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A facile synthesis and the asymmetric catalytic activity of BINOL-based thiazole (thiadiazole) thioether ligands

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Abstract

Four new BINOL-based thiazole (thiadiazole) thioether ligands (S)-**1**, (S)-**2**, (S,S)-**3** and (S)-**4** were prepared. When their catalytic effectiveness was tested, good results (up to 93% ee and 97% yield) were obtained in the asymmetric addition of diethylzinc to aldehydes while poor results were obtained in the asymmetric conjugate addition of diethylzinc to enones.
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Keywords: BINOL; Diethylzinc; Titanium tetraisopropoxide; Copper trifluoromethanesulfonate; Asymmetric addition

1. Introduction

In catalytic asymmetric systems, small changes in the donating ability of a ligand or the size of a substituent can have dramatic effect on the catalytic efficiency and enantioselectivity [1]. 1,1′-Binaphthol (BINOL) is one of the most effective chiral ligands in asymmetric catalysis [2]. Substituents at the 3-position of BINOL are normally introduced via a two-step protocol that involves treatment of a suitably protected BINOL with an organolithium reagent, followed by reaction with an electrophile [3]. BINOL ligands substituted by the introduction of hetero-aromatic groups at the 3 or 3,3′-positions are less reported [4]. In our previous research, some nitrogen-contained aromatic heterocycle groups such as 1,3,5-triazin-2-yl, 2-quinolyl and 1,2,4-triazol-1-ylmethyl were, respectively, introduced to the 3 or 3,3′-positions of BINOL, and their catalytic applicability in the addition of diethylzinc to aldehydes was also reported [5].

In recent years, chiral S-donor ligands have proved to be useful as other classical asymmetric ligands, especially when combined with other donor atoms [6]. Despite of the vast knowledge on sulfur-metal interactions in coordination chemistry [7], the use of chiral BINOL ligands containing sulfur atoms in asymmetric catalysis appears to be still rather undeveloped. Sulfur has somewhat less donor and acceptor character. In addition to this electronic consideration, the sulfur atom, in thioether ligands, for example, has only two substituents which can create a less hindered environment. Woodward [8] developed copper-catalyzed asymmetric conjugate additions of various organometallic reagents to linear enones in the presence of sulfur-containing BINOL ligands, and the sulfur atom proved to be necessary in this reaction. Kang [9] reported some BINOL-based ligands containing sulfur were effective in promoting 1,4-additions of organometallics to various enones. To the best of our knowledge, BINOL-based ligands bounded with both sulfur-contained heterocycle (thiazole or thiadiazole) and thioether block in which the sulfur might serve as a talent anchor have never been reported. Therefore, it should be of interest to explore the catalytic ability of this kind of BINOL ligands. Herein, we report the synthesis of new chiral ligands (S)-3-(5-methyl-1,3,4-thiadiazol-2-ylthio)methyl-BINOL [(S)-**1**], (S)-3-(benzothiazol-2-ylthio)methyl-BINOL [(S)-**2**], (S,S)-2,5-bis(2,2′-dihydroxy-1,1′-binaphthalen-3-yl)-1,3,4-thiadiazole [(S,S)-**3**], and (S)-3,3′-bis[(5-methyl-1,3,4-thiadiazol-

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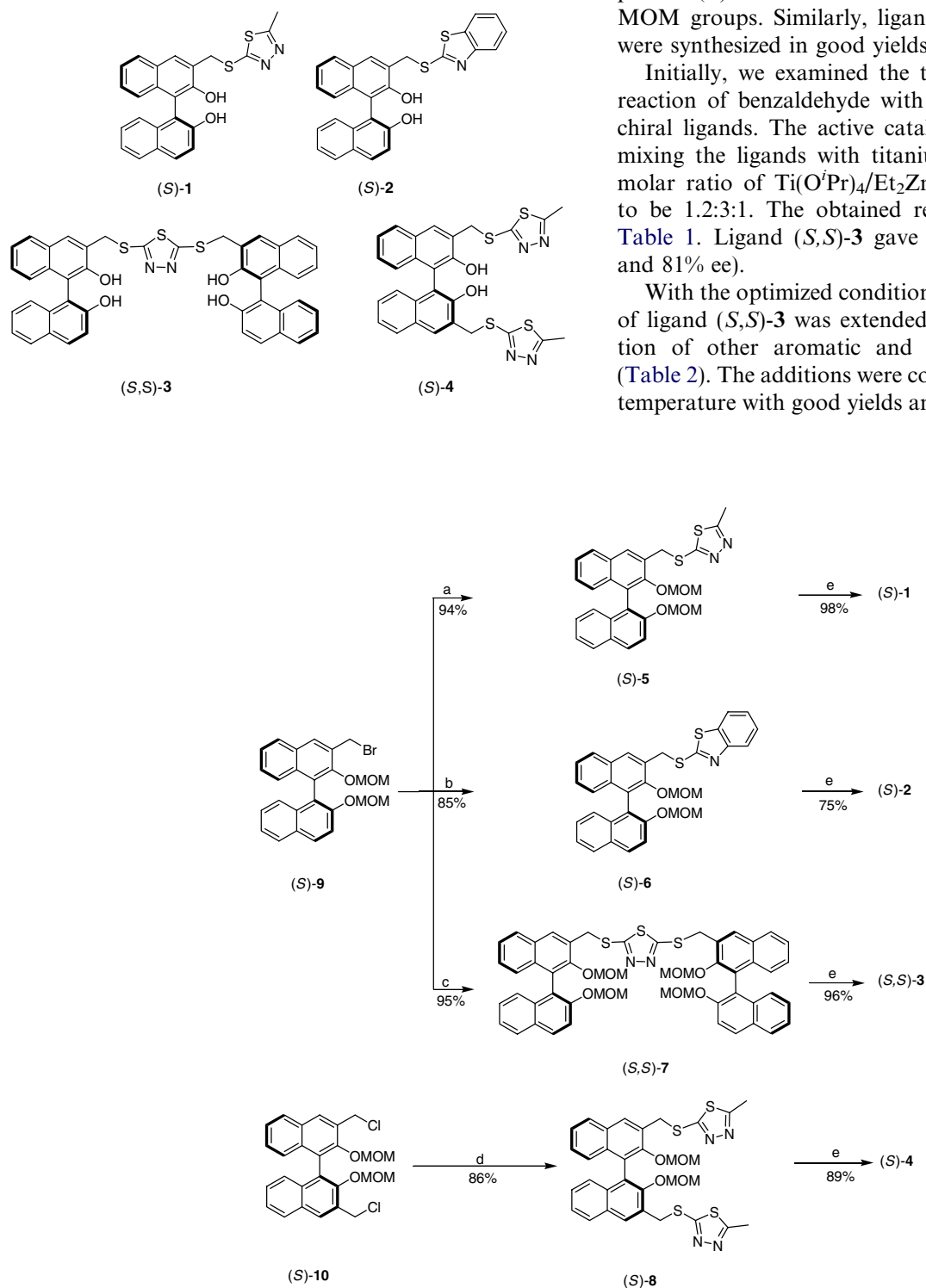*E-mail address:* jinshan_li2001@yahoo.com.cn (J.-S. Li).

2-ylthio)methyl]-BINOL [(*S*)-**4**] and their application in asymmetric addition of diethylzinc to aldehydes in the presence of titanium tetraisopropoxide and in asymmetric conjugate addition of diethylzinc to enones in the presence of Cu(OTf)$_2$.

2. Results and discussion

The synthetic route for ligands (*S*)-**1**, (*S*)-**2**, (*S*,*S*)-**3** and (*S*)-**4** is outlined in Scheme 1. (*S*)-**5** was easily prepared by the reaction of (*S*)-**9** with 2-mercapto-5-methyl-1,3,4-thiadiazole in high yield, and the corresponding target compound (*S*)-**1** was obtained after deprotection of the MOM groups. Similarly, ligands (*S*)-**2**, (*S*,*S*)-**3** and (*S*)-**4** were synthesized in good yields.

Initially, we examined the titanium-catalyzed addition reaction of benzaldehyde with diethylzinc using the four chiral ligands. The active catalyst was formed *in situ* by mixing the ligands with titanium tetraisopropoxide. The molar ratio of Ti(O^{i}Pr)$_4$/Et$_2$Zn/benzaldehyde was set up to be 1.2:3:1. The obtained results were summarized in Table 1. Ligand (*S*,*S*)-**3** gave the best result (95% yield and 81% ee).
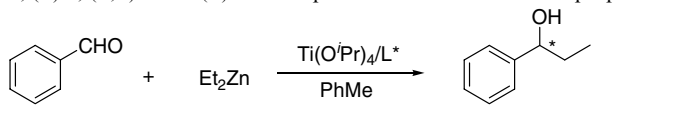
With the optimized conditions for benzaldehyde, the use of ligand (*S*,*S*)-**3** was extended to the asymmetric ethylation of other aromatic and α,β-unsaturated aldehydes (Table 2). The additions were completed within 5 h at room temperature with good yields and ee values for all the alde-

Scheme 1. Synthesis of (*S*)-**1**, (*S*)-**2**, (*S*,*S*)-**3** and (*S*)-**4**. Reagents and conditions: (a) 1 equiv 2-mercapto-5-methyl-1,3,4-thiadiazole, KOH, reflux for 2 h; (b) 1 equiv 2-mercaptobenzothiazole, KOH, reflux for 2 h; (c) 0.5 equiv 2, 5-dimercapto-1,3,4-thiadiazole, KOH, reflux for 2 h; (d) 2 equiv 2-mercapto-5-methyl-1,3,4-thiadiazole, KOH, reflux for 2 h; (e) CH$_2$Cl$_2$, CH$_3$OH, 6 M HCl, r.t.

Table 1

Addition of diethylzinc (2 M in hexane) to benzaldehyde using ligands (S)-**1**, (S)-**2**, (S,S)-**3** and (S)-**4** in the presence of titanium tetraisopropoxide

Entry	Ligand (mol%) [a]	Yield (%) [b]	ee (%) [c]	Config. [d]
1	(S)-**1** (20)	93	76	S
2	(S)-**1** (10)	90	54	S
3	(S)-**2** (20)	91	78	S
4	(S)-**2** (15)	92	74	S
5	(S)-**2** (10)	91	69	S
6	(S,S)-**3** (20)	95	81	S
7	(S,S)-**3** (15)	95	77	S
8	(S,S)-**3** (10)	90	62	S
9	(S)-**4** (20)	98	70	S
10	(S)-**4** (10)	96	66	S

[a] Ti(O^{i}Pr)$_4$/Et$_2$Zn/benzaldehyde = 1.2:3:1; Reaction temperature: r.t.; Reaction time: 5 h.
[b] Isolated yield.
[c] Data were determined by GC analysis using a chiral column (Chiral beta-DEX 120 capillary column).
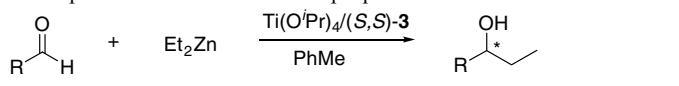[d] The absolute configurations of the products were determined by comparison to the literature data.

hydes. The best enantioselectivity up to 93% ee was obtained with o-methoxybenzaldehyde (Entry 5).

Furthermore, the effectiveness of the four ligands in the copper-catalyzed conjugate addition of diethylzinc to enones was tested. Cyclohexenone and 4-chloro-chalcone were chosen as typical substrates of cyclic and acyclic enones, respectively. The conjugate addition of diethylzinc to enones were carried out in the presence of Cu(OTf)$_2$ (5 mol%) and chiral ligand (10 mol%) in THF at 0 °C for 2 h producing 3-ethyl ketones. The obtained results are summarized in Table 3. (S)-**4** gave the best result when cyclohexenone was the substrate while (S,S)-**3** was the best ligand when 4-chloro-chalcone was the substrate. With

Table 2

Addition of diethylzinc (2 M in hexane) to aldehydes using ligand (S,S)-**3** in the presence of titanium tetraisopropoxide

Entry	R [a]	Yield (%) [b]	ee (%) [c]	Config. [d]
1	Ph	95	81	S
2	p-ClC$_6$H$_4$	94	89	S
3	p-BrC$_6$H$_4$	95	91	S
4	p-MeOC$_6$H$_4$	91	87	S
5	o-MeOC$_6$H$_4$	97	93	S
6	PhCH=CH	94	87	S
7	1-Naphthyl	92	86	S

[a] (S,S)-**3**/Ti(O^{i}Pr)$_4$/Et$_2$Zn/aldehyde = 0.2:1.2:3:1; Reaction temperature: r.t.; Reaction time: 5 h.
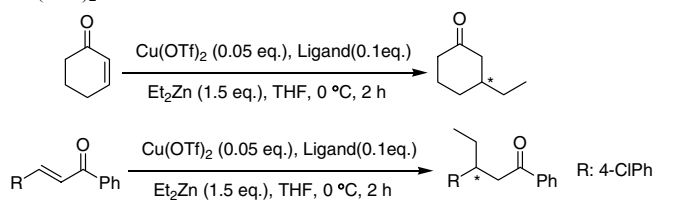[b] Isolated yield.
[c] Data were determined by GC analysis using a chiral column (Chiral beta-DEX 120 capillary column).
[d] The absolute configurations of the products were determined by comparison to the literature data.

Table 3

Asymmetric conjugate addition of Et$_2$Zn to enones in the presence of Cu(OTf)$_2$

Entry	Substrate	Ligand [a]	Yield (%) [b]	ee (%) [c]
1	Cyclohexenone	(S)-**1**	71	19 [d]
2	Cyclohexenone	(S)-**2**	70	19 [d]
3	Cyclohexenone	(S,S)-**3**	68	15 [d]
4	Cyclohexenone	(S)-**4**	76	33 [d]
5	4-Chloro-chalcone	(S)-**1**	68	24 [e]
6	4-Chloro-chalcone	(S)-**2**	69	26 [e]
7	4-Chloro-chalcone	(S,S)-**3**	75	33 [e]
8	4-Chloro-chalcone	(S)-**4**	65	11 [e]

[a] Ligand/Cu(OTf)$_2$/Et$_2$Zn/Substrate = 0.1: 0.05:1.5:1; Reaction temperature: 0 °C; Reaction time: 2 h.
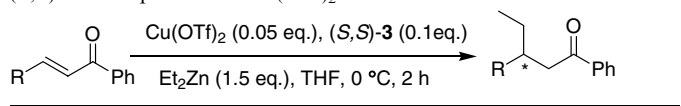[b] Isolated yield.
[c] The absolute configurations of the products were not determined.
[d] Data were determined by GC analysis using a chiral column (Chiral GAMA-DEX 225 capillary column).
[e] Data were determined by HPLC (Chiracel OJ-H column).

Table 4

Asymmetric conjugate addition of Et$_2$Zn to acyclic enones using ligand (S,S)-**3** in the presence of Cu(OTf)$_2$

Entry	R [a]	Yield (%) [b]	ee (%) [c]
1	Ph	62	13
2	4-MeOPh	60	10
3	4-Cl	75	33

[a] (S,S)-**3**/Cu(OTf)$_2$/Et$_2$Zn/Substrate = 0.1:0.05:1.5:1; Reaction temperature: 0 °C; Reaction time: 2 h.
[b] Isolated yield.
[c] Data were determined by HPLC (Chiracel OJ-H column). The absolute configurations of the products were not determined.

ligand (S,S)-**3**, various chalcones were converted into the corresponding chiral ketones (Table 4). The results showed that the electron-withdrawing substituent of the chalcone obviously increased the enantioselectivity and the yield (entry 3) while the electron-donating group slightly decreased the enantioselectivity and the yield (entry 2).

3. Conclusion

In conclusion, we prepared four new chiral modified BINOL ligands (S)-**1**, (S)-**2**, (S,S)-**3** and (S)-**4**. It was found that the four chiral ligands could catalyze both the asymmetric addition of diethylzinc to aldehydes and the asymmetric conjugate addition of diethylzinc to enones. The titanium complex of (S,S)-**3** was found to be an efficient

catalyst in the asymmetric addition of diethylzinc to aldehydes. Poor enantioselectivities were obtained when the four ligands were applied in the asymmetric conjugate addition of diethylzinc to enones in the presence of $Cu(OTf)_2$.

4. Experimental

4.1. General

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 instrument in $CDCl_3$ solution with TMS as internal standard. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. The high-resolution mass spectra (MALDI-HRMS) were measured on an Ionspec FT MS 7.0T spectrometer. All experiments which are sensitive to moisture or air were carried out under an argon atmosphere using standard Schlenk techniques. Diethylzinc (2 M in hexane) was purchased from Aldrich. All anhydrous solvents were purified and dried by standard techniques just before use. (S)-**9** [10] and (S)-**10** [11] were prepared according to the literature method, respectively.

4.1.1. (S)-3-(5-methyl-1,3,4-thiadiazol-2-ylthio)methyl-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene [(S)-5] [Typical procedure for the synthesis of (S)-5, (S)-6, (S,S)-7 and (S)-8]

To a solution of (S)-**9** (1.868 g, 4 mmol) in 20 mL dry ethanol was added 2-mercapto-5-methyl-1,3,4-thiadiazole (0.528 g, 4 mmol) and KOH (0.224 g, 4 mmol). The reaction process was monitored by TLC. After refluxing for 2 h, the reaction mixture was concentrated and washed with water. The oil layer was extracted with ethyl acetate (3×20 mL) and dried over anhydrous $MgSO_4$. After evaporation of the volatiles, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate 3:1) to give (S)-**5** (1.95 g, 94% yield) as a white solid. M.p. 112 °C. $[\alpha]_D^{25} = -47.7$ ($c = 2.83$ THF). ^{1}H NMR (300 MHz, $CDCl_3$) 8.12–7.14 (m, 11H), 5.09 (dd, $J = 18.00$, 2H), 4.90 (s, 2H), 4.65 (d, $J = 5.70$, 1H), 4.53 (d, $J = 5.70$, 1H), 3.19 (s, 3H), 3.06 (s, 3H), 2.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.57, 162.39, 152.88, 152.62, 133.80, 130.71, 130.27, 130.03, 129.67, 127.94, 126.85, 126.44, 125.69, 125.42, 125.21, 124.21, 116.46, 99.44, 94.92, 56.96, 56.03, 34.13, 15.66. HR-MS Calc. for $C_{28}H_{27}N_2O_4S_2$ ($M^+ + H$): 519.1407. Found: 519.1402.

4.1.2. (S)-3-(Benzothiazol-2-ylthio)methyl-2,2'-bis(methoxymethoxy)-1,1'-binaphtha-lene [(S)-6]

Semi-solid. yield: 85%, $[\alpha]_D^{25} = -75.1$ ($c = 3.34$, CHCl₃). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.18 (s, 1H), 7.99–7.14 (m, 14H), 5.09 (dd, $J = 19.05$, 2H), 4.98 (s, 2H), 4.70 (d, $J = 5.7$, 1H), 4.57 (d, $J = 5.4$, 1H), 3.18 (s, 3H), 3.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.35, 153.21, 152.92, 150.19, 133.88, 130.27, 130.18, 130.01, 129.71, 128.86, 128.03, 127.81, 126.84, 126.04, 125.72, 125.50,

125.17, 124.95, 124.42, 124.21, 123.63, 121.56, 121.40, 120.94, 117.25, 116.53, 99.45, 94.95, 56.93, 55.96, 33.30. HR-MS Calc. for $C_{32}H_{28}NO_4S_2$ ($M^+ + H$): 554.1454. Found: 554.1452.

4.1.3. (S,S)-2,5-Bis{[2,2'-bis(methoxymethoxy)-1,1'-binaphthyl-3-yl]methylthio}-1,3,4-thiadiazole [(S,S)-7]

Yellow solid. Yield: 95%, m.p. 90–92 °C. $[\alpha]_D^{25} = -41.9$ ($c = 5.57$, CHCl₃). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.12–7.16 (m, 22H), 5.09 (dd, $J = 11.10$, 4H), 4.90 (s, 4H), 4.65 (d, $J = 5.70$, 2H), 4.52 (d, $J = 5.40$, 2H), 3.19 (d, $J = 3.00$, 6H), 3.06 (d, $J = 3.00$, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.37, 162.35, 152.88, 152.63, 133.86, 130.73, 130.31, 130.07, 129.69, 129.55, 127.97, 126.91, 126.51, 125.78, 125.63, 125.43, 125.28, 124.24, 120.39, 116.45, 99.46, 94.90, 56.98, 56.05, 34.41, 22.69. HR-MS Calc. for $C_{52}H_{47}N_2O_8S_3$ ($M^+ + H$): 923.2489. Found: 923.2483.

4.1.4. (S)-3,3'-Bis[(5-methyl-1,3,4-thiadiazol-2-ylthio)methyl]-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene [(S)-8]

Yellow solid. Yield: 86%, m.p. 154–156 °C. $[\alpha]_D^{25} = -38.5$ ($c = 0.41$, CHCl₃). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.16 (s, 2H), 7.86 (d, $J = 8.10$, 2H), 7.43–7.12 (m, 6H), 4.90 (s, 4H), 4.58 (d, $J = 5.70$, 2H), 4.50 (d, $J = 6.00$, 2H), 3.03 (s, 6H), 2.73 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.30, 165.05, 162.34, 152.79, 133.88, 130.87, 130.58, 129.98, 128.06, 126.93, 125.89, 125.40, 125.32, 99.43, 56.98, 33.97, 15.63. HR-MS Calc. for $C_{32}H_{31}N_4O_4S_4$ ($M^+ + H$): 663.1223. Found: 663.1226.

4.1.5. (S)-3-(5-Methyl-1,3,4-thiadiazol-2-ylthio)methyl-BINOL [(S)-1] (Typical procedure for the deprotection of the MOM groups)

To a solution of (S)-**5** (0.518 g, 1 mmol) in CH_2Cl_2 (10 mL) and MeOH (20 mL) was added 6 M HCl (5 mL) and the mixture was stirred at room temperature for 12 h. The mixture was poured into water (40 mL), extracted with CH_2Cl_2, washed with water and saturated $NaHCO_3$, dried over anhydrous $MgSO_4$ and finally concentrated in vacuo to give a white solid. Yield: 98%, m.p. 208–210 °C. $[\alpha]_D^{25} = -97.1$ ($c = 0.48$, CHCl₃). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.11 (s, 1H), 7.99–7.85 (m, 3H), 7.40–7.10 (m, 7H), 6.33 (s, 1H), 5.10 (s, 1H), 4.80 (s, 2H), 2.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.26, 162.35, 152.61, 151.21, 133.44, 133.35, 131.78, 131.19, 129.42, 129.07, 128.37, 128.30, 127.48, 127.30, 125.57, 124.34, 123.88, 117.91, 112.67, 111.64, 33.50, 15.62. HR-MS Calc. for $C_{24}H_{19}N_2O_2S_2$ ($M^+ + H$): 431.0883. Found: 431.0861.

4.1.6. (S)-3-(Benzothiazol-2-ylthio)methyl-BINOL [(S)-2]

White solid. Yield: 75%, m.p. 102–104 °C. $[\alpha]_D^{25} = -105.8$ ($c = 2.17$, CHCl₃). ^{1}H NMR (300 MHz,

CDCl$_3$) δ: 8.03 (s, 1H), 7.90–7.64 (m, 4H), 7.32–6.99 (m, 10H), 4.76 (s, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 161.32, 151.14, 151.08, 150.68, 134.06, 132.58, 130.77, 129.59, 128.35, 128.19, 127.23, 127.07, 126.37, 125.98, 125.72, 125.44, 125.25, 123.52, 123.27, 122.56, 120.37, 119.96, 116.72, 113.11, 112.22, 32.18. HR-MS Calc. for C$_{28}$H$_{20}$NO$_2$S$_2$ (M$^+$ + H): 466.0930. Found: 466.0936.

4.1.7. (S,S)-2,5-Bis(2,2'-dihydroxy-1,1'-binaphthalen-3-yl)-1,3,4-thiadiazole [(S,S)-3]

Yellow foam. Yield: 96%, m.p. 160–162 °C. $[\alpha]_D^{25} = -74.2$ ($c = 1.18$, CHCl$_3$). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.09 (s, 2H), 7.98–7.82 (m, 6H), 7.38–7.09 (m, 14H), 6.00 (s, 2H), 5.11 (s, 2H), 4.76 (s, 4H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 165.65, 162.34, 152.65, 151.09, 133.40, 133.32, 131.84, 131.35, 129.46, 129.09, 128.42, 127.59, 127.45, 125.24, 124.42, 124.27, 123.98, 118.90, 117.88, 112.38, 111.30, 33.75. HR-MS Calc. for C$_{44}$H$_{31}$N$_2$O$_4$S$_3$ (M$^+$ + H): 747.1441. Found: 747.1470.

4.1.8. (S)-3,3'-Bis[(5-methyl-1,3,4-thiadiazol-2-ylthio)methyl]-BINOL [(S)-4]

Yellow solid. Yield: 89%, m.p. 204–206 °C. $[\alpha]_D^{25} = -54.4$ ($c = 0.75$, CHCl$_3$). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.06 (s, 2H), 7.83 (d, $J = 7.80$, 2H), 7.35–7.04 (m, 6H), 4.78 (s, 4H), 2.66 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 165.42, 162.33, 151.08, 133.38, 131.59, 129.06, 128.25, 127.33, 125.52, 124.42, 124.19, 113.39, 33.71, 15.59. HR-MS Calc. for C$_{28}$H$_{23}$N$_4$O$_2$S$_4$ (M$^+$ + H): 575.0698. Found: 575.0697.

4.1.9. A typical procedure for the asymmetric addition of diethylzinc to aldehydes

Titanium tetraisopropoxide (1.2 mmol) was added to a solution of (S,S)-3 (0.20 mmol) in 3 mL dry toluene at room temperature and the reaction mixture was stirred for 30 min followed by addition of diethylzinc (2 M in hexane, 3 mmol) with continuous stirring for 15 min. The solution was cooled to 0 °C and benzaldehyde (1 mmol) was added. The reaction was quenched with 20 mL of saturated NH$_4$Cl solution after 5 h. The reaction mixture was filtered to remove the insoluble material and the filtrate was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na$_2$SO$_4$ and concentrated to the solvent free. The residue was purified by column chromatography on silica gel affording 1-phenyl-1-propanol as a pale yellow liquid. The enantiomeric excess of the product was determined by GC on a Chiral beta-DEX 120 capillary column.

4.1.10. A typical procedure for the asymmetric conjugate addition of diethylzinc to enones

A solution of Cu(OTf)$_2$ (0.05 mmol) and ligand (0.1 mmol) in THF (5 mL) was stirred under argon atmosphere at room temperature for 30 min. The solution was cooled to 0 °C, then Et$_2$Zn solution in hexane (1.5 mmol) and the enone (1 mmol) were added

in turn. After stirring at 0 °C for 2 h, the reaction was quenched by aqueous NH$_4$Cl and the mixture was extracted with ethyl acetate (3 × 20 mL). The organic phases were combined, dried over Na$_2$SO$_4$, filtered, and concentrated. The crude product was purified by chromatography on a silica gel column. The ee values of cyclic ketones were determined by chiral GC (Chiral GAMA-DEX 225 capillary column), and the ee values of acyclic ketone were determined by chiral HPLC (Chiracel OJ-H column).

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