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Asymmetric Hydroformylations of Sulfur-Containing Olefins Catalyzed by BINAPHOS—Rh(I) Complexes

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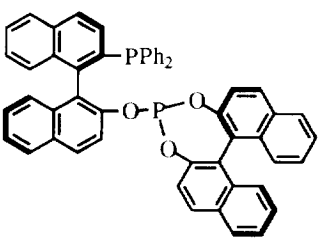
Abstract: Asymmetric hydroformylations of vinyl sulfides, allyl sulfides, and allyl sulfones catalyzed by (*R*,*S*)-BINAPHOS / Rh(acac)(CO)$_2$ afforded the corresponding branched *oxo* aldehydes as major products in 60—89% *ee*. Use of bulkier substituents on the sulfur in vinyl sulfides gave the branched *oxo*-aldehydes in higher regio- and enantioselectivities.

Hydroformylation is one of the most versatile methods for the functionalization of C=C double bonds. Recently asymmetric hydroformylation has been attracting much attention, because optically active *oxo*-aldehydes are very important and useful intermediates for the synthesis of many biologically active compounds.[1] In this context, much effort has been focused on the development of new efficient catalysts and expansion of olefinic substrates available to asymmetric hydroformylation. We have found that (*R*,*S*)- and (*S*,*R*)-BINAPHOS—Rh(I) complexes [(*R*,*S*)-BINAPHOS = ( )-2-diphenylphosphino-1,1'-binaphthalen-2'-yl (*S*)-1,1'-binaphthalen-2,2'-diyl phosphite] are highly efficient catalysts for asymmetric hydroformylations of a variety of olefins such as arylethenes,[3] vinyl esters,[3] *N*-vinylphthalimide,[3] fluoroalkyl- and fluoroarylethenes,[4] and 1,3-dienes.[5] In order to expand the utility of our catalysts, we have investigated the asymmetric hydroformylation of some sulfur-containing olefins.[6,7]

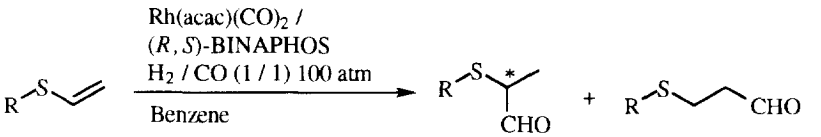


(*R*,*S*)-BINAPHOS

A solution of vinyl sulfides **1a**—**f**, catalytic amounts of Rh(acac)(CO)$_2$ and (*R*,*S*)-BINAPHOS, and ferrocene (internal standard) in benzene was stirred at 40—55 °C for 22—96 h in a 50-mL autoclave under hydrogen and carbon monoxide pressure (1 : 1 ratio, total 100 atom). The conversions of the substrates and the branched / normal ratios (*i* / *n*) of the products were determined by ^{1}H NMR analysis. Enantiomeric excesses

were determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as a chiral shift reagent for **2a—d** or by HPLC analysis of the corresponding alcohols derived from **2e** and **2f**.

Some representative results of the asymmetric hydroformylation of vinyl sulfides are given in Table 1.



1a: R = Et
1b: R = *iso*-Pr
1c: R = *tert*-Bu
1d: R = *c*-C_6H_{11}
1e: R = Ph
1f: R = *p*-MeC_6H_4

2a—f **3a—f**

Table1. Asymmetric Hydroformylations of Vinyl Sulfides Catalyzed by (*R*, *S*)-BINAPHOS / Rh(acac)(CO)$_2$[a]

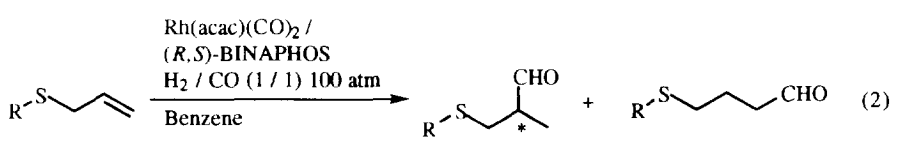
run	substrate[b]	S / C[c]	temp. °C	time, h	conv. %[d]	*i* / *n*[d]	*ee*, %[e]	config.[e]
1	**1a**	502	50	96	60	86 / 14	66[f]	(-)
2	**1b**	488	50	48	>99	92 / 8	72[f]	(-)
3	**1c**	497	40	27	70	96 / 4	89[f]	(-)
4	**1d**	500	55	66	76	88 / 12	60[f]	(-)
5	**1d**	503	40	36	32	91 / 9	72[f]	(-)
6	**1e**	996	40	34	97	98 / 2	76[g]	(-)
7	**1f**	1002	40	20	96	96 / 4	74[g]	(*S*)-(-)

[a] Reactions were carried out in benzene (solvent / substrate = 0.7—6.4) with the substrate **1** (0.9—9.8 mmol) and Rh(acac)(CO)$_2$ (0.17—2.0 x 10^{-2} mmol) in a 50-mL autoclave under 1 : 1 mixture of H_2 and CO at initial total pressure of 100 atm. [b] Ligand / [Rh] = 4.0—4.4. [c] S / C: substrate / [Rh] ratio. [d] Conversions and *i* / *n* ratios were determined based on ^{1}H NMR using ferrocene as an internal standard. [e] Determined by the signs of specific rotations which are given in parentheses. [f] Determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as a chiral shift reagent. [g] Determined by HPLC analysis of the alcohols derived from the corresponding aldehydes with DAICEL CHIRALCEL OD column.

The absolute configuration of **2f** has been assigned based on the sign of specific rotation.[8] In all cases, hydrogenated products of the starting vinyl sulfides were not detected by ^{1}H NMR analysis. The observed high *i* / *n* ratios might be attributed to the presence of highly polarizable sulfur atom attached to the C=C bonds. Aryl vinyl sulfides also afforded significantly high *i* / *n* ratio. Notably, higher *ee*'s were obtained as the bulkiness of the substituents on the sulfur atom increased. The use of bulkier alkyl substituents are also in a favour of the formation of branched aldehydes, though the reason still remains to be elucidated. It is also noteworthy that a similar tendency has been observed for asymmetric hydroformylation of vinyl carboxylates.[4] The reaction of **1a** which has less bulky substituent on the sulfur atom proceeded more slowly than those of other substrates. For example, compound **1a** was recovered almost unchanged in the reaction at 40 °C, while the reactions of **1b**—**1f** proceeded in reasonable conversions. This suggests that a strong interaction between the sulfur atom and the metal catalytic center results in decrease in reaction rates. All of these facts imply that the reaction might not proceed by so-called chelation control, though such a mechanism has been suggested for hydroformylation of vinyl acetate.[9]

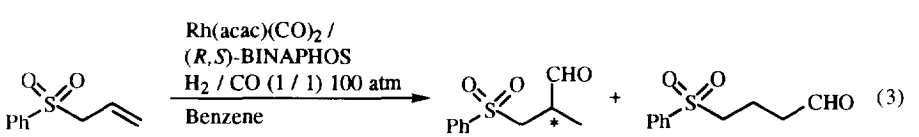
Similarly, asymmetric hydroformylation of allyl sulfides and allyl sulfones have been investigated (eqs (2) and (3)). The results are given in Table 2.

For all of these substrates, formation of hydrogenation products were not observed as analyzed by ^{1}H NMR spectroscopy. Neither isomerization of the starting substrates nor formation of 2-thiobutanals was detected. Although lower *i* / *n* ratios were obtained for **4a** and **4b** compared to **1c** and **1e**, respectively, the values are still much higher compared to that obtained for 1-hexene (*i* / *n* = 24 / 76, 75% *ee*). This shows that the sulfur atom at allylic position also exerts relatively large influence on the regioselectivity of hydroformylation. Introduction of an electron-withdrawing sulfonyl group at allylic position also influenced on the regioselectivity of the reaction to a large extent, resulting in high selectivity for branched aldehyde.



4a: R = *tert*-Bu
4b: R = Ph

5a—b **6a—b**



7 **8** **9**

Table 2. Asymmetric Hydroformylations of Allyl Sulfides and Allyl Sulfones Catalyzed by (*R*, *S*)-BINAPHOS / Rh(acac)$(CO)_2$[a]

run	substrate[b]	S / C	temp. °C	time, h	conv. %[c]	*i* / *n*[c]	*ee*, %[d]
1	**4a**	497	50	47	76	56 / 44	64[e] (-)
2	**4b**	991	50	48	100	67 / 33	80[f] (-)
3	**7**	455	40	46	75	86 / 14	65[g] (+)

[a] Reactions were carried out in benzene (solvent / substrate = 1.2—7.4) with the substrate **1** (0.9—2.2 mmol) and Rh(acac)$(CO)_2$ (2.0—3.5 x 10^{-3} mmol) in a 50-mL autoclave under 1 : 1 mixture of H_2 and CO at initial total pressure of 100 atm. [b] Ligand / [Rh] = 4.0—4.4. [c] Conversions and *i* / *n* ratios were determined based on ^{1}H NMR using ferrocene as an internal standard. [d] The signs of specific rotations are given in parentheses. [e] Determined by ^{1}H NMR analysis of MTPA esters derived from the corresponding aldehydes. [f] Determined by ^{19}F NMR analysis of MTPA esters derived from the corresponding aldehydes. [g] Determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as a chiral shift agent.

To the best of our knowledge, the present work provides the first example of the asymmetric hydroformylation of olefins containing sulfide moiety. Optically active α- and β-thioaldehydes and β- and γ-hydroxysulfides derived from them have rarely been synthesized, though they have potential use as intermediates for the synthesis of physiologically active compounds. Optically active 2-methyl-3-phenylthiopropanol which can be derived from **5a** has been shown to be a useful building block of macrolide antibiotic (+)-milbemycin β_3.[10] Thus, the above results show that asymmetric hydroformylation of sulfur containing olefins catalyzed by BINAPHOS—Rh(I) complexes provides a new route to synthetically useful optically active sulfides and sulfones.

Experimental Section

General

Nuclear magnetic resonance [H (270 MHz) and ^{19}F (254 MHz) NMR] spectra were recorded on a JEOL JNM-EX270 spectrometer with TMS (^{1}H internal) and 20% CF_3COOH (^{19}F external) as references, respectively. Optical rotations were measured on a JASCO DIP-360. High resolution mass spectra (HRMS) were taken on a Hitachi M-80B spectrometer.

HPLC analyses were performed on a Shimadzu LC-4A equipped with an SPD-2AS spectrophotometric detector and a UV-8000 detector. All manipulation involving air- and moisture-sensitive organometallic compounds were carried out with the standard Schlenk-tube technique under argon atmosphere purified by passing it through a BASF-Catalyst R3-11 column. Deuteriochloroform was distilled over P_4O_{10} and transferred into an NMR tube by bulb-to-bulb distillation prior to use. Benzene-d_6 was distilled over Na-K alloy

and transferred into an NMR tube by bulb-to-bulb distillation prior to use. Methanol was distilled over $Mg(OCH_3)_2$ under argon atmosphere. Ethanol was distilled over $Mg(OCH_2CH_3)_2$ under argon atmosphere. Benzene was distilled over P_4O_{10} under argon. Complex $Rh(acac)(CO)_2$ was purchased from Aldrich Chemical Company Inc. and used without further purification. Thiols were purchased from Tokyo Kasei Kogyo Co., Ltd. and used without purification. Ethyl vinyl sulfide and phenyl vinyl sulfide were purchased from Tokyo Kasei Kogyo Co., Ltd. and were degassed after distillation. Other vinyl sulfides were synthesized according to the literature procedures.[11]

*iso-Propyl Vinyl Sulfide (**1b**)*

^1H NMR ($CDCl_3$) δ 1.32 (d, J = 6.6 Hz, $2CH_3$), 3.16 (heptet, $CH(CH_3)_2$)), 5.22 (d, J = 16.8 Hz, $CH=CH_2$ (trans)), 5.23 (d, J = 10.2 Hz, $CH=CH_2$ (cis)), 6.38 (dd, $CH=CH_2$).

*tert-Butyl Vinyl Sulfide (**1c**)*

^1H NMR ($CDCl_3$) δ 1.36 (s, $3CH_3$), 5.30 (d, J = 9.6 Hz, $CH=CH_2$ (cis)), 5.38 (d, J = 16.8 Hz, $CH=CH_2$ (trans)), 6.54 (dd, $CH=CH_2$). B.p. 114—115 °C.

*Cyclohexyl Vinyl Sulfide (**1d**)*

^1H NMR ($CDCl_3$) δ 1.2—1.4 (m, 5H), 1.6—1.7 (m, 1H), 1.7—1.8 (m, 2H), 2.0—2.1 (m, 2H) (cyclohexyl), 2.8—2.9 (m, CHS), 5.20 (d, J = 9.9 Hz, $CH=CH_2$ (cis)), 5.21 (d, J = 16.8 Hz, $CH=CH_2$ (trans)), 6.38 (dd, $CH=CH_2$).

*p-Tolyl Vinyl Sulfide (**1f**)*

^1H NMR ($CDCl_3$) δ 2.35 (s, CH_3), 5.24 (d, J = 15.8 Hz, $CH=CH_2$ (trans)), 5.30 (d, J = 8.6 Hz, $CH=CH_2$ (cis)), 6.55 (dd, $CH=CH_2$), 7.15 (d, J = 8.0 Hz, 2H) and 7.31 (d, 2H) (aromatic protons). B.p. 101—102 °C (13 mmHg).

*Hydroformylation of Ethyl Vinyl Sulfide (**1a**)*

A solution of ethyl vinyl sulfide (**1a**) (221 mg, 2.51 mmol), (*R,S*)-BINAPHOS (15.4 mg, 2.00 x 10^{-2} mmol), and $Rh(acac)(CO)_2$ (1.3 mg, 5.0 x 10^{-3} mmol) in benzene (0.5 ml) was prepared in a 20-mL Schlenk tube. The mixture was degassed by freeze-thaw cycles for three times and transferred into a 50-mL autoclave. Then the solution was stirred at 50 °C for 96 h under H_2 / CO (1 / 1) pressure of 100 atm. The conversion of **1a** (60%) and the ratio of 2-(ethylthio)propanal (**2a**) / 3-(ethylthio)propanal (**3a**) (86 / 14) were determined by ^1H NMR analysis. The enantiomeric excess (66% *ee*) was determined by ^1H NMR analysis using $Eu(hfc)_3$ as the chiral shift reagent. The sign of specific rotation of the major enantiomer was (-). **2a**: ^1H NMR ($CDCl_3$) δ 1.23 (t, J = 7.3 Hz, CH_2CH_3), 1.36 (d, J = 6.9 Hz, $CHCH_3$), 2.41 (q, CH_2CH_3), 3.25 (dq, J = 4.3 and 6.9 Hz, CHCHO), 9.23 (d, CHO). HRMS (EI); Calcd. for $C_5H_{10}OS$ (M^+): 118.0451. Found: 118.0488.

*Hydroformylation of iso-Propyl Vinyl Sulfide (**1b**)*

iso-Propyl vinyl sulfide (**1b**) (840 mg, 9.75 mmol), (*R,S*)-BINAPHOS (67.7 mg, 8.80 x 10^{-2} mmol), $Rh(acac)(CO)_2$ (5.2 mg, 2.0 x 10^{-2} mmol), and benzene (2 ml) were placed in a 20-mL Schlenk tube. The mixture was degassed by freeze-thaw cycles for three times, transferred into a 50-mL autoclave under argon, and then stirred at 50 °C for 48 h under H_2 / CO (1 / 1) pressure of 100 atm. The conversion of **1b** (>99%) and

the ratio of 2-(*iso*-propylthio)propanal (**2b**) / 3-(*iso*-propylthio)propanal (**3b**) (92 / 8) were determined by ^{1}H NMR analysis. The enantiomeric excess (72% *ee*) was determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as the chiral shift reagent. The sign of specific rotation of the major enantiomer was (-). **2b**: ^{1}H NMR ($CDCl_3$) δ 1.24 (d, J = 6.9 Hz, CH_3CHCH_3), 1.28 (d, J = 6.6 Hz, CH_3CHCHO), 1.35 (d, J = 6.9 Hz, CH_3CHCH_3), 2.83 (heptet, $CH(CH_3)_2$), 3.28 (dq, J = 4.6 and 6.6 Hz, $CHCHO$), 9.22 (d, J = 4.6 Hz, CHO). HRMS (EI); Calcd. for $C_6H_{12}OS$ (M^+): 132.0608. Found: 132.0624.

*Hydroformylation of tert-Butyl Vinyl Sulfide (**1c**)*

In a 20-mL Schlenk tube were placed *tert*-butyl vinyl sulfide (**1c**) (98.2 mg, 0.845 mmol), (*R,S*)-BINAPHOS (5.8 mg, 7.5 x 10^{-3} mmol), Rh(acac)$(CO)_2$ (0.44 mg, 1.7 x 10^{-3} mmol), and benzene (0.7 ml). The degassed mixture was transferred into an autoclave under argon and stirred at 40 °C for 27 h under H_2 / CO (1 / 1) pressure of 100 atm. The conversion of **1c** (70%) and the ratio of 2-(*tert*-butylthio)propanal (**2c** / 3-(*tert*-butylthio)propanal (**3c**) (96 / 4) were determined by ^{1}H NMR analysis. The enantiomeric excess (89% *ee*) was determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as the chiral shift reagent. The sign of specific rotation of the major enantiomer was (-). **2c**: ^{1}H NMR ($CDCl_3$) δ 1.34 (d, J = 7.0 Hz, $CHCH_3$), 1.35 (s, $3CH_3$), 3.34 (dq, J = 4.0 and 7.1 Hz, $CHCHO$), 9.34 (d, CHO). HRMS (EI); Calcd. for $C_7H_{14}OS$ (M^+): 146.0764. Found: 146.0728.

*Hydroformylation of Cyclohexyl Vinyl Sulfide (**1d**)*

A solution of cyclohexyl vinyl sulfide (**1d**) (494 mg, 3.47 mmol), (*R,S*)-BINAPHOS (23.4 mg, 3.04 x 10^{-2} mmol), and Rh(acac)$(CO)_2$ (1.8 mg, 6.9 x 10^{-3} mmol) in benzene (0.7 ml) placed in a 20-mL Schlenk tube was degassed by freeze-thaw cycles for three times. The solution was transferred into an autoclave under argon and stirred at 40 °C for 36 h under H_2 / CO (1 / 1) pressure of 100 atm. The conversion of **1d** (32%) and the ratio of 2-(cyclohexylthio)propanal (**2d**) / 3-(cyclohexylthio)propanal (**3d**) (91 / 9) were determined by ^{1}H NMR analysis. The enantiomeric excess (72% *ee*) was determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as the chiral shift reagent. The sign of specific rotation of the major enantiomer was (-). **2d**: ^{1}H NMR ($CDCl_3$) δ 1.34 (d, J = 6.9 Hz, $CHCH_3$), 1.2—2.0 (m, 10H, cyclohexyl protons), 2.5—2.6 (m, CHS), 3.30 (dq, J = 4.6 and 6.9 Hz, $CHCHO$), 9.22 (d, J = 4.6 Hz, CHO). Anal. Calcd. for $C_9H_{16}OS$: C, 62.74; H, 9.36. Found: C, 62.59; H, 9.59.

*Hydroformylation of Phenyl Vinyl Sulfide (**1e**)*

A solution of phenyl vinyl sulfide (**1e**) (352 mg, 2.59 mmol), (*R,S*)-BINAPHOS (8.8 mg, 1.1 x 10^{-2} mmol), Rh(acac)$(CO)_2$ (0.67 mg, 2.6 x 10^{-3} mmol) in benzene (0.3 ml) was prepared in a 20-mL Schlenk tube and degassed by freeze-thaw cycles for three times. The mixture was transferred into an autoclave under argon and stirred at 40 °C for 34 h under H_2 / CO (1 / 1) pressure of 100 atm. The conversion of **1e** (97%) and the ratio of 2-(phenylthio)propanal (**2e**) / 3-(phenylthio)propanal (**3e**) (98 / 2) were determined by ^{1}H NMR analysis. The enantiomeric excess (76% *ee*) was determined by HPLC analysis of the corresponding alcohol obtained by the reduction with $NaBH_4$ / MeOH. The sign of specific rotation of the major enantiomer was (-). **2e**: ^{1}H NMR ($CDCl_3$) δ 1.33 (d, J = 6.6 Hz, $CHCH_3$), 3.57 (dq, J = 3.3 and 6.6 Hz, $CHCHO$), 7.2—7.6 (m, 5H, aromatic protons), 9.38 (d, CHO). HRMS (EI); Calcd. for $C_9H_{10}OS$ (M^+): 166.0452. Found: 166.0459.

*Hydroformylation of p-Tolyl Vinyl Sulfide (**1f**)*

To a 20-mL Schlenk tube were added *p*-tolyl vinyl sulfide (**1f**) (753 mg, 5.01 mmol), (*R,S*)-BINAPHOS (15.4 mg, 2.00 x 10^{-2} mmol), Rh(acac)$(CO)_2$ (1.3 mg, 5.0 x 10^{-3} mmol), and benzene (0.5 ml). The resulting solution was degassed by freeze-thaw cycles for three times and transferred into an autoclave under argon. The mixture was stirred at 40 °C for 20 h under H_2 / CO (1 / 1) pressure of 100 atm. The conversion of **1f** (96%) and the ratio of 2-(*p*-tolylthio)propanal (**2f**) / 3-(*p*-tolylthio)propanal (**3f**) (96 / 4) were determined by ^{1}H NMR analysis. The enantiomeric excess (74% *ee*) was determined by HPLC analysis of the corresponding alcohol derived through the reduction by using $NaBH_4$ / MeOH. The absolute configuration of the major enantiomer was determined to be *S* by comparison of the sign (-) of specific rotation of the sample with that of the reported one.[8] **2f**: ^{1}H NMR ($CDCl_3$) δ 1.37 (d, *J* = 6.9 Hz, $CHCH_3$), 2.33 (s, $C_6H_4CH_3$), 3.56 (dq, *J* = 3.0 and 6.9 Hz, CHCHO), 7.11 (d, *J* = 8.0 Hz, 2H) and 7.25 (d, 2H) (aromatic protons), 9.45 (d, *J* = 3.0 Hz, CHO).

*Synthesis of Allyl tert-Butyl Sulfide (**4a**) and Allyl Phenyl Sulfide (**4b**)*

A solution of sodium ethoxide (9.00 g, 0.132 mol) in ethanol (100 mL) was placed in a three-necked flask. To the solution was added *tert*-butyl mercaptan (10 mL, 89 mmol) slowly from a dropping funnel. After the mixture was stirred for additional 15 min, to this was added slowly allyl chloride (7.6 mL, 93 mmol). The mixture was stirred further for 1.5 h and, then the solvent was removed by slow distillation at atmospheric pressure. To the residue were added water and ether and the organic layer was separated. The aqueous layer was extracted with ether for several times. The combined organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by fractional distillation of the residue afforded allyl phenyl sulfide (**4a**) (1.55 g, 10.3 mmol, 12% yield) as a colorless liquid. The product was distilled over sodium hydride before further use for asymmetric hydroformylation. ^{1}H NMR δ 1.34 (s, $3CH_3$), 3.22 (d with fine splitting, *J* = 7.3 Hz, $CH_2CH{=}CH_2$), 5.0—5.2 (m, $CH{=}CH_2$), 5.8—6.0 (m, $CH{=}CH_2$). B.p. 59 °C (35 mmHg). Allyl phenyl sulfide (**4b**) was similarly synthesized from allyl chloride and thiophenol (72% yield) as a colorless liquid. The product was distilled over sodium before use for catalytic reaction. ^{1}H NMR ($CDCl_3$) δ 3.55 (d with fine splitting, *J* = 6.9 Hz, $CH_2CH{=}CH_2$), 5.0—5.2 (m, $CH{=}CH_2$), 5.8—6.0 (m, $CH{=}CH_2$), 7.1—7.4 (m, aromatic protons).

*Hydroformylation of Allyl tert-Butyl Sulfide (**4a**)*

Allyl *tert*-butyl sulfide (**4a**) (262 mg, 1.74 mmol), (*R,S*)-BINAPHOS (10.8 mg, 1.40 x 10^{-2} mmol), Rh(acac)$(CO)_2$ (0.90 mg, 3.5 x 10^{-3} mmol), and benzene (0.4 ml) were placed in a 20-mL Schlenk tube. The mixture was degassed by freeze-thaw cycles for three times and then transferred into an autoclave under argon. The reaction was carried out at 50 °C for 47 h under H_2 / CO (1 / 1) pressure of 100 atm. The conversion of **4a** (76%) and the ratio of 2-methyl-3-(*tert*-butylsulfenyl)propanal (**5a**) / 4-(*tert*-butylsulfenyl)butanal (**6a**) (56 / 44) were determined by ^{1}H NMR analysis. The enantiomeric excess (64% *ee*) was determined by H NMR analysis of MTPA ester of the corresponding alcohol obtained by the reduction with $NaBH_4$ / MeOH. **5a**: ^{1}H NMR ($CDCl_3$) δ 1.21 (d, *J* = 6.9 Hz, $CHCH_3$), 1.33 (s, $C(CH_3)_3$), 2.5—2.6 (m, SCH(H)CH), 2.8—2.9 (m, SCH(H)CH), 9.68 (d, *J* = 1.3 Hz, CHO). Anal. Calcd. for $C_8H_{16}OS$: C, 59.95; H, 10.06. Found: C, 59.88; H, 9.83.

*Hydroformylation of Allyl Phenyl Sulfide (**4b**)*

To a 20 mL Schlenk tube were added allyl phenyl sulfide (**4b**) (328 mg, 2.18 mmol), (*R,S*)-BINAPHOS

(7.4 mg, 9.7 x 10^{-3} mmol), $Rh(acac)(CO)_2$ (0.57 mg, 2.2 x 10^{-3} mmol), and benzene (1.2 ml). The mixture was degassed by freeze-thaw cycles for three times and was transferred into an autoclave, which was stirred at 50 °C for 48 h under H_2 / CO (1 / 1) pressure of 100 atm. The conversion of the reactant (100%) and the ratio of 2-methyl-3-phenylthiopropanal (**5b**) / 4-phenylthiobutanal (**6b**) (67 / 33) were determined by ^1H NMR analysis. The enantiomeric excess (80% *ee*) was determined by ^1H NMR analysis of the MTPA ester of the alcohol obtained by the reduction of **5b** with $NaBH_4$ in MeOH. **5b**: ^1H NMR (C_6D_6) δ 0.93 (d, J = 7.9 Hz, $CHC\underline{H}_3$), 2.22 (m, C<u>H</u>CHO), 2.59 (d of ABq, J = 7.3 and 13.5 Hz, $SC\underline{H}(H)$), 3.06 (d of ABq, J = 6.3 and 13.5 Hz, $SCH(\underline{H})$), 7.0—7.2 (m, 2H) and 7.3—7.4 (m, 3H) (aromatic protons), 9.33 (d, J = 1.3 Hz, CHO). Anal. Calcd. for $C_{10}H_{12}OS$: C, 66.63; H, 6.71. Found: C, 66.37; H, 6.69.

Synthesis of Allyl Phenyl Sulfone (7)

Allyl phenyl sulfone (**7**) was synthesized according to the literature procedure (71% yield).[12] ^1H NMR ($CDCl_3$) δ 3.81 (d with fine splitting, J = 7.3 Hz, SO_2CH_2), 5.15 (d with fine splitting, J = 17.2 Hz, $CH{=}C\underline{H}_2$ (trans), 5.33 (d with fine splitting, J = 9.2 Hz, $CH{=}C\underline{H}_2$ (cis)), 5.7—5.9 (m, $SO_2CH_2C\underline{H}$), 7.5—7.7 (m, 3H, aromatic protons), 7.8—7.9 (m, 2H, aromatic protons).

Hydroformylation of Allyl Phenyl Sulfone (7)

A solution of allyl phenyl sulfone (**7**) (199 mg, 0.91 mmol), (*R,S*)-BINAPHOS (6.8 mg, 8.8 x 10^{-3} mmol), $Rh(acac)(CO)_2$ (0.52 mg, 2.0 x 10^{-3} mmol) in benzene (1.2 ml) was prepared in a 20-mL Schlenk tube under argon, which was transferred into an autoclave and stirred at 40 °C for 46 h under H_2 / CO (1 / 1) pressure of 100 atm. The conversion of **7** (75%) and the ratio of 2-methyl-3-(phenylsulfonyl)propanal (**8**) / 4-(phenylsulfonyl)butanal (**9**) (86 / 14) were determined by ^1H NMR analysis. The enantiomeric excess was determined by ^{19}F NMR analysis of the corresponding MTPA esters derived from the alcohols obtained by the reduction of the products with $NaBH_4$ / MeOH. The sign of specific rotation of the major enantiomer was (+). **8**: ^1H NMR ($CDCl_3$) δ 1.35 (d, J = 7.3 Hz, CH_3), 2.98 (d of ABq, J = 6.9 and 13.9 Hz, $SO_2CH(\underline{H})$), 3.0—3.1 (m, C<u>H</u>CHO), 3.71 (d of ABq, J = 5.0 and 13.9 Hz, $SO_2CH(\underline{H})$), 7.5—7.7 (m, 3H, aromatic protons), 7.9—8.0 (m, 2H, aromatic protons), 9.60 (s, CHO). HRMS (CI); Calcd. for $C_{10}H_{12}O_3S$ (M^+ + H): 213.0585. Found: 213.0607.

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