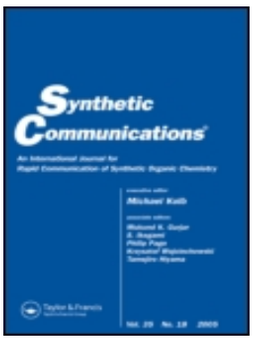

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CATALYTIC ASYMMETRIC OXIDATION OF SULFIDES MEDIATED BY A SERIES OF NOVEL OXAZOLINES-TITANIUM COMPLEXES

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ABSTRACT

A series of chiral oxazoline-titanium complexes were found to be efficient catalysts for the enantioselective oxidation of sulfides. The reactivity and enantioselectivity were strongly influenced by the structure of the oxazolines. When (4*S*,5*S*)-4,5-dihydro-4,5-diphenyl-2-(2′-hydroxy-3′-*tert*-butylphenyl) oxazoline was used as ligand, the sulfoxide was obtained in 96%e.e.

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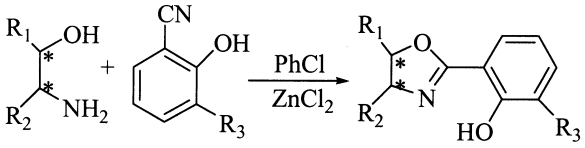
Optically active sulfoxides have been increasingly used as building blocks and chiral auxiliaries in asymmetric synthesis.[1] The most attractive method for their preparation is the enantioselective oxidation of the readily available prochiral sulfides. In the past several years, the asymmetric oxidation of sulfides had constituted a very active research area, and excellent results had been obtained.[2–10] In those asymmetric catalytic reactions, the ligands were mainly limited in the chiral diols and Schiff bases. Oxazoline as a class of chiral ligands had been successfully employed in the asymmetric Baeyer-Villiger reaction,[11] Mukaiyama Aldol reaction, cyclopropanation reaction, and many other catalytic asymmetric reactions.[12] Bolm tried to use bis[(4*S*)-4-isopropyl-4,5-dihydro-2-(oxazolinyl)phenolato]oxovanadium-(IV) as catalyst to mediate the oxidation of methyl phenyl sulfide, but he obtained racemic sulfoxide.[13] These results prompted us to explore the feasibility of catalytic enantioselective oxidation of sulfides using chiral oxazoline-titanium complexes as catalysts. We thought that if we design some oxazolines with suitable structure, we could achieve this transformation with good enantioselectivity. Herein, we wish to report our efforts in the study of enantioselective oxidation of sulfides catalyzed by chiral oxazoline-titanium complexes.

The chiral oxazolines (**1a–1f**) were prepared via the reaction of the corresponding amino alcohols and nitriles (Scheme 1).[14]



(4*S*, 5*R*)-**1a**: R_1=R_2=Ph, R_3=*t*-Bu
(4*S*, 5*S*)-**1b**: R_1=R_2=Ph, R_3=*t*-Bu
(4*S*, 5*R*)-**1c**: R_1=R_2=Ph, R_3=H
(4*S*, 5*S*)-**1d**: R_1=R_2=Ph, R_3=H
(4*S*)-**1e**: R_1=H, R_2=Ph, R_3=*t*-Bu
(4*S*)-**1f**: R_1=H, R_2=$PhCH_2$, R_3=*t*-Bu

Scheme 1.

Our studies started with methyl phenyl sulfide as a test substrate (Table 1). The oxidation reaction of sulfide with *tert*-butylhydroperoxide (TBHP) was carried out in CH_2Cl_2/CCl_4 at 0°C for 24 h catalyzed by the complexes formed *in situ* from a series of oxazolines, titanium alkoxide and water (Scheme 2).

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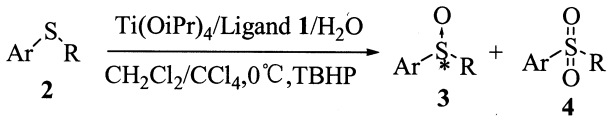
Table 1. The Enantioselective Oxidation of Methyl Phenyl Sulfide by TBHP in the Presence of $Ti(O^iPr)_4$ and Chiral Ligands[a]

Entry	Ligand	Yield (%)[b]		Selectivity		Configuration of 3[d]
		Total yield	Sulfoxide (3)	Chemo (3:4)	E.e. of 3 (%)[c]	
1	1a	67	41	62:38	11	*R*
2	1b	66	31	48:52	72	*R*
3	1c	23	23	100:0	9	*R*
4	1d	58	13	78:22	12	*R*
5	1e	72	40	56:44	9	*S*
6	1f	96	68	70:30	0	

[a]Conditions: sulfide/oxazoline 1/$Ti(O^iPr)_4$/H_2O = 1.0/0.1/0.05/1.0; reaction temperature = 0°C; reaction time = 24 h; 1.1 equiv. of TBHP(*tert*-butyl hydroperoxide, 70% in water) was used; CH_2Cl_2/CCl_4 = 3:7 was used as solvent; [b]Isolated yield; [c]Determined by HPLC on a Daicel Chiralcel OB column; [d]The absolute configuration was assigned by comparison with literature values.[2a,7a]



Scheme 2.

The results listed in Table 1 indicated that the chemoselectivity and enantioselectivity were strongly influenced by the structure of the oxazolines. **1b** was found to be the most efficient ligand and gave 72% e.e. for the sulfoxide. If the configuration of C(5) in the oxazoline was inverted from S to R, the e.e. of the sulfoxide was found to decrease from 72% to 11% (Table 1, entries 2 and 1). If the phenyl group attached to C(5) was replaced by H, opposite configuration of sulfoxide was observed (Table 1, entries 2 and 5). So the configuration of C(5) had a strong influence on the enantioselectivity. The substituent attached to C(4) had an influence on the enantioselectivity too. When the phenyl was replaced by a benzyl, the e.e. of the sulfoxide decreased from 9% to 0 (Table 1, entries 5 and 6). The *tert*-butyl group (R_3) was also necessary for good enantioselectivity. For example, when the chiral oxazoline changed from **1b** to **1d**, only 12% e.e. was obtained in the sulfoxide (Table 1, entry 4).

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We screened a series of solvents including C_6H_6, C_7H_8, Et_2O, THF, CH_2Cl_2, CCl_4, DCE (1,2-dichloroethane) and investigated their function on the reaction. A mixture of CH_2Cl_2 and CCl_4 ($CH_2Cl_2/CCl_4 = 3{:}7$) was found to give the best results in both chemoselectivity and enantioselectivity. The oxidation of methyl phenyl sulfide with Ti(IV)-**1b** as catalyst and 1.4 equiv. of oxidant, the enantioselectivity was found to be 63% e.e. in CH_2Cl_2 and 70% e.e. in CCl_4, respectively. However, when a mixed solvent ($CH_2Cl_2/CCl_4 = 3{:}7$) was used under identical conditions, the enantioselectivity increased to 80% e.e. Further studies showed that the influence of the ligand-to-metal ratio was not obvious for both the reactivity and selectivity. The best results were obtained when 2.0 equivalents of oxazoline were used per Ti (Table 1, entry 2). We also investigated the effect of the amount of catalyst on the chemoselectivity and enantioselectivity of the reaction. The chemoselectivity and enantioselectivity were not obviously influenced by the catalyst level too. The best catalyst level used was 5 mol%. The effect of temperature was also tested. The experiments showed that the reactivity and enantioselectivity varied with the temperature from $-25^{\circ}C$ to $20^{\circ}C$. An optimum reaction temperature was found to be $0^{\circ}C$. We optimized the amount of water and the kind of oxidant in this reaction system. The influence of the amount of water was not obviously in the range of literature reported,[6b] the best amount of water relative to the sulfide was 1.0 equiv. We also found that TBHP (70% in water) was superior to TBHP (5–6 M in decane), H_2O_2 (30%) and MCPBA.

A phenomenon of kinetic resolution was observed in the enantioselective oxidation of sulfides. When other reaction conditions were kept constant in the oxidation of methyl phenyl sulfide, the amount of oxidant increased from 1.1 equiv. to 1.4 equiv., the yield of sulfoxide increased from 31% (72%e.e.) to 33% (80%e.e.). The isolated yield of sulfone increased from 35% to 54%. In order to confirm this phenomenon, racemic methyl phenyl sulfoxide was treated with 5 mol% Ti(O^iPr)$_4$/**1b** complex and 0.55 equiv. TBHP in CH_2Cl_2/CCl_4, the e.e. value of the recovered sulfoxide was found to be 45% (R) (isolated yield, 50%).

$$k_{rel} = k_f/k_s = \ln[(1 - C)(1 - \text{e.e.})/\ln(1 - C)(1 + \text{e.e.}) = 4$$

The $k_{rel}{}^{15}$ was lower than the literature reported ($k_{rel}{}^{15}$).[6c] So this system was inferior to the Ti-binaphthol complex in the catalytic kinetic resolution of sulfoxides.

Encouraged by the result obtained for the enactioselective oxidation of methyl phenyl sulfide, we investigated other sulfides by using the [(**1b**)$_2$-Ti(O^iPr)$_4$] catalyst system. As shown in Table 2, moderate isolated yield and good to high e.e.'s were obtained for most of substrates. In the

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Table 2. The Enantioselective Oxidation of Sulfides (ArSR)[a]

			Yield (%)[b]		Enantioselectivity	
Entry	Ar	R	Total yield	Sulfoxide (3)	Chemo (3:4)	E.e of 3 (%)[c]
1	Ph	Me	87	33	38:62	80 (*R*)
2[d]	Ph	Me	95	16	17:83	96 (*R*)
3	Ph	Et	79	32	41:59	72 (*R*)
4	p-BrC_6H_4	Me	78	27	34:66	75 (*R*)
5	p-MeC_6H_4	Me	90	38	42:58	81 (*R*)
6	Ph	$PhCH_2$	86	37	43:57	70 (*R*)[e]
7	Pyridyl	Me	88	50	57:43	21 (*R*)

[a]Conditions: sulfide/ligand-**1b**/$Ti(O^iPr)_4/H_2O = 1.0/0.1/0.05/1.0$; reaction temperature = 0°C; reaction time = 24 h; 1.4 equiv. of TBHP (70% in water) was used; $CH_2Cl_2/CCl_4 = 3{:}7$ was used as solvent; [b]Isolated yield; [c]Determined by HPLC on a Daicel Chiralcel OB column; [d]CCl_4 as solvent, 2.0 equiv. of TBHP (70% in water) was used; [e]Determined by HPLC on a Daicel Chiralcel OD column.

oxidation of methyl pyridyl sulfide, only 21%e.e. was obtained (Table 2, entry 7). When 2.0 equiv. of TBHP was used in the oxidation of methyl phenyl sulfide, up to 96%e.e. was obtained, even though the chemoselectivity was lower (ratio of **3** and **4** was 17:83) (Table 2, entry 2). The high e.e. might be due to concomitant kinetic resolution of the sulfoxide.

In conclusion, we have first probed and set up a novel oxazoline-titanium catalytic system for the enantioselective oxidation of sulfide. Good to high enantiomeric excess was obtained (up to 96%e.e.). Further efforts will be devoted to the optimization of the oxazoline structure to enhance both chemoselectivity and enantioselectivity for the enantioselective oxidation of sulfides.

EXPERIMENTAL

Melting points were determined on a Southend SS25PH apparatus and were uncorrected. Elemental analyses were recorded on a Carlo Erba-1106 instrument. HPLC analyses were performed on a Beckman-110A chromatography with a Beckman 165 variable wavelengh detector. ^{1}H-NMR and ^{13}C-NMR spectra were performed on a Bruker 300 MHz NMR spectrometer. Optical rotations were measured on a Perkin-Elmer 341 polarimeter. OB and OD Column was purchased from Daicel Chemical Industries, LTD.

General Procedure for the Syntheses of Oxazolines

In a 50 mL three-necked flask, 27.2 mg (0.2 mmol) of zinc chloride was melted under high vacuum and cooled under argon. After cooling to room temp., 10 mL of chlorobenzene was added followed by 5 mmol of the corresponding benzonitrile and 5 mmol of the amino alcohol. The mixture was refluxed for 20 h. The solvent was removed under reduced pressure to give an oily residue, which was dissolved in 20 mL dichloromethane. The solution was extracted for three times with 20 mL of water and the aqueous phase with 10 mL of dichloromethane. The combined organic phases were dried over anhydrous sodium sulfate and the solvent was removed in vacuum. The residue was purified by flash chromatography (petroleum ether/ethyl acetate 40:1).

(4*S*,5*R*)-4,5-Dihydro-4,5-diphenyl-2-(2′-hydroxy-3′-*tert*-butylphenyl)-oxazoline 1a: (1.19 g, 65%); Yellow solid; M.p. = 145∼146°C; $[\alpha]_D^{25} = -9.8°$ (c 0.24, EtOH); IR (mull) ν (cm^{-1}) 1633 (C = N), 1251 (C-O-C), 1213 (C-OH). ^{1}H-NMR ($CDCl_3$, 300 MHz); δ 1.47 (s, 9H, $C(CH_3)_3$), 5.81 (d, 1H, J = 10.09 Hz, NCH), 5.98 (d, 1H, J = 10.1 Hz, OCH), 6.88 (t, 1H, J = 7.72 Hz, ArH), 7.04 (m, 10H, ArH), 7.47 (dd, 1H, J = 7.75 Hz, 1.45 Hz, ArH), 7.76 (dd, 1H, J = 7.77 Hz, 1.43 Hz, ArH), 12.76 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 167.9, 160.3, 138.1, 137.8, 136.54, 131.64, 128.45, 128.42, 128.39, 128.36, 127.91, 127.12, 116.72, 110.96, 84.94, 73.99, 35.74, 30.11. EIMS (M/Z): 371 (M^+), 204, 161, 91 (100), 77, 41. Anal. Calcd for $C_{25}H_{25}NO_2$: C, 80.83; H, 6.78; N, 3.77. Found: C, 80.96; H, 6.90; N, 3.87.

(4*S*,5*S*)-4,5-Dihydro-4,5-diphenyl-2-(2′-hydroxy-3′-*tert*-butylphenyl)-oxazoline 1b: (1.54 g, 84%); Yellow solid; M.p. = 94 ∼ 95.5°C; $[\alpha]_D^{25} = +94.4°$ (c 0.77, EtOH); IR (mull) ν (cm^{-1}): 1632 (C = N), 1251 (C-O-C), 1208 (C-OH); ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.46 (s, 9H, C $(CH_3)_3$), 5.28 (d, 1H, J = 7.8 Hz, NCH), 5.36 (d, 1H, J = 7.8 Hz. OCH), 6.84 (t, 1H, J = 7.86 Mz, ArH), 7.35 (m, 10H, ArH), 7.44 (dd, 1H, J = 7.71 Hz, 1.41 Hz, ArH), 7.71 (dd, 1H, J = 7.92 Hz, 1.38 Hz, ArH), 12.67 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 167.0, 160.2, 141.9, 140.2, 138.0, 131.5, 129.6, 129.3, 128.6, 127.2, 127.1, 126.5, 118.6, 111.0, 88.6, 78.3, 35.7, 30.0; EIMS (M/Z): 371 (M^+), 204 (100), 161, 91, 77, 41. Anal. Calcd for $C_{25}H_{25}NO_2$: C, 80.83; H, 6.78; N, 3.77; Found: C, 80.92; H, 6.78; N, 3.76.

(*4S*,*5R*)-4,5-Dihydro-4,5-diphenyl-2-(2′–hydroxyphenyl)oxazoline 1c: (1.09 g, 69%); M.p. = 51–52°C; $[\alpha]_D^{20} = -42.4°$(c 1.53, EtOH); IR (mull) ν (cm^{-1}) 3030 (O-H), 1641 (C = N), 1490, 1258, 1069; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 4.8 (s, 1H, OH), 5.77 (d, 1H, J = 10.02 Hz, NCH), 5.96 (d, 1H, J = 10.02 Hz, OCH), 6.9 (m, 5H, ArH), 7.0 (m, 5H, ArH), 7.4 (m, 3H, ArH), 7.84 (d, 1H, J = 7.74 Hz, ArH): ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 167.2, 161.0, 137.7, 136.3, 134.5, 131.4, 129.2, 129.1, 129.0, 128.9, 128.6,

128.46, 128.3, 127.9, 127.6, 127, 119.5, 117.6, 110.9, 85.2, 73.8; EMIS (M/Z): 315 (M^+), 209, 195, 148, 121, 104, 91 (100), 77, 65, 51, 39, 27; Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44; Found: C, 79.95; H, 5.56; N, 4.40.

(4*S*,5*S*)-4,5-Dihydro-4,5-diphenyl-2-(2′-hydroxyphenyl)oxazoline 1d: (1.34 g, 85%); M.p. = 70 ~ 71°C; $[\alpha]_D^{20} = +42.9°$(c 0.99, EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.28 (d, 1H, J = 7.83 Hz, NCH), 5.36 (d, 1H, J = 7.71 Hz, OCH), 6.91 (t, 1H, J = 7.60 Hz, ArH), 7.07 (d, 1H, J = 8.43 Hz, ArH), 7.4 (m, 11H, ArH), 7.8 (d, 1H, J = 7.89 Hz, ArH), 12.1 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 165.9, 160.4, 140.6, 138.9, 134.2, 129.0, 128.97, 128.91, 128.5, 128.1, 126.4, 125.9, 118.8, 117.1, 109.6, 88.5, 76.7. IR (mull) v (cm^{-1}) 3028 (O-H), 1642 (C = N), 1617, 1584, 1455, 1258, 1065; EIMS (M/Z): 315 (M^+), 209 (100), 195, 165, 148, 121, 105, 89, 77, 65, 51, 28; Anal. Calcd for $C_{21}H_{17}NO_2$:C, 79.98; H, 5.43; N, 4.44; Found: C, 79.96; H, 5.55; N, 4.35.

(4*S*)-4,5-Dihydro-4-phenyl-2-(2′-hydroxy-3′-*tert*-butylphenyl)oxazoline 1e: (0.99 g, 67%); M.p. = 139~140°C; $[\alpha]_D^{20} = +69.7°$ (c 0.90, EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.35 (s, 9H, $C(CH_3)_3$), 4.12 (t, 1H, J = 8.35 Hz, NCH), 4.66 (t, 1H, J = 9.24 Hz, OCH), 5.35 (t, 1H, J = 9.18 Hz, OCH), 6.74 (t, 1H, J = 7.74 Hz, ArH), 7.27 (m, 6H, ArH), 7.53 (d, 1H, J = 7.71 Hz, ArH), 12.6 (s, 1H, OH); ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 166.9, 159.2, 141.5, 137.2, 130.6, 128.8, 127.8, 126.5, 126.2, 117.8, 110.4, 73.7, 68.8, 34.9, 29.3; IR (mull) v (cm^{-1}) 3031 (O-H), 1628 (C = N); EIMS (M/Z): 295 (M^+), 280, 252, 161 (100), 120, 91, 77, 65, 41, 27; Anal. Calcd for $C_{19}H_{21}NO_2$, C, 77.26, H, 7.17, N, 4.74; Found: C, 76.99, H, 7.23, N, 4.57.

(4*S*)-4,5-Dihydro-4-benzyl-2-(2′-hydroxy-3′-*tert*-butylphenyl)oxazoline 1f: (1.24 g, 80%); M.p. = 39~40°C; $[\alpha]_D^{20} = +13.4°$(c 0.74, EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.44 (s, 9H, $C(CH_3)_3$), 2.78 (dd, 1H, J = 13.71 Hz, 8.07 Hz; PhCH), 3.17 (dd, 1H, J = 13.71 Hz, 5.94 Hz; PhCH), 4.1 (t, 1H, J = 7.92 Hz, OCH_2); 4.35 (t, 1H, J = 8.76 Hz, OCH_2), 4.62 (m, 1H, NCH), 6.8 (t, 1H, J = 7.74 Hz, ArH), 7.3 (m, 6H, ArH), 7.5 (d, 1H, J = 6.87 Hz, ArH), 12.7 (s, 1H); ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 166.1, 159.1, 137.6, 137.1, 130.4, 129.1, 128.6, 126.6, 126.0, 117.7, 110.5, 70.9, 66.7, 41.8, 34.9, 29.3; IR (mull) v (cm^{-1}) 3050 (O-H), 1633 (C = N), 1497, 1455, 1433, 1367, 1252, 1211; EIMS (M/Z): 309 (M^+), 294, 266, 218, 176, 161, 132, 105, 91 (100), 77, 65, 51, 41, 27; Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53; Found: C, 77.56; H, 7.52; N, 4.44.

General Procedure for the Asymmetric Oxidation of Sulfides

To a solution of oxazoline (0.05 mmol) in a suitable solvent was introduced $Ti(O^iPr)_4$ (0.025 mmol) by means of a syringe under an argon

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atmosphere. This solution was stirred for 2 h at rt. and the solvent was removed under reduced pressure, and then an appropriate solvent (2.5 mL) and water (9 mL) were added. After the mixture was stirred at rt. for 1 h, the sulfide (0.50 mmol) was introduced by means of a syringe and the mixture was cooled to the appropriate temperature. After 0.5 h, TBHP (70% in water) was introduced by means of a syringe, and the mixture was stirred for 24 h. The reaction mixture was directly purified by flash chromatograph. (petroleum ether/ethyl acetate 2:1).

Methyl phenyl sulfoxide: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.72 (s, 3H), 7.58 (m, 5H, ArH); IR (KBr) ν (cm^{-1}) 1477, 1443, 1415, 1089, 1036 (S=0). (R) 81% e.e.; $[\alpha]_D^{27} = +34.4^\circ$(c 0.36, CH_3COCH_3).

***p*-Methylphenyl methylsulfoxide**: ^{1}H-NMR($CDCl_3$, 300 MHz): δ 2.42 (s, 3H, $PhCH_3$), 2.71 (s, 3H, $SOCH_3$), 7.33 (d, 2H, $J = 7.98$ Hz, ArH), 7.54 (d, $J = 7.89$ Hz, 2H, ArH); IR(KBr) ν(cm^{-1}) 1493, 1421, 1088, 1048 (S, S=O). (R) 80.7% e.e.; $[\alpha]_D^{27} = +53.5^\circ$ (c 1.0, CH_3COCH_3).

***p*-Bromophenyl methylsulfoxide**: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.72 (s, 3H, CH_3), 7.60 (m, 4H, ArH); IR (KBr) ν(cm^{-1}) 1469, 1417, 1387, 1084, 1043 (S=O), 1008, 516 (C-Br). (R) 75% e.e.; $[\alpha_D^{27}] = +37.6^\circ$ (c 0.60, CH_3COCH_3).

Ethyl phenyl sulfoxide: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.20 (t, 3H, $J = 7.36$ Hz, CH_3), 2.80 (m, 2H, CH_2), 7.60 (m, 5H, ArH); IR (KBr) ν (cm^{-1}) 1443, 1086, 1044 (S=O), 1021. (R) 71.8% e.e.; $[\alpha]_D^{27} = +65.2^\circ$ (c 1.0, CH_3COCH_3).

Benzylphenyl sulfoxide: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 4.0 (d, 1H, $J = 12.57$ Hz, CH_2), 4.06 (d, 1H, $J = 12.57$ Hz, CH_2), 6.96–7.45 (m, 10H, ArH); IR (KBr) ν(cm^{-1}) 1494, 1455, 1034 (S=O). (R) 70% e.e.; $[\alpha]_D^{27} = +75.5^\circ$(c 1.56, CH_3COCH_3).

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