New Asymmetric Reactions of 2-Formyl- and 2-Acyl-1-[(2,4,6-triisopropylphenyl)sulfinyl]naphthalenes via Diastereomeric Rotamers

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Nucleophilic reactions with Grignard reagents and the Mukaiyama aldol reactions of the naphthaldehydes having the (2,4,6-triisopropylphenyl)sulfinyl group produced products with high stereoselectivity. In these reactions, the stereochemistry of the major products changes depending on the Lewis acids used. Reduction of the 2-acyl-1-[(2,4,6-triisopropylphenyl)sulfinyl]naphthalenes also proceeds with high stereoselectivity but with a different stereochemistry depending on the reducing agents. We have demonstrated, by the mechanistic consideration based on the X-ray crystal structures as well as the ^{1}H and ^{13}C NMR spectral data, that the extremely high and specific stereoselectivities of these reactions are due to the predominant rotamer around the C_{naph}−S axis. Synthesis of enantiomerically pure 2-naphthylmethanol is provided as an example.

Introduction

Since the first resolution of a chiral biphenyl compound by Christie and Kenner,[1] axially chiral biaryl compounds such as binaphthyl and biphenyl compounds have been widely used as chiral ligands or chiral auxiliaries.[2] Recently, the asymmetric reactions of nonbiaryl axially chiral compounds have been reported, e.g., high stereoselectivity has been achieved in the reactions of (*o*-*tert*-butylphenyl)maleimide,[3] *N*-acyl-*o*-*tert*-butylanilides,[4] and *N*,*N*-diisopropylnaphthamides.[5] The substrates in these reactions enable the separation of the atropisomer due to the high rotational barrier about the C−N bond, but resolution of the optically active isomers is always needed prior to undertaking the reaction.[4c,e,g,h,6] We were interested in the asymmetric reactions of 1-sulfinylnaphthalene derivatives. The barriers to rotation about the C_{naph}−S bond of sulfinylnaphthalenes have been estimated to be generally lower than those around the C−N axis, and isolation of the atropisomers have never been reported.[7] Thus, there have been no reports on the asymmetric reactions of 2-substituted 1-sulfinylnaphthalenes using the rotational barrier about the C_{naph}−S bond prior to our preliminary report of this type of reaction.[8] Such rotamers around the C−S axis consist of diastereomers. Therefore, we thought that each rotamer would stay in a different equilibrating state depending on the steric or electronic demands of the chiral sulfinyl group and affect the diastereoselectivity in the nucleophilic additions to the carbonyl at the 2-position. Furthermore, nucleophilic additions to the carbonyl of γ-ketosulfoxides[9] are known to proceed with rather low stereoselectivity in contrast to the highly stereoselective reactions of β-ketosulfoxides.[10] We now report in detail the stereoselective reactions of 2-formyl- and 2-acyl-1-sulfinylnaphthalenes bearing the (2,4,6-triisopropylphenyl)sulfinyl group with nucleophiles and reducing agents

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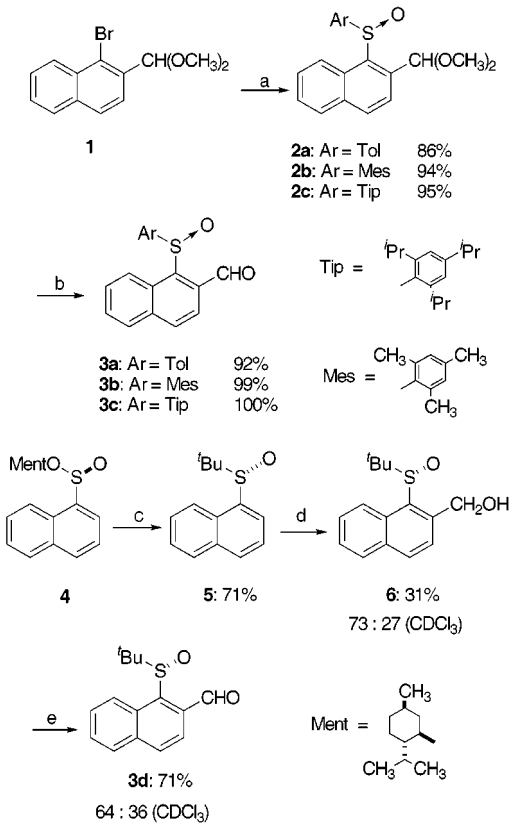
Scheme 1[a]



[a] (a) (1) *n*-BuLi, (2) ArS(O)O^{i}Pr, Et_2O, −78 °C; (b) H_2SO_4, SiO_2, CH_2Cl_2, rt; (c) ^{t}BuMgCl, THF, 0 °C; (d) (1) *n*-BuLi, (2) $(CH_2O)_n$, THF, −78 °C → rt; (e) PCC, CH_2Cl_2, rt.

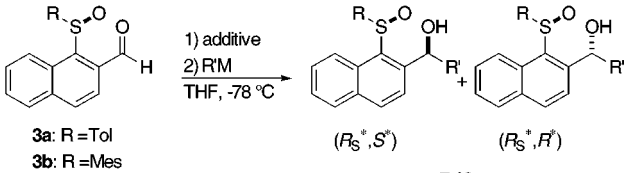
without prior resolution of the axially chiral or diastereomeric isomer. We also describe the stereochemical course possibly derived from the predominantly formed rotamer around the C_{naph}−S bond axis, and the transformation of the product into the enantiomerically pure 2-naphthylmethanol.

Results

Scheme 1 summarizes the synthetic routes for the preparation of various racemic 1-sulfinyl-2-naphthaldehydes **3a**−**d** for the study of the stereoselectivity in the addition of nucleophiles.

Treatment of the *p*-toluene-, 2,4,6-trimethylbenzene-, 2,4,6-triisopropylbenzenesulfinates with 1-lithio-2-naphthaldhyde dimethyl acetal[11] at −78 °C in Et_2O, followed by deprotection upon treatment with silica gel containing a small amount of sulfuric acid in CH_2Cl_2,[12] gave the corresponding 1-(arylsulfinyl)-2-naphthaldehydes **3a**−**c** in high yields. Since the 1,1-dimethylethanesulfinate did not react with 1-lithio-2-naphthaldehyde dimethyl acetal, (−)-menthyl (*S*)-naphthalenesulfinate **4** was treated with *tert*-BuMgCl. The obtained sulfoxide **5** was lithiated and then allowed to react with paraformaldehyde to give alcohol **6**, which was converted to aldehyde **3d** by oxidation of **6** with PCC (Scheme 1). Notably, we confirmed, by ^{1}H NMR spectral analyses in $CDCl_3$, that each sulfoxide **3d** or **6** exists as two rotamers, each ratio of which was 64:36 or 73:27, respectively (vide infra).

Table 1. Stereoselective Reaction of 1-Sulfinyl-2-naphthaldehydes 3a−d with Nucleophiles



3a: R = Tol
3b: R = Mes
3c: R = Tip
3d: R = ^{t}Bu (*S*)

entry	R	R′M	additive	product	yield (%)	ratio[a]
1	Tol	PhMgBr	-	**7**	80	61:39
2	Tol	PhMgBr	$Yb(OTf)_3$	**7**	81	66:34
3	Mes	PhMgBr	-	**8**	82	87:13
4	Mes	PhMgBr	$Ti(O^iPr)_4$	**8**	34	67:33
5	Mes	PhMgBr	$Yb(OTf)_3$	**8**	70	77:23
6	Tip	PhMgBr	-	**9**	96	98:2
7	Tip	PhLi	-	**9**	78	95:5
8	Tip	PhMgBr	$ZnBr_2$	**9**	49	91:9
9	Tip	PhMgBr	$Ti(O^iPr)_4$	**9**	81	76:24
10	Tip	PhMgBr[b]	$Ti(O^iPr)_4$	**9**	-	-
11	Tip	PhMgBr	$Ti(O^iPr)_2Cl_2$	**9**	58	75:25
12	Tip	PhMgBr	$TiCl_4$	**9**	83	79:21
13	Tip	PhMgBr	Et_2AlCl	**9**	71	91:9
14	Tip	PhMgBr	$Yb(OTf)_3$	**9**	76	31:69
15	Tip	PhMgBr	$Yb(OTf)_3$[c]	**9**	80	30:70
16	Tip	MeMgI	-	**10**	94	80:20
17	Tip	^{i}BuMgBr	-	**11**	60[d]	>98:2
18	Tip	AllylMgBr	-	**12**	80	74:26
19	^{t}Bu	PhMgBr	-	**13**	80	68:32

[a] Determined by ^{1}H NMR. [b] The reaction was carried out in Et_2O. [c] $Yb(OTf)_3$ (2.0 equiv) was used. [d] The (1-sulfinyl-2-naphthyl)methanol was obtained (35%).

Treatment of a THF solution of 1-sulfinyl-2-naphthaldehydes **3a**−**d** with 1.5 equiv of Grignard reagents or PhLi gave the 2-naphthylmethanols **7**−**13**. The reaction in the presence of a Lewis acid was carried out by stirring a THF solution of **3a**−**c** and the Lewis acid (1.1 equiv) for 1 h before the addition of a solution of R′M. These results are shown in Table 1.

As expected, the stereoselectivity varied, depending upon the groups attached to the sulfinyl group. It is apparent that 1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthaldehyde **3c** shows high stereoselectivity in comparison with the (*p*-tolylsulfinyl)- and [(2,4,6-trimethylphenyl)sulfinyl]naphthaldehydes **3a** and **3b**. Thus, the reaction of **3c** with PhMgBr and PhLi gave the 2-naph-

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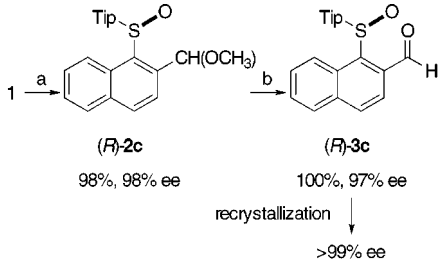
Scheme 2[a]



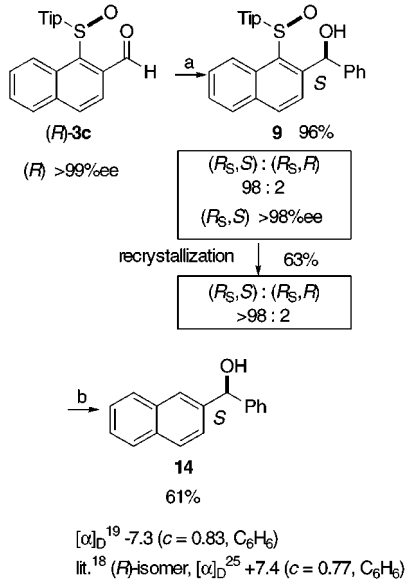
[a] (a) (1) *n*-BuLi, 2) (*R*)-diacetone D-glucosyl 2,4,6-triisopropylbenzenesulfinate, Et_2O, −105 °C; (b) H_2SO_4, SiO_2, CH_2Cl_2, rt.

thylmethanol **9** in a ratio of 98:2 and 95:5, respectively, favoring the (R_S*,*S**)-isomer (entries 6 and 7). Their stereochemistry was determined by X-ray crystallography. The stereoselectivity was reduced when the reaction was performed in the presence of 1.1 equiv of Lewis acids. Notably, $Yb(OTf)_3$ reversed the stereoselectivity favoring the (R_S*,*R**)-isomer (entries 14 and 15). The stereoselectivity also changed depending on the size of the Grignard reagents. A higher diastereoselectivity was obtained as the size of the nucleophile was bulkier (entries 16−18). Thus, the addition product **11** was obtained with complete selectivity in the reaction with *iso*-BuMgBr, although a significant amount of the (1-sulfinyl-2-naphthyl)-methanol was formed by the abnormal Grignard reaction.[13] It should be noted that the naphthaldehyde **3d** bearing a bulky *tert*-butylsulfinyl group gave the product **13** with low selectivity (entry 19).[14] These results show that higher stereoselectivity is not always obtained in the reaction of the sulfinylnaphthaldehydes bearing a bulkier substituent and the stereochemistry-determining step would be strongly related to the rotational barrier around the C_{naph}−S bond as discussed in detail in the discussion section.

Having established a high diastereoselectivity in the reaction of **3c**, we next confirmed that this nucleophilic reaction could be applied to the preparation of enantiomerically pure 2-naphthylmethanol by starting with the chiral [(2,4,6-triisopropylphenyl)sulfinyl]naphthaldehyde (*R*)-**3c**. Scheme 2 summarizes the route for the preparation of (*R*)-**3c** from **1**.

To avoid the racemization of the sulfoxide, the reaction was immediately quenched after the addition of the precooled solution of (*R*)-diacetone D-glucosyl 2,4,6-triisopropylbenzenesulfinate[15] to lithiated **1** in one portion at −105 °C. This gave a 98% yield of sulfoxide (*R*)-**2c** with 98% ee.[16] Acetal (*R*)-**2c** was deprotected to quantitatively give (*R*)-**3c** with 97% ee. The enantiomerically pure sulfoxide (*R*)-**3c** was obtained by recrystallization from hexane/ethyl acetate. The reaction of the chiral (*R*)-**3c** with PhMgBr at −78 °C gave the product in a ratio of 98:2 (Scheme 3).

Scheme 3[a]



[a] (a)PhMgBr, THF, −78 °C; (b) *n*-BuLi, THF, −78 °C

Recrystallization from hexane/ethyl acetate yielded the enantiomerically as well as diastereomerically pure adduct (R_S,*S*)-**9**. Cleavage of the sulfinyl moiety using *n*-BuLi[17] gave enantiomerically pure 2-naphthylmethanol **14**. The absolute configuration of **14** was assigned to be *S* by comparison of the specific rotation with the reported value.[18] This reaction provides a convenient method for the preparation of the optically pure 2-naphthylmethanols via the nucleophilic reaction of the sulfinylnaphthaldehyde in combination with cleavage of the sulfinyl group.

The Mukaiyama Aldol Reaction of 1-Sulfinyl-2-naphthaldehydes. We studied the Mukaiyama aldol reaction of sulfinylnaphthaldehydes **3a**−**c** with the trimethyl- and *tert*-butyldimethylsilylketene acetals. The reaction was carried out by stirring a CH_2Cl_2 solution of **3a**−**c** and a Lewis acid (1.1 or 2.0 equiv) for 1 h at −78 °C and subsequent addition of the ketene acetals. These results are shown in Table 2.

The reactions of **3a** and **3b** with the ketene thioacetal in the presence of 2 equiv of BF_3·OEt_2 gave products **15** and **16** with high selectivity in ratios of 79:21 and 95:5, respectively (entries 1 and 3). On the other hand, **3c** gave (R_S*,*S**)-**17** with complete selectivity (entry 5), whose structure was confirmed by X-ray crystallography. The stereochemical outcome in the presence of $TiCl_4$ is noteworthy. The reaction of **3a** and **3b** revealed good stereoselectivity, favoring the same diastereomers as those preferably obtained with BF_3·OEt_2. The stereoselectivity was reversed to 30:70 in the reaction of **3c** in the presence of $TiCl_4$, favoring the (R_S*,*R**)-isomer (entries 6 and 7).[19] We also examined the reaction of **3c** with

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(14) The absolute stereochemistry of **13** was determined by cleavage of the sulfinyl group using *n*-BuLi.

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(16) The reaction carried out at −78 °C or stirred for a longer time caused racemization of the sulfoxide. The exchange reaction of lithium for magnesium using $MgBr_2$·Et_2O was also examined, but enantiomeric pure product could not be obtained, see: Girodier, L.; Maignan, C.; Rouessac, F. *Tetrahedron: Asymmetry* **1992**, *3*, 857.

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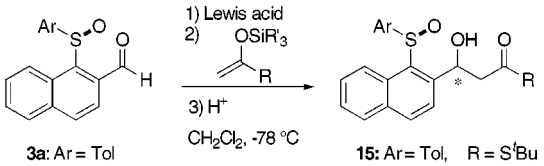
(19) Other Lewis acids such as Et_2AlCl, $MeAlCl_2$, $Yb(OTf)_3$, $MgBr_2$·OEt, and $SnCl_4$ were also examined, but no significant results were obtained.

Table 2. The Mukaiyama Aldol Reaction of the 1-Sulfinyl-2-naphthaldehydes 3a−c



3a: Ar = Tol
3b: Ar = Mes
3c: Ar = Tip

15: Ar = Tol, R = S^{t}Bu
16: Ar = Mes, R = S^{t}Bu
17: Ar = Tip, R = S^{t}Bu
18: Ar = Tip, R = Ph

entry	Ar	R	SiR′$_3$	reaction time (h)	Lewis acid	product	yield (%)	ratio[a]
1	Tol	S^{t}Bu	$SiMe_3$	7	BF_3·OEt_2[b]	**15**	91	79:21[c]
2	Tol	S^{t}Bu	$SiMe_3$	7	$TiCl_4$	**15**	77	80:20[c]
3	Mes	S^{t}Bu	$SiMe_3$	5	BF_3·OEt_2[b]	**16**	81	95:5[c]
4	Mes	S^{t}Bu	$SiMe_3$	10	$TiCl_4$	**16**	78	73:27[c]
5	Tip	S^{t}Bu	$SiMe_3$	2	BF_3·OEt_2[b]	**17**	90	>98:2
6	Tip	S^{t}Bu	$SiMe_3$	7	$TiCl_4$	**17**	82	30:70
7	Tip	S^{t}Bu	$SiMe_3$	3	$TiCl_4$[b]	**17**	90	39:61
8	Tip	OEt	Si^{t}BuMe$_2$	4	BF_3·OEt_2[b]		0[d]	-
9	Tip	OEt	Si^{t}BuMe$_2$	3	$TiCl_4$		0[d]	-
10	Tip	S^{t}Bu	Si^{t}BuMe$_2$	10	BF_3·OEt_2[b]	**17**	62	>98:2
11	Tip	S^{t}Bu	Si^{t}BuMe$_2$	6	$TiCl_4$	**17**	22	10:90
12	Tip	S^{t}Bu	Si^{t}BuMe$_2$	3	$TiCl_4$	**17**	42[d]	12:88
13	Tip	Ph	$SiMe_3$	4	BF_3·OEt_2[b]	**18**	81	>98:2
14	Tip	Ph	$SiMe_3$	5	$TiCl_4$	**18**	40	2:>98

[a] Determined by ^{1}H NMR. [b] The Lewis acid (2.0 equiv) was used. [c] The relative stereochemistry was not determined. [d] The reaction mixture was warmed to room temperature.

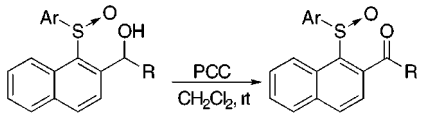
several silyl enol ethers derived from ethyl acetate, *tert*-butyl thioacetate, and acetophenone, which have often been used in the Mukaiyama aldol reaction.[20] The reaction with *O*-*tert*-butyldimethylsilyl *O*-ethyl ketene acetal gave no Mukaiyama aldol product in the presence of a Lewis acid such as BF_3·OEt_2 or $TiCl_4$ (entries 8 and 9). The reaction of the ketene thioacetal, prepared from *tert*-butyl thioacetate and *tert*-butyldimethylsilyl chloride, with **3c** gave only (R_S*,*S**)-**17** in the presence of BF_3·OEt_2 (entry 10) although in lower yield when compared with the reaction using the *O*-trimethylsilyl ketene thioacetal. $TiCl_4$ again reversed the stereoselectivity, favoring the (R_S*,*R**)-isomer (entries 11 and 12). The reaction of the trimethylsilyl enol ether of acetophenone proceeded with extremely high stereoselectivity. Thus, each diastereomer **18** could be prepared with complete selectivity by using either BF_3·OEt_2 or $TiCl_4$ as a Lewis acid (entries 13 and 14). Since we have already assigned the stereochemistry of the predominantly formed product from the ketene thioacetal as the (R_S*,*S**)-isomer with BF_3·OEt_2, and hence the (R_S*,*R**)-isomer with $TiCl_4$, the stereochemistry of the product **18** was deduced as such.

Reduction of the 2-Acyl-1-arylsulfinylnaphthalenes. The pyridinium chlorochromate (PCC) oxidation of the (1-arylsulfinyl-2-naphthyl)methanols **7**−**10** and **12**, which had been already prepared in the former reaction, gave 2-acyl-1-(arylsulfinyl)naphthalenes **19a**−**e**. (Scheme 4).

The stereochemical outcome of the reduction including the stereochemistry and stereoselectivity was found to be quite different among **19a**, **19b**, and **19c**−**e**, bearing *p*-tolyl, 2,4,6-trimethylphenyl, and (2,4,6-triisopropylphenyl)sulfinyl groups, respectively (Table 3).

Furthermore, the remarkable role of the (2,4,6-triisopropylphenyl)sulfinyl group was again shown through

Scheme 4



7: Ar = Tol, R = Ph
8: Ar = Mes, R = Ph
9: Ar = Tip, R = Ph
10: Ar = Tip, R = Me
12: Ar = Tip, R = $CH_2CH{=}CH_2$

19a: 74%
19b: 65%
19c: 81%
19d: 62%
19e: 66%

the stereoselective reductions. The reduction of **19a** with DIBAL gave alcohol **7** in an isomer ratio of 81:19, favoring the (R_S*,*S**)-isomer, whereas the reduction with $LiAlH_4$ gave **7** in a ratio of 35:65, favoring the (R_S*,*R**)-isomer (entries 1 and 2). On the other hand, the reductions of **19b** with DIBAL and $LiAlH_4$ both favor the formation of the (R_S*,*R**)-isomers (entries 3 and 4). In the reduction of **19c**, a higher stereoselectivity with DIBAL was obtained in CH_2Cl_2 than in THF (97:3) and the reversed stereoselectivity was obtained with $LiAlH_4$ (4:96)[21] (entries 5−7). These results show that the reaction mechanism of **19c** may be different from that of **19a** and **19b**. The reduction of **19c** with other reducing agents was also examined (Table 3, entries 8 and 9). Reaction with $NaBH_4$ failed (entry 10). Methyl and allyl ketones **19d** and **19e** showed a stereochemical outcome similar to that of phenyl ketone **19c**, showing the dependence on the reducing agents (entries 11−14). The relative configurations of the alcohols **7**−**10** and **12** were determined by comparison of the HPLC behavior with those obtained in the previous nucleophilic reactions (Table 1).

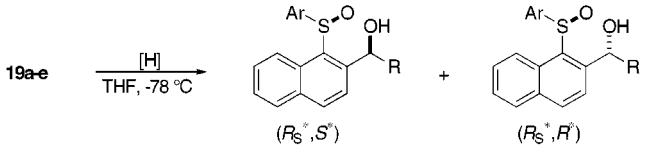
Discussion

In the ^{1}H NMR spectrum of the (*tert*-butylsulfinyl)-naphthaldehyde **3d** measured at −78 °C in THF-d_8, two

(20) Gennari, C. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, pp 629−660.

(21) Addition of $Yb(OTf)_3$, $ZnCl_2$ or BF_3·OEt_2 did not significantly affect the stereoselectivity in the reduction with DIBAL, see: refs 9a−d and 10.

Table 3. Stereoselective Reduction of Ketones 19a−e



7-10,12

entry	Ar	R	reducing agent	temp (°C)	product	yield (%)	ratio[a] (R_S*,*S*): (R_S*,*R*)
1	Tol	Ph	DIBAL	−78 → 0	**7**	52	81:19
2	Tol	Ph	$LiAlH_4$	−78	**7**	98	35:65
3	Mes	Ph	DIBAL	−78 → 0	**8**	51	36:64
4	Mes	Ph	$LiAlH_4$	−78 → 0	**8**	36	33:67
5	Tip	Ph	DIBAL	−78 → 0	**9**	15	72:28
6	Tip	Ph	DIBAL[b]	−78	**9**	91	97: 3
7	Tip	Ph	$LiAlH_4$	−78	**9**	80	4:96
8	Tip	Ph	L-selectride	−78 → 0	**9**	48	6:94
9	Tip	Ph	Super-Hydride	−78	**9**	91	79:21
10	Tip	Ph	$NaBH_4$	−78→ 0	**9**	-	-
11	Tip	Me	$LiAlH_4$	−78	**10**	72	26:74
12	Tip	Me	DIBAL[b]	−78	**10**	78	90:10
13	Tip	$-CH_2-CH=CH_2$	$LiAlH_4$	−78	**12**	64	20:80
14	Tip	$-CH_2-CH=CH_2$	DIBAL[b]	−78	**12**	80	80:20

[a] Determined by ^1H NMR. [b] Reaction was carried out in CH_2Cl_2.

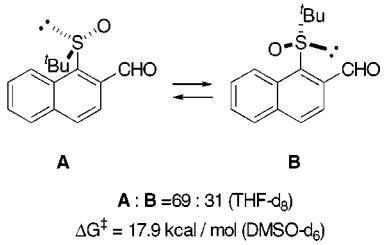


Figure 1. The barrier to rotation around the $C_{naph}-S$ bond for **3d**.

sets of signals due to the *tert*-butyl protons appeared at 1.27 and 1.23 ppm, the peri-H^8 proton at 8.62 and 9.86 ppm, and the formyl proton at 10.8 and 11.7 ppm, which were obviously derived from the restricted rotation about the $C_{naph}-S$ bond. Thus, **3d** exists as two conformers, either having the sulfinyl oxygen close to the formyl group (**A**-isomer) or close to the peri-H^8 of the naphthalene (**B**-isomer) as shown in Figure 1. This result is not unusual; the barriers to rotation around the $C_{naph}-S$ bond for several 2-substituted 1-sulfinylnaphthalenes have been measured to be relatively high.[7]

The minor conformer was assigned to be rotamer **B** on the basis of the downfield shift of the peri-H^8 proton due to the anisotropic effect of the sulfinyl oxygen.[22] The **A**/**B** ratio was 69:31 in the ^1H NMR spectrum at −78 °C in THF-d_8. It is of interest that the **A**-isomer is the more stable, because the 2-substituted, e.g., 2-fluoro, chloro, bromo, methoxy, isopropoxycarbonyl, and methyl, 1-(alkylsulfinyl)naphthalenes are known to generally prefer the isomer having the sulfinyl oxygen close to the peri-H^8 proton than the other isomer.[7a,b,d] The rate constant of the rotation was found to be $k = 64\ s^{-1}$ at 80 °C in DMSO-d_6 by the line shape analysis of the broadened *tert*-butyl proton signal in the region of coalescence. From the rate constant, k, the activation energy ($\Delta G^{\ddagger}$) of rotation was calculated using Eyring's equation[23] to be 17.9 kcal/mol. Hence, the **A**/**B** rotamer ratio at room temperature turned out to be 69:31 which is essentially the same as the product ratio of 68:32 (Table 1, entry 19). It can be estimated that the rotameric forms remain long enough to react at −78 °C (a half-life of 2470 h at −78 °C) and indicating that the ratio of the rotamers **A** and **B** would reflect the diastereomer ratio of the product **13** on the basis of the rotational barrier (17.9 kcal/mol). Hence, it can be reasonably assumed that the reaction of **3d** with a nucleophile proceeds faster than the rotation of the rotamers and, therefore, that the reaction proceeds under dynamic thermodynamic control. Sulfoxide **3c** bearing a sterically bulky triisopropylphenyl group may also have a relatively high rotational barrier, although the ^1H NMR analyses of the other sulfoxides **3a**−**c** at −95 °C in CD_2Cl_2 failed to detect the corresponding rotamers that originated from the rotational barrier around the $C_{naph}-S$ axis. The reactions of **3c** with PhMgBr and PhLi showed high stereoselectivity favoring the same diastereomer (Table 1, entries 6 and 7). These results are in contrast to those reported by Clayden and co-workers.[5a] They observed the reversal in stereoselectivity in each reaction of the 2-formyl-1-naphthamide with RMgX or RLi, which can be ascribed to a chelated (RMgX) or nonchelated (RLi) transition state. Furthermore, the reaction of **3c** with PhMgBr in the presence of $Yb(OTf)_3$ predominantly afforded a stereoisomer different from the one preferably obtained without a Lewis acid. These results indicate that both reactions of **3c** with PhMgBr and PhLi would proceed through a nonchelated transition state.

The configuration of product **9** was (R_S*,*S*), and the origin of this stereochemistry can be directly rationalized from the X-ray crystal structure of **3c**, which showed the sulfoxide oxygen situated away from the peri-H^8 proton, the carbonyl group almost on the plane of the naphthalene ring, and the carbonyl oxygen away from the sulfoxide (Figure 2). In this structure, one face of the formyl group is highly hindered by the 2,4,6-triisopropylphenyl group, while the other is much more exposed to attack. Thus, the Grignard reagent or phenyllithium predominantly approaches from the side opposite the bulky aryl group to give (R_S*,*S*)-**9**. The stable conformer of **3c**, like that of **3d**, was also different from that of 1-(alkylsulfinyl)naphthalenes having a substituent at the

(22) Lett, R.; Marquet, A. *Tetrahedron* **1974**, *30*, 3379.
(23) Eyring, H. *Chem. Rev.* **1935**, *17*, 65.

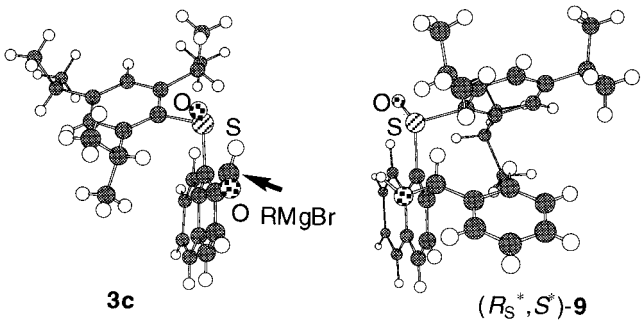


Figure 2. The Chem 3D structure derived from the X-ray crystallography of **3c** and (R_S*,*S**)-**9**.

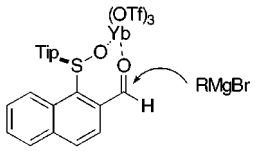


Figure 3. Chelated structure of **3c** with $Yb(OTf)_3$.

2-position other than the formyl group. The 2-formyl group definitely affects the stability of the rotamer around the C_{naph}−S axis. The reason is still unclear, although the effect of the dipole−dipole and/or stereoelectronic interactions for this peculiar arrangement might play a role. Furthermore, the (2,4,6-triisopropylphenyl)sulfinyl group rotates around the C_{naph}−S axis and the sulfinyl oxygen is now placed close to the peri-H^8 proton in the X-ray structure of (R_S*,*S**)-**9** (Figure 2).

The reaction of **3c** in the presence of $Yb(OTf)_3$ proceeds through a rigid conformation fixed by chelation between the sulfinyl and carbonyl oxygen, in which one face of the formyl group is highly covered by 2,4,6-triisopropylphenyl group and RMgBr approaches from the less hindered side to give predominantly (R_S*,*R**)-**9** (Figure 3). The slightly lower stereoselectivity in the reaction with $Yb(OTf)_3$ compared to those without $Yb(OTf)_3$ is due probably to the incomplete chelate formation.

To obtain a more quantitative insight, we calculated the relative energies for the conformers of **3c** using the MOPAC 93/PM3 method.[24] The relative energies of the optimized structures **C**, **D**, **E**, and **F** are depicted in Figure 4.

Conformer **C**, which turned out to be the most stable, was substantially the same rotamer as the solid structure confirmed by X-ray crystallography, indicating that the reaction predominantly proceeds through this conformer to give the (R_S*,*S**)-isomer with high selectivity. Conformer **F** was the most stable among the rotamers presumably affording the (R_S*,*R**)-isomer, but its energy was higher than that of conformer **C** by 1.81 kcal/mol, which corresponds in theory to a ratio of 99.1:0.9 at −78 °C, favoring the (R_S*,*S**)-isomer. Conformer **D** is another optimized rotamer having the sulfinyl oxygen close to the peri-H^8 proton of the naphthalene ring and is less stable than conformer **C** by 1.98 kcal/mol. These data indicate that **3c** would be present to a large extent as conformer **C**, which suggests why only the signal due to one rotamer in the ^1H NMR spectra of **3c** could be detected even at low temperature.

The highly stable structure derived from the MO calculation as well as the X-ray crystallography was also confirmed in solution. The anisotropic effect of the sulfinyl and sulfonyl oxygens in the ^1H and ^{13}C NMR spectra enables us to determine whether the oxygens is close to or away from the peri-H^8 proton[25] (Figure 5).

Thus, it is reasonable that the peri-H^8 proton of the sulfone **20d** is shifted downfield for **B** but not for **A**, whereas the formyl carbon is shifted downfield conversely. For **3a**, **3b**, and **3c**, on the other hand, no separated signals for the peri-H^8 proton and the formyl carbon were observed in the ^1H and ^{13}C NMR spectra. Taking into account the downfield shifts of the protons and the carbons by converting the sulfinyl group to sulfonyl, we can expect the most stable rotamers which are depicted in Figure 5. The stable conformer for **3c** thus assigned by the NMR spectral analyses is in good accord with the X-ray crystal structure (Figure 2) as well as the most stable conformer **C** predicted by the MO calculation. The structure of the stable rotamer for **3a** seems to be different from that of **3c**, i.e., the rotamer bearing the sulfinyl oxygen close to the peri-H^8 proton is more stable than the other one.[26] Although the exact rotational barrier cannot be estimated by these spectral results, the barrier to rotation about the C_{naph}−S bond is expected to be definitely higher as the sulfinyl group is bulkier. The poor stereoselectivity obtained in the reaction of **3a** may be due to the low barrier to rotation. On the basis of these considerations, we have concluded that the nucleophilic reactions of **3c** would predominantly proceed through the thermodynamically most stable rotamer as depicted in Figures 2 and 5.[27]

The results in the Mukaiyama aldol reaction of **3c** also support the reaction pathway through the rotamer in which the sulfinyl oxygen is directed toward the formyl group. We examined two Lewis acids, $BF_3{\cdot}OEt_2$ (2 equiv) and $TiCl_4$ (1.1 equiv), which showed completely different stereochemical behavior from one another, giving predominantly the (R_S*,*S**)- and (R_S*,*R**)-isomers, respectively. Two boron trifluoride molecules independently coordinate with the sulfinyl and carbonyl oxygens as shown in Figure 6. A silyl enol ether approaches the carbonyl from the side away from the 2,4,6-triisopropylphenyl group. $TiCl_4$, on the other hand, coordinates with the sulfinyl and carbonyl oxygens to form a seven-membered cyclic intermediate. A silyl enol ether approaches the carbonyl face from the direction avoiding any steric interaction with the 2,4,6-triisopropylphenyl group, giving the aldol product in a product distribution different from that obtained in the reaction using $BF_3{\cdot}OEt_2$. The Mukaiyama aldol reaction needs a Lewis acid to activate the carbonyl group and thus resulted in higher stereocontrol than the Grignard reaction with the Lewis acids. Obviously, attack of the silyl enol ether in the $TiCl_4$-chelated seven-membered cyclic intermediate occurs on the same carbonyl face as that in the Grignard reaction in the presence of $Yb(OTf)_3$ (Table 1 and Figure 3).

The treatment of 2-[(2,4,6-triisopropylphenyl)sulfinyl]-benzaldehyde **21** with the silyl enol ether in the presence

(24) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(25) For NMR spectral analyses of 2-sulfinylnaphthalene derivatives, see: refs 7a,b,d.

(26) Preference of this rotamer for **3a** was also confirmed by the MO calculation using the PM3 method.

(27) Although all the evidence we obtained supports our conclusion, the kinetic pathway cannot be strictly ruled out because we are unable to determine the barrier to rotation for **3c**.

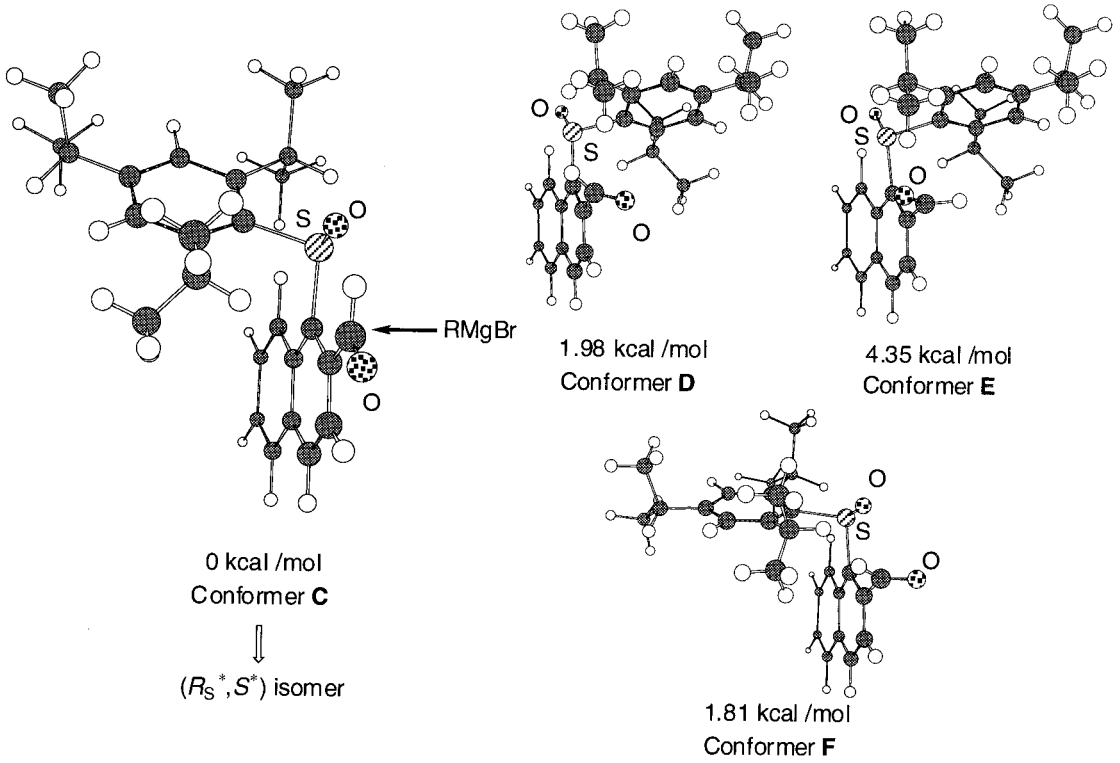


Figure 4. Geometry optimization of **3c** by MOPAC 93/PM3.

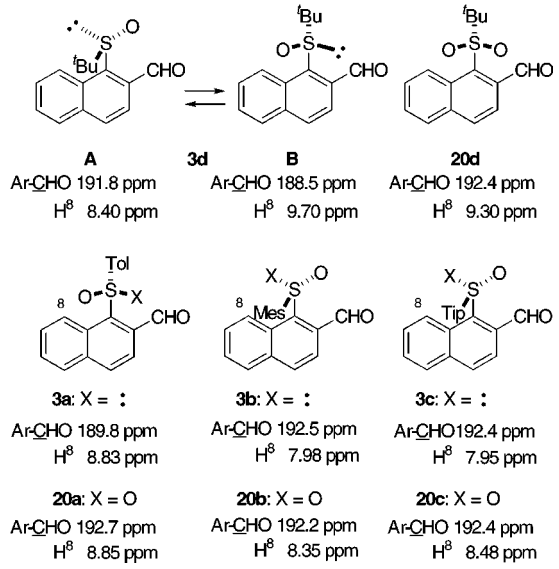


Figure 5. Significant ^{1}H and ^{13}C NMR chemical shifts for the 1-sulfinyl- and 1-sulfonyl-2-naphthaldehydes.

of $BF_3{\cdot}OEt_2$ was found to give the product[28] with much lower stereoselectivity than that from the reaction of the naphthaldehyde **3c** (Scheme 5). The barrier to rotation of **21** would be very low, and the product would be kinetically formed. These results suggest that the stereochemical outcome in the reactions of **3c** is strongly related to the rotational barrier about the $C_{naph}-S$ bond derived from the significant role of the peri-H^8 proton.[29]

The stereoselectivity in the reduction of **19c** with $LiAlH_4$ giving (R_S*,*R**)-**9** can also be explained from the X-ray crystal structure of **19c**, in which the sulfinyl

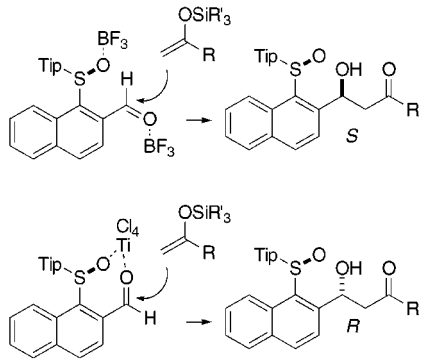


Figure 6. Nonchelated and chelated intermediate in the Mukaiyama aldol reactions of **3c** with $BF_3{\cdot}OEt_2$ and $TiCl_4$.

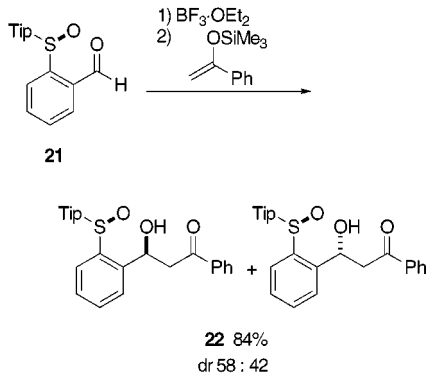
oxygen is directed to the carbonyl group as in the structure of **3c**, but the carbonyl face probably rotates by the stereoelectronic effect, so that the phenyl group is arranged in the direction opposite to the 2,4,6-triisopropylphenyl group (Figure 7): The dihedral angle between the carbonyl and the naphthalene bond is 64.7°.

In this structure, one carbonyl face is highly hindered by the 2,4,6-triisopropylphenyl group, and the other face is open to attack. Attack from the side opposite to the triisopropylphenyl group produces (R_S*,*R**)-**9**. Reduction of **19c** with DIBAL proceeds through a seven-membered cyclic transition state while maintaining the conforma-

(28) The structure of the minor product was confirmed by the X-ray crystallography as shown in Scheme 5.

(29) Both reactions of **21** with PhMgBr in the presence and absence of $Yb(OTf)_3$ gave the same (R_S*,*S**)-isomer with high stereoselectivities (>98:2). The stereochemical outcome is different from the one in the reaction of **3c** with PhMgBr, forming the (R_S*,*S**)-isomer through the nonchelating intermediate and the (R_S*,*R*)-isomer in the presence of $Yb(OTf)_3$. Both reactions of **21** probably proceed through a similar chelating transition state involving the coordination of an ytterbium or magnesium ion with the sulfinyl and carbonyl oxygens, although freely rotating **21** would form the chelation structure different from the ytterbium-chelating **3c**.

Scheme 5



tion of the rotamer to yield (R_S*,S*)-**9**. We assume that the high selectivity obtained in the reduction of **19c**, **19d**, and **19e** is controlled entirely by the restricted rotational barrier around the C_{naph}−S bond and the steric effect of the bulky 2,4,6-triisopropylphenylsulfinyl group.

Conclusion

We have described new and excellent carbonyl-face selective reactions of 2-formyl- and 2-acylnaphthalenes bearing the bulky (2,4,6-triisopropylphenyl)sulfinyl group, which can be performed without isolation of the diastereomeric rotamers. We have demonstrated that high diastereoselectivity is obtained under dynamic thermodynamic control due to the restricted rotation around the C_{naph}−S bond having the bulky (2,4,6-triisopropylphenyl)-sulfinyl group by viewing a combination of the stereochemical behavior in comparison with the *p*-tolyl- and mesitylsulfinylnaphthalene derivatives, and (2,4,6-triisopropylphenyl)sulfinylbenzaldehyde, and the X-ray crystal structures supported by the MO calculation as well as the ^{1}H and ^{13}C NMR spectral data. In addition, removal of the sulfinyl group from the products would provide a convenient and efficient method for preparation of the optically active 2-naphthylalkanols.

Experimental Section

Representative Procedure for the Preparation of the Sulfoxides. 1-(2,4,6-Triisopropylphenyl)sulfinyl-2-naphthaldehyde Dimethyl Acetal (2c). To a solution of 1-bromo-2-naphthaldehyde dimethyl acetal (1.15 g, 4.07 mmol) in Et_2O (10 mL) was added *n*-butyllithium (1.51 mol L^{-1}, 2.70 mL, 4.07 mmol) at −78 °C, and the mixture was stirred for 30 min. A solution of isopropyl 2,4,6-triisopropylbenzenesulfinate (1.15 g, 3.70 mmol) in Et_2O (10 mL) was then added. After stirring for 1 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 30 g, hexane/ethyl acetate = 96:4) to afford **2c** (1.60 g, 95%): R_f = 0.49 (hexane/ethyl acetate=80:20); HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate 0.5 mL/min) t_R 11.3 (*S*) and 16.7 min (*R*); ^{1}H NMR δ 0.81 (d, 6H, J = 6.6 Hz), 1.19 (d, 3H, J = 6.9 Hz), 1.20 (d, 3H, J = 6.9 Hz), 1.29 (d, 6H, J = 6.6 Hz), 2.84 (hep, 1H, J = 6.9 Hz), 3.35 (s, 3H), 3.56 (s, 3H), 4.13 (hep, 2H, J = 6.6 Hz), 6.97 (s, 1H), 7.03 (s, 2H), 7.20−7.50 (m, 2H), 7.78 (d, 1H, J = 7.2 Hz), 7.90 (s, 2H), 8.16 (d, 1H, J = 8.5 Hz), 9.49 (d, 1H, J = 8.9 Hz); ^{13}C NMR δ 23.7, 24.6, 28.9, 34.2, 55.1, 55.5, 98.7, 123.3, 123.7, 125.1, 126.2, 126.3, 128.6, 129.1, 130.9, 133.4, 137.2, 138.8, 149.7, 153.0; IR (neat) 2960, 1180, 1060 cm^{-1}; EIMS *m*/*z* (rel intensity) 452 (M^+, 20), 435 (74), 389 (72), 341 (100), 203 (96). Anal. Calcd for $C_{28}H_{36}O_3S$: C,74.30; H, 8.02. Found: C, 74.10; H, 8.23.

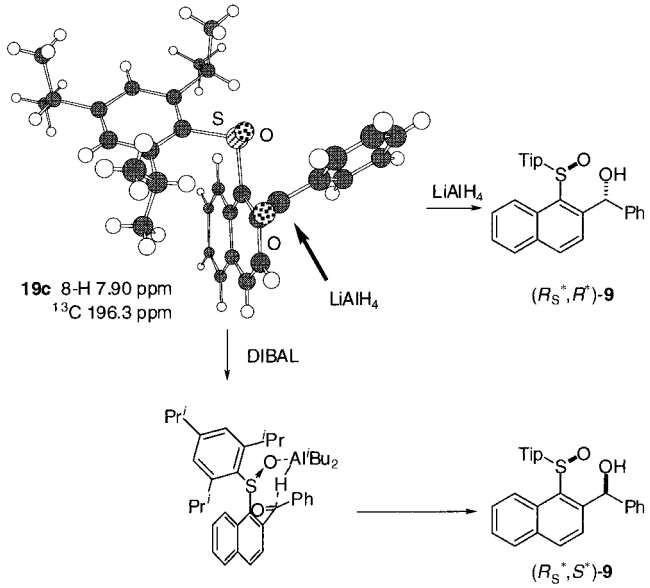


Figure 7. X-ray crystallography of **19c** and the assumed reaction direction.

1-(2,4,6-Triisopropylphenyl)sulfinyl-2-naphthaldehyde (3c). To a suspension of silica gel (2.8 g) in CH_2Cl_2 (5.8 mL) was added 10 drops of a 15% sulfuric acid solution, and the mixture was stirred for 5 min. Then a solution of **2c** (1.27 g, 2.81 mmol) in CH_2Cl_2 (5.8 mL) was added. After stirring for 1 h, a small amount of $NaHCO_3$ was added. The mixture was stirred for 5 min, filtered, and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 50 g, hexane/ethyl acetate = 90:10) to afford **3c** (1.14 g, 100%): mp 164−165 °C (from hexane/ethyl acetate); R_f = 0.37 (hexane/ethyl acetate = 80:20); HPLC (COSMOSIL hexane/ethyl acetate = 90:10, flow rate 0.5 mL/min) t_R 16.7 min, (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate 0.5 mL/min) 16.2 (*S*) and 18.7 min (*R*); ^{1}H NMR δ 0.76 (d, 6H, J = 6.8 Hz), 1.18 (d, 3H, J = 6.9 Hz), 1.19 (d, 3H, J = 6.9 Hz), 1.34 (d, 6H, J = 6.9 Hz), 2.83 (hep, 1H, J = 6.9 Hz), 3.98 (hep, 2H, J = 6.8 Hz), 7.01 (s, 2H), 7.29−7.38 (m, 1H), 7.46−7.55 (m, 1H), 7.77−7.88 (m, 1H), 7.95 (d, 1H, J = 8.5 Hz), 11.3 (s, 1H); ^{13}C NMR δ 23.5, 24.7, 28.8, 34.3, 123.4, 124.3, 125.2, 127.0, 127.9, 128.4, 130.9, 134.7, 136.8, 137.9, 150.4, 154.0, 192.4; IR (KBr) 2980, 1680, 1040 cm^{-1}; EIMS *m*/*z* (rel intensity) 406 (M^+, 15), 389 (74), 347 (100), 203 (80). Anal. Calcd for $C_{26}H_{30}O_2S$: C, 76.81; H, 7.44. Found: C,76.68; H, 7.57.

(*R*)-*tert*-Butyl 1-Naphthyl Sulfoxide [(*R*)-5]. A solution of *tert*-butylmagnesium chloride (2.50 mol L^{-1} solution in Et_2O, 12 mL, 2.80 mmol) was slowly added to a THF (10 mL) solution of (−)-menthyl (S_S)-1-naphthylsulfinate at 0 °C, and the mixture was stirred for 6 h. Saturated aqueous NH_4Cl was then added, and the mixture was extracted with CH_2Cl_2. Usual workup gave the crude product which was purified by column chromatography (silica gel 50 g, hexane/ethyl acetate = 85:15) to afford (*R*)-**5** (420 mg, 71%): R_f = 0.45 (hexane/ethyl acetate = 90:10); HPLC (Daicel Chiralpac AD, hexane/*i*-PrOH = 80:20, flow rate 0.5 mL/min) t_R 17.4 (*S*) and 25.8 min (*R*); $[\alpha]^{23}_D$ +264 (*c* 0.50, toluene, 80% ee) lit.[30] $[\alpha]^{23}_D$ +333 (*c* 1.1, toluene); ^{1}H NMR δ 1.22 (s, 9H), 7.50−7.70 (m, 3H), 7.85−8.30 (m, 4H); ^{13}C NMR δ 23.2, 57.9, 123.2, 124.9, 125.5, 126.2, 126.5, 128.5, 131.3, 131.5, 133.0, 136.8.

(*R*)-[1-(*tert*-Butylsulfinyl)-2-naphthyl]methanol [(*R*)-6]. To a solution of **5** (420 mg, 1.80 mmol) in THF (10 mL) was

(30) Baker, R. W.; Hockless, D. C. R.; Pocock, G. R.; Sargent, M. V.; Skelton, B. W.; Sobolev, A. N.; Twiss, E.; White, A. H. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2615.

added *n*-butyllithium (1.48 mol L^{-1}, 1.34 mL, 1.99 mmol) at −78 °C. After stirring for 10 min, a THF (5 mL) solution of paraformaldehyde (274 mg, 9.04 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 1 h. Usual workup gave the crude product which was purified by column chromatography (silica gel 30 g, hexane/ethyl acetate = 70:30) to afford (*R*)-**6** (145.4 mg, 31%). The atropisomer ratio was determined to be 73:27 by the ^{1}H NMR analysis of the product in $CDCl_3$ at room temperature: R_f = 0.17 (hexane/ethyl acetate = 50:50); HPLC (Daicel Chiralpac AD, hexane/*i*-PrOH = 70:30, flow rate 0.5 mL/min) t_R 16.6 (*S*) and 19.5 min (*R*); $[\alpha]^{23}_D$ +164.6 (*c* 0.253, $CHCl_3$, 80% ee); ^{1}H NMR δ 1.22 (s, 9H, the major isomer), 1.30 (s, 9H, the minor isomer), 4.15−4.60 (m, 2H), 5.20−5.40 (m, 1H, the minor isomer), 5.70−5.85 (m, 1H, the major isomer), 7.60−8.00 (m, 5H), 8.20−8.40 (m, 1H, the major isomer), 9.35−9.50 (m, 1H, the minor isomer); ^{13}C NMR δ 24.8, 25.0, 60.3, 60.7, 60.9, 64.4, 124.1, 125.0, 126.2, 126.4, 126.5, 126.7, 128.3, 128.5, 130.3, 132.0, 132.3, 132.9, 133.1, 143.0; IR (KBr) 3320, 2970, 1060, cm^{-1}; EIMS *m*/*z* (rel intensity) 262 (M^+, 0.1), 188 (100), 115 (50). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92. Found: C, 68.56; H, 7.03.

(*R*)-1-(*tert*-Butylsulfinyl)-2-naphthaldehyde [(*R*)-3d]. To a solution of PCC (179.2 mg, 0.83 mmol) in CH_2Cl_2 (1.5 mL) was added a solution of **6** (145.4 mg, 0.55 mmol) in CH_2Cl_2 (1.5 mL) at room temperature. After stirring for 5 h, Et_2O was added, and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly washed with Et_2O. The ethereal solution was concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 20 g, hexane/ethyl acetate = 70:30) to give (*R*)-**3d** (103.3 mg, 71%). The atropisomer ratio was determined to be 69:31 by the ^{1}H NMR analysis of the product in THF-d_8 at −78 °C: R_f = 0.58 (hexane/ethyl acetate = 50:50); HPLC (COSMOSIL, hexane/ethyl acetate = 75:25, flow rate 0.6 mL/min) t_R 15.0 min, (Daicel Chiralpac AD, hexane/*i*-PrOH = 80:20, flow rate 0.5 mL/min) t_R 26.2 (*S*) and 35.2 min (*R*); $[\alpha]^{26}_D$ +155.7 (*c* 0.184, $CHCl_3$, 80% ee); ^{1}H NMR δ 1.23 (s, 9H), 7.50−7.70 (m, 2H) 7.80−8.10 (m, 3H), 8.35−8.45 (m, 1H, the major isomer), 9.65−9.72 (m, 1H, the minor isomer), 10.8 (s, 1H, the major isomer), 11.6 (s, 1H, the minor isomer); ^{13}C NMR δ 24.1, 24.9, 60.3, 61.1, 122.7, 123.9, 125.5, 127.4, 127.7, 127.8, 128.0, 128.3, 128.5, 128.6, 128.8, 129.2, 131.6, 132.5, 134.7, 136.8, 138.8, 139.0, 188.5, 191.8; IR (neat) 2980, 1680, 1050 cm^{-1}; EIMS *m*/*z* (rel intensity) 260 (M^+, 0.3), 204 (90), 187 (100), 158 (32), 115 (34). Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19. Found: C, 69.28; H, 6.11; $\Delta G^{\ddagger}_{C-S}$ = 17.9 kcal/mol (DMSO-d_6).

Reaction of the 1-Sulfinyl-2-naphthaldehydes with Nucleophiles. (R_S*,*S)- and (R_S*,*R**)-1-Phenyl-1-[1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthyl]methanols [(R_S*,*S**)-9 and (R_S*,*R**)-9].** To a solution of **3c** (15.0 mg, 0.037 mmol) in THF (0.4 mL) was added PhMgBr (0.965 mol L^{-1}, 0.045 mL, 0.043 mmol) at −78 °C, and the mixture was stirred for 15 min. Usual workup gave the crude product which was purified by column chromatography (silica gel 10 g, hexane/CH_2Cl_2/Et_2O = 50:48:2) to afford a mixture of (R_S*,*S**)-**9** and (R_S*,*R**)-**9** (17.0 mg, 96%). The diastereomer ratio was determined to be 98:2 by ^{1}H NMR analysis and HPLC analysis of the crude product: R_f = 0.41 (CH_2Cl_2/Et_2O = 95:5); HPLC (COSMOSIL, hexane/ethyl acetate = 90:10, flow rate 0.5 mL/min) t_R 24.7 min, (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min) t_R 9.0 (R_S,*R*) and 37.7 min (R_S,*S*); ^{1}H NMR δ 0.78 (d, 6H, *J* = 6.3 Hz), 1.18 (d, 6H, *J* = 6.6 Hz), 1.22 (d, 6H, *J* = 6.3 Hz), 2.85 (hep, 1H, *J* = 6.6 Hz), 3.70−3.90 (m, 2H), 4.00 (hep, 2H, *J* = 6.3 Hz), 7.03 (s, 2H), 7.10−7.50 (m, 8H), 7.70−7.85 (m, 2H), 8.17 (d, 1H, *J* = 8.7 Hz); ^{13}C NMR δ 25.1, 25.2, 25.7, 30.8, 35.8, 70.5, 124.9, 125.4, 127.7, 127.9, 128.3, 129.3, 129.5, 130.1, 132.5, 132.8, 135.0, 140.1, 144.0, 144.8, 151.3, 154.9; IR (KBr) 3320, 2980, 1040 cm^{-1}; EIMS *m*/*z* (rel intensity) 484 (M^+, 0.1), 389 (54), 347 (96), 203 (100). Anal. Calcd for $C_{32}H_{36}O_2S$: C, 79.30; H, 7.49. Found: C, 79.50; H, 7.45.

(R_S*,*S)- and (R_S*,*R**)-1-[1-[(2,4,6-Triisopropylphenyl)-sulfinyl]-2-naphthyl]ethanols [(R_S*,*S**)-10 and (R_S*,*R*)-10].** The reaction was carried as described above except using **3c** (41.1 mg, 0.037 mmol) and MeMgI (2.83 mol L^{-1}, 0.080 mL, 0.226 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel 8 g, hexane/ethyl acetate = 90:10) to afford (R_S*,*S**)-**10** (32.0 mg, 75%) and (R_S*,*R**)-**10** (8.0 mg, 19%). The diastereomer ratio was determined to be 80:20 by the ^{1}H NMR analysis of the crude product: (R_S*,*S**)-**10**: R_f = 0.13 (hexane/ethyl acetate = 80:20); HPLC (COSMOSIL, hexane/ethyl acetate = 80:20, flow rate 0.5 mL/min) t_R 32.3 min; ^{1}H NMR δ 0.70 (d, 6H, *J* = 6.8 Hz), 0.85 (d, 6H, *J* = 6.0 Hz), 1.06 (d, 6H, *J* = 6.8 Hz), 1.20 (d, 6H, *J* = 6.8 Hz), 2.80 (hep, 1H, *J* = 6.9 Hz), 3.75 (hep, 2H, *J* = 6.8 Hz), 4.70 (br, 1H), 5.80−5.90 (m, 1H), 7.05 (s, 2H), 7.30−7.70 (m, 2H), 7.70−8.00 (m, 3H), 9.00−9.10 (m, 1H); ^{13}C NMR δ 15.7, 23.6, 19.8, 34.4, 64.2, 122.9, 123.0, 124.6, 128.6, 131.5, 132.0, 144.2, 149.8, 153.3; IR (KBr) 3350, 3000, 1060 cm^{-1}; EIMS *m*/*z* (rel intensity) 422 (M^+, 0.2), 345 (40), 203 (100). Anal. Calcd for $C_{27}H_{34}SO_2$: C, 76.73; H, 8.11. Found: C, 76.54; H, 8.30. (R_S*,*R**)-**10**: R_f = 0.24 (hexane/ethyl acetate = 80:20); HPLC (COSMOSIL, hexane/ethyl acetate = 80:20, flow rate 0.5 mL/min) t_R 22.5 min; ^{1}H NMR δ 0.43 (d, 6H, *J* = 6.8 Hz), 0.82 (d, 6H, *J* = 6.0 Hz), 1.05 (d, 6H, *J* = 6.8 Hz), 1.16 (d, 6H, *J* = 6.8 Hz), 2.80 (hep, 1H, *J* = 6.9 Hz), 3.75 (hep, 2H, *J* = 6.8 Hz), 4.35 (br, 1H), 5.30−5.50 (m, 1H), 6.94 (s, 2H), 7.35−7.60 (m, 2H), 7.70−7.95 (m, 3H), 8.40−8.60 (m, 1H); ^{13}C NMR δ 22.1, 23.2, 23.6, 24.2, 29.2, 34.2, 64.1, 123.1, 123.8, 124.5, 125.9, 126.6, 128.5, 131.4, 131.9, 133.6, 138.7, 144.1, 149.8, 153.3; IR (KBr) 3320, 2980, 1060 cm^{-1}; EIMS *m*/*z* (rel intensity) 422 (M^+, 10), 345 (55), 203 (100). Anal. Calcd for $C_{27}H_{34}SO_2$: C, 76.73; H, 8.11. Found: C, 76.79; H, 8.02.

(R_S*,*S)-3-Methyl-1-[1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthyl]-1-butanol [(R_S*,*S**)-11].** The reaction was carried as described above except using **3c** (46.3 mg, 0.114 mmol) and ^{i}BuMgBr (1.0 mol L^{-1}, 0.17 mL, 0.17 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel 10 g, hexane/ethyl acetate = 92:8) to afford (R_S*,*S**)-**11** (31.7 mg, 60%) and 1-[1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthyl]methanol (16.3 mg, 35%). The diastereomer ratio was determined to be >98:2 by the ^{1}H NMR analysis of the crude product. (R_S*,*S**)-**11**: R_f = 0.41 (hexane/ethyl acetate = 80/20): ^{1}H NMR δ 0.77 (d, 6H, *J* = 6.7 Hz), 0.93 (d, 3H, *J* = 6.7 Hz), 0.97 (d, 3H, *J* = 6.7 Hz), 1.15−1.25 (m, 12H), 1.45−1.60 (m, 1H), 1.70−1.90 (m, 1H, *J* = 6.7 Hz), 1.90−2.10 (m, 1H), 2.84 (hep, 1H, *J* = 6.7 Hz), 3.75 (br, 1H), 3.91 (hep, 2H, *J* = 6.7 Hz), 5.90−6.00 (m, 1H), 7.10 (s, 2H), 7.15−7.30 (m, 1H), 7.30−7.45 (m, 1H), 7.70−8.00 (m, 4H);^{13}C NMR δ 22.5, 23.4, 23.6, 23.8, 24.2, 25.2, 29.1, 34.2, 45.9, 68.0, 123.3, 123.7, 125.9, 128.3, 129.5, 130.9, 132.9, 138.2, 144.5, 149.6, 153.1; IR (KBr) 3420, 2980, 1060 cm^{-1}; EIMS *m*/*z* (rel intensity) 464 (M^+, 0.3), 447 (80), 243 (92), 203 (100). Anal. Calcd for $C_{30}H_{40}SO_2$: C, 77.54; H, 8.68. Found: C, 77.41; H, 8.81.

(R_S*,*S)- and (R_S*,*R**)-1-[1-[(2,4,6-Triisopropylphenyl)-sulfinyl]-2-naphthyl]-3-butene-1-ols [(R_S*,*S**)-12 and (R_S*,*R*)-12].** The reaction was carried as described above except using **3c** (60.0 mg, 0.148 mmol) and CH_2=$CHCH_2MgBr$ (0.125 mol L^{-1} solution in THF, 1.77 mL, 0.221 mmol). Usual workup gave the crude product that was purified by column chromatography (silica gel 10 g, hexane/CH_2Cl_2/Et_2O = 50:48:2) to afford a mixture of (R_S*,*S**)-**12** and (R_S*,*R**)-**12** (53 mg, 80%). The diastereomer ratio was determined to be 76:24 by the ^{1}H NMR analysis of the crude product: R_f = 0.24 (hexane/ethyl acetate = 80:20); HPLC (COSMOSIL, hexane/ethyl acetate = 90:10, flow rate 0.5 mL/min) t_R 38.1 and 42.8 min; ^{1}H NMR δ 0.54 (d, 6H, *J* = 6.8 Hz, the major isomer), 0.85 (d, 6H, *J* = 6.8 Hz, the minor isomer), 1.10−1.40 (m, 12H), 2.15−2.40 (m, 1H), 2.40−3.00 (m, 2H), 3.70−4.20 (m, 2H), 4.80−5.20 (m, 2H), 5.40−5.90 (m, 2H), 6.98 (s, 2H, the major isomer), 7.05 (s, 2H, the minor isomer), 7.20−8.00 (m, 5H), 8.60 (d, 1H, *J* = 8.0 Hz, the minor isomer), 9.00 (d, 1H, *J* = 8.0 Hz, the major isomer); ^{13}C NMR δ 23.4, 23.7, 23.8, 24.3, 28.8, 29.3, 34.2, 34.3, 41.4, 41.9, 67.3, 70.3, 117.5, 117.6, 123.2, 123.5, 123.9, 125.1, 126.0, 126.1, 126.4, 126.7, 128.5, 131.1,

131.4, 133.4, 134.5, 134.7, 142.8, 149.6; IR (KBr) 3350, 2980, 1060 cm^{-1}; EIMS *m/z* (rel intensity) 448 (M^+, 0.1), 430 (66), 347 (100), 227 (32), 203 (30). Anal. Calcd for $C_{29}H_{36}O_2S$: C, 77.64; H, 8.09. Found: C, 77.81; H, 7.99.

(*R*S,*S*)- and (*R*S,*R*)-1-[1-(*tert*-Butylsulfinyl)-2-naphthyl]-1-phenylmethanols [(*R*S,*S*)-13 and (*R*S,*R*)-13]. The reaction was carried as described above except using (*R*)-**3d** (103.3 mg, 0.397 mmol) and PhMgBr (1.0 mol L^{-1}, 0.4 mL, 0.40 mmol). Usual workup gave the crude product that was purified by column chromatography (silica gel 10 g, hexane/ethyl acetate = 90:10) to afford the mixture of (*R*S,*S*)-**13** and (*R*S,*R*)-**13** (107.4 mg, 80%). The diastereomer ratio was determined to be 68:32 by the HPLC analysis of the crude product. The diastereomeric atropisomer ratio a:b:c:d was determined to be 52:16:32:0 by the ^{1}H NMR analysis of the crude product: R_f = 0.34 (hexane/ethyl acetate = 50:50); HPLC (COSMOSIL, hexane/ethyl acetate = 75:25, 0.6 mL/min) t_R 24.9 and 28.0 min;^{1}H NMR δ 1.32 (s, 9H, a), 1.36 (s, 9H, b), 1.49 (s, 9H, c), 3.20 (br, 1H, a), 3.60 (br, 1H, b), 5.00 (br, 1H, c), 6.70 (s, 1H, a), 6.80 (s, 1H, c), 7.00−8.00 (m, 10H), 8.30−8.50 (m, 1H, a+c)), 9.50−9.70 (m, 1H, b), two singlet 1.32 and 1.36 ppm appeared at 1.34 ppm as a singlet at 60 °C; IR (KBr) 3300, 2980, 1080 cm^{-1}; EIMS *m/z* (rel intensity) 338 (M^+, 0.1), 266 (70), 247 (100). Anal. Calcd for $C_{21}H_{22}O_2S$: C, 74.52; H, 6.55. Found: C, 74.42; H, 6.65.

Preparation of the Chiral Sulfoxides. (*R*)-[1-(2,4,6-Triisopropylphenyl)sulfinyl]-2-naphthaldehyde Dimethyl Acetal [(*R*)-2c]. The reaction was carried out as described in the preparation of racemic-**3c** except using (−)-1,1-diacetone-D-glucosyl 2,4,6-triisopropylbenzenesulfinate (1.14 g, 2.24 mmol), 1-bromo-2-naphthaldehyde dimethyl acetal (599.8 mg, 2.13 mmol) and *n*-butyllithium (1.51 mol L^{-1}, 1.48 mL, 2.24 mmol) at −105 °C. Usual workup gave the crude product which was purified by column chromatography (silica gel 50 g, hexane/ethyl acetate = 96:4) to afford (*R*)-**2c** (950.5 mg, 98%). See the HPLC data of **2c**.

(*R*)-1-(2,4,6-Triisopropylphenyl)sulfinyl-2-naphthaldehyde [(*R*)-3c]. The reaction was carried as described in the preparation of racemic-**3c** except using 6 drops of 15% sulfuric acid solution, silica gel (1.50 g), and (*R*)-**2c** (631.9 mg, 1.40 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel 20 g, hexane/ethyl acetate = 96:4) to afford (*R*)-**3c** (565 mg, 100%). The enantiomer ratio was determined to be >98:2 by the HPLC analysis using Chiralcel OD-H; see the data of **3c**: $[\alpha]^{20}_D$ −20.0 (*c* 0.724, $CHCl_3$).

Reaction of (*R*)-3c with PhMgBr. (*R*S,*S*)-1-Phenyl-1-[1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthyl]methanol [(*R*S,*S*)-9]. The reaction was carried as described in the preparation of racemic-**9** except using (*R*)-**3c** (33.5 mg, 0.082 mmol) and PhMgBr (0.72 mol L^{-1}, 0.172 mL, 0.124 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel 10 g, hexane/CH_2Cl_2/Et_2O = 50:48:2) to afford a mixture of (*R*S,*S*)-**9** and (*R*S,*R*)-**9** (38.3 mg, 96%). The diastereomer ratio was determined to be 98:2 by the ^{1}H NMR analysis of the crude product. Recrystallization from hexanes−ethyl acetate afforded (*R*S,*S*)-**9** with 98% ee; see the HPLC data of **9**: $[\alpha]^{20}_D$ −96.9 (*c* 0.98, $CHCl_3$).

Preparation of (*S*)-1-(2-naphthyl)-1-phenylmethanol [(*S*)-14]. To a solution of (*R*S,*S*)-**9** (28.0 mg, 0.058 mmol) in THF (0.2 mL) was added *n*-BuLi (0.19 mL, 1.51 mol L^{-1} in hexane, 0.289 mmol) at −78 °C, and the mixture was stirred for 10 min. Usual workup gave the crude product which was purified by column chromatography (silica gel 7 g, hexane/CH_2Cl_2/Et_2O = 50:47.5:2.5) to afforded (*S*)-**14** (8.3 mg, 61%): HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 93:7, flow rate 1.0 mL/min) t_R 36.6 (*S*) and 44.8 min(*R*); $[\alpha]^{19}_D$ −7.3 (*c* 0.83, benzene) lit.[18] $[\alpha]^{20}_D$ +7.4 (*c* 0.77, benzene) for the (*R*)-isomer: R_f = 0.61 (CH_2Cl_2/Et_2O = 95:5); ^{1}H NMR δ 2.45 (br, 1H, −OH), 6.05 (s, 1H, −CH−), 7.20−7.60 (m,8H, Ar), 7.80−8.00 (m, 4H, Ar); IR (KBr) 3600, 3040 cm^{-1}.

Representative Procedure for the Mukaiyama Aldol Reaction of the Sulfoxides. *tert*-Butyl (*R*S*,*S)-3-Hydroxy-3-[1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthyl]thiopropanoate [(*R*S*,*S**)-17].** To a solution of **3c** (23.0 mg, 0.057 mmol) in CH_2Cl_2 (0.5 mL) was added BF_3·OEt_2 (1.34 mol L^{-1} solution in CH_2Cl_2, 0.084 mL, 0.113 mmol) at −78 °C and the mixture was stirred for 1 h. A solution of S-*tert*-butyl *O*-trimethylsilylketene acetal (28.0 mg, 0.137 mmol) in CH_2Cl_2 (0.5 mL) was then added. After stirring for 2 h, HCl (1 mol L^{-1}) was added, and the mixture was stirred for 15 min. Usual workup gave the crude product which was purified by column chromatography (silica gel 10 g, hexane/CH_2Cl_2/Et_2O = 50:48:2) to afford (*R*S*,*S**)-**17** (27.5 mg, 90%). The diastereomer ratio was determined to be >98:2 by the ^{1}H NMR analysis of the crude product: mp 184−185 °C; R_f = 0.43 (CH_2Cl_2/Et_2O = 95:5); ^{1}H NMR δ 0.73 (d, 6H, *J* = 6.7 Hz), 1.22 (d, 6H, *J* = 7.0 Hz), 1.30 (d, 6H, *J* = 6.7 Hz), 1.45 (s, 9H), 2.25 (dd, 1H, *J* = 2.6, 16.1 Hz), 2.84 (dd, 1H, *J* = 9.4, 16.1 Hz), 2.85 (hep, 1H, *J* = 7.0 Hz), 4.03 (hep, 2H, *J* = 6.7 Hz), 4.17 (d, 1H, *J* = 3.9 Hz), 6.11 (ddd, 1H, *J* = 2.6, 3.9, 9.4 Hz), 7.03 (s, 2H), 7.25−7.50 (m, 3H), 7.65−7.95 (m, 2H), 8.68 (d, 1H, *J* = 8.9 Hz); ^{13}C NMR δ 23.5, 23.9, 24.6, 29.4, 29.8, 34.3, 48.6, 50.7, 66.0, 123.4, 123.8, 125.0, 126.2, 126.4, 128.5, 130.8, 131.1, 133.3, 140.7, 149.9, 200.0; IR (KBr) 3320, 2980, 1670, 1160, 1070 cm^{-1}; EIMS *m/z* (rel intensity) 538 (M^+, 12), 431 (20), 389 (40), 347 (60), 203 (100). Anal. Calcd for $C_{32}H_{42}O_3S_2$: C, 71.33; H, 7.86. Found: C, 71.23; H, 7.96.

***tert*-Butyl (*R*S*,*R**)- and (*R*S*,*S**)-3-Hydroxy-3-[1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthyl]thiopropanoates [(*R*S*,*R**)-17 and (*R*S*,*S**)-17].** To a solution of **3c** (48.3 mg, 0.119 mmol) in CH_2Cl_2 (1.0 mL) was added $TiCl_4$ (0.015 mL, 0.137 mmol) at −78 °C and the mixture was stirred for 1 h. A solution of S-*tert*-butyl O-*tert*-butyldimethylsilylketene acetal (35.2 mg, 0.143 mmol) in CH_2Cl_2 (0.5 mL) was then added. After stirring for 7 h, HCl (1 mol L^{-1}) was added, and the mixture was stirred for 15 min. Usual workup gave the crude product which was purified by column chromatography (silica gel 10 g, hexane/CH_2Cl_2/Et_2O = 50:48:2) to afford a mixture of (*R*S*,*R**)-**17** and (*R*S*,*S**)-**17** (27.1 mg, 42%). The diastereomer ratio was determined to be 88:12 by the ^{1}H NMR analysis of the crude product. (*R*S*,*R**)-**17**: R_f = 0.43 (CH_2Cl_2/Et_2O = 95:5); ^{1}H NMR δ 0.81 (d, 6H, *J* = 6.7 Hz), 1.10−1.40 (m, 12H), 1.42 (s, 9H), 2.75−2.95 (m, 1H), 3.08 (dd, 1H, *J* = 5.4, 15.2 Hz), 3.20 (dd, 1H, *J* = 8.0, 15.2 Hz), 3.90−4.00 (m, 2H), 4.68 (d, 1H, *J* = 6.7 Hz), 5.85−6.00 (m, 1H), 7.05 (s, 2H), 7.20−7.50 (m, 2H), 7.60−7.90 (m, 3H), 8.20 (d, 1H, *J* = 8.6 Hz); ^{13}C NMR δ 14.1, 22.7, 23.7, 24.3, 29.1, 29.7, 52.3, 69.8, 123.5, 123.7, 126.2, 126.4, 126.9, 128.6, 129.0, 131.3, 137.8, 141.4, 149.8, 153.2, 198.7; IR (KBr) 3360, 2980, 1680, 1040 cm^{-1}; EIMS *m/z* (rel intensity) 538 (M^+, 20), 431 (15), 389 (70), 203 (100). Anal. Calcd for $C_{32}H_{42}O_3S_2$: C, 71.33; H, 7.86. Found: C, 71.35; H, 7.81.

(*R*S*,*S)-3-Hydroxy-1-phenyl-3-[1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthyl]-1-propanone [(*R*S*,*S**)-18].** The reaction was carried as described above except using **3c** (37.3 mg, 0.092 mmol), BF_3·OEt_2 (1.34 mol L^{-1} solution in CH_2Cl_2, 0.15 mL, 0.201 mmol), and the *O*-trimethylsilyl enol ether of acetophenone (26.5 mg, 0.138 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel 10 g, hexane/ethyl acetate = 90:10) to afford (*R*S*,*R**)-**18** (39.2 mg, 81%). The diastereomer ratio was determined to be >98:2 by the ^{1}H NMR analysis of the crude product: mp 168−169 °C; R_f = 0.20 (hexane/ethyl acetate = 80:20); ^{1}H NMR δ 0.76 (d, 6H, *J* = 6.8 Hz), 0.92 (d, 3H, *J* = 6.9 Hz), 0.99 (d, 3H, *J* = 6.9 Hz), 1.28 (d, 6H, *J* = 6.8 Hz), 2.50 (dd, 1H, *J* = 3.0, 17.9 Hz), 2.55 (hep, 1H, *J* = 6.8 Hz), 3.16 (dd, 1H, *J* = 9.6, 17.9 Hz), 4.14 (hep, 2H, *J* = 6.9 Hz), 4.22 (d, 1H, *J* = 3.0 Hz), 6.18 (ddd, 1H, *J* = 3.0, 3.0, 9.6 Hz), 6.93 (s, 2H), 7.30−7.60 (m, 5H), 7.70−8.00 (m, 5H), 9.08 (d, 1H, *J* = 9.3 Hz); ^{13}C NMR δ 23.2, 23.4, 24.6, 29.5, 33.9, 45.6, 64.9, 123.1, 123.8, 124.6, 126.2, 127.8, 127.9, 128.0, 128.6, 131.3, 133.5, 135.0, 136.4, 139.0, 140.7, 150.0, 153.3, 199.5; IR (KBr) 3400, 2980, 1600, 1070 cm^{-1}; EIMS *m/z* (rel intensity) 526 (M^+, 1), 390 (33), 347 (100), 203 (64), 105 (98). Anal. Calcd for $C_{34}H_{38}O_3S$: C, 77.53; H, 7.27. Found: C, 77.42; H, 7.38.

(*R*S*,*R)-3-Hydroxy-1-phenyl-3-[1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthyl]-1-propanone [(*R*S*,*R**)-18].** The reaction was carried as described above except using **3c** (32.3 mg, 0.079 mmol), $TiCl_4$ (1.41 mol L^{-1} solution in CH_2-

Cl_2, 0.06 mL, 0.085 mmol), and *O*-trimethylsilyl enol ether of acetophenone (24.0 mg, 0.125 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel 10 g, hexane/ethyl acetate = 92:8) to afford (R_S*,*S**)-**18** (16.7 mg, 40%) and **3c** (17.8 mg, 55%). The diastereomer ratio was determined to be >98:2 by the ^{1}H NMR analysis of the crude product: R_f = 0.20 (hexane/ethyl acetate=80:20); ^{1}H NMR δ 0.86 (d, 6H, J = 6.8 Hz), 1.16 (d, 6H, J = 6.8 Hz), 1.18 (d, 6H, J = 6.8 Hz), 2.80 (hep, 1H, J = 6.8 Hz), 3.40−3.75 (m, 2H), 4.05 (hep, 2H, J = 6.8 Hz), 4.65 (d, 1H, J = 5.5 Hz), 6.08−6.20 (m, 1H), 7.03 (s, 2H), 7.25−7.60 (m, 5H), 7.70−8.10 (m, 5H), 8.38 (d, 1H, J = 8.5 Hz); ^{13}C NMR δ 23.6, 23.9, 24.2, 28.9, 34.2, 47.1, 68.6, 123.4, 123.9, 126.2, 126.3, 126.5, 128.3, 128.6, 130.1, 131.6, 133.4, 136.8, 137.3, 142.0, 149.7, 153.0, 199.4; IR (neat) 3380, 2960, 1680, 1040 cm^{-1}; EIMS *m*/*z* (rel intensity) 526 (M^+, 1), 390 (40), 347 (100), 203 (64), 105 (80). Anal. Calcd for $C_{34}H_{38}O_3S$: C, 77.53; H, 7.27. Found: C, 77.51; H, 7.30.

Representative Procedure for the Preparation of the 2-Acyl-1-sulfinylnaphthalenes. 1-[(2,4,6-Triisopropylphenyl)sulfinyl]-2-benzonaphthone (19c). To a solution of PCC (11.0 mg, 0.051 mmol) in CH_2Cl_2 (0.1 mL) was added **9** (16.5 mg, 0.034 mmol) at room temperature. After stirring for 3 h, Et_2O was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly washed with Et_2O. The ethereal solution was concentrated under reduced pressure to leave a residue which was purified by column chromatography (silica gel 10 g, hexane/CH_2Cl_2/Et_2O = 50:48:2) to afford **19c** (13.3 mg, 81%): mp 92−93 °C (from hexane/ethyl acetate); R_f = 0.50 (CH_2Cl_2/Et_2O = 95:5); ^{1}H NMR δ 0.66 (d, 6H, J = 6.6 Hz), 1.09 (d, 6H, J = 6.9 Hz), 1.22 (d, 6H, J = 6.6 Hz), 2.73 (hep, 1H, J = 6.9 Hz), 3.96 (hep, 2H, J = 6.6 Hz), 6.91 (s, 2H), 7.18−7.50 (m, 6H), 7.60−7.75 (m, 3H), 7.80−7.90 (m, 2H); ^{13}C NMR δ 23.5, 23.6, 28.6, 34.2, 123.2, 123.8, 125.9, 126.9, 128.3, 126.9, 128.3, 128.7, 128.8, 128.9, 130.4, 132.3, 133.5, 136.3, 138.3, 138.4, 140.8, 150.8, 153.7, 196.3; IR (KBr) 3420, 3030, 1670, 1660, 1050 cm^{-1}; EIMS *m*/*z* (rel intensity) 482 (M^+, 70), 377 (80), 263 (64), 234 (100), 149 (50), 105 (80). Anal. Calcd for $C_{32}H_{34}O_2S$: C, 79.63; H, 7.10. Found: C, 79.59; H, 7.14.

Representative Procedure for the Reduction of the 2-Acyl-1-sulfinylnaphthalenes. Reduction of 19c with DIBAL. (R_S*,*S)- and (R_S*,*R**)-1-Phenyl-1-[1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthyl]methanol [(R_S*,*S**)-9 and (R_S*,*R**)-9].** To a solution of **19c** (15.7 mg, 0.033 mmol) in CH_2Cl_2 (0.35 mL) was added DIBAL (0.95 mol L^{-1} solution in hexane, 0.070 mL, 0.067 mmol) at −78 °C, and the mixture was stirred for 1 h. MeOH was then added and the mixture was extracted with CH_2Cl_2. Usual workup gave the crude product which was purified by column chromatography (silica gel 3 g, hexane/CH_2Cl_2/Et_2O = 50:48:2) to afford a mixture of (R_S*,*S**)-**9** and (R_S*,*R**)-**9** (14.4 mg, 91%). The diastereomer ratio was determined to be 97:3 by the ^{1}H NMR analysis of the crude product.

Reduction of 19c with $LiAlH_4$. (R_S*,*R)-1-Phenyl-1-[1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthyl]methanol [(R_S*,*R**)-9].** To a solution of $LiAlH_4$ (1.6 mg, 0.042 mmol) in THF (0.2 mL) was added a solution of **19c** (13.3 mg, 0.028 mmol) in THF (0.2 mL) at −78 °C, and the mixture was stirred for 40 min. Usual workup gave the crude product which was purified by column chromatography (silica gel 2 g, hexane/CH_2Cl_2/Et_2O = 50:48:2) to afford a mixture of (R_S*,*R**)-**9** and (R_S*,*S**)-**9** (10.6 mg, 80%). The diastereomer ratio was determined to be 96:4 by the ^{1}H NMR analysis of the crude product. Recrystallization from hexanes−ethyl acetate afforded (R_S*,*R**)-**9** with >98% de: R_f = 0.42 (CH_2Cl_2/Et_2O = 95:5); HPLC (COSMOSIL, hexane/ethyl acetate = 90:10, flow rate 0.5 mL/min) t_R 20.7 min, (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 90:10, 1.0 mL/min) t_R 15.8 (R_S,*R*) and 37.7 min (R_S,*S*); ^{1}H NMR δ 0.87 (d, 6H, J = 6.8 Hz), 1.08 (d, 6H, J = 6.8 Hz), 1.22 (d, 3H, J = 6.9 Hz), 2.97 (hep, 1H, J = 6.9 Hz), 3.93 (d 1H, J = 5.4 Hz), 4.12 (hep, 2H, J = 6.8 Hz), 6.81 (d 1H, J = 5.4 Hz), 7.08 (s, 2H), 7.15−7.55 (m, 8H), 7.75−7.85 (m, 2H), 8.50−8.60 (m, 1H); ^{13}C NMR δ 23.7, 23.8, 24.3, 28.8, 34.2, 71.2, 123.5, 123.6, 126.2, 126.4, 126.9, 127.9, 128.0, 128.2, 128.7, 131.5, 133.2, 142.5, 142.5, 142.9, 149.7, 152.9; IR (KBr) 3400, 2960, 1660, 1100 cm^{-1}; EIMS *m*/*z* (rel intensity) 484 (M^+, 0.1), 389 (60), 347 (90), 203 (100). Anal. Calcd for $C_{32}H_{36}O_2S$: C, 79.30; H, 7.49. Found: C, 79.10; H, 7.30.

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Supporting Information Available: Spectroscopic characterization of the products **2a**,**b**, **3a**,**b**, **7**, **8**, **15**, **16**, **19a**,**b**,**d**,**e**, **20**−**22** and X-ray crystallographic data of **3c**, **9**, **17**, **19c**, and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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