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Novel thiazolidine derivatives as chiral catalysts in the enantioselective addition of diethylzinc to aldehydes

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Abstract

New chiral thiazolidine derivatives were synthesized conveniently from natural L-cysteine and showed good enantioselectivity (up to 90% ee) in the addition of diethylzinc to aldehydes. The catalytic efficiency of the thiazolidine derivatives is influenced by the different structures of the thiazolidine rings and the bulkiness of R moiety in the ester groups. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Enantioselective addition of dialkylzinc to aldehydes in the presence of catalytic amounts of chiral catalysts is one of the most important asymmetric C–C bond formation reactions. In most cases chiral β-amino alcohols or their analogues were used as efficient catalysts in this reaction.[1]

Several chiral catalysts based on the thiazolidine ring have been reported, which showed moderate enantioselectivity.[2–4] Here we report a new type of thiazolidine derivatives **1**–**4** (Scheme 1), which were obtained from natural L-cysteine and showed good enantioselectivity as chiral catalysts in the addition of diethylzinc to aldehydes. Thiazolidines **1**–**4** bear a carboxylic acid ester group. Esters or their derivatives were seldom used as efficient catalysts. We paid particular attention to the influence that different structures of the thiazolidine rings and the bulkiness of R had on the catalytic efficiency of **1**–**4**.

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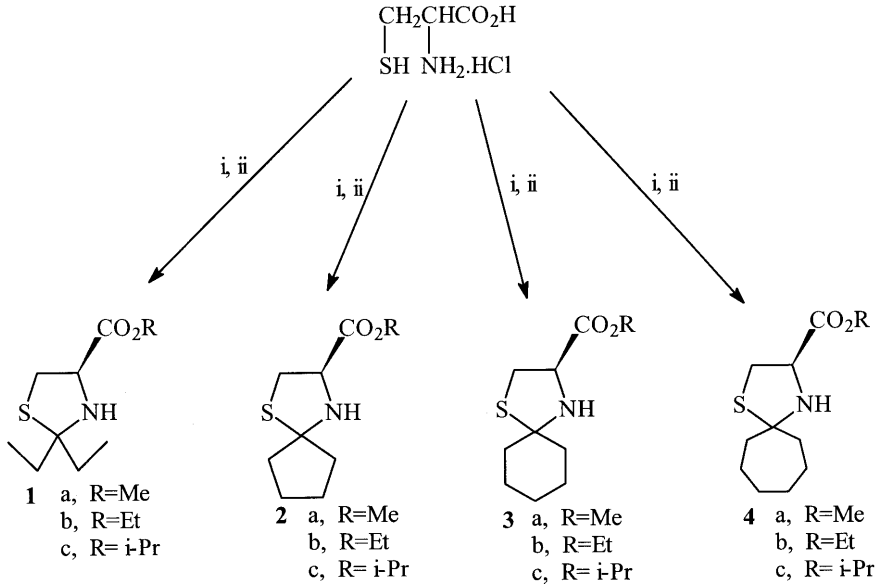


Scheme 1. (i) ROH, HCl (g); (ii) corresponding ketone, *p*-TsOH and benzene/reflux

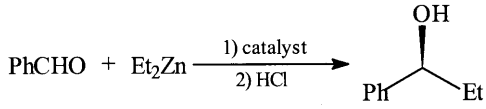
2. Results and discussion

The chiral catalysts **1**–**4** were synthesized from L-cysteine in moderate yields first by esterification and then cyclization with the corresponding ketones (Scheme 1).

The catalytic efficiency of **1**–**4** was examined in the enantioselective addition of diethylzinc to benzaldehyde at room temperature and the results are summarized in Table 1. The thiazolidine derivatives promoted the formation of (*S*)-phenethanol in 65–99% yields and 79–90% ee under 8 mol% catalytic conditions, showing moderate to high enantioselectivity.

The results of the catalytic reactions are shown in Fig. 1. We found that the bulkiness of R in the carboxylic acid ester group did affect the enantioselectivity of the catalysts. The larger R became (Me→Et→*i*-Pr) in **1**–**4**, the higher enantioselectivity the catalysts usually showed. It is probable that the carbonyl group in the carboxylic acid ester of thiazolidine derivatives takes part in the coordination with diethylzinc, so that the bulkiness of R affected the results of the catalytic reactions as R is near to the carbonyl group. Additionally, the different structures of the thiazolidine rings also affected the enantioselectivity of the catalysts. It is quite evident that **1** and **4** showed higher enantioselectivity than **2** and **3**. We believe that the ethyls in **1** and the cycloheptyl in **4** have greater freedom of movement than the corresponding cyclopentyl in **2** and cyclohexyl in **3**. Therefore **1** and **4** could present a larger steric bulk than **2** and **3** near the nitrogen and sulfur atoms in the catalysts, which play an important role in coordinating with diethylzinc in the catalytic reactions. We hold that the thiazolidine derivatives tend to show higher enantioselectivity when they have larger steric bulk in the thiazolidine rings. The enantioselectivity of the catalysts was also affected by their amounts in the catalytic reactions. In the reaction **1c** was used in different amounts (Entries 3–5) and showed relatively low enantioselectivity in 2 mol% consistency, while it showed equally high enantioselectivity at 4 and

Table 1
Enantioselective addition of diethylzinc to benzaldehyde catalyzed by **1**–**4**[a]



Entry	Catalyst	Mol%	Yield (%)[b]	ee (%)[c]	Config.[d]
1	**1a**	8	74	85	*S*
2	**1b**	8	70	88	*S*
3	**1c**	2	78	71	*S*
4	**1c**	4	99	89	*S*
5	**1c**	8	98	90	*S*
6	**2a**	8	65	79	*S*
7	**2b**	8	67	82	*S*
8	**2c**	8	77	89	*S*
9	**3a**	8	83	79	*S*
10	**3b**	8	90	80	*S*
11	**3c**	8	74	81	*S*
12	**4a**	8	90	86	*S*
13	**4b**	8	99	88	*S*
14	**4c**	8	90	89	*S*

[a] The molar ratio of aldehyde:Et_2Zn:catalyst is usually 1:2.4:0.08 and the reactions were performed at room temperature for 48 h.

[b] Yields were based on the isolated products.

[c] Determined by using HPLC on a CHIRAL OJ column (*i*-PrOH:hexane = 5:95, flow rate = 0.700 ml/min, Waters 2487 Dual λ Absorbance Detector).

[d] Reported value for (*S*)-phenylpropanol in 98% ee is $[\alpha]_D^{22} = -47.6$ ($c = 6.11$, $CHCl_3$).[5]

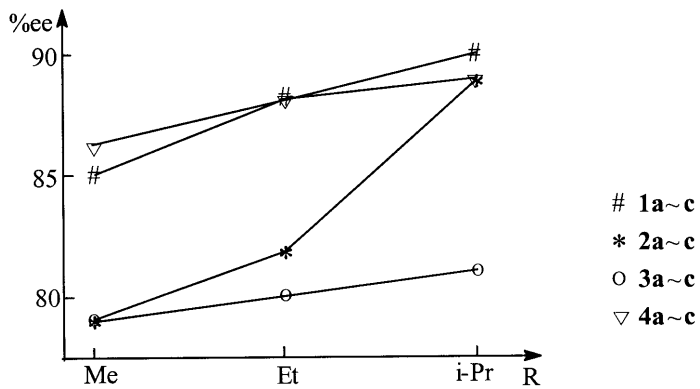


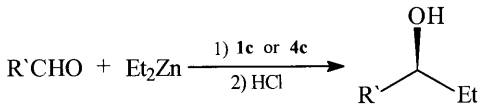
Figure 1. Relationship between the ees of chiral 1-phenyl-1-propanol and the bulkiness of R in the thiazolidine derivatives **1**–**4** in catalyzing the addition of diethylzinc to benzaldehyde

8 mol%. This means the catalysts can exhibit satisfactory enantioselectivity at only 4 mol%, although 8 mol% was used in most reactions.

Chiral catalysts **1c** and **4c** were also used in the enantioselective addition of diethylzinc to some other aldehydes and the results are summarized in Table 2. Medium to high purity of

reaction products (68–88% ee) could usually be obtained when aromatic aldehydes were used in the reaction, while moderate selectivities (52–56% ee) were obtained when *n*-heptanal was used.

Table 2
Enantioselective addition of diethylzinc to aldehydes catalyzed by **1c** and **4c**[a]



Entry	Catalyst	Mol%	R′	Yield (%)	ee (%)	Config.
15	**1c**	8	4-Cl-C_6H_4	71	88[b]	*S*
16	**1c**	8	4-MeO-C_6H_4	96	78[c]	*S*
17	**1c**	8	2-Furyl	43	78[d]	*S*
18	**1c**	8	(*E*)-C_6H_5-CH=CH	79	75[e]	*S*
19	**1c**	8	*n*-C_6H_{13}	75	52[f]	*S*
20	**4c**	8	4-Cl-C_6H_4	70	86[b]	*S*
21	**4c**	8	4-MeO-C_6H_4	99	76[c]	*S*
22	**4c**	8	2-Furyl	45	78[d]	*S*
23	**4c**	8	(*E*)-C_6H_5-CH=CH	76	68[e]	*S*
24	**4c**	8	*n*-C_6H_{13}	79	56[f]	*S*

[a] Reaction conditions are the same as in Table 1.
[b] $[\alpha]_D^{22} = -28.2$ ($c = 5.01$, benzene) for (*S*)-1-(4-chlorophenyl)-1-propanol in 100% ee.[6]
[c] $[\alpha]_D^{22} = -17.2$ (benzene) for (*S*)-1-(4-methoxyphenyl)-1-propanol in 43% ee.[7]
[d] $[\alpha]_D^{22} = -17.9$ ($c = 1.75$, chloroform) for (*S*)-1-(2-furyl)-1-propanol in 91% ee.[8]
[e] $[\alpha]_D^{20} = -6.6$ ($c = 3.18$, chloroform) for (*S*,*E*)-1-phenyl-1-penten-3-ol in 75% ee.[9]
[f] $[\alpha]_D^{24} = +9.07$ ($c = 7.2$, chloroform) for (*S*)-3-nonanol in 88% ee.[10]

In conclusion the chiral thiazolidine derivatives can be obtained conveniently from L-cysteine and have successfully been used as chiral catalysts in the enantioselective addition of diethylzinc to aldehydes, which will encourage further study on the use of easily prepared chiral catalysts in asymmetric catalysis and synthesis from readily available amino acids. Further studies on the preparation of efficient catalysts from L-cysteine are in progress.

3. Experimental

^{1}H NMR spectra were recorded on a Varian Mercury 200 MHz FT-NMR spectrometer. IR spectra were taken on a Brucker VECTOR 22 FT-IR spectrometer. Mass spectra were measured on a Hewlett Packard GC/MS System 5988A spectrometer. Elemental analysis was performed on an Elementar Vario EL instrument. Optical rotations were recorded on a Perkin Elmer 241 Polarimeter. Optical purity of 1-phenyl-1-propanol was determined on a CHIRALCEL OJ column and the specific rotation $[\alpha]_D^{20} = -47$ ($c = 2.25$, hexane)[5] for its (*S*)-enantiomer was used to determine the configuration. Silica gel H 60 was used for flash column chromatography. Diethylzinc was obtained by preparation.

3.1. General procedure of **1–4**

L-Cysteine hydrochloride (4.0 g, 25 mmol) was dissolved in 50–70 ml of corresponding anhydrous alcohol ROH and dry HCl gas was added in 0°C. The resulting solution was warmed to room temperature gradually and stirred at 40–50°C for 8 h. The alcohol was removed under reduced pressure. The resulting product was recrystallized from corresponding ROH/diethyl ether and white needles were obtained. The resulting L-cysteine ester hydrochloride was cyclized with the corresponding ketone under catalytic amounts of *p*-toluenesulfonic acid. The reaction solution was neutralized to pH 9 with a saturated K_2CO_3 solution. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with a saturated NaCl solution before drying over anhydrous K_2CO_3. The solvent was removed under reduced pressure and the obtained yellow oil was purified by flash column chromatography (ethyl acetate:petroleum = 1:3–10) to give pure **1–4**.

3.1.1. (R)-2,2-Diethyl-4-methoxycarbonylthiazolidine **1a**[3]

Colorless oil; yield: 68%; $[\alpha]_D^{20} = -139$ ($c = 1.5$, ethyl acetate); bp 232–234°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.03 (dd, $J = 6.4$, 9.4 Hz, 1H), 3.79 (s, 3H), 3.30 (dd, $J = 6.4$, 10.2 Hz, 1H), 2.84 (dd, $J = 9.6$, 10.2 Hz, 1H), 2.42 (s, 1H), 1.67–1.99 (m, 4H), 1.04 (t, $J = 7.2$ Hz, 3H), 0.92 (t, $J = 7.2$ Hz, 3H); IR (film): 3309, 2967, 1744, 1436, 1347, 1273, 1226, 1175, 847 cm^{-1}. Calcd for $C_9H_{17}NO_2S$: C, 53.17; H, 8.43; N, 6.89. Found: C, 53.05; H, 8.39; N, 6.97. MS (EI): m/z (relative intensity) 114 (38), 144 (33), 156 (45), 174 (100), 203 (M^+, 29).

3.1.2. (R)-2,2-Diethyl-4-ethoxycarbonylthiazolidine **1b**

Colorless oil; yield: 68%; $[\alpha]_D^{20} = -139$ ($c = 1.5$, ethyl acetate); bp 240–242°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.22 (dq, $J = 2.0$, 7.2 Hz, 2H), 4.00 (dd, $J = 7.0$, 9.6 Hz, 1H), 3.30 (dd, $J = 6.6$, 10.4 Hz, 1H), 2.84 (dd, $J = 9.4$, 10.2 Hz, 1H), 2.43 (s, 1H), 1.67–1.99 (m, 4H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.04 (t, $J = 7.2$ Hz, 3H), 0.92 (t, $J = 7.2$ Hz, 3H); IR (film): 3309, 2969, 1740, 1459, 1371, 1337, 1223, 1179, 1027, 850 cm^{-1}. Calcd for $C_{10}H_{19}NO_2S$: C, 55.26; H, 8.81; N, 6.44. Found: C, 55.02; H, 8.93; N, 6.44. MS (EI): m/z (relative intensity) 114 (38), 144 (28), 170 (25), 188 (100), 217 (M^+, 22).

3.1.3. (R)-2,2-Diethyl-4-(1-methylethoxy)carbonylthiazolidine **1c**

Colorless oil; yield: 78%; $[\alpha]_D^{20} = -132$ ($c = 1.5$, ethyl acetate); bp 248–250°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.09 (m, 1H), 3.98 (dd, $J = 6.8$, 9.2 Hz, 1H), 3.29 (dd, $J = 6.6$, 10.4 Hz, 1H), 2.82 (dd, $J = 9.4$, 10.4 Hz, 1H), 2.44 (s, 1H), 1.70–1.99 (m, 4H), 1.28 (dd, $J = 3.6$, 6.0 Hz, 6H), 1.05 (t, $J = 7.2$ Hz, 3H), 0.93 (t, $J = 7.2$ Hz, 3H); IR (film): 3310, 2971, 1736, 1458, 1375, 1320, 1226, 1177, 1107, 851 cm^{-1}. Calcd for $C_{11}H_{21}NO_2S$: C, 57.11; H, 9.15; N, 6.05. Found: C, 56.97; H, 9.03; N, 6.35. MS (EI): m/z (relative intensity) 114 (54), 144 (73), 184 (15), 202 (100), 231 (M^+, 38).

3.1.4. (R)-3-Methoxycarbonyl-1-thia-4-azaspiro[4.4]nonane **2a**

Light yellow oil; yield: 51%; $[\alpha]_D^{18} = -134$ ($c = 1.1$, ethyl acetate); bp >220°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.94 (dd, $J = 7.0$, 9.4 Hz, 1H), 3.79 (s, 3H), 3.38 (dd, $J = 6.8$, 10.2 Hz, 1H), 2.99 (dd, $J = 9.2$, 10.2 Hz, 1H), 2.51 (s, 1H), 1.75–2.17 (m, 8H); IR (film): 3302, 2955, 1744, 1437, 1343, 1227, 1168, 835 cm^{-1}. Calcd for $C_9H_{15}NO_2S$: C, 53.70; H, 7.51; N, 6.96. Found: C, 53.60; H, 7.32; N, 6.97. MS (EI): m/z (relative intensity) 114 (57), 142 (78), 154 (77), 172 (100), 201 (M^+, 40).

*3.1.5. (*R*)-3-Ethoxycarbonyl-1-thia-4-azaspiro[4.4]nonane* ***2b***[4]

Light yellow oil; yield: 53%; $[\alpha]_D^{19}=-136$ ($c=1.2$, ethyl acetate); bp >230°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.24 (dq, $J=1.8$, 7.2 Hz, 2H), 3.92 (dd, $J=7.2$, 9.2 Hz, 1H), 3.39 (dd, $J=7.2$, 10.4 Hz, 1H), 2.98 (dd, $J=9.4$, 10.0 Hz, 1H), 2.51 (s, 1H), 1.78–2.17 (m, 8H), 1.31 (t, $J=7.2$ Hz, 3H); IR (film): 3302, 2962, 1739, 1446, 1370, 1335, 1224, 1116, 1027, 831 cm^{-1}. Calcd for $C_{10}H_{17}NO_2S$: C, 55.78; H, 7.96; N, 6.51. Found: C, 55.58; H, 7.86; N, 6.59. MS (EI): m/z (relative intensity) 114 (44), 142 (93), 168 (59), 186 (100), 215 (M^+, 76).

*3.1.6. (*R*)-3-(1-Methylethoxy)carbonyl-1-thia-4-azaspiro[4.4]nonane* ***2c***

Light yellow oil; yield: 61%; $[\alpha]_D^{18}=-124$ ($c=1.2$, ethyl acetate); bp >230°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.10 (m, 1H), 3.90 (dd, $J=7.2$, 9.2 Hz, 1H), 3.38 (dd, $J=7.2$, 10.4 Hz, 1H), 2.96 (dd, $J=9.2$, 10.2 Hz, 1H), 2.54 (s, 1H), 1.73–2.31 (m, 8H), 1.28 (dd, $J=2.6$, 6.0 Hz, 6H); IR (film): 3303, 2962, 1735, 1450, 1361, 1325, 1227, 1169, 1107, 822 cm^{-1}. Calcd for $C_{11}H_{19}NO_2S$: C, 57.61; H, 8.35; N, 6.11. Found: C, 57.81; H, 8.40; N, 5.88. MS (EI): m/z (relative intensity) 114 (25), 142 (100), 182 (11), 200 (41), 229 (M^+, 43).

*3.1.7. (*R*)-3-Methoxycarbonyl-1-thia-4-azaspiro[4.5]decane* ***3a***

Colorless oil; yield: 51%; $[\alpha]_D^{20}=-138$ ($c=1.0$, ethyl acetate); bp 234–236°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.07 (dd, $J=6.8$, 9.4 Hz, 1H), 3.79 (s, 3H), 3.30 (dd, $J=6.6$, 10.4 Hz, 1H), 2.88 (dd, $J=9.6$, 10.4 Hz, 1H), 2.43 (s, 1H), 1.29–1.91 (m, 10H); IR (film): 3300, 2931, 1744, 1437, 1348, 1232, 1199, 1157, 878, 802 cm^{-1}. Calcd for $C_{10}H_{17}NO_2S$: C, 55.78; H, 7.96; N, 6.51. Found: C, 55.88; H, 7.99; N, 6.48. MS (EI): m/z (relative intensity) 41 (98), 59 (100), 156 (23), 168 (38), 172 (49), 215 (M^+, 25).

*3.1.8. (*R*)-3-Ethoxycarbonyl-1-thia-4-azaspiro[4.5]decane* ***3b***[4]

Colorless oil; yield: 58%; $[\alpha]_D^{20}=-142$ ($c=1.5$, ethyl acetate); bp 248–250°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.26 (dq, $J=2.0$, 7.2 Hz, 2H), 4.04 (dd, $J=6.6$, 9.6 Hz, 1H), 3.30 (dd, $J=6.6$, 10.4 Hz, 1H), 2.87 (dd, $J=9.6$, 10.2 Hz, 1H), 2.43 (s, 1H), 1.46–1.91 (m, 10H), 1.31 (t, $J=7.2$ Hz, 3H); IR (film): 3301, 2932, 1739, 1447, 1371, 1341, 1191, 1157, 1026, 880, 800 cm^{-1}. Calcd for $C_{11}H_{19}NO_2S$: C, 57.61; H, 8.35; N, 6.11. Found: C, 57.48; H, 8.76; N, 6.30. MS (EI): m/z (relative intensity) 156 (73), 182 (84), 186 (100), 229 (M^+, 82).

*3.1.9. (*R*)-3-(1-Methylethoxy)carbonyl-1-thia-4-azaspiro[4.5]decane* ***3c***

Colorless oil; yield: 54%; $[\alpha]_D^{20}=-144$ ($c=1.2$, ethyl acetate); bp >252°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.10 (m, 1H), 4.01 (dd, $J=6.6$, 9.4 Hz, 1H), 3.29 (dd, $J=6.4$, 10.2 Hz, 1H), 2.84 (dd, $J=9.4$, 10.0 Hz, 1H), 2.44 (s, 1H), 1.46–1.92 (m, 10H), 1.28 (dd, $J=3.4$, 6.2 Hz, 6H); IR (film): 3301, 2932, 1736, 1448, 1362, 1232, 1194, 1158, 1107, 878, 801 cm^{-1}. Calcd for $C_{12}H_{21}NO_2S$: C, 59.22; H, 8.70; N, 5.76. Found: C, 59.03; H, 8.75; N, 5.82. MS (EI): m/z (relative intensity) 156 (14), 196 (20), 200 (55), 243 (M^+, 100).

*3.1.10. (*R*)-3-Methoxycarbonyl-1-thia-4-azaspiro[4.6]undecane* ***4a***

Colorless oil; yield: 67%; $[\alpha]_D^{20}=-124$ ($c=1.8$, ethyl acetate); bp 240–242°C; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.02 (dd, $J=6.6$, 9.2 Hz, 1H), 3.78 (s, 3H), 3.34 (dd, $J=6.8$, 10.6 Hz, 1H), 2.91 (dd, $J=9.6$, 10.6 Hz, 1H), 2.48 (s, 1H), 1.58–2.15 (m, 12H); IR (film): 3305, 2928, 2855, 1744, 1437, 1345, 1220, 1170, 1007, 942, 850, 790 cm^{-1}. Calcd for $C_{11}H_{19}NO_2S$: C, 57.61; H, 8.35; N, 6.11. Found: C, 57.57; H, 8.05; N, 6.14. MS (EI): m/z (relative intensity) 95 (60), 112 (78), 170 (60), 172 (100), 182 (90), 196 (94), 229 (M^+, 71).

3.1.11. (R)-3-Ethoxycarbonyl-1-thia-4-azaspiro[4.6]undecane ***4b***

Colorless oil; yield: 38%; $[\alpha]_D^{20} = -137$ ($c = 2.0$, ethyl acetate); bp >254°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.20 (dq, $J = 2.0$, 7.2 Hz, 2H), 3.98 (dd, $J = 6.8$, 9.2 Hz, 1H), 3.33 (dd, $J = 6.4$, 10.2 Hz, 1H), 2.89 (dd, $J = 9.2$, 10.2 Hz, 1H), 2.35 (s, 1H), 1.66–2.14 (m, 12H), 1.31 (t, $J = 7.2$ Hz, 3H); IR (film): 3306, 2980, 2928, 2856, 1740, 1459, 1371, 1337, 1212, 1178, 1026, 853, 789 cm^{-1}. Calcd for $C_{12}H_{21}NO_2S$: C, 59.22; H, 8.70; N, 5.76. Found: C, 59.17; H, 8.50; N, 5.62. MS (EI): m/z (relative intensity) 95 (67), 112 (93), 170 (100), 186 (97), 196 (92), 210 (96), 243 (M^+, 72).

3.1.12. (R)-3-(1-Methylethoxy)carbonyl-1-thia-4-azaspiro[4.6]undecane ***4c***

Colorless oil; yield: 34%; $[\alpha]_D^{20} = -124$ ($c = 1.5$, ethyl acetate); bp >254°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.09 (m, 1H), 3.95 (dd, $J = 6.8$, 9.2 Hz, 1H), 3.32 (dd, $J = 6.8$, 10.2 Hz, 1H), 2.86 (dd, $J = 9.2$, 10.4 Hz, 1H), 2.41 (s, 1H), 1.57–2.14 (m, 12H), 1.28 (dd, $J = 2.6$, 6.2 Hz, 6H); IR (film): 3306, 2980, 2929, 2856, 1736, 1459, 1364, 1322, 1220, 1179, 1108, 993, 852, 795 cm^{-1}. Calcd for $C_{13}H_{23}NO_2S$: C, 60.66; H, 9.01; N, 5.44. Found: C, 60.47; H, 8.87; N, 5.76. MS (EI): m/z (relative intensity) 112 (63), 168 (46), 170 (100), 200 (36), 210 (31), 224 (43), 257 (M^+, 46).

3.2. A typical procedure for the addition of diethylzinc to aldehyde catalyzed by ***1–4***

A solution of 0.16 mmol chiral catalyst in 15 ml of dry toluene and hexane (v/v = 1:1) was cooled to 0°C and diethylzinc (0.5 ml, 4.8 mmol) was added under a nitrogen atmosphere. After 20 min, 2 mmol aldehyde was added under stirring. The reaction mixture was gradually warmed to room temperature and stirred for 48 h. The reaction mixture was quenched by 10% hydrochloric acid at 0°C, then the organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed by saturated $NaHCO_3$ and NaCl solutions, respectively, before drying over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by flash column chromatography (ethyl acetate:petroleum ether = 1:10) and distilled under vacuum to afford the optically active secondary alcohol.

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