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Preparation of novel *N*-sulfonylated (*S*,*S*)-2,3-diaminosuccinate-type chiral auxiliaries and application to an asymmetric 1,3-dipolar cycloaddition reaction of nitrile oxides to allyl alcohol

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Abstract—Novel *N*-sulfonylated (*S*,*S*)-2,3-diaminosuccinate-type chiral auxiliaries, which have the tartaric acid-like framework with a sulfonamide group instead of a hydroxyl group, were synthesized from L-aspartic acid. The synthesized (*S*,*S*)-2,3-diaminosuccinate derivatives were applied to an asymmetric 1,3-dipolar cycloaddition reaction of nitrile oxides to allyl alcohol to afford the corresponding optically active 2-isoxazolines, with the enantioselectivities of up to 73% ee. The enantiofacial differentiation was intriguingly opposite to that by using diisopropyl tartrate as a chiral auxiliary.

1. Introduction

Enantiomerically pure vicinal diamines and their derivatives have recently attracted a great deal of attention in asymmetric synthesis, as chiral auxiliaries.[1,2] In particular, chiral vicinal bis-sulfonamides play significant roles due to their acidic protons and ready formation of metal amides.[1,3] Recently, we have developed new asymmetric reactions utilizing tartaric acid ester as a chiral auxiliary.[4] If the two hydroxyl groups in tartaric acid esters are replaced by nitrogen functional groups, an alternative affinity for metals and different stereocontrols by substituents on nitrogen atoms are anticipated. Herein we wish to describe a synthesis of new (*S*,*S*)-2,3-diaminosuccinate-type chiral auxiliaries[5] that have the tartaric acid framework with a sulfonamide group instead of a hydroxyl group, and their application to the asymmetric 1,3-dipolar cycloaddition reaction of nitrile oxides to allyl alcohol.

2. Results and discussion

The synthesis of chiral auxiliaries was accomplished as outlined in Scheme 1. The 2,3-diaminosuccinate backbone was constructed according to the reported procedure from L-aspartic acid via its *N*-9-phenylfluorenylated ester derivative **1** to give a diastereomeric mixture of (2*S*,3*S*)-**2** and (2*R*,3*S*)-**2**.[5a] Diastereomerically pure (2*S*,3*S*)-**2** was obtained by recrystallization. Catalytic hydrogenolysis of the 9-phenylfluorenyl and azide groups afforded (*S*,*S*)-2,3-diaminosuccinate **3**, followed by sulfonylation with various sulfonylating reagents to give the desired chiral auxiliaries **4a**–**f** having the tartaric acid framework with a sulfonamide group instead of a hydroxyl group. Hydrolysis of the methyl ester by aqueous NaOH solution followed by esterification furnished the ^{i}Pr ester **6** and ^{t}Bu esters **7a**–**f** without racemization.

The ability of chiral induction of compounds **4a**, **6** and **7a**–**f** prepared above was probed by an asymmetric 1,3-dipolar cycloaddition of a nitrile oxide to allyl alcohol **8** (Scheme 2),[6] that is, treatment of allyl alcohol with 1.0 molar amount of diethylzinc, 1.0 molar amount of chiral sulfonamide, 1.1 molar amounts of the second diethylzinc and 1.1 molar amounts of *p*-(methoxy)benzohydroximoyl chloride; this may form the bis-zinc containing intermediate **9**, in which the nitrile oxide generated coordinates to zinc metal(s). The following 1,3-dipolar cycloaddition was expected to proceed enantioselectively within this complex to afford the corresponding optically active 2-isoxazoline **10A**.

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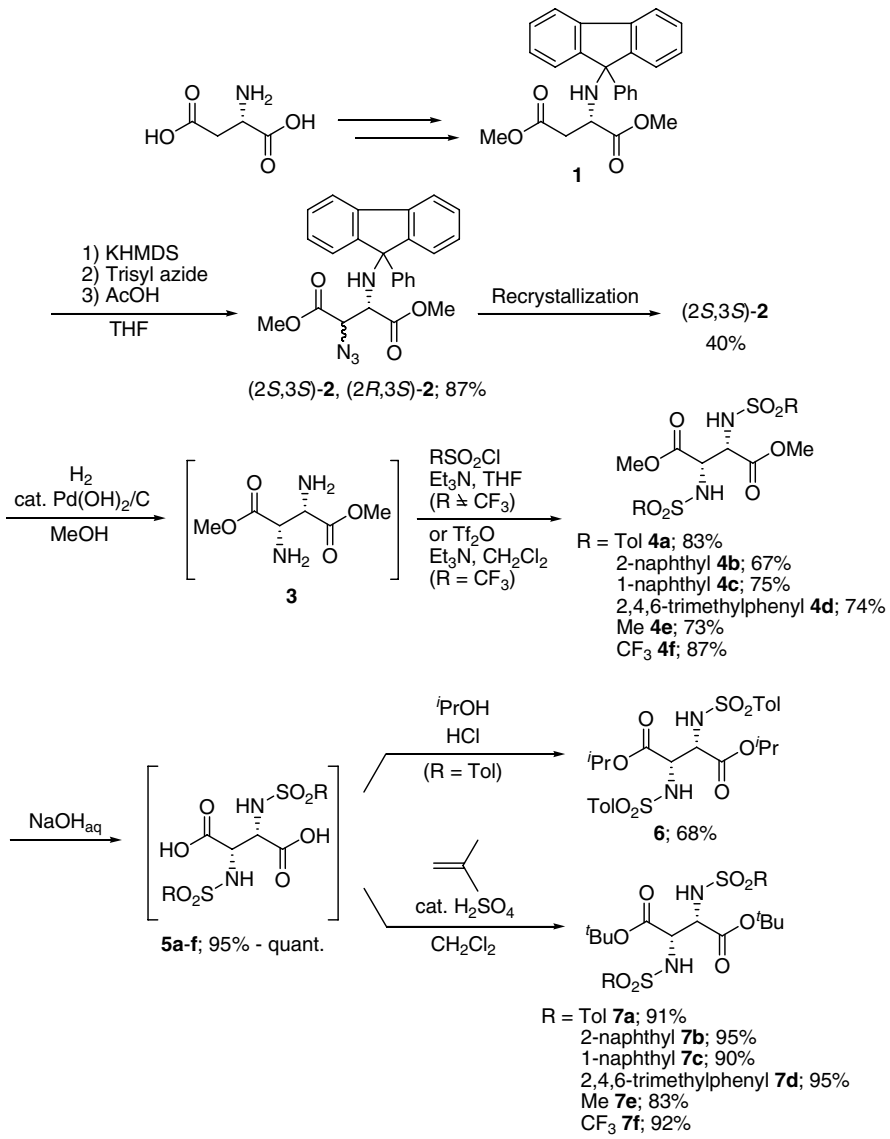
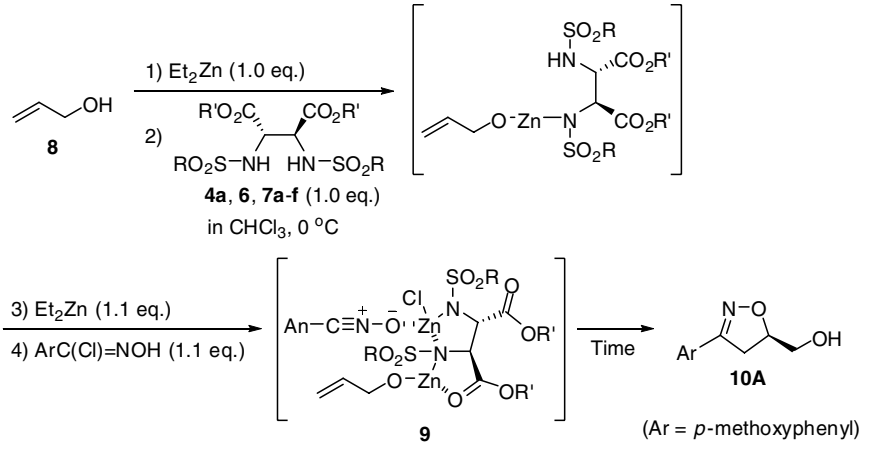


Scheme 1.



Scheme 2.

Table 1.

Entry	R	R′	Chiral sulfonamide	Time (h)	Yield of **10A** (%)	ee (%)
1	Tol	Me	**4a**	24	67	24
2	Tol	^{i}Pr	**6**	24	70	37
3	Tol	^{t}Bu	**7a**	23	60	40
4	2-Naphthyl	^{t}Bu	**7b**	23	56	37
5	1-Naphthyl	^{t}Bu	**7c**	24	56	11
6	2,4,6-Trimethylphenyl	^{t}Bu	**7d**	24	63	13
7	Me	^{t}Bu	**7e**	24	67	18
8	CF_3	^{t}Bu	**7f**	24	67	50

First in order to investigate the influence of the ester groups in the chiral auxiliaries, the chiral auxiliaries with the tosyl group on the nitrogen atom were used for the 1,3-dipolar cycloaddition (Table 1, entries 1–3). Although the use of methyl ester **4a** afforded cycloadduct **10A** with poor enantioselectivity (entry 1), bulkier esters enhanced the enantioselectivity. In the case of *t*-butyl ester **7a**, enantioselectivity was improved to 40% ee (entry 3).

Next, the effect of the substituents on the nitrogen in the chiral auxiliaries was investigated (entries 3–8). Sulfonamides **7b–d** with bulkier groups and **7e** with a smaller Me group were less effective than **7a**. A smaller electron-withdrawing trifluoromethanesulfonyl (Tf) group was found to be more effective than **7a** and the enantioselectivity was improved to 50% ee (entry 8).

Table 2.

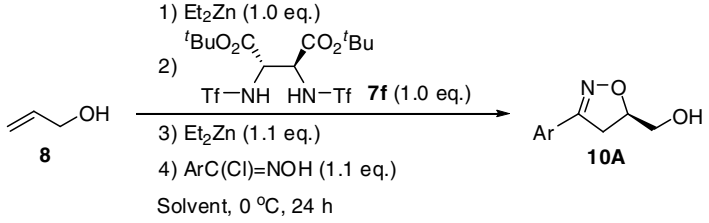
Entry	Solvent	Yield (%)	ee (%)
1	$CHCl_3$	67	50
2	CH_2Cl_2	56	45
3	MeCN	35	0
4	THF	24	1
5	Et_2O	31	28
6	^{t}BuOMe	67	33
7	Toluene	49	52
8	Toluene/THF[a]	46	2
9	Toluene/DMTHF[a,b]	53	11
10	Toluene/DME[a]	53	14
11	Toluene/Et_2O[a]	53	39
12	Toluene/^{t}BuOMe[a]	63	65
13	Benzene/^{t}BuOMe[a]	73	61
14	Ethylbenzene/^{t}BuOMe[a]	73	73
15[c]	Ethylbenzene/^{t}BuOMe[a]	74	71
16	*n*-Propylbenzene/^{t}BuOMe[a]	73	67
17	Cumene/^{t}BuOMe[a]	67	69
18	Xylene/^{t}BuOMe[a,d]	73	68
19	Mesitylene/^{t}BuOMe[a]	73	67

[a] Solvent/co-solvent ratio was 13/1.
[b] DMTHF is 2,5-dimethyltetrahydrofuran.
[c] MS 3 Å was added.
[d] A mixture of xylene isomers was used.

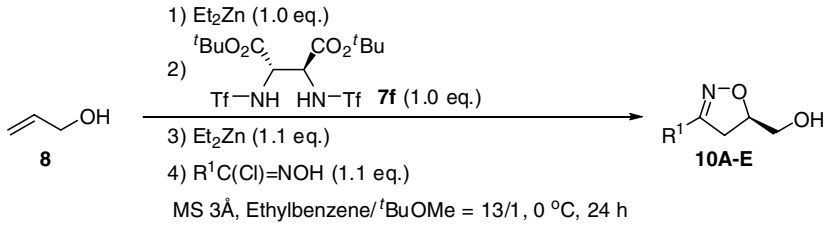
The effect of solvent was also examined (Scheme 3) and the results are listed in Table 2. Dichloromethane afforded a comparable result with $CHCl_3$ (entry 2). Coordinative solvents, such as MeCN or ethers, decreased the enantioselectivity (entries 3–6). Enantioselectivity in toluene was similar to that in halogenated solvents (entry 7), even though **7f** was almost insoluble and the reaction mixture was heterogeneous throughout the reaction. In order to dissolve **7f**, a small amount of etheral solvent was added as a co-solvent. It was found that the enantioselectivity was varied by the type of added ethers (entries 8–12). Strongly coordinative ethers, such as THF and DME, considerably lowered the enantioselectivity. When weakly coordinative ^{t}BuOMe was used, the enantiomeric excess was further improved to 65% ee (entry 12). Furthermore, other aromatic solvents were examined (entries 12–19), and it was found that substituted benzenes afforded product **10A** with slightly enhanced enantioselectivity. Especially, ethylbenzene was the solvent of choice to furnish 2-isoxazoline **10A** in 73% ee (entry 14). It was found that the presence of MS 3 Å in the reaction mixture was effective to realize reproducibile enantioselectivity (entry 15), probably to avoid the influence of moisture.

The asymmetric 1,3-dipolar cycloaddition of benzonitrile oxide, pivalonitrile oxide, 4-bromobenzonitrile oxide and 4-cyanobenzonitrile oxide was carried out under the optimized reaction conditions (Scheme 4, Table 3). The corresponding 2-isoxazolines **10B–E** were obtained with moderate enantioselectivity.

The absolute configurations of 2-isoxazolines **10B** and **10C** were determined to be (*R*) by comparison of their specific rotations with the reported data, respectively.[7] The absolute configurations of **10A**,**D**,**E** were tentatively determined to be (*R*). Interestingly, based on these results, the enantio-



Scheme 3.



Scheme 4.

facial differentiation of the present system was found to be opposite to the case utilizing diisopropyl tartrate (DIPT) as a chiral auxiliary. (*S*,*S*)-2,3-Diaminosuccinate **7f** afforded the (*R*)-2-isoxazoline, whereas (*R*,*R*)-DIPT gave the (*R*)-2-isoxazoline, which means that (*S*,*S*)-DIPT would produce the (*S*)-2-isoxazoline.[6]

Table 3.

Entry	R^1	**10**	Yield (%)	ee (%)
1	4-$MeOC_6H_4$ (Ar)	**A**	74	71
2	Ph	**B**	72	55
3	^{t}Bu	**C**	78	50
4	4-BrC_6H_4	**D**	82	57
5	4-NCC_6H_4	**E**	79	49

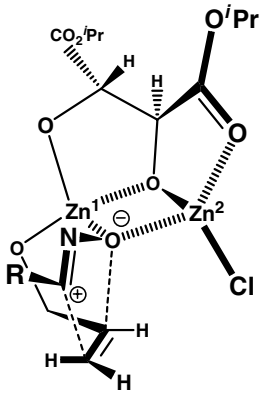


Figure 1.

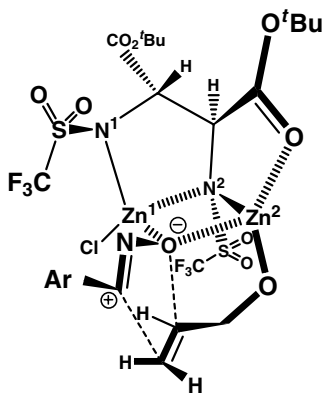


Figure 2.

We had proposed that the stereochemical course in asymmetric 1,3-dipolar cycloadditions using (*S*,*S*)-DIPT could be explained by using a bimetallic transition state model as depicted in Figure 1, in which a rigid 5/5-fused bicyclic structure was formed by zinc bridging. The nitrile oxide coordinating to the two zinc metals was well-activated and added from the *si*-face of allyl alcohol to give the (*S*)-2-isoxazoline.

On the other hand, in the present case using a chiral sulfonamide, such as **7f**, the asymmetric 1,3-dipolar cycloaddition might proceed through the two zinc bridging transition states as depicted in Figure 2. The reversal of enantioselection might be due to the influence of the substituents on nitrogen atoms which are absent in the case of DIPT (Fig. 1). Nitrile oxide coordinates to the two zinc metals Zn^1 and Zn^2 in a similar manner to the case of DIPT; however, the substituents on nitrogen atoms influence the steric relationship between nitrile oxide and allyl alcohol moiety. The allyl alcohol moiety might be bound to Zn^2 as shown in Figure 4, rather than Zn^1 to avoid the steric interaction with the bulky sulfonamide on N^1 (Fig. 3). Nitrile oxide would approach the *re*-face of the allyl alcohol (Fig. 4), which is opposite to that in the case of DIPT. The strongly electron-withdrawing Tf group makes zinc metals more Lewis acidic, and the interaction between the zinc metals and a nitrile oxide may become more effective to enhance the stereoselectivity.

3. Conclusion

In conclusion, a series of new (*S*,*S*)-2,3-diaminosuccinate-type chiral auxiliaries were prepared from L-aspartic acid, and their asymmetric induction properties were investigated for the asymmetric 1,3-dipolar cycloaddition reaction of nitrile oxides to allyl alcohol. The corresponding 2-isoxazolines were obtained with an enantioselectivity of upto 73% ee, whose enantiofacial differentiation was opposite to the case utilizing DIPT as a chiral auxiliary.

4. Experimental

4.1. General

All of the melting points were determined by a micro melting apparatus (Yamagimoto-Seisakusho) and are uncorrected. The ^{1}H NMR spectra were recorded on JEOL Lambda 400, JEOL Lambda 300 (only for (2*S*,3*S*)-**2**), and JEOL JNM-GX 400 spectrometers. The chemical shifts were determined in the δ-scale relative to tetrameth-

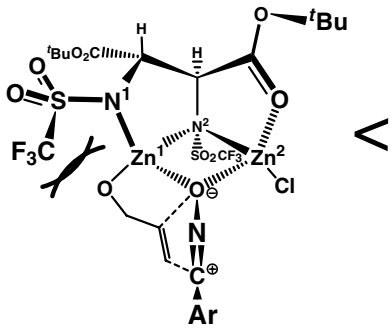


Figure 3.

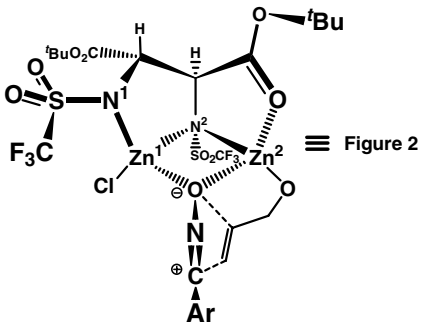


Figure 4.

ylsilane ($\delta = 0$) as an internal standard. The IR spectra were measured by a JASCO FT/IR-230 spectrometer. The optical rotations were recorded on a JASCO DIP-370 spectrometer. $CHCl_3$ was treated with Merck's aluminum oxide 90 active basic (0.063–0.200 mm, activity stage I, Art. 101076) and dried over MS 4 Å just before use. THF and Et_2O were freshly distilled from sodium diphenylketyl. All other solvents were distilled and stored over drying agents. Flash column chromatography and thin-layer chromatography (TLC) were performed on Cica-Merck's silica gel 60 (No. 9385-5B) and Merck's silica gel 60 PF_{254} (Art. 107749), respectively.

4.2. Preparation of chiral auxiliaries

4.2.1. Dimethyl (2*S*,3*S*)-2-azido-3-(9-phenyl-9*H*-fluoren-9-ylamino)succinate (2*S*,3*S*)-2.[5a] To a THF (35 ml) solution of dimethyl (*S*)-*N*-(9-phenyl-9*H*-fluoren-9-yl)aspartate **1** (1.27 g, 3.16 mmol) was added KHMDS (4.10 mmol, 4.6 ml of 20% solution (ca. 0.9 M) in toluene) at −78 °C under a nitrogen atmosphere and the reaction mixture was kept at −78 °C for 1 h. A precooled (−78 °C) THF (12 ml) solution of (2,4,6-triisopropyl)benzenesulfonyl azide (1.27 g, 4.10 mmol) was added to the above enolate solution. After stirring for 6 min, the reaction was quenched with AcOH (15.2 mmol, 0.87 ml) and the resulting mixture was stirred for 2 h at 25 °C, and then extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/AcOEt = 6/1) to give a mixture of (2*S*,3*S*)-**2** and (2*R*,3*S*)-**2** (1.22 g, 87%, (2*S*,3*S*)-**2**:(2*R*,3*S*)-**2** = ca. 2:1). Recrystallization of the mixture from hexane/AcOEt gave pure (2*S*,3*S*)-**2** (0.56 g, 40%). Mp 150.5–151.5 °C (from hexane/AcOEt); $[\alpha]_D^{25} = -324$ (*c* 0.22, $CHCl_3$); IR (KBr) 3309, 3064, 2952, 2844, 2142, 2109, 1749, 1598, 1543, 1489, 1436, 1353, 1340, 1301, 1272, 1213, 1182, 1141, 1060, 1022, 984, 931, 908, 889, 835, 805, 757, 734, 700 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.19$ (dd, $J = 3.12$, 10.09 Hz, 1H), 3.37 (d, $J = 10.09$ Hz, 1H), 3.40 (s, 3H), 3.52 (s, 3H), 3.76 (d, $J = 3.12$ Hz, 1H), 7.18–7.42 (m, 11H), 7.65 (d, $J = 7.52$ Hz, 1H), 7.70 (d, $J = 7.52$ Hz, 1H). Found: C, 67.83; H, 5.08; N, 12.55. Calcd for $C_{25}H_{22}N_4O_4$: C, 67.86; H, 5.01; N, 12.66.

4.2.2. Dimethyl (*S*,*S*)-2,3-bis(4-methylphenylsulfonamido)-succinate 4a. To a suspension of (2*S*,3*S*)-**2** (1.85 g, 4.18 mmol) in MeOH (35 ml) was added $Pd(OH)_2$/C (350 mg, 20% Pd) and the mixture was stirred under an H_2 atmosphere for 11 h at room temperature. The resulting suspension was filtered and the filtrate was evaporated under reduced pressure to give crude diamine **3**. To crude **3** was added a catalytic amount of DMAP (31 mg, 0.25 mmol) and replaced with N_2 atmosphere. THF (45 ml), Et_3N (2.03 ml, 14.6 mmol) and a THF (15 ml) solution of *p*-toluenesulfonyl chloride (2.39 g, 12.5 mmol) were added and the solution was stirred for 24 h at room temperature. The reaction was quenched by the addition of water and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The residue was purified by recrystallization from hexane/AcOEt to give **4a** (1.28 g, 63%). The mother liquor was condensed and the residue was separated by column chromatography on SiO_2 (hexane/AcOEt = 5/1 and then hexane/AcOEt = 2/1) to give the almost pure **4a**. The product was purified by recrystallization from hexane/AcOEt to give **4a** (284 mg, 14%). The mother liquor was condensed and the residue was purified by TLC (SiO_2, $CHCl_3$/MeCN = 5/1) to give additional **4a** (112 mg, 6%). Mp 207–208 °C (from hexane/AcOEt); $[\alpha]_D^{25} = +123$ (*c* 0.23, $CHCl_3$); IR (KBr) 3261, 3231, 3069, 2960, 2921, 1740, 1718, 1597, 1496, 1458, 1343, 1283, 1214, 1169, 1125, 1088, 1019, 982, 956, 915, 861, 817, 802, 790, 717, 704, 665 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.42$ (s, 6H), 3.61 (s, 6H), 4.38 (d, $J = 8.05$ Hz, 2H), 5.56 (d, $J = 8.05$ Hz, 2H), 7.29 (d, $J = 7.81$ Hz, 4H), 7.69 (d, $J = 7.81$ Hz, 4H). Found: C, 49.35; H, 5.00; N, 5.70. Calcd for $C_{20}H_{24}N_2O_8S_2$: C, 49.57; H, 4.99; N, 5.78.

In a similar manner, dimethyl 2,3-diaminosuccinates **4b–e** were prepared using the corresponding sulfonyl chloride.

4.2.3. Dimethyl (*S*,*S*)-2,3-bis(naphthalene-2-sulfonamido)-succinate 4b. Mp 190–191 °C (from hexane/AcOEt); $[\alpha]_D^{25} = +138$ (*c* 0.26, $CHCl_3$); IR (KBr) 3260, 3055, 2958, 1737, 1713, 1626, 1591, 1504, 1438, 1345, 1283, 1213, 1166, 1132, 1105, 1075, 1017, 967, 910, 864, 819, 783, 746, 708, 660 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.47$ (s, 6H), 4.46 (d, $J = 8.54$ Hz, 2H), 5.72 (d, $J = 8.54$ Hz, 2H), 7.61 (dd, $J = 6.83$, 8.54 Hz, 2H), 7.66 (dd, $J = 6.83$, 8.05 Hz, 2H), 7.77 (d, $J = 8.54$ Hz, 2H), 7.90 (d, $J = 8.05$ Hz, 2H), 7.94 (d, $J = 8.54$ Hz, 4H), 8.36 (s, 2H). Found: C, 55.95; H, 4.41; N, 5.04. Calcd for $C_{26}H_{24}N_2O_8S_2$: C, 56.10; H, 4.35; N, 5.03.

4.2.4. Dimethyl (*S*,*S*)-2,3-bis(naphthalene-1-sulfonamido)-succinate 4c. Mp 172–173 °C (from hexane/AcOEt); $[\alpha]_D^{25} = +146$ (*c* 0.23, $CHCl_3$); IR (KBr) 3366, 3267, 3055, 2957, 2849, 1765, 1736, 1594, 1507, 1437, 1340, 1267, 1218, 1202, 1166, 1133, 1104, 1049, 1026, 985, 951, 893, 866, 828, 808, 770, 703, 676 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.18$ (s, 6H), 4.26 (d, $J = 8.54$ Hz, 2H), 5.80 (d, $J = 8.54$ Hz, 2H), 7.50 (dd, $J = 7.32$, 8.29 Hz, 2H), 7.61 (dd, $J = 6.83$, 8.05 Hz, 2H), 7.70 (dd, $J = 6.83$, 8.78 Hz, 2H), 7.92 (d, $J = 8.05$ Hz, 2H), 8.06 (d, $J = 8.29$ Hz, 2H), 8.14 (d, $J = 7.32$ Hz, 2H), 8.57 (d, $J = 8.78$ Hz, 2H). Found: C, 55.99; H, 4.39; N, 5.03. Calcd for $C_{26}H_{24}N_2O_8S_2$: C, 56.10; H, 4.35; N, 5.03.

4.2.5. Dimethyl (*S*,*S*)-2,3-bis(2,4,6-trimethylphenylsulfonamido)succinate 4d. Mp 198.5–199.5 °C (from hexane/AcOEt); $[\alpha]_D^{25} = +81$ (*c* 0.31, $CHCl_3$); IR (KBr) 3349, 3332, 3306, 3288, 2978, 1767, 1757, 1603, 1561, 1427, 1380, 1343, 1263, 1212, 1194, 1165, 1139, 1109, 1056, 977, 938, 882, 861, 780, 721, 697 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.28$ (s, 6H), 2.60 (s, 12H), 3.55 (s, 6H), 4.26 (d, $J = 8.54$ Hz, 2H), 5.57 (d, $J = 8.54$ Hz, 2H), 6.94 (s, 4H). Found: C, 53.24; H, 5.97; N, 5.25. Calcd for $C_{24}H_{32}N_2O_8S_2$: C, 53.31; H, 5.97; N, 5.18.

4.2.6. Dimethyl (*S*,*S*)-2,3-di(methylsulfonamido)succinate 4e. Mp 162–163 °C (from hexane/AcOEt); $[\alpha]_D^{25} = +32$ (*c* 0.20, $CHCl_3$); IR (KBr) 3327, 3292, 3021, 2985, 2942, 1746, 1440, 1337, 1309, 1279, 1229, 1207, 1184, 1165, 1108, 984, 924, 887, 790, 750, 698 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.98$ (s, 6H), 3.88 (s, 6H), 4.74 (d, $J = 8.54$ Hz, 2H), 5.68 (d, $J = 8.54$ Hz, 2H). Found: C, 29.02; H, 4.90; N, 8.37. Calcd for $C_8H_{16}N_2O_8S_2$: C, 28.91; H, 4.85; N, 8.43.

4.2.7. Dimethyl (*S*,*S*)-2,3-bis(trifluoromethylsulfonamido)-succinate 4f. In a similar manner for the preparation of **4a**, crude **3** was obtained by the reduction of (2*S*,3*S*)-**2** (1.00 g, 1.81 mmol). Then, to the crude **3** was added a catalytic amount of DMAP (34 mg, 0.28 mmol) under an N_2 atmosphere. After the addition of CH_2Cl_2 (25 ml) and Et_3N (0.786 ml, 5.65 mmol), the mixture was cooled to 0 °C, and then trifluoromethanesulfonic anhydride (0.779 ml, 4.75 mmol) was added, followed by stirring for 1 h at 0 °C and for 17 h at room temperature. The reaction was quenched by the addition of water and stirred for 30 min and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The residue was dissolved in a small amount of EtOH, and the solution was adjusted to pH 11 by the addition of 1 M aq NaOH solution and stirred for 1 min. The mixture was washed with Et_2O. The aqueous layer was acidified to pH 4 by the addition of 1 M aq HCl solution and extracted with Et_2O. The combined extracts were washed with brine, dried over Na_2SO_4, and condensed under reduced pressure to give crude **4f** (866 mg, 87%). Crude **4f** was used in the following reaction without further purification. A small amount of **4f** was recrystallized for characterization and analysis. Mp 85.5–86.5 °C (from hexane/Et_2O); $[\alpha]_D^{25} = +26$ (*c* 0.22, EtOH); IR (KBr) 3257, 3156, 2984, 2968, 2928, 2856, 2799, 1751, 1724, 1685, 1654, 1636, 1483, 1454, 1439, 1391, 1296, 1266, 1236, 1200, 1139, 1095, 1018, 977, 917, 870, 799, 768 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.91$ (s, 6H), 4.71 (s, 2H), Signals of the amide protons were not observed clearly.. Found: C, 22.04; H, 2.36; N, 6.65. Calcd for $C_8H_{10}N_2O_8F_6S_2$: C, 21.82; H, 2.29; N, 6.36.

4.2.8. Diisopropyl (*S*,*S*)-2,3-bis(4-methylphenylsulfonamido)succinate 6. Sulfonamide **4a** (700 mg, 1.14 mmol) was treated with 0.6 M aq NaOH solution (40 ml, 24 mmol) at room temperature and the mixture was stirred for 13 h. The solution was neutralized to pH 8 by the addition of 1 M aq HCl solution and washed with AcOEt. The aqueous phase was acidified to pH 3 by the addition of 1 M aq HCl solution and extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4, and condensed under reduced pressure to give crude **5a** (670 mg, quant.). Dry HCl gas was bubbled into the *i*-PrOH (10 ml) solution of **5a** (20 mg, 0.0438 mmol) for 10 min and the mixture was stirred for 98 h at room temperature. The resulting solution was condensed under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/AcOEt = 2/1) to give **6** (16 mg, 68%). Mp 175.5–176.5 °C (from hexane/AcOEt); $[\alpha]_D^{25} = +63$ (*c* 0.15, EtOH); IR (KBr) 3272, 3219, 3069, 3029, 2985, 2933, 2767, 1728, 1709, 1599, 1471, 1458, 1441, 1343, 1309, 1283, 1170, 1104, 1087, 970, 952, 909, 817, 804, 779, 700, 663 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.08$ (d, $J = 6.10$ Hz, 6H), 1.18 (d, $J = 6.10$ Hz, 6H), 2.40 (s, 6H), 4.27 (d, $J = 8.78$ Hz, 2H), 4.86 (hep, $J = 6.10$ Hz, 2H), 5.39 (d, $J = 8.78$ Hz, 2H), 7.28 (d, $J = 8.05$ Hz, 4H), 7.68 (d, $J = 8.05$ Hz, 4H). Found: C, 53.19; H, 5.96; N, 5.24. Calcd for $C_{24}H_{32}N_2O_8S_2$: C, 53.31; H, 5.97; N, 5.18.

4.2.9. Di-*tert*-butyl (*S*,*S*)-2,3-bis(4-methylphenylsulfonamido)succinate 7a. In the same manner for the preparation of **6**, the hydrolysis of **4a** was carried out to give crude **5a**. After cooling a solution of **5a** (850 mg, 1.86 mmol) in CH_2Cl_2 (40 ml) to −40 °C in a pressure bottle, isobutene (ca. 3.4 g, 60.6 mmol) was bubbled and a catalytic amount of H_2SO_4 was added. The mixture was stirred for 74 h at room temperature. The reaction was quenched by the addition of water and neutralized to pH 8 by the addition of saturated aq $NaHCO_3$ solution. The mixture was extracted with AcOEt and the combined extracts were washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The residue was purified by recrystallizing from hexane/AcOEt to give **7a** (894 mg, 84%). The mother liquor was condensed and the residue was purified by TLC (SiO_2, $CHCl_3$/MeCN = 10/1) to give additional **7a** (69 mg, 7%). Mp 179.5–180.5 °C (decomp., recrystallized from toluene/hexane); $[\alpha]_D^{25} = +103$ (*c* 0.21, $CHCl_3$); IR (KBr) 3271, 3245, 3066, 2992, 2928, 1728, 1710, 1685, 1473, 1458, 1438, 1396, 1373, 1365, 1352, 1301, 1260, 1171, 1087, 964, 917, 845, 815, 802, 768, 699, 664 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.30$ (s, 18H), 2.40 (s, 6H), 4.22 (d, $J = 9.03$ Hz, 2H), 5.26 (d, $J = 9.03$, 2H), 7.29 (d, $J = 8.05$, 4H), 7.69 (d, $J = 8.05$ Hz, 4H). Found: C, 54.86; H, 6.34; N, 4.91. Calcd for $C_{26}H_{36}N_2O_8S_2$: C, 54.91; H, 6.38; N, 4.93.

In a similar manner, di-*tert*-butyl *N*-sulfonylated 2,3-diaminosuccinates **7b–d** were prepared from the corresponding dimethyl 2,3-diaminosuccinates **4b–d**.

4.2.10. Di-*tert*-butyl (*S*,*S*)-2,3-bis(naphthalene-2-sulfonamido)succinate 7b. Mp 175.5–176.5 °C (decomp., recrystallized from hexane/AcOEt); $[\alpha]_D^{25} = +131$ (*c* 0.20, $CHCl_3$); IR (KBr) 3274, 3060, 2983, 2965, 2929, 1728, 1713, 1590, 1505, 1455, 1395, 1366, 1352, 1295, 1259, 1168, 1132, 1095, 1076, 966, 916, 868, 855, 828, 794, 768, 746, 697, 661 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.13$ (s, 18H), 4.31 (d, $J = 8.54$ Hz, 2H), 5.40 (d, $J = 8.54$ Hz, 2H), 7.61 (dd, $J = 6.83$, 7.81 Hz, 2H), 7.65 (dd, $J = 6.83$, 8.54 Hz, 2H), 7.76 (d, $J = 8.54$ Hz, 2H), 7.89 (d, 7.81 Hz, 2H), 7,94 (d, $J = 8.54$ Hz, 4H), 8.36 (s, 2H). Found: C, 59.73; H, 5.67; N, 4.47. Calcd for $C_{32}H_{36}N_2O_8S_2$: C, 59.98; H, 5.66; N, 4.37.

4.2.11. Di-*tert*-butyl (*S*,*S*)-2,3-bis(naphthalene-1-sulfonamido)succinate 7c. Mp 137.5–138.5 °C (from toluene/hexane); $[\alpha]_D^{25} = +104$ (*c* 0.20, EtOH); IR (KBr) 3304, 3060, 2980, 2932, 2871, 1737, 1594, 1508, 1457, 1395, 1370, 1350, 1298, 1259, 1231, 1201, 1167, 1104, 1027, 980, 934, 890, 837, 805, 771, 712, 679 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.03$ (s, 18H), 4.16 (d, $J = 8.54$ Hz, 2H), 5.62 (d, $J = 8.54$ Hz, 2H), 7.51 (dd, $J = 7.32$, 8.30 Hz, 2H), 7.61 (dd, $J = 7.08$, 7.81 Hz, 2H), 7.70 (dd, $J = 7.08$, 8.54 Hz, 2H), 7.93 (d, $J = 7.81$ Hz, 2H), 8.06 (d, $J = 8.30$ Hz, 2H), 8.16 (d, $J = 7.32$ Hz, 2H), 8.64 (d, $J = 8.54$ Hz, 2H). Found: C, 59.86; H, 5.74; N, 4.38. Calcd for $C_{32}H_{36}N_2O_8S_2$: C, 59.98; H, 5.66; N, 4.37.

4.2.12. Di-*tert*-butyl (*S*,*S*)-2,3-bis(2,4,6-trimethylphenylsulfonamido)succinate 7d. Mp 171–172 °C (from hexane/AcOEt); $[\alpha]_D^{25} = +89$ (*c* 0.24, $CHCl_3$); IR (KBr) 3328, 2976, 2940, 2876, 1758, 1743, 1604, 1564, 1457, 1429, 1370, 1344, 1313, 1282, 1222, 1188, 1169, 1153, 1109, 1056, 1037, 966, 937, 851, 784, 753, 720, 709, 657 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.29$ (s, 18H), 2.27 (s, 6H), 2.63 (s, 12H), 4.07 (d, $J = 8.78$ Hz, 2H), 5.49 (d, $J = 8.78$ Hz, 2H), 6.93 (s, 4H). Found: C, 57.41; H, 7.17; N, 4.51. Calcd for $C_{30}H_{44}N_2O_8S_2$: C, 57.66; H, 7.10; N, 4.48.

4.2.13. Di-*tert*-butyl (*S*,*S*)-2,3-di(methylsulfonamido)succinate 7e. In a similar manner for the preparation of **6**, the hydrolysis of **4e** (128 mg, 0.386 mmol) was carried out. The solution was neutralized to pH 8 by the addition of 1 M aq HCl solution and washed with AcOEt. The aqueous phase was acidified to pH 3 by the addition of 1 M aq HCl solution and the water was evaporated under reduced pressure, since product **5e** is water soluble. The residual oil was extracted with AcOEt and the combined extracts were condensed under reduced pressure to give crude **5e** (118 mg, quant.). In a similar manner for the preparation of **7a**, the esterification was carried out. Mp 149–150 °C (from hexane/AcOEt); $[\alpha]_D^{25} = -5$ (*c* 0.20, $CHCl_3$); IR (KBr) 3329, 3274, 2977, 2939, 2880, 2779, 1733, 1716, 1652, 1645, 1634, 1505, 1454, 1396, 1370, 1349, 1328, 1284, 1261, 1158, 1109, 1043, 987, 940, 840, 785, 773, 670 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.54$ (s, 18H), 2.97 (s, 6H), 4.61 (d, $J = 9.27$ Hz, 2H), 5.48 (d, $J = 9.27$ Hz, 2H). Found: C, 40.16; H, 6.80; N, 6.73. Calcd for $C_{14}H_{28}N_2O_8S_2$: C, 40.37; H, 6.78; N, 6.73.

4.2.14. Di-*tert*-butyl (*S*,*S*)-2,3-bis(trifluoromethylsulfonamido)succinate 7f. In a similar manner for the preparation of **6**, the hydrolysis of **4f** was carried out to give crude **5f**. After cooling a solution of **5f** (1.44 g, 1.86 mmol) in CH_2Cl_2 (60 ml) to –40 °C in a pressure bottle, isobutene (ca. 12.1 g, 216 mmol) was bubbled into the above solution and a catalytic amount of H_2SO_4 was added. The mixture was stirred for 95 h at room temperature. The reaction mixture was quenched by the addition of water and adjusted to pH 4 by the addition of saturated aq $NaHCO_3$ solution. The mixture was extracted with AcOEt and the combined extracts were washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The remaining **5f** and monoester in the residue were separated by column chromatography (SiO_2, hexane/EtOH = 4/1). Most of the solvent of the eluent containing **7f** was evaporated under reduced pressure. After hexane was added to the residue, the precipitated **7f** was filtered off (877 mg, 48%). The filtrate was condensed and the residue was dissolved in a small amount of MeOH. The solution was adjusted to pH 11 by the addition of 1 M aq NaOH solution and stirred for 1 min. After being washed with Et_2O, the aqueous layer was acidified to pH 4 by the addition of 1 M aq HCl solution and extracted with Et_2O. The combined extracts were washed with brine, dried over Na_2SO_4, and condensed under reduced pressure to give the almost pure **7f**. Compound **7f** obtained was once dissolved in a small amount of MeOH, and most of the MeOH was evaporated under reduced pressure. To the residue was added hexane and the precipitated **7f** was filtered off (597 mg, 33%). The filtrate was condensed and the residue was purified by TLC (SiO_2, hexane/*i*-PrOH = 8/1, twice) to give **7f** (210 mg, 11%). Mp 155–156 °C (decomp., recrystallized from hexane/EtOH); $[\alpha]_D^{25} = +10$ (*c* 0.22, $CHCl_3$); IR (KBr) 3210, 2988, 2921, 1719, 1465, 1388, 1339, 1285, 1235, 1200, 1148, 1102, 984, 947, 829, 793, 772, 713 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.52$ (s, 18H), 4.48 (s, 2H), 6.16 (br, 2H). Found: C, 32.09; H, 4.30; N, 5.62. Calcd for $C_{14}H_{22}N_2O_8F_6S_2$: C, 32.06; H, 4.23; N, 5.34.

4.3. Asymmetric 1,3-dipolar cycloaddition

4.3.1. Representative procedure for asymmetric 1,3-dipolar cycloaddition of a nitrile oxide to allyl alcohol (Table 2, entry 15). To a suspension of ethylbenzene (3.75 ml) solution of allyl alcohol **8** (20 mg, 0.344 mmol) with powdered MS 3Å (200 mg) was added diethylzinc (0.344 mmol, 0.344 ml of 1.00 M solution in hexane) at 0 °C under an argon atmosphere, and the mixture was stirred for 10 min. After adding a solution of chiral sulfonamide **7f** (181 mg, 0.345 mmol) in ethylbenzene (6.0 ml) and ^{t}BuOMe (1.25 ml), the mixture was stirred for 1 h at 0 °C. To the solution, diethylzinc (0.379 mmol, 0.379 ml of 1.00 M solution in hexane) was added and the mixture was stirred for 10 min at 0 °C. A precooled (0 °C) ethylbenzene (6.5 ml) solution of *p*-methoxybenzohydroximoyl chloride (70 mg, 0.377 mmol) was then added all at once and the mixture was stirred for 24 h at 0 °C. The reaction was quenched by the addition of a saturated aq NH_4Cl solution. After filtration of the precipitate, the filtrate was extracted with AcOEt. The combined extracts were washed with brine, dried over Na_2SO_4, and condensed under reduced pressure. The residue was separated by TLC on SiO_2. The chiral auxiliary was separated first (hexane/*i*-PrOH/AcOH = 6/1/0.03), then the part containing

product **10A** was eluted and again developed on TLC to separate **10A** ($CHCl_3$/MeCN = 7/1) in 74% (53 mg) yield. The enantioselectivity was determined by HPLC (Daicel Chiralcel OD-H, hexane/EtOH = 15/1, detected at 254 nm) analysis to be 71% ee.

4.3.2. Recovery of the chiral auxiliary. The part of TLC containing chiral auxiliary **7f** was eluted and condensed under reduced pressure to give the almost pure **7f** quantitatively. Compound **7f** obtained was washed with a small amount of benzene/hexane (1/1) and dissolved in a small amount of MeOH. After evaporation of most of the MeOH, hexane was added and the resulting precipitate was filtered off and washed with benzene to recover the enantiomerically pure **7f** (66 %).

4.3.3. (*R*)-5-(Hydroxymethyl)-3-(4-methoxyphenyl)-2-isoxazoline 10A. Mp 166–167 °C (from EtOH); $[\alpha]_D^{25} = -94$ (*c* 0.53, MeOH, 71% ee); IR (KBr) 3380, 3010, 2950, 2850, 1600, 1510, 1450, 1440, 1410, 1360, 1300, 1290, 1250, 1170, 1100, 1040, 1010, 990, 950, 920, 900, 860, 820, 800, 780 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.88$ (t, $J = 7.02$ Hz, 1H), 3.25 (dd, $J = 7.63$, 16.48 Hz, 1H), 3.27 (dd, $J = 10.68$, 16.48 Hz, 1H), 3.68 (ddd, $J = 4.88$, 7.02, 12.51 Hz, 1H), 3.84 (s, 3H), 3.86 (m, 1H), 4.84 (m, 1H), 6.92 (d, $J = 8.85$ Hz, 2H), 7.61 (d, $J = 8.85$ Hz, 2H). Found: C, 63.57; H, 6.40; N, 6.72. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76%. The enantioselectivity was determined by HPLC (Daicel Chiralcel OD-H, hexane/EtOH = 15/1, detected at 254 nm).

4.3.4. (*R*)-5-(Hydroxymethyl)-3-phenyl-2-isoxazoline 10B.[7] Mp 67–68 °C (from hexane/AcOEt); $[\alpha]_D^{25} = -92$ (*c* 0.44, $CHCl_3$, 55% ee) [lit.,[7b] $[\alpha]_D^{25} = -161$ (*c* 1.0, $CHCl_3$, 100% ee)]; IR (KBr) 3360, 3060, 2920, 2840, 1580, 1490, 1460, 1440, 1350, 1100, 1040, 1010, 910, 880, 800, 740, 680 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.12$ (br, 1H), 3.28 (dd, $J = 7.81$, 16.59 Hz, 1H), 3.39 (dd, $J = 10.73$, 16.59 Hz, 1H), 3.69 (dd, $J = 4.88$, 12.20 Hz, 1H), 3.88 (dd, $J = 3.17$, 12.20 Hz, 1H), 4.82–4.94 (m, 1H), 7.37–7.44 (m, 3H), 7.63–7.71 (m, 2H). The enantioselectivity was determined by HPLC (Daicel Chiralcel OB-H, hexane/EtOH = 2/1, detected at 254 nm).

4.3.5. (*R*)-3-(1,1-Dimethylethyl)-5-hydroxymethyl-2-isoxazoline 10C.[7] An oil; $[\alpha]_D^{25} = -53$ (*c* 0.17, $CHCl_3$, 50% ee) [lit.,[7b] $[\alpha]_D^{25} = -127$ (*c* 1.0, $CHCl_3$, 100% ee)]; IR (neat) 3400, 2967, 2933, 2871, 1647, 1613, 1479, 1462, 1436, 1396, 1366, 1337, 1257, 1219, 1206, 1168, 1086, 1051, 950, 879, 827, 808 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.21$ (s, 9H), 2.38 (br, 1H), 2.87 (dd, $J = 7.32$, 16.83 Hz, 1H), 3.02 (dd, $J = 10.49$, 16.83 Hz, 1H), 3.56 (dd, $J = 4.88$, 11.95 Hz, 1H), 3.76 (dd, $J = 3.17$, 11.95 Hz, 1H), 4.67 (dddd, $J = 3.17$, 4.88, 7.32, 10.49 Hz, 1H). The enantioselectivity was determined by HPLC (Daicel Chiralcel OB-H, hexane/EtOH = 30/1, detected at 220 nm).

4.3.6. (*R*)-5-(Hydroxymethyl)-3-(4-bromophenyl)-2-isoxazoline 10D. Mp 122.5–123.5 °C (from hexane/EtOH); $[\alpha]_D^{25} = -61$ (*c* 0.29, MeOH, 57% ee); IR (KBr) 3388, 2937, 2923, 2866, 1593, 1490, 1438, 1400, 1375, 1358, 1307, 1248, 1184, 1105, 1070, 1050, 1008, 995, 959, 937, 908, 864, 828, 808, 707 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.84$ (dd, $J = 5.37$, 7.32 Hz, 1H), 3.26 (dd, $J = 8.05$, 16.59 Hz, 1H), 3.36 (dd, $J = 10.73$, 16.59 Hz, 1H), 3.69 (ddd, $J = 4.39$, 7.32, 12.20 Hz, 1H), 3.89 (ddd, $J = 3.17$, 5.37, 12.20 Hz, 1H), 4.89 (dddd, $J = 3.17$, 4.39, 8.05, 10.73 Hz, 1H), 7.54 (s, 4H). Found: C, 46.73; H, 3.96; N, 5.43. Calcd for $C_{10}H_{10}NO_2Br$: C, 46.90; H, 3.94; N, 5.47%. The enantioselectivity was determined by HPLC (Daicel Chiralcel OD-H, hexane/EtOH = 15/1, detected at 254 nm).

4.3.7. (*R*)-5-(Hydroxymethyl)-3-(4-cyanophenyl)-2-isoxazoline 10E. Mp 128–129 °C (from hexane/EtOH); $[\alpha]_D^{25} = -75$ (*c* 0.22, MeOH, 49% ee); IR (KBr) 3422, 3075, 3048, 2952, 2935, 2871, 2224, 1608, 1595, 1508, 1433, 1410, 1398, 1361, 1283, 1251, 1104, 1049, 990, 969, 939, 909, 852, 838, 812, 776 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.85$ (dd, $J = 5.37$, 7.81 Hz, 1H), 3.31 (dd, $J = 8.05$, 16.59 Hz, 1H), 3.38 (dd, $J = 10.73$, 16.59 Hz, 1H), 3.71 (ddd, $J = 4.15$, 7.81, 12.44 Hz, 1H), 3.93 (ddd, $J = 3.17$, 5.37, 12.44 Hz, 1H), 4.94 (dddd, $J = 3.17$, 4.15, 8.05, 10.73 Hz, 1H), 7.70 (d, $J = 8.54$ Hz, 2H), 7.77 (d, $J = 8.54$ Hz, 2H). Found: C, 65.13; H, 5.03; N, 13.74. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.98; N, 13.86%. The enantioselectivity was determined by HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 7/1, detected at 254 nm).

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