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Enantioselective reaction of α-lithiated thiazolidines as new chiral formyl anion equivalents

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Abstract—The reaction of lithiated *N*-Boc-thiazolidine and *N*-Boc-benzothiazolidine with benzophenone in the presence of (−)-sparteine afforded the products with up to 97% ee and 93% ee, respectively. The reaction with various aromatic and aliphatic aldehydes also afforded the products with high enantioselectivity and moderate diastereoselectivity. Each diastereomer could be converted to optically active diols. Consequently, lithiated *N*-Boc-thiazolidine and *N*-Boc-benzothiazolidine serve as chiral formyl anion equivalents. The reaction was confirmed to proceed through a dynamic thermodynamic resolution pathway.

1. Introduction

Chiral formyl anion equivalents are useful tools for asymmetric synthesis. There are many examples of chiral formyl anion equivalents using various chiral auxiliaries. Diastereoselective reactions of carbanions derived from dithioacetals,[1] N,S-acetals,[2] hemithioacetals,[3] 1,3-dioxolanes[4] and 1,3-oxazolidines,[5] have been reported. On the other hand, there are only a few enantioselective reactions reported and reactions of carbanions derived from dithioacetals[6] and oxazolidines[7] have been reported. We have previously reported highly enantioselective lithiation–substitution reactions of α-thio carbanion of various sulfides in the presence of bis(oxazoline)s,[8,9] and an enantioselective reaction using unsymmetrical dithioacetals as chiral formyl anion equivalents.[10] We recently reported the first highly enantioselective reaction of the thiazolidine.[11] Herein we report in detail an enantioselective reaction of lithiated *N*-Boc-thiazolidine and *N*-Boc-benzothiazolidine with benzophenone and various aromatic and aliphatic aldehydes and the subsequent transformation of the products to chiral 1,2-ethanediols.

2. Results and discussion

2.1. Reaction of Li-1 and Li-2 with benzophenone

We first examined the reaction of lithiated *N*-Boc-thiazolidine Li-**1** and *N*-Boc-benzothiazolidine Li-**2** with benzophenone using either (−)-sparteine **5**, 2,2-bis{2-[(4*S*)-alkyl-1,3-dioxazolinyl]}propane **6a–c** [bis(oxazoline)–R], or (1*R*,2*R*)-*N*,*N*,*N*′*N*′-tetramethylcyclohexane-1,2-diamine **7**, as a chiral ligand (Scheme 1). *N*-Boc-thiazolidine **1** and *N*-Boc-benzothiazolidine **2** were treated with 1.2 equiv of *n*-BuLi for 15 min at an appropriate temperature and subsequently with 1.2 equiv of a chiral ligand for 1 h. To the resultant solution was added 1.3 equiv of benzophenone with the corresponding enantiomeric products **3** and **4** obtained. The results are shown in Table 1. The reaction in THF in the presence of (−)-sparteine at −78 °C gave product **3** in good yield but with low enantioselectivity (entry 1), while when the reaction was performed in Et_2O and hexane, good enantioselectivity was obtained (entries 2 and 3). On the other hand, the reaction in cumene showed high enantioselectivity (entries 4 and 5). The reaction in toluene at −78 °C also showed excellent enantioselectivity (entry 6), while at −95 °C the enantioselectivity (entry 7) was slightly lowered. The enantioselectivity also decreased when performed at higher temperatures (entries 8 and 9). The reaction using *s*-BuLi or *t*-BuLi did not improve the yield (entries 10 and 11). Bis(oxazoline)-^{i}Pr **6a** and bis(oxazoline)-^{t}Bu **6b** showed rather low

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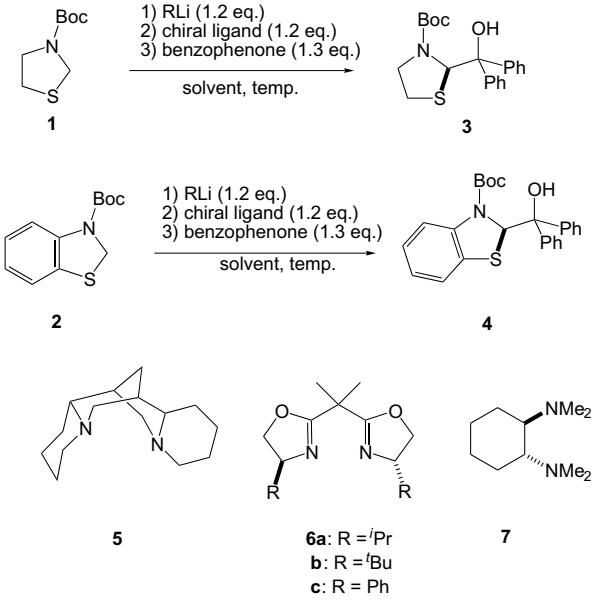


Scheme 1.

enantioselectivity[12] (entries 12 and 13), whereas with bis(oxazoline)-Ph **6c**, **3** was obtained with good enantioselectivity but with the opposite stereochemistry of that obtained above (entry 14). Cyclohexanediamine **7** did not afford a satisfactory result (entry 15). The reaction of lithiated *N*-Boc-benzothiazolidine **2** with benzophenone using (−)-sparteine **5** in toluene or cumene both at −78 °C and at −95 °C gave good enantiomeric purity of product **4** in good yield (entries 16–19).

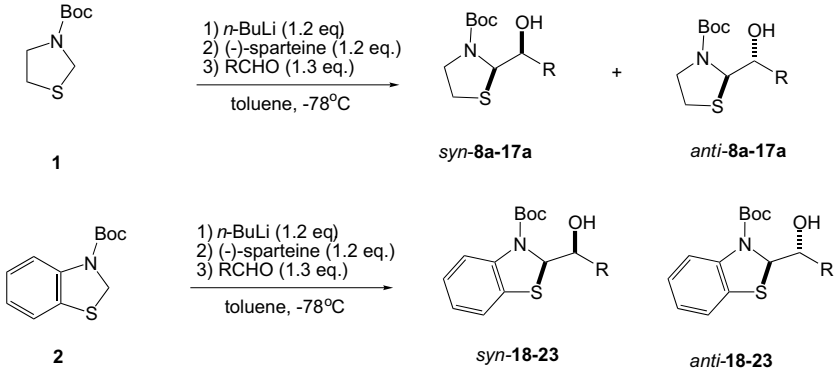
2.2. Reaction of Li-1 and Li-2 with aldehydes

The enantioselective reaction of lithiated *N*-Boc-thiazolidine Li-**1** and lithiated *N*-Boc-benzothiazolidine Li-**2** with various aldehydes was next examined (Scheme 2, Table 2). Treatment of *N*-Boc-thiazolidine **1** with 1.2 equiv of *n*-BuLi and 1.2 equiv of (−)-sparteine in toluene at −78 °C for 1 h, followed by the addition of various aldehydes, gave the corresponding alcohols **8a**–**17a** in good yields. Since each diastereomer derived from the reaction with aromatic aldehydes could not be separated by column chromatography, the obtained alcohols **8a**–**13a** were converted to the corresponding acetates **8b**–**13b**, which could be easily separated by column chromatography. When benzaldehyde was used, product **8a** was obtained in 74% yield and in a 42:58 diastereomer ratio. The enantiomeric excess of the *syn*- and *anti*-isomers were determined to be 93% and 88% ee, respectively, by the HPLC analysis after conversion to the corresponding acetate (entry 1). The reaction of lithiated *N*-Boc-thiazolidine Li-**1** with other aromatic aldehydes such as *p*-tolualdehyde, *p*-anisaldehyde, *p*-chlorobenzaldehyde, 1-naphthaldehyde, and 2-naphthaldehyde gave the corresponding products **9a**–**13a**, each *syn*- and *anti*-isomer of which had high enantiomeric purity (entries 2–6). Although the reaction with propanal afforded product **14a** with moderate enantioselectivity (entry 7), the reaction with other aliphatic aldehydes, such as 3-methylbutanal, cyclohexanecarbaldehyde and 2,2-dimethylpropanal, afforded products **15a**–**17a** with high enantioselectivities (entries 8–10). The *syn*- and *anti*-isomers of **14a**–**17a** could be separated by column chromatography. The reaction of lithiated *N*-Boc-benzothiazolidine Li-**2** with various aldehydes gave the corresponding alcohols **18**–**23** in high yields. Both the *syn*- and *anti*-isomers were formed with high enantioselectivity. In the reaction of **2**, the *syn*- and *anti*-isomers of alcohols **18**–**23** were easily separable by column chromatography. When benzaldehyde was used, alcohol **18** was obtained in 93% yield in a 60:40 diastereomer ratio, with the enantiomeric excesses of the *syn*- and *anti*-isomers were determined to be 93% and 88% ee, respectively, (entry 11). The reaction with various aromatic aldehydes afforded the corresponding products

Table 1. Enantioselective reaction of lithiated *N*-Boc-thiazolidine **1** and *N*-Boc-benzothiazolidine **2** with benzophenone

Entry	Substrate	RLi	Solvent	Chiral ligand	Reaction temperature (°C)	Product	Yield (%)	Ee (%)[a]
1	**1**	*n*-BuLi	THF	**5**	−78	**3**	76	19
2	**1**	*n*-BuLi	Et_2O	**5**	−78	**3**	43	60
3	**1**	*n*-BuLi	Hexane	**5**	−78	**3**	44	84
4	**1**	*n*-BuLi	Cumene	**5**	−78	**3**	54	92
5	**1**	*n*-BuLi	Cumene	**5**	−95	**3**	36	97
6	**1**	*n*-BuLi	Toluene	**5**	−78	**3**	65	97
7	**1**	*n*-BuLi	Toluene	**5**	−95	**3**	32	92
8	**1**	*n*-BuLi	Toluene	**5**	−50	**3**	69	64
9	**1**	*n*-BuLi	Toluene	**5**	−30	**3**	35	−13
10	**1**	*s*-BuLi	Toluene	**5**	−78	**3**	31	53
11	**1**	*t*-BuLi	Toluene	**5**	−78	**3**	36	35
12	**1**	*n*-BuLi	Toluene	**6a**	−78	**3**	53	−13
13	**1**	*n*-BuLi	Toluene	**6b**	−78	**3**	57	−68
14	**1**	*n*-BuLi	Toluene	**6c**	−78	**3**	17	82
15	**1**	*n*-BuLi	Toluene	**7**	−78	**3**	21	−19
16	**2**	*n*-BuLi	Toluene	**5**	−78	**4**	74	93[b]
17	**2**	*n*-BuLi	Cumene	**5**	−78	**4**	70	94[b]
18	**2**	*n*-BuLi	Toluene	**5**	−95	**4**	60	92[b]
19	**2**	*n*-BuLi	Cumene	**5**	−95	**4**	53	93[b]

[a] Determined by the HPLC analysis using chiralcel OD-H.
[b] Determined by the HPLC analysis using chiralpak AD-H.



Scheme 2.

Table 2. Enantioselective reaction of Li-**1** and Li-**2** with various aldehydes

Entry	Substrate	R	Product	Yield (%)	*syn*/*anti*[a]	*syn* Ee (%)[b]	*anti* Ee (%)[b]
1	**1**	Ph	**8a**	74	42:58	93[c]	88 [c]
2	**1**	*p*-MeC_6H_4	**9a**	65	46:54	69[c]	89[c]
3	**1**	*p*-$MeOC_6H_4$	**10a**	58	43:57	66[c]	90[c]
4	**1**	*p*-ClC_6H_4	**11a**	65	42:58	60[c]	88[c]
5	**1**	1-Naphthyl	**12a**	55	22:78	64[c]	88[c]
6	**1**	2-Naphthyl	**13a**	72	42:58	65[c]	90[c]
7	**1**	Et	**14a**	67	59:41	46	—[d]
8	**1**	*i*-Pr	**15a**	54	53:47	77	87
9	**1**	*c*-Hex	**16a**	69	61:39	73	89
10	**1**	*tert*-Bu	**17a**	63	51:49	72	87
11	**2**	Ph	**18**	93	60:40	93	88
12	**2**	*p*-MeC_6H_4	**19**	92	53:47	75	93
13	**2**	*p*-$MeOC_6H_4$	**20**	92	55:45	72	88
14	**2**	*p*-ClC_6H_4	**21**	96	51:49	78	89
15	**2**	1-Naphthyl	**22**	89	57:43	71	86
16	**2**	2-Naphthyl	**23**	97	58:42	73	86

[a] Determined by the ^1H NMR analysis.
[b] Determined by the HPLC analysis using chiralcel OD-H, OJ-H, or chiralpak AD-H.
[c] Determined by the HPLC analysis after conversion to the acetate.
[d] The enantiomeric purity could not be determined by various chiral columns.

19–**23**, the *syn*- and *anti*-isomers of which were formed with high enantioselectivity (entries 12–16).[13] Generally, the *anti*-isomers had higher enantiomeric purity than the *syn*-isomers except for **18** (entry 11). The *syn*-isomers formed from *N*-Boc-benzothiazolidine **2** had higher enantioselectivities than those from *N*-Boc-thiazolidine **1**, whereas the *anti*-isomers obtained from *N*-Boc-thiazolidine **1** and *N*-Boc-benzothiazolidine **2** had the same range of enantiomeric excess.

2.3. Configuration of the stereochemistry of 8b–13b and 18–23

The relative stereochemistry of *syn*-**8b** and *syn*-**18** was confirmed by X-ray crystallographic analysis (Fig. 1), and the absolute configuration was determined by transformation to the known chiral 1-phenyl-1,2-ethanediol (vide infra).

The chemical shifts of the H_a and H_b protons and their coupling constants in the ^1H NMR spectra of **8a**–**13a** and **18**–**23** are shown in Table 3. Generally, the *anti*-isomers of **8b**–**13b** showed larger $J_{a,b}$ values and downfield shifts for the H_b protons in comparison with those of the corresponding *syn*-isomers. On the other hand, the $J_{a,b}$ values of *syn*-**18**–**23** were not clearly defined because both protons of H_a and H_b appeared as broad singlets. The H_a and H_b protons of *syn*-**18**–**23** appeared at higher and lower field, respectively, than those of the corresponding *anti*-isomers. Thus, the relative stereochemistry of **9b**–**13b**, that is, **9a**–**13a**, and **19**–**23** was tentatively assigned by comparison of the $J_{a,b}$ values and the chemical shifts for the H_a and H_b protons with those for **8b** and **18**.

2.4. Conversion to optically active 1,2-ethanediols

In order to define the absolute configuration, the *syn*- and *anti*-isomers of **8b**–**13b** and **18**–**23** were separately converted to the chiral 1,2-ethanediols. Thus, *syn*- and *anti*-**8b**–**13b** were treated with mercury(II) chloride in aqueous CH_3CN at room temperature for 6–12 h to give the corresponding 2-acetoxy-2-arylacetaldehydes, which, without isolation, were subjected to reduction with $LiAlH_4$ in THF at 0 °C. Optically active 1-aryl-1,2-ethanediols **24**–**29** were obtained in good yields

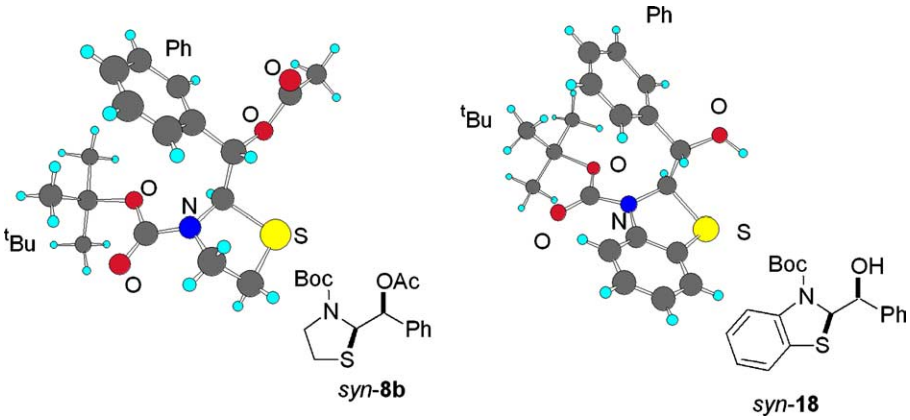
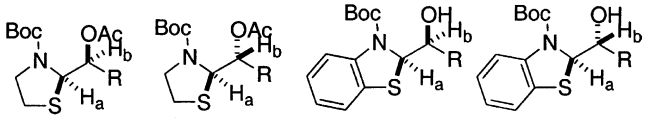


Figure 1. The Chem 3D structures derived from the X-ray crystallography of *syn*-**8b** and *syn*-**18**.

Table 3. The ^{1}H NMR analysis for the products **8b**–**13b** and **18**–**23**



syn-**8b**-**13b** *anti*-**8b**-**13b** *syn*-**18**-**23** *anti*-**18**-**23**

Compound[a]	$J_{a,b}$ (Hz)	δ H_a (ppm)	δ H_b (ppm)
syn-**8b**	4.2	5.96	5.34
anti-**8b**	6.6	5.98	5.45
syn-**9b**	4.2	5.94	5.29
anti-**9b**	6.8	5.90	5.44
syn-**10b**	4.2	5.91	5.30
anti-**10b**	6.8	5.93	5.43
syn-**11b**	4.2	5.92	5.25
anti-**11b**	6.8	5.94	5.39
syn-**12b**	4.2	6.80	5.59
anti-**12b**	6.2	6.63	5.84
syn-**13b**	3.8	6.13	5.43
anti-**13b**	6.4	6.11	5.58
syn-**18**	—[b]	5.83	4.80
anti-**18**	7.8	5.95	4.74
syn-**19**	—[b]	5.81	4.80
anti-**19**	7.8	5.92	4.67
syn-**20**	—[b]	5.80	4.78
anti-**20**	7.8	5.91	4.68
syn-**21**	—[b]	5.76	4.75
anti-**21**	7.0	5.90	4.73
syn-**22**	—[b]	6.11	5.55
anti-**22**	6.2	6.31	5.54
syn-**23**	—[b]	5.90	4.98
anti-**23**	7.6	6.04	4.87

[a] The relative stereochemistry is the one tentatively assigned except for **8b** and **18**.

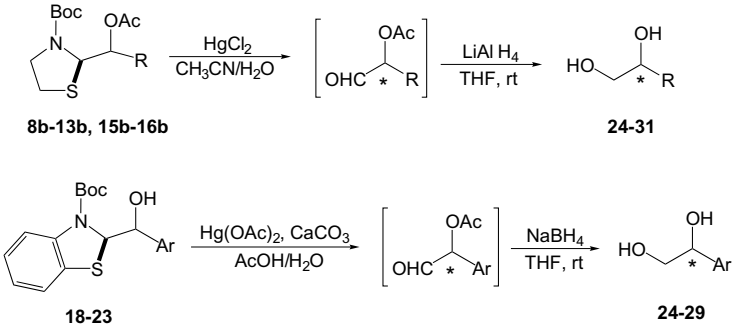
[b] Each H_a and H_b proton appeared as a broad signal.

(Scheme 3, Table 4). The reaction of *syn*-**8b** and *anti*-**8b** gave optically active 1-phenyl-1,2-ethanediol **24** in 66% and 57% yields, respectively, without loss of the enantiomeric purity. The absolute configurations of the 1,2-ethanediols **24** derived from *syn*-**8b** and *anti*-**8b** were assigned to be *S* and *R*, respectively, by comparison of the values of the specific rotation with those reported (entries 1 and 2).[14] Therefore, the absolute configurations of *syn*-**8b** and *anti*-**8b** were determined to be (1′*S*,2*R*) and (1′*R*,2*R*), respectively. Chiral 1,2-ethanediols **25**–**29** were also obtained from **9b**–**13b**. Under similar reaction conditions, products **15b** and **16b** formed in the reaction of **1** and aliphatic aldehydes could be converted to the corresponding 1,2-ethanediols **30** and **31** with moderate yields without loss of the enantiomeric purity (entries 13–16). Since the deprotection of **18** using mercury(II) chloride afforded product **24** in rather low yield, **18**–**23** were treated with mercury(II) acetate in aqueous acetic acid for 6 h at 50 °C to give the corresponding 2-hydroxy-2-arylacetaldehydes, which were subjected to reduction with $NaBH_4$ in MeOH at room temperature to give the corresponding chiral 1,2-ethanediols **24**–**29** in good yields (entries 13–24). Similarly, the absolute configurations of *syn*-**18**–**23** and *anti*-**18**–**23** were determined to be (1′*S*,2*R*) and (1′*R*,2*R*), respectively. Therefore, the major isomers of **3** and **4** obtained in the reaction of Li-**1** and Li-**2** with benzophenone were tentatively assigned to be the *R*-isomer.

Recrystallization of the products was attempted to increase the enantiopurity. For example, a single recrystallization of *anti*-**8b** (88% ee) from hexane was found to increase the enantiomeric purity to 99% ee. It was converted to the corresponding optically active 1,2-ethanediol (*R*)-**24** with 99% ee (Scheme 4). The enantiomeric purity of other crystalline products could also be improved by recrystallization. Thus, the present enantioselective reaction of lithiated N,S-acetals provides an efficient method for the synthesis of enantiomerically pure 1,2-ethanediols.

2.5. Reaction mechanism

It is important to determine whether the reaction proceeds through asymmetric deprotonation[15] or asymmetric substitution.[16] We examined the reaction of Li-**1** and racemic *tert*-butyl 2-(tributylstannyl)thiazolidine-3-carboxylate **32** that was prepared from lithiated **1** with tributylstannyl chloride with benzophenone in the presence of (−)-sparteine.[17] Treatment of **32** with a mixture of 1.2 equiv of *n*-BuLi and (−)-sparteine at −78 °C for 15 min in toluene followed by the addition of 1.3 equiv of benzophenone gave the product (*R*)-**3** with 60% ee (Scheme 5). The enantiomeric purity of (*R*)-**3** was slightly diminished, reduced from that (76% ee) obtained



Scheme 3.

Table 4. Conversion of **8b**–**13b** and **18**–**23** to chiral 1,2-ethanediols **24**–**31**

Entry	Substrate			1,2-Ethanediols[a]		
		R	Ee (%)		Yield (%)	Ee[b] (%)
1	*syn*-**8b**	Ph	93	(*S*)-**24**	66	92
2	*anti*-**8b**	Ph	88	(*R*)-**24**	57	87
3	*syn*-**9b**	*p*-MeC_6H_4	69	(*S*)-**25**	68	67
4	*anti*-**9b**	*p*-MeC_6H_4	89	(*R*)-**25**	75	88
5	*syn*-**10b**	*p*-$MeOC_6H_4$	66	(*S*)-**26**	55	66
6	*anti*-**10b**	*p*-$MeOC_6H_4$	90	(*R*)-**26**	58	90
7	*syn*-**11b**	*p*-ClC_6H_4	60	(*S*)-**27**	73	60
8	*anti*-**11b**	*p*-ClC_6H_4	88	(*R*)-**27**	62	88
9	*syn*-**12b**	1-Naphthyl	64	(*S*)-**28**	60	63
10	*anti*-**12b**	1-Naphthyl	88	(*R*)-**28**	62	87
11	*syn*-**13b**	2-Naphthyl	65	(*S*)-**29**	52	64
12	*anti*-**13b**	2-Naphthyl	90	(*R*)-**29**	54	88
13	*syn*-**15b**	*i*-Pr	77	(*S*)-**30**	44	77
14	*anti*-**15b**	*i*-Pr	87	(*R*)-**30**	49	85
15	*syn*-**16b**	*c*-Hex	73	(*S*)-**31**	69	70
16	*anti*-**16b**	*c*-Hex	89	(*R*)-**31**	57	89
17	*syn*-**18**	Ph	93	(*S*)-**24**	74	93
18	*anti*-**18**	Ph	88	(*R*)-**24**	59	88
19	*syn*-**19**	*p*-MeC_6H_4	75	(*S*)-**25**	54	74
20	*anti*-**19**	*p*-MeC_6H_4	93	(*R*)-**25**	67	89
21	*syn*-**20**	*p*-$MeOC_6H_4$	72	(*S*)-**26**	61	69
22	*anti*-**20**	*p*-$MeOC_6H_4$	88	(*R*)-**26**	55	88
23	*syn*-**21**	*p*-ClC_6H_4	78	(*S*)-**27**	62	78
24	*anti*-**21**	*p*-ClC_6H_4	89	(*R*)-**27**	71	87
25	*syn*-**22**	1-Naphthyl	71	(*S*)-**28**	57	69
26	*anti*-**22**	1-Naphthyl	86	(*R*)-**28**	61	82
27	*syn*-**23**	2-Naphthyl	73	(*S*)-**29**	58	73
28	*anti*-**23**	2-Naphthyl	86	(*R*)-**29**	49	85

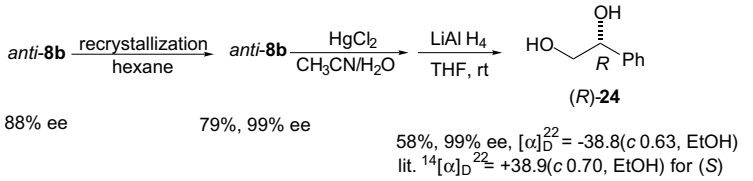
[a] The absolute configuration was determined by comparison of the value of the specific rotation with those reported.
[b] Calculated by comparison of the value of the specific rotation with those reported.

in the reaction of *N*-Boc-thiazolidine **1** under similar conditions, which are different from those performed in the reaction described earlier in Scheme 1, but 60% ee of the product is enough to rule out the asymmetric deprotonation, because the reaction through asymmetric deprotonation should afford the racemic product. Thus, the reaction proceeds through asymmetric substitution.

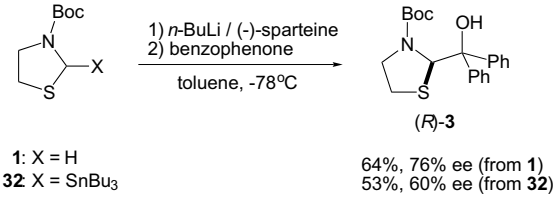
The Beak test using a deficient amount of the electrophile[16f,18] was examined. After treatment of **1** with *n*-BuLi and (−)-sparteine in toluene at −78 °C, 0.1 equiv of benzophenone was added (Scheme 6). The enantiomeric purity of the product **3** was 79% ee, which was lower than that (97% ee) obtained in the reaction with 1.3 equiv of benzophenone (entry 6, Table 1). These results indicate that the reaction of lithiated *N*-Boc-thiazolidine with benzophenone, and hence possibly with aromatic and aliphatic aldehydes, should proceed through a dynamic thermodynamic resolution pathway.

3. Conclusion

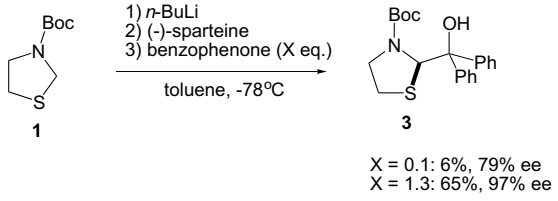
In summary, the enantioselective reaction of lithiated *N*-Boc-thiazolidine and *N*-Boc-benzothiazolidine with various carbonyl compounds in the presence of (−)-sparteine proceeded with high enantioselectivity and moderate diastereoselectivity. The reaction was found to proceed through a dynamic thermodynamic resolution pathway.



Scheme 4.



Scheme 5.



Scheme 6.

Each diastereomer was converted to optically active 1,2-ethanediols without substantial racemization during the reaction. The present new chiral formyl anion equivalents provide a convenient method for the preparation of optically active 1,2-ethanediols.

4. Experimental section

4.1. Synthesis of *tert*-Butyl thiazolidine-3-carboxylate 1 and *tert*-butyl benzothiazolidine-3-carboxylate 2

4.1.1. *tert*-Butyl thiazolidine-3-carboxylate 1.[19] A solution of thiazolidine (1.42 g, 15.9 mmol) and di-*tert*-butyl dicarbonate (3.47 g, 15.9 mmol) in THF (30 mL) and water (30 mL) was stirred for 20 h at room temperature. The reaction mixture was extracted with ethyl acetate. The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel 100 g, hexane/ethyl acetate = 96:4) to give 1 (3.0 g, 100%); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.47 (9H, s), 2.97 (2H, t, J = 6.2 Hz), 3.67 (2H, t, J = 6.2 Hz), 4.42 (2H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ 29.7, 32.2, 48.7, 51.5, 80.3, 153.2; IR (neat): 2975, 2880, 1698, 1476, 1455, 1391, 1260, 1161, 874, 768 cm^{-1}; MS (FAB) *m/z* (%): 190 (M^++1, 13), 132 (19), 88 (8), 57 (100). Anal. Calcd for $C_8H_{15}NO_2S$: C, 50.76; H, 7.99; N, 7.40. Found: C, 50.77; H, 8.20; N, 7.17.

4.1.2. *tert*-Butyl benzothiazolidine-3-carboxylate 2.[20] To a solution of benzothiazolidine (1.68 g, 12.2 mmol) and di-*tert*-butyl dicarbonate (2.67 g, 12.2 mmol) in acetonitrile (20 mL) was added 4-dimethylaminopyridine (150 mg, 1.23 mmol). The reaction mixture was stirred for 24 h at room temperature. Saturated aqueous NH_4Cl was added and the mixture extracted with ethyl acetate. The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel 100 g, hexane/ethyl acetate = 99:1) to give **2** (1.54 g, 53%); ^{1}H NMR ($CDCl_3$): δ 1.56 (9H, s), 5.19 (2H, s), 6.88–7.12 (3H, m), 7.51–7.78 (1H, m); ^{13}C NMR ($CDCl_3$): δ 28.5, 51.2, 81.2, 116.5, 122.0, 123.3, 125.0, 151.8; IR (neat): 2978, 2929, 1714, 1580, 1474, 1367, 1274, 1158, 1014, 854, 746 cm^{-1}; MS (FAB) *m/z* (%): 237 (M^+, 11), 180 (10), 136 (51), 57 (100). Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37; N, 5.90. Found: C, 60.69; H, 6.39; N, 5.77.

4.2. Typical procedure for the reaction of 1 and 2 with benzophenone

4.2.1. *tert*-Butyl 2-(1-hydroxy-1,1-diphenylmethyl)thiazolidine-3-carboxylate 3. To a solution of **1** (24 mg, 0.127 mmol) in toluene (0.6 mL) was added *n*-BuLi (0.10 mL, 1.49 mol L^{-1} solution in hexane, 0.152 mmol) dropwise over a period of 5 min at −78 °C, and the reaction mixture stirred for 15 min. Then a solution of (−)-sparteine (36 mg, 0.152 mmol) in toluene (0.3 mL) was added. After the reaction mixture was stirred for 1 h, a solution of benzophenone (30 mg, 0.165 mmol) in toluene (0.3 mL) was added and the mixture stirred for an additional 20 min. Saturated aqueous NH_4Cl was added and the mixture extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to leave a residue, which was purified by column chromatography (silica gel 10 g, hexane/EtOAc = 95:5) to give **3** (31 mg, 65%). Mp 148–149 °C; ^{1}H NMR ($CDCl_3$): δ 1.17 (9H, s), 2.79–2.97 (2H, m), 3.42–3.76 (2H, m), 4.51 (1H, br), 6.29 (1H, s), 7.17–7.54 (10H, m); ^{13}C NMR ($CDCl_3$): δ 27.9, 31.8, 49.6, 70.6, 80.8, 81.4, 126.6, 126.8, 127.3, 128.0, 142.6, 144.8, 153.3; IR (KBr): 3404, 3054, 2973, 1692, 1493, 1450, 1403, 1272, 1151, 1095, 1063, 982, 887, 740, 697 cm^{-1}; MS (FAB) *m/z* (%): 372 (M^++1, 6), 354 (4), 298 (80), 254 (44), 188 (47), 154 (22), 132 (76), 105 (27), 88 (40), 57 (100). Anal. Calcd for $C_{21}H_{25}NO_3S$: C, 67.89; H, 6.78; N, 3.77. Found: C, 67.90; H, 6.88; N, 3.65; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 10.8 (*S*) and 12.8 (*R*) min.

4.2.2. *tert*-Butyl 2-(1-hydroxy-1,1-diphenylmethyl)benzothiazolidine-3-carboxylate 4. The reaction was carried out as described above except for using **2** (27 mg,

0.110 mmol), *n*-BuLi (0.10 mL, 1.32 mol L^{-1} solution in hexane, 0.132 mmol), (−)-sparteine (32 mg, 0.138 mmol), and benzophenone (26 mg, 0.144 mmol). Usual work-up gave the crude product, which was purified by column chromatography (silica gel 10 g, hexane/EtOAc = 98:2) to afford **4** (34 mg, 74%). Mp 165–166 °C; ^{1}H NMR ($CDCl_3$): δ 1.22 (9H, s), 3.15 (1H, br), 6.76 (1H, s), 6.95–7.52 (14H, m); ^{13}C NMR ($CDCl_3$): δ 27.9, 72.2, 82.3, 82.5, 118.7, 121.3, 124.0, 125.1, 126.7, 127.2, 127.5, 128.2, 141.3, 143.6, 151.8; IR (KBr): 3437, 3056, 2977, 1691, 1467, 1367, 1336, 1161, 1060, 859, 755, 732 cm^{-1}; MS (FAB) *m/z* (%): 420 (M^++1, 4), 402 (6), 346 (51), 302 (33), 236 (49), 180 (37), 154 (58), 136 (100), 105 (32), 57 (100). Anal. Calcd for $C_{25}H_{25}NO_3S$: C, 71.57; H, 6.01; N, 3.34. Found: C, 71.38; H, 6.20; N, 3.33; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min) t_R 32.8 (*R*) and 42.4 (*S*) min.

4.3. General procedure for the reaction of 1 and 2 with aldehydes.

To a solution of **1** or **2** in toluene was added *n*-BuLi (1.2 equiv) dropwise over a period of 5 min at −78 °C. The mixture was stirred for an additional 15 min at the same temperature and then a solution of (−)-sparteine (1.2 equiv) in toluene added. After the reaction mixture was stirred for 1 h, a solution of an aldehyde (1.3 equiv) in toluene was added, and then the reaction mixture stirred for an appropriate time. Saturated aqueous NH_4Cl was added and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to leave a residue, which was purified by column chromatography to give the corresponding alcohol.

Since the diastereomers of alcohol **8a**–**13a** were not separated, spectral and analytical data of the mixture of the diastereomers are shown below. These alcohols were converted into the acetates (vide infra).

4.3.1. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-(1-hydroxy-1-phenylmethyl)thiazolidine-3-carboxylate *syn*-8a and *anti*-8a. ^{1}H NMR ($CDCl_3$): δ 1.45 (9H, s), 2.40–2.75 (2H, m), 3.15–3.41 (2H, m), 3.87–4.05 (1H, m), 4.83 (0.6H, d, *J* = 6.2 Hz, *anti*), 4.89 (0.4H, br, *syn*), 5.31 (0.4H, br, *syn*), 5.36 (0.6H, d, *J* = 6.2 Hz, *anti*), 7.20–7.35 (5H, m); ^{13}C NMR ($CDCl_3$): δ 28.4, 30.2, 49.6, 53.5, 68.0, 81.3, 127.1, 127.5, 127.8, 140.0, 153.8; IR (neat): 3441, 2977, 1693, 1475, 1454, 1392, 1257, 1163, 909, 850, 733, 700 cm^{-1}; MS (FAB) *m/z* (%): 296 (M^++1, 16), 222 (89), 188 (34), 132 (58), 88 (38), 57 (100). Anal. Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74. Found: C, 60.86; H, 7.42; N, 4.62.

4.3.2. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-hydroxy-1-(4-tolyl)methyl]thiazolidine-3-carboxylate *syn*-9a and *anti*-9a. ^{1}H NMR ($CDCl_3$): δ 1.46 (9H, s), 2.33 (3H, s), 2.55–2.77 (2H, m), 3.21–3.46 (2H, m), 4.16–4.30 (1H, m), 4.75 (0.5H, d, *J* = 6.6 Hz, *anti*), 4.84 (0.5H, d, *J* = 4.2 Hz, *syn*), 5.31 (0.5H, br, *syn*), 5.34 (0.5H, d, *J* = 6.6 Hz, *anti*), 7.09–7.27 (4H, m); ^{13}C NMR ($CDCl_3$): δ 21.3, 28.4, 30.2, 49.5, 53.5, 68.0, 81.2, 127.0, 128.5, 137.1, 137.4, 154.6; IR (neat): 3442, 2977, 2936, 1694, 1514, 1475, 1392, 1265, 1163, 1111, 1061, 895, 853, 765, 737, 703 cm^{-1}; MS (FAB) *m/z* (%): 310 (M^++1, 5), 236 (100), 188 (47), 132 (65), 88 (38), 57 (82). Anal. Calcd for $C_{16}H_{23}NO_3S$: C, 62.11; H, 7.49; N, 4.53. Found: C, 62.12; H, 7.55; N, 4.46.

4.3.3. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-hydroxy-1-(4-methoxyphenyl)methyl]thiazolidine-3-carboxylate *syn*-10a and *anti*-10a. ^{1}H NMR ($CDCl_3$): δ 1.48 (9H, s), 2.51–2.80 (2H, m), 3.23–3.38 (2H, m), 3.80 (3H, s), 3.88–4.07 (1H, m), 4.76 (0.6H, d, *J* = 6.6 Hz, *anti*), 4.82 (0.4H, br, *syn*), 5.30 (0.4H, br, *syn*), 5.33 (0.6H, d, *J* = 6.6 Hz, *anti*), 6.86 (2H, d, *J* = 8.6 Hz), 7.29 (2H, d, *J* = 8.6 Hz); ^{13}C NMR ($CDCl_3$): δ 28.5, 30.2, 49.5, 53.5, 55.3, 68.2, 81.4, 113.3, 128.3, 132.2, 158.7, 159.1; IR (neat): 3447, 2976, 2836, 1693, 1513, 1457, 1392, 1249, 1171, 1111, 1034, 894, 828, 768, 737, 703 cm^{-1}; MS (FAB) *m/z* (%): 326 (M^++1, 4), 252 (100), 208 (57), 188 (62), 132 (87), 88 (51), 57 (100). Anal. Calcd for $C_{16}H_{23}NO_4S$: C, 59.05; H, 7.12; N, 4.30. Found: C, 59.21; H, 7.11; N, 4.24.

4.3.4. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-hydroxy-1-(4-chlorophenyl)-methyl]thiazolidine-3-carboxylate *syn*-11a and *anti*-11a. ^{1}H NMR ($CDCl_3$): δ 1.46 (9H, s), 2.60–2.80 (2H, m), 3.10–3.25 (2H, m), 3.92–4.15 (1H, m), 4.77 (0.6H, d, 6.6 Hz, *anti*), 4.85 (0.4H, br, *syn*), 5.27 (0.4H, d, *J* = 4.0 Hz, *syn*), 5.29 (0.6H, d, *J* = 6.6 Hz, *anti*), 7.24–7.36 (4H, m); ^{13}C NMR ($CDCl_3$): δ 28.3, 30.2, 49.6, 53.5, 67.9, 81.4, 127.8, 128.5, 133.5, 138.6, 155.0; IR (neat): 3441, 2977, 1693, 1475, 1454, 1392, 1257, 1163, 909, 850, 733, 700 cm^{-1}; MS (FAB) *m/z* (%): 330 (M^++1, 28), 256 (100), 212 (38), 188 (100), 132 (100), 88 (75), 57 (100). Anal. Calcd for $C_{15}H_{20}ClNO_3S$: C, 54.62; H, 6.11; N, 4.25. Found: C, 54.73; H, 6.02; N, 4.18.

4.3.5. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-hydroxy-1-(1-naphthyl)methyl]thiazolidine-3-carboxylate *syn*-12a and *anti*-12a. ^{1}H NMR ($CDCl_3$): δ 1.42 (9H, s), 2.62–2.91 (2H, m), 3.09–3.38 (2H, m), 3.95–4.17 (1H, m), 5.22 (0.8H, d, *J* = 5.2 Hz, *anti*), 5.28 (0.2H, br, *syn*), 5.57 (0.2H, d, *J* = 3.2 Hz, *syn*), 5.70 (0.8H, d, *J* = 5.2 Hz, *anti*), 7.34–8.06 (7H, m); ^{13}C NMR ($CDCl_3$): δ 27.9, 30.8, 49.2, 53.4, 68.0, 80.8, 125.0, 125.2, 125.4, 125.7, 128.1, 128.4, 130.1, 133.2, 153.7; IR (KBr): 3426, 3051, 2975, 2931, 1686, 1475, 1392, 1257, 1161, 1099, 892, 858, 774 cm^{-1}; MS (FAB) *m/z* (%): 346 (M^++1, 12), 272 (100), 228 (29), 188 (31), 132 (51), 88 (31), 57 (69). Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05. Found: C, 66.05; H, 6.85; N, 3.87.

4.3.6. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-hydroxy-1-(2-naphthyl)methyl]thiazolidine-3-carboxylate *syn*-13a and *anti*-13a. ^{1}H NMR ($CDCl_3$): δ 1.44 (9H, s), 2.56–2.78 (2H, m), 3.23–3.41 (2H, m), 3.93–4.18 (1H, m), 4.92 (0.6H, d, *J* = 6.6 Hz, *anti*), 4.97 (0.4H, d, *J* = 4.6 Hz, *syn*), 5.43 (0.4H, br, *syn*), 5.45 (0.6H, d, *J* = 6.6 Hz, *anti*), 7.44–7.53 (3H, m), 7.79–7.84 (4H, m); ^{13}C NMR ($CDCl_3$): δ 28.4, 30.3, 49.7, 53.5, 68.2, 81.5, 124.9, 125.9, 127.4, 127.6, 127.8, 132.8, 133.0, 137.6, 154.9; IR (KBr): 3439, 3055, 2977, 2936, 1693, 1475,

1392, 1267, 1162, 1109, 890, 858, 819, 741, 703 cm^{-1}; MS (FAB) *m/z* (%): 346 (M^++1, 3), 272 (100), 228 (44), 188 (27), 132 (56), 88 (36), 57 (100). Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05. Found: C, 66.10; H, 6.83; N, 3.89.

4.3.7. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-(1-hydroxypropyl)thiazolidine-3-carboxylate *syn*-16a and *anti*-16a. *syn*-**16a**: ^{1}H NMR ($CDCl_3$): δ 1.00 (3H, t, J = 7.4 Hz), 1.47 (9H, s), 1.40–1.60 (2H, m), 2.31 (1H, br), 2.84–3.10 (2H, m), 3.48–3.69 (2H, m), 4.10 (1H, br), 5.10 (1H, br); ^{13}C NMR ($CDCl_3$): δ 10.4, 22.8, 28.5, 30.5, 49.4, 68.0, 75.0, 80.8, 153.6; IR (neat): 3458, 2974, 2936, 2884, 1694, 1457, 1392, 1256, 1167, 1108, 1051, 972, 880, 770, 737 cm^{-1}; MS (FAB) *m/z* (%): 248 (M^++1, 44), 230 (2), 192 (89), 188 (49), 174 (80), 132 (56), 88 (36), 57 (100); Anal. Calcd for $C_{11}H_{21}NO_3S$: C, 53.41; H, 8.56; N, 5.66. Found: C, 53.25; H, 8.68; N, 5.83; HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 10.1 (1′*S*,2*S*) and 13.9 (1′*R*,2*R*) min (46% ee). *anti*-**14a**: ^{1}H NMR ($CDCl_3$): δ 1.02 (3H, t, J = 7.2 Hz), 1.48 (9H, s), 1.40–1.60 (2H, m), 2.24 (1H, br), 2.90–3.00 (2H, m), 3.35–3.48 (2H, m), 4.16 (1H, d, J = 6.8 Hz), 5.13 (1H, d, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 10.0, 21.2, 28.4, 31.2, 48.2, 64.1, 76.5, 80.7, 154.0; IR (neat): 3455, 2974, 2935, 2881, 1693, 1392, 1256, 1167, 1109, 1051, 971, 880, 770, 733 cm^{-1}; MS (FAB) *m/z* (%): 248 (M^++1, 51), 230 (3), 192 (100), 188 (50), 174 (80), 132 (59), 88 (34), 57 (96). Anal. Calcd for $C_{11}H_{21}NO_3S$: C, 53.41; H, 8.56; N, 5.66. Found: C, 53.44; H, 8.68; N 5.51. The enantiomeric purity could not be determined by the HPLC analysis using various chiral columns.

4.3.8. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-(1-hydroxy-2-methylpropyl)thiazolidine-3-carboxylate *syn*-15a and *anti*-15a. *syn*-**15a**: $[\alpha]_D^{20}$ = +66.0 (*c* 1.54, $CHCl_3$, 77% ee); ^{1}H NMR ($CDCl_3$): δ 0.91 (3H, d, J = 6.6 Hz), 1.06 (3H, d, J = 8.6 Hz), 1.48 (9H, s), 1.79–1.99 (1H, m), 2.16 (1H, d, J = 7.0 Hz), 2.83–3.03 (2H, m), 3.40–3.56 (2H, m), 4.15 (1H, br), 5.30 (1H, br); ^{13}C NMR ($CDCl_3$): δ 18.4, 19.6, 28.5, 30.6, 32.3, 49.2, 66.4, 78.2, 80.7, 153.0; IR (neat): 3473, 2965, 2877, 1694, 1472, 1391, 1256, 1166, 1106, 1064, 995, 907, 884, 766, 736 cm^{-1}; MS (FAB) *m/z* (%): 262 (M^++1, 38), 244 (4), 206 (82), 188 (100), 132 (44), 88 (31), 57 (68). Anal. Calcd for $C_{12}H_{23}NO_3S$: C, 55.14; H, 8.87; N, 5.36. Found: C, 54.94; H, 8.99; N, 5.17; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 16.4 (1′*S*,2*S*) and 19.3 (1′*R*,2*R*) min (77% ee). *anti*-**15a**: $[\alpha]_D^{20}$ = +51.3 (*c* 0.427, $CHCl_3$, 87% ee); ^{1}H NMR ($CDCl_3$): δ 0.91 (3H, d, J = 6.6 Hz), 1.06 (3H, d, J = 8.6 Hz), 1.48 (9H, s), 1.79–1.99 (1H, m), 2.28 (1H, br), 2.82–3.06 (2H, m), 3.32–3.48 (2H, m), 4.13 (1H, br), 5.18 (1H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$):δ 14.8, 20.0, 28.4, 30.1, 30.8, 48.9, 64.9, 79.8, 81.5, 155.2; IR (neat): 3462, 2967, 2875, 1702, 1469, 1392, 1270, 1162, 1109, 1053, 1005, 911, 876, 771, 734 cm^{-1}; MS (FAB) *m/z* (%): 262 (M^++1, 27), 244 (6), 206 (48), 188 (100), 132 (51), 88 (36), 57 (74). Anal. Calcd for $C_{12}H_{23}NO_3S$: C, 55.14; H, 8.87; N, 5.36. Found: C, 55.34; H, 8.92; N 5.11. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min) t_R 24.0 (1′*R*,2*S*) and 28.2 (1′*S*,2*R*) min (87% ee).

4.3.9. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-(1-hydroxy-1-cyclohexyl)thiazolidine-3-carboxylate *syn*-16a and *anti*-16a. *syn*-**16a**: $[\alpha]_D^{20}$ = +55.9 (*c* 0.583, $CHCl_3$, 73% ee); ^{1}H NMR ($CDCl_3$): δ 1.47 (9H, s), 1.01–1.73 (11H, m), 2.22 (1H, d, J = 8.2 Hz), 2.82–3.08 (2H, m), 3.40–3.54 (2H, m), 4.11 (1H, br), 5.30 (1H, br); ^{13}C NMR ($CDCl_3$): δ 26.0, 26.1, 26.3, 28.4, 29.8, 41.6, 49.1, 53.4, 66.0, 77.2, 80.6, 152.9; IR (KBr): 3468, 2976, 2926, 2852, 1695, 1475, 1392, 1258, 1164, 1105, 903, 737 cm^{-1}; MS (FAB) *m/z* (%): 302 (M^++1, 34), 246 (58), 228 (60), 202 (42), 188 (52), 132 (82), 88 (39), 57 (100). Anal. Calcd for $C_{15}H_{27}NO_3S$: C, 59.77; H, 9.03; N, 4.65. Found: C, 59.96; H, 8.83; N, 4.65; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 23.2 (1′*R*,2*R*) and 28.4 (1′*S*,2*S*) min (73% ee). *anti*-**16a**: $[\alpha]_D^{20}$ = +58.0 (*c* 0.470, $CHCl_3$, 89% ee); ^{1}H NMR ($CDCl_3$): δ 1.47 (9H, s), 1.20–1.75 (11H, m), 2.63 (1H, br), 2.83–3.05 (2H, m), 3.24–3.43 (2H, m), 4.10 (1H, br), 5.26 (1H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$): 25.5, 26.2, 26.6, 28.4, 30.7, 40.1, 49.0, 53.5, 64.4, 79.8, 81.5, 155.1; IR (neat): 3453, 2977, 2926, 2853, 1694, 1392, 1258, 1163, 1104, 910, 734 cm^{-1}; MS (FAB) *m/z* (%): 302 (M^++1, 30), 246 (69), 228 (76), 202 (30), 188 (44), 132 (89), 88 (41), 57 (100). Anal. Calcd for $C_{15}H_{27}NO_3S$: C, 59.77; H, 9.03; N, 4.65. Found: C, 59.96; H, 9.08; N, 4.67; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min) t_R 19.6 (1′*R*,2*S*) and 24.5 (1′*S*,2*R*) min (89% ee).

4.3.10. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-(1-hydroxy-2,2-dimethylpropyl)thiazolidine-3-carboxylate *syn*-17a and *anti*-17a. *syn*-**17a**: $[\alpha]_D^{20}$ = +54.8 (*c* 0.386, $CHCl_3$, 72% ee); ^{1}H NMR ($CDCl_3$): δ 0.94 (9H, s), 1.48 (9H, s), 2.56 (1H, d, J = 10.4 Hz), 2.77–3.00 (2H, m), 3.35–3.56 (2H, m), 4.26 (1H, br), 5.42 (1H, br); ^{13}C NMR ($CDCl_3$): δ 26.5, 28.5, 30.8, 35.1, 48.5, 53.4, 64.8, 80.5, 152.5; IR (neat): 3474, 2960, 2877, 1697, 1476, 1393, 1367, 1263, 1162, 1098, 1016, 982, 893, 765, 734 cm^{-1}; MS (FAB) *m/z* (%): 276 (M^++1, 25), 258 (3), 220 (40), 202 (11), 188 (47), 132 (59), 88 (31), 57 (100). Anal. Calcd for $C_{13}H_{25}NO_3S$: C, 56.69; H, 9.15; N, 5.09. Found: C, 56.84; H, 9.15; N 4.94. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min) t_R 17.7 (1′*R*,2*R*) and 21.0 (1′*S*,2*S*) min (72% ee). *anti*-**17a**: $[\alpha]_D^{20}$ = +36.4 (*c* 0.566, $CHCl_3$, 87% ee); ^{1}H NMR ($CDCl_3$): δ 1.01 (9H, s), 1.48 (9H, s), 2.63 (1H, br), 2.80–3.09 (2H, m), 3.22–3.47 (2H, m), 4.25 (1H, br), 5.37 (1H, d, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$): δ 26.7, 28.5, 30.3, 34.1, 49.2, 53.5, 60.2, 80.5, 82.3, 154.8; IR (neat): 3489, 2977, 2871, 1698, 1478, 1392, 1367, 1268, 1162, 1094, 1077, 1012, 902, 786, 734 cm^{-1}; MS (FAB) *m/z* (%): 276 (M^++1, 41), 258 (3), 220 (74), 202 (21), 188 (56), 132 (67), 88 (36), 57 (100). Anal. Calcd for $C_{13}H_{25}NO_3S$: C, 56.69; H, 9.15; N, 5.09. Found: C, 56.60; H, 9.39; N, 5.08. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 99:1, 0.5 mL/min) t_R 23.1 (1′*R*,2*S*) and 27.5 (1′*S*,2*R*) min (87% ee).

4.3.11. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-(1-hydroxy-1-phenylmethyl)benzothiazolidine-3-carboxylate *syn*-18 and *anti*-18. *syn*-**18**: Mp 115–117 °C; $[\alpha]_D^{20}$ = +75.5 (*c* 1.84, $CHCl_3$, 93% ee); ^{1}H NMR ($CDCl_3$): δ 1.36 (9H, s), 2.88 (1H, d, J = 5.2 Hz), 4.80 (1H, br), 5.83 (1H, br),

6.93–7.64 (9H, m); ^{13}C NMR ($CDCl_3$): δ 28.4, 72.1, 75.2, 82.3, 117.9, 122.2, 124.0, 125.2, 125.6, 126.2, 127.2, 127.8, 128.1, 138.8, 151.1; IR (KBr): 3407, 2975, 1716, 1468, 1368, 1313, 1252, 1150, 1065, 1013, 748, 700 cm^{-1}; MS (FAB) *m/z* (%): 344 (M^++1, 9), 270 (21), 236 (14), 180 (9), 136 (35), 57 (100). Anal. Calcd for $C_{19}H_{21}NO_3S$: C, 66.45; H, 6.16; N, 4.08. Found: C, 66.34; H, 6.27; N, 4.07; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 27.1 (1′*S*,2*R*) and 32.4 (1′*R*,2*S*) min (93% ee). Crystal data for *syn*-**18**: $C_{19}H_{21}NO_3S$, M = 343.44, (0.48 × 0.47 × 0.30 mm), triclinic, P-1 (#2), α = 11.483(6), β = 12.896(6), γ = 12.942(4) Å, α = 69.80(3), β = 75.50(3), γ = 77.14(3), V = 1721(1) Å^3, μ = 1.807 mm, Z = 4, 18311 reflections measured. 5920 unique (R_{int} = 0.071). Final R indices [$I > 3\sigma(I)$]: R = 0.066, R_w = 0.068. CCDC reference number 244746. *anti*-**18**: mp 109–110 °C; $[\alpha]_D^{20}$ = +117.2 (*c* 0.812, $CHCl_3$, 88% ee); ^{1}H NMR ($CDCl_3$): δ 1.55 (9H, s), 3.08 (1H, br), 4.74 (1H, d, *J* = 7.8 Hz), 5.95 (1H, d, *J* = 7.8 Hz), 6.88–7.51 (9H, m); ^{13}C NMR ($CDCl_3$): δ 28.3, 53.5, 69.9, 83.0, 118.2, 121.9, 124.0, 124.8, 127.4, 127.9, 128.1, 128.7, 137.6, 138.8, 151.2; IR (KBr): 3456, 3031, 2979, 1694, 1581, 1469, 1368, 1254, 1159, 1018, 910, 745, 699 cm^{-1}; MS (FAB) *m/z* (%): 344 (M^++1, 3), 270 (42), 236 (23), 180 (20), 136 (78), 57 (100). Anal. Calcd for $C_{19}H_{21}NO_3S$: C, 66.45; H, 6.16; N, 4.08. Found: C, 66.54; H, 6.17; N, 4.08; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 16.9 (1′*S*,2*S*) and 23.2 (1′*R*,2*R*) min (88% ee).

4.3.12. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-hydroxy-1-(4-tolyl)methyl]benzothiazolidine-3-carboxylate *syn*-19 and *anti*-19. *syn*-**19**: $[\alpha]_D^{20}$ = +76.7 (*c* 0.830, $CHCl_3$, 75% ee); ^{1}H NMR ($CDCl_3$): δ 1.38 (9H, s), 2.34 (3H, s), 2.78 (1H, d, *J* = 5.6 Hz), 4.80 (1H, br), 5.81 (1H, br), 6.93–7.65 (8H, m); ^{13}C NMR ($CDCl_3$): δ 21.3, 28.1, 72.2, 75.1, 82.3, 117.8, 122.2, 124.0, 125.2, 125.6, 126.0, 128.8, 135.8, 137.5, 138.5, 151.1; IR (neat): 3456, 2978, 1714, 1581, 1469, 1367, 1254, 1161, 1016, 909, 819, 744 cm^{-1}; MS (FAB) *m/z* (%): 358 (M^++1, 7), 340 (6), 284 (98), 236 (78), 180 (47), 136 (100), 57 (100). Anal. Calcd for $C_{20}H_{23}NO_3S$: C, 67.20; H, 6.49; N, 3.92. Found: C, 67.10; H, 6.58; N, 3.93; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 29.6 (1′*S*,2*R*) and 34.4 (1′*R*,2*S*) min (75% ee). *anti*-**19**: $[\alpha]_D^{20}$ = +110.6 (*c* 0.550, $CHCl_3$, 93% ee); ^{1}H NMR ($CDCl_3$): δ 1.55 (9H, s), 2.31 (3H, s), 3.13 (1H, br), 4.67 (1H, dd, *J* = 4.0, 7.8 Hz), 5.92 (1H, d, *J* = 7.8 Hz), 6.88–7.52 (8H, m); ^{13}C NMR ($CDCl_3$): δ 21.3, 28.3, 52.6, 69.9, 82.9, 118.3, 121.9, 124.0, 124.8, 127.3, 128.6, 128.8, 136.0, 137.5, 137.8, 151.2; IR (neat): 3453, 2975, 2929, 1713, 1580, 1469, 1368, 1254, 1160, 1017, 818, 745 cm^{-1}; MS (FAB) *m/z* (%): 358 (M^++1, 5), 340 (9), 284 (100), 236 (89), 180 (66), 136 (100), 57 (100). Anal. Calcd for $C_{20}H_{23}NO_3S$: C, 67.20; H, 6.49; N, 3.92. Found: C, 67.06; H, 6.62; N, 3.96; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 31.9 (1′*S*, 2*S*) and 36.1 (1′*R*,2*R*) min (93% ee).

4.3.13. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-hydroxy-1-(4-methoxyphenyl)methyl]benzothiazolidine-3-carboxylate *syn*-20 and *anti*-20. *syn*-**20**: Mp 131–132 °C; $[\alpha]_D^{20}$ = +51.2 (*c* 0.707, $CHCl_3$, 72% ee); ^{1}H NMR ($CDCl_3$): 1.39 (9H, s), 2.73 (1H, d, *J* = 4.2 Hz), 3.79 (3H, s), 4.78 (1H, br), 5.80 (1H, br), 6.86–7.64 (8H, m); ^{13}C NMR ($CDCl_3$): δ 28.0, 55.2, 72.0, 74.8, 82.1, 113.4, 117.7, 122.1, 123.9, 125.0, 127.3, 128.1, 131.0, 138.3, 151.1, 158.9; IR (KBr): 3460, 2975, 1679, 1607, 1581, 1511, 1471, 1252, 1146, 1093, 1069, 1017, 832, 752 cm^{-1}; MS (FAB) *m/z* (%): 374 (M^++1, 6), 356 (11), 300 (71), 236 (53), 180 (30), 136 (100), 57 (100). Anal. Calcd for $C_{20}H_{23}NO_4S$: C, 64.32; H, 6.21; N, 3.75. Found: C, 64.36; H, 6.28; N, 3.62; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95:5, 1.0 mL/min) t_R 24.1 (1′*S*,2*R*) and 27.4 (1′*R*,2*S*) min (72% ee). *anti*-**20**: mp 142.5–143.5 °C; $[\alpha]_D^{20}$ = +120.1 (*c* 0.460, $CHCl_3$, 88% ee); ^{1}H NMR ($CDCl_3$): 1.56 (9H, s), 3.08 (1H, br), 3.78 (3H, s), 4.68 (1H, dd, *J* = 3.8, 7.8 Hz), 5.91 (1H, d, *J* = 7.8 Hz), 6.81–7.52 (8H, m); ^{13}C NMR ($CDCl_3$): δ 28.4, 53.5, 55.3, 70.0, 83.0, 113.4, 118.3, 121.9, 124.0, 124.8, 128.6, 128.8, 131.1, 137.4, 153.0, 159.3; IR (KBr): 3456, 2967, 1699, 1514, 1470, 1368, 1251, 1160, 1036, 832, 746 cm^{-1}; MS (FAB) *m/z* (%): 374 (M^++1, 3), 356 (4), 300 (84), 236 (44), 180 (40), 136 (100), 57 (100). Anal. Calcd for $C_{20}H_{23}NO_4S$: C, 64.32; H, 6.21; N, 3.75. Found: C, 64.30; H, 6.39; N, 3.59; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95:5, 1.0 mL/min) t_R 26.9 (1′*S*,2*S*) and 31.0 (1′*R*,2*R*) min (88% ee).

4.3.14. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-hydroxy-1-(4-chlorophenyl)methyl]benzothiazolidine-3-carboxylate *syn*-21 and *anti*-21. *syn*-**21**: mp 145–147 °C; $[\alpha]_D^{20}$ = +71.5 (*c* 1.20, $CHCl_3$, 78% ee); ^{1}H NMR ($CDCl_3$): δ 1.38 (9H, s), 2.96 (1H, d, *J* = 4.0 Hz), 4.75 (1H, br), 5.76 (1H, br), 6.94–7.61 (8H, m); ^{13}C NMR ($CDCl_3$): δ 28.1, 71.8, 74.8, 82.6, 117.9, 122.3, 124.2, 125.3, 127.6, 127.8, 128.2, 133.6, 137.3, 138.2, 151.2; IR (KBr): 3461, 2974, 1705, 1671, 1469, 1369, 1255, 1154, 1014, 732 cm^{-1}; MS (FAB) *m/z* (%): 378 (M^++1, 7), 304 (26), 236 (32), 180 (20), 136 (88), 57 (100). Anal. Calcd for $C_{19}H_{20}ClNO_3S$: C, 60.39; H, 5.33; N, 3.71. Found: C, 60.24; H, 5.51; N, 3.58; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 25.8 (1′*S*, 2*R*) and 33.8 (1′*R*,2*S*) min (78% ee). *anti*-**21**: mp 152–153 °C; $[\alpha]_D^{20}$ = +107.3 (*c* 0.833, $CHCl_3$, 89% ee); ^{1}H NMR ($CDCl_3$): 1.55 (9H, s), 3.28 (1H, br), 4.73 (1H, dd, *J* = 4.0, 7.0 Hz), 5.90 (1H, d, *J* = 7.0 Hz), 6.89–7.53 (8H, m); ^{13}C NMR ($CDCl_3$): δ 28.4, 53.5, 69.8, 83.2, 118.2, 121.9, 124.1, 125.0, 128.0, 128.5, 128.8, 133.9, 137.2, 137.6, 151.2; IR (KBr): 3442, 2976, 2929, 1713, 1580, 1469, 1368, 1254, 1158, 1069, 1015, 830, 742 cm^{-1}; MS (FAB) *m/z* (%): 378 (M^++1, 3), 304 (16), 236 (40), 180 (26), 136 (95), 57 (100). Anal. Calcd for $C_{19}H_{20}ClNO_3S$: C, 60.39; H, 5.33; N, 3.71. Found: C, 60.21; H, 5.37; N, 3.74; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 16.9 (1′*S*,2*S*) and 27.1 (1′*R*,2*R*) min (89% ee).

4.3.15. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-hydroxy-1-(1-naphthyl)methyl]benzothiazolidine-3-carboxylate *syn*-22 and *anti*-22. *syn*-**22**: Mp 133–134 °C; $[\alpha]_D^{20}$ = +30.1 (*c* 0.308, $CHCl_3$, 71% ee); ^{1}H NMR ($CDCl_3$): δ 1.20 (9H, s), 2.85 (1H, d, *J* = 5.2 Hz), 5.55 (1H, br), 6.11 (1H, br), 6.94–7.61 (11H, m); ^{13}C NMR ($CDCl_3$): δ

28.0, 71.6, 72.8, 82.4, 118.1, 122.1, 123.2, 124.1, 125.0, 125.2, 125.4, 125.9, 128.5, 128.6, 130.6, 133.4, 134.3, 138.6, 151.1; IR (KBr): 3453, 2977, 2932, 1713, 1580, 1469, 1393, 1367, 1253, 1161, 1015, 790, 774, 740 cm^{-1}; MS (FAB) *m/z* (%): 394 (M^++1, 3), 376 (3), 320 (49), 276 (59), 236 (53), 180 (50), 136 (100), 57 (100). Anal. Calcd for $C_{23}H_{23}NO_3S$: C, 70.20; H, 5.89; N, 3.56. Found: C, 70.26; H, 6.06; N, 3.32; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 96:4, 0.5 mL/min) t_R 38.6 (1′*S*,2*R*) and 44.0 (1′*R*,2*S*) min (71% ee). *anti*-**22**: mp 50–51 °C; $[\alpha]_D^{20} = +56.4$ (*c* 0.246, $CHCl_3$, 86% ee); ^1H NMR ($CDCl_3$): δ 1.32 (9H, s), 2.98 (1H, br), 5.54 (1H, d, *J* = 6.2 Hz), 6.31 (1H, d, *J* = 6.2 Hz), 6.90–8.16 (11H, m); ^{13}C NMR ($CDCl_3$): δ 28.1, 53.1, 69.1, 83.5, 118.1, 121.7, 123.0, 124.0, 124.9, 125.3, 125.4, 125.9, 128.6, 128.8, 130.7, 133.4, 134.1, 138.5, 152.3; IR (KBr): 3446, 3060, 2975, 1716, 1580, 1512, 1469, 1359, 1153, 1068, 856, 744 cm^{-1}; MS (FAB) *m/z* (%): 394 (M^++1, 2), 376 (4), 320 (40), 276 (38), 236 (40), 180 (32), 136 (100), 57 (100). Anal. Calcd for $C_{23}H_{23}NO_3S$: C, 70.20; H, 5.89; N, 3.56. Found: C, 70.24; H, 6.10; N, 3.30; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 96:4, 1.0 mL/min) t_R 21.7 (1′*S*,2*S*) and 27.6 (1′*R*,2*R*) min (86% ee).

4.3.16. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-hydroxy-1-(2-naphthyl)methyl]benzothiazolidine-3-carboxylate *syn*-23 and *anti*-23. *syn*-**23**: $[\alpha]_D^{20} = +30.4$ (*c* 1.64, $CHCl_3$, 73% ee); ^1H NMR ($CDCl_3$): δ 1.23 (9H, s), 3.01 (1H, d, *J* = 5.6 Hz), 4.98 (1H, br), 5.90 (1H, br), 6.93–7.82 (11H, m); ^{13}C NMR ($CDCl_3$): δ 27.9, 72.1, 75.3, 82.3, 117.8, 122.2, 123.9, 124.0, 125.2, 125.8, 126.0, 127.4, 127.8, 128.0, 132.8, 132.9, 136.3, 138.5, 151.1; IR (neat): 3423, 3058, 2956, 1714, 1581, 1508, 1468, 1367, 1253, 1161, 1069, 1016, 858, 744 cm^{-1}; MS (FAB) *m/z* (%): 394 (M^++1, 3), 376 (3), 320 (72), 276 (83), 236 (50), 180 (46), 136 (100), 57 (100). Anal. Calcd for $C_{23}H_{23}NO_3S$: C, 70.20; H, 5.89; N, 3.56. Found: C, 70.16; H, 5.96; N, 3.66; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95:5, 1.0 mL/min) t_R 17.2 (1′*S*,2*R*) and 23.1 (1′*R*,2*S*) min (73% ee). *anti*-**23a**: $[\alpha]_D^{20} = +76.4$ (*c* 0.513, $CHCl_3$, 86% ee); ^1H NMR ($CDCl_3$): δ 1.52 (9H, s), 3.36 (1H, br), 4.87(1H, dd, *J* = 4.0, 7.6 Hz), 6.04 (1H, d, *J* = 7.6 Hz), 6.89–7.80 (11H, m); ^{13}C NMR ($CDCl_3$): δ 28.3, 53.5, 69.9, 83.1, 118.3, 121.9, 124.1, 124.8, 124.9, 125.9, 127.0, 127.4, 127.8, 128.8, 132.7, 133.1, 136.3, 138.4, 153.0; IR (neat): 3423, 3060, 2976, 1712, 1581, 1508, 1469, 1369, 1255, 1160, 1017, 909, 858, 742 cm^{-1}; MS (FAB) *m/z* (%): 394 (M^++1, 2), 376 (2), 320 (36), 276 (49), 236 (23), 180 (27), 136 (91), 57 (100). Anal. Calcd for $C_{23}H_{23}NO_3S$: C, 70.20; H, 5.89; N, 3.56. Found: C, 69.92; H, 5.97; N, 3.64; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 92:8, 0.5 mL/min) t_R 30.9 (1′*S*,2*S*) and 38.1 (1′*R*,2*R*) min (86% ee).

4.4. General procedure for the acetylation of alcohols 8a–13a to acetates 8b–13b

To a solution of alcohols **8a**–**13a** in pyridine was added a catalytic amount of 4-dimethylaminopyridine (0.1 equiv) and acetic anhydride (5.0 equiv) and then the mixture was stirred for 3 h at room temperature. Saturated aqueous NH_4Cl was then added and the aqueous layer was extracted with CH_2Cl_2, The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue, which was purified by column chromatography to give acetates **8b**–**13b**.

4.4.1. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-(1-acetoxy-1-phenylmethyl)thiazolidine-3-carboxylate *syn*-8b and *anti*-8b. *syn*-**8b**: Mp 88–89 °C; $[\alpha]_D^{20} = +43.9$ (*c* 0.544, $CHCl_3$, 93% ee); $[\alpha]_D^{20} = +46.0$ (*c* 0.390, $CHCl_3$, 97% ee, after recrystallization from hexane); ^1H NMR ($CDCl_3$): 1.36 (9H, s), 2.14 (3H, s), 2.83–3.05 (2H, m), 3.52 (2H, t, *J* = 6.2 Hz), 5.34 (1H, d, *J* = 4.2 Hz), 5.96 (1H, d, *J* = 4.2 Hz), 7.40–7.30 (5H, m); ^{13}C NMR ($CDCl_3$): δ 21.4, 28.2, 30.5, 49.2, 66.6, 76.7, 80.9, 126.6, 128.0, 137.0, 152.9, 169.3; IR (KBr): 2973, 1749, 1700, 1455, 1369, 1229, 1162, 1106, 1027, 931, 893, 855, 748, 699 cm^{-1}; MS (FAB) *m/z* (%): 338 (M^++1, 3), 222 (100), 188 (41), 132 (47), 88 (27), 57 (60). Anal. Calcd for $C_{17}H_{23}NO_4S$: C, 60.51; H, 6.87; N, 4.15. Found: C, 60.44; H, 7.10; N, 4.34; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min) 22.7 (1′*R*,2*S*) and 25.2 (1′*S*,2*R*) min (93% ee). Crystal data for *syn*-**8b**: $C_{17}H_{23}NO_4S$, *M* = 337.43, (0.31 × 0.18 × 0.08 mm), orthorhombic, P212121 (#19), *a* = 8.23(1), *b* = 9.09(2), *c* = 22.54(4) Å, β = 90, *V* = 1689(4) $Å^3$, μ = 1.871 mm, *Z* = 4, 31284 reflections measured. 2909 unique (R_{int} = 0.058). Final *R* indices [$I > 3\sigma(I)$]: *R* = 0.066, R_w = 0.068. CCDC reference number 241322. *anti*-**8b**: mp 64–65 °C; $[\alpha]_D^{20} = +32.3$ (*c* 0.362, $CHCl_3$, 88% ee); $[\alpha]_D^{20} = +36.6$ (*c* 0.253, $CHCl_3$, 99% ee, after recrystallization from hexane); ^1H NMR ($CDCl_3$): δ 1.50 (9H, s), 2.09 (3H, s), 2.68–2.86 (2H, m), 3.18 (2H, t, *J* = 6.2 Hz), 5.45 (1H, d, *J* = 6.6 Hz), 5.98 (1H, d, *J* = 6.6 Hz), 7.37–7.30 (5H, m); ^{13}C NMR ($CDCl_3$): 21.3, 28.5, 30.3, 48.9, 65.4, 75.8, 81.0, 127.8, 128.0, 135.9, 152.8, 169.3; IR (KBr): 2977, 1747, 1696, 1496, 1476, 1455, 1370, 1231, 1162, 1106, 1034, 969, 928, 857, 761, 701 cm^{-1}; MS (FAB) *m/z* (%): 338 (M^++1, 3), 222 (98), 188 (49), 132 (63), 88 (40), 57 (100). Anal. Calcd for $C_{17}H_{23}NO_4S$: C, 60.51; H, 6.87; N, 4.15. Found: C, 60.65; H, 6.84; N, 4.06; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 99:1, 0.5 mL/min) 16.2 (1′*S*,2*S*) and 26.5 (1′*R*,2*R*) min (88% ee).

4.4.2. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-acetoxy-1-(4-tolyl)methyl]thiazolidine-3-carboxylate *syn*-9b and *anti*-9b. *syn*-**9b**: Mp 127–128 °C; $[\alpha]_D^{20} = +45.4$ (*c* 0.524, $CHCl_3$, 69% ee); $[\alpha]_D^{20} = +64.6$ (*c* 0.407, $CHCl_3$, 98% ee, after recrystallization from hexane); ^1H NMR ($CDCl_3$): δ 1.37 (9H, s), 2.13 (3H, s), 2.32 (3H, s), 2.80–3.05 (2H, m), 3.40–3.52 (2H, m), 5.29 (1H, d, *J* = 4.2 Hz), 5.94 (1H, d, *J* = 4.2 Hz), 7.10–7.25 (4H, m); ^{13}C NMR ($CDCl_3$): δ 21.9, 22.7, 29.4, 31.9, 49.2, 65.1, 75.3, 80.9, 125.1, 127.3, 133.9, 137.8, 152.9, 169.3; IR (KBr): 2977, 2929, 1747, 1701, 1371, 1231, 1163, 1107, 1034, 962, 931, 857, 815, 738, 704 cm^{-1}; MS (FAB) *m/z* (%): 352 (M^++1, 3), 292 (9), 236 (100), 188 (51), 132 (53), 88 (27), 57 (68). Anal. Calcd for $C_{18}H_{25}NO_4S$: C, 61.51; H, 7.17; N, 3.99. Found: C, 61.61; H, 7.12; N, 3.87; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98.5:1.5, 0.8 mL/min) t_R 18.1

(1′*R*,2*S*) and 29.1 (1′*S*,2*R*) min (69% ee). *anti*-**9b**: $[\alpha]_D^{20} = +22.9$ (*c* 1.07, $CHCl_3$, 89% ee); ^1H NMR ($CDCl_3$): δ 1.50 (9H, s), 2.08 (3H, s), 2.34 (3H, s), 2.62–2.80 (2H, m), 3.10–3.25 (2H, m), 5.44 (1H, d, $J = 6.8$ Hz), 5.90 (1H, d, $J = 6.8$ Hz), 7.11–7.30 (4H, m); ^{13}C NMR ($CDCl_3$): δ 21.3, 21.4, 28.5, 30.4, 48.8, 65.4, 75.8, 80.9, 127.7, 128.7, 133.0, 138.2, 153.2, 169.4; IR (neat): 2976, 2929, 1745, 1702, 1516, 1453, 1368, 1232, 1164, 1107, 1036, 968, 864, 813, 767, 723 cm^{-1}; MS (FAB) *m*/*z* (%): 352 (M^++1, 3), 292 (13), 236 (100), 188 (52), 132 (56), 88 (30), 57 (70). Anal. Calcd for $C_{18}H_{25}NO_4S$: C, 61.51; H, 7.17; N, 3.99. Found: C, 61.58; H, 7.23; N, 4.20; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min) t_R 21.4 (1′*S*,2*S*) and 24.6 (1′*R*,2*R*) min (89% ee).

4.4.3. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-acetoxy-1-(4-methoxyphenyl)methyl]thiazolidine-3-carboxylate *syn*-10b and *anti*-10b. *syn*-**10b**: Mp 88–89 °C; $[\alpha]_D^{20} = +42.1$ (*c* 0.587, $CHCl_3$, 66% ee); $[\alpha]_D^{20} = +61.1$ (*c* 0.183, $CHCl_3$, 95% ee, after recrystallization from hexane); ^1H NMR ($CDCl_3$): δ 1.39 (9H, s), 2.12 (3H, s), 2.80–2.97 (2H, m), 3.37–3.49 (2H, m), 3.78 (3H, s), 5.30 (1H, d, $J = 4.2$ Hz), 5.91 (1H, d, $J = 4.2$ Hz), 6.82–6.89 (2H, m), 7.24–7.29 (2H, m); ^{13}C NMR ($CDCl_3$): δ 21.4, 28.3, 49.2, 53.5, 55.3, 66.5, 76.5, 80.9, 113.5, 128.0, 129.0, 153.1, 159.2, 169.3; IR (KBr): 2976, 2929,1747, 1698, 1515, 1458, 1369, 1232, 1174, 1114, 1034, 912, 733 cm^{-1}; MS (FAB) *m*/*z* (%): 368 (M^++1, 3), 308 (24), 252 (100), 208 (100), 188 (100), 132 (100), 88 (69), 57 (100). Anal. Calcd for $C_{18}H_{25}NO_3S$: C, 58.83; H, 6.86; N, 3.81. Found: C, 58.92; H, 7.07; N, 3.70; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 99.5:0.5, 0.5 mL/min) t_R 48.3 (1′*S*,2*R*) and 53.4 (1′*R*,2*S*) min (66% ee). *anti*-**10b**: mp 71–72 °C; $[\alpha]_D^{20} = +18.8$ (*c* 0.823, $CHCl_3$, 90% ee); $[\alpha]_D^{20} = +20.7$ (*c* 0.627, $CHCl_3$, >99% ee, after recrystallization from hexane); ^1H NMR ($CDCl_3$): δ 1.51 (9H, s), 2.08 (3H, s), 2.62–2.78 (2H, m), 3.11–3.24 (2H, m), 3.80 (3H, s), 5.43 (1H, d, $J = 6.8$ Hz), 5.93 (1H, d, $J = 6.8$ Hz), 6.83–6.89 (2H, m), 7.29–7.33 (2H, m); ^{13}C NMR ($CDCl_3$): δ 21.3, 28.4, 48.7, 53.5, 55.2, 65.4, 75.4, 80.8, 113.4, 128.0, 129.0, 153.2, 159.4, 169.3; IR (KBr): 2977, 2936, 1745, 1697, 1515, 1457, 1369, 1232, 1174, 1034, 909, 733 cm^{-1}; MS (FAB) *m*/*z* (%): 368 (M^++1, 3), 308 (34), 252 (100), 208 (97), 188 (86), 132 (96), 88 (50), 57 (100). Anal. Calcd for $C_{18}H_{25}NO_5S$: C, 58.83; H, 6.86; N, 3.81. Found: C, 58.75; H, 7.05; N, 3.72; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 19.7 (1′*S*,2*S*) and 22.1 (1′*R*,2*R*) (90% ee).

4.4.4. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-acetoxy-1-(4-chlorophenyl)methyl]thiazolidine-3-carboxylate *syn*-11b and *anti*-11b. *syn*-**11b**: Mp 122–123 °C; $[\alpha]_D^{20} = +44.9$ (*c* 0.670, $CHCl_3$, 60% ee); $[\alpha]_D^{20} = +72.4$ (*c* 0.387, $CHCl_3$, 97% ee, after recrystallization from hexane); ^1H NMR ($CDCl_3$): δ 1.38 (9H, s), 2.14 (3H, s), 2.80–3.05 (2H, m), 3.42–3.51 (2H, m), 5.25 (1H, d, $J = 4.2$ Hz), 5.92 (1H, d, $J = 4.2$ Hz), 7.25–7.33 (4H, br); ^{13}C NMR ($CDCl_3$): δ 21.3, 28.3, 30.5, 49.3, 66.4, 76.2, 81.1, 128.1, 128.3, 134.0, 135.5, 149.9, 169.2; IR (KBr): 2974, 2936, 1747, 1692, 1496, 1405, 1232, 1158, 1089, 1037, 932, 871, 785, 762 cm^{-1}; MS (FAB) *m*/*z* (%): 372 (M^++1, 6), 312 (8), 256 (100), 212 (38), 188 (53), 132 (58), 88 (31), 57 (89); Anal. Calcd for $C_{17}H_{22}ClNO_4S$: C, 54.91; H, 5.96; N, 3.77. Found: C, 54.96; H, 6.00; N, 3.67; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 99.5:0.5, 0.5 mL/min) t_R 23.6 (1′*S*,2*R*) and 26.4 (1′*R*,2*S*) min (60% ee). *anti*-**11b**: mp 84–85 °C; $[\alpha]_D^{20} = +38.7$ (*c* 0.426, $CHCl_3$, 88% ee); $[\alpha]_D^{20} = +44.1$ (*c* 0.520, $CHCl_3$, >99% ee, after recrystallization from hexane); ^1H NMR ($CDCl_3$): δ 1.50 (9H, s), 2.09 (3H, s), 2.40–2.80 (2H, m), 3.10–3.25 (2H, m), 5.39 (1H, d, $J = 6.8$ Hz), 5.94 (1H, d, $J = 6.8$ Hz), 7.28–7.35 (4H, m); ^{13}C NMR ($CDCl_3$): δ 21.2, 28.5, 30.2, 49.0, 65.3, 75.1, 81.1, 128.2, 129.1, 134.3, 134.5, 153.2, 169.2; IR (KBr): 2978, 2929, 1742, 1698, 1493, 1456, 1369, 1231, 1162, 1092, 1039, 1014, 906, 865, 819, 768, 737 cm^{-1}; MS (FAB) *m*/*z* (%): 372 (M^++1, 5), 312 (10), 256 (100), 212 (46), 188 (56), 132 (62), 88 (36), 57 (100). Anal. Calcd for $C_{17}H_{22}ClNO_4S$: C, 54.91; H, 5.96; N, 3.77. Found: C, 54.91; H, 5.99; N, 3.74; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min) t_R 19.4 (1′*S*,2*S*) and 21.9 (1′*R*,2*R*) min (88% ee).

4.4.5. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-acetoxy-1-(1-naphthyl)methyl]thiazolidine-3-carboxylate *syn*-12b and *anti*-12b. *syn*-**12b**: $[\alpha]_D^{20} = -16.0$ (*c* 0.418, $CHCl_3$, 64% ee); ^1H NMR ($CDCl_3$): δ 1.36 (9H, s), 2.19 (3H, s), 2.87–3.22 (2H, m), 3.47–3.73 (2H, m), 5.59 (1H, d, $J = 4.2$ Hz), 6.80 (1H, d, $J = 4.2$ Hz), 7.35–8.26 (7H, m); ^{13}C NMR ($CDCl_3$): δ 21.9, 28.8, 30.3, 50.2, 60.2, 76.6, 82.0, 123.4, 125.3, 125.9, 126.4, 128.5, 129.0, 130.6, 133.2, 153.9, 169.6; IR (neat): 3053, 2978, 1747, 1695, 1598, 1512, 1476, 1368, 1228, 1161, 1106, 1068, 932, 898, 863, 775, 736, 704 cm^{-1}; MS (FAB) *m*/*z* (%): 388 (M^++1, 3), 272 (100), 228 (60), 188 (62), 132 (84), 88 (56), 57 (100); Anal. Calcd for $C_{21}H_{25}NO_4S$: C, 65.09; H, 6.50; N, 3.61. Found: C, 64.92; H, 6.71; N. 3.55; HPLC (Daicel Chiralpak AD-H, Hexane/*i*-PrOH = 98:2, 0.5 mL/min) t_R 24.2 (1′*R*, 2*S*) and 30.6 (1′*S*,2*R*) min (64% ee). *anti*-**12b**: $[\alpha]_D^{20} = -11.3$ (*c* 1.34, $CHCl_3$, 88% ee); ^1H NMR ($CDCl_3$): δ 1.39 (9H, s), 2.11 (3H, s), 2.66–2.85 (2H, m), 3.16–3.37 (2H, m), 5.84 (1H, d, $J = 6.2$ Hz), 6.63 (1H, d, $J = 6.2$ Hz), 7.35–8.26 (7H, m); ^{13}C NMR ($CDCl_3$): δ 21.3, 28.4, 31.0, 48.5, 65.0, 76.1, 80.8, 123.3, 124.8, 125.5, 126.2, 128.6, 129.1, 131.9, 133.5, 153.6, 169.4; IR (neat): 2977, 1693, 1475, 1454, 1392, 1257, 1163, 909, 850, 733, 700 cm^{-1}; MS (FAB) *m*/*z* (%): 388 (M^++1, 3), 272 (100), 228 (62), 188 (31), 132 (52), 88 (33), 57 (66). Anal. Calcd for $C_{21}H_{25}NO_4S$: C, 65.09; H, 6.50; N, 3.61. Found: C, 64.99; H, 6.66; N, 3.54; HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 95:5, 0.5 mL/min) t_R 16.0 (1′*R*,2*R*) and 20.1 (1′*S*,2*S*) min (88% ee).

4.4.6. (1′*S*,2*R*)- and (1′*R*,2*R*)-*tert*-Butyl 2-[1-acetoxy-1-(2-naphthyl)methyl]thiazolidine-3-carboxylate *syn*-13b and *anti*-13b. *syn*-**13b**: $[\alpha]_D^{20} = +42.5$ (*c* 0.273, $CHCl_3$, 65% ee); ^1H NMR ($CDCl_3$): δ 1.27 (9H, s), 2.18 (3H, s), 2.80–3.10 (2H, m), 3.45–3.57 (2H, m), 5.43 (1H, d, $J = 3.8$ Hz), 6.13 (1H, d, $J = 3.8$ Hz), 7.43–7.48 (3H, m), 7.79–7.83 (4H, m); ^{13}C NMR ($CDCl_3$): δ 21.4, 28.2, 30.6, 49.2, 66.7, 77.2, 81.0, 124.2, 126.0, 127.4, 127.8, 128.0, 132.7, 133.0, 134.4, 153.2, 169.3; IR (neat): 3058, 2977, 2936, 1747, 1698, 1475, 1456, 1368, 1228,

1161, 1107, 1035, 911, 858, 819, 733, 647 cm^{-1}; MS (FAB) *m/z* (%): 388 (M^++1, 4), 272 (100), 228 (78), 188 (57), 132 (82), 88 (52), 57 (100). Anal. Calcd for $C_{21}H_{25}NO_4S$: C, 65.09; H, 6.50; N, 3.61. Found: C, 65.13; H, 6.73; N, 3.55; HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 99:1, 0.5 mL/min) t_R 28.2 (1′*R*,2*S*) and 34.3 (1′*S*,2*R*) min (65% ee). *anti*-**13b**: mp 114–115 °C; $[\alpha]_D^{20} = +13.5$ (*c* 2.40, $CHCl_3$, 90% ee); $[\alpha]_D^{20} = +15.0$ (*c* 0.830, $CHCl_3$, >99% ee, after recrystallization from hexane); ^1H NMR ($CDCl_3$): δ 1.51 (9H, s), 2.12 (3H, s), 2.50–2.85 (2H, m), 3.10–3.30 (2H, m), 5.58 (1H, d, *J* = 6.4 Hz), 6.11 (1H, d, *J* = 6.4 Hz), 7.45–7.49 (3H, m), 7.79–7.86 (4H, m); ^{13}C NMR ($CDCl_3$): δ 21.4, 28.5, 30.3, 48.9, 65.5, 76.1, 81.0, 125.2, 126.0, 127.5, 127.7, 128.0, 132.6, 133.1, 133.4, 153.1, 169.4; IR (KBr): 3060, 2977, 2936, 1740, 1680, 1475, 1368, 1238, 1167, 1098, 1047, 940, 865, 810, 749, 716 cm^{-1}; MS (FAB) *m/z* (%): 388 (M^++1, 3), 272 (100), 228 (37), 188 (36), 132 (43), 88 (24), 57 (66). Anal. Calcd for $C_{21}H_{25}NO_4S$: C, 65.09; H, 6.50; N, 3.61. Found: C, 65.14; H, 6.48; N, 3.58; HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98:2, 0.6 mL/min) t_R 23.9 (1′*S*, 2*S*) and 30.2 (1′*R*,2*R*) min (90% ee).

4.5. Typical procedure for the preparation of optically active 1,2-ethanediols 24–29 from 8b–16b

To a solution of *syn*-**8b** (121 mg, 0.36 mmol) in acetonitrile (2.4 mL) and water (0.6 mL) was added $HgCl_2$ (293 mg, 1.08 mmol), and then the mixture stirred for 6 h at room temperature. The reaction mixture was diluted with water and filtered, and the filtrate then extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure to give an oil including 2-acetoxy-2-phenylacetaldehyde, which was dissolved in THF (0.5 mL) and added to a solution of $LiAlH_4$ (68 mg, 1.80 mmol) in THF (2 mL) at 0 °C. The reaction mixture was stirred for 3 h at room temperature. 1 mol/L HCl solution was added slowly and the mixture extracted with diethyl ether, dried over Na_2SO_4 and concentrated under reduced pressure to leave a residue that was purified by column chromatography (hexane/EtOAc = 70:30) to give (*S*)-**24** (32 mg, 66%).

4.5.1. (*S*)-1-Phenyl-1,2-ethanediol (*S*)-24. $[\alpha]_D^{22} = +36.2$ (*c* 0.30, EtOH, 92% ee) lit.[14] $[\alpha]_D^{22} = +38.9$ (*c* 3.60, EtOH); mp 59–60 °C; ^1H NMR ($CDCl_3$): δ 2.09 (1H, br), 2.55 (1H, br), 3.61–3.79 (2H, m), 4.82 (1H, dd, *J* = 3.6, 8.0 Hz), 7.29–7.38 (5H, m); ^{13}C NMR ($CDCl_3$): δ 68.0, 74.7, 125.8, 127.7, 128.3, 140.2; IR (KBr): 3300–3200, 3031, 2933, 2871, 1448, 1100, 1072, 1052, 750, 698 cm^{-1}. HPLC (Daicel Chiralpak OB-H, hexane/*i*-PrOH = 90:10, 0.5 mL/min) t_R 15.2 (*R*) and 17.8 (*S*) min.

(*R*)-1-Phenyl-1,2-ethanediol (*R*)-**24**: $[\alpha]_D^{22} = -34.2$ (*c* 0.43, EtOH, 88% ee).

4.5.2. (*S*)-1-(4-Tolyl)-1,2-ethanediol (*S*)-25. $[\alpha]_D^{22} = +46.2$ (*c* 0.80, $CHCl_3$, 67% ee) lit.[14] $[\alpha]_D^{22} = +69.2$ (*c* 1.10, $CHCl_3$); mp: 64–66 °C; ^1H NMR ($CDCl_3$): δ 2.04 (1H, br), 2.35 (3H, s), 2.46 (1H, br), 3.61–3.74 (2H, m), 4.80 (1H, dd, *J* = 3.6, 8.0 Hz), 7.17–7.28 (4H, m); ^{13}C NMR ($CDCl_3$): δ 21.3, 68.1, 74.5, 125.8,129.0, 137.1, 137.5; IR (KBr): 3450–3250, 2925, 2886, 1401, 1093, 1069, 1037, 897, 821 cm^{-1}.

(*R*)-1-(4-Tolyl)-1,2-ethanediol (*R*)-**25**: $[\alpha]_D^{23} = -60.8$ (*c* 0.83, $CHCl_3$, 88% ee).

4.5.3. (*S*)-1-(*p*-Methoxyphenyl)-1,2-ethanediol (*S*)-26. $[\alpha]_D^{22} = +51.6$ (*c* 0.49, $CHCl_3$, 66% ee) lit.[14] $[\alpha]_D^{22} = +74.1$ (*c* 0.52, $CHCl_3$ 95% ee); mp 73–74 °C; ^1H NMR ($CDCl_3$): δ 2.14 (1H, br), 2.39 (1H, br), 3.60–3.77 (2H, m), 3.80 (3H, s), 4.77 (1H, dd, *J* = 4.2, 7.8 Hz), 6.86–6.91 (2H, m), 7.25–7.30 (2H, m); ^{13}C NMR ($CDCl_3$): δ 55.4, 68.1, 74.3, 113.8, 127.2, 132.1, 159.2; IR (KBr): 3400–3300, 2959, 2934, 1699, 1515, 1246, 1081, 1026, 834 cm^{-1}.

(*R*)-1-(*p*-Methoxyphenyl)-1,2-ethanediol (*R*)-**26**: $[\alpha]_D^{22} = -70.5$ (*c* 0.53, $CHCl_3$, 90% ee).

4.5.4. (*S*)-1-(4-Chlorophenyl)-1,2-ethanediol (*S*)-27. $[\alpha]_D^{23} = +37.0$ (*c* 0.82, $CHCl_3$, 60% ee); mp 79–81 °C; ^1H NMR ($CDCl_3$): δ 2.56 (1H, br), 3.04 (1H, br), 3.53–3.75 (2H, m), 4.77 (1H, dd, *J* = 3.6, 8.2 Hz), 7.23–7.33 (4H, m); ^{13}C NMR ($CDCl_3$): δ 67.9, 74.0, 127.2, 128.5, 133.5, 138.6; IR (KBr): 3400–3300, 2932, 2895, 1493, 1088, 1037, 900, 831 cm^{-1}.

(*R*)-1-(4-Chlorophenyl)-1,2-ethanediol (*R*)-**27**: $[\alpha]_D^{23} = -53.7$ (*c* 0.23, $CHCl_3$, 88% ee) lit.[21] $[\alpha]_D^{23} = -60.0$ (*c* 1.0, $CHCl_3$, 98% ee).

4.5.5. (*S*)-1-(1-Naphthyl)-1,2-ethanediol (*S*)-28. $[\alpha]_D^{24} = +56.5$ (*c* 0.38, $CHCl_3$, 63% ee); mp 38–39 °C; ^1H NMR ($CDCl_3$): δ 1.85 (1H, br), 2.40 (1H, br), 3.70–3.81 (2H, m), 5.62 (1H, dd, *J* = 2.8, 8.0 Hz), 7.43–7.50 (3H, m), 7.80–7.85 (4H, m); ^{13}C NMR ($CDCl_3$): δ 67.5, 71.6, 122.4, 123.3, 125.2, 125.5, 126.1, 128.2, 128.7, 130.6, 133.4, 136.0; IR (KBr): 3350–3150, 2929, 2876, 1459, 1374, 1334, 1107, 1079, 1033, 799, 779 cm^{-1}.

(*R*)-1-(1-Naphthyl)-1,2-ethanediol (*R*)-**28**: $[\alpha]_D^{24} = -78.9$ (*c* 0.38, $CHCl_3$, 87% ee) lit.[22] $[\alpha]_D^{23} = -90.2$ (*c* 1.0, $CHCl_3$).

4.5.6. (*S*)-1-(2-Naphthyl)-1,2-ethanediol (*S*)-29. $[\alpha]_D^{23} = +20.5$ (*c* 0.70, EtOH, 64% ee); mp 104–106 °C; ^1H NMR ($CDCl_3$): δ 2.04 (1H, br), 2.58 (1H, br), 3.70–3.90 (2H, m), 4.99 (1H, dd, *J* = 3.8, 8.0 Hz), 7.43–7.50 (3H, m), 7.80–7.85 (4H, m); ^{13}C NMR ($CDCl_3$): δ 68.1, 74.8, 123.7, 124.8, 125.9, 126.1, 127.5, 127.7, 128.1, 132.9, 133.0, 137.6; IR (KBr): 3400–3200, 2925, 2862, 1465, 1362, 1086, 824, 742 cm^{-1}.

(*R*)-1-(2-Naphthyl)-1,2-ethanediol (*R*)-**29**: $[\alpha]_D^{23} = -28.6$ (*c* 0.79, EtOH, 88% ee) lit.[22] $[\alpha]_D^{23} = -31.2$ (*c* 1.0, EtOH).

4.5.7. (*S*)-3-Methyl-1,2-butanediol (*S*)-30. $[\alpha]_D^{20} = +7.9$ (*c* 0.26, $CHCl_3$, 77% ee) lit.[23] $[\alpha]_D^{20} = +10.3$ (*c* 1.15, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 0.93 (3H, d, *J* = 11.6), 0.97 (3H, d, *J* = 11.6), 1.63–1.79 (1H, m), 2.13 (2H, br), 3.38–3.56 (2H, m), 3.70 (1H, dd, *J* = 2.2,

10.2); ^{13}C NMR ($CDCl_3$): δ 18.4, 18.9, 31.1, 65.0, 77.2; IR (neat): 3500–3100, 2960, 2925, 2883, 1467, 1065, 1012, 876 cm^{-1}.

(*R*)-3-Methyl-1,2-butanediol (*R*)-**30**: $[\alpha]_D^{20} = -8.8$ (*c* 0.31, $CHCl_3$, 85% ee).

(*S*)-1-Cyclohexyl-1,2-ethanediol (*S*)-**31**: $[\alpha]_D^{23} = +3.7$ (*c* 0.76, $CHCl_3$, 70% ee).

(*R*)-1-Cyclohexyl-1,2-ethanediol (*R*)-**31**: $[\alpha]_D^{23} = -4.7$ (*c* 0.73, $CHCl_3$, 89% ee) lit.[22] $[\alpha]_D^{23} = -4.8$ (*c* 0.92, $CHCl_3$), 91% ee for *R*; ^{1}H NMR ($CDCl_3$): δ 0.88–1.89 (11H, m), 2.68 (2H, br), 3.38–3.56 (2H, m), 3.69 (1H, dd, J = 2.2, 10.4 Hz); ^{13}C NMR ($CDCl_3$): δ 26.2, 26.5, 28.8, 29.1, 31.7, 40.8, 64.8, 76.5; IR (neat): 3500–3100, 2923, 2855, 1449, 1069, 892, 756 cm^{-1}.

4.6. Typical procedure for the preparation of optically active 1,2-ethanediols 24–29 from 18–23

To a solution of *syn*-**18** (156 mg, 0.45 mmol) in acetic acid (3.2 mL) and water (0.8 mL) was added $Hg(OAc)_2$ (435 mg, 1.36 mmol). Calcium carbonate (137 mg, 1.36 mmol) was added to adjust the pH of the reaction mixture to 7.0. The mixture was stirred for 6 h at 50 °C under argon, and then cooled to room temperature. The precipitates were filtered through a Celite bed and washed with CH_2Cl_2. The filtrate was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give the crude 2-hydroxy-2-phenylacetaldehyde, which was added to a solution of $NaBH_4$ (18 mg, 0.48 mmol) in MeOH (2 mL) at room temperature. The reaction mixture was stirred for 3 h at room temperature. MeOH was evaporated under reduced pressure to leave a residue, to which brine was added. The solution was extracted with diethyl ether. The resultant combined extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue that was purified by column chromatography (hexane/EtOAc = 70:30) to give (*S*)-**24** (46 mg, 74%).

4.7. Preparation of *tert*-butyl 2-tributylstannylthiazolidine-3-carboxylate 32

To a solution of **1** (220 mg, 1.16 mmol) in THF (2.0 mL) was added *n*-BuLi (0.95 mL, 1.49 mol L^{-1} solution in hexane, 1.40 mmol) dropwise over a period of 5 min at −78 °C. After the mixture was stirred for 15 min, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.21 mL, 1.40 mmol) was added. The reaction mixture was stirred for 30 min, before the addition of tributylstannyl chloride (492 mg, 1.51 mmol). The mixture was stirred for an additional 20 min at −78 °C. Saturated aqueous NH_4Cl was added and the mixture was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to leave a residue that was purified by column chromatography (hexane/benzene = 85:15) to give **32** (310 mg, 56%). ^{1}H NMR ($CDCl_3$): δ 1.45 (9H, s), 0.85–1.60 (27H, m), 2.93 (2H, t, J = 6.6 Hz), 3.48–3.64 (2H, m), 4.12 (1H, s); ^{13}C NMR ($CDCl_3$): δ 11.8, 14.0, 27.6, 28.6, 29.2, 33.1, 48.3, 49.4, 79.7, 153.7; IR (neat): 2955, 1680, 1477, 1456, 1402, 1366, 1250, 1149, 1045, 874, 767, 673 cm^{-1}; MS (EI) *m*/*z* (%): 422 ($M^+ - {}^t$Bu). Anal. Calcd for $C_{20}H_{41}NO_2SSn$: C, 50.22; H, 8.64; N, 2.93. Found: C, 50.45; H, 8.64; N, 2.97.

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