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Catalytic and Asymmetric [2,3]Sigmatropic Rearrangement: Co(III)-Salen Catalyzed *S*-Ylide Formation from Allyl Aryl Sulfides and Their Rearrangement

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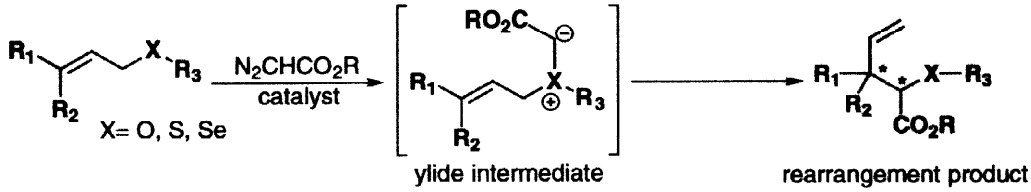
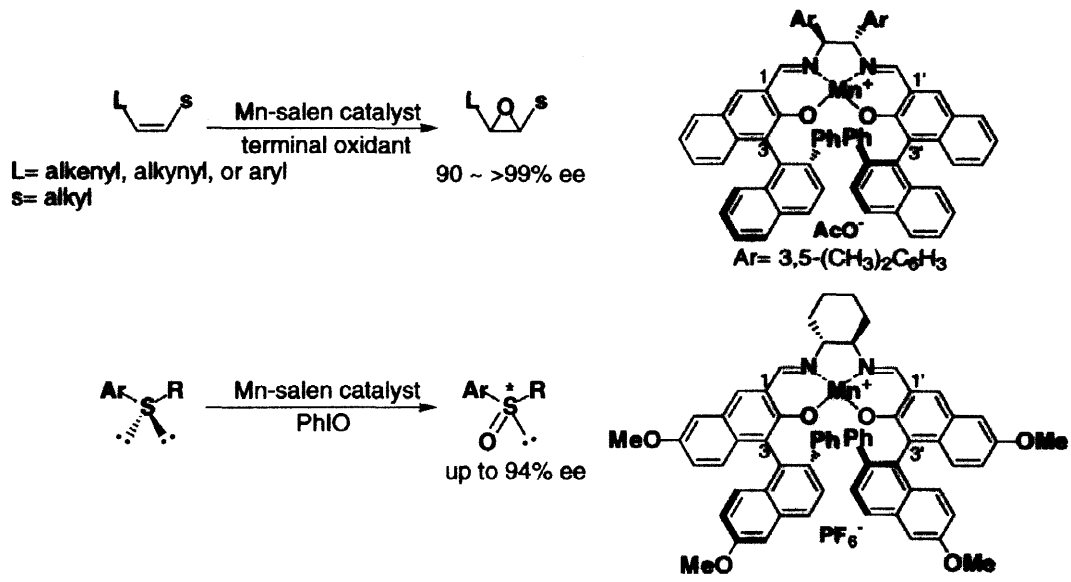
Abstract: Reaction of allyl aryl sulfides and α-diazoacetic acid esters in the presence of optically active Co(III)-salen complex (**8-Br**) provided 3-substituted 2-arylthio-4-pentenoic acid esters stereoselectively by way of enantioselective *S*-ylide formation and subsequent diastereoselective [2,3]sigmatropic rearrangement. For example, the reaction of cinnamyl phenyl sulfide and (-)-menthyl α-diazoacetate provided (-)-menthyl (2*R*,3*S*)-2-phenylthio-3-phenyl-4-pentenoate of 74% de preferentially.

Carbon-carbon bond formation reaction accompanied with generation of two vicinal asymmetric carbons is of high synthetic use as a tool for the construction of carbon skeleton. Naturally, this type of reactions such as aldol condensation, [3,3] and [2,3]sigmatropic rearrangement,[1] and Diels-Alder reactions are now widely used in organic synthesis, and most of these reactions can be carried out in a catalytic and enantioselective manner. However, examples of catalytic and enantioselective [2,3]sigmatropic rearrangement are still rare and their stereoselectivity is not satisfactory. This is probably due to difficulty in generation of carbanion α to heteroatom in a catalytic manner. On the other hand, carbene is known to react with a heteroatom such as oxygen and sulfur atoms and to produce the corresponding ylides.[2] Thus, treatment of a substrate such as allyl ethers or allyl sulfides with carbene or carbenoid species is expected to give the corresponding ylides which can undergo [2,3]sigmatropic rearrangement (Scheme 1). As a matter of course, stereochemistry of this reaction is dependent upon enantioselectivity in the ylide formation and diastereoselectivity in the rearrangement. Several years ago, Doyle *et al.* reported that the reaction of allyl ether and α-diazoacetate in the presence of $Rh_2(OAc)_4$ proceeded with moderate to good diastereoselectivity (79:21-97:3), giving the corresponding [2,3]sigmatropic rearrangement products by way of the intermediary oxonium ylides formed by the reaction of carbenoid and ether oxygen atom (Scheme 1, X= O).[3] This example showed that the second rearrangement step proceeded with moderate to good diastereoselectivity but no asymmetric version of this reaction has been reported. In 1995, Uemura *et al.* first reported the catalytic asymmetric [2,3]sigmatropic rearrangement of allylic chalcogen-ylides that were prepared by treatment of allylic sulfides or selenides with diazoacetate in the presence of Cu(I)-bis(oxazoline)[4] or $Rh_2(5S\text{-MEPY})_4$,[5] respectively, which were efficient catalysts for asymmetric cyclopropanation reaction (Scheme 1, X= S or Se). These reactions, however, proceeded with only moderate enantioselectivity (up to 41% ee).[6]



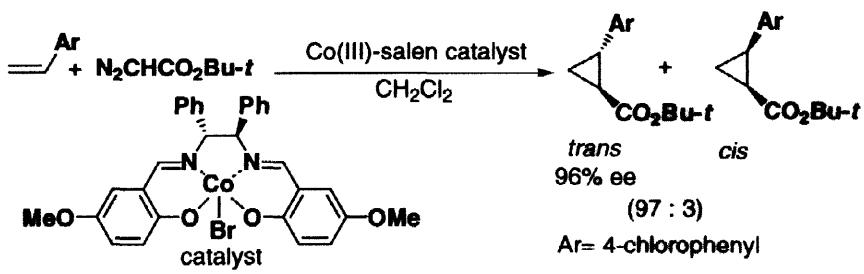
Scheme 1

PII: S0040-4020(98)01065-5



Scheme 2

On the other hand, we have reported that the well-designed (salen)manganese(III) complexes (hereafter referred to as Mn-salen complexes) bearing bulky groups at C3- and C3'-carbons are efficient catalysts for asymmetric epoxidation of conjugated olefins[7] and asymmetric oxidation of alkyl aryl sulfides[8] in the course of our study on metallosalen complexes (Scheme 2). Furthermore, we recently found that a (salen)cobalt(III) complex (hereafter referred to as Co(III)-salen complex) prepared by the treatment of the corresponding Co(II)-salen complex with halogen (bromine or iodine) is an efficient catalyst for asymmetric cyclopropanation of styrene derivatives using α-diazoacetate as a carbenoid source[9] (up to 96% ee) (Scheme 3). This cyclopropanation reaction has been considered to proceed through an intermediary cobalt-carbenoid species, therefore, we expected that the reaction of allylic sulfides and diazoacetate in the presence of a Co(III)-salen would also proceed with high enantioselectivity to give the corresponding *S*-ylide which undergoes [2,3]sigmatropic rearrangement. Along this line, we examined the stereoselective [2,3]sigmatropic rearrangement of the chiral *S*-ylide which was formed *in situ* by the reaction of allyl aryl sulfides and α-diazoacetates in the presence of an optically active Co(III)-salen complex. After we had reported our preliminary communication[10] on this study, Doyle *et al.* reported that the reaction of allyl phenyl ether proceeded with high enantioselectivity when the modified chiral rhodium complex was used as a catalyst.[11]

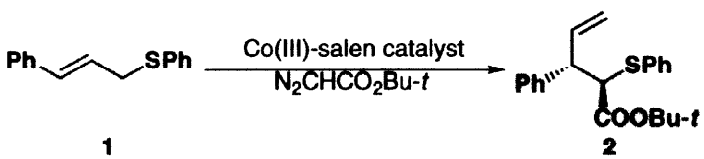


Scheme 3

Asymmetric [2,3]sigmatropic rearrangement of the chiral S-ylides derived from allyl aryl sulfides using Co(III)-salen complexes

In order to explore the above possibility, we first examined the reaction of *trans*-cinnamyl phenyl sulfide **1** and *tert*-butyl α-diazoacetate using various Co(III)-salen complexes as catalysts in dichloromethane (Table 1).

Since we had found that Mn-salen catalyzed asymmetric epoxidation and oxidation of sulfides have common features in many respects,[7,8] we also expected that Co(III)-salen catalyzed asymmetric cyclopropanation[9] and *S*-ylide formation would also show similar features. Co(III)-salen catalysts bearing substituents at C3 and C3' show no catalytic activity for cyclopropanation reaction. In accord with this, Co(III)-salen complexes (**4-I** or **7-I**) bearing bulky *tert*-butyl group at C3 and C3' did not catalyze asymmetric [2,3]sigmatropic rearrangement reaction of **1** *via* the corresponding *S*-ylide (Table 1, entries 2 and 5). In contrast to this, complexes **3-I**, **5-I** and **6-I** which had no C3- and C3'-substituent catalyzed the desired reaction with modest enantioselectivity (42-48% ee) and with similar level of *anti-syn* selectivity (83:17-85:15) (Table 1, entries 1, 3 and 4). The reaction with complex **8-I** bearing electron-donating methoxy group at C5- and C5'-carbons showed a slightly improved enantioselectivity, but complex **9-I** bearing electron-donating acetonide groups showed no improvement in enantioselectivity (entries 6 and 7). Further improvement of enantioselectivity up to 64% ee was observed, when complex **8-Br** was used as a catalyst (entry 8). This was probably attributed to the poorer *trans*-effect of axial bromide ligand as compared with iodide ligand.[9b] However, no improvement in diastereoselectivity was observed (entry 8). These results strongly suggested that *S*-ylide formation was performed in the coordination sphere of a chiral Co-salen catalyst but rearrangement of the *S*-ylide proceeded out of the coordination sphere, that is, the resulting *S*-ylide was not coordinated to the catalyst. Thus, the diastereoselectivity in [2,3]sigmatropic rearrangement was not affected by the catalysts used.

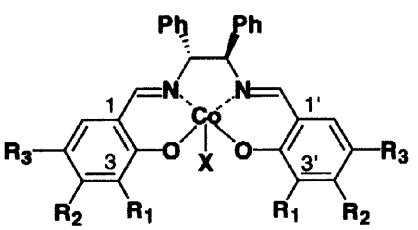


1 2

Table 1. Co(III)-salen catalyzed asymmetric [2,3]sigmatropic rearrangement using *trans*-cinnamyl phenyl sulfide as the substrate

entry	catalyst	yield (%)	*anti* : *syn*[a]	% ee[b,c]
1	**3-I**	31	85:15	48
2	**4-I**	-[d]	-	-
3	**5-I**	53	83:17	42
4	**6-I**	74	83:17	47
5	**7-I**	-[d]	-	-
6	**8-I**	64	82:18	50
7	**9-I**	77	84:16	47
8	**8-Br**	81	85:15[e]	64

a) Determined by ^{1}H NMR analysis (270 MHz).
b) The enantiomeric excess of the *anti*-isomer.
c) Determined by HPLC analysis using DAICEL CHIRALPAK AD (hexane/*i*-PrOH = 100/1).
d) The formation of only a trace amount of the product was detected by TLC analysis.
e) The enantiomeric excess of *syn*-isomer was determined to be 64% by HPLC analysis using DAICEL CHIRALPAK AD (hexane/*i*-PrOH = 100/1).



3-I: R^1= H, R^2=H, R^3= H, X= I
4-I: R^1= *t*-Bu, R^2= H, R^3= H, X= I
5-I: R^1= H, R^2= *t*-Bu, R^3= H, X= I
6-I: R^1= H, R^2= H, R^3= *t*-Bu, X= I
7-I: R^1= *t*-Bu, R^2= H, R^3= *t*-Bu, X= I
8-I or 8-Br: R^1= H, R^2= H, R^3= OMe, X= I or Br
9-I: R^1= H, R^2,R^3= $OC(CH_3)_2O$, X= I

Since solvent was thought to affect the stereochemical course and the yield, the reaction of **1** and *tert*-butyl α-diazoacetate was examined with aid of **8-Br**[12] in various other solvents (Table 2). The reaction in ethanol

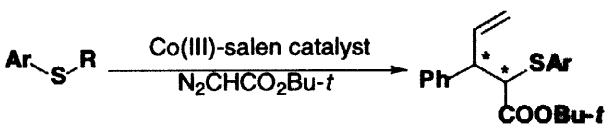
Table 2. Solvent effect in the reaction of **1** and *tert*-butyl α-diazoacetate using **8-Br** as catalyst

entry	solvent	yield (%)	*anti* : *syn*[a]	% ee[b,c]
1	EtOH	quantitative	75:15	56
2	C_6H_6	55	84:16	61
3	$CHCl_3$	81	81:19	60
4	CH_3CN	-[d]	-	-
5	AcOEt	-[d]	-	-

a) Determined by ^1H NMR analysis (270 MHz).
b) The enantiomeric excess of the *anti*-isomer.
c) Determined by HPLC analysis using DAICEL CHIRALPAK AD (hexane/*i*-PrOH = 100/1).
d) The formation of only a trace amount of the product was detected by TLC analysis.

proceeded smoothly to give the desired rearrangement product in quantitative yield but both the *anti-syn* and enantio-selectivity was diminished (entry 1). Non-polar solvents such as benzene and chloroform gave the slightly inferior results to dichloromethane in terms of chemical yield and stereoselectivity (entries 2 and 3). The reaction was sluggish in aprotic polar solvent such as acetonitrile and ethyl acetate (entries 4 and 5). In the event, dichloromethane turned out to be the solvent of choice and thus used for the following experiments.

The reaction of *trans*-cinnamyl 2-methoxyphenyl sulfide **10** and *tert*-butyl α-diazoacetate also showed a good diastereoselectivity and moderate enantioselectivity, when complex **8-Br** was used as a catalyst (Table 3, entry 1). We also examined the reaction using *cis*-cinnamyl phenyl sulfide **12** as a substrate and **8-Br** as a catalyst. The reaction proceeded with good *anti*-selectivity, though enantioselectivity was diminished to some extent (entry 2).[13]



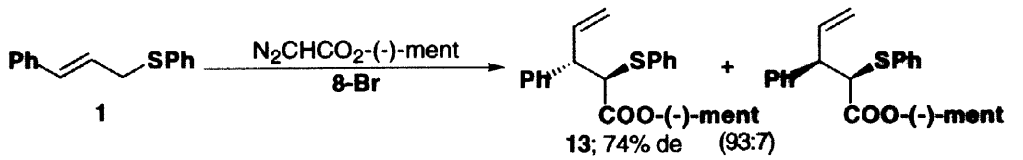
10: R= *trans*-cinnamyl, Ar= 2-methoxyphenyl **11**: Ar= 2-methoxyphenyl
12: R= *cis*-cinnamyl, Ar= phenyl **2**: Ar= phenyl

Table 3. Co-salen catalyzed asymmetric [2,3]sigmatropic rearrangement of other substrates

entry	catalyst	substrate	product	yield (%)	*anti* : *syn*[a]	% ee[b]
1	**8-Br**	**10**	**11**	75	83:17	60[c]
2	**8-Br**	**12**	**2**	87	87:13	51[c,d]

a) Determined by ^1H NMR analysis (270 MHz) unless otherwise noted.
b) The enantiomeric excess of the *anti*-isomer.
c) Determined by HPLC analysis using DAICEL CHIRALPAK AD (hexane/*i*-PrOH = 100/1).
d) Configuration of *anti*-isomer was (2*R*,3*S*).

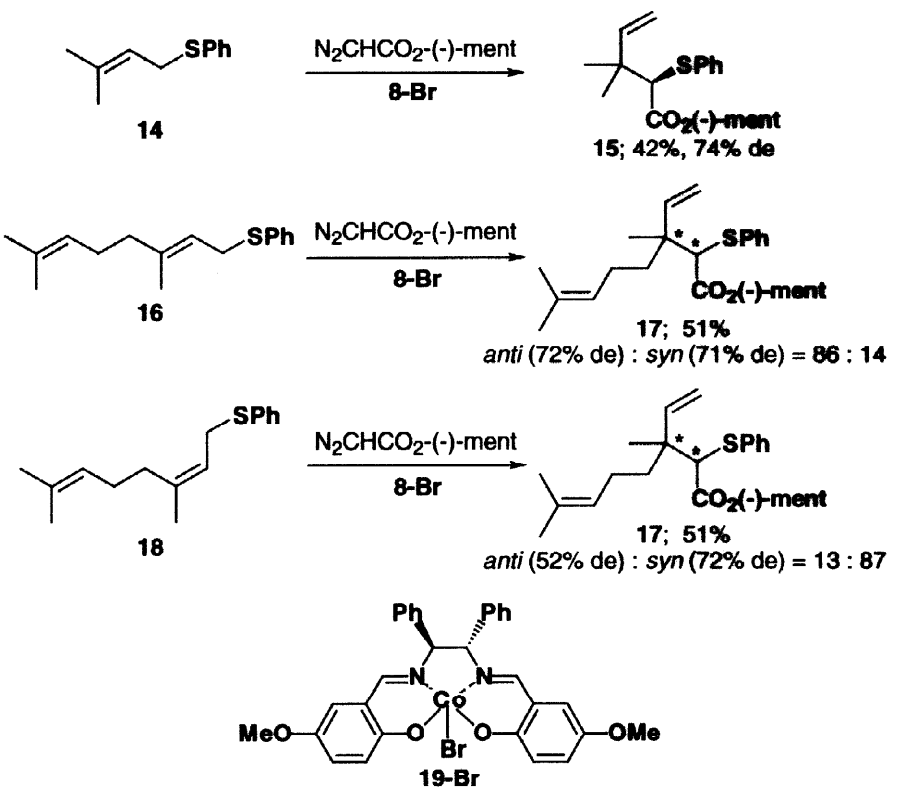
The above conjecture that *S*-ylides were not coordinated to Co-salen catalyst, indicated that the diastereoselectivity of the reaction could not be improved by modification of the catalyst. Therefore, we next examined the reaction using chiral α-diazoacetate with expectation of matched double diastereodifferentiation. Fortunately, both the enantioselectivity in *S*-ylide formation and *anti-syn* ratio of the product were improved to 74% ee and to 93:7, respectively, when (-)-menthyl α-diazoacetate was used. This means that the sense of asymmetric induction by the (-)-menthyl moiety matches that by **8-Br** (Scheme 4).



13; 74% de (93:7)

Scheme 4

To clarify the scope of the reaction, we further examined the reactions of phenyl prenyl sulfide **14**, geranyl phenyl sulfide **16** and neryl phenyl sulfide **18**, under the same reaction conditions (Scheme 5). The reaction of phenyl prenyl sulfide and (-)-menthyl diazoacetate in the presence of catalyst **8-Br** proceeded with good stereoselectivity of 74% de. As expected from the previous conjecture that the sense of asymmetric induction by catalyst **8-Br** matched that by (-)-menthyl moiety (*vide supra*), the same reaction in the presence of **19-Br**, which is the enantiomer of **8-Br**, showed only poor selectivity (8% de).[14] The reaction of geranyl phenyl sulfide **16** proceeded with good enantio- and *anti*-stereoselectivity.[15] The reaction of neryl phenyl sulfide **18** showed opposite *syn*-selectivity reflecting the geometry of the allyl moiety.

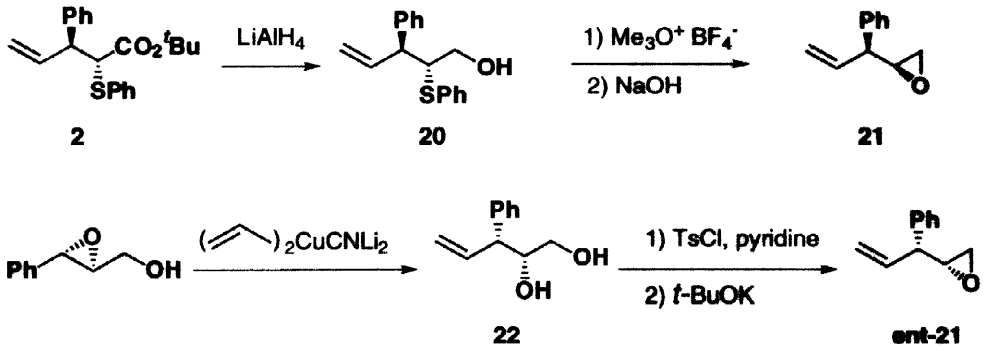


Scheme 5

Determination of the absolute configuration of the major rearrangement products in the reactions of cinnamyl phenyl sulfide and phenyl prenyl sulfide

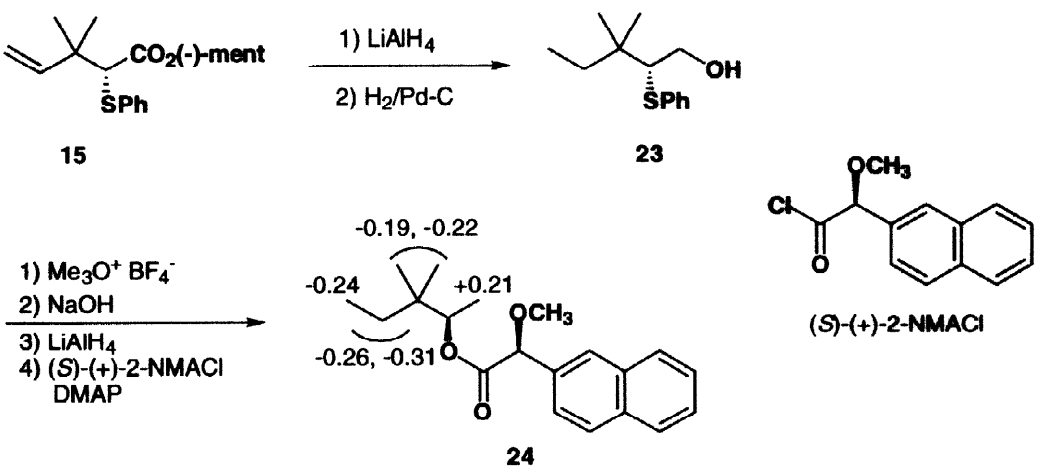
The absolute configuration of the major *anti*-isomer obtained by the reaction of cinnamyl phenyl sulfide was determined to be 2*R*,3*S* by chemical correlation and chiroptical comparison as follows (Scheme 6): *tert*-Butyl 2-phenylthio-3-phenyl-4-pentenoate **2** was converted into alcohol **20** by $LiAlH_4$ reduction. Successive treatment of **20** with trimethyloxonium tetrafluoroborate and with aqueous solution of NaOH gave epoxide **21**[16]. On the other hand, (2*S*,3*S*)-2,3-epoxycinnamyl alcohol that was prepared according to the reported procedure[17] was treated with higher order cuprate reagent $(CH_2CH)_2CuCNLi_2$[18] to give (2*R*,3*R*)-3-phenyl-4-penten-1,2-diol **22**. The diol was converted into **21** by the sequence: i) treatment with *p*-toluenesulfonyl chloride and ii) *tert*-BuOK treatment of the resulting tosylate. The specific rotations of the samples are opposite to each other in sign and the absolute configuration of **2** was determined to be 2*R* ,3*S*.

The absolute configuration of the newly formed stereogenic center of the major isomer in the reaction of phenyl prenyl sulfide was determined to be *R* as follows (Scheme 7): (-)-Menthyl 3,3-dimethyl-2-phenylthio-4-pentenoate **15** was converted into alcohol **23** of 74% ee by $LiAlH_4$ reduction and subsequent hydrogenation. Compound **23** was converted into diastereomeric 2NMA esters **24** by the sequence: i) treatment with



Scheme 6

trimethyloxonium tetrafluoroborate, ii) NaOH treatment of the resulting sulfonium salt, iii) $LiAlH_4$ reduction of epoxide, and iv) esterification with (*S*)-(+)-methoxy(2-naphthyl)acetyl chloride (2NMA chloride). The distribution pattern of the signs of the $\Delta\delta$ values (δ_{minor}-δ_{major}, where the subscripts refer to the minor and major diastereomers, respectively) in **24** unambiguously proved the absolute configuration of C2-carbon to be *R* according to Kusumi's method[19] and, therefore, the configuration of the C2 carbon in **15** to be *R*.

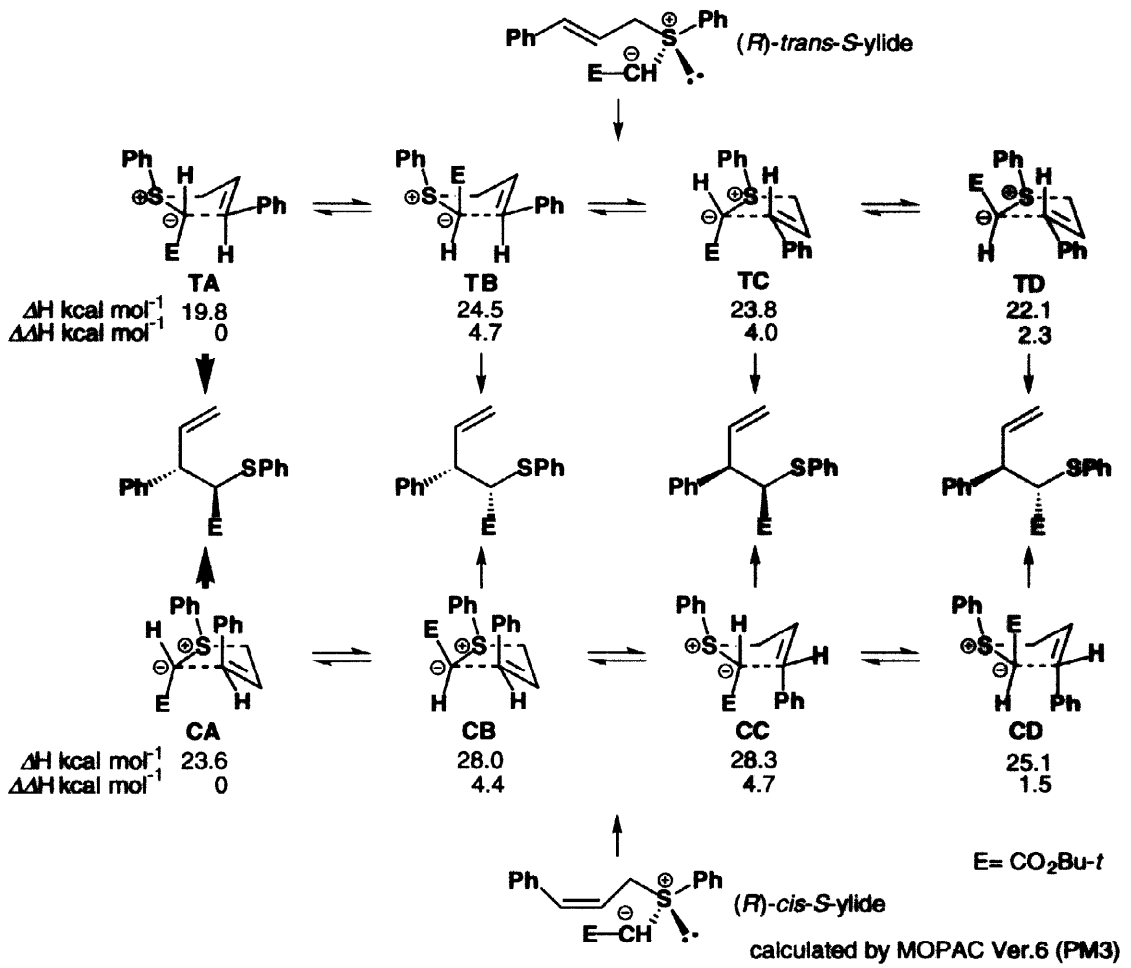


Scheme 7

Consideration on the stereochemistry of [2,3]sigmatropic rearrangement of S-ylide

To understand the stereochemical course of the [2,3]sigmatropic rearrangement of *S*-ylide, heat of formation (ΔH) of the diastereomeric transition structures of the reaction of the *S*-ylide derived from *trans*- and *cis*-cinnamyl phenyl sulfides was evaluated by semi-empirical calculation (Scheme 8).[20,21] Calculation suggests that the reaction starting from (*R*)-*trans*-*S*-ylide proceeds through transition state TA to give (2*R*,3*S*)-*anti*-product preferentially, in accord with the results obtained. On the other hand, in the reaction of *cis*-cinnamyl phenyl sulfide, transition states CB and CC suffer from unfavorable gauche interaction between phenyl group on the allyl moiety and ester group. Transition state CD also suffers from eclipsed interaction between phenyl group on the S atom and ester group. Thus, the reaction starting from (*R*)-*cis*-*S*-ylide proceeds through transition state CA, showing *anti*-selectivity. This is in accord with the experimental result (Table 3, entry 2). These calculations support our proposal that both the reactions of *trans*- and *cis*-cinnamyl phenyl sulfides and α-diazo ester in the presence of complex **8-Br** give the (*R*)-*S*-ylides preferentially (*vide infra*).

In the reactions of 3,3-dialkylsubstituted allyl sulfides such as **14** and (-)-menthyl α-diazoacetate, there are four transition states of low energy for the rearrangement step. The lowest transition state (DA1) and the next

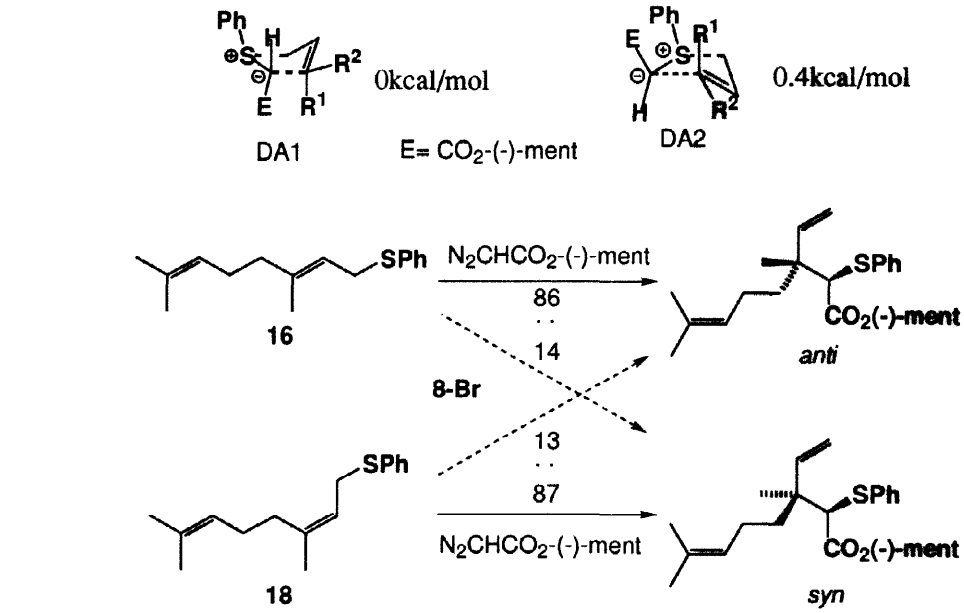


Scheme 8

lowest DA2 are described in Scheme 9 (the relative heat of formations of each transition state shown in the scheme are calculated for the reaction of **14**, R^1=R^2=Me). Two transition states shows the same diastereoselectivity (*anti-syn* selectivity) when $R^1 \neq R^2$. Therefore, the geometry of the double bond in the substrates such as **16** and **18** should be reflected into the relative configuration of the product. In accord with this discussion, geranyl (**16**) and neryl (**18**) sulfides gave *anti*- and *syn*-isomers as major products, respectively.

We have recently reported that the stereochemistry of the Co(III)-salen catalyzed cyclopropanation can be readily explained by assuming that the salen ligand of the intermediary Co(V)-salen carbenoid species has a non-planar structure as drawn by using TRIPOS-SYBYL on an IRIS Indigo 2 (Fig. 1) and that olefins approach Co(V)-salen species from the sterically less congested front side, orientating their bulky substituent away from the bulky *tert*-butoxycarbonyl group.[9] The fact that Co(III)-salen complexes bearing substituents at C3 and C3' did not show any catalytic activity for asymmetric cyclopropanation supported this assumption. In the present reaction, Co(III)-complexes bearing *tert*-butyl group at C3 and C3' also showed no or very poor catalytic activity (Table 1, entries 2 and 5). This also strongly supports that sulfides approach Co(V)-salen carbenoid species from its front side, directing its phenyl group away from the carbenoid ester group. Thus, the reaction of *trans*- and *cis*-cinnamyl phenyl sulfides in the presence of complex **8-Br** is expected to give the corresponding (*R*)-*S*-ylides in preference, which undergo the rearrangement via transition states TA and CA, respectively, to give the products of (2*R*,3*S*)-configuration (Scheme 8).

In conclusion, we could demonstrate that Co(III)-salen complex **8-Br** was an efficient catalyst for enantioselective *S*-ylide formation from allyl aryl sulfides as well as for asymmetric cyclopropanation of styrene



Scheme 9

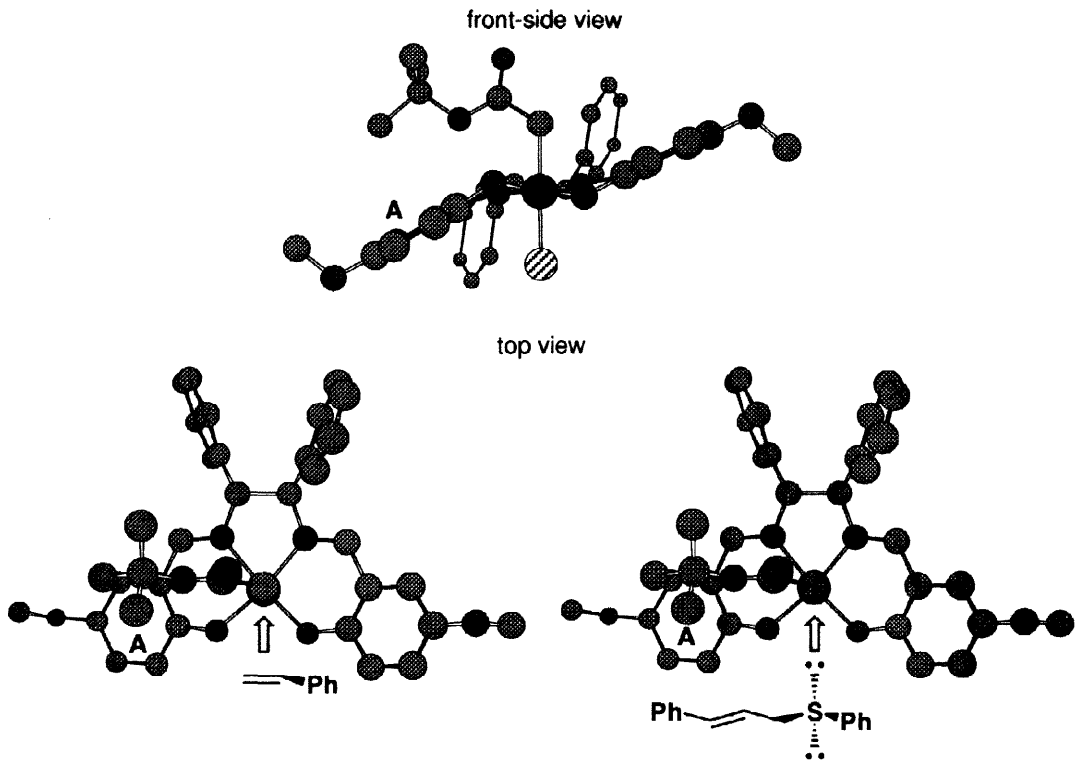


Fig. 1 The frontside and top views of carbene Co(V)-salen complex derived from the corresponding Co(III)-complex (**8-Br**)

derivatives and that the stereochemistry of the ylide formation reaction could be explained in a similar manner to that of cyclopropanation reaction, while the stereochemistry of the subsequent rearrangement is irrelevant to the Co-salen catalyst used. We also revealed that complex **8-Br** and (-)-menthyl α-diazoacetate showed the same sense of asymmetric induction in ylide formation and, therefore, a combining use of **8-Br** and (-)-menthyl α-diazoacetate realized good enantioselectivity of 74% de.

Experimental

NMR spectra were recorded at 270 MHz on a JEOL EX-270 instrument or at 400 MHz on a JEOL GX-400 instrument. All signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ-value in $CDCl_3$). IR spectra were obtained with a SHIMADZU FTIR-8600 instrument. Optical rotation was measured with a JASCO DIP-360 automatic digital polarimeter. High resolution mass spectra were recorded on a JEOL JMS-SX/SX 102A instrument. Column chromatography was conducted on Silica Gel BW-820MH, 70-200 mesh ASTM, available from FUJI SILYSIA CHEMICAL LTD. Preparative thin layer chromatography was performed on 0.5 mm x 20 cm x 20 cm E. Merck silica gel plate (60 F-254). Solvents were dried and distilled shortly before use. *trans*-Cinnamyl phenyl sulfide **1** was prepared according to the literature procedure.[22] All the Co(III)-salen complexes used in the present reaction were prepared according to the previously reported method.[9b] Co(II) complex **8** was also subjected to aerobic oxidation in the presence of HBr to give the analytical sample of **8-Br**. Reactions were carried out under an atmosphere of nitrogen if necessary. HPLC analysis of enantiomeric excess was carried out using Hitachi L-4000 equipped with an appropriate optically active column, as described in the footnotes of Table 1 and Table 3.

Co(III)-Salen 8-Br

To a suspension of Co(II)-salen complex (**8**, 100 mg, 0.19 mmol) in EtOH (4 ml) was added ethanolic HBr (2 ml, *ca.* 0.1 mol dm^{-3}). After 7 h of vigorous stirring under O_2, the resulting precipitate was collected by suction filtration, washed with a limited amount of EtOH, and dried *in vacuo*. **8-Br**; yield 103.3 mg (87%); IR (KBr): 3447, 3055, 3030, 3001, 2999, 2901, 2831, 1628, 1612, 1564, 1533, 1493, 1466, 1425, 1358, 1313, 1271, 1256, 1219, 1200, 1161, 1040, 1009, 951, 856, 822, 762, 704 cm^{-1}. Calcd. for $C_{30}H_{26}N_2O_4CoBr \cdot 0.5H_2O$: C, 57.52; H, 4.34; N, 4.47%. Found: C, 57.30; H, 4.31; N, 4.41%.

trans-Cinnamyl 2-methoxyphenyl sulfide 10

trans-Cinnamyl 2-methoxyphenyl sulfide **10** was synthesized from *trans*-cinnamyl alcohol and 2-methoxybenzenethiol in the same procedure[22] as described for the synthesis of *trans*-cinnamyl phenyl sulfide except for purification. Crude **10** was purified successively by column chromatography (SiO_2, hexane-AcOEt= 9:1) and recrystallization (hexane-CH_2Cl_2) to give pure **10** as colorless crystals in 75% yield. **10**; IR (KBr): 2997, 2937, 2837, 1574, 1475, 1450, 1435, 1304, 1277, 1240, 1182, 1132, 1072, 1042, 1020, 989, 972, 914, 845, 789, 750, 714, 683 cm^{-1}. ^1H NMR (270 MHz): δ 7.36-7.17 (m, 7H), 6.93-6.84 (m, 2H), 6.43 (br d, *J*= 15.7 Hz, 1H), 6.25 (dt, *J*= 7.0 and 15.7 Hz, 1H), 3.89 (s, 3H), 3.71 (dd, *J*= 1.0 and 7.0 Hz, 2H). HREIMS m/z. Calcd. for $C_{16}H_{16}OS$ (M^+): 256.0922. Found: 256.0922. Calcd. for $C_{16}H_{16}OS$: C, 74.96; H, 6.29%. Found: C, 74.66; H, 6.45%.

cis-Cinnamyl phenyl sulfide 12

To a solution of ethanol (21.2 ml) and 2 N aqueous NaOH (1.13 ml) was added $NaBH_4$ (883 mg, 23.3 mmol) at room temperature. After being stirred for 10 min, the mixture was filtered through a pad of Celite. A portion (12.0 ml) of the filtrate was added dropwise to a suspension of $Ni(OAc)_2 \cdot 4H_2O$ (2.39 g, 9.60 mmol) in ethanol (226 ml) with vigorous stirring under hydrogen. To this mixture were added ethylenediamine (1.92 ml, 28.7 mmol) and 1-phenyl-1-propyn-3-ol (5.08 g, 38.4 mmol) in ethanol (102 ml). After being stirred for 4 h, the mixture was diluted with water and extracted with AcOEt. The extract was dried over Na_2SO_4 and concentrated. Silica gel chromatography of the residue (hexane-AcOEt= 8:2) gave pure *cis*-cinnamyl alcohol (4.63 g, 90%) as an oil[23]. *cis*-Cinnamyl alcohol; IR (neat): 3331, 3103, 3082, 3057, 3022, 2928, 2866, 1601, 1576, 1495, 1447, 1339, 1317, 1248, 1217, 1182, 1078, 1018, 947, 916, 800, 773, 700 cm^{-1}. ^1H NMR (270 MHz): δ 7.38-7.19 (m, 5H), 6.57 (br d, *J*= 11.7 Hz, 1H), 5.87 (dt, *J*= 6.4 and 11.7 Hz, 1H), 4.43 (dd, *J*= 1.6 and 6.4 Hz, 2H), 1.69 (s, OH). HREIMS m/z. Calcd. for $C_9H_{10}O$ (M^+): 134.0732. Found: 134.0732. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51%. Found: C, 80.50; H, 7.60%.

Butyllithium (21.6 ml, 1.60 mol dm^{-3} in hexane) was added to the solution of the above *cis*-cinnamyl alcohol (4.41 g, 32.9 mmol) in ether (33 ml) over 20 min at -78 °C. The mixture was gradually raised to room

temperature and diluted with *N,N*-dimethylformamide (20 ml).

On the other hand, butyllithium (24.7 ml, 1.60 mol dm^{-3} in hexane) was added to a solution of thiophenol (4.05 ml, 39.4 mmol) in ether (24.7 ml) at -78 °C. The mixture was gradually raised to room temperature and then diluted with *N,N*-dimethylformamide (20 ml).

The above lithium *cis*-cinnamyl alkoxide solution was added to a solution of methanesulfonyl chloride (2.80 ml, 36.2 mmol) in *N,N*-dimethylformamide (20 ml) and ether (21.6 ml) at 0 °C over 1 h and stirred for 30 min. To the mixture, was added the above lithium thiophenoxide solution and the whole mixture was gradually raised to room temperature. After being stirred overnight, the mixture was quenched with 2 N NaOH (100 ml) and extracted with ether. The extract was washed successively with 2 N aqueous NaOH, water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexane-AcOEt= 1:0 to 8:2) to give **12** (4.22 g, 57%) as a colorless oil. **12**; IR (neat): 3076, 3057, 3020, 2924, 1583, 1479, 1439, 1223, 1090, 1072, 1026, 964, 918, 895, 810, 772, 739, 691 cm^{-1}. ^1H NMR (270 MHz): δ 7.36-7.12 (m, 10H), 6.57 (br d, *J*= 11.4 Hz, 1H), 5.79 (dt, *J*= 7.8 and 11.4 Hz, 1H), 3.80 (dd, *J*= 1.3 and 7.8 Hz, 2H). HREIMS m/z. Calcd. for $C_{15}H_{14}S$ (M^+): 226.0816. Found: 226.0816.

Phenyl prenyl sulfide 14

Phenyl prenyl sulfide **14** was synthesized from 3-methyl-2-buten-1-ol and thiophenol in the same procedure[22] as described for the synthesis of **1** except for purification. Crude **14** was further purified by distillation (100 °C, 1 mmHg) after column chromatography (SiO_2, hexane), to give pure **14** (57%) as a colorless oil. **14**; IR (neat): 3057, 2968, 2930, 2912, 1583, 1479, 1439, 1375, 1217, 1088, 1061, 1026, 843, 739, 691 cm^{-1}. ^1H NMR (270 MHz): δ 7.36-7.14 (m, 5H), 5.33-5.27 (m, 1H), 3.54 (br d, *J*= 7.7 Hz, 2H), 1.71 (s, 3H), 1.58 (s, 3H). HREIMS m/z. Calcd. for $C_{11}H_{14}S$ (M^+): 178.0816. Found: 178.0816. Calcd. for $C_{11}H_{14}S$: C, 74.10; H, 7.91%. Found: C, 74.12; H, 7.95%.

Geranyl phenyl sulfide 16

NaH (60% in oil, 524 mg, 13.1 mmol) was washed with THF and suspended in THF (40 ml). To the suspension was added thiophenol at 0 °C and stirred for 1 h. To this solution was added geranyl bromide (2.0 ml, 10.1 mmol) at the same temperature and the whole mixture was gradually warmed to room temperature. The mixture was stirred overnight at room temperature and quenched with 2 N aqueous NaOH (40 ml). The mixture was extracted with ether, washed successively with 2 N aqueous NaOH, water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexane-AcOEt= 1:0 to 9:1) to give **16** (2.46 g, 99%) as a colorless oil. **16**; IR (neat): 3057, 2966, 2924, 2855, 1583, 1479, 1439, 1375, 1227, 1107, 1026, 737, 691 cm^{-1}. ^1H NMR (270 MHz): δ 7.36-7.14 (m, 5H), 5.34-5.27 (m, 1H), 5.09-5.03 (m, 1H), 3.55 (d, *J*= 7.7 Hz, 2H), 2.08-1.96 (m, 4H), 1.67 (s, 3H), 1.58 (d, *J*= 3.0 Hz, 3H), 1.57 (d, *J*= 0.5 Hz, 3H). ^{13}C NMR (270 MHz): δ 139.9, 136.7, 131.6, 139.8, 128.6, 125.9, 123.9, 119.2, 39.5, 32.1, 26.4, 25.6, 17.6, 16.0. HREIMS m/z. Calcd. for $C_{16}H_{22}S$ (M^+): 246.1442. Found: 246.1442. Calcd. for $C_{16}H_{22}S$: C, 77.99 H, 9.00%. Found: C, 78.19; H, 9.02%.

Neryl phenyl sulfide 18

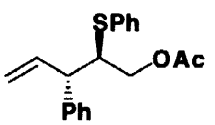
Neryl phenyl sulfide **18** was synthesized from nerol and thiophenol in the same procedure as described for the synthesis of **12** except for purification. Column chromatography (SiO_2, hexane-AcOEt= 9:1) was run to give pure **18** as a colorless oil. **18** (75%); IR (neat): 3058, 2966, 2926, 2856, 1583, 1479, 1439, 1375, 1221, 1090, 1026, 837, 737, 691 cm^{-1}. ^1H NMR (270 MHz): δ 7.36-7.13 (m, 5H), 5.35-5.29 (m, 1H), 5.13-5.07 (m, 1H), 3.55 (dd, *J*= 0.9 and 7.8 Hz, 2H), 2.04 (br d, *J*= 3.1 Hz, 4H), 1.72 (d, *J*= 1.2 Hz, 3H), 1.68 (s, 3H), 1.60 (s, 3H). ^{13}C NMR: δ 139.9, 137.0, 131.9, 129.3, 128.7, 125.8, 123.8, 119.8, 31.9, 31.8, 26.5, 25.6, 23.3, 17.6. HREIMS m/z. Calcd. for $C_{16}H_{22}S$ (M^+): 246.1442. Found 246.1442. Calcd. for $C_{16}H_{22}S$: C, 77.99 H, 9.00%. Found: C, 78.21 H, 9.04%.

General procedure for asymmetric [2,3]sigmatropic rearrangement using Co(III)-salen complex as a catalyst

Representative procedure is exemplified by the reaction of *trans*-cinnamyl phenyl sulfide with *t*-butyl diazoacetate in the presence of complex **8-Br**: Co(II)-salen complex **8**[9b] (13.4 mg, 0.25 μmol) was dissolved in CH_2Cl_2 (3 ml) and treated with a solution of bromine in CH_2Cl_2 (0.12 M, 102 μl, 12 μmol) at room temperature for 1 h. A solution of *trans*-cinnamyl phenyl sulfide (113 mg, 0.50 mmol) in CH_2Cl_2 (3 ml) was loaded and the mixture was stirred for another 10 min. *t*-Butyl diazoacetate (70 μl, 0.50 mmol) was added to this mixture and stirred for 24 h at room temperature. The reaction mixture was concentrated *in vacuo* and the residue was chromatographed on silica gel (hexane-AcOEt= 8:1) to give a mixture of *t*-butyl *anti*- and *syn*-3-phenyl-2-phenylthio-4-pentenoates as crystals (138 mg, 81%). The *anti-syn* ratio was determined to be 85:15 by ^{1}H NMR analysis. **2** (a mixture of *anti*- and *syn*-isomers); ^{1}H NMR (270 MHz): δ 7.55-7.49 (m, 2H), 7.35-7.15 (m, 8H), 6.19-5.96 (m, 1H), 5.21-5.07 (m, 2H), 3.96-3.91 (m, 1H), 3.77-3.64 (m, 1H), 1.32 (s, 1.48H), 1.02 (s, 7.52H). Calcd. for $C_{21}H_{24}O_2S$: C, 74.08 H, 7.10%. Found: C, 74.10; H, 7.17%. The % ee's of the products were determined to be 64% ee by HPLC analysis as described in the footnote to Table 1. The crystalline mixture was recrystallized twice from hexane at 0 °C to afford the enantiomerically pure *anti* isomer (6.3 mg, 3.7%). M.p. 79.5-80.5 °C. $[\alpha]_D^{25}$ +147° (*c* 0.244, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.52 (dd, *J*= 1.6 and 7.8 Hz, 2H), 7.32-7.17 (m, 8H), 6.12 (ddd, *J*= 8.3, 9.3, and 17.1 Hz, 1H), 5.18 (d, *J*= 9.3 Hz, 1H), 5.15 (d, *J*= 17.1 Hz, 1H), 3.93 (d, *J*= 11.7 Hz, 1H), 3.68 (dd, *J*= 8.3 and 11.7 Hz, 1H), 1.02 (s, 9H). IR (KBr): 3422, 3080, 3059, 3028, 3005, 2978, 2928, 1958, 1884, 1720, 1641, 1601, 1582, 1493, 1475, 1454, 1441, 1420, 1391, 1367, 1350, 1339, 1286, 1256, 1200, 1151, 1090, 1070, 1028, 995, 910, 862, 841, 772, 748, 727, 700, 669 cm^{-1}. HREIMS m/z. Calcd. for $C_{21}H_{24}O_2S$ (M^+): 340.1497. Found 340.1497.

***tert*-Butyl 2-(2-methoxyphenylthio)-3-phenyl-4-pentenoate 11** (as a mixture of *anti*- and *syn*-isomers); ^{1}H NMR (270 MHz): δ 7.49 (dd, *J*= 1.7 and 8.0 Hz, 1H), 7.36-7.15 (m, 8H), 6.22-5.98 (m, 1H), 5.24-5.15 (m, 2H), 4.25-4.16 (m, 1H), 3.92 (s, 2.59H), 3.85 (s, 0.41H), 3.77-3.70 (m, 1H), 1.23 (s, 1.53H), 1.02 (s, 7.47H). The *anti-syn* ratio was determined to be 83:17 by comparison of peak areas of the signals of *tert*-butyl groups in a pair of diastereomers (δ 1.23 and 1.02). IR (KBr): 3439, 3082, 3063, 3030, 3003, 2976, 2934, 2837, 2043, 1948, 1728, 1638, 1601, 1582, 1477, 1456, 1433, 1393, 1367, 1333, 1275, 1146, 1070, 1042, 1024, 988, 964, 920, 860, 839, 797, 754, 700, 685, 667 cm^{-1}. Calcd. for $C_{22}H_{26}O_3S$: C, 71.32 H, 7.07%. Found: C, 71.17; H, 7.00%.

(-)-Menthyl 3-phenyl-2-phenylthio-4-pentenoate 13 (as a mixture of two *anti*- and two *syn*-isomers); ^{1}H NMR (400 MHz): δ 7.54-7.50 (m, 2H), 7.32-7.17 (m, 8H), 6.19-6.00 (m, 1H), 5.20-5.06 (m, 2H), 4.37-4.31 (m, 1H), 4.06 (d, *J*= 11.5 Hz, 0.121H), 4.04 (d, *J*= 11.5 Hz, 0.819H), 4.03 (d, *J*= 11.5 Hz, 0.042H), 4.02 (d, *J*= 11.0 Hz, 0.018H), 3.81-3.71 (m, 1H), 1.70-0.29 (m, 18H). Calcd. for $C_{27}H_{34}O_2S$: C, 76.73 H, 8.11%. Found: C, 76.53; H, 8.26%. The *anti-syn* ratio was determined after **13** was converted into acetate **29** by the sequence: i) treatment of **13** with $LiAlH_4$ and ii) acetylation of resulting alcohol with Ac_2O in the presence of DMAP and Et_3N. **29**: ^{1}H NMR (400 MHz): δ 7.36-7.18 (m, 10H), 6.25-6.16 (m, 1H), 5.25-5.14 (m, 2H), 4.23-4.05 (m, 2H), 3.72-3.60 (m, 2H), 3.81-3.71 (m, 1H), 1.98 (s, 0.22H), 1.94 (s, 2.78H). IR (KBr): 3423, 3080, 3061, 3030, 2959, 2920, 2866, 2108, 1952, 1882, 1720, 1639, 1601, 1582, 1491, 1468, 1452, 1443, 1416, 1385, 1367, 1337, 1278, 1240, 1204, 1169, 1123, 1097, 1080, 1038, 1028, 982, 961, 914, 880, 841, 808, 748, 702, 667 cm^{-1}. Evaluation of integrals of methyl signals (δ 1.94 and 1.98) in acetyl groups indicated diastereomer ratio to be 93:7.



29

(-)-Menthyl 3,3-dimethyl-2-phenylthio-4-pentenoate 15 (as a mixture of two diastereomers); ^{1}H NMR (400 MHz): δ 7.46-7.42 (m, 2H), 7.29-7.20 (m, 3H), 6.08-5.99 (m, 1H), 5.13-5.05 (m, 2H), 4.64-4.57 (m, 1H), 3.62 (s, 0.13H), 3.58 (s, 0.87H), 2.04-0.56 (m, 24H). The diastereomer excess was determined to be 74% de by comparison of peak areas of the signals of C2-protons in a pair of diastereomers (δ 3.62 and 3.58). IR (KBr): 3435, 2957, 2930, 2870, 1734, 1639, 1583, 1458, 1416, 1385, 1367, 1298, 1261, 1146, 1096, 1040, 1011, 988, 916, 845, 773, 741, 691 cm^{-1}. **15** (74% de); $[\alpha]_D^{22}$ +24.8° (*c* 1.97, $CHCl_3$). HREIMS m/z. Calcd. for $C_{16}H_{22}S$ (M^+): 374.2280. Found 374.2280.

(-)-Menthyl 3-methyl-3-(4-methyl-3-pentenyl)-2-phenylthio-4-pentenoate 17 (obtained from sulfide **16** as a mixture of two *anti*- and two *syn*-isomers); ^{1}H NMR (400 MHz): δ 7.45-7.42 (m, 2H), 7.28-7.20 (m, 3H), 6.02-5.83 (m, 1H), 5.21-5.05 (m, 3H), 4.68-4.57 (m, 1H), 3.70 (s, 0.121H), 3.66 (s, 0.024H), 3.64 (s, 0.737H), 3.61 (s, 0.118H), 1.92-0.55 (m, 31H). IR (KBr): 3443, 2957, 2926, 2870, 1734, 1638, 1583, 1454, 1414, 1375, 1342, 1304, 1259, 1146, 1097, 1038, 1011, 988, 916, 741, 691 cm^{-1}. Calcd. for $C_{28}H_{42}O_2S$: C, 75.97 H, 9.56%. Found: C, 75.93; H, 9.55%. The *anti-syn* ratio was determined to be 83:17 by the comparison of peak areas of the signals of C2-protons in pairs of diastereomers. The signals at δ 3.70 and 3.64 were assigned to *anti*-isomers and the signals at δ 3.66 and 3.61 to *syn*-isomers by the comparison of ^{1}H NMR data with those of **17** synthesized from neryl phenyl sulfide.

(2*R*,3*S*)-3-Phenyl-2-phenylthio-4-penten-1-ol 20

To a solution of **2** (27.8 mg, 0.082 mmol, *anti*, >99% ee) in THF (0.5 ml) was added $LiAlH_4$ (6.2 mg, 0.16 mmol) at 0 °C. The mixture was stirred for 2 h at the temperature and followed by addition of $LiAlH_4$ (6.2 mg, 0.16 mmol) to complete the reduction. After another 1 h of stirring at 0 °C, the reaction was quenched with saturated KF (60 μl). The suspension was passed through a short column of silica gel and eluted with a 4:1 mixture of hexane and AcOEt, and then with AcOEt. The product obtained was further purified by preparative TLC (SiO_2, hexane-AcOEt= 1:1) to give analytically pure **20** (22.2 mg 99%) as a colorless oil. **20**; $[\alpha]_D^{24}$ -28° (*c* 0.042, C_2H_5OH). ^{1}H NMR (400 MHz): δ 7.40-7.37 (m, 2H), 7.34-7.21 (m, 8H), 6.23 (ddd, *J*= 8.8, 10.3, and 17.1 Hz, 1H), 5.20 (d, *J*= 10.3 Hz, 1H), 5.14 (d, *J*= 17.1 Hz, 1H), 3.59 (dd, *J*= 8.8 and 8.3 Hz, 1H), 3.57-3.45 (m, 2H), 3.36 (ddd, *J*= 4.9, 6.4, and 11.2 Hz, 1H), 2.14 (t, *J*= 6.4 Hz, OH). IR (KBr): 3420, 3059, 3028, 2931, 2877, 1638, 1601, 1583, 1477, 1452, 1439, 1418, 1387, 1067, 1024, 922, 748, 700, 517 cm^{-1}. HREIMS m/z. Calcd. for $C_{17}H_{18}OS$ (M^+): 270.1078. Found 270.1081.

(4*S*,3*S*)-4,5-Epoxy-3-phenyl-1-pentene 21

Trimethyloxonium tetrafluoroborate (37.5 mg, 0.25 mmol) was added all at once to a stirred solution of **20** (22.2 mg, 0.082 mmol) in dry CH_2Cl_2 (0.5 ml) at 0 °C. After 2 h of stirring at room temperature, the mixture was cooled to 0 °C and treated with 10% aqueous NaOH (1.1 ml). Stirring was further continued for 3 h before the reaction mixture was neutralized with saturated NH_4Cl. The suspension was passed through a short column of silica gel by using a 10:1 mixture of hexane and AcOEt as the eluate. The product obtained was further purified by preparative TLC (SiO_2, hexane-AcOEt= 10:1) to give analytically pure **21** (7.8 mg, 60%) as a colorless oil[16]. **21**; $[\alpha]_D^{24}$ +33° (*c* 0.029, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.36-7.24 (m, 5H), 6.00 (ddd, *J*= 6.8, 10.3, and 17.1 Hz, 1H), 5.19 (d, *J*= 10.3 Hz, 1H), 5.16 (d, *J*= 17.1 Hz, 1H), 3.32 (dd, *J*= 6.3 and 6.8 Hz, 1H), 3.23 (ddd, *J*= 2.9, 3.9, and 6.3 Hz, 1H), 2.84 (dd, *J*= 3.9 and 4.9 Hz, 1H), 2.58 (dd, *J*= 2.9 and 4.9 Hz, 1H). IR (KBr): 3456, 3084, 3061, 3030, 2984, 2922, 1638, 1603, 1493, 1452, 1408, 1259, 1130, 1101, 1074, 1030, 995, 922, 860, 812, 754, 702, 527 cm^{-1}. HREIMS m/z. Calcd. for $C_{11}H_{12}O$ (M^+): 160.0888. Found 160.0892.

(2*R*,3*R*)-3-phenyl-4-penten-1,2-diol 22

tert-Butyllithium (5.8 ml, 1,7 mol cm^{-3} in pentane) was added to vinyl bromide (5.0 ml, 1.0 mol dm^{-3} in THF) dropwise over 15 min at -78 °C and the mixture was allowed to warm to -10 °C with stirring for 1 h. The obtained solution was transferred to a suspension of CuCN (222 mg, 2.5 mmol), which was azeotropically dried

with toluene (2 ml x 2) before use, in THF (2 ml) at -78 °C and the mixture was gradually warmed to -20 °C with vigorous stirring for 40 min. A solution of (2*S*,3*S*)-2,3-epoxycinnamyl alcohol (113 mg, 0.75 mmol, 84% ee) in THF (1 ml) was added dropwise with a subsequent wash with THF (0.5 ml) and the mixture was stirred at 0 °C for 11 h. The reaction was quenched with a mixture of saturated NH_4Cl (9 ml) and 28% aqueous NH_3 (1 ml) and stirring was continued at room temperature until a blue clear aqueous phase was obtained. The phases were separated and the aqueous layer was extracted with AcOEt (10 ml x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The residue was subjected to column chromatography (SiO_2, hexane-AcOEt= 2:1 to 1:1) to give diol **22** (82 mg, 61%) as a colorless oil. **22**; $[\alpha]_D^{25}$ -85.3° (*c* 0.213, C_2H_5OH). ^1H NMR (400 MHz): 7.36-7.32 (m, 2H), 7.27-7.23 (m, 3H), 5.98 (ddd, *J*= 8.7, 10.3, and 17.1 Hz, 1H), 5.18-5.11 (m, 2H), 3.96, (ddd, *J*= 2.9, 6.8, and 8.3 Hz, 1H), 3.77 (dd, *J*= 2.9 and 11.2 Hz, 1H), 3.55 (dd, *J*= 6.8 and 11.2 Hz, 1H), 3.41 (dd, *J*= 8.3 and 8.8 Hz, 1H), 2.32 (br s, OH), 2.12 (br s, OH). IR (KBr): 3418, 3383, 3082, 3063, 3028, 2928, 2883, 2253, 1638, 1601, 1493, 1452, 1416, 1132, 1092, 1069, 1030, 995, 923, 876, 837, 760, 702, 677, 525 cm^{-1}. Calcd. for $C_{11}H_{14}O_2$: C, 74.13 H, 7.92%. Found: C, 74.20; H, 7.95%.

(4*R*,3*R*)-4,5-Epoxy-3-phenyl-1-pentene ent-21

Diol **22** (12 mg, 0.067 mmol) was dissolved in pyridine (0.5 ml) and treated with *p*-toluenesulfonyl chloride (15 mg, 0.077 mmol) at room temperature. After 12 h of stirring at room temperature, the reaction mixture was dried up and the residue was dissolved in THF (0.5 ml) followed by addition of *t*-BuOK (22 mg, 0.20 mmol). After 2 h of stirring at room temperature, water (2 ml) was added and the mixture was extracted with AcOEt (2 ml x 4). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was subjected to column chromatography (SiO_2, hexane-AcOEt= 8:1) to give **21** (5.7 mg, 53%) as a colorless oil. **ent-21**; $[\alpha]_D^{24}$ -15.2° (*c* 0.382, C_2H_5OH).

(*R*)-3,3-Dimethyl-2-phenylthio-4-pentan-1-ol 23

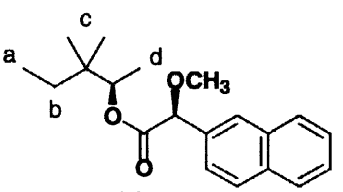
To a solution of **15** (78.2 mg, 0.21 mmol, 74% de) in THF (0.5 ml) was added $LiAlH_4$ (16 mg, 0.42 mmol) at 0 °C. After stirring for 13 h at the temperature, the reaction mixture was treated with saturated KF (30 µl) at 0 °C. The resulting suspension was filtered through a pad of Celite and the filtrate was concentrated to dryness. The residue was subjected to column chromatography (SiO_2, hexane-CH_2Cl_2= 4:1) and further purified by preparative TLC (SiO_2, CH_2Cl_2) to give (*R*)-3,3-Dimethyl-2-phenylthio-4-penten-1-ol (32.7 mg 66%) as a colorless oil; $[\alpha]_D^{24}$ -24.5° (*c* 0.933, C_2H_5OH). ^1H NMR (400 MHz): 7.50-7.47 (m, 2H), 7.31-7.20 (m, 3H), 5.92 (dd, *J*= 10.8 and 14.2 Hz, 1H), 5.05 (dd, *J*= 1.5 and 14.2 Hz, 1H), 5.04 (dd, *J*= 1.5 and 10.8 Hz, 1H), 3.87 (ddd, *J*= 4.4, 9.3, and 11.7 Hz, 1H), 3.55 (ddd, *J*= 4.9, 8.3, and 11.7 Hz, 1H), 3.10 (dd, *J*= 4.4 and 8.3 Hz, 1H), 2.34 (dd, *J*= 4.9 and 9.3 Hz, OH) 1.19 (s, 3H), 1.16 (s, 3H). IR (KBr): 3445, 3084, 2986, 2928, 2882, 2363, 2341, 1638, 1582, 1477, 1462, 1439, 1414, 1379, 1362, 1261, 1170, 1076, 1057, 1024, 997, 918, 746, 694 cm^{-1}. HREIMS m/z. Calcd. for $C_{13}H_{18}OS$ (M^+): 222.1078. Found 222.1056.

The alcohol (14.1 mg, 0.063 mmol) was stirred over palladium on charcoal (10 %, 5 mg) in AcOEt (2 ml) under hydrogen atmosphere at room temperature for 15 h. The mixture was filtered through a pad of Celite and concentrated. The residue was purified by TLC (SiO_2, CH_2Cl_2) to give **23** (13.1 mg, 92%) as a colorless oil. **23**; $[\alpha]_D^{24}$ 19.1° (*c* 0.479, C_2H_5OH). ^1H NMR (400 MHz): 7.50-7.47 (m, 2H), 7.30-7.26 (m, 2H), 7.23-7.19 (m, 1H), 3.89 (ddd, *J*= 4.4, 9.3, and 11.7 Hz, 1H), 3.61 (ddd, *J*= 3.9, 8.8, and 11.7 Hz, 1H), 3.14 (dd, *J*= 4.4 and 8.8 Hz, 1H), 2.44 (dd, *J*= 3.9 and 9.3 Hz, 1H), 1.55 (B of ABdq *J*= 7.8 and 13.7 Hz, 1H), 1.41 (A of ABdq, *J*= 7.3 and 13.7 Hz, OH), 1.02 (s, 3H), 0.99 (s, 3H), 0.79 (dd, *J*= 7.3 and 7.8 Hz, 3H). IR (KBr): 3445, 3059, 2964, 2937, 2878, 1638, 1583, 1477, 1439, 1387, 1366, 1252, 1178, 1086, 1051, 1024, 1007, 742, 692 cm^{-1}. HREIMS m/z. Calcd. for $C_{13}H_{20}OS$ (M^+): 224.1234. Found 224.1238.

(*R*)-3,3-Dimethyl-2-pentyl (*S*)-(+)-methoxy(2-naphthyl)acetate 24

Trimethyloxonium tetrafluoroborate (15.5 mg, 0.10 mmol) was added all at once to a stirred solution of **23** (7.6 mg, 0.034 mmol) in CH_2Cl_2 (0.5 ml) at 0 °C. After stirring for 3 h at room temperature, the mixture was cooled to 0 °C and treated with 10% aqueous NaOH (0.5 ml). Stirring was further continued for 2 h at room

temperature before the reaction mixture was extracted with diethyl ether (2 ml x 3) and then dried over Na_2SO_4. The drying agent was filtered off and the solvent was distilled off under ambient pressure. The residue was dissolved in diethyl ether (1 ml) and to the solution was added $LiAlH_4$ (10 mg, 0.26 mmol) at 0 °C. After 4 h of stirring at room temperature, the reaction mixture was concentrated on heating under ambient pressure and dissolved again in diethyl ether (2 ml) followed by addition of saturated sodium potassium tartrate (4 ml) at 0 °C. The mixture was further stirred at room temperature until a clear biphasic solution was obtained. The phase was separated and the aqueous layer was extracted with diethyl ether (2 ml x 4). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue thus obtained and *N,N*-4-dimethylaminopyridine (9,5 mg, 0.078 mmol) were dissolved in CH_2Cl_2 (2 ml) and the solution was added to 2NMA chloride prepared from (*S*)-(+)-2NMA acid (13.4 mg, 0.043 mmol) according to the known procedures. After 2 h of stirring at room temperature, the reaction mixture was concentrated and purified by preparative TLC (SiO_2, hexane-AcOEt= 4:1) to give 2NMA ester **24** (2.4 mg, 22% from **23**) as a colorless oil. **24** (as a mixture of diastereomers); ^{1}H NMR (400 MHz): 7.92 (br s, 1H), 7.86-7.81 (m, 3H), 7.55 (dd, *J*= 1.8 and 8.6 Hz, 1H), 7.52-7.47 (m, 2H), 4.91 and 4.89 (s, 1H), 4.82 and 4.76 (q, *J*= 6.4 Hz, 1H), 3.47 and 3.45 (s, 3H), 1.29 and 0.98 (B of ABdq, *J*= 7.8 and 13.7 Hz, 1H), 1.21 and 0.94 (A of ABdq, *J*= 7.3 and 13.7 Hz, 1H), 1.15 and 0.94 (d, *J*= 6.4 Hz, 3H), 0.82 and 0.63 (s, 3H), 0.81 and 0.59 (s, 3H), 0.79 and 0.55 (dd, *J*= 7.3 and 7.8 Hz, 3H). IR (KBr): 3059, 2968, 2937, 2880, 2827, 1746, 1728, 1632, 1603, 1510, 1464, 1379, 1367, 1335, 1283, 1269, 1192, 1126, 1109, 1080, 1032, 1007, 860, 810, 750, 478 cm^{-1}. HREIMS m/z. Calcd. for $C_{20}H_{26}O_3$ (M^+): 314.1882. Found 314.1882.



24

Table 3. ^{1}H NMR data (chemical shifts and Δδ values) of **24**

	δ_{minor} (ppm)	δ_{major} (ppm)	$\Delta\delta$ (δ_{minor}-δ_{major})
a	0.55	0.79	-0.24
b	0.98	1.29	-0.31
	0.95	1.21	-0.26
c	0.63	0.82	-0.19
	0.59	0.81	-0.22
d	1.15	0.94	+0.21

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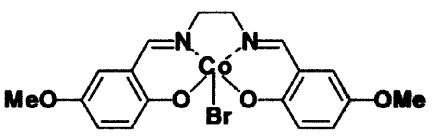
12 Isolated Co(III)-salen complex **8-Br** (see Experimental Section) was used for the study of solvent effect.

13 It has been reported that the [2,3]Wittig rearrangement of both (*E*)- and (*Z*)-(2-alkenyloxy)acetic acid esters showed *syn*-selectivity (ref. 1a).

14 To consider more about double diastereodifferentiation, we synthesized complex **i** and examined the reaction of **14** and (-)-menthyl α-diazoacetate using the complex as a catalyst. However, the reaction was sluggish, suggesting that the presence of the phenyl groups on the ethylenediamine moiety accelerated the desired reaction. The mechanism of this ligand acceleration is unclear at present.



i

15 Configuration of the major diastereomer was tentatively assigned to be *anti* by the mechanical analogy with [2,3]sigmatropic rearrangement of the *S*-ylide derived from cinnamyl phenyl sulfide.

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