Enantioselective Diels−Alder Reaction Using Chiral Mg Complexes Derived from Chiral 2-[2-[(Alkyl- or 2-[2-[(Arylsulfonyl)amino]phenyl]-4-phenyl-1,3-oxazoline

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Magnesium complexes derived from (*R*)-2-[2-[(alkyl- or (*R*)-2-[2-[(arylsulfonyl)amino]phenyl]-4-phenyl-1,3-oxazolines and methylmagnesium iodide were found to be efficient Lewis acid catalysts for the Diels−Alder reaction of 3-alkenoyl-1,3-oxazolidin-2-one with cyclopentadiene. Chiral ligands were easily prepared from readily available D-phenylglycinol in good yields. The reaction of 3-acryloyl-1,3-oxazolidin-2-one with cyclopentadiene catalyzed by a stoichiometric amount of the Lewis acid gave exclusively the *endo*-cycloaddition product in up to 92% ee. The sulfonamide group on the chiral ligand strongly influenced the enantiofacial selectivity: the use of a toluene-, benzene-, 1- or 2-naphthalene-, or methanesulfonamide group in the chiral ligand gave the *endo*-(2*R*)-cycloaddition product, while a trifluoromethanesulfonamide group predominantly gave its enantiomer, the *endo*-(2*S*)-cycloaddition product, in 65% ee. The scope and limitations of the catalytic effect of chiral Mg(II) complexes on the enantioselectivity of the Diels−Alder reaction were investigated. The reaction mechanism of the Mg(II)-catalyzed reaction is also discussed on the basis of the experimental results.

Introduction

The investigation of effective chiral Lewis acid catalysts has recently attracted considerable interest.[1] Among them, B,[2] Al,[3] Ti,[4] Sn,[5] and lanthanide[6] complexes have been shown to be effective Lewis acid catalysts for asymmetric carbon−carbon bond formation. The Diels−Alder reaction has long been recognized as one of the most important methods for preparing cyclohexene derivatives, which are versatile chiral building blocks for the synthesis of numerous natural products because both the absolute and relative stereochemistry at all four newly created asymmetric centers can potentially be controlled.[7] The control of enantioselectivity for chiral Lewis acid-catalyzed Diels−Alder reactions has been demonstrated by several groups.[8] However, only a few reports are available regarding the preparation of both enantiomers of [4 + 2] cycloadducts.[9] Since one enantiomer is prepared from one chiral source and the other enantiomer is synthesized using another chiral source, both enantiomers are not always available, e.g., amino acids, sugars, from most chiral sources. On the other hand, although Grignard reagents are readily available and the asymmetric addition to ketones and aldehydes has been reported by a few groups,[10] only one group has demonstrated that a magnesium complex prepared from a Grignard reagent is an effective Lewis acid for asymmetric carbon−carbon bond-forming reactions.[11] Recently, we reported that the Mg complex **5a** prepared from chiral 2-[2-[(tolylsulfonyl)amino]phenyl]-4-phenyl-1,3-oxazoline (**4a**) and methylmagnesium iodide was an effective Lewis acid catalyst for the enantioselective Diels−Alder reaction of 3-alkenoyl-1,3-oxazolidin-2-one with cyclopentadiene.[12] In the present work, the scope and limitations of this reaction and the catalytic effect of Mg complexes **5a**−**g** on the enantioselectivity of the Diels−Alder reaction were investigated, and enantiofacial discrimination was found to be greatly influenced by the substituent on the sulfonamide group. The details of the

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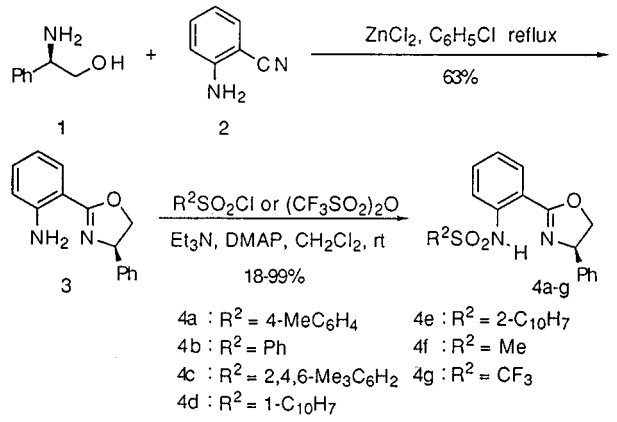
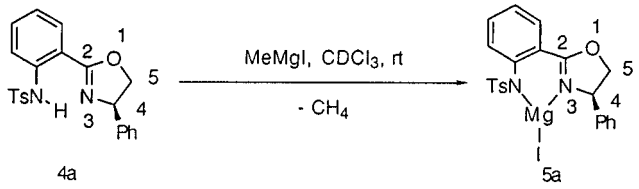
Scheme 1



Scheme 2



asymmetric Diels–Alder reaction promoted by a chiral magnesium catalyst are discussed.

Results and Discussion

Chiral 2-[2-[(aryl- or [2-[(alkylsulfonyl)amino]phenyl]-4-phenyl-1,3-oxazolines were easily prepared from commercially available D-phenylglycinol (**1**) in a two-step procedure (Scheme 1). In the presence of zinc chloride, the reaction of D-phenylglycinol (**1**) and 2-aminobenzonitrile (**2**) in chlorobenzene gave oxazoline **3** in 63% yield.[13] The amino group was then sulfonylated by treatment with aryl- or alkylsulfonyl chloride or trifluoromethanesulfonic anhydride in the presence of triethylamine and DMAP in dichloromethane to give the corresponding sulfonamides **4a**–**g** in moderate to good yields. Compounds **4a**,**c**–**f** could be purified by recrystallization from ethyl acetate and hexane.

Mg(II)-containing complexes were readily prepared by the reaction of methylmagnesium iodide with chiral ligands in dry dichloromethane at 0 °C for 5 min under an argon atmosphere. NMR investigations of the complexes were performed under the following conditions. To a solution of the chiral ligand **4a** in dichloromethane was added a solution of MeMgI in ether at 0 °C (Scheme 2). After stirring for 15 min, the solvent was removed under reduced pressure (0.8 mmHg) at rt for 30 min, $CDCl_3$ was then added to the resulting white powder, and the whole mixture was transferred to an NMR tube. Peaks of diethyl ether were detected by ^1H and ^{13}C NMR despite repeated evaporation under highly reduced pressure, which suggests that coordination or interaction of ether with the magnesium complex is likely.[14] The signal of the acidic proton (δ 12.31 ppm) of the sulfonamide group disappeared in the ^1H NMR spectrum, while two different sets of diastereotopic carbons were seen in the ^{13}C NMR spectrum for complex **5a** prepared from **4a** and methylmagnesium iodide in $CDCl_3$ at room temperature.

Table 1. ^{13}C Chemical Shifts of Chiral Ligand 4a and Magnesium Complex 5a[a]

	δ, ppm		
	4a	**5a**	
C–CH_3	21.51	21.12	21.46
C-5	69.59	68.43	68.70
C-4	73.50	73.69	74.71

[a] At 67.5 MHz in $CDCl_3$ at room temperature.

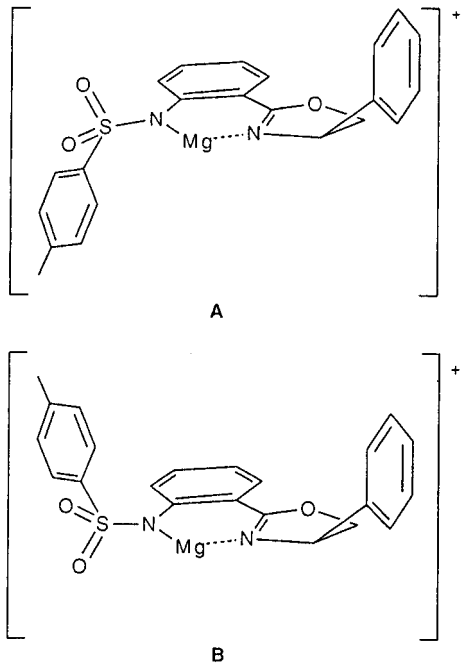


Figure 1.

The ^{13}C chemical shifts of chiral ligand **4a** and magnesium complex **5a** are shown in Table 1. The ratio of the peak intensities of the two diastereotopic carbons at CH_3 of the tolyl group was 7:3. This ratio did not agree well with that based on the calculated difference of 0.904 kcal/mol, which implies a roughly 8:2 mixture of the two complexes. These findings strongly suggest the presence of six-membered ring chelation between the chiral ligand and magnesium, which reflects the observed ratio of the conformers. There seem to be two stable conformations at room temperature in $CDCl_3$ due to hindered rotation of the sulfonyl group. Using MM2 calculations,[15] two stable conformations **A** and **B** of magnesium complex were found, as shown in Figure 1. Conformation **A** was more stable (0.904 kcal/mol) than conformation **B**. Therefore, this catalyst probably behaves like a C_2-symmetric ligand and is responsible for the highly asymmetric induction observed in the Diels–Alder reactions (vide infra).

3-(2′-Propenoyl)-1,3-oxazolidin-2-one **(6)**,[16] which is highly reactive as a dienophile, was chosen for the cycloaddition reaction with cyclopentadiene **7** (Scheme 3). In all cases, the reaction was carried out at −78 °C in the presence of stoichiometric amounts of complex without removal of diethyl ether derived from Grignard

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(14) In the ^{13}C NMR spectrum, an upfield shift of the diethyl ether Mg complex **5a** (δ 65.8, CH_2CH_3; 14.9, CH_2CH_3) was observed from the original peaks (δ 67.4, CH_2CH_3; 17.1, CH_2CH_3).

(15) These conformations were supported by MM-2 calculations perfomed on the CAChe system.

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Scheme 3

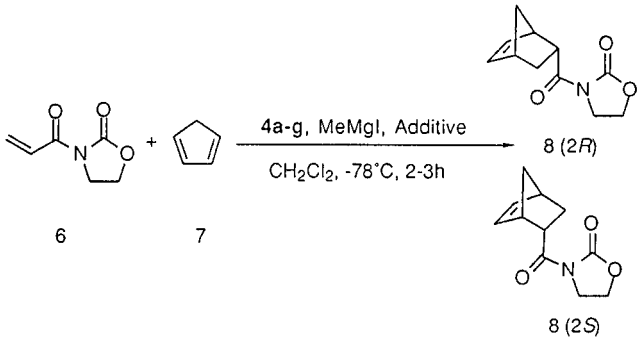


Table 2. Effect of a Substituent on the Chiral Ligand in the Diels−Alder Reaction between 6 and 7[a]

entry	additive	ligand	yield (%)[b]	% ee	config
1	none	**4a**	60	7	*R*
2	$NaBPh_4$	**4a**	70	17	*R*
3	$AgSbF_6$	**4a**	80	60	*R*
4	I_2	**4a**	69	92	*R*
5	I_2	**4a**	81	91	*R*[c]
6	I_2	**4a**	64[d]	0	
7	I_2	**4b**	82	89	*R*
8	I_2	**4c**	71	29	*S*
9	I_2	**4d**	55	14	*R*
10	I_2	**4e**	81	86	*R*
11	I_2	**4f**	70	62	*R*
12	I_2	**4g**	44	65	*S*

[a] The reaction was carried out with 0.2 mmol of **6**, 3.0 equiv of **7**, 1.0 equiv of additive, 1.0 equiv of **4a**−**g**, and 1.0 equiv of MeMgI at −78 °C for 2−3 h. [b] Isolated yield. [c] With the use of 50 mol % of the complex. [d] Carried out at −93 °C.

reagent under an argon atmosphere. The results are summarized in Table 2.[17] The *endo*-adduct was obtained exclusively under these conditions. The enantioselectivity was determined by HPLC analysis using a chiral column (Chiralcel OJ), and the absolute configuration of the *endo*-adduct was determined by comparison of the optical rotation with that reported in the literature.[18] To obtain high enantioselectivity and high yield, strong conformational rigidity of the dienophile and an increase in the Lewis acidity of the magnesium complex were necessary. Therefore, additives were used to try to increase the Lewis acidity of the magnesium cationic complex.[19] Although the use of 1 equiv of catalyst **5a** gave cycloaddition product **8** in 60% yield with 7% ee (entry 1), the use of sodium tetraphenyl borate as an additive slightly increased the enantioselectivity (entry 2), and silver hexafluoroantimonate improved the selectivity up to 60% ee (entry 3). The highest enantioselectivity of 92% ee was obtained using iodine (entry 4). These additives may act by dissociating the iodine anion as an iodinate, as reported by Corey.[8d,e] The use of 50 mol % of the catalyst was also effective to give the product in high yield and enantioselectivity (entry 5), while reducing the amount of the complex to 20 or 10 mol % decreased the enantioselectivity of the product (82% yield, 80% ee, and 95% yield, 51% ee). The reaction temperature was important in this magnesium-catalyzed Diels−Alder reaction, and the best result for the reaction of **6** with **7** was obtained at −78 °C. Interestingly, at −93 °C, a racemic cycloaddition product was obtained when magnesium complex **5a** was used (entry 6).

(17) The solvent proportion was CH_2Cl_2−Et_2O = 30:1.

(18) Pikul, S.; Corey, E. J. *Org. Synth.* **1992**, *71*, 30.

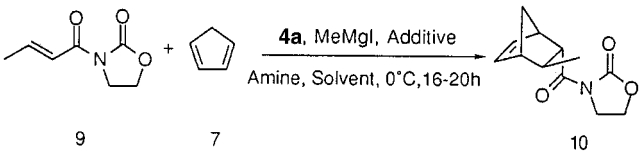
(19) Recently Corey et al. reported that a cationic oxazaborinane catalyst was an effective catalyst for enantioselective Diels−Alder reactions: Hayashi, Y.; Rohde, J. J.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 5502.

Table 3. Diels−Alder Reaction between 3-((*E*)-2′-Butenoyl)-1,3-oxazolin-2-one (9) and Cyclopentadiene Catalyzed by 5a To Provide Cycloadduct 10[a]

entry	additive	amine (equiv)	solvent	yield (%)[b]	% ee[c]	$[\alpha]_D^{23}$ (*c*, CCl_4)
1			CH_2Cl_2	10	11	+20.0 (0.10)
2	$AgSbF_6$		CH_2Cl_2	68	57	+118.5 (0.60)
3	$NaBPh_4$		CH_2Cl_2	61	84	+175.0 (0.54)
4	I_2		CH_2Cl_2	62	72	+152.7 (0.55)
5	I_2	Et_3N (0.1)	CH_2Cl_2	79	89	+183.9 (0.69)
6	I_2	DMAP (0.1)	CH_2Cl_2	82	88	+181.9 (0.72)
7	I_2	pyridine (0.1)	CH_2Cl_2	70	70	+145.2 (0.62)
8	I_2	iPr_2NEt (0.1)	CH_2Cl_2	61	72	+147.3 (0.54)
9	I_2	*N*-ethylpiperidine (0.1)	CH_2Cl_2	56	70	+146.6 (0.50)
10	I_2	DMAP (0.05)	CH_2Cl_2	77	82	+169.6 (0.68)
11	I_2	DMAP (0.2)	CH_2Cl_2	63	91	+188.5 (0.56)
12	I_2	DMAP (0.3)	CH_2Cl_2	73	89	+184.0 (0.62)
13	I_2	DMAP (0.4)	CH_2Cl_2	62	88	+181.9 (0.51)
14	I_2	DMAP (0.1)	Et_2O	50	25	+52.0 (0.44)
15	I_2	DMAP (0.1)	THF	23	10	+21.0 (0.20)
16	I_2	DMAP (0.1)	$CHCl_3$	50	43	+88.3 (0.44)
17	I_2	DMAP (0.1)	toluene	68	72	+149.3 (0.60)

[a] All reactions were carried out with 0.2 mmol of **9**, 3.0 equiv of **7**, 1.0 equiv of additive, 1.0 equiv of **4a**, and 1.0 equiv of MeMgI at 0 °C for 16−20 h. [b] Isolated yield. [c] Determined by comparison of the optical rotation with that reported in the literature.[18]

Scheme 4



The enantioselectivity of the Diels−Alder adduct was influenced by the substituent on the sulfonamide group of the chiral ligand. Except for the cases using sulfonamide **4c** and **4g** (entries 8 and 12), the reaction gave the 2*R*-product exclusively. The benzenesulfonamide **4b** and the 2-naphthalenesulfonamide **4e** also provided high enantioselectivity (89% ee and 86% ee, entries 7 and 10), and the methanesulfonamide **4f** gave a cycloadduct with good yield and selectivity (70% yield and 62% ee, entry 11), whereas the results with the 1-naphthyl derivative **4d** were disappointing (14% ee, entry 9). Surprisingly, reversal of the enantioselectivity was observed when catalysts **4c** and **4g** were used, and the 2*S*-product was predominantly obtained (29% ee and 65% ee, entries 8 and 12).

As shown in Table 3, the reaction of 3-((*E*)-2′-butenoyl)-1,3-oxazolidin-2-one **(9)**[16] with cyclopentadiene **7** was examined to increase the utility of the chiral Lewis acid (Scheme 4). The *endo*-adduct was obtained exclusively, and no *exo*-isomer could be detected. The enantioselectivity and absolute configuration of the *endo*-adduct were determined by comparison of the optical rotation with that reported in the literature.[20] The presence of a tertiary amine was crucial for good chiral induction in this reaction, in which DMAP and triethylamine were effective additives to give the cycloadduct with high enantiofacial selectivity (88% ee and 89% ee, entries 5 and 6). The enantiomeric purity of the products was affected by the amount of the amine. The use of 20 mol % of the amine gave the cycloadduct in up to 91% ee, while no improvement in enantioselectivity was observed with the use of greater amounts of DMAP to 30 and 40 mol % (entries 12 and 13). In the present system, the

(20) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340.

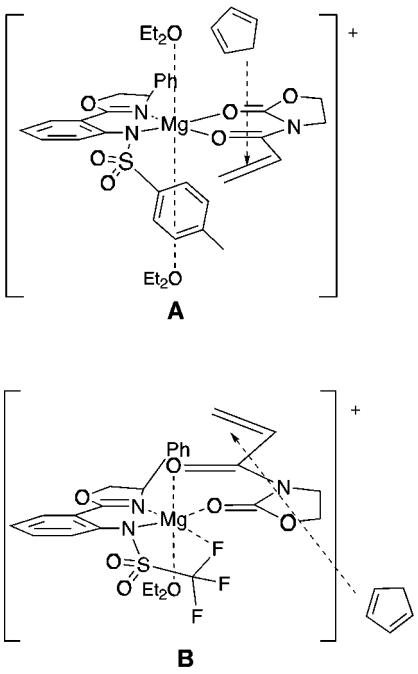


Figure 2.

solubility of iodine was very low, and upon addition of these amines, the reaction mixture became homogeneous. Therefore, amines do not seem to coordinate or interact with the catalyst, but rather merely improve its solubility. The use of nonpolar solvents was suitable for this reaction, and among them dichloromethane was effective, whereas solvents with an oxygen atom which could potentially interact with magnesium led to the formation of cycloaddition product with poor yields and lower enantioselectivities due to the low solubility of the chiral magnesium complex.

The high degree of enantioselection of the Diels−Alder reaction may be explained as follows: a bis(oxazoline)−magnesium complex with the *S*-configuration gives Diels−Alder product **8** with predominantly an *R*-configuration, as previously reported by Corey et al.[8e] On the other hand, in the presence of magnesium perchlorate and 2 equiv of water, a bis(oxazoline) with an *R*-configuration predominantly produces the cycloadduct **8** with *R*-stereochemistry. This stereochemical outcome was explained by Desimoni et al. in terms of a catalysis via an octahedral coordination, which is in contrast to the opposite stereochemical results obtained by Corey and Desimoni in the absence of water, which involved a tetrahedral coordination.[9b,c] In the present case, magnesium complexes **5a**−**g** probably form an octahedral complex with chiral ligands **4a**−**g**, bidentate dienophiles **6** and **9**, and diethyl ether.[17] In fact, ^{1}H and ^{13}C NMR spectra showed the coordination of Et_2O to the center metal of chiral magnesium complexes. Thus, the present magnesium complexes **5a**−**g** probably assume an octahedral arrangement.[9b,c,14] On the other hand, the dienophile assumes an *s-cis* conformation (**A,** Figure 2), and the *endo-Si*-attack of cyclopentadiene from the sterically less-hindered side appears to be favored, leading to the observed 2*R*-configuration. The reversal of enantioselectivity using the magnesium complex derived from trifluoromethyl ligand **4g** may be explained as follows: the trifluoromethyl group could coordinate or interact weakly with the magnesium cation.[21] Furthermore, the use of a (trifluoromethyl)sulfonyl group increased the Lewis acidity of the center metal, which may have led to coordination of the oxygen atom of the sulfonyl group at the chiral ligand.[22] In the case of the Mg complex derived from ligand **4g**, coordination of the fluorine or oxygen presumably occupies one of the equatorial positions, and the dienophile coordinates with the oxygen at the equatorial and axial positions, as depicted in **B** (Figure 2). On the basis of this molecular arrangement, the *endo-Re*-attack of the dienes appears to be favored, providing the 2*S*-configuration. The use of catalyst **5c** gave the cycloadduct with low *S*-enantioselectivity due to shielding of the coordination site of the magnesium cation by the methyl group of the arylsulfonyl group, and the dienophile could not bind to the metal by its two carbonyl groups. Several conformations of the dienophile would be involved under these circumstances. 3-((*E*)-2′-Cinnamoyl)-1,3-oxazolidin-2-one, which was used as a dienophile in the present reaction, also gave a cycloaddition product in moderate yield and with high enantioselectivity (51% yield, 88% ee) at room temperature.

A new chiral ligand was developed for the Diels−Alder reaction of cyclopentadiene **7** with 3-alkenoyl-1,3-oxazolidin-2-ones **6** and **9**. The chiral ligand was prepared from optically active amino acid by a straightforward procedure. The magnesium Lewis acid was easily prepared from readily available Grignard reagent with the new chiral ligand, and promoted the cycloaddition reaction between cyclopentadiene **7** and dienophile **6** or **9** to give the *endo*-isomer as a sole product. The addition of iodine, sodium tetraphenylborate, or silver hexafluoroantimonate was crucial to dissociate the iodinate anion from the magnesium cation to provide high enantioselectivity during the Diels−Alder process. The reaction of acryloyl derivative **6** and cyclopentadiene **7** also gave cycloaddition products with good enantioselectivity. Changing the sulfonamide moiety of the chiral ligand resulted in a reversal of the observed enantioselectivity. The addition of a catalytic amount of tertiary amine, DMAP, or triethylamine was necessary for the reaction of crotonoyl derivative **9** and cyclopentadiene **7** to proceed at an appreciable rate due in part to its ability to solvate iodine.

Experimental Section

Infrared spectra were determined on a JASCO IR-810 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with JEOL α-500 and JNM EX-270 spectrometers using tetramethylsilane or trichlorofluoromethane as an internal standard. High performance liquid chromatography (HPLC) was carried out using a Hitachi L-4000 detector, Hitachi L-6000 pump, and a Daicel Chiralcel OJ column. Optical rotations were measured with a Union PM-101 polarimeter. Exact mass spectra were taken on a JEOL JMS-DX303-HF spectrometer. All melting points are uncorrected. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl immediately before use. Dichloromethane was pretreated with diphosphorus pentoxide, distilled from CaH_2, and stored over 4A molecular sieves. Pyridine was pretreated with potassium hydroxide, distilled from CaH_2, and stored over 4A molecular sieves. Purification of products was performed by column chromatography on silica gel Wakogel C-300 or Merck Silica Gel-60, and/or preparative TLC on silica gel Merck Kisel Gel PF254 or Wakogel B-5F. The starting materials 3-((*E*)-2′-butenoyl)-1,3-oxazolidin-2-one[16] and 3-(2′-propenoyl)-1,3-oxazolidin-2-one[16,17] were synthesized according to the literature procedures. Methylmagnesium iodide in diethyl ether was prepared according to a typical procedure.[23] Iodine,

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4-(*N*,*N*-dimethylamino)pyridine and triphenylphosphine were used as received from Wako Pure Chemical Industrial Ltd. All reactions were carried out under an argon atmosphere. Reaction flasks were sealed with a red rubber septum, unless otherwise mentioned. Anhydrous solvents and reaction mixtures were transferred by an oven-dried syringe or cannula.

(4*R*)-2-(2-Aminophenyl)-4-phenyloxazoline (3). To a mixture of D-(−)-phenylglycinol (8.1 g, 59 mmol) and 2-aminobenzonitrile (7.0 g, 59 mmol) in dichloromethane (140 mL) was added zinc chloride (8.0 g, 59 mmol) at room temperature, and the reaction mixture was heated at 140 °C for 2 days. The reaction mixture was cooled to room temperature and was quenched with 50 mL of saturated aqueous ammonium chloride. The resultant mixture was extracted 3 times with 50 mL of ethyl acetate. The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel using 20% ethyl acetate−hexane as eluent to afford 8.9 g (63%) of the title compound as a colorless solid. $[\alpha]^{23}_D = -189.5$ (*c* 1.01, $CHCl_3$); mp 71 °C; R_f = 0.5 (20% ethyl acetate−hexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.13 (t, *J* = 8.25 Hz, 1H), 4.69 (dd, *J* = 8.25, 1.65 Hz, 1H), 5.45 (dd, *J* = 8.25, 1.65 Hz, 1H), 6.15 (br s, 2H), 6.66−6.73 (m, 2H), 7.21−7.22 (m, 6H), 7.74−7.78 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.17, 73.04, 108.64, 115.67, 115.97, 126.58, 127.51, 128.67, 129.75, 132.25, 142.73, 148.76, 165.00; IR (neat) 3295, 1628, 1490 cm^{-1}; MS (EI) *m*/*z* (relative intensity) 238 (100), 207 (36), 118 (47), calcd for $C_{15}H_{14}N_2O$ 238.1106; found 238.1111. Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.80; H, 5.83; N, 11.75.

General Protocol for the Sulfonylation of (4*R*)-2-(2-Aminophenyl)-4-phenyloxazoline. To a solution of (4*R*)-2-(2-aminophenyl)-4-phenyloxazoline in dry dichloromethane (∼0.15 M) at 0 °C were added 5 equiv of triethylamine and 0.01 equiv of 4-(*N*,*N*-dimethylamino)pyridine, and after 5 min the appropriate sulfonyl chloride (1.2 equiv) was added. The mixture was stirred for 24−48 h at room temperature. The reaction was quenched with excess saturated aqueous ammonium chloride and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The product was purified by flash chromatography on silica gel and recrystallized from ethyl acetate−hexane to afford the desired compounds.

(4*R*)-2-[2-[(Tolylsulfonyl)amino]phenyl]-4-phenyloxazoline (4a): yield 100%; $[\alpha]^{23}_D = -49.3$ (*c* 0.75, $CHCl_3$); mp 134−135 °C; R_f = 0.3 (25% ethyl acetate−hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.20 (dd, *J* = 1.83, 7.94 Hz, 1H), 4.71 (dd, *J* = 1.83, 8.55 Hz, 1H), 5.49 (dd, *J* = 7.94, 8.55 Hz, 1H), 7.00−7.42 (m, 9H), 7.66−7.82 (m, 4H), 12.31 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.51, 69.59, 73.50, 113.30, 118.02, 122.41, 126.46, 127.17, 127.86, 128.82, 129.46, 129.55, 132.72, 136.86, 139.41, 141.47, 143.47, 164.55; IR ($CHCl_3$): 1630, 1600 cm^{-1}; MS (EI) *m*/*z* (relative intensity) 392 (100), 328 (39), 208 (41), 91 (52), calcd for $C_{22}H_{20}N_2O_3S$ 392.1259; found 392.1234. Anal. Calcd for $C_{22}H_{20}N_2O_3S$: C, 67.33; H, 5.14; N, 7.14. Found: C, 67.60; H, 4.92; N, 7.09.

NMR Study of Magnesium Complex 5a in $CDCl_3$. To a solution of the chiral ligand **4a** (78.5 mg, 0.2 mmol) in dichloromethane (3 mL) was added a solution of MeMgI[23] in ether (0.98 M, 0.2 mL) at 0 °C. After stirring for 15 min, the solvent was removed in vacuo (0.8 mmHg at rt) and dried over 30 min. Anhydrous $CDCl_3$ (1 mL) was added to the residue and transferred into NMR tube.

General Procedure for the Asymmetric Diels−Alder Reaction between 6 and 7 Using a Stoichiometric Amount of the Mg(II) Complex. To a solution of 1.0 equiv of a chiral ligand in dichloromethane was added a solution of MeMgI in ether (0.98 M, 0.2 mL)[23] at 0 °C. After stirring for 30 min, iodine (0.2 mmol) and additives were added to the resulting solution in one portion at the same temperature (*without removal of diethyl ether!*). The reaction mixture was cooled to −78 °C. After 5 min a dichloromethane solution (2 mL) of 3-(2′-propenoyl)-1,3-oxazolidin-2-one (0.2 mmol) was added and the mixture was stirred for 30 min. A solution of cyclopentadiene (0.6 mmol) in dichloromethane (2 mL) was added to the mixture over 40 min and stirred for 2−3 h. A solution of triphenylphosphine (0.4 mmol) in dichloromethane (2 mL) was added to remove iodine and to quench the reaction at the same temperature. The color of reaction mixture changed from brown to yellow, and aqueous sodium thiosulfate was added. The organic materials were extracted with ethyl acetate, and the combined extracts were dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was purified on thin layer silica gel chromatography (hexane−ethyl acetate = 2:1, R_f = 0.3) to give the pure 3-[((1′*R*,2′*R*,4′*S*)-bicyclo[2.2.1]hept-5′-en-2′-yl)carbonyl]-1,3-oxazolin-2-one (**8**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.39−1.50 (m, 3H), 1.95 (ddd, *J* = 12.6, 9.3, 3.7 Hz, 1H), 2.92−2.93 (m, 1H), 3.29−3.30 (m, 1H), 3.90−4.00 (m, 3H), 4.35−4.41 (m, 2H), 5.87 (dd, *J* = 5.5, 2.8 Hz, 1H), 6.24 (dd, *J* = 5.5, 3.1 Hz, 1H); IR ($CHCl_3$) 1775, 1696 cm^{-1}. The enantioselectivity was determined by HPLC analysis using a chiral column (Chiralcel OJ, hexane−*i*-PrOH = 10:1), and the absolute configuration of the *endo*-adduct was determined by comparison of the optical rotation value with that reported in the literature ($[\alpha]_D$ −152.0 (*c* 1.5, $CHCl_3$)) [89% ee (1′*S*,2′*S*,4′*R*)].[18]

General Procedure for the Asymmetric Diels−Alder Reaction between 9 and 7 Using a Stoichiometric Amount of the Mg(II) Complex. To a solution of 1.0 equiv of a chiral ligand in dichloromethane was added a solution of MeMgI in ether (0.98 M, 0.2 mL) at 0 °C. After stirring for 30 min, iodine (0.2 mmol) and additives were added to the resulting solution in one portion at the same temperature. A dichloromethane solution (2 mL) of 3-((*E*)-2′-butenoyl)-1,3-oxazolidin-2-one (0.2 mmol) was added to the reaction mixture followed by cyclopentadiene (0.6 mmol), and the mixture was stirred overnight at 0 °C. A solution of triphenylphosphine (0.4 mmol) in dichloromethane (2 mL) was added to remove iodine and to quench the reaction. The color of reaction mixture changed from brown to yellow, and aqueous sodium thiosulfate was added. The organic materials were extracted with ethyl acetate, and the combined extracts were dried over anhydrous sodium sulfate. After evaporation of the solvent, the crude product was purified on thin layer silica gel chromatography (hexane−ethyl acetate = 2:1, R_f = 0.3) to give pure 3-[((1′*R*,2′*R*,3′*S*,4′*S*)-3′-methylbicyclo[2.2.1]hept-5′-en-2′-yl)carbonyl]-1,3-oxazolin-2-one (**10**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.13 (d, *J* = 6.92 Hz, 3H), 1.44−1.48 (m, 1H), 1.67−1.73 (m, 1H), 2.07−2.17 (m, 1H), 2.53−2.54 (m, 1H), 3.28−3.29 (m, 1H), 3.53−3.55 (m, 1H), 3.88−4.13 (m, 2H), 4.38−4.44 (m, 2H), 5.78 (dd, *J* = 2.64, 5.61 Hz, 1H), 6.36−6.39 (dd, *J* = 3.30, 5.61 Hz, 1H); IR (neat) 1775, 1695 cm^{-1}. The enantioselectivity and the absolute configuration of the *endo*-adduct were determined by comparison of the optical rotation with that reported in the literature ($[\alpha]_D$ −191 (*c* 3.6, CCl_4) [(92% ee (1′*S*,2′*S*,3′*R*,4′*R*)].[18]

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of chiral ligands **3** and **4a**−**g** (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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