Lewis Acid-Catalyzed Asymmetric Diels–Alder Reactions Using Chiral Sulfoxide Ligands: Chiral 2-(Arylsulfinylmethyl)-1,3-oxazoline Derivatives

Kazuhiro WATANABE, Takashi HIRASAWA, and Kunio HIROI*

Tohoku Pharmaceutical University, 4–4–1 Komatsushima, Aoba-ku, Sendai, Miyagi 981–8558, Japan.
Received October 29, 2001; accepted November 22, 2001

New chiral sulfoxide-1,3-oxazoline ligands have been developed as chiral ligands for Lewis acid-catalyzed asymmetric Diels–Alder reactions. The use of chiral sulfinyl 1,3-oxazoline ligands in copper(II)-catalyzed asymmetric Diels–Alder reactions provided an *endo* cycloadduct as a major product with moderate enantioselectivity. A rationale is proposed for the mechanism of the asymmetric induction.

Key words chiral sulfoxide; chiral 1,3-oxazoline; chiral ligand; asymmetric Diels–Alder reaction; Lewis acid; copper catalyst

A catalytic asymmetric carbon–carbon bond-forming reaction has received much attention for the creation of complex organic molecules with stereochemical efficiency. A number of methodologies have been proposed for asymmetric Diels–Alder reactions by introducing chiral auxiliaries into substrates for the stereoselective formation of six-membered carbo- and heterocycles.[1] Currently, however, catalytic asymmetric Diels–Alder reactions are receiving attention due to their efficiency, and chiral ligands of various kinds have been developed.[2]

The use of chiral sulfinyl functionality as chiral auxiliaries in organic synthesis has been investigated, and numerous asymmetric syntheses have been achieved with this methodology. However, few precedents for the use of chiral sulfoxides as chiral ligands have been reported.[3] We have developed chiral sulfoxide ligands of various types, and applied them to palladium-catalyzed asymmetric allylic alkylations.[4] Chiral sulfoxide functionality has two possibilities for the formation of chelates by coordination of sulfinyl oxygen or sulfur atoms to metals, depending on the metals employed. As we have already reported, a chiral sulfoxide provides a chelate coordinated by the sulfur atom with a palladium catalyst.[5]

We describe here the use of chiral sulfoxides as chiral ligands in Lewis acid-catalyzed asymmetric Diels–Alder reactions.

Chiral sulfoxide ligands were prepared by the following procedure starting from readily available α-amino acids. 1,3-Oxazolines were readily obtainable by the reaction of ethyl acetimidate hydrochloride[6] with β-amino alcohols derived from commercially available α-amino acids in dichloromethane (CH_2Cl_2) at room temperature.[7] Sulfinylation of 1,3-oxazolines **3a**—**f**[6] with (*S*s)-**4** was carried out in tetrahydrofuran (THF) at −78 °C using lithium diisopropylamide (LDA) as the base to give (*R*s)-**5a**—**f**. Methylation of (*R*s)-**5a**—**f** with methyl iodide (LDA, THF, at −78 °C—room temperature) gave (*R*s)-**6a**—**f**, which were further methylated by the reaction of methyl iodide using potassium hexamethyldisilazide (KHMDS) as the base at −78 °C—room temperature, affording (*S*s)-**7a**—**f**.[8]

Similar procedures were applied to chiral β-amino alcohols (1*R*,2*S*)-**8** and (1*S*,2*R*)-**13**. 1,3-Oxazoline (4*S*,5*R*)-**9** was obtained by the reaction of (1*R*,2*S*)-**8** with **2** in CH_2Cl_2 at room temperature. Sulfinylation of (4*S*,5*R*)-**9** with (*S*s)-**4** gave (4*S*,5*R*,*R*s)-**10**. Methylation of (4*S*,5*R*,*R*s)-**10** with methyl iodide was carried out in a similar way as described above, giving (4*S*,5*R*,*S*s)-**12** through (4*S*,5*R*,*R*s)-**11**. The same procedures as described above were applied to the synthesis of another chiral 2-(arylsulfinylmethyl)-1,3-oxazoline ligand (4*S*,5*R*,*S*s)-**17** from chiral β-amino alcohol (1*S*,2*R*)-**13**.

The use of chiral sulfoxides obtained above as chiral ligands was studied in the Lewis acid-catalyzed asymmetric Diels–Alder reactions of *N*-acryloyl-1,3-oxazolidinone (**18**) with cyclopentadiene (**19**).[9] Initially, the effects of Lewis acids in the asymmetric Diels–Alder reaction were studied using (*R*s,*S*)-**5d** as a ligand and $MgBr_2 \cdot OEt_2$, MgI_2, $Mg(OTf)_2$, $Zn(OTf)_2$, $Cu(OTf)_2$, $Cu(AbF_6)_2$, $Cu(ClO_4)_2$, or FeI_3 as a Lewis acid.[10]

The reactions of **18** with **19** (5.0 eq) were carried out in dichloromethane at −20—78 °C in the presence of a Lewis acid such as $MgBr_2 \cdot OEt_2$, $Mg(OTf)_2$, $Zn(OTf)_2$, $Cu(OTf)_2$ or FeI_3 to give an *endo* adduct **20a** as a main product along with an *exo* adduct **20b** as a minor product. The ratios of **20a** (*endo* adduct) to **20b** (*exo* adduct) and the enantiomeric excess of the major product **20a** obtained were determined by the HPLC analysis with Chiralcel OD eluted with 10% iso-PrOH in hexane.[11]

Surprisingly, in this case with chiral 2-(arylsulfinylmethyl)-1,3-oxazolines[12] as ligand, substantially different effects on enantioselectivity depending on the Lewis acids used were observed, compared with the case with 2-[2-(arylsulfinyl)pheny]-1,3-oxazolines,[12] when the use of MgI_2 as a Lewis acid was apparently the most effective in achieving the highest enantioselectivity. In the present case, however, MgI_2 was not as useful for increasing the enantioselectivity. The use of other Lewis acids such as $Mg(OTf)_2$, $Zn(OTf)_2$, and FeI_3 in the above reaction provided much lower enantioselectivity.

The results of the $MgBr_2 \cdot OEt_2$-catalyzed asymmetric Diels–Alder reactions of **18** with **19** using **5a**—**f**, **7a**—**f**, **10**, **12**, **15**, and **17** as chiral ligands are summarized in Table 1.

As shown in Table 1, chiral 2-(*p*-toluenesulfinylmethyl)-4-substituted-1,3-oxazolines were not useful as chiral ligands in the $MgBr_2 \cdot OEt_2$-catalyzed Diels–Alder reactions of **18** with **19**, giving very poor enantioselectivity. Interestingly, however, the chiral 4,5-disubstituted-1,3-oxazolines **10** and **15** resulted in a slight increase in the enantioselectivity of (2*S*)-**20a** with a high ratio of *endo*-**20a** to *exo*-**20b**. Against expectations, the use of cupric salts such as cupric trifrate,

* To whom correspondence should be addressed. e-mail: khiroi@tohoku-pharm.ac.jp

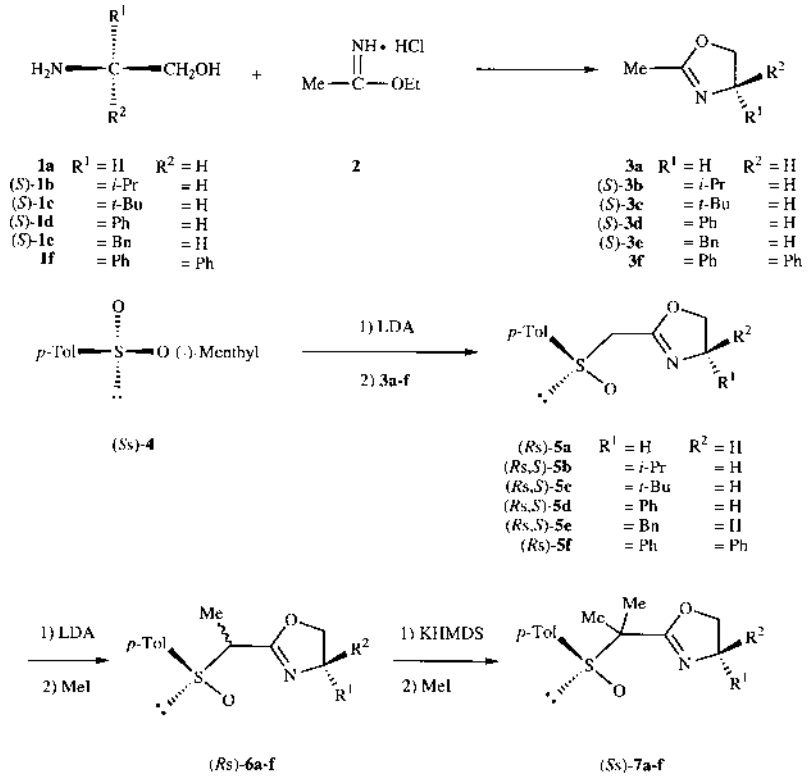

Chart 1

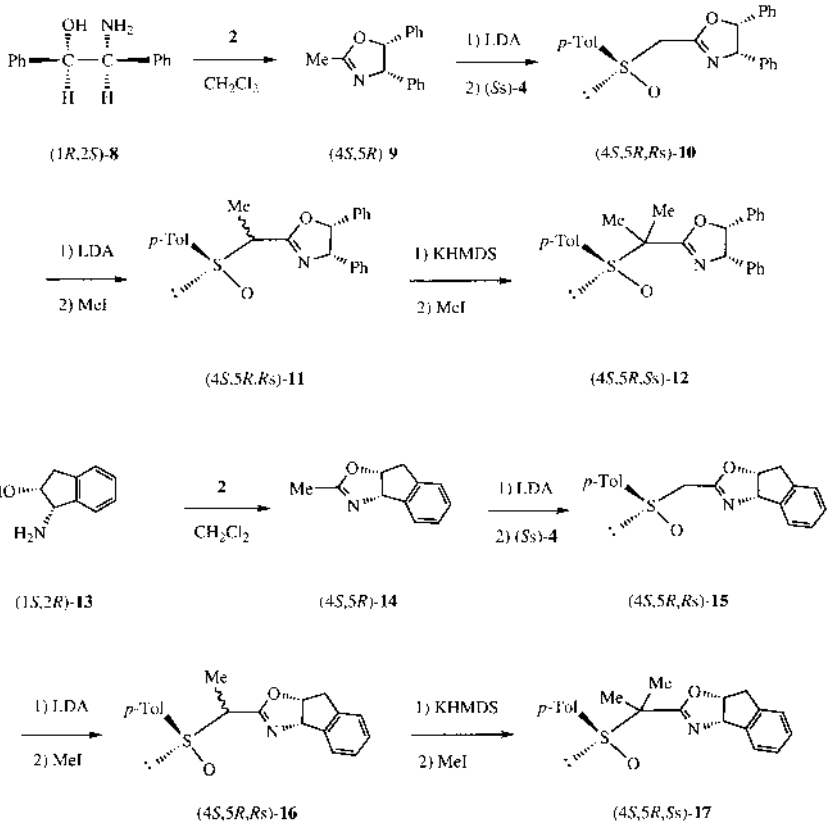

Chart 2

hexafluoroantimonate, and perchlorate as Lewis acids in the above Diels–Alder reaction provided the rather high enantioselectivity of **20a** with the use of the types of ligands mentioned above.

The copper(II)-catalyzed asymmetric Diels–Alder reactions of **18** with **19** were studied using the chiral sulfoxide

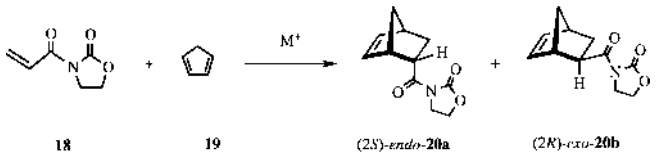

Chart 3

ligands 2-(*p*-toluenesulfinylmethyl)-1,3-oxazolines **5a**—**f**, **10**, and **15**. The results are summarized in Table 2.

The copper(II) complexes CuX_2 (X=OTf, ClO_4, SbF_6) were prepared by reacting the chiral ligands **5a**—**f**, **10**, and **15** with $CuCl_2$ in CH_2Cl_2 at room temperature for 4 h in the presence of silver(I) salts such as silver triflate, perchlorate, and hexafluoroantimonate.

Table 1. Studies on the $MgBr_2 \cdot OEt_2$-Catalyzed Asymmetric Diels–Alder Reactions of **18** with **19** Using Chiral Ligands **5a**—**f**, **7a**—**f**, **12**, and **17**[a)]

Entry	Ligand (mol%)	Time (h)	Yield (%)	*endo*/*exo* **20a**/**20b**	ee (%) of (*S*)-**20a**
1	**5a** (10)	24	81	90/10	<1
2	**5b** (10)	24	79	89/11	8
3	**5c** (10)	24	88	88/12	13
4	**5d** 10)	24	82	83/17	8
5	**5e** (10)	24	82	87/13	6
6	**5f** (10)	24	81	89/11	7
7	**10** (10)	24	83	91/ 9	15
8	**15** (10)	24	94	89/11	32
9	**15** (20)	20	92	90/10	27
10	**15** (30)	18	93	91/ 9	29
11	**7a** (10)	24	91	91/ 9	<1
12	**7b** (10)	24	90	93/ 7	3
13	**7c** (10)	24	88	93/ 7	5
14	**7d** (10)	24	82	92/ 8	3
15	**7e** (10)	24	86	91/ 9	3
16	**7f** (10)	24	84	92/ 8	5
17	**12** (10)	24	92	90/10	7
18	**17** (10)	24	93	93/ 7	5

a) The reactions of **18** with **19** (5.0 eq) were carried out at −78 °C in CH_2Cl_2 in the presence of $MgBr_2 \cdot OEt_2$ and chiral ligands **5a**—**f**, **7a**—**f**, **12**, and **17**.

Table 2. Studies on the Cu(II)-Catalyzed Asymmetric Diels–Alder Reactions of **18** with **19** Using Chiral Ligands **5a**—**f**, **10**, and **15**[a)]

Entry	Couterion	Ligand (mol%)	Solvent	Time (h)	Yield (%)	*endo*/*exo* **20a**/**20b**	ee (%) of **20a**
1	OTf	**5a** (10)	CH_2Cl_2	12	89	92/ 8	2 (*S*)
2	ClO_4	**5a** (10)	CH_2Cl_2	12	88	91/ 9	3 (*S*)
3	SbF_6	**5a** (10)	CH_2Cl_2	10	91	94/ 6	1 (*S*)
4	OTf	**5b** (10)	CH_2Cl_2	24	90	87/13	6 (*S*)
5	ClO_4	**5b** (10)	CH_2Cl_2	24	87	86/14	8 (*S*)
6	SbF_6	**5b** (10)	CH_2Cl_2	6	96	94/ 6	10 (*S*)
7	OTf	**5c** (5)	CH_2Cl_2	16	85	94/ 6	50 (*S*)
8	OTf	**5c** (10)	CH_2Cl_2	10	90	96/ 4	59 (*S*)
9	OTf	**5c** (15)	CH_2Cl_2	9	99	95/ 5	48 (*S*)
10	OTf	**5c** (20)	CH_2Cl_2	8	99	96/ 4	57 (*S*)
11	OTf	**5c** (10)	Toluene	36	63	91/ 9	21 (*S*)
12	OTf	**5c** (10)	THF	24	80	95/ 5	57 (*S*)
13	ClO_4	**5c** (10)	CH_2Cl_2	10	93	95/ 5	23 (*S*)
14	SbF_6	**5c** (10)	CH_2Cl_2	8	89	97/ 3	34 (*S*)
15	OTf	**5d** (10)	CH_2Cl_2	24	61	81/19	48 (*R*)
16	ClO_4	**5d** (10)	CH_2Cl_2	24	69	83/17	21 (*R*)
17	SbF_6	**5d** (10)	CH_2Cl_2	10	88	91/ 9	7 (*R*)
18	OTf	**5e** (10)	CH_2Cl_2	22	86	89/11	39 (*R*)
19	ClO_4	**5e** (10)	CH_2Cl_2	22	90	88/12	34 (*R*)
20	SbF_6	**5e** (10)	CH_2Cl_2	10	85	94/ 6	66 (*R*)
21	OTf	**5f** (10)	CH_2Cl_2	24	89	93/ 7	13 (*S*)
22	ClO_4	**5f** (10)	CH_2Cl_2	24	87	91/ 9	11 (*S*)
23	SbF_6	**5f** (10)	CH_2Cl_2	10	93	92/ 8	9 (*S*)
24	OTf	**10** (10)	CH_2Cl_2	24	86	93/ 7	29 (*S*)
25	ClO_4	**10** (10)	CH_2Cl_2	24	83	93/ 7	25 (*S*)
26	SbF_6	**10** (10)	CH_2Cl_2	10	87	93/ 7	16 (*S*)
27	OTf	**15** (10)	CH_2Cl_2	24	80	84/16	23 (*R*)
28	ClO_4	**15** (10)	CH_2Cl_2	24	75	82/18	18 (*R*)
29	SbF_6	**15** (10)	CH_2Cl_2	8	93	88/12	16 (*R*)

a) The reactions of **18** with **19** (5.0 eq) were carried out at −78 °C in the presence of copper complexes CuX_2 (X=OTf, ClO_4, and SbF_6), which were prepared by reacting ligands **5**, **10**, and **15** with $CuCl_2$ at room temperature in CH_2Cl_2 for 4 h.

Table 3. Studies on the Cu(II)-Catalyzed Asymmetric Diels–Alder Reactions of **18** with **19** Using Chiral Ligands **7a**—**f**, **12**, and **17**[a)]

Entry	Couterion	Ligand	Time (h)	Yield (%)	*endo*/*exo* **20a**/**20b**	ee (%) of (*R*)-**20a**
1	OTf	**7a**	24	70	91/ 9	5
2	ClO_4	**7a**	24	67	90/10	2
3	SbF_6	**7a**	12	69	92/ 8	3
4	OTf	**7b**	24	68	90/10	20
5	ClO_4	**7b**	24	63	88/12	13
6	SbF_6	**7b**	12	72	89/11	17
7	OTf	**7c**	19	60	91/ 9	50
8	ClO_4	**7c**	19	52	87/13	28
9	SbF_6	**7c**	6	77	89/11	46
10	OTf	**7d**	24	65	88/12	36
11	ClO_4	**7d**	24	60	89/11	24
12	SbF_6	**7d**	24	62	86/14	49
13	OTf	**7e**	24	63	88/12	28
14	ClO_4	**7e**	24	61	86/14	21
15	SbF_6	**7e**	24	65	89/11	32
16	OTf	**7f**	24	71	88/12	18
17	ClO_4	**7f**	24	72	88/12	16
18	SbF_6	**7f**	18	72	89/11	25
19	OTf	**12**	24	71	87/13	26
20	ClO_4	**12**	24	68	89/11	18
21	SbF_6	**12**	20	68	90/10	14
22	OTf	**17**	24	62	86/14	40
23	ClO_4	**17**	24	60	87/13	31
24	SbF_6	**17**	18	65	87/13	33

a) The reactions of **18** with **19** (5.0 eq) were carried out in CH_2Cl_2 at −78 °C in the presence of copper complexes CuX_2 (X=OTf, ClO_4, and SbF_6), which were prepared by reacting ligands **7**, **12**, and **17** (0.1 eq) with $CuCl_2$ at room temperature in CH_2Cl_2 for 4 h.

The solvent effects in the copper(II)-catalyzed asymmetric Diels–Alder reactions are shown in Table 2. Among the solvent examined, the rather high enantioselectivity (59—58%) of (*S*)-**20a** was provided with the use of CH_2Cl_2 or THF as solvent, as listed in entries 8, 11, and 12 of Table 2, using cupric triflate (10 mol%) as a catalyst.

The chirality of the sulfoxide in **5** was not so effective for the asymmetric Diels–Alder reactions with copper(II) catalysts, since the loss of the chiralities on the 1,3-oxazolines provided lower enantioselectivity of (*S*)-**20a** (entries 1—3, 21—23 in Table 2).

The steric bulk of the substituents on the 1,3-oxazolines were effective in achieving high enantioselectivity. The chiral ligand (*R*s,*S*)-**5b** including iso-propyl was not useful for the asymmetric induction, while the use of the ligands (*R*s,*S*)-**5c**—**e** with *tert*-butyl, phenyl, and benzyl groups provided higher enantioselectivity of (2*S*)- and (2*R*)-**20a**, respectively, except for the case of the copper(II) catalyst derived from ligand **5d** with hexafluoroantimonate (entry 17), presumably due to the steric interference between the phenyl substituent and the bulky counterion. Surprisingly, however, the absolute configuration of the resulting *endo* adduct **20a** was dependent on the ligands and the counterions employed. Introduction of a phenyl or benzyl group as the chiral center at the C_3 position on the 1,3-oxazoline rings provided (2*R*)-**20a**, which was inversed in the absolute configuration to that obtained above with (*R*s,*S*)-**5c**.

The anchored effects by dimethyl substituents were studied with cupric catalysts using 2-[1-methyl-1-(*p*-toluenesulfinyl)ethyl]-1,3-oxazoline ligands (*S*s)-**7a**—**f**, **12**, and **17**. The results obtained are summarized in Table 3. Similar effects of counterions and substituents on the 1,3-oxazolines were observed as those by **5a**—**f**, **10**, and **15**. The use of (*S*s,*S*)-**7c** with cupric triflate provided (2*R*)-**20a** with rather high enantioslectivity (50%). Similarly, cupric triflate was useful achieving rather high enantioselectivity in the case of (4*S*,5*R*,*S*s)-**17**. However, with (*S*s,*S*)-**7e** as a ligand, cupric hexafluoroantimonate was more effective, as shown in Table 2. The highest enantioselectivity (66%) of (2*R*)-**20a** was obtained with (*R*s,*S*)-**5e** as a chiral ligand using hexafluoroantimonate as a counterion.

The following mechanism of these catalytic asymmetric reactions is proposed for the rationalization of the stereochemical results obtained. Based on the rather high level of the asymmetric induction with these chiral ligands, the formation of a six-membered square planar copper chelate coordinated by the nitrogen atom of the 1,3-oxazoline and the sulfinyl oxygen atom should be predicted as an intermediate. In the conformational equilibrium of the copper chelate of the 1,3-oxazoline ligands with bulky substituents such as iso-propyl and *tert*-butyl groups on the rings, conformer **21b** would be preferred to conformer **21a** because of the existence of the rather severe $A^{1,3)}$ strain between the bulky groups and X (the counterion or the reaction substrate) in **21a**. Therefore cyclopentadiene attacks the dienophile part in the substrate preferentially from the sterically less crowded side (*Re* face in **21b**-II), giving (*S*)-**20a** as a main product. A similar explanation is applicable to the case with **10**, since the intermediate derived from **10** has rather severe steric interference by the phenyl group at the 4 position on the 1,3-oxazolines, due to the conformational rigidity induced by the adjacent phenyl group at the 5 position.

On the other hand, in the case of the chiral ligands with phenyl or benzyl groups, conformer **22a** would be favorable to **22b** because of the existence of the less crowded steric space arised due to the less bulky groups or the π–π stacking

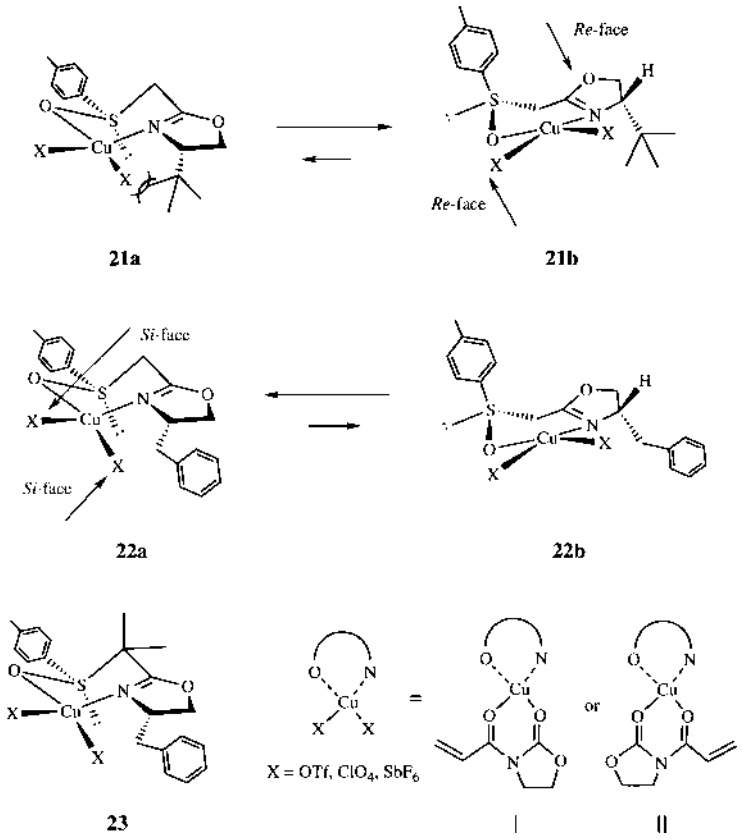

Chart 4

interaction between the phenyl or benzyl group and the carbon–carbon double bond in **22a**-II. Therefore cyclopentadiene attacks the reaction site from the *Si*-face in **22a**-I or in **22a**-II, affording (*R*)-**20a** as a main product.

In the case of chiral ligands **7a**—**f**, **12**, and **17** anchored by dimethyl groups, the sterically more stable isomer **23** is preferentially formed due to the conformational fixation of the six-membered chelate with an equatorial tolyl group. The attack of cyclopentadiene occurs in the same way as mentioned above in **22a** to give (*R*)-**20a** as a main product.

In conclusion, we have prepared chiral sulfinyl 1,3-oxazoline derivatives and applied them as chiral ligands to catalytic asymmetric Diels–Alder reactions, in which moderate asymmetric induction was observed. The degree of the asymmetric induction and the absolute configuration of the product were dependent on the steric bulk of the substituents at the chiral centers on the 1,3-oxazolines. A novel mechanism of asymmetric induction with these new chiral sulfoxide ligands is proposed for the rationalization of the steric results obtained.

Experimental

Infrared (IR) spectra were obtained in the indicated state with a JASCO DR-81 Fourier-transform infrared spectrometer. Nuclear magnetic resonance (NMR) spectra were determined in the indicated solvents with a JEOL GSX-400 (^{1}H-NMR, 400 MHz; ^{13}C-NMR, 100 MHz), EX-270 (^{1}H-NMR, 270 MHz; ^{13}C-NMR, 67.5 MHz), or JNM PMX-60SI (60 MHz) high-resolution NMR spectrometer; chemical shifts are given in parts per million with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on a JEOL JMS-DX 303/JMA-DA 5000 system. Optical rotations were measured with a JASCO DIP-370 polarimeter. High-performance liquid chromatographic (HPLC) data were obtained with a Tosoh UV-8010, CCPM (column, Daicel chiralpack OD). Flash column chromatography was performed with Merck silica gel 60 (230—400 mesh). Thin-layer or thick-layer plates (preparative TLC) were made of Merck silica gel 60PF-254 activated by drying at 140 °C for 3.5 h.

2-Methyl-2-oxazoline (3a) To a stirred solution of ethyl acetimidate hydrochloride[6] (**2**) (376.5 mg, 3 mmol) in dichloromethane (15 ml) at 0 °C was added a solution of ethanolamine (183 mg, 3 mmol) in dichloromethane (10 ml). The resulting solution was slowly allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into water (10 ml) and extracted with dichloromethane (3×10 ml). The combined organic layers were dried over anhydrous Na_2SO_4, and the solvent was removed by distillation at atmospheric pressure. Distillation gave 2-methyl-2-oxazoline (**3a**) (181.1 mg, 71%) as a colorless liquid, bp 109—110 °C.

3a: IR ν_{max}^{film} cm^{-1}: 1674 (O–C=N). ^{1}H-NMR ($CDCl_3$) δ: 1.96 (3H, s, CH_3), 3.76—3.84 (2H, m, O–CH_2 or N–CH), 4.19—4.26 (2H, m, O–C<u>H</u>$_2$ or N–C<u>H</u>). ^{13}C-NMR ($CDCl_3$) δ: 18.6, 52.4, 56.6, 164.2. MS *m*/*z*: 85 (M^+), 74, 60, 55, 43 (BP). Exact mass determination: 85.0550 (Calcd for C_4H_7NO: 85.0527).

The cyclization of **1b**—**f** with ethyl acetimidate hydrochloride (**2**) was carried out using the same procedure as described above to give (*S*)-isopropyl-(**3b**), (*S*)-*tert*-butyl-(**3c**), (*S*)-phenyl-(**3d**), (*S*)-benzyl-(**3e**), 4,4-diphenyl-(**3f**), (4*S*,5*R*)-4,5-diphenyl-2-methyl-2-oxazole (**9**), and (3a*S*,8a*R*)-3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazole (**14**), respectively.

(*S*)-**3b**: 70% yield. Colorless oil. $[\alpha]_D$ −87.3° (*c*=2.51, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1678 (O–C=N). NMR ($CDCl_3$) δ: 0.85—0.89 (6H, d, *J*=7.2 Hz, $CH(CH_3)_2$), 2.09 (3H, d, *J*=1.3 Hz, CH_3), 3.81—3.82 (1H, m, O–C<u>H</u>$_2$ or N–C<u>H</u>), 3.99—4.05 (1H, t, *J*=8.4 Hz, O–C<u>H</u>$_2$ or N–C<u>H</u>), 4.13—4.18 (1H, dd, *J*=8.4, 10.1 Hz, O–C<u>H</u>$_2$ or N–C<u>H</u>). ^{13}C-NMR ($CDCl_3$) δ: 17.4, 17.8, 18.9, 27.9, 58.5, 69.3. MS *m*/*z*: 127 (M^+), 101 (BP), 90. Exact mass determination: 127.2234 (Calcd for $C_7H_{13}NO$: 127.2230).

(*S*)-**3c**[7]: 75% yield.

(*S*)-**3d**: 68% yield. Colorless oil. $[\alpha]_D$ −98.2° (*c*=1.66, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1672 (O–C=N), 1605, 1493, 756 (aromatic). NMR ($CDCl_3$) δ: 2.09 (3H, d, *J*=1.5 Hz, CH_3), 4.05—4.11 (1H, t, *J*=8.3 Hz, O–C<u>H</u>$_2$ or N–C<u>H</u>), 4.55—4.63 (1H, dd, *J*=8.3, 10.1 Hz, O–C<u>H</u>$_2$ or N–C<u>H</u>), 5.12—5.19 (1H, ddd, *J*=1.5, 8.3, 10.1 Hz, O–C<u>H</u>$_2$ or N–C<u>H</u>), 7.21—7.52 (5H, m, $CHC_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 13.8, 69.7, 74.5, 126.4, 126.6, 127.4, 128.2, 128.6, 142.3, 165.7. MS *m*/*z*: 161 (M^+), 130 (BP), 119, 104, 90. Exact mass deter-

mination: 161.0825 (Calcd for $C_{10}H_{11}NO$: 161.0841).

(*S*)-**3e**: 65% yield. Colorless oil. $[\alpha]_D$ −47.9° (*c*=5.60, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1671 (O–C=N), 1603, 1496, 750 (aromatic). NMR ($CDCl_3$) δ: 1.96 (3H, d, *J*=1.3 Hz, CH_3), 2.60—2.68 (1H, dd, *J*=8.5, 13.9 Hz, $C\underline{H}_2$–C_6H_5), 3.04–3.11 (1H, dd, *J*=8.5, 13.9 Hz, $C\underline{H}_2$–C_6H_5), 3.89—3.95 (1H, dd, *J*=7.4, 8.5 Hz, O–$C\underline{H}_2$), 4.12—4.19 (1H, t, *J*=8.5 Hz, O–$C\underline{H}_2$), 4.29—4.41 (1H, m, N–C$\underline{H}$), 7.12—7.32 (5H, m, $CH_2C_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 13.8, 30.8, 41.7, 68.8, 71.7, 128.4, 129.0, 129.1, 129.2, 137.9, 164.9. MS *m*/*z*: 175 (M^+), 84, 56 (BP). Exact mass determination: 175.1007 (Calcd for $C_{11}H_{13}NO$: 175.0997).

3f: 63% yield. Colorless column ($CHCl_3$–hexane), mp 77 °C. IR ν_{max}^{film} cm^{-1}: 1671 (O–C=N), 1599 (aromatic). NMR ($CDCl_3$) δ: 2.11 (3H, s, CH_3), 4.76 (2H, s, O–$C\underline{H}_2$), 7.18—7.62 (10H, m, $CC_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 14.1, 79.2, 79.3, 126.4, 126.9, 127.2, 127.8, 128.4, 128.6, 146.1, 163.9. MS *m*/*z*: 237 (M^+), 207, 194, 178, 165 (BP). Exact mass determination: 237.1150 (Calcd for $C_{16}H_{15}NO$: 237.1154). *Anal.* Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.90; H, 6.39; N, 5.83.

(4*S*,5*R*)-**9**: 93% yield. Colorless column ($CHCl_3$–hexane), mp 204—205 °C. $[\alpha]_D$ −123.2° (*c*=1.01, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1671 (O–C=N), 1599 (aromatic). NMR ($CDCl_3$) δ: 2.27 (3H, d, *J*=1.5 Hz, CH_3), 5.49—5.54 (1H, m, N–C$\underline{H}$ or O–C$\underline{H}$), 5.81—5.85 (1H, m, N–C$\underline{H}$ or O–C$\underline{H}$), 6.86—7.31 (10H, m, C_6H_4). ^{13}C-NMR ($CDCl_3$) δ: 23.5, 85.3, 126.3, 126.5, 127.3, 127.5, 127.6, 127.7, 127.8, 128.0, 128.1, 136.6, 136.9, 137.8, 139.7, 166.0. MS *m*/*z*: 237 (M^+), 194, 180, 130 (BP). Exact mass determination: 237.1357 (Calcd for $C_{16}H_{15}NO$: 237.1355). *Anal.* Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.88; H, 6.31; N, 5.98.

(4*S*,5*R*)-**14**: 90% yield. Colorless column ($CHCl_3$-hexane), mp 67—68 °C. $[\alpha]_D$ −327.2° (*c*=1.91, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1659 (O–C=N), 1480, 1224, 1199 (aromatic). NMR ($CDCl_3$) δ: 1.94 (3H, d, *J*=1.2 Hz, CH_3), 3.19—3.26 (1H, dd, *J*=1.6, 17.8 Hz, $C\underline{H}_2$–C_6H_4), 3.38—3.47 (1H, dd, *J*=6.8, 17.8 Hz, $C\underline{H}_2$–C_6H_4), 5.26—5.33 (1H, m, O–C$\underline{H}$), 5.48—5.51 (1H, dd, *J*=1.2, 8.1 Hz, N–C$\underline{H}$), 7.21—7.48 (4H, m, C_6H_4). ^{13}C-NMR ($CDCl_3$) δ: 14.0, 39.8, 76.6, 82.9, 125.2, 125.3, 127.4, 128.4, 139.7, 142.1, 165.0. MS *m*/*z*: 173 (M^+), 144, 132, 115, 104 (BP). Exact mass determination: 173.0824 (Calcd for $C_{11}H_{11}NO$: 173.0841). *Anal.* Calcd for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.15; H, 6.36; N, 8.18.

(*Rs*)-2-(*p*-Toluenesulfinylmethyl)-1,3-oxazoline (5a) A 50-ml two-necked flask equipped with a septum inlet and magnetic stirring bar was flushed with argon and maintained under a positive pressure of argon. A 1.5 M hexane solution of *n*-butyllithium (1.47 ml, 2.2 mmol) was added at −78 °C to a solution of diisopropylamine (0.31 ml, 2.2 mmol) in THF (7 ml). The mixture was stirred at −78 °C for 30 min. Then a solution of **3a** (85 ml, 1 mmol) in THF (3 ml) was added to the above solution. The reaction mixture was stirred at −78 °C for 1 h. A solution of (−)-menthyl (*S*)-*p*-toluenesulfinate (**4**) (323.4 mg, 1.1 mmol) in THF (10 ml) was added to the above solution, and the reaction mixture was stirred at −78 °C for 12 h. The reaction solution was diluted with $CHCl_3$ and the solution was washed with saturated aqueous NH_4Cl and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (AcOEt : hexane=1 : 1) to give (*Rs*)-**5a** (138.3 mg, 62% yield).

(*Rs*)-**5a**: Colorless column ($CHCl_3$–hexane), mp 105—107 °C. $[\alpha]_D$ +97.5° (*c*=1.5, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1665 (O–C=N), 1525, (aromatic), 1047 (S–O). NMR ($CDCl_3$) δ: 2.42 (3H, s, $C_6H_4C\underline{H}_3$), 3.62—3.64 (1H, d, *J*=1.2 Hz, S–$C\underline{H}_2$), 3.80—3.88 (3H, m, S–$C\underline{H}_2$, O–CH_2), 4.18—4.31 (2H, m, N–$C\underline{H}_2$), 7.29—7.60 (4H, m, $CH_3C_6\underline{H}_4$). ^{13}C-NMR ($CDCl_3$) δ: 20.9, 52.8, 57.3, 57.6, 123.2, 123.5, 130.1, 130.5, 140.1, 143.1, 163.6. MS *m*/*z*: 223 (M^+), 207, 175, 139 (BP), 123, 111, 105, 91. Exact mass determination: 223.0702 (Calcd for $C_{11}H_{13}NO_2S$: 223.0667). *Anal.* Calcd for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; N, 6.27. Found: C, 59.22; H, 5.81; N, 6.20.

The sulfinylation of **3b**—**f**, **9**, and **14** with (*Ss*)-**4** was carried out using the same procedure as described above to give (*Rs*,*S*)-4-iso-propyl-2-(*p*-toluenesulfinylmethyl)-(**5b**), (*Rs*,*S*)-4-*tert*-butyl-2-(*p*-toluenesulfinylmethyl)-(**5c**), (*Rs*,*S*)-4-phenyl-2-(*p*-toluenesulfinylmethyl)-(**5d**), (*Rs*,*S*)-4-benzyl-2-(*p*-toluenesulfinylmethyl)-(**5e**), (*Rs*)-4,4-diphenyl-2-(*p*-toluenesulfinylmethyl)-(**5f**), (4*S*,5*R*,*Rs*)-4,5-diphenyl-2-(*p*-toluenesulfinylmethyl)-1,3-oxazoline (**10**), and (3a*S*,8a*R*)-3a,8a-dihydro-2-(*p*-toluenesulfinylmethyl)-8*H*-indeno[1,2-*d*]1,3-oxazole (**15**), respectively.

(*Rs*,*S*)-**5b**: 58% yield. Colorless oil. $[\alpha]_D$ +56.8° (*c*=1.1, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1663 (O–C=N), 1595, 1468 (aromatic), 1053, 812 (S–O). NMR ($CDCl_3$) δ: 0.83—0.85 (3H, d, *J*=6.8 Hz, CH_3), 0.91—0.93 (3H, d, *J*=6.8 Hz, CH_3), 2.42 (3H, s, $C\underline{H}_3C_6H_4$), 3.62—3.67 (1H, d, *J*=12.4 Hz, S–$C\underline{H}_2$), 3.79—3.85 (1H, d, *J*=12.4 Hz, S–$C\underline{H}_2$), 3.82—3.96 (2H, m, N–C$\underline{H}$ or O–$C\underline{H}_2$), 4.20—4.31 (1H, m, N–C$\underline{H}$ or O–$C\underline{H}_2$), 7.14—7.65 (4H, m, $CH_3C_6\underline{H}_4$). ^{13}C-NMR ($CDCl_3$) δ: 18.2, 18.8, 21.4, 30.9, 32.6, 55.9, 70.9, 72.6, 77.2, 124.3, 129.9, 140.1, 142.2, 158.7. MS *m*/*z*: 265 (M^+), 249, 217, 206, 174, 149, 139 (BP). Exact mass determination: 265.1098 (Calcd for $C_{14}H_{19}NO_2S$: 265.1136).

(*Rs*,*S*)-**5c**: 56% yield. Colorless oil. $[\alpha]_D$ +137.6° (*c*=1.97, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1668 (O–C=N), 1541 (aromatic), 1057, 812 (S–O). NMR ($CDCl_3$) δ: 0.85 (9H, s, $C(C\underline{H}_3)_3$), 2.42 (3H, s, $C_6H_4C\underline{H}_3$), 3.62—3.68 (1H, d, *J*=13.5 Hz, S–$C\underline{H}_2$), 3.80—3.85 (1H, d, *J*=13.5 Hz, S–$C\underline{H}_2$), 3.82—3.90 (1H, m, N–C$\underline{H}$), 4.00—4.06 (1H, t, *J*=8.5 Hz, O–$C\underline{H}_2$), 4.20—4.24 (1H, t, *J*=8.5 Hz, O–$C\underline{H}_2$), 7.26—7.65 (4H, m, $CH_3C_6\underline{H}_4$). ^{13}C-NMR ($CDCl_3$) δ: 21.4, 25.7, 33.5, 56.1, 69.3, 76.2, 77.2, 124.3, 129.9, 140.3, 142.2. MS *m*/*z*: 279 (M^+), 231, 174, 139 (BP). Exact mass determination: 279.1290 (Calcd for $C_{15}H_{21}NO_2S$: 279.1293).

(*Rs*,*S*)-**5d**: 53% yield. Colorless oil. $[\alpha]_D$ +50.4° (*c*=1.40, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1659 (O–C=N), 1541 (aromatic), 1053, 812 (S–O). NMR ($CDCl_3$) δ: 2.43 (3H, s, $C_6H_4C\underline{H}_3$), 3.74—3.80 (1H, dd, *J*=1.3, 12.2 Hz, S–$C\underline{H}_2$), 3.90—3.96 (1H, d, *J*=12.9 Hz, S–$C\underline{H}_2$), 4.05—4.11 (1H, t, *J*=8.5 Hz, O–$C\underline{H}_2$), 4.61—4.67 (1H, dd, *J*=1.8, 8.5 Hz, O–$C\underline{H}_2$), 5.15—5.22 (1H, m, N–C$\underline{H}$), 7.10—7.65 (9H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 21.5, 55.7, 63.5, 69.9, 75.2, 77.2, 77.8, 98.1, 124.3, 126.6, 127.7, 128.7, 130.1, 139.9, 141.2, 142.3, 160.1. MS *m*/*z*: 299 (M^+), 283, 251, 209, 139 (BP). Exact mass determination: 299.0994 (Calcd for $C_{17}H_{17}NO_2S$: 299.0980).

(*Rs*,*S*)-**5e**: 53% yield. Colorless oil. $[\alpha]_D$ +41.3° (*c*=1.56, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1660 (O–C=N), 1597, 1495 (aromatic), 1053, 812 (S–O). NMR ($CDCl_3$) δ: 2.43 (3H, s, $C_6H_4C\underline{H}_3$), 2.49—2.60 (1H, m, C_6H_5–$C\underline{H}_2$–CH), 3.74—3.80 (1H, dd, *J*=1.3, 12.2 Hz, S–$C\underline{H}_2$), 3.90—3.96 (1H, d, *J*=12.2 Hz, S–$C\underline{H}_2$), 4.05—4.11 (1H, t, *J*=8.5 Hz, O–$C\underline{H}_2$), 4.61—4.67 (1H, dd, *J*=1.8, 8.5 Hz, O–$C\underline{H}_2$), 5.15—5.22 (1H, m, N–C$\underline{H}$), 7.10—7.65 (9H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 20.9, 37.5, 57.9, 61.4, 65.7, 123.4, 123.6, 125.8, 128.4, 128.6, 128.7, 128.8, 130.3, 130.5, 138.8, 140.1, 143.1, 164.2. MS *m*/*z*: 313 (M^+), 297, 265, 222, 206, 174, 139, 117, 91 (BP). Exact mass determination: 313.1102 (Calcd for $C_{18}H_{19}NO_2S$: 313.1136).

(*Rs*)-**5f**: 52% yield. Colorless oil. $[\alpha]_D$ +10.9° (*c*=1.10, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1663 (O–C=N), 1597 (aromatic), 1055, 810 (S–O). NMR ($CDCl_3$) δ: 2.38 (3H, s, $C_6H_4C\underline{H}_3$), 3.77—3.82 (1H, d, *J*=13.4 Hz, S–$C\underline{H}_2$), 3.99—4.04 (1H, d, *J*=13.4 Hz, S–$C\underline{H}_2$), 4.73 (2H, s, O–$C\underline{H}_2$), 7.13—7.73 (14H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_5$, $C_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 21.5, 44.5, 69.0, 77.2, 125.5, 126.4, 126.5, 126.6, 127.2, 127.3, 127.5, 127.7, 128.3, 128.4, 128.5, 128.6, 129.8, 129.9, 139.6, 141.9, 142.3, 144.1, 145.2, 145.3, 158.2. MS *m*/*z*: 375 (M^+), 359, 320, 227, 182, 165, 139 (BP). Exact mass determination: 375.1279 (Calcd for $C_{23}H_{21}NO_2S$: 375.1293).

(4*S*,5*R*,*Rs*)-**10**: 61% yield. Colorless column ($CHCl_3$–hexane), mp 124 °C. $[\alpha]_D$ +40.9° (*c*=1.1, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1669 (O–C=N), 1541 (aromatic), 1053, 812 (S–O). NMR ($CDCl_3$) δ: 2.45 (3H, s, $C_6H_4C\underline{H}_3$), 3.87—3.93 (1H, d, *J*=12.5 Hz, S–$C\underline{H}_2$), 4.07—4.13 (1H, d, *J*=12.5 Hz, S–$C\underline{H}_2$), 5.54—5.58 (1H, d, *J*=10.6 Hz, O–C$\underline{H}$ or N–C$\underline{H}$), 5.86—5.90 (1H, d, *J*=10.6 Hz, O–C$\underline{H}$ or N–C$\underline{H}$), 6.90—7.73 (14H, m, $CH_3C_6\underline{H}_4$, N–CH–$C_6\underline{H}_5$, O–CH–$C_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 21.5, 56.3, 74.4, 77.2, 86.0, 124.5, 126.4, 127.0, 127.5, 127.6, 127.7, 127.8, 130.2, 135.7, 136.8, 140.3, 142.5, 160.3. MS *m*/*z*: 375 (M^+), 359, 236, 194, 180, 130 (BP). Exact mass determination: 375.1314 (Calcd for $C_{23}H_{21}NO_2S$: 375.1293). *Anal.* Calcd for $C_{23}H_{21}NO_2S$: C, 73.57; H, 5.64; N, 3.73. Found: C, 73.45; H, 5.55; N, 3.83.

(1*R*,2*S*,*Rs*)-**15**: 81% yield. Colorless column ($CHCl_3$–hexane), mp 85—87 °C. $[\alpha]_D$ −249.0° (*c*=1.1, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1657 (O–C=N), 1601 (aromatic), 1051, 810 (S–O). NMR ($CDCl_3$) δ: 2.35 (3H, s, $C_6H_4C\underline{H}_3$), 2.96—3.03 (1H, dd, *J*=7.1, 18.2 Hz, O–CH–$C\underline{H}_2$–C_6H_4), 3.30—3.39 (1H, dd, *J*=7.1, 18.2 Hz, O–CH–$C\underline{H}_2$–C_6H_4), 3.57—3.61 (1H, d, *J*=12.5 Hz, S–$C\underline{H}_2$), 3.82—3.87 (1H, d, *J*=12.5 Hz, S–$C\underline{H}_2$), 5.22—5.30 (1H, m, O–C$\underline{H}$), 5.50—5.53 (1H, d, *J*=8.1 Hz, N–C$\underline{H}$), 7.07—7.51 (8H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_4$). ^{13}C-NMR ($CDCl_3$) δ: 21.4, 30.9, 39.5, 55.3, 76.8, 77.2, 83.7, 124.2, 125.2, 125.4, 127.5, 128.6, 129.7, 139.3, 139.5, 141.3, 141.9, 159.1. MS *m*/*z*: 311(M^+), 262, 220, 172, 139 (BP). Exact mass determination: 311.1004 (Calcd for $C_{18}H_{17}NO_2S$: 311.0980). *Anal.* Calcd for $C_{18}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85. Found: C, 60.18; H, 7.21; N, 5.91.

(*Rs*)-2-[1-(*p*-Toluenesulfinyl)ethyl]-1,3-oxazoline (6a) A 50-ml two-necked flask equipped with a septum inlet and magnetic stirring bar was flushed with argon and maintained under a positive pressure of argon. A 1.5 M hexane solution of *n*-butyllithium (1.47 ml, 2.2 mmol) was added at −78 °C to a solution of diisopropylamine (0.31 ml, 2.2 mmol) in THF (10 ml). The mixture was stirred at −78 °C for 30 min. Then a solution of (*Rs*)-2-(*p*-toluenesulfinylmethyl)-1,3-oxazoline (**5a**) (223 mg, 1 mmol) in THF (5 ml) was added to the above solution. The reaction mixture was stirred at −78 °C for 1 h. A solution of iodomethane (312.2 mg, 2.2 mmol) in THF (5 ml) was added to the above solution, and the reaction mixture was

stirred at −78 °C for 12 h. The reaction solution was diluted with $CHCl_3$ and the solution was washed with saturated aqueous NH_4Cl and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (AcOEt : hexane = 1 : 1) to give **6a** (97.2 mg, 41% yield) and **7a** (57.7 mg, 23% yield).

(*Rs*)-**6a**: 68% yield (**7b**: 23% yield). Colorless oil. $[\alpha]_D$ +22.4° (*c* = 1.38, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1664 (O–C=N), 1526 (aromatic), 1047, 752 (S–O). NMR ($CDCl_3$) δ: 1.31—1.55 (3H, m, S–CH–C$\underline{H}_3$), 2.41 (3H, s, C_6H_4–C$\underline{H}_3$), 3.48—3.55 (1H, m, S–CH), 3.75—3.96 (2H, m, N–CH_2 or O–CH_2), 4.18—4.26 (2H, m, N–CH_2 or O–C$\underline{H}_2$), 7.27—7.55 (4H, m, $C_6\underline{H}_4$–CH_3). ^{13}C-NMR ($CDCl_3$) δ: 7.8, 20.8, 53.2, 57.4, 60.7, 123.3, 123.5, 130.4, 130.5, 140.1, 143.1, 164.6. MS *m/z*: 237 (M^+), 210, 188, 151, 140 (BP). Exact mass determination: 237.1287 (Calcd for $C_{12}H_{15}NO_2S$: 237.1293).

The methylation of **5b**—**f**, **10**, and **15** with iodomethane was carried out using the same procedure as described above to give (*Rs*,*S*)-2-[1-(*p*-toluenesulfinyl)ethyl]-4-iso-propyl-(**6b**), (*Rs*,*S*)-4-*tert*-butyl-2-[1-(*p*-toluenesulfinyl)ethyl]-(**6c**), (*Rs*,*S*)-2-[1-(*p*-toluenesulfinyl)ethyl]-4-phenyl-(**6d**), (*Rs*,*S*)-4-benzyl-2-[1-(*p*-toluenesulfinyl)ethyl)-(**6e**), (*Rs*)-4,4-diphenyl-2-[1-(*p*-toluenesulfinyl)ethyl]-(**6f**), (4*S*,5*R*,*Rs*)-2-[1-(*p*-toluenesulfinyl)ethyl]-4,5-diphenyl-1,3-oxazoline (**11**), and (3a*S*,8a*R*,*Rs*)-3a,8a-dihydro-2-[1-(*p*-toluenesulfinyl)ethyl]-8*H*-indeno[1,2-*d*]1,3-oxazole (**16**), respectively.

(*Rs*,*S*)-**6b**: 68% yield (**7b**: 23% yield). Colorless oil. $[\alpha]_D$ +12.3° (*c* = 1.87, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1660 (O–C=N), 1456 (aromatic), 1053, 812 (S–O). NMR ($CDCl_3$) δ: 0.81—0.94 (6H, m, CH(C$\underline{H}_3$)$_2$), 1.33—1.52 (3H, m, S–CH–C$\underline{H}_3$), 2.41 (3H, s, C_6H_4–C$\underline{H}_3$), 3.48—3.55 (1H, m, S–CH), 3.75—3.96 (2H, m, N–CH, O–CH_2), 4.18—4.26 (1H, m, N–CH, O–C$\underline{H}_2$), 7.27—7.55 (4H, m, $C_6\underline{H}_4$–CH_3). ^{13}C-NMR ($CDCl_3$) δ: 7.8, 17.4, 17.7, 20.8, 27.9, 59.3, 61.0, 70.1, 123.4, 123.5, 130.4, 130.6, 140.5, 143.3, 164.1. MS *m/z*: 279 (M^+), 263, 231, 210, 188, 151, 140 (BP). Exact mass determination: 279.1287 (Calcd for $C_{15}H_{21}NO_2S$: 279.1293).

(*Rs*,*S*)-**6c**: 54% yield (**7c**: 22% yield). Colorless oil. $[\alpha]_D$ +26.5° (*c* = 1.62, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1665 (O–C=N), 1480 (aromatic), 1053, 812 (S–O). NMR ($CDCl_3$) δ: 0.85 (9H, s, C(C$\underline{H}_3$)$_3$), 1.30—1.33, 1.47—1.50 (3H, dd, S–CH–C$\underline{H}_3$), 2.41 (3H, s, C_6H_4–C$\underline{H}_3$), 3.49—3.57 (1H, m, S–CH), 3.75—3.87 (1H, m, N–CH or O–CH_2), 4.00—4.09 (1H, m, N–CH or O–CH_2), 4.13—4.21 (1H, m, N–CH or O–CH_2), 7.27—7.65 (4H, m, $C_6\underline{H}_4$–CH_3). ^{13}C-NMR ($CDCl_3$) δ: 7.8, 20.9, 24.5, 24.8, 24.9, 31.0, 56.6, 61.3, 78.1, 123.3, 123.9, 130.1, 130.7, 140.1, 143.1, 164.2. MS *m/z*: 293 (M^+), 277, 245, 220, 188, 168, 154 (BP). Exact mass determination: 293.1474 (Calcd for $C_{16}H_{23}NO_2S$: 293.1450).

(*Rs*,*S*)-**6d**: 71% yield (**7d**: 14% yield). Colorless oil. $[\alpha]_D$ −21.2° (*c* = 1.23, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1657 (O–C=N), 1493 (aromatic), 1051, 812 (S–O). NMR ($CDCl_3$) δ: 1.43—1.45, 1.56—1.59 (3H, m, S–CH–C$\underline{H}_3$), 3.42 (3H, s, C_6H_4–C$\underline{H}_3$), 3.59—3.69 (1H, m, CH_3–C$\underline{H}$), 3.87—3.95 (1H, m, CH_3–C$\underline{H}$), 4.02—4.13 (1H, m, O–C$\underline{H}_2$ or N–C$\underline{H}$), 4.58—4.66 (1H, m, O–C$\underline{H}_2$ or N–CH), 5.11—5.18 (1H, m, O–C$\underline{H}_2$ or N–C$\underline{H}$), 7.10—7.56 (9H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 10.2, 21.5, 58.3, 69.5, 74.9, 77.2, 124.8, 125.2, 126.6, 127.6, 128.7, 129.8, 138.8, 141.3, 142.0, 142.2, 163.9. MS *m/z*: 313 (M^+), 297, 265 (BP), 209, 174, 158, 139, 120. Exact mass determination: 313.1115 (Calcd for $C_{18}H_{19}NO_2S$: 313.1136).

(*Rs*,*S*)-**6e**: 62% yield (**7e**: 20% yield). Colorless oil. $[\alpha]_D$ +10.5° (*c* = 3.89, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1657 (O–C=N), 1493, 1452 (aromatic), 1051, 812 (S–O). NMR ($CDCl_3$) δ: 1.35—1.51 (3H, m, CHC$\underline{H}_3$), 2.42 (3H, s, C_6H_4–C$\underline{H}_3$), 2.49—2.60 (1H, m, C_6H_5–C$\underline{H}_2$–CH), 2.94—3.09 (1H, m, C_6H_5–C$\underline{H}_2$–CH), 3.44—3.54 (1H, m, C$\underline{H}$–CH_3), 3.82—3.95 (1H, m, O–C$\underline{H}_2$), 4.10—4.18 (1H, m, O–C$\underline{H}$), 4.27—4.40 (1H, m, N–CH), 7.12—7.54 (8H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_4$). ^{13}C-NMR ($CDCl_3$) δ: 7.5, 20.4, 37.4, 61.0, 61.7, 65.6, 123.2, 123.6, 125.7, 128.1, 128.3, 128.5, 128.8, 130.2, 130.5, 138.8, 140.1, 143.2, 164.2. MS *m/z*: 327 (M^+), 279, 210, 188, 139, 91 (BP). Exact mass determination: 327.1267 (Calcd for $C_{19}H_{21}NO_2S$: 327.1293).

(*Rs*,*S*)-**6f**: 51% yield (**7f**: 31% yield). Colorless column ($CHCl_3$–hexane), mp 92—94 °C. $[\alpha]_D$ +4.4° (*c* = 2.25, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1653 (O–C=N), 1541, 1491 (aromatic), 1053, 812 (S–O). NMR ($CDCl_3$) δ: 1.42—1.67 (3H, m, S–CH–CH_3), 2.33—2.42 (3H, m, C_6H_4–C$\underline{H}_3$), 3.64—4.02 (1H, m, S–CH), 4.64—4.80 (2H, m, O–C$\underline{H}_2$), 7.07—7.84 (14H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_4$). ^{13}C-NMR ($CDCl_3$) δ: 7.8, 20.9, 61.5, 72.0, 75.8, 123.2, 123.6, 126.0, 126.5, 128.1, 128.3, 128.5, 128.6, 129.0, 129.2, 129.4, 129.5, 130.1, 130.4, 140.2, 143.0, 143.2, 143.3, 164.2. MS *m/z*: 389 (M^+), 373, 341, 320, 304, 180, 165, 139 (BP). Exact mass determination: 389.1402 (Calcd for $C_{24}H_{23}NO_2S$: 389.1450). *Anal.* Calcd. for $C_{24}H_{23}NO_2S$: C, 74.01; H, 5.95; N, 3.60. Found: C, 73.90; H, 5.87; N, 3.65.

(*Rs*,*S*)-**11**: 53% yield (12: 27% yield). Colorless column ($CHCl_3$–hexane), mp 85—87 °C. $[\alpha]_D$ −14.3° (*c* = 3.90, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1663 (O–C=N), 1541, 1495 (aromatic), 1051, 812 (S–O). NMR ($CDCl_3$) δ: 1.47—1.69 (3H, m, S–CH–C$\underline{H}_3$), 2.44 (3H, s, C_6H_4–C$\underline{H}_3$), 3.72—3.80, 4.03—4.11 (1H, m, S–C$\underline{H}$–CH_3), 5.50—5.56 (1H, m, N–C$\underline{H}$ or O–CH), 5.81—5.89 (1H, m, N–C$\underline{H}$ or O–CH), 6.83—7.67 (14H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_4$). ^{13}C-NMR ($CDCl_3$) δ: 7.6, 20.7, 61.4, 70.8, 75.2, 123.4, 123.6, 125.7, 127.4, 127.5, 127.6, 127.7, 127.9, 128.3, 128.5, 128.6, 128.8, 130.2, 130.4, 140.1, 140.2, 140.9, 143.2, 164.8. S *m/z*: 389 (M^+), 341, 196, 165, 143 (BP), 116, 89. Exact mass determination: 389.1424 (Calcd for $C_{24}H_{23}NO_2S$: 389.1450). *Anal.* Calcd for $C_{24}H_{23}NO_2S$: C, 74.01; H, 5.95; N, 3.60. Found: C, 74.16; H, 5.93; N, 3.55.

(*Rs*,*S*)-**16**: 96% yield. Colorless column ($CHCl_3$–hexane), mp 105—107 °C. $[\alpha]_D$ −184.1° (*c* = 1.13, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1649 (O–C=N), 1597 (aromatic), 1051, 812 (S–O). NMR ($CDCl_3$) δ: 1.32—1.36 (3H, d, *J* = 7.1 Hz, CHC$\underline{H}_3$), 1.60—1.63, 2.33—2.34 (3H, d, *J* = 7.2 Hz, C$\underline{H}_3$–C_6H_4), 2.75—2.81, 3.09—3.16 (2H, d, *J* = 18.0 Hz, O–CH–C$\underline{H}_2$–C_6H_4), 3.25—3.52 (1H, m, CH_3–C$\underline{H}$), 5.17—5.29 (1H, m, O–C$\underline{H}$), 5.47—5.53 (1H, t, *J* = 8.1 Hz, N–C$\underline{H}$), 6.98—7.56 (8H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_4$). ^{13}C-NMR ($CDCl_3$) δ: 8.4, 12.6, 21.5, 39.5, 39.6, 57.3, 60.2, 76.5, 76.8, 83.1, 83.5, 124.9, 125.2, 125.5, 125.6, 127.5, 128.6, 129.4, 129.5. MS *m/z*: 325(M^+), 309, 277, 186, 115 (BP). Exact mass determination: 325.1154 (Calcd for $C_{19}H_{19}NO_2S$: 325.1137). *Anal.* Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.89; N, 4.30. Found: C, 70.06; H, 5.94; N, 4.24.

(*Rs*)-2-[1-Methyl-1-(*p*-toluenesulfinyl)ethyl]-1,3-oxazoline (7a) A 25-ml two-necked flask equipped with a septum inlet and magnetic stirring bar was flushed with argon and maintained under a positive pressure of argon. A 0.5 M toluene solution of potassium hexamethyldisilazide (KHMDS) (1.5 ml, 0.75 mmol) was added at −78 °C to a solution of **6a** (118.5 mg, 0.5 mmol) in THF (8 ml). A solution of iodomethane (0.07 ml, 1.1 mmol) in THF (3 ml) was added to the above solution, and the reation mixture was stirred at room temperature for 24 h. The reaction solution was diluted with $CHCl_3$ and the solution was washed with saturated aqueous NH_4Cl and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (AcOEt : hexane = 1 : 1) to give (*Rs*)-**7a** (92.9 mg, 74% yield).

(*Rs*)-**7a**: 71% yield. Colorless column ($CHCl_3$–hexane), mp 76 °C. $[\alpha]_D$ −35.9° (*c* = 1.48, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1671 (O–C=N), 1589 (aromatic), 1051, 812 (S–O). NMR ($CDCl_3$) δ: 0.80—0.83 (3H, d, *J* = 6.8 Hz, CH(C$\underline{H}_3$)$_2$), 0.89—0.92 (3H, d, *J* = 6.8 Hz, CH(C$\underline{H}_3$)$_2$), 1.30 (3H, s, CC$\underline{H}_3$), 1.59 (3H, s, CC$\underline{H}_3$), 1.63—1.76 (1H, m, C$\underline{H}$(CH$_3$)$_2$), 2.40 (3H, s, C_6H_5–C$\underline{H}_3$), 3.75—3.84 (2H, m, N–C$\underline{H}_2$), 3.92—3.99 (1H, t, *J* = 8.5 Hz, O–C$\underline{H}_2$), 4.17—4.20 (1H, t, *J* = 8.5 Hz, O–C$\underline{H}_2$), 7.25—7.49 (4H, m, $C_6\underline{H}_4$–CH_3). ^{13}C-NMR ($CDCl_3$) δ: 20.8, 14.8, 14.9, 53.5, 57.7, 65.3, 123.1, 123.8, 130.1, 130.5, 140.1, 143.3, 164.5. MS *m/z*: 294 (M^+), 251, 181, 154, 140, 110, 91, 69, 41 (BP). Exact mass determination: 251.1475 (Calcd for $C_{13}H_{17}NO_2S$: 251.1450). *Anal.* Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.01; H, 6.88; N, 5.48.

The methylation of **6b**—**f**, **11**, and **16** with iodomethane was carried out using the same procedure as described above to give (*Rs*,*S*)-2-[1-methyl-1-(*p*-toluenesulfinyl)ethyl]-4-iso-propyl-(**7b**), (*Rs*,*S*)-4-*tert*-butyl-2-[1-methyl-1-(*p*-toluenesulfinyl)ethyl]-(**7c**), (*Rs*,*S*)-2-[1-methyl-1-(*p*-toluenesulfinyl)ethyl]-4-phenyl-(**7d**), (*Rs*,*S*)-4-benzyl-2-[1-methyl-1-(*p*-toluenesulfinyl)ethyl]-(**7e**), (*Rs*)-4,4-diphenyl-2-[1-methyl-1-(*p*-toluenesulfinyl)-ethyl]-(**7f**), (4*S*,5*R*,*Rs*)-2-[1-methyl-1-(*p*-toluenesulfinyl)ethyl]-4,5-diphenyl-1,3-oxazoline (**12**), and (3a*S*,8a*R*,*Rs*)-3a,8a-dihydro-2-[1-methyl-1-(*p*-toluenesulfinyl)ethyl]-8*H*-indeno[1,2-*d*]1,3-oxazole (**17**), respectively.

(*Rs*,*S*)-**7b**: 73% yield. Colorless oil. $[\alpha]_D$ −50.3° (*c* = 1.77, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1658 (O–C=N), 1589 (aromatic), 1051, 812 (S–O). NMR ($CDCl_3$) δ: 0.80—0.83 (3H, d, *J* = 6.8 Hz, CH(C$\underline{H}_3$)$_2$), 0.89—0.92 (3H, d, *J* = 6.8 Hz, CH(C$\underline{H}_3$)$_2$), 1.30 (3H, s, CC$\underline{H}_3$), 1.59 (3H, s, CC$\underline{H}_3$), 1.63—1.76 (1H, m, C$\underline{H}$(CH$_3$)$_2$), 2.40 (3H, s, C_6H_5–C$\underline{H}_3$), 3.75—3.84 (1H, m, N–C$\underline{H}$), 3.92—3.99 (1H, t, *J* = 8.5 Hz, O–C$\underline{H}_2$), 4.17—4.20 (1H, t, *J* = 8.5 Hz, O–C$\underline{H}_2$), 7.25—7.49 (4H, m, $C_6\underline{H}_4$–CH_3). ^{13}C-NMR ($CDCl_3$) δ: 14.5, 14.9, 17.3, 17.6, 20.9, 27.7, 59.6, 65.4, 70.5, 123.2, 123.6, 130.5, 130.7, 140.5, 143.3, 164.8. S *m/z*: 294 (M^+), 225, 181, 154, 140, 110, 91, 69, 41 (BP). Exact mass determination: 293.1475 (Calcd for $C_{16}H_{23}NO_2S$: 293.1450).

(*Rs*,*S*)-**7c**: 86% yield. Colorless oil. $[\alpha]_D$ −41.5° (*c* = 1.52, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1661 (O–C=N), 1478 (aromatic), 1051, 812 (S–O). NMR ($CDCl_3$) δ: 0.84 (9H, s, C(C$\underline{H}_3$)$_3$), 1.29 (3H, s, S–C(C$\underline{H}_3$)$_2$), 1.58 (3H, s, S–C(C$\underline{H}_3$)$_2$), 2.40 (3H, s, C_6H_4–C$\underline{H}_3$), 3.71—3.77 (1H, dd, *J* = 2.5, 7.6 Hz, N–C$\underline{H}$), 4.06—4.19 (2H, m, O–C$\underline{H}_2$), 7.25—7.56 (4H, m, $C_6\underline{H}_4$–CH_3). ^{13}C-NMR ($CDCl_3$) δ: 14.3, 14.8, 20.7, 24.5, 24.6, 24.9, 31.1, 57.3, 65.7, 78.6, 123.2, 123.6, 130.1, 130.5, 140.3, 143.1, 164.2. MS *m/z*: 307 (M^+), 168, 153, 140, 112, 92, 69, 57 (BP). Exact mass determination: 307.1682 (Calcd for $C_{17}H_{25}NO_2S$: 307.1606).

(*Rs*,*S*)-**7d**: 75% yield. Colorless oil. $[\alpha]_D$ −69.2° (*c* = 2.66, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1653 (O–C=N), 1599, 1493 (aromatic), 1051, 812 (S–O). NMR

($CDCl_3$) δ: 1.41 (3H, s, S–C($C\underline{H}_3$)$_2$), 1.66 (3H, s, S–C($C\underline{H}_3$)$_2$), 2.41 (3H, s, C_6H_4–$C\underline{H}_3$), 4.04—4.10 (1H, t, J=8.6 Hz, N–C$\underline{H}$ or O–C$\underline{H}_2$), 4.59—4.66 (1H, t, J=8.6 Hz, N–CH or O–C$\underline{H}_2$), 5.06—5.13 (1H, m, N–CH or O–C$\underline{H}_2$), 7.10–7.49 (9H, m, $C_6\underline{H}_4$–CH_3, $C_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 17.4, 20.7, 21.5, 60.9, 69.5, 75.0, 124.3, 125.7, 126.6, 126.7, 127.7, 128.7, 129.3, 129.6, 130.1, 136.8, 141.5, 142.2, 167.4. MS *m*/*z*: 327 (M^+), 279, 214, 188, 172, 157, 140, 117, 91 (BP). Exact mass determination: 327.1338 (Calcd for $C_{19}H_{21}NO_2S$: 327.1293).

(*Rs*,*S*)-**7e**: 70% yield. Colorless oil. $[\alpha]_D$ −45.3° (c=1.17, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1653 (O–C=N), 1493, 1454 (aromatic), 1051, 812 (S–O). NMR ($CDCl_3$) δ: 1.33 (3H, s, C$\underline{H}_3$), 1.54 (3H, s, C$\underline{H}_3$), 2.40 (3H, s, C_6H_4–$C\underline{H}_3$), 2.51–2.59 (1H, dd, J=4.6, 8.6 Hz, C_6H_5–C$\underline{H}_2$), 2.99—3.06 (1H, dd, J=4.6, 8.6 Hz, C_6H_5–C$\underline{H}_2$), 3.91—3.97 (1H, dd, J=0.8, 7.6 Hz, O–C$\underline{H}_2$), 4.10—4.17 (1H, dd, J=0.8, 8.6 Hz, O–C$\underline{H}_2$), 4.23—4.34 (1H, m, N–CH), 7.13—7.42 (9H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 14.7, 14.9, 20.9, 37.6, 62.1, 65.6, 65.9, 123.2, 123.5, 125.8, 128.2, 128.4, 128.7, 128.8, 130.2, 130.5, 138.9, 140.5, 143.1, 164.1. MS *m*/*z*: 341 (M^+), 202, 140, 110, 91 (BP). Exact mass determination: 341.1441 (Calcd for $C_{20}H_{23}NO_2S$: 341.1450).

(*Rs*,*S*)-**7f**: 72% yield. Colorless column ($CHCl_3$–hexane), mp 74—77 °C. $[\alpha]_D$ −40.2° (c=1.64, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1653 (O–C=N), 1491, 1447 (aromatic), 1051, 812 (S–O). NMR ($CDCl_3$) δ: 1.41 (3H, s, C$\underline{H}_3$), 1.71 (3H, s, C$\underline{H}_3$), 2.29 (3H, s, C_6H_4–$C\underline{H}_3$), 4.73 (2H, d, J=8.6 Hz, O–C$\underline{H}_2$), 6.87—7.80 (14H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_5$). ^{13}C-NMR ($CDCl_3$) δ: 14.7, 14.9, 20.7, 65.8, 72.4, 76.1, 123.6, 123.7, 126.0, 126.3, 128.2, 128.4, 128.6, 128.9, 129.2, 129.3, 129.5, 129.8, 130.4, 130.6, 140.3, 143.3, 143.5, 143.8, 164.2. MS *m*/*z*: 403 (M^+), 334 (BP), 264, 233, 211, 196, 139. Exact mass determination: 403.1620 (Calcd for $C_{25}H_{25}NO_2S$: 403.1606). *Anal.* Calcd for $C_{25}H_{25}NO_2S$: C, 74.41; H, 6.25; N, 3.47. Found: C, 74.34; H, 6.31; N, 3.38.

(*Rs*,*S*)-**12**: 72% yield. Colorless column ($CHCl_3$–hexane), mp 93—94 °C. $[\alpha]_D$ −70.6° (c=2.65, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1655 (O–C=N), 1541, 1491 (aromatic), 1049, 812 (S–O). NMR ($CDCl_3$) δ: 1.47 (3H, s, C$\underline{H}_3$), 1.77 (3H, s, C$\underline{H}_3$), 2.43 (3H, s, C_6H_4–$C\underline{H}_3$), 5.44—5.48 (1H, d, J=10.6 Hz, N–C$\underline{H}$ or O–C$\underline{H}$), 5.85—5.89 (1H, d, J=10.6 Hz, N–C$\underline{H}$ or O–C$\underline{H}$), 6.83—7.64 (14H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_4$). ^{13}C-NMR ($CDCl_3$) δ: 14.4, 14.9, 20.9, 71.1, 75.8, 65.8, 123.2, 123.6, 125.7, 127.3, 127.4, 127.5, 127.8, 127.9, 128.3, 128.4, 128.6, 128.7, 130.6, 130.8, 140.1, 140.2, 140.9, 143.2, 164.1. MS *m*/*z*: 339 (M^+), 196, 165, 143 (BP). Exact mass determination: 339.2354 (Calcd for $C_{20}H_{21}NO_2S$: 339.2341). *Anal.* Calcd for $C_{20}H_{21}NO_2S$: C, 70.77; H, 6.24; N, 4.13. Found: C, 70.69; H, 6.31; N, 4.08.

(*Rs*,*S*)-**17**: 72% yield. Colorless column ($CHCl_3$–hexane), mp 96 °C. $[\alpha]_D$ −196.0° (c=1.26, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 1639 (O–C=N), 1597 (aromatic), 1049, 814 (S–O). NMR ($CDCl_3$) δ: 1.27 (3H, s, C$\underline{H}_3$), 1.61 (3H, s, C$\underline{H}_3$), 2.34 (3H, s, C_6H_4–$C\underline{H}_3$), 3.00—3.06 (1H, d, J=18.1 Hz, O–CH–C$\underline{H}_2$–C_6H_4), 3.33—3.42 (1H, dd, J=7.2,18.1 Hz, O–CH–C$\underline{H}_2$–C_6H_4), 5.22—5.30 (1H, m, O–C$\underline{H}$), 5.50—5.53 (1H, d, J=8.1 Hz, N–C$\underline{H}$), 6.97—7.59 (8H, m, $CH_3C_6\underline{H}_4$, $C_6\underline{H}_4$). ^{13}C-NMR ($CDCl_3$) δ: 15.7, 21.4, 22.6, 39.7, 60.3, 76.7, 77.2, 83.2, 125.2, 125.5, 125.7, 127.5, 128.6, 129.1, 136.7, 139.7, 141.4, 141.7, 166.6. MS *m*/*z*: 339 (M^+), 262, 214, 199 (BP), 170, 140. Exact mass determination: 339.1258 (Calcd for $C_{20}H_{21}NO_2S$: 339.1293). *Anal.* Calcd for $C_{20}H_{21}NO_2S$: C, 70.77; H, 6.24; N, 4.13. Found: C, 70.68; H, 6.31; N, 4.06.

The Copper(II)-Catalyzed Asymmetric Diels–Alder Reactions of 18 with 19 Genaral Procedure: Anhydrous $CuCl_2$ (5.4 mg, 0.04 mmol) is reacted with chiral 2-(arylsulfinylmethyl)-1,3-oxazoline (**5**, **7**, **10**, **12**, **15**, or **17**) (0.04 mmol) in dichloromethane (1 ml) at room temperature for 4 h under an argon atomosphere. Another 25-ml two-necked flask equipped with a septum inlet and a magnetic stirring bar and containing AgX_2 (X=OTf, ClO_4, and SbF_6) (0.08 mmol) was flushed with argon, and maintained under a positive pressure of argon. The above solution was added and the mixture was stirred for 4 h at room temperature. The resulting mixture was cooled to −78 °C with a dry ice–CH_3OH bath, and a solution of *N*-acyl-1,3-oxazolidine-2-one (**18**) (56.4 mg, 0.4 mmol) in CH_2Cl_2 (2 ml) and freshly distilled cyclopentadiene (**19**) (132 mg, 2 mmol) were sequentially added dropwise. The reaction mixture was stirred under the conditions listed in Tables 1—3. After the reaction time described, the reaction was quenched with saturated aqueous NaCl solution. The mixture was extracted with $CHCl_3$ (3×10 ml) and the combined organic layer was dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a crude product that was purified by column chromatography over silca gel (35% acetone in hexane as eluent) to provide a cycloadduct, (2*S*)-*endo*-**20a**. The results obtained are listed in Tables 1—3.

The standard analysis of **20** was performed by HPLC analysis on a Daicel OD column with 10% 2-propanol in hexane as the eluent [1 ml/min; average retention times: 19.9 and 20.7 min for *exo*-**20b** enantiomers, 21.9 min for (2*S*)-*endo*-**20a** and 24.6 min for (2*R*)-*endo*-**20a**]. The *endo* and *exo* ratio was determined by ^{1}H-NMR analysis.[11]

References

1) Seyden-Penne J., "Chiral Auxiliaries and Ligands in Asymmetric Synthesis," John Wiley & Sons, New York, 1995, pp. 536—592.
2) Johnson J. S., Evans D. A., *Acc. Chem. Res*., **33**, 325—335 (2000); Jorgensen K. A., *Angew Chem. Int. Ed*., **39**, 3558—3588 (2000); Simonse K. B., Svenstrup N., Roberson M., Jorgensen K. A., *Chem. Eur. J*., **6**, 123—128 (2000); Yao S., Saaby S., Hazell R. G., Jorgensen K. A., *ibid*., **6**, 2435—2448 (2000); Crosignani S., Desimoni G., Faita G., Filippone S., Mortoni A., Righetti P., Zema M., *Tetrahedron Lett*., **40**, 7007—7010, (1999); Evans D. A., Barnes D. M., Johnson J. S., Lectka T., Matt P. V., Miller S. J., Murry J. A., Norcross R. D., Shaughnessy E. A., Campos K. R., *J. Am. Chem. Soc*., **121**, 7582—7594 (1999); Lipkowitz K. B., Schefzick S., *ibid*., **123**, 6710—6711 (2001).
3) Khiar N., Fernandez I., Alcudia F., *Tetrahedron Lett*., **34**, 123—126 (1993); Ordonez M., Guerrero-de la Rosa V., Labastida V., Llera J. M., *Tetrahedron Asymm*., **7**, 2675—2686 (1996); Quite recently, chiral bis(sulfinyl)imidamidine ligands were reported; Owens T. D., Hollander F. J., Oliver A. G., Ellman J. A., *J. Am. Chem. Soc*., **123**, 1539—1540 (2001); Bolm C., Simic O., *ibid*., **123**, 3830—3831 (2001).
4) Hiroi K., Suzuki Y., *Heterocycles*, **46**, 77—81 (1997); Hiroi K., Suzuki Y., Abe I., Hasegawa Y., Suzuki K., *Tetrahedron Asymm*., **9**, 3797—3817 (1998); Suzuki Y., Abe I., Hiroi K., *Heterocycles*, **50**, 89—94 (1999); Hiroi K., Suzuki Y., Abe I., *Chem. Lett*., **1999**, 149—150; Hiroi K., Suzuki Y., *Tetrahedron Lett*., **39**, 6499—6502 (1998); Hiroi K., Suzuki Y., Kawagishi R., *ibid*., **40**, 715—718 (1999); Hiroi K., Suzuki Y., Abe I., Kawagishi R., *Tetrahedron*, **56**, 4701—4710 (2000).
5) Hiroi K., Umemura M., Tomikawa Y., Kaneko M., Kato F., *Chem. Pharm. Bull*., **45**, 759—764 (1997); Hiroi K., Umemura M., *Tetrahedron Lett*., **33**, 3343—3346 (1992); *Idem*, *Tetrahedron*, **49**, 1831—1840 (1993).
6) "Organic Syntheses," Collective Vol. I, John Wiley & Sons, Inc., New York, 1941, pp. 5—7.
7) Meyers A. I., Shipman M., *J. Org. Chem*., **56**, 7098—7102 (1991).
8) Khiar N., Fernandez I., Alcudia F., *Tetrahedron Lett*., **34**, 123—126 (1993).
9) Narasaka K., Inoue M., Okada N., *Chem. Lett*., **7**, 1109—1112 (1986).
10) Brunel J. M., Campo B. D., Buono G., *Tetrahedron Lett*., **39**, 9663—9666 (1998); Crosignani S., Desimoni G., Faita G., Righetti P. P., *Tetrahedron*, **54**, 15721—15730 (1998); Ghosh A. K., Cho H., Cappiello J., *Tetrahedron Asymm*., **9**, 3687—3691 (1998); Desimoni G., Faita G., Righetti P. P., *Tetrahedron Lett*., **37**, 3027—3030 (1996); Crosignani S., Desimoni G., Faita G., Filippone S., Mortoni A., Righetti P. P., Zema M., *ibid*., **40**, 7007—7010 (1999); Peer M., de Jong J. C., Kiefer M., Langer T., Rieck H., Schell H., Sennhenn P., Sprinz J., Steinhagen H., Wiese B., Helmchen G., *Tetrahedron*, **52**, 7547—7583 (1996); Pyne S. G., Hayipour A. R., Prabakaran K., *Tetrahedron Lett*., **35**, 645—648 (1994).
11) Nishida A., Yamanaka M., Nakagawa M., *Tetrahedron Lett*., **40**, 1555—1558 (1999).
12) Hiroi K., Watanabe K., Abe I., Koseki M., *Tetrahedron Lett*., **42**, 7617—7619 (2001).