Pergamon

Tetrahedron: Asymmetry Vol. 6, No. 12, pp. 2991-3000, 1995
Elsevier Science Ltd
Printed in Great Britain
0957-4166/95 $9.50+0.00

0957-4166(95)00395-9

Asymmetric Synthesis of a Xanthine Dehydrogenase Inhibitor (*S*)-(-)-BOF-4272 : Utility of Chiral Alkoxysulfonium Salts

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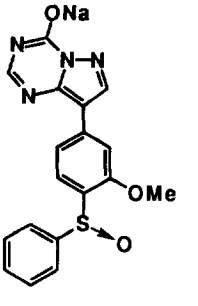
Abstract: A practical synthetic method for a xanthine dehydrogenase inhibitor, (*S*)-(-)-BOF-4272, was established utilizing an asymmetric oxidation of diaryl sulfide BOF-4269. The oxidation of the sulfide with 1-chlorobenzotriazole carried out in the presence of 4-cyanopyridine and chiral 2-phenylcyclohexanol gave a high enantiomeric excess (73%*ee*). The sulfoxides in each enantiomerically pure form could be obtained by treating with alkaline hydrolysis or thermolysis of one of the diastereomeric intermediate sulfonium salts (>99%*de*). Thus the transformation into the sulfoxides occur with virtually perfect inversion (alkaline hydrolysis) or retention (thermolysis). It is therefore possible to obtain the target sulfoxide, (*S*)-(-)-BOF-4272, from both the two diastereomeric sulfonium intermediates.

Introduction

BOF-4272 (**1**) is a pyrazolotriazine derivative which shows a potent inhibition of the biosynthesis of uric acid by interfering with the xanthine oxidase / xanthine dehydrogenase system[1]. Of the two optical isomers, the (*S*)-(-)-isomer[2] shows 100 fold more active[3] than the (+)-isomer. We wish to report first asymmtric synthesis of (*S*)-(-)-BOF-4272.

In recent years, a variety of synthetic methods to obtain optically active sulfoxides have been reported. However, only a few methods are applicable to the production of chiral diaryl sulfoxides such as BOF-4272, since the scope of the asymmetric oxidation[4] seems to be limited to alkyl aryl sulfides. Substitution reactions[5] of enantiomerically pure sulfinate analogues represented by Andersen's synthesis appear to be promising for the achievement of high stereocontrol. The application for BOF-4272, however, was not successful mainly due to the existing heterocyclic ring in the molecule.

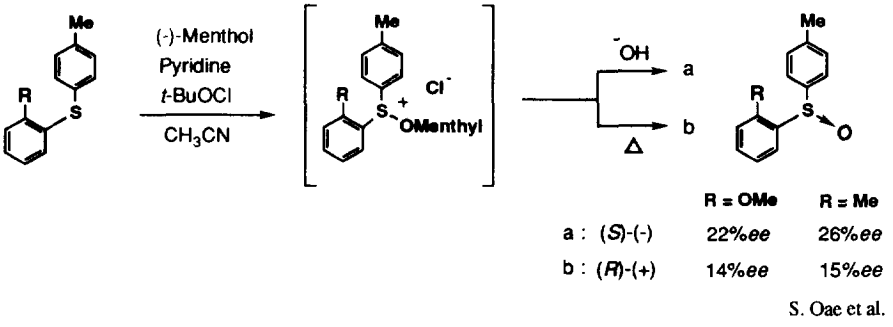


BOF-4272

1

In 1976, a convenient method for asymmetric oxidation of diaryl sulfides using (-)-menthol, pyridine and *t*-butylhypochlorite was reported by Oae's group[6] (Scheme 1).

Scheme 1



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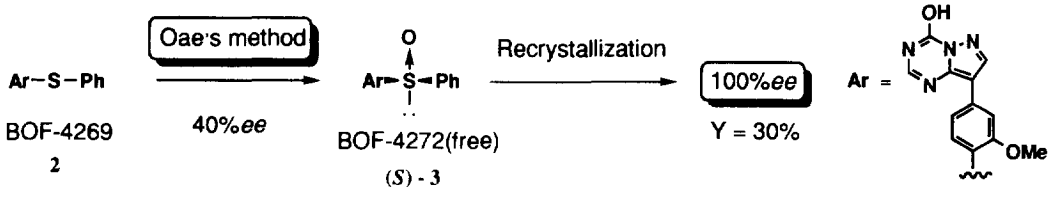
An interesting observation is that the opposite enantiomers can be produced depending on the work-up treatment on the intermediate sulfonium salt. This suggests a possibility for asymmetric production of a sulfoxide in its desired configuration.

Results and discussion

Synthesis of (*S*)-(-)-BOF-4272(free) : Modification of Oae's method

We studied the synthetic conditions required to achieve a high enantiomeric excess, since the oxidation of BOF-4269 (**2**)[7] under Oae's original condition resulted in only 40%*ee*. Subsequent recrystallization gave pure (*S*)-(-)-isomer (**3**) with an overall yield of 30% (Scheme 2).

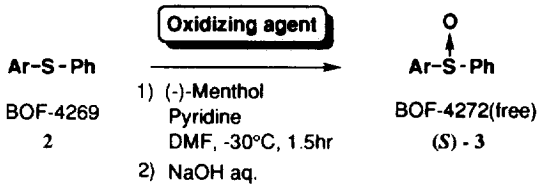
Scheme 2

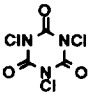
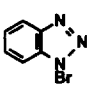
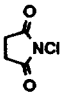
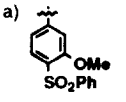
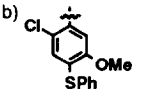


Firstly a variety of halo-cation reagents were examined, as shown in Table 1. The variation of the oxidants exerted little influence on the enantioselectivity and chemical yield. Therefore, 1-chlorobenzotriazole[8](CBT) was chosen in view of its safety and convenience in handling compared to *t*-butylhypochlorite originally used (Table 1).

As for the solvents, *N*,*N*-dimethylformamide was found to be the most adequate in terms of the chemical yield, the optical yield, and the purity of the product (**3**) (Table 2).

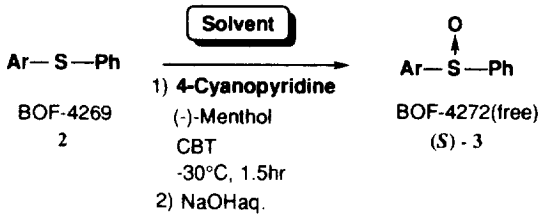
Table 1 : Influence of the Oxidizing Agent



Oxidant	 (CBT)				
ee (%)	43	39	38	——	——
Yield (%)	87	83	87	a) 	b) 

a) In stead of sulfoxide, sulfone was obtained as only product.
b) Chlorination on aromatic ring took place mainly.

Table 2 : Solvent Effect in the Oxidation

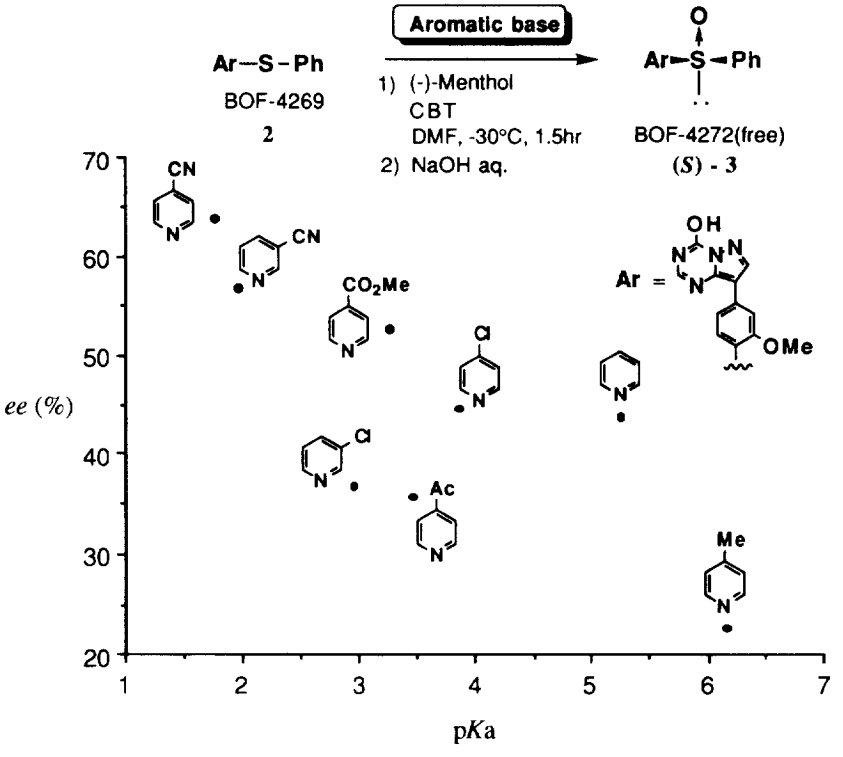


Solvent	DMF	CH_2Cl_2*	MeCN*	Diglyme*	THF*	Toluene*	Acetone*	AcOEt*
Time (hr)	1.5	1.5	20.5	1.5	1.5	24	22	3
ee (%)	63	60	44	7.5	0	——	——	——
Yield (%)	93	84	87	93	95	28	26	N.R.

*) Substrate was almost insoluble.

Oae's oxidation recipe involves pyridine. We found an intricate dependence of the enantiomerical excess on the p*K*a value of pyridine bases. The enantiomeric excess appears to increase with decrease in basicity of pyridines (Figure 1). And in case of 4-cyanopyridine, we could obtain the best result of 63%*ee*. The trend, however, is limited to a certain range of 3- and 4-substituted pyridine derivatives. For example, tetrafluoropyridine a base weaker than 4-cyanopyridine, gave only about 50%*ee*. Also, we could not rationalize the deviation observed for 3-chloro- and 4-acetylpyridine. How does the pyridine base participate in the oxidation reaction remains to be elucidated.

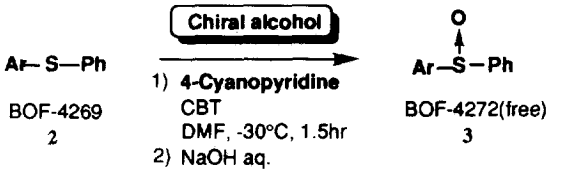
Figure 1 : Influence of the base

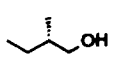
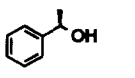
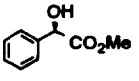
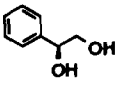
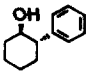
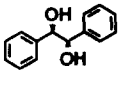
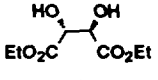
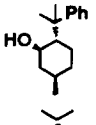
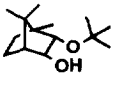
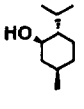
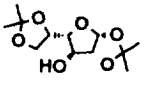


In the absence of the base, the enantioselectivity was 50%*ee*.

We also studied the variation of chiral alcohols. Chiral 2-substituted cyclohexanol was quite effective. Thus the enantiomeric excess of 73% was obtained when (1*R*,2*S*)-(-)-2-phenylcyclohexanol was used (Table 3), a quite high value for the asymmetric oxidation of a diaryl sulfide. On the other hand, we found poor enantioselectivity in the case of diols, acyclic secondary or primary alcohols.

Table 3 : Effect of Chiral Alcohols



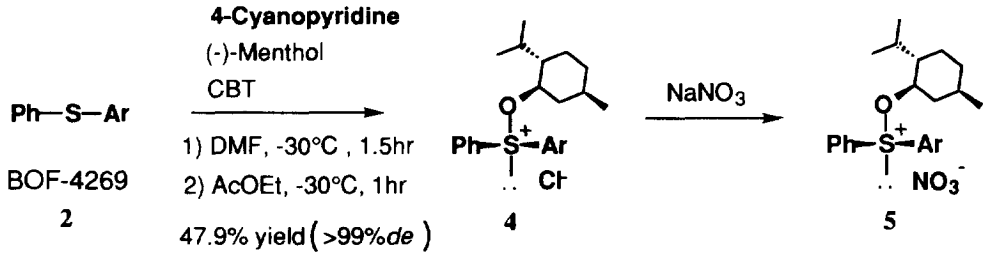
Chiral alcohol	*ee* (%)	Yield (%)	Configuration of (3)	Chiral alcohol	*ee* (%)	Yield (%)	Configuration of (3)
	0	95	—		20	50*	*R*
	11	87	*S*		22	80	*R*
	20	39	*S*		43	54*	*S*
	5	96	*S*		73	78*	*S*
	20	68	*S*		18	78	*S*
	11	39*	*S*		15	89	*S*
	12	63*	*S*		48	38*	*S*
	63	93	*S*		6	27*	*S*

*) Chlorination on Ar ring took place as a side reaction.

Synthesis of (*S*)-(-)-BOF-4272 : Utility of menthoxy sulfonium salts

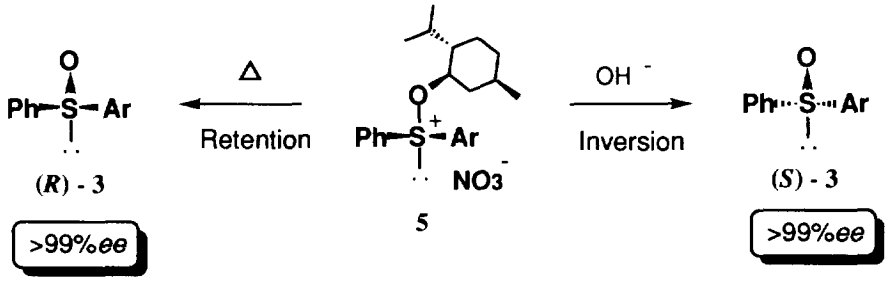
We were able to isolate the intermediate menthoxy sulfonium salt (**4**) (>99%*de*) by choosing an appropriate solvent system (Scheme 3)[9]. Thus the reaction sequence involving a sulfonium salt postulated by Oae et al.[6] was verified. We found that the transformation of the sulfonium chloride into a more moisture-stable nitrate can be effected by replacing the counter anion with sodium nitrate (Scheme 3).

Scheme 3



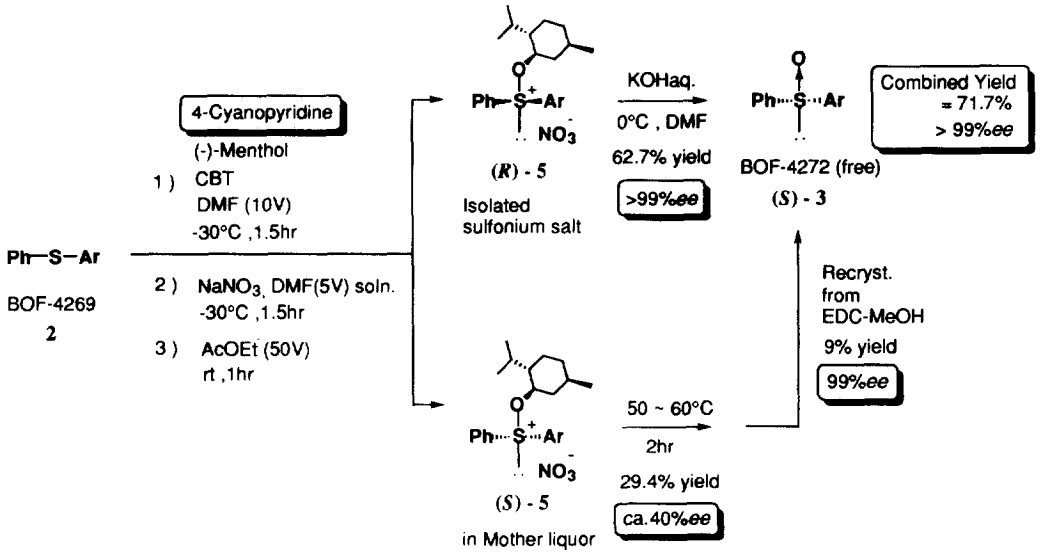
The most amazingly property of the salt is the ability which allows stereospecific transformation into the enantiomerically pure sulfoxides. Thus the (*S*)-(-)-isomer of (**3**) was isolated in >99%*ee* by alkaline hydrolysis whereas (*R*)-(+)-isomer of (**3**) was obtained with >99%*ee* by thermolysis (Scheme 4). Further, the absolute configuration of the sulfonium salt obtained could be determined by its stereospecific transformation into enantiomerically pure sulfoxides. The alkaline hydrolysis of chiral sulfonium salt is known to proceed through SN2 type reaction[6]. Accordingly we recovered (-)-menthol. In contrast, in the thermal reaction we observed the formation of menthene. Since the absolute configuration (-)-BOF-4272 has been established to be *S*[2], the stereochemistries of these transformations can be depicted in Scheme 4.

Scheme 4



Based on the observation described above we established an effective synthetic method for (*S*)-(-)-BOF-4272(free form) (**3**). Namely two stereospecific transformations separately effected on each diastereomeric component of the sulfonium intermediates, yield one enantiomerically pure sulfoxide. Following the modified Oae's oxidation (see the Experimental part), we are able to obtain BOF-4272(free form) (**3**) in its desired configuration in 71.7% overall yield[10] (Scheme 5).

Scheme 5 Divergent Asymmetric Synthesis of (-)-BOF-4272



All Chemical yields are based on BOF-4269.

Free acid of (*S*)-BOF-4272 (**3**) was easily converted to sodium salt (*S*)-BOF-4272 (**1**) by treatment with sodium hydroxide.

Conclusion

We found a combination of 4-cyanopyridine, chiral 2-phenylcyclohexanol, and 1-chlorobenzotriazole to be a good recipe for the asymmetric oxidation of a diarylsulfide BOF-4269. Further an effective synthesis of (*S*)-(-)-BOF-4272 (**1**) was achieved by the new methodology, "conversion of both of diastereomeric intermediates into one enantiomerically pure product, a sulfoxide enantiomer".

Experimental

Melting points were determined on a Yamato Melting Point Apparatus MP-21 and uncorrected. ^{1}H NMR spectra were recorded on a Varian XL-200 (200MHz) and JEOL JNM-A500 (500MHz), using either $CDCl_3$ or DMSO-d_6 as the solvent with TMS as internal standard. Mass spectra were obtained on a Shimadzu GCMS QP1000 or JEOL JMS SX-102A spectrometer. The *de* values were calculated from ^{1}H NMR spectra and the *ee* values by HPLC on a CHIRALCEL®OD (DAICEL) column (eluent : EtOH / hexane / HCO_2H = 350 / 650 / 1). Optical rotations were measured on a JASCO DIP-360 polarimeter. BOF-4269 was prepared essentially following the published method[7b].

(*S*)-(-)-8-[3-methoxy-4-(phenylsulfinyl)phenyl]pyrazolo[1,5-*a*]-1,3,5-triazin-4(1*H*)-one (3) : General procedure for the modified Oae's method. To a solution of 19.35g of BOF-4269 (**2**) (55.3 mmol), 19.33g of (-)-menthol (124 mmol) and 5.75 g of 4-cyanopyridine (55.3 mmol) in 200 ml of DMF was added a solution of 9.33 g of 1-chlorobenzotriazole (60.8 mmol) in 110ml of acetonitril at -30°C under stirring. Stirring was continued for 1.5h at -30°C. An aqueous 5 *N* solution (130 ml) of NaOH was then added to the mixture. After the temperature of the mixture was allowed to reach to room temperature, 100 ml of deionized water was added and the resulting solution was washed with 200 ml of toluene. Neutralization of the aqueous layer with an aqueous citric acid solution gave 20.30g of a crude product (**3**) (93%, 63%*ee*) which was recrystallized from MeOH-1,2-dichloroethane to give 8.95g of (*S*)-(**3**) (44.2%, >99%*ee*). ^{1}H NMR (DMSO-d_6, 200MHz) δ 3.88 (s, 3H), 7.49-7.55 (m, 3H), 7.66-7.93 (m, 4H), 7.91 (dd, *J* = 8.2Hz, 1.4Hz, 1H), 8.14 (s, 1H), 8.64 (s, 1H), 12.84 (bs, 1H); $[\alpha]_D^{20}$ = -174 (*c* 0.5, DMF). mp = 265-268°C (dec.); Anal. Calcd for $C_{18}H_{14}N_4O_3S$: C, 59.00; H, 3.85; N, 15.29; found : C, 58.74; H, 3.55; N, 14.99

[1*R*-(1α,2β,5α)]-[[5-methyl-2-(1-methylethyl)cyclohexyl]oxy][2-methoxy-4-(1*H*-4-oxopyrazolo[1,5,*a*]-1,3,5-triazin-7-yl)phenyl] phenyl sulfonium chloride (4). To a solution of 313 mg of BOF-4269 (**2**) (0.90 mmol), 341 mg of (-)-menthol (2.18 mmol) and 97 mg of 4-cyanopyridine (0.93 mmol) in 3.2 ml of DMF (dried with activated 4Å molecular sieves) was added 159 mg of 1-chlorobenzotriazole (1.04 mmol) at -30°C under stirring. The reaction mixture was stirred for 1h at -30°C. Ethyl acetate (22 ml) was then added to the reaction mixture and the mixture was further stirred for 1h at -30°C. Collecting the crystalline precipitates afforded 232 mg of (**4**) (48%, >99%*de*). ^{1}H NMR (DMSO-d_6, 200MHz) δ 0.54 (d, *J* = 6.8Hz, 3H), 0.81 (d, *J* = 7.2Hz, 3H), 0.95 (d, *J* = 6.2Hz, 3H), 0.90-1.95 (m, 7H), 2.20 (m, 1H), 4.03 (s, 3H), 4.39 (m, 1H), 7.60-8.21 (m, 8H), 8.26 (s, 1H), 8.88 (s, 1H), 13.30 (bs, 1H); HRMS calcd for $C_{28}H_{32}O_3N_4SCl$ (M-H)$^-$ 539.1883, found 539.1891

[1*R*-(1α,2β,5α)]-[[5-methyl-2-(1-methylethyl)cyclohexyl]oxy][2-methoxy-4-(1*H*-4-oxopyrazolo[1,5,*a*]-1,3,5-triazin-7-yl)phenyl] phenyl sulfonium nitrate (5). To a solution of 5.02 g of BOF-4269 (**2**) (14.3 mmol), 5.79 g of (-)-menthol (37.1 mmol) and 1.49 g of 4-cyanopyridine (14.3 mmol) in 50 ml of DMF (dried with activated 4Å molecular sieves) was added 2.20 g of 1-chlorobenzotriazole (14.3 mmol) at -30°C under stirring. After stirring for 1.5h at -30°C, sodium nitrate (1.58 g, 18.5 mmol) in 15 ml of DMF was added. The mixture was stirred for 1.5h at -30°C. Ethyl acetate (250 ml) was then added and the mixture was further stirred for 1.5h at -30°C. Then stirring being continued, the temperature was allowed to reach to the room temperature during 1h. Collecting the crystalline precipitates afforded the mixture (6.35 g) of (**5**) (>99%*de*) and sodium chloride as a by-product. This was employed in the next step without further purification. ^{1}H NMR ($CDCl_3$, 500MHz) δ 0.63 (d, *J* = 6.8Hz, 3H), 0.85 (d, *J* = 6.8Hz, 3H), 0.89-1.95 (m, 8H), 2.65 (m, 1H), 4.07 (s, 3H), 4.55 (m, 1H), 7.32 (d, *J* = 9.4Hz, 1H), 7.46 (dd, *J* = 9.4, 0.2Hz, 1H), 7.75-7.95 (m, 3H), 7.81 (s, 1H), 8.05-8.20 (m, 2H), 8.09 (s,1H), 13.22 (bs, 1H); HRMS calcd for $C_{28}H_{32}O_6N_5S$ (M-H)$^-$ 566.2073, found 566.2064

(*S*)-8-[3-methoxy-4-(phenylsulfinyl)phenyl]pyrazolo[1,5-*a*]-1,3,5-triazin-4(1*H*)-one (3) : Hydrolysis of l-menthoxy sulfonium nitrate compound. To a solution of a mixture (349 mg) of sulfonium nitrate (**5**) and sodium chloride in 1.6 ml of DMF was added an excess of 2.5 *N* aqueous NaOH at 0°C under stirring and stirring was continued for 1h at 0°C. Deionized water (10ml) being added to the solution, the mixture was washed with 5 ml of toluene. Neutralization of the aqueous layer with an aqueous citric acid solution gave 170 mg of (*S*)-(**3**) (>99%*ee*) as crystalline precipitates.

(*R*)-8-[3-methoxy-4-(phenylsulfinyl)phenyl]pyrazolo[1,5-*a*]-1,3,5-triazin-4(1*H*)-one (3) : Thermolysis of l-menthoxy sulfonium nitrate compound. A solution of a mixture(156 mg) of sulfonium nitrate (**5**) and sodium chloride in 20 ml of DMF was stirred for 6h at 60°C. Deionized water (30 ml) being added to the solution, the solution was washed with 5 ml of toluene. Neutralization of the aqueous layer with an aqueous citric acid solution afforded 78.3 mg of (*R*)-(**3**) (>99%*ee*) as crystalline precipitates. ^{1}H NMR (DMSO-d_6, 200MHz) δ 3.88 (s, 3H), 7.49-7.55 (m, 3H), 7.66-7.93 (m, 4H), 7.90 (dd, *J* = 9.2Hz, 1.4Hz, 1H), 8.13 (s, 1H), 8.63 (s, 1H); $[\alpha]_D^{20}$ = +174 (*c* 0.5, DMF); mp = 265-268°C (dec.)

(*S*)-8-[3-methoxy-4-(phenylsulfinyl)phenyl]pyrazolo[1,5-*a*]-1,3,5-triazin-4(1*H*)-one (3) : Divergent asymmetric synthesis. To a solution of 5.02 g of BOF-4269 (**2**) (14.3 mmol), 5.79 g of (-)-menthol (37.1 mmol) and 1.49 g of 4-cyanopyridine (14.3 mmol) in 50 ml of DMF was added 2.20 g of 1-chlorobenzotriazole (14.3 mmol) at -30°C under stirring. Stirring was continued for 1.5h at -30°C. Sodium nitrate (1.58 g, 18.5 mmol) in 15 ml of DMF being added, the mixture was stirred for 1.5h at -30°C. Ethyl acetate (250 ml) was then added to the reaction mixture. And the mixture was stirred for 1.5h at -30°C. Temperature of mixture was allowed to reach to the room temperature and stirred for 1h at ambient temperature to precipitate only (*R*)-sulfonium nitrate (**5**). The separated (*R*)-salt (>99%*de*) was effectively converted to (*S*)-(**3**) (>99%*ee*) in a 62.7% yield by treating the crystalline sulfonium precipitates with an excess of 2.5 *N* aqueous NaOH in DMF at 0°C. After the mixture was allowed to stand at room temperature, 100 ml of deionized water was added. After the solution was washed with 20 ml of toluene, neutralization of the aqueous layer with an aqueous citric acid solution gave 3.28 g of (*S*)-(**3**) (62.7%, >99%*ee*). On the other hand, (*S*)-salt (about 40%*de*) stayed in the mother liquor also gave the (*S*)-(**3**) (99%*ee*) in a 9% yield by thermolysis followed by recrystallization. Namely, after the mother liquor was stirred for 2h at 60°C, the reaction mixture was extracted with 2.5*N* NaOH. Neutralization of the aqueous layer with an aqueous citric acid solution gave 1.54 g of a crude (*S*)-(**3**) (29.4%, 38%*ee*). The product was recrystallized from MeOH-1,2-dichloroethane to give 0.645 g of (*S*)-(**3**) (8.5%, >99%*ee*). The combined yield was 71.7%.

(*S*)-(-)-Sodium-8-[3-methoxy-4-(phenylsulfinyl)phenyl]pyrazolo[1,5-*a*]-1,3,5-triazin-4-olate monohydrate : (*S*)-(-)-BOF-4272 (1). To a solution of 145 mg of sodium hydroxide in 100 ml of deionized water was added 1.3 g of (**3**) in 50 ml of ethanol at room temperature and the mixture was stirred at room temperature until it became clear solution. After the solvent was evaporated, ethyl acetate (100 ml) was added to the residue and heated under reflux for 30min. After the mixture was cooled to room temperature, precipitated crystalline was collected to give 1.20 g of (**1**) (83.3%, >99%*ee*). ^{1}H NMR (DMSO-d_6, 200MHz) δ 3.86 (s, 3H), 7.49-7.75 (m, 7H), 7.84 (dd, *J* = 9.2Hz, 1.4Hz, 1H), 7.89 (s, 1H), 8.30 (s, 1H); $[\alpha]_D^{20}$ = -245 (*c* 0.5, DMF); mp = 228-235°C (dec.); Anal. Calcd for $C_{18}H_{13}N_4NaO_3S.H_2O$: C, 53.20; H, 3.72; N, 13.79; found : C, 53.02; H, 3.54; N, 13.77

References and Notes

1. a) Uematsu, T.; Nakashima, M. *J. Pharmacol. Exp. Ther.*, **1994**, *270 (2)*, 453; b) Yamamoto, T.; Mori waki, Y.; Suda, M.; Nasako, Y.; Takahashi, S.; Hiroishi, K.; Nakano, T.; Hada, T.; Higashino, K. *Biochem. Pharmacol.* **1993**, *46(12)*, 2277; c) Iwahara, R.; Emoto, S.; Kaga, J.; Imura, Y.; Aoki, M.; Asakawa, K. *Iyakuhin Kenkyu* **1994**, *25(6)*, 42; d) Nishimura, M.; Yamaoka, K.; Yasui, H.; Naito, S.; Nakagawa, T. *Biol. Pharm. Bull.* **1995**, *18(7)*, 980.
2. The absolute configuration of BOF-4272 was determined by a single crystal X ray analysis using an *N*-alkyl derivative bearing a chiral auxiliary (*S*)-(+)-1-bromo-2-methylbutane.
3. a) Okamoto, K. *Yokohama Igaku*, **1994**, *45 (1)*, 47; b) Okamoto, K. Nishino, T. *J. Biol. Chem.* **1995**,

270(14), 7816.

4. a) Walker, A. J. *Tetrahedron: Asymmetry* **1992**, *3*, 961; b) Komatsu, N.; Uemura, S. *J. Org. Synth. Chem. Jpn.*, **1995**, *53*, 268; c) Kagan, H. B. "Catalytic Asymmetric Synthesis", ed. by Ojima, I. VCH, New York, **1993**, p203; d) Pitchen, P.; Dunach, E.; Deeshmukh, M. N.; Kagan, H. B. *J. Am. Chem. Soc.*, **1984**, *106*, 8818; e) Davis, F. A.; Chattopadhyay, S.; Harakal, M. E.; Towson, J. C.; Watoson, W. H.; Tavanaiepour, I. *J. Am. Chem. Soc.*, **1987**, *109*, 3370; f) Palucki, M.; Hanson, P.; Jacobsen, E. N. *Tetrahedron Lett.*, **1992**, *33*, 7111; g) Komatsu, N.; Hashizume, M.; Sugita, T.; Uemura, S. *J. Org. Chem.*, **1993**, *58*, 4529; h) Noda, K.; Hosoya, N.; Yanai, K.; Irie, R.; Katsuki, T. *Tetrahedron Lett.*, **1994**, *35*, 1887.
5. a) Andersen, K. K.; Gaffield, W.; Papanikolaov, N. E.; Perkins, R. I. *J. Am. Chem. Soc.*, **1964**, *86*, 5637; b) Rebiere, F.; Kagan, H. B. *J. Org. Chem.*, **1991**, *56*, 5991; c) Evans, D. A.; Faul, M. M.; Colombo, L.; Bisaha, J. J.; Clandy, J.; Cherry, D. *J. Am. Chem. Soc.*, **1992**, *114*, 5977; d) Fernandes, I.; Khiar, N.; Llera, J. M.; Alcudia, F. *J. Org. Chem.*, **1992**, *57*, 6789; e) Whitesell, J. K.; Wong, M. *J. Org. Chem.*, **1994**, *59*, 597.
6. Moriyama, M.; Yoshimura, T.; Furukawa, N.; Numata, T.; Oae, S. *Tetrahedron*, **1976**, *32*, 3003.
7. a) Fujii, S.; Kawamura, H.; Kiyokawa, H.;Yamada, S. *Eur. Pat. Appl.* EP 269859 (Cl. C07D487104), 08. Jun. 1988, CA **1988**, *109*, 211092p; b) Prous, J.; Graul, A.; Castaner, J. *Drugs of the Future* **1993**, *18(9)*, 791.
8. Johnson, C. R.; Bacon, C. C.; Kingsbury, W. D. *Tetrahedron Lett.*, **1972**, 501.
9. a) Ray III, D. G.; Koser, G. F. *J. Am. Chem. Soc.*, **1990**, *112*, 5672; b) Kimura, T.; Nakayama, H.; Furukawa, N. *Chem. Lett.*, **1994**, 27.
10. The reproducibility of this route is confirming with scale of Kg.

(*Received in Japan* 7 *September* 1995)