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(Salen)Ti(IV) complex catalyzed asymmetric ring-opening of epoxides using dithiophosphorus acid as the nucleophile

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Abstract

A series of chiral bis-Schiff bases were synthesized starting from (1*R*,2*R*)-(+)-diaminocyclohexane, (+)-*cis*-1,2,2-trimethyl-1,3-diaminocyclopentane, (*R*)-2,2′-diamino-1,1′-binaphthalene, and (1*S*,2*S*)-diphenyl-1,2-ethanediamine. The enantioselective ring-opening of *meso* epoxides with dithiophosphorus acids catalyzed by a (salen)Ti(IV) complex formed *in situ* upon the treatment of Ti(OPr-*i*)$_4$ and the aforementioned chiral Schiff base was realized. The resulting products were obtained with low to good enantioselectivities (up to 73% ee). The (salen)Ti(IV) complex containing the backbone of 1,2-diaminocyclohexane exhibited the best enantioselectivity. The substituents in dithiophosphorus acids and those on the salen aromatic ring have a significant influence on the reaction. Moderate enantioselectivity were obtained for the (salen)Ti(IV) complex catalyzed ring-opening of racemic monosubstituted epoxides. High regioselectivity was observed for the alkyl substituted epoxides, whereas poor regioselectivity was obtained for the aryl substituted ones.

Keywords: (Salen)Ti(IV) complex; Asymmetric ring-opening; Epoxide; Dithiophosphorus acid

1. Introduction

As an important strategy for the formation of 1,2-bifunctionalized chiral building blocks, the enantioselective ring-opening of epoxides with different nucleophiles has attracted much attention from the organic chemists. A wide variety of nucleophiles, such as alcohols, phenols, carboxylic acids, amines, azide ions, thiols, cyanide ions and halide ions are utilized in the aforementioned reaction [1]. Among them, sulfur nucleophiles are important ones, which lead to the formation of synthetically valuable β-hydroxylsulfides or β-hydroxymercaptan. The common used sulfur nucleophiles are alkane- or arenethiol [2]. In addition, some other sulfur nucleophiles containing silicon [3] or phosphorus [4] have also been documented. A lot of good results were obtained in the asymmetric ring-opening of *meso* epoxides with nitrogen, oxygen, carbon nucleophiles as well as halogen ions in recent years, while few deals with the sulfur nucleophiles. Almost all the few reported sulfur nucleophiles in asymmetric ring-opening of *meso* epoxides are thiols or thiophenols. In 1988, Yamashita reported a catalytic asymmetric ring-opening of epoxides with thiols using a zinc tartrate catalyst to provide β-hydroxysulfides in good yield and enantioselectivity [2l]. Although high enantioselectivity was obtained by Shibasaki employing gallium–lithium (*R*)-binaphthoxide as the catalyst, the nucleophile was limited to *tert*-butylthiol [2h]. Jacobsen has realized the (salen)Cr(III)-catalyzed asymmetric ring-opening of *meso* epoxides. High enantioselectivity was observed when dithiol was employed as the nucleophile, whereas the reaction was poorly enantioselective when monothiols was used [2g]. Dai has also investigated the (salen)Ti(IV)-catalyzed ring-opening of epoxides. The resulting β-hydroxysulfides were formed only with moderate ee values [2f]. Some outstanding results are obtained in the chiral catalytic kinetic resolution of racemic epoxides, especially for monosubstituted epoxides. The most used ring-opening reagents are oxygen and nitrogen nucleophiles

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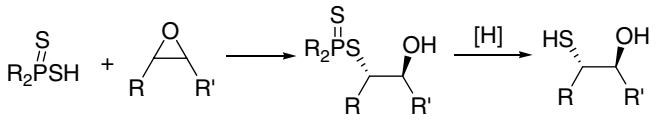
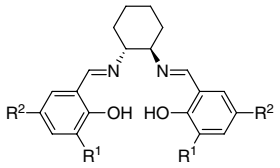
[1a,5]. Yamashita reported the only one catalytic kinetic resolution of racemic epoxides using thiol as the nucleophile, while the corresponding product was obtained only with a highest selectivity of 27% ee [2l]. As for asymmetric ring-opening of monosubstituted epoxide only one example was documented using halogen ion as the nucleophile, and the resulting product was obtained with poor regioselectivity and enantioselectivity [6]. There is no report about the application of sulfur nucleophiles in the asymmetric ring-opening of racemic monosubstituted epoxides.

Although several examples were documented about the reaction of *O*,*O*-diethyl dithiophosphoric acid with α-substituted epoxides since Pudovik firstly reported this type of reaction in 1965 [4c,4d,4e]. However, there has no systematic investigation on the regio- and stereoselectivity of this reaction. Recently, highly regio- and stereoselective ring-opening of epoxides was realized employing a series of organic dithiophosphorus acids as the nucleophiles under mild conditions without any catalyst in our research group. The corresponding products could afford the synthetically valuable β-hydroxymercaptan through reduction [4a]. This procedure has provided a new convenient and practical method for the synthesis of this type of compounds in terms of the mild reaction condition and ready availability of the nucleophile dithiophosphoric acid. Based on these results, herein we will report the chiral (salen)Ti(IV) complex catalyzed enantioselective ring-opening of epoxides with dithiophosphorus acids.

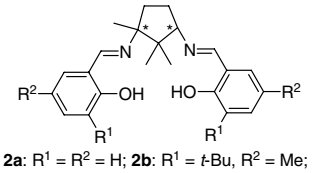


2. Results and discussion

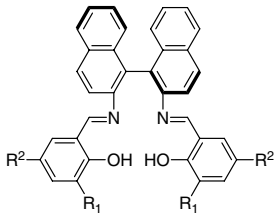
Chiral salen ligands 1, 2, 3, and 4 were synthesized according to the literature procedure [7–10].



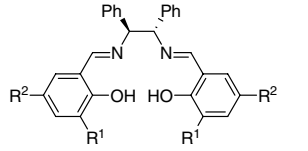
1a: $R^1 = R^2 = H$; **1b**: $R^1 = t$-Bu, R^2 = Me; **1c**: $R^1 = R^2 = t$-Bu; **1d**: $R^1 = R^2 = t$-Pentyl; **1e**: R^1 = Cl, R^2 = Br



2a: $R^1 = R^2 = H$; **2b**: $R^1 = t$-Bu, R^2 = Me; **2c**: $R^1 = R^2 = t$-Bu; **2d**: $R^1 = R^2 = t$-Pentyl; **2e**: $R^1 = R^2$ = Cl



3a: $R^1 = R^2 = H$; **3b**: $R^1 = R^2 = t$-Bu; **3c**: R^1 = t-Bu, R^2 = OMe



4a: $R^1 = R^2 = t$-Bu; **4b**: $R^1 = t$-Bu, R^2 = Me

The reaction conditions were optimized using the (salen)Ti(IV) complex formed *in situ* upon the treatment of a 1:1 mixture of chiral salen ligand **1c** and Ti(OPr-*i*)$_4$ catalyzed ring-opening of cyclohexene epoxide with *O*,*O*-diethyl dithiophosphoric acid as the model reaction. After evaluation of a number of solvents, arene, such as toluene and benzene, was found to be the best solvent, which resulted in the best results both in yield and ee value. The better ones for this reaction were THF, diethyl ether, hexane, and methylene chloride. The reaction was worst conducted in DMF, which led to quite low yield and enantioselectivity. The enantioselectivity was almost independent of the amount of the chiral Schiff base used when the loading of the chiral Schiff base was varied from 50 mol% to 10 mol%. However, further reduction the amount of chiral Schiff base to 5 mol% resulted in a decrease both in yield and enantioselectivity. Thus, the optimal loading of the chiral Schiff base was 10 mol%. Moreover, the reaction was carried out at different temperature variation from −78 °C to 50 °C to determine the optimal reaction temperature. Satisfactory results were obtained for those conducted at 0–25 °C.

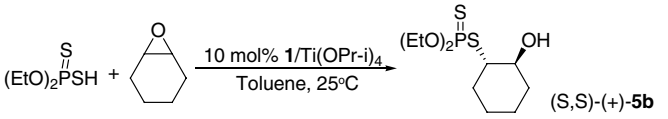
We have done some additional experiments to clarify the role of the chiral catalysts. First, racemic product was obtained for the blank experiment using only the chiral Schiff base **1c**. Second, the corresponding ring-opening product was obtained with 69% ee when isolated chiral (salen)Ti complex prepared from salen **1c** and Ti(OPr-*i*)$_4^{II}$ [11] was employed as the catalyst, which was matched to the results observed for the (salen)Ti complex formed *in situ* upon the treatment of **1c** and Ti(OPr-*i*)$_4$. Therefore, it is very clear that the desired chiral Ti complexes bearing the salen ligand do be formed, and function as the catalysts in the reaction.

A series of chiral salen ligand **1**/Ti(OPr-*i*)$_4$ catalyzed asymmetric ring-opening of cyclohexene epoxide with *O*,*O*-diethyl dithiophosphoric acid was examined under the aforementioned optimal reaction conditions (10 mol% of chiral Schiff base, 25 °C, and toluene as the solvent). The results are listed in Table 1.

As shown in Table 1, the nature of the chiral salen ligand **1** was found to be an essential factor to this reaction. For example, better catalytic activity (excellent chemical yield and good enantioselectivity) was observed for those have bulky group substituted at 3 and 5-position on the salen aromatic ring, such as **1c** and **1d**. This finding revealed that steric effect plays an important role in the reaction. Moreover, electronic effect of the substituent on the salen aromatic ring also has a significant influence on the reaction. For instance, compound **1e** containing electron-withdrawing group led to the worst result (only 21% ee was observed, entry 5).

With these results, we have extended the application of chiral salen ligand **1c**, which demonstrated the best catalytic activity, to other substrates. The results from **1c**/Ti(OPr-*i*)$_4$ catalyzed asymmetric ring-opening of *meso* cyclic epoxides with different ring size with a variety of dithiophosphorus acids are summarized in Table 2.

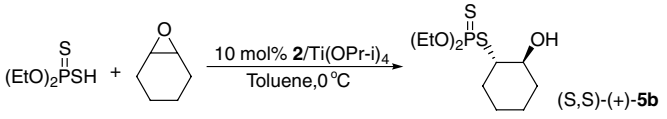
Table 1
1/Ti(OPr-*i*)$_4$ catalyzed ring-opening of cyclohexene epoxide with $(EtO)_2P(S)SH$



Entry	**1** (10 mol%)	Yield (%)[a]	ee (%) [b]	Configuration[c]
1	**a**	67	35	*S*,*S*
2	**b**	76	51	*S*,*S*
3	**c**	90	73	*S*,*S*
4	**d**	92	64	*S*,*S*
5	**e**	67	21	*S*,*S*

[a] Isolated yield.
[b] Determined by chiral HPLC analysis (OD column,hexane:isopropanol = 95:5, flow rate 1.0 mL/min, $t_{1(minor)} = 9.31$ min, $t_{2(major)} = 10.23$ min).
[c] According to Ref. [4a], compound **5b** was transformed into the configuration known (*S*,*S*)-(+)-2-hydroxycyclohexanemercaptan [2]. This process was retention of configuration. Thus, the absolute configuration of compound **5b** is 1*S*, 2*S*.

Table 3
2/Ti(OPr-*i*)$_4$ catalyzed ring-opening of cyclohexene epoxide with $(EtO)_2P(S)SH$



Entry	**2** (30 mol%)	Yield (%)[a]	ee (%)[b]	Configuration[d]
1	**a**	76	0[c]	/
2	**b**	87	62	*S*,*S*
3	**c**	83	15	*S*,*S*
4	**d**	81	13	*S*,*S*
5	**e**	84	4[c]	*S*,*S*

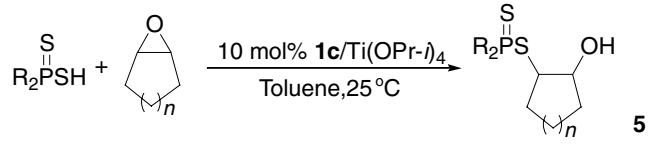
[a] Isolated yield.
[b] Determined by chiral HPLC analysis (OD column, hexane:isopropanol = 99:1, flow rate 1.0 mL/min, $t_{1(minor)} = 9.11$ min, $t_{2(major)} = 10.03$ min).
[c] Determined by comparison of specific rotation value: $[\alpha]_D$ +22.5 (*c* 2, CH_2Cl_2) with 73% ee. $[\alpha]_D$ 0 and +4 (*c* 2, CH_2Cl_2) for entries 1 and 5, respectively.
[d] See note 4 in Table 1.

As shown in Table 2, both the nature of the nucleophile, dithiophosphorus acid, and the substrate cyclic epoxide have a moderate influence on the enantioselectivity of the reaction. For example, the nucleophiles in which R equals to ethoxy or ethyl resulted in good enantioselectivity. The ee value of cyclohexene epoxide ($n = 2$) was higher than those of cyclopentene epoxide ($n = 1$) and cyclooctene epoxide ($n = 4$).

The results of (Salen)Ti(IV) complex formed *in situ* by the reaction of equivalent chiral salen ligand **2** and Ti(OPr-*i*)$_4$ catalyzed ring-opening of cyclohexene epoxide with *O*,*O*-diethyl dithiophosphoric acid are listed in Table 3.

As shown in Table 3, compared to salen **1**, lower catalytic activity in terms of enantioselectivity was obtained for the salen **2** derived from (+)-*cis*-1,2,2-trimethyl-1,3-diaminocyclopentane. Enantioselectivity of up to 62% ee was observed when the reaction was carried out at lower temperature (0 °C) with a 30 mol % loading of ligand **2b** which containing a bulky tertiary butyl group at the 3-position.

Table 2
Asymmetric ring-opening of *meso* epoxides with $R_2P(S)SH$



Product **5**	R	*n*	Yield (%)[a]	Ee (%)[b]
a	MeO	2	85	44
b	EtO	2	90	73
c	Et	2	89	69
d	Ph	2	92	60
e	EtO	1	93	53
f	EtO	4	89	66

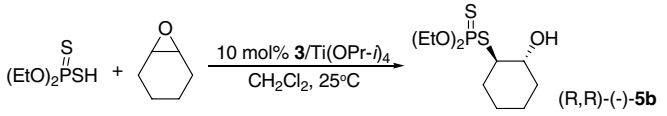
[a] Isolated yield.
[b] Determined by chiral HPLC analysis.

Salen ligand **3**/Ti(OPr-*i*)$_4$ catalyzed ring-opening of cyclohexene epoxide was carried out in methylene chloride because of its poor solubility in toluene and THF. The other conditions are same as the Salen ligand **1**/Ti(OPr-*i*)$_4$ catalyzed reaction. The results are listed in Table 4.

As shown in Table 4, the molar ratio of salen ligand **3** to Ti(OPr-*i*)$_4$ has a moderate influence on the enantioselectivity of the reaction. The results of the reaction conducted with a 1:3 or 1:4 molar ratio of **3** to Ti(OPr-*i*)$_4$ (entries 3 and 4) were better than those of the reaction carried out with a 1:1 or 1:2 molar ratio of **3** to Ti(OPr-*i*)$_4$ (entries 1 and 2). This phenomenon was not observed in the salen **1** and **2** Ti(OPr-*i*)$_4$ catalyzed ring-opening reaction. Salen ligand **3** are derived from aromatic diamine, which are distinguishable from the other three types of ligands. Therefore, the molar ratio of salen ligand **3** to Ti(OPr-*i*)$_4$ has a moderate influence on the enantioselectivity of the reaction, which may attribute to the increase of loading of Ti(OPr-*i*)$_4$ favored the formation of the chiral Ti complexes. Better enantioselectivity was observed for the reaction with a 20 mol% ligand loading compared to those with a 5 mol%, 10 mol% and 30 mol% ligand loading. As for the nature of the chiral salen ligand **3**, it was found that the existence of a bulky group substituted at the 3-position on the salen aromatic ring is necessary to the selectivity of the reaction, while the change of R^2 group at the 5-position exhibited less influence on the reaction. In addition, different to the results of salen ligand **1** and **2**, the major product of **3**/Ti(OPr-*i*)$_4$ catalyzed reaction has a *R*,*R* configuration.

Salen ligand **4**/Ti(OPr-*i*)$_4$ catalyzed ring-opening of cyclohexene epoxide with *O*,*O*-diethyl dithiophosphoric

Table 4
3/Ti(OPr-*i*)$_4$ catalyzed ring-opening of cyclohexene epoxide with $(EtO)_2P(S)SH$



Entry	**3** (mol%)	Ti(OPr-*i*)$_4$ (mol%)	Yield (%)[a]	ee (%)[b]	Configuration[d]
1	**3b** (10)	10	80	35	*R*,*R*
2	**3b** (10)	20	81	41	*R*,*R*
3	**3b** (10)	30	81	47	*R*,*R*
4	**3b** (10)	40	81	47	*R*,*R*
5	**3b** (5)	15	78	47	*R*,*R*
6	**3b** (10)	30	80	47	*R*,*R*
7	**3b** (20)	60	77	51	*R*,*R*
8	**3b** (30)	90	75	47	*R*,*R*
9	**3a** (10)	30	80	2[c]	*R*,*R*
10	**3c** (10)	30	75	41	*R*,*R*

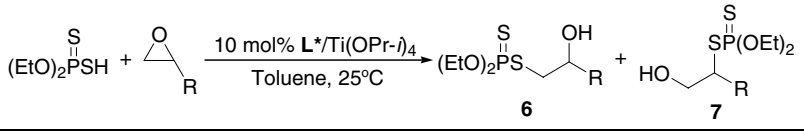
[a] Isolated yield.
[b] Determined by chiral HPLC analysis, OD column, hexane:isopropanol = 99:1, flow rate 1.0 mL/min, $t_{1(major)} = 9.11$ min, $t_{2(minor)} = 10.03$ min.
[c] Determined by comparison of specific rotation value: $[\alpha]_D$ +22.5 (*c* 2, CH_2Cl_2) with 73% ee. $[\alpha]_D$ −0.5 (*c* 2, CH_2Cl_2) for entry 9.
[d] See note 4 in Table 1.

acid was conducted in toluene at 0°C. The catalytic effect of salen ligand **4** was much worse than those of salen ligand **1**, **2** and **3**. For example, the corresponding ring-opening product was obtained in 89% yield with 19% ee for salen **4a**, and in 81% yield with 11% ee for ligand **4b**, respectively. The lack of rigidity of ligand **4** may be the major factor led to the low enantioselectivity of the ring-opening reaction.

The chiral catalytic ring-opening of racemic monosubstituted epoxides has been preliminarily investigated.[12] The results of L*/Ti(OPr-*i*)$_4$ catalyzed ring-opening of monosubstituted epoxides with *O*,*O*-diethyl dithiophosphoric acid are listed in Table 5.

As shown in Table 5, when R group in the epoxide equals to alkyl, the reaction took place with high regioselectivity and poor enantioselectivity (entries 1–3). When R equals to phenyl or substituted phenyl group, poor regioselectivity was observed, whereas better enantioselectivity was obtained (entries 5, 9, 11, 13). In some cases, moderate enantioselectivity was observed. The electronic nature of the substituent on the benzene ring of the substrate epoxide had a moderate influence on the reaction. The introduction of electron deficient group, such as chloro and nitro group, resulted in a moderate decrease of the regioselectivity (entries 8, 9, 12, 13), and vice versa (entry 10). Moreover, when unsubstituted or electron donating group substitute styrene oxide was used, the enantiomeric excess of product **6** which formed from the nucleophilic attack takes place at the unsubstituted carbon of the epoxide was higher than that of **7** which obtained from the nucleophilic attack takes place at the substituted carbon of the epoxide. When electron-withdrawing group substituted styrene oxide was employed, the enantiomeric excess of product **7** was higher than that of **6**. The nature of the chiral salen ligand was

Table 5
Asymmetric ring-opening of racemic monosubstituted epoxides with $(EtO)_2P(S)SH$



Entry	Product **6** or **7**	R	L[ast] (10 mmol%)	Yield (%)[a]	**6**:**7**[b]	ee%[c]	
						6	**7**
1	**a**	Et	**1b**	82	93:7	/	/
2	**b**	Pr	**1b**	52	91:9	24	–
3	**c**	CH_2Cl	**1b**	78	100:0	3	–
4	**d**	C_6H_5	**1a**	75	30:70	55	31
5	**d**	C_6H_5	**1b**	74	28:72	55	29
6	**d**	C_6H_5	**3b**	70	33:67	4	2
7	**d**	C_6H_5	**3c**	69	34:66	5	11
8	**e**	3-ClC_6H_4	**1a**	72	43:57	39	40
9	**e**	3-ClC_6H_4	**1b**	73	46:54	35	47
10	**f**	3-$MeOC_6H_4$	**1a**	71	25:75	42	24
11	**f**	3-$MeOC_6H_4$	**1b**	72	34:66	54	41
12	**g**	3-$O_2NC_6H_4$	**1a**	74	57:43	14	57
13	**g**	3-$O_2NC_6H_4$	**1b**	73	56:44	24	57

[a] Isolated yield (total yield of **6** and **7**).
[b] Determined by calculation the ratio of peak area corresponding to compounds **6** and **7** in ^{31}P NMR spectra.
[c] Determined by chiral HPLC analysis.

found to be an essential factor to this reaction. For example, In terms of selectivity (enantio- and regioselectivity) the salen ligands derived from (1*R*,2*R*)-(+)-diaminocyclohexane (entries 4, 5) are better those have a backbone of 2,2′-diamino-1,1′-binaphthalene (entries 6, 7).

We further try to improve the catalytic effect through changing the central metal atom in the catalyst. The regioselectivity was significantly improved in the ring-opening of styrene oxide with *O*,*O*-diethyl dithiophosphoric acid using the (salen)Fe(III), (salen)Co(II), (salen)Co(III) complexes prepared from salen ligand **1a** as the catalyst (ratio of **6** to **7** are 7:93, 0:100 and 0:100, respectively). However, very poor enantioselectivity was observed (1–2% ee). Both poor regioselectivity (ratio of **6** to **7** is 27:73) and enantioselectivity (4–5% ee) was obtained for (salen)VO(IV) complex of salen **1a**.

In conclusion, several types of (salen)TI(IV) complexes catalyzed asymmetric ring-opening of epoxides with a novel nucleophile, dithiophosphorus acid, was investigated. The corresponding ring-opening products were obtained in excellent chemical yield with good ee values (up to 73% ee) when *meso* epoxides were used as the substrates. Synthetically valuable optically active β-hydroxymercaptan could be obtained through further reduction. When racemic monosubstituted epoxides were employed as the substrates, good to excellent regioselectivity was obtained for the alkyl substituted epoxides although very poor enantioselectivity was observed. Moreover, moderated enantioselectivity was obtained for aryl substituted epoxides, whereas it suffered form poor regioselectivity. More catalytic system need to be evaluated to realized this reaction with both high regioselectivity and enantioselectivity.

3. Experimental

3.1. General methods

^{1}H and ^{31}P NMR were recorded in $CDCl_3$ on a Bruker AMX-300 or AC-P 200 instrumental using TMS as an internal standard for ^{1}H NMR and 85% H_3PO_4 as an external standard for ^{31}P NMR. Specific rotations were measured on a Perkin–Elmer 341MC polarimeter. Enantiomeric excesses were determined on a HP-1100 instrument (chiral column; mobile phase: Hexane/*i*-PrOH). Elemental analyses were conducted on a Yanaco CHN Corder MT-3 automatic analyzer. Melting points were determined on a T-3 melting point apparatus. All temperatures and pressures were uncorrected. All of the solvent was dried according to the standard method and used after fresh distillation.

3.2. Preparation of salen ligand 1 [7]

For **1a**. Thick liquid, 92% yield, $[\alpha]_D^{20}$ −397.5 (*c* 1, CH_2Cl_2). ^{1}H NMR(δ, $CDCl_3$, 300 MHz): 1.74–1.95(m, 8H), 3.27–3.32(m, 2H), 6.73–7.26(m, 8H$_{arom}$), 8.24(s, 2H), 13.32(br., 2H).

For **1b**. Pale yellow solid, 77% yield, m.p. 83–85 °C, $[\alpha]_D^{20}$ −439.0 (*c* 1, CH_2Cl_2). ^{1}H NMR(δ, $CDCl_3$, 300 MHz): 1.37(s, 18H), 1.54–1.97(m, 8H), 2.17(s, 6H), 3.25–3.30(m, 2H), 6.76–7.01(m, 4H$_{arom}$), 8.21(s, 2H), 13.59(br., 2H).

For **1c**. Pale yellow solid, 78% yield, m.p. 201–202 °C, $[\alpha]_D^{20}$ −308.7 (*c* 1, CH_2Cl_2). ^{1}H NMR(δ, $CDCl_3$, 300 MHz): 1.27(s, 36H), 1.45–2.00(m, 8H), 3.31–3.70(m, 2H), 7.02–7.34(m, 4H$_{arom}$), 8.34(s, 2H), 13.76(br. 2H) (Ref. [7a]: m.p. 200–203 °C, $[\alpha]_D^{20}$ −315.0 (*c* 1, CH_2Cl_2)).

For **1d** [7b]. Pale yellow solid, 76% yield, m.p. 151–153 °C, $[\alpha]_D^{20}$ −293.7 (*c* 1, CH_2Cl_2). ^{1}H NMR(δ, $CDCl_3$, 300 MHz): 0.54(t, $J = 7.0$ Hz, 12 H), 1.19(s, 24H), 1.44(m, 8H), 1.75–1.92(m, 8H), 3.20–3.23(m, 2H), 6.80–7.08(m, 4H$_{arom}$), 8.17(s, 2H), 13.53(br. 2H).

For **1e**. Pale yellow solid, 62% yield, m.p. 150–152 °C, $[\alpha]_D^{20}$ −285.8 (*c* 1, CH_2Cl_2). ^{1}H NMR(δ, $CDCl_3$, 300 MHz): 1.45–1.90(m, 8H), 3.28–3.30(m, 2H), 7.15–7.43(m, 4H$_{arom}$), 8.11(s, 2H), 14.16(br. 2H). Anal. Calc. for $C_{20}H_{18}Br_2Cl_2N_2O_2$: C, 43.75; H, 3.30; N, 5.10. Found: C, 43.65; H, 2.98; N, 4.95%.

3.3. Preparation of salen ligand 2 [8]

For **2a** [8]. Yellow solid, 80% yield, m.p. 159–161 °C, $[\alpha]_D^{25}$ +34.0 (*c* 2, $CHCl_3$).

For **2b** [8]. Yellow solid, 80% yield, m.p. 137–139 °C, $[\alpha]_D^{25}$ +41.9 (*c* 2, $CHCl_3$).

For **2c**. Yellow solid, 76% yield, m.p. 237–239 °C, $[\alpha]_D^{25}$ +25.0 (*c* 1.2, $CHCl_3$). ^{1}H NMR(δ, $CDCl_3$): 0.91(s, 3H, 2CH$_3$), 1.07(s, 3H, 2CH$_3$), 1.33(s, 18H, 2*t*-Bu), 1.39(s, 18H, 2*t*-Bu), 1.80–2.35(m, 7H, 2CH$_2$ and CH$_3$), 3.35(t, 1H, $J = 6.9$ Hz, CH), 7.04(s, 1H, CH=N), 7.17–7.21(m, 2H$_{arom}$), 7.36(s, 1H, CH=N), 7.76–7.80(m, 2H$_{arom}$), 7.90(s, 1H, OH), 13.45(s, 1H, OH). Anal. Calc. for $C_{38}H_{58}N_2O_2$: C, 79.39; H, 10.17; N, 4.87. Found: C, 79.20; H, 10.05; N, 5.01%.

For **2d**. Yellow solid, 87% yield, m.p. 64–68 °C, $[\alpha]_D^{25}$ +14.1 (*c* 1, $CHCl_3$). ^{1}H NMR(δ, $CDCl_3$): 0.69(t, 12H, $J = 6.9$ Hz, 2CH$_3$), 0.97(s, 6H, 2CH$_3$), 1.30(s, 24H, 8CH$_3$), 1.32(s, 3H, 2CH$_3$), 1.39(q, 8H, $J = 6.9$ Hz, 4CH$_2$), 1.63(m, 4H, 2CH$_2$), 3.57(t, 1H, $J = 6.9$ Hz, CH), 7.04–7.26(m, 4H$_{arom}$), 8.01(s, 1H, OH), 8.34(s, 2H, 2CH=N), 13.32(s, 1H, OH). Anal. Calc. for $C_{42}H_{66}N_2O_2$: C, 79.95; H, 10.54; N, 4.44. Found: C, 79.91; H, 10.52; N, 4.36%.

For **2e** [8]. Yellow solid, 77% yield, m.p. 237–240 °C, $[\alpha]_D^{25}$ +37.7 (*c* 1, $CHCl_3$).

3.4. Preparation of salen ligand 3 [9]

For **3a** [9a]. Pale yellow solid, 81% yield, $[\alpha]_D^{20}$ −521.2 (*c* 0.1, acetone). ^{1}H NMR(δ, $CDCl_3$): 6.69–8.12(m, 20H$_{arom}$), 8.67(s, 2H, CH=N), 12.10(br., 2H, 2OH).

For **3b** [9a]. Pale yellow solid, 73% yield, $[\alpha]_D^{20}$ −498.8 (*c* 0.1, acetone). ^{1}H NMR(δ, $CDCl_3$): 1.25(s, 36H, 4*t*-Bu), 6.98–8.04(m, 16H$_{arom}$), 8.51(s, 2H, CH=N), 12.62(br., 2H, 2OH).

For **3c** [9a]. Orange solid, 81% yield, $[\alpha]_D^{20}$ − 437.0 (*c* 0.1, acetone). ^{1}H NMR(δ, $CDCl_3$): 1.20(s, 18H, 2*t*-Bu), 3.67(s, 6H, $2OCH_3$), 6.44–8.09(m, $16H_{arom}$), 8.52(s, 2H, CH=N), 12.51(br., 2H, 2OH).

3.5. Preparation of salen ligand 4 [10]

For **4a**. Yellow crystal, 76% yield, m.p. 197–199 °C, $[\alpha]_D^{20}$ + 35.7 (*c* 0.3, $CHCl_3$) (Ref. [10]: m.p. 199–200 °C, $[\alpha]_D^{20}$ + 32.4 (*c* 0.25, $CHCl_3$)).

For **4b**. Yellow crystal, 64% yield, m.p. 136–138 °C, $[\alpha]_D^{20}$ + 119.0 (*c* 0.1, $CHCl_3$). ^{1}H NMR(δ, $CDCl_3$): 1.41(s, 18H, 6CH3), 2.17(s, 6H, $2CH_3$), 3.50(s, 2H, 2CH), 4.68(broad, 2H, 2OH), 6.77-7.26(m, $14H_{arom}$), 8.30(s, 2H, CH=N). Anal. Calc. for $C_{38}H_{44}N_2O_2$: C, 81.39; H, 7.91; N, 5.00. Found: C, 81.31; H, 7.92; N, 5.13%.

3.6. Preparation of *O,O*-dimethyl dithiophosphoric acid and *O,O*-diethyl dithiophosphoric acid

According to the general method, *O,O*-dimethyl dithiophosphoric acid was afforded through the reaction of anhydrous methanol and phosphorus pentasulfide, b.p. 59–60 °C/160 Pa, n_D^{20} 1.5318 (Ref. [13]: b.p. 34–35 °C/20 Pa, n_D^{20} 1.5328).

O,O-diethyl dithiophosphoric acid was synthesized by the treatment of anhydrous ethanol and phosphorus pentasulfide following the same procedure, b.p. 136–138 °C/2.67 kPa, n_D^{20} 1.5110 (Ref. [13]: b.p. 92–94 °C/1.20 kPa, n_D^{20} 1.5120).

3.7. Preparation of diethyldithiophosphinic acid

Diethylthiophosphinic acid. According to Kabachnik's method [14], the reaction of *O,O*-diethyl phosphite with ethylmagnesiumbromide resulted in the formation of diethylphosphinite, the latter was treatment with sulfur to provide diethylthiophosphinic acid with 68% yield, b.p. 118–119 °C/267 Pa, n_D^{20} 1.5256 (Ref. [14]: b.p. 88.5–89 °C/200 Pa, n_D^{20} 1.5267).

Diethylthiophosphinyl chloride was synthesized through the reaction of diethylthiophosphinic acid with phosphorus pentachloride following Mastryukova's procedure [15], 90% yield, b.p. 135–138 °C/2.67 kPa, n_D^{20} 1.5260 (Ref. [15]: b.p. 60–61 °C/533 Pa, n_D^{20} 1.5281).

The reaction of diethylthiophosphinyl chloride with sodium hydrosulfide afforded diethyldithiophosphinic acid in 52% yield, b.p. 148–150 °C/2.00 kPa, n_D^{20} 1.5820 (Ref. [15]: b.p. 130–131 °C/1.73 kPa, n_D^{20} 1.5858).

3.8. Preparation of diphenyldithiophosphinic acid [16]

According to Higgins' method, diphenyldithiophosphinic acid was prepared by the reaction of benzene and phosphorus pentasulfide in the presence of aluminum chloride with a yield of 41%, m.p. 58–59 °C (Ref. [16]: m.p. 55–56 °C).

3.9. Ring-opening of meso epoxides with dithiophosphoric (dithiophosphinic) acids (general procedure)

To a 25 mL of 4-necked flask was placed 0.1 mmol of **1**, 5 mL of dry toluene, and 0.1 mmol of Ti(OPr-*i*)$_4$ at room temperature under a nitrogen atmosphere. After stirring for 1 h, 1 mmol of dithiophosphorus acid was added dropwise to the resulting mixture. The reaction was stirred for additional 0.5 h. Then 1 mmol of epoxide was added and the whole was stirred for 20 min. After removal of solvent, the crude product was purified by column chromatography on silica gel (200–300 mesh, gradient eluted with petroleum ether/ethyl acetate) to provide the ring-opening product as a pale yellow liquid. The ee value of the product was determined by comparison of specific rotation value with literature or by chiral HPLC analysis.

For **5a**: 85% yield, n_D^{20} 1.5432, $[\alpha]_D^{25}$ + 19.5 (*c* 2, CH_2Cl_2), 44% ee. ^{31}P NMR(δ, $CDCl_3$): 99.24; ^{1}H NMR(δ, $CDCl_3$): 1.26–1.71(m, 6H, $3CH_2$), 2.10(m, 2H, CH_2), 2.39(s, 1H, OH), 3.10(m, 1H, CH), 3.45(m, 1H, CH), 3.79(d, 6H, J_{P-H} = 10.1 Hz, $2CH_3O$). Anal. Calc. for $C_8H_{17}O_3PS_2$: C, 37.49; H, 6.68. Found: C, 37.21; H, 6.74%. HPLC conditions: OD column, hexane:isopropanol = 95:5, flow rate 1.0 mL/min, t_R = 10.45 and 11.97 min.

For **5b**: 90% yield, n_D^{20} 1.5262, $[\alpha]_D^{25}$ + 22.5 (*c* 2, CH_2Cl_2), 73% ee. ^{31}P NMR(δ, $CDCl_3$): 94.18; ^{1}H NMR(δ, $CDCl_3$): 1.30(t, 6H, *J* = 7.1 Hz, $2CH_3$), 1.34–1.69(m, 6H, $3CH_2$), 2.10(m, 2H, CH_2), 2.61(s, 1H, OH), 3.10(m, 1H, CH), 3.36(m, 1H, CH), 4.16(m, 4H, $2CH_2O$). Anal. Calc. for $C_{10}H_{21}O_3PS_2$: C, 42.23; H, 7.44. Found: C, 42.15; H, 7.56%. HPLC conditions: OD column, hexane:isopropanol = 99:1, flow rate 1.0 mL/min, t_R = 9.30 and 10.20 min.

For **5c**: 89% yield, n_D^{20} 1.5513, $[\alpha]_D^{25}$ + 25.0 (*c* 2, CH_2Cl_2), 69% ee. ^{31}P NMR(δ, $CDCl_3$): 81.86; ^{1}H NMR(δ, $CDCl_3$): 0.80(m, 2H, CH_2), 1.22–1.80(m, 10H, $2CH_2$ and $2CH_3$), 2.05(m, 6H, $3CH_2$), 2.25(s, 1H, OH), 3.35(m, 2H, 2CH). Anal. Calc. for $C_{10}H_{21}OPS_2$: C, 47.59; H, 8.39; Found: C, 47.65; H, 8.14%. HPLC conditions: OD column, hexane:isopropanol = 90:10, flow rate 1.0 mL/min, t_R = 9.31 and 10.23 min.

For **5d**: 92% yield, thick liquid, $[\alpha]_D^{25}$ − 2.5 (*c* 2, CH_2Cl_2), 60% ee. ^{31}P NMR(δ, $CDCl_3$): 64.18; ^{1}H NMR(δ, $CDCl_3$): 1.19–1.64(m, 6H, $3CH_2$), 2.03(m, 2H, CH_2), 2.85(s, 1H, OH), 3.12(m, 1H, CH), 3.52(m, 1H, CH), 7.42–7.92(m, $10H_{arom}$). Anal. Calc. for $C_{18}H_{21}OPS_2$: C, 62.04; H, 6.08. Found: C, 62.07; H, 6.04%. HPLC conditions: OD column, hexane:isopropanol = 90:10, flow rate 0.8 mL/min, t_R = 9.71 and 11.13 min.

For **5e**: 93% yield, n_D^{20} 1.5268, $[\alpha]_D^{25}$ − 7.2 (*c* 2, CH_2Cl_2), 53% ee. ^{31}P NMR(δ, $CDCl_3$): 93.70; ^{1}H NMR(δ, $CDCl_3$): 1.32(t, 6H, *J* = 7.0 Hz, $2CH_3$), 1.57–1.90(m, 6H, $3CH_2$), 2.20(m, H, CH), 2.70(s, 1H, OH), 3.30(m, 1H, CH), 4.12(m, 4H, $2CH_2O$). Anal. Calc. for $C_9H_{19}O_3PS_2$: C, 39.99; H, 7.08. Found: C, 39.80; H, 7.30%. HPLC conditions: OJ column, hexane:isopropanol = 90:10, flow rate 1.0 mL/min, t_R = 6.01 and 6.92 min.

For **5f**: 89% yield, n_D^{20} 1.5210, $[\alpha]_D^{25}$ + 27.7 (*c* 2, CH_2Cl_2), 66% ee. ^{31}P NMR(δ, $CDCl_3$): 94.96; ^{1}H NMR(δ, $CDCl_3$):

1.29(t, 6H, $J = 7.0$ Hz, $2CH_3$), 1.57–2.20(m, 12H, $6CH_2$), 2.54(s, 1H, OH), 3.50(m, 1H, CH), 3.80(m, 1H, CH), 4.14(m, 4H, $2CH_2O$). Anal. Calc. for $C_{12}H_{25}O_3PS_2$: C, 46.13; H, 8.07. Found: C, 46.06; H, 7.92%. HPLC conditions: OD column, hexane:isopropanol = 90:10, flow rate 0.8 mL/min, $t_R = 5.58$ and 6.89 min.

3.10. Ring-opening of racemic epoxides with O,O-diethyl dithiophosphoric acid (general procedure)

To a 25 mL of 4-necked flask was placed 0.1 mmol of chiral salen ligand, 5 mL of dry toluene, and 0.1 mmol of $Ti(OPr\text{-}i)_4$ at room temperature under a nitrogen atmosphere. After stirring for 1 h, 1 mmol of dithiophosphorus acid was added dropwise to the resulting mixture. The reaction was stirred for additional 0.5 h. Then 1 mmol of epoxide was added and the whole was stirred for 5–10 min (monitored by TLC). After removal of solvent, the crude product was analyzed by ^{31}P NMR, and then purified by column chromatography on silica gel (200–300 mesh, gradient eluted with petroleum ether/ethyl acetate) to provide the ring-opening product **6** and **7**. The ee value of the product was determined by chiral HPLC analysis.

For **6a**: R = Et, 82% yield, n_D^{20} 1.5138. ^{31}P NMR(δ, $CDCl_3$): 95.45; ^1H NMR(δ, $CDCl_3$): 0.96(t, 3H, $J = 7.1$ Hz, CH_3), 1.31(t, 6H, $J = 7.1$ Hz, $2CH_3$), 1.52(m, 2H, CH_2), 2.24(broad, 1H, OH), 3.10(m, 2H, CH_2), 3.72(m, 1H, CH), 4.13(m, 4H, $2CH_2O$). Anal. Calc. for $C_8H_{19}O_3PS_2$: C, 37.21; H, 7.36. Found: C, 37.19; H, 7.42%. HPLC conditions: OJ column, hexane:isopropanol = 90:10, flow rate 0.8 mL/min, $t_R = 6.75$ and 7.16 min.

For **6b**: R = n-Pr, 52% yield, 24% ee. ^{31}P NMR(δ, $CDCl_3$): 95.65; ^1H NMR(δ, $CDCl_3$): 0.91(t, 3H, $J = 7.1$ Hz, CH_3), 1.34(t, 6H, $J = 7.1$ Hz, $2CH_3$), 1.30–1.59(m, 4H, $2CH_2$), 2.50(broad, 1H, OH), 2.80–3.15(m, 2H, CH_2), 3.80(m, 1H, CH), 4.18(m, 4H, $2CH_2O$). Anal. Calc. for $C_9H_{21}O_3PS_2$: C, 39.69; H, 7.77. Found: C, 39.75; H, 7.65%. HPLC conditions: OJ column, hexane:isopropanol = 90:10, flow rate 0.8 mL/min, $t_R = 7.03$ and 8.21 min.

For **6c**: R = CH_2Cl, 78% yield, 3% ee. ^{31}P NMR(δ, $CDCl_3$): 96.21; ^1H NMR(δ, $CDCl_3$): 1.37(t, 6H, $J = 6.9$ Hz, $2CH_3$), 2.67(broad, 1H, OH), 3.08–3.18(m, 2H, CH_2), 3.60–3.72(m, 2H, CH_2), 4.14–4.19(m, 1H, CH), 4.20(m, 4H, $2CH_2O$). Anal. Calc. for $C_7H_{16}ClO_3PS_2$: C, 30.16; H, 5.79. Found: C, 29.89; H, 5.81%. HPLC conditions: AD-H column, hexane:isopropanol = 92:8, flow rate 0.8 mL/min, $t_R = 9.10$ and 9.51 min.

For **6d**: R = Ph, 21% yield, 55% ee. ^{31}P NMR(δ, $CDCl_3$): 95.71; ^1H NMR(δ, $CDCl_3$): 1.24(t, 6H, $J = 7.1$ Hz, $2CH_3$), 2.44(broad, 1H, OH), 2.93-3.21(m, 2H, CH_2S), 4.04(m, 4H, $2CH_2O$), 4.80(dd, 1H, $J = 3.6$ and 3.9 Hz, CHO), 7.18–7.26(m, $5H_{arom}$). Anal. Calc. for $C_{12}H_{19}O_3PS_2$: C, 47.04; H, 6.25. Found: C, 46.98; H, 6.21%. HPLC conditions: AD column, hexane:isopropanol = 95:5, flow rate 1.0 mL/min, $t_R = 15.94$ and 17.47 min.

For **7d**: R = Ph, 53% yield, 29% ee. ^{31}P NMR(δ, $CDCl_3$): 92.36; ^1H NMR(δ, $CDCl_3$): 1.20(t, 3H, $J = 6.9$ Hz, $2CH_3$), 1.28(t, 3H, $J = 6.9$ Hz, CH_3), 2.03(broad, 1H, OH), 3.95(d, 2H, $J = 6.9$ Hz, CH_2), 3.84–4.20(m, 4H, $2CH_2O$), 4.40(dt, 1H, $J = 6.9$ Hz, $J_{P-H} = 14.4$ Hz, CHS), 7.26–7.36(m, $5H_{arom}$). Anal. Calc. for $C_{12}H_{19}O_3PS_2$: C, 47.04; H, 6.25. Found: C, 47.01; H, 6.32%. HPLC conditions: AD column, hexane:isopropanol = 98:2, flow rate 0.8 mL/min, $t_R = 10.87$ and 12.13 min.

For **6e**: R = m-ClC_6H_4, 32% yield, 35% ee. ^{31}P NMR(δ, $CDCl_3$): 95.31; ^1H NMR(δ, $CDCl_3$): 1.37(t, 6H, $J = 6.9$ Hz, $2CH_3$), 2.58(broad, 1H, OH), 3.02–3.28(m, 2H, CH_2S), 4.10–4.28(m, 4H, $2CH_2O$), 4.91(dd, 1H, $J = 3.6$ and 3.9 Hz, CHO), 7.23–7.40(m, $4H_{arom}$). Anal. Calc. for $C_{12}H_{18}ClO_3PS_2$: C, 42.29; H, 5.32. Found: C, 42.19; H, 5.26%. HPLC conditions: AD column, hexane:isopropanol = 90:10, flow rate 1.0 mL/min, $t_R = 7.34$ and 8.59 min.

For **7e**: R = m-ClC_6H_4, 41% yield, 47% ee. ^{31}P NMR(δ, $CDCl_3$): 91.71; ^1H NMR(δ, $CDCl_3$): 1.23(t, 3H, $J = 6.9$ Hz, CH_3), 1.29(t, 3H, $J = 6.9$ Hz, CH_3), 2.13(broad, 1H, OH), 3.94(d, 2H, $J = 6.9$ Hz, CH_2O), 4.08–4.19(m, 4H, $2CH_2O$), 4.41(dt, 1H, $J = 6.9$ Hz, $J_{P-H} = 13.8$ Hz, CHS), 7.25–7.37(m, $4H_{arom}$). Anal. Calc. for $C_{12}H_{18}ClO_3PS_2$: C, 42.29; H, 5.32. Found: C, 42.31; H, 5.29%. HPLC conditions: AS column, hexane:isopropanol = 99:1, flow rate 0.8 mL/min, $t_R = 40.21$ and 42.56 min.

For **6f**: R = m-$MeOC_6H_4$, 49% yield, 54% ee. ^{31}P NMR(δ, $CDCl_3$): 95.43; ^1H NMR(δ, $CDCl_3$): 1.36(t, 6H, $J = 6.9$ Hz, $2CH_3$), 2.51(broad, 1H, OH), 3.05–3.33(m, 2H, CH_2S), 3.81(s, 3H, CH_3O), 4.09–4.28(m, 4H, $2CH_2O$), 4.90(dd, 1H, $J = 3.6$ and 3.9 Hz, CHO), 6.82–7.30(m, $4H_{arom}$). Anal. Calc. for $C_{13}H_{21}O_4PS_2$: C, 46.41; H, 6.29. Found: C, 46.29; H, 6.31%. HPLC conditions: AS column, hexane:isopropanol = 92:8, flow rate 0.8 mL/min, $t_R = 15.62$ and 18.31 min.

For **7f**: R = m-$MeOC_6H_4$, 23% yield, 41% ee. ^{31}P NMR(δ, $CDCl_3$): 92.12; ^1H NMR(δ, $CDCl_3$): 1.22(t, 3H, $J = 6.9$ Hz, CH_3), 1.29(t, 3H, $J = 6.9$ Hz, CH_3), 2.26(broad, 1H, OH), 3.80(s, 3H, CH_3O), 3.92(d, 2H, $J = 6.9$ Hz, CH_2O), 4.03–4.20(m, 4H, $2CH_2O$), 4.39(dt, 1H, $J = 6.9$ Hz, $J_{P-H} = 14.1$ Hz, CHS), 6.81–7.28(m, $4H_{arom}$). Anal. Calc. for $C_{13}H_{21}O_4PS_2$: C, 46.41; H, 6.29. Found: C, 46.45; H, 6.38%. HPLC conditions: AS-H column, hexane:isopropanol = 90:10, flow rate 0.9 mL/min, $t_R = 10.34$ and 11.31 min.

For **6g**: R = m-$O_2NC_6H_4$, 41% yield, 24% ee. ^{31}P NMR(δ, $CDCl_3$): 95.66; ^1H NMR(δ, $CDCl_3$): 1.37(t, 6H, $J = 6.9$ Hz, $2CH_3$), 3.07(broad, 1H, OH), 3.10–3.39(m, 2H, CH_2S), 4.10–4.28(m, 4H, $2CH_2O$), 5.09(dd, 1H, $J = 3.6$ and 3.9 Hz, CHO), 7.55(d, $J = 7.8$ Hz, $1H_{arom}$), 7.76(d, $J = 7.8$ Hz, $1H_{arom}$), 8.12(d, $J = 7.8$ Hz, $1H_{arom}$), 8.28(s, $1H_{arom}$). Anal. Calc. for $C_{12}H_{18}NO_5PS_2$: C, 41.02; H, 5.16; N, 3.99. Found: C, 41.13; H, 5.20; N, 4.01%. HPLC conditions: OD column, hexane:isopropa-

nol = 99:1, flow rate 1.0 mL/min, $t_R = 10.16$ and 10.85 min.

For **7g**: R = *m*-$O_2NC_6H_4$, 32% yield, 57% ee. ^{31}P NMR(δ, $CDCl_3$): 91.70; ^1H NMR(δ, $CDCl_3$): 1.24(t, 3H, $J = 6.9$ Hz, CH_3), 1.27(t, 3H, $J = 6.9$ Hz, CH_3), 2.36(broad, 1H, OH), 4.03(d, 2H, $J = 6.9$ Hz, CH_2O), 3.92–4.21(m, 4H, $2CH_2O$), 4.57(dt, 1H, $J = 6.9$ Hz, $J_{P-H} = 14.1$ Hz, CHS), 7.55(d, $J = 7.8$ Hz, $1H_{arom}$), 7.75(d, $J = 7.8$ Hz, $1H_{arom}$), 8.15(d, $J = 7.8$ Hz, $1H_{arom}$), 8.27(s, $1H_{arom}$). Anal. Calc. for $C_{12}H_{18}NO_5PS_2$: C, 41.02; H, 5.16; N, 3.99. Found: C, 40.90; H, 5.02; N, 4.03%. HPLC conditions: OA column, hexane:isopropanol = 90:10, flow rate 0.8 mL/min, $t_R = 24.78$ and 26.27 min.

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References

[1] (a) I.M. Pastor, M. Yus, Curr. Org. Chem. 9 (2005) 1;
(b) D.M. Hodgson, A.R. Gibbs, G.D. Lee, Tetrahedron 52 (1996) 14361;
(c) I. Paterson, D.J. Berrisford, Angew. Chem., Int. Ed. Engl. 31 (1992) 1197.
[2] (a) R.H. Fan, X.L. Hou, J. Org. Chem. 68 (2003) 726;
(b) J.S. Yadav, B.V.S. Reddy, G. Baishya, Chem. Lett. (9) (2002) 906;
(c) M.R. Younes, M.M. Chaabouni, A. Baklouti, Tetrahedron Lett. 42 (2001) 3167;
(d) V. Kwsavan, D.B. Delpon, J.P. Begue, Tetrahedron Lett. 41 (2000) 2895;
(e) H. Adams, R. Bell, Y.Y. Cheung, Tetrahedron: Asymmetry 10 (1999) 4129;
(f) J. Wu, X.L. Hou, L.X. Dai, L.J. Xia, M.H. Tang, Tetrahedron: Asymmetry 9 (1998) 3431;
(g) M.A. Wu, E.N. Jacobsen, J. Org. Chem. 63 (1998) 5252;
(h) T. Iida, N. Yamamoto, H. Sasai, M. Shibasaki, J. Am. Chem. Soc. 119 (1997) 4783;
(i) S.-I. Fukuzawa, H. Kato, M. Ohtaguchi, Y. Hayashi, H. Yamazaki, J. Chem. Soc., Perkin Trans. 1 (1997) 3059;
(j) D. Albanese, D. Landin, M. Penso, Synthesis (1994) 34;
(k) A.K. Maiti, P. Bhattacharyya, Tetrahedron 50 (1994) 10483;
(l) H. Yamashita, Bull. Chem. Soc. Jpn. 61 (1988) 1213;
(m) Y.K. Soo, K.B. Sharpless, J. Org. Chem. 51 (1986) 5413;
(n) J.M. Chong, K.B. Sharpless, J. Org. Chem. 50 (1985) 1560;
(o) M. Caron, K.B. Sharpless, J. Org. Chem. 50 (1985) 1557.
[3] (a) J.C.J. Pomar, J.A. Soderquist, Tetrahedron Lett. 39 (1998) 4409;
(b) Y. Tanabe, M. Mori, Y. Yoshida, J. Chem. Soc., Perkin Trans. 1 (1997) 671;
(c) J. Brittain, Y. Gareau, Tetrahedron Lett. 34 (1993) 3363.
[4] (a) Z.M. Li, Z.H. Zhou, K.Y. Li, L.X. Wang, Q.L. Zhou, C.C. Tang, Tetrahedron Lett. 43 (2002) 7609;
(b) Y. Tamura, T. Kawasaki, H. Yasuda, J. Chem. Soc., Perkin Trans. 1 (1981) 1577;
(c) A.N. Pudovik, E.M. Faezurrin, G.E. Zhuravrev, Zh. Obshch. Khim. 36 (1965) 718;
(d) J.M. Ndong Mebah, J.L. Mieloszynski, D. Paquer, Phosphorus Sulfur Silicon 78 (1993) 215;
(e) A. Aldasheva, Zh. Beishekeev, K.D. Dzhundubaev, T. Toktobekova, Izv. Akad. Nauk. Kirg. SSR 4 (1980) 52 (Chem. Abstr. 1981, 94, 12134).
[5] E.N. Jacobsen, Acc. Chem. Res. 33 (2000) 421.
[6] S. Bruns, G. Haufe, Tetrahedron: Asymmetry 10 (1999) 1563.
[7] (a) J.F. Larrow, E.N. Jacobsen, J. Org. Chem. 59 (1994) 1939;
(b) S. Liang, X.R. Bu, J. Org. Chem. 67 (2002) 2702.
[8] Z.H. Yang, L.X. Wang, Z.H. Zhou, Q.L. Zhou, C.C. Tang, Tetrahedron: Asymmetry 12 (2001) 1579.
[9] (a) X.G. Zhou, J.S. Huang, P.H. Ko, K.K. Cheung, C.M. Che, J. Chem. Soc., Dalton Trans. (1999) 3303;
(b) K.D.S. Bernado, A. Robert, F. Dahan, B. Meunier, New J. Chem. 19 (1995) 129;
(c) N. Takenaka, Y. Huang, V.H. Rawal, Tetrahedron 58 (2002) 8299.
[10] Y.Z. Jiang, L.Z. Gong, X.M. Feng, W.H. Hu, W.D. Pan, Z. Li, A.Q. Mi, Tetrahedron 53 (1997) 14327.
[11] E.F. DiMauro, M.C. Kozlowski, J. Am. Chem. Soc. 124 (2002) 12668.
[12] Z.H. Zhou, Q.Y. Wang, B. Liu, G.F. Zhao, Q.L. Zhou, C.C. Tang, Lett. Org. Chem. 2 (2005) 752.
[13] R.S. Edmundson (Ed.), Dictionary of Organophosphorus Compounds D-00898 (Me ester), D-00384 (Et ester), Chapman and Hall, London, 1988.
[14] M.I. Kabachnik, T.A. Mastryukova, A.E. Shipov, T.A. Melent'eva, Tetrahedron 16 (1960) 10.
[15] T.A. Mastryukova, A.E. Shipov, M.I. Kabachnik, Zh. Obshch. Khim. 31 (1961) 507.
[16] W.A. Higgins, P.W. Vogel, W.G. Craig, J. Am. Chem. Soc. 77 (1955) 1864.