^{23}_{436}$ −335°, $[\alpha]^{23}_{365}$ −715° (*c* 0.32, $CHCl_3$).

2-[(Methylthio)methyl]-2′-[(phenylthio)methyl]-1,1′-binaphthyl (7e). Method A. A stock solution of sulfonium iodide **6a** (7 mL of 0.074 M solution) was rapidly evaporated at rt in vacuo. The residue was dissolved under argon in anhyd THF (3 mL), and the THF solution was added to a suspension of potassium thiophenoxide (0.775 mmol), which was prepared from potassium *tert*-butoxide (0.775 mmol) and thiophenol (80 μL, 0.779 mmol) in anhyd THF (3 mL) at rt. The reaction mixture was kept at rt for 10 min, poured into a saturated NaCl solution (10 mL), and extracted with $CHCl_3$ (4 × 10 mL). The combined extracts were washed with a saturated solution of NaCl (2 × 10 mL) and dried over Na_2SO_4. The solvent was evaporated in vacuo, and flash chromatography of the residue in light petroleum ether–ether–acetone (98:1:1) afforded 28 mg (17%) of sulfide **5** and 176 mg (78%) of oily thiophenyl derivative **7e**.

Method B. Perchlorate **6c** (100 mg, 0.234 mmol) was treated with potassium thiophenoxide in a manner analogous to that described for sulfonium iodide **6a** to give 100 mg (98%) of oily thiophenyl derivative **7e**: ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 3 H), 3.39 and 3.49 (AB system, 2 × d, J = 13.9 Hz, 2 H), 3.84 and 3.91 (AB system, 2 × d, J = 13.0 Hz, 2 H), 6.98–8.01 (m, 17 H); IR (CCl_4) 2957, 2917, 2854, 1585, 1480, 700, 676, 668 cm^{-1}; EI MS m/z (rel intensity) 436 (M$^+$, 17), 389 ((M − CH_3S)$^+$, 3), 327 ($C_{23}H_{19}S$, 60), 281 ($C_{22}H_{17}$, 53), 279 ($C_{22}H_{15}$, 100), 266 (32), 265 ($C_{21}H_{13}$, 37), 252 ($C_{20}H_{12}$, 6). Anal. Calcd for $C_{29}H_{24}S_2$: C, 79.77; H, 5.54; S, 14.69. Found: C, 79.64; H, 5.60; S, 14.80.

2-[(Methylthio)methyl]-2′-[(phenylseleno)methyl]-1,1′-binaphthyl (7f). A stock solution of sulfonium iodide **6a** (10 mL of 0.074 M solution, 0.740 mmol) was rapidly evaporated at rt in vacuo, and the residue was suspended in anhyd THF (4 mL) under argon. The suspension was mixed with a solution of sodium selenophenoxide (1.11 mmol), which was prepared from diphenyl diselenide (173 mg, 0.554 mmol) and sodium borohydride (42 mg, 1.11 mmol) in absolute ethanol (3 mL) at rt. After standing at rt for 10 min, the mixture was concentrated in vacuo, and the residue was flash chromatographed in light petroleum ether–ether–acetone (98:1:1) to yield sulfide **5** (40 mg, 17%) and oily selenophenyl derivative **7f** (285 mg, 80%): ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 3 H), 3.39 and 3.51 (AB system, 2 × d, J = 13.7 Hz, 2 H), 3.87 and 3.90 (AB system, 2 × d, J = 5.0 Hz, 2 H), 7.00–8.03 (m, 17 H); IR (CCl_4) 2956, 2916, 2854, 1579, 1477, 661, 572 cm^{-1}; EI MS m/z (rel intensity) 484 (M$^+$, 2), 437 ((M − CH_3S)$^+$, 1), 327 ($C_{23}H_{19}S$, 100), 281 ($C_{22}H_{17}$, 77), 279 ($C_{22}H_{15}$, 57), 266 (44), 265 ($C_{21}H_{13}$, 42), 252 ($C_{20}H_{12}$, 7). Anal. Calcd for $C_{29}H_{24}SSe$: C, 72.04; H, 5.00. Found: C, 71.99; H, 5.08.

2-(Acetoxymethyl)-2'-[(methylthio)methyl]-1,1'-binaphthyl (7g). Method A. A mixture of sulfonium perchlorate **6c** (100 mg, 0.234 mmol), anhyd sodium acetate (29 mg, 0.354 mmol), and dry DMF (1 mL) was allowed to stand at rt for 2 d. The reaction mixture was then poured into water (10 mL) and extracted with peroxide-free ether (4 × 10 mL). The combined extracts were washed with water (2 × 10 mL) and dried over Na_2SO_4, and the solvent was evaporated in vacuo. The residue was filtered through a short column of alumina (elution with light petroleum ether–ether (2:1) and then with benzene) to give 31 mg (49%) of oily compound **7g**.

Method B. The reaction mixture was heated at 50 °C for 6 h and then worked up as described under method A to yield 56 mg (89%) of oily compound **7g**: ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 6 H), 3.41 (s, 2 H), 4.80 and 4.87 (AB system, 2 × d, J = 13.0 Hz, 2 H), 6.98–8.05 (m, 12 H); IR (CCl_4) 2917, 1743, 1230, 1045, 701, 685 cm^{-1}; EI MS m/z (rel intensity) 386 (M^+, 9), 371 ($(M - CH_3)^+$, 1.4), 326 ($(M - CH_3CO_2H)^+$, 9), 312 (2), 295 (4), 279 ($C_{22}H_{15}$, 100), 277 (32), 267 (17), 266 (20), 265 ($C_{21}H_{13}$, 22), 252 ($C_{20}H_{12}$, 9). Anal. Calcd for $C_{25}H_{22}O_2S$: C, 77.69; H, 5.74; S, 8.30. Found: C, 77.75; H, 5.90; S, 8.18.

Decomposition of Sulfonium Iodide 6a in the Presence and Absence of Sodium Acetate. A stock solution of sulfonium iodide **6a** (5 mL of 0.074 M solution, 0.370 mmol) was rapidly evaporated at rt in vacuo, and the residue was dissolved in dry DMF (4 mL). The solution was mixed with anhyd sodium acetate (58 mg, 0.708 mmol). Except for unchanged sulfonium salt **6a**, only sulfide **5** (53%) was detected after the reaction mixture stood at rt for 4 days. A blank experiment performed in the absence of sodium acetate afforded identical results.

2-(Acetoxymethyl)-2'-[(ethylthio)methyl]-1,1'-binaphthyl (7h). Method A. Sulfonium tetrafluoroborate **6d** (100 mg, 0.233 mmol) was treated with anhyd sodium acetate (29 mg, 0.354 mmol) as described for the preparation of acetoxy derivative **7g** to yield 39 mg (42%) of oily product **7h**.

Method B. The reaction mixture was heated at 50 °C for 6 h and then worked up as described for method A to yield 85 mg (91%) of product **7h** as an oil: ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.5 Hz, 3 H), 1.85 (s, 3 H), 2.26 (q, J = 7.5 Hz, 2 H), 3.39 and 3.48 (AB system, 2 × d, J = 13.3 Hz, 2 H), 4.81 and 4.89 (AB system, 2 × d, J = 12.9 Hz, 2 H), 7.00–8.04 (m, 12 H); IR (CCl_4) 2971, 2927, 2872, 2855, 1743, 1229, 1045, 686, 676 cm^{-1}; EI MS m/z (rel intensity) 400 (M^+, 9), 385 ($(M - CH_3)^+$, 3), 356 (1), 340 (8), 311 (2), 295 (4), 279 ($C_{22}H_{15}$, 100), 277 (35), 267 (16), 266 (20), 265 ($C_{21}H_{13}$, 23), 252 ($C_{20}H_{12}$, 9). Anal. Calcd for $C_{28}H_{24}O_2S$: C, 77.97; H, 6.04; S, 8.01. Found: C, 78.00; H, 5.94; S, 8.10.

2-(Cyanomethyl)-2'-[(methylthio)methyl]-1,1'-binaphthyl (7i). Method A. A stock solution of sulfonium iodide **6a** (4.3 mL of 0.074 M solution, 0.318 mmol) was rapidly evaporated at rt in vacuo. The residue was dissolved in dry DMF (2 mL), mixed with NaCN (23 mg, 0.469 mmol), and kept at rt for 1.5 h. The mixture was poured into saturated aqueous ammonium sulfate (10 mL) and extracted with peroxide-free ether (5 × 10 mL). The combined ethereal phases were washed with water (4 × 10 mL) and dried over Na_2SO_4, and the solvent was evaporated in vacuo. According to the ^{1}H NMR spectrum, the crude reaction mixture contained **7i** and **5** in a 75:25 ratio. Flash chromatography on alumina in light petroleum ether–benzene (2:1) afforded 22 mg (22%) of sulfide **5** and 76 mg (68%) of oily **7i**.

Method B. A mixture of sulfonium perchlorate **6c** (100 mg, 0.234 mmol), NaCN (17 mg, 0.347 mmol), and dry DMF (1 mL) was allowed to stand at rt for 1.5 h and then processed as described under method A. Flash chromatography of the crude mixture of **7i** and **5** (74:26 according to ^{1}H NMR spectrum) on alumina in light petroleum ether–benzene (2:1) afforded 18 mg (25%) of sulfide **5** and 58 mg (70%) of oily cyano derivative **7i**.

7i: ^{1}H NMR ($CDCl_3$) δ 1.91 (s, 3 H), 3.31 (AB system, d, J = 12.8 Hz, 1 H), 3.34 (AB system, d, J = 18.8 Hz, 1 H), 3.45 (AB system, d, J = 12.8 Hz, 1 H), 3.66 (AB system, d, J = 18.8 Hz, 1 H), 6.95–8.10 (m, 12 H); IR (CCl_4) 2963, 2917, 2857, 2250, 701, 684 cm^{-1}; EI MS m/z (rel intensity) 353 (M^+, 50), 305 ($(M - CH_3SH)^+$, 82), 290 (14), 277 (33), 266 (100), 265 ($C_{21}H_{13}$, 72), 252 ($C_{20}H_{12}$, 11). Anal. Calcd for $C_{24}H_{19}NS$: C, 81.55; H, 5.42; N, 3.96; S, 9.07. Found: C, 81.67; H, 5.60; N, 3.81; S, 9.19.

2-(Cyanomethyl)-2'-[(ethylthio)methyl]-1,1'-binaphthyl (7j). A mixture of sulfonium tetrafluoroborate **6d** (100 mg, 0.233 mmol), NaCN (17 mg, 0.347 mmol), and dry DMF (1 mL) was set aside at rt for 1.5 h, poured into water (10 mL), and extracted with peroxide-free ether (4 × 10 mL). The combined organic phases were washed with water (2 × 10 mL) and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was filtered through a short column of alumina (elution with light petroleum ether–benzene (2:1) and then with benzene) to give 76 mg (89%) of oily compound **7j**: ^{1}H NMR ($CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 3 H), 2.32 (q, J = 7.3 Hz, 2 H), 3.28 (AB system, d, J = 12.7 Hz, 1 H), 3.34 (AB system, d, J = 18.6 Hz, 1 H), 3.52 (AB system, d, J = 12.7 Hz, 1 H), 3.70 (AB system, d, J = 18.6 Hz, 1 H), 6.98–8.11 (m, 12 H); IR (CCl_4) 2971, 2927, 2872, 2854, 2250, 687, 676 cm^{-1}; EI MS m/z (rel intensity) 367 (M^+, 58), 338 ($(M - C_2H_5)^+$, 2), 305 ($(M - C_2H_5SH)^+$, 100), 290 (16), 277 (38), 266 (97), 265 ($C_{21}H_{13}$, 78), 252 ($C_{20}H_{12}$, 13). Anal. Calcd for $C_{25}H_{21}NS$: C, 81.70; H, 5.76; N, 3.81; S, 8.72. Found: C, 81.78; H, 5.71; N, 3.76; S, 8.77.

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Supplementary Material Available: ^{1}H NMR spectrum of **6a** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.