Remote Asymmetric Induction in Lewis Acid-Catalyzed Diels–Alder Reaction of α,β-Unsaturated Enones Having a Chiral Sulfinyl-Substituted, 5-Membered Aromatic Heterocycle[1)]

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Two types of chiral sulfoxides as Diels–Alder dienophiles were synthesized and high levels of diastereoselectivity were observed in cycloadditions. 2-Furyl and 2-thienyl α,β-enones, bearing a chiral sulfinyl group in the heterocycle, served as efficient dienophiles in Diels–Alder reactions, where the catalytic use of aluminium chloride or a lanthanide triflate effected the cycloaddition with cyclopentadiene affording the *endo* adduct with high diastereoselectivity, ranging from 91% to 98%.

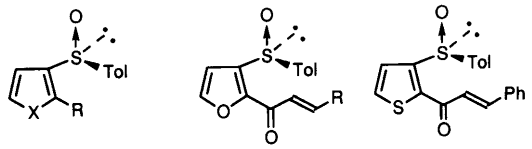
Key words Diels–Alder reaction; chiral sulfoxide; Lewis acid; remote asymmetric induction

Chiral sulfoxides are useful for asymmetric carbon–carbon bond formation in organic synthesis.[3)] Among reactions using chiral sulfoxides, the Diels–Alder reaction is a fascinating strategy which enables the construction of up to four chiral centers in one step.[4)] To effect asymmetric Diels–Alder reaction, chiral sulfinyl dienophiles,[5)] dienes[6)] and catalyst[7)] have been exploited to date. Most studies on cycloadditions using chiral dienophiles have dealt with α-sulfinyl acrylate derivatives, whose sulfinyl oxygen and carbonyl oxygen should coordinate tightly with a Lewis acid, resulting in a conformationally rigid six-membered chelate. High levels of asymmetric induction should result with an auxiliary which effects steric control due to the three ligands in the sulfinyl center. However, little work has been done on asymmetric Diels–Alder reactions of dienophiles that possess a reaction site which is remote from the sulfinyl group. To realize such a remote induction in chiral sulfoxide chemistry, we previously devised five-membered aromatic heterocycles **1** and **2**, derived from **3** and **4**, bearing a chiral sulfinyl moiety. The use of the furan- and thiophene-compounds, **1** and **2** resulted in highly asymmetric allylation[8)] and hetero Diels–Alder reaction.[9)] As part of our studies on asymmetric addition using chiral sulfoxides whose sulfinyl group is remote from the reaction site, we now detail the Lewis acid-catalyzed Diels–Alder reaction of the novel sulfinyl dienophiles **5** and **6** with cyclopentadiene.[10)]

Results and Discussion

Preparation of Sulfinyl Dienophiles Bearing 5-Membered Aromatic Heterocycles Sulfinyl dienophiles were prepared by the following sequence (Chart 1). Treatment of **3** with lithium diisopropylamide (LDA) and (*E*)-cinnamaldehyde afforded the alcohol **7a** as a 1 : 1 diastereoisomeric mixture in 98% yield. Allylic oxidation of **7a** with MnO_2 produced **5a** (mp 149—150 °C, $[\alpha]_D^{24}$ −771.8°) in 86% yield. In a similar manner to **5a**, the crotonyl derivative **5b** (mp 84—85 °C, $[\alpha]_D^{26}$ −591.5°) was obtained by treatment of **3** with (*E*)-crotonaldehyde and LDA followed by MnO_2 oxidation of the resulting alcohol **7b** in 72% yield. The corresponding thiophene derivative **6** (mp 167—169 °C, $[\alpha]_D^{21}$ −720.5°) was also prepared from **4** in 74% yield according to a similar sequence (*via* **8**).

Diels–Alder Reaction of 5 with Cyclopentadiene Having obtained the sulfinyl dienophiles, we set out to explore the diastereoselectivity of the Diels–Alder reaction with cy-



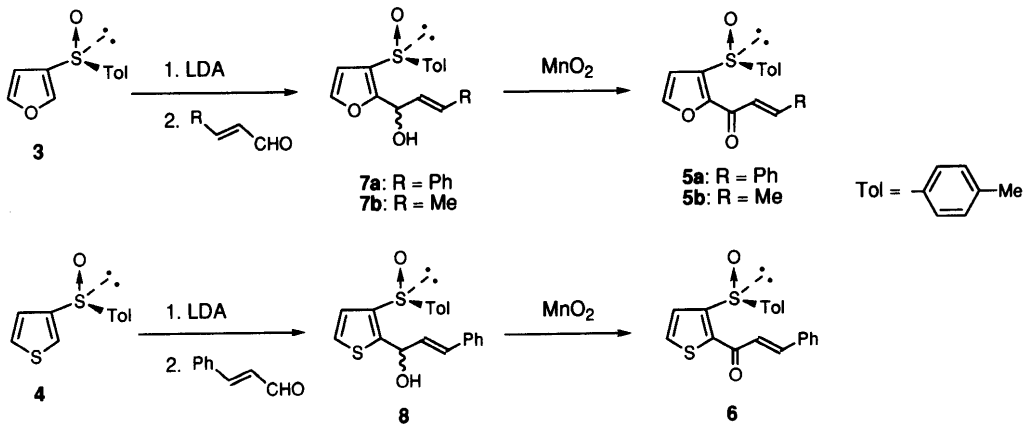


Chart 1

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Table 1. Diels–Alder Reaction of **5a** with Cyclopentadiene

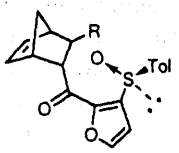
Entry	Lewis acid	(eq used)	Solvent	Temp./°C	Time/h	Total yield/%	Product ratio[a] **9a**:**10a**:**11a**:**12a**	*endo*/*exo*	de of *endo*/%
1	None		CH_2Cl_2	25	20	13	37:37:13:13	74/26	0
2	None		Benzene	80	7	72	27:36:17:20	63/37	−14[b]
3	$TiCl_4$	(1.0)	CH_2Cl_2	−20	16	0	—	—	—
4	$BF_3 \cdot Et_2O$	(1.0)	CH_2Cl_2	−20	20	100	65:32: 2: 1	97/3	34
5	$AlCl_3$	(1.0)	CH_2Cl_2	−20	3	100	94: 2: 4: *ca.* 0	96/4	97
6	$AlCl_3$	(0.2)	CH_2Cl_2	25	16	100	88: 4: 7: 1	92/8	91
7	$Yb(OTf)_3$	(0.2)	Toluene	25	20	49	53:21:17: 9	74/26	44
8	$Yb(OTf)_3$	(0.2)	THF	25	20	39	71:10:13: 6	81/19	75
9	$Yb(OTf)_3$	(1.0)	CH_2Cl_2	25	3	96	84:10: 4: 2	94/6	78
10	$Yb(OTf)_3$	(0.2)	CH_2Cl_2	25	20	98	83: 6: 9: 2	89/11	87
11	$Nd(OTf)_3$	(0.2)	CH_2Cl_2	25	20	100	88: 4: 7: 1	92/8	92
12	$Sm(OTf)_3$	(0.2)	CH_2Cl_2	25	20	100	89: 3: 6: 2	92/8	93

a) Product ratio was determined by HPLC analysis. *b*) Negative sign indicates that **10a** in excess is diastereoisomeric to **9a**.

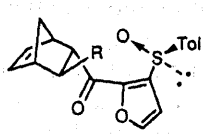
Table 2. Diels–Alder Reaction of **5b** with Cyclopentadiene in CH_2Cl_2

Entry	Lewis acid	(eq used)	Temp./°C	Time/h	Total yield/%	Product ratio[a] **9b**:**10b**:**11b**:**12b**	*endo*/*exo*[b]	de of *endo*/%
1	$AlCl_3$	(1.0)	−20	25	80	91: 4:4:1	95/5	92
2	$AlCl_3$	(1.0)	25	3	100	89: 3:7:1	92/8	91
3	$AlCl_3$	(0.2)	25	24	87	74:16:8:2	90/10	64
4	$Yb(OTf)_3$	(0.2)	25	20	94	87: 4:7:2	91/9	91
5	$Nd(OTf)_3$	(0.2)	25	20	100	89: 5:5:1	94/6	89
6	$Sm(OTf)_3$	(0.2)	25	20	97	90: 4:5:1	94/6	91

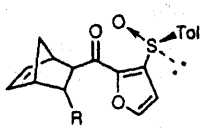
a) Product ratio of **9b** and **10b** was determined by ^{1}H-NMR analysis. Product ratio of **11b** and **12b** was determined by HPLC analysis. *b*) Determined by HPLC analysis.



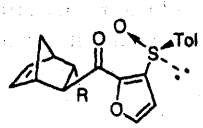
9a: R = Ph
9b: R = Me



10a: R = Ph
10b: R = Me



11a: R = Ph
11b: R = Me



12a: R = Ph
12b: R = Me

clopentadiene. Results of the reaction of **5a** are shown in Table 1. All reactions were carried out with **5a** and an excess of cyclopentadiene (30 eq) in the absence or presence of a Lewis acid. Attempts to conduct the reactions without a Lewis acid were not fruitful, resulting in poor yields and/or in the production of nearly 1 : 1 mixtures of both *endo* and *exo* adducts (entries 1—2). Attempts to perform reaction with $TiCl_4$ or $SnCl_4$ as a promoter were unsuccessful, resulting in polymerization of the substrate even though reactions were conducted at −20 °C (*cf.* entry 3). Reaction with Lewis acids in tetrahydrofuran (THF) or toluene as a solvent also gave poor results. Although the reaction with $BF_3 \cdot Et_2O$ as a Lewis acid proceeded smoothly, selectivity was poor (entry 4).

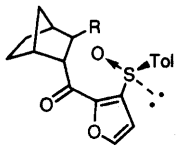
Reaction of **5a** in the presence of 1 eq of $AlCl_3$ at −20 °C proceeded to afford the *endo* adduct **9a** (97% de) as the major product. Even when the reaction was conducted with a catalytic amount (0.2 eq) of $AlCl_3$ at room temperature, the selectivity did not significantly decrease (91% de), although a longer reaction time (16 h) was required for completion of the reaction. Lanthanide triflates also proved to be excellent catalysts for the reaction. With $Yb(OTf)_3$, the same adduct **9a** was produced exclusively (87% de). Other lanthanide triflates such as $Nd(OTf)_3$ and $Sm(OTf)_3$ enhanced both the *endo*/*exo* stereoselectivity [(**9a**+**10a**) *vs.* (**11a**+**12a**)] and the *endo* diastereoselectivity (**9a** *vs.* **10a**).

Since it was found that use of $AlCl_3$ or lanthanide triflates as reaction promoters was effective, these conditions were applied to the reaction of **5b**. Data are presented in Table 2. As anticipated, the reaction with $AlCl_3$ (1.0 eq) or lanthanide triflates (0.2 eq) gave high diastereoselectivity. The reactions with **5b** were comparable with the results obtained with **5a**. Under these conditions *endo* adducts (**9b** and **10b**) were produced with high *endo*/*exo* stereoselectivity [(**9b**+**10b**) *vs.* (**11b**+**12b**)] and a high level of diastereoselectivity for the *endo* adducts (**9b** *vs.* **10b**) was achieved in all cases (89—91% de).

Adducts **9**—**12** were inseparable from each other without the aid of HPLC. However, the major adducts **9a** and **9b** were readily isolated by crystallization of the product mixture obtained in the highly stereoselective reactions. The absolute stereochemistry of **9a** was established by X-ray analysis[10] of a suitable crystal of product **13a**, obtained by hydrogenation of the 5,6-double bond of **9a**. The stereochemistry of the other *endo* diastereoisomer **10a** was confirmed by the following reaction sequence. Deoxygenation of the sulfinyl group in

9a with Zn–$TiCl_4$[11] afforded the corresponding sulfide, which was transformed into the sulfoxides **9a** and the enantiomer of **10a** (*ent*-**10a**) in an approximate 1 : 1 ratio by oxidation with 3-chloroperoxybenzoic acid (*m*-CPBA). Since the mixture was separable by HPLC, the *endo* configuration could be ascertained for **10a**. For a sample for HPLC analysis, all four possible isomers were also obtained by Zn–$TiCl_4$ reduction of the original product mixture followed by *m*-CPBA oxidation. Both the *endo* isomers and the *exo* isomers obtained by this sequence showed nearly equal peak intensities by HPLC analysis. The stereochemistry of the *exo* adducts **11a** and **12a** was tentatively assigned on the basis of the reaction mechanism previously proposed by us (*vide infra*).[5a] In a similar manner to the sequence for **9a**, the adducts **9b**—**12b** derived from the Diels–Alder reaction of **5b** were characterized and stereochemistries were assigned.

To date, numerous efforts to access chiral bicyclo[2.2.1]-heptane and -heptene systems *via* asymmetric Diels–Alder reactions have been reported;[12] however, surprisingly no structural determination of a simple system such as **14a** has appeared. The major adducts **9a** and **9b** were transformed into chiral bicyclo[2.2.1]heptane-2-carboxylic acids **14a** and **14b**, respectively. Treatment of **13a** with RuO_4 (prepared from $RuCl_3$ and $NaIO_4$ in a CCl_4–H_2O–MeCN solvent system)[13] gave the acid **14a**[14] [mp 97—99 °C, $[\alpha]_D^{25}$ −94° (c=1, $CHCl_3$)], which was further transformed into the methyl ester **15** [$[\alpha]_D^{25}$ −70.5° (c=0.5, $CHCl_3$)]. Judging from the high optical purity (98% ee) of **15** by chiral HPLC, the ee of **14a** was estimated as ≥98%. Similarly the major adduct **9b** was converted into acid **14b** [mp 36—38 °C, $[\alpha]_D^{22}$ −43.6° (c=0.53, EtOH), lit.[15] $[\alpha]_D$ +45.9° (c=5.42, 95% EtOH) for enantiomer] by hydrogenation followed by oxidative degradation of the furan ring in **13b**.



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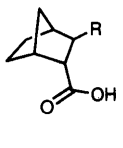
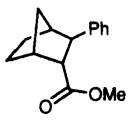
13b: R = Me



14a: R = Ph
14b: R = Me



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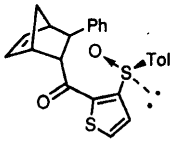
Diels–Alder Reaction of 6 with Cyclopentadiene As summarized in Table 3, the diastereoselectivities of the reactions with **6** were excellent and were in the same sense as observed for reactions of **5**. In a similar manner to the transformation of **9**—**12**, the product ratio of **16**—**19** was determined as follows: Deoxygenation of the crude adducts **16**—**19** (**16** enriched) afforded **20** as a major sulfide, which was isolated pure after column chromatography, followed by crystallization. Exposure of isomerically pure **20** to *m*-CPBA gave **16** and the enantiomer of **17** (*ent*-**17**) as a *ca.* 1 : 1 mixture. Although the *exo* adducts **18** and **19** were not obtained in substantial yields, these isomers formed in the Diels–Alder reaction could be detected by chemical correlation as follows: the mixture of sulfides, obtained from the mother liquor after crystallization of **20**, was oxidized with *m*-CPBA to give **16**, *ent*-**17**, **18** and *ent*-**19**, whose ^{1}H-NMR signals were observed in the original Diels–Alder adducts. The product ratio of the *exo* adducts could not be determined because of unsatisfactory base-line separation both in ^{1}H-NMR analysis and HPLC. The stereochemistry of the adducts **16**—**19** were tentatively assigned by analogy with the reaction mechanism of the Diels–Alder cycloaddition of **5**.

A vast number of asymmetric, Lewis acid-catalyzed and -promoted Diels–Alder reactions have been reported; nevertheless, understanding of the reaction mechanism and characterization of the actual species involved in the Lewis acid complex is difficult. Some efforts aimed at theoretical interpretation of the stereochemical outcome of cycloadditions using chiral sulfoxides have been reported.[16] Although further study is required to fully elucidate the stereochemical outcome of the Diels–Alder reaction, the observed excellent diastereoselectivity should be consistent with the previous proposal (Fig. 1).[5] With dienophiles **5** and **6**, the results can be accommodated by the cyclic transition state models A or B, which are assembled with a Lewis acid, giving a favored seven-membered complex or a five-membered chelate. Cyclopentadiene should thus attack not from the sterically hindered *p*-tolyl group, but from the less hindered lone-paired electron site, giving the major adducts **9a**, **9b** or **16**. The decrease and reversal

Table 3. Diels–Alder Reaction of **6** with Cyclopentadiene in CH_2Cl_2

Entry	Lewis acid	(eq used)	Temp./°C	Time/h	Total yield/%	Product ratio[a] **16**:**17**:(**18**+**19**)	*endo*/*exo*[b]	de of *endo*/%
1	$BF_3 \cdot Et_2O$	(1.0)	25	46	50	54:38:8	92/8	17
2	$AlCl_3$	(1.0)	−20	3	99	95: 1:4	96/4	98
3	$Nd(OTf)_3$	(1.0)	25	5	91	90: 4:6	94/6	91
4	$Sm(OTf)_3$	(1.0)	25	5	92	91: 4:5	95/5	92
5	$Nd(OTf)_3$	(0.2)	25	22	93	88: 3:9	91/9	93
6	$Sm(OTf)_3$	(0.2)	25	22	99	89: 2:9	91/9	96

a) Product ratio of **16** and **17** was determined by HPLC. Diastereoisomeric ratio of the *exo* adducts **18** and **19** was not determined. *b*) Determined by HPLC analysis.



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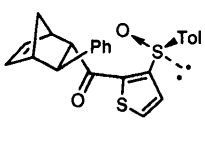

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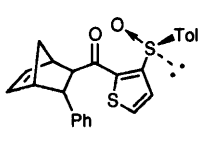

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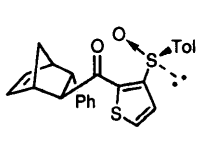

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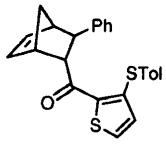

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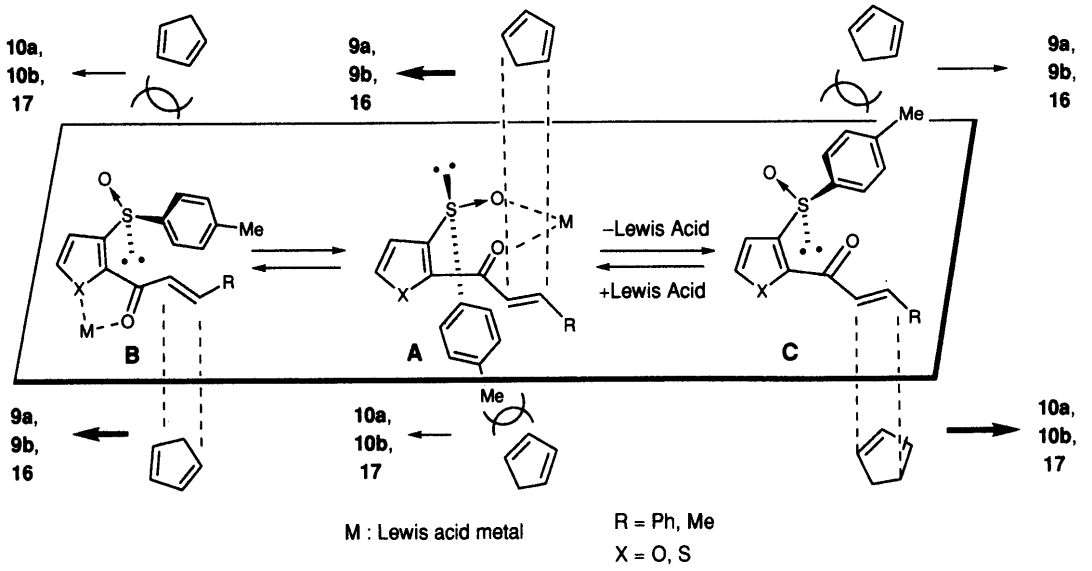

Fig. 1. Stereochemical Outcome of *Endo* Addition of Dienophiles **5**—**6** with Cyclopentadiene

of the diastereoselectivity observed in reactions carried out without a Lewis acid may indicate that the transition state C is favored over those approximated by A or B (but not chelate form). Furthermore, the reasons for the high selectivity in $AlCl_3$-promoted cycloadditions are not yet clear, especially since other typical Lewis acids give poor to moderate levels of diastereoselectivity. In $AlCl_3$-promoted reactions of furan-2-carbonyl compounds, it is suggested that the reactions proceed *via* 5-membered coordination[17] of $AlCl_3$ with the oxygen atom of the furan ring and the 2-carbonyl oxygen. Such a chelating species may be in agreement with the transition model B for the Diels–Alder reaction of **5** and **6**. It is also probable that the use of a lanthanide triflate as a catalyst would facilitate a chelating species,[18] due to the large ionic radii of the Lewis acid metals.

In conclusion, we have demonstrated that Diels–Alder reaction of novel sulfinyl dienophiles **5** and **6** proceeds smoothly to give adduct with high levels of *endo* selectivity and diastereoselectivity by means of a catalytic amount of a Lewis acid.

Experimental

Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. IR spectra were recorded in $CHCl_3$ solution on a JASCO IRA-1 spectrometer. NMR spectra were taken in $CDCl_3$ solution with tetramethylsilane as internal standard. ^{1}H-NMR spectra were measured on a JEOL JNM-GX270 (270 MHz) or EX-400 (400 MHz) spectrometer. The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), doublet of dd (ddd), multiplet (m) and broad (br). Mass spectra were taken with a JEOL JMS-D300 or JMS-SX102A spectrometer. Optical rotations were recorded on a JASCO DIP-360 digital polarimeter. Extracts were dried over anhydrous $MgSO_4$ before evaporation of solvents on a rotary evaporator under reduced pressure. Dry THF and diethyl ether were freshly distilled from sodium benzophenone ketyl prior to use. Dry dichloromethane was distilled from CaH_2 prior to use. *m*-CPBA was used after purification by washing with pH 7.5 phosphate buffer, according to the literature method.[19] TLC analyses were performed using Merck precoated silica $60F_{254}$ plates (0.2 mm). Column chromatography was carried out on Merck silica (70—230 mesh) or Merck silica (230—400 mesh). Preparative TLC was carried out with a Merck $60F_{254}$ plate (2 mm). Analytical HPLC was performed on a 5 μ Develosil 60® column (4.6 × 250 mm). Preparative HPLC was carried out with a 5 μ silica gel prepacked column (Kusano Kagaku). Chiral HPLC analyses were performed using a chiral column, Chiralcel OD® (4.6 × 250 mm). Peak ratios by HPLC were determined with an integrator (Shimadzu Chromatopac C-R6A).

(1*R*/1*S*,*S*$_s$)-1-[3-(*p*-Tolylsulfinyl)-2-furyl]-*trans*-cinnamyl Alcohol (7a) BuLi (1.68 M in hexane, 0.87 ml, 1.46 mmol) was added slowly to an ice-cooled solution of diisopropylamine (0.2 ml, 1.46 mmol) in dry THF (12 ml) under an argon atmosphere. After stirring for 15 min, the solution was cooled to −78 °C and sulfinyl furan **3**[20] (250 mg, 1.21 mmol) in dry THF (3 ml) was added. The mixture was stirred at the same temperature for 11 h. The reaction mixture was then treated with saturated NH_4Cl (100 ml) and the aqueous phase was extracted with EtOAc (30 ml × 3). The combined organic phase was washed with saturated brine (50 ml), dried, and concentrated. The residue was purified by column chromatography on silica with hexane–EtOAc (1 : 1) as the eluent to afford **7a** (400 mg, 98%) as a colorless oil as a *ca.* 1 : 1 diastereoisomeric mixture, $[\alpha]_D^{22}$ +13.6° (*c* = 1.06, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 2.36, 2.38 (total 3H, each s, Me), 4.44, 4.53 (total 1H, each d, *J* = 7.3, 6.5 Hz, OH), 5.60, 5.66 (total 1H, each t, *J* = 7.3, 6.5 Hz, CHOH), 6.24, 6.26 (total 1H, each d, *J* = 2.2, 2.0 Hz, furan), 6.42, 6.45 (total 1H, each dd, *J* = 15.9, 6.5 Hz, CH=), 6.69 (1H, dd, *J* = 15.9, 1.2 Hz, CH=), 7.20—7.45 (8H, m, Ph + Tol + furan), 7.54, 7.61 (total 2H, each d, *J* = 8.1 Hz, Tol). IR: 3300, 3020, 1500, 1080, 1035, 1010, 965, 805 cm^{-1}. MS *m*/*z*: 338 (M^+), 320, 319, 279, 243, 217. HRMS Calcd for $C_{20}H_{18}O_3S$ (M^+): 338.0976. Found: 338.0959.

(*S*$_s$)-*trans*-2-Cinnamoyl-3-(*p*-tolylsulfinyl)furan (5a) A mixture of **7a** (400 mg, 1.18 mmol) and finely powdered MnO_2 (2.5 g) in $CHCl_3$ (20 ml) was stirred vigorously at room temperature for 0.5 h. After filtration with the aid of a short pad of Celite, the solid filter was washed with warm $CHCl_3$ (30 ml). The combined washings and filtrate were concentrated to give **5a** (342 mg, 86%) as a pale yellow solid. **5a**: mp 149—150 °C (EtOAc), $[\alpha]_D^{24}$ −771.8° (*c* = 1.04, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 2.36 (3H, s, Me), 7.14 (1H, d, *J* = 1.6 Hz, furan), 7.26 (2H, d, *J* = 8.1 Hz, Tol), 7.48 (1H, d, *J* = 16.1 Hz, CH=), 7.4—7.5 (3H, m, Ph), 7.61 (1H, d, *J* = 1.6 Hz, furan), 7.6—7.7 (2H, m, Ph), 7.80 (2H, d, *J* = 8.1 Hz, Tol), 7.89 (1H, d, *J* = 16.1 Hz, CH=). IR: 3000, 1645, 1590, 1465, 1365, 1325, 1130, 965 cm^{-1}. MS *m*/*z*: 336 (M^+), 320, 287, 229, 217, 201, 103. *Anal.* Calcd for $C_{20}H_{16}O_3S$: C, 71.41; H, 4.79. Found: C, 71.22; H, 4.82.

(1*R*/1*S*,*S*$_s$)-1-[3-(*p*-Tolylsulfinyl)-2-furyl]-*trans*-crotyl Alcohol (7b) Alcohol **7b** was obtained in 99% yield in a similar manner to **7a** as a colorless oil. **7b**: $[\alpha]_D^{26}$ −10.6° (*c* = 1.06, $CHCl_3$) (1 : 1 mixture). ^{1}H-NMR (270 MHz) δ: 1.70 (3H, d, *J* = 3.9 Hz, Me), 2.40 (3H, s, Me), 4.0—4.2 (1H, br, OH), 5.4—5.5 (1H, br, CH), 5.80 (2H, m, CH=), 6.22, 6.23 (total 1H, each d, *J* = 2.4 Hz, furan), 7.3 (3H, m, Tol + furan), 7.53, 7.68 (total 2H, each d, *J* = 8.3 Hz, Tol). IR: 3340, 3020, 1730, 1490, 1130, 1035, 1010, 965 cm^{-1}. MS *m*/*z*: 276 (M^+), 259, 243, 217, 201, 167. HRMS Calcd for $C_{15}H_{16}O_3S$ (M^+): 276.0820. Found: 276.0830.

(*S*$_s$)-2-*trans*-Crotonyl-3-(*p*-tolylsulfinyl)furan (5b) Enone **5b** was ob-

tained in 73% yield from **7b** by a similar method as described for **5a**. **5b**: mp 84—85 °C (hexane–EtOAc), $[\alpha]_D^{26}$ −591.5° (c=1.1, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 2.00 (3H, dd, J=6.8, 1.6 Hz, Me), 2.36 (3H, s, Me), 6.86 (1H, dd, J=15.5, 1.6 Hz, CH=), 7.09 (1H, d, J=1.7 Hz, furan), 7.20 (1H, dd, J=15.5, 6.8 Hz, CH=), 7.25 (2H, d, J=8.3 Hz, Tol), 7.55 (1H, d, J=1.7 Hz, furan), 7.76 (2H, d, J=8.3 Hz, Tol). IR: 3020, 1665, 1615, 1470, 1375, 1040, 895 cm^{-1}. HRMS Calcd for $C_{15}H_{14}O_3S$: 274.0664. Found: 274.0671. MS m/z: 274 (M^+), 257, 243, 225, 217, 167. *Anal.* Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.41; H, 5.19.

(1*R*/1*S*,*S*$_s$)-1-[3-(*p*-Tolylsulfinyl)-2-thienyl]-*trans*-cinnamyl Alcohol (8) Alcohol **8** was obtained in 88% yield from **4**[20] and *trans*-cinnamaldehyde in a similar manner to the procedure for **7a**, as a semi-solid, 1:1 diastereoisomeric mixture. ^{1}H-NMR (270 MHz) δ: 2.34, 2.36 (total 3H, each s, Me), 4.33 (0.5H, br, OH), 4.65 (0.5H, br, OH), 5.83 (0.5H, dd, J=5.9, 1.1 Hz, CHOH), 6.01 (0.5H, dd, J=6.4, 1.1 Hz, CHOH), 6.39 (0.5H, dd, J=15.8, 6.4 Hz, CH=), 6.39 (0.5H, dd, J=15.9, 5.9 Hz, CH=), 6.71 (0.5H, dd, J=15.8, 1.1 Hz, CH=), 6.72 (0.5H, dd, J=15.9, 1.1 Hz, CH=), 6.87, 7.06 (total 1H, each d, J=5.3 Hz, thiophene), 7.20, 7.21 (total 1H, each d, J=5.3 Hz, thiophene), 7.2—7.4 (7H, m, Ph+Tol), 7.51, 7.54 (total 2H, each d, J=8.2 Hz, Tol). IR: 3320, 3015, 1600, 1495, 1030, 985 cm^{-1}. MS m/z: 354 (M^+), 336, 259, 233. HRMS Calcd for $C_{20}H_{18}O_2S_2$ (M^+): 354.0748. Found: 354.0761.

(*S*$_s$)-2-*trans*-Cinnamoyl-3-(*p*-tolylsulfinyl)thiophene (6) Enone **6** was obtained in 84% yield by a similar method as described for **5**. **6**: mp 167—169 °C (hexane–EtOAc), $[\alpha]_D^{21}$ −720.5° (c=2.1, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 2.34 (3H, s, Me), 7.22 (1H, d, J=15.6 Hz, CH=), 7.24 (2H, d, J=8.2 Hz, Tol), 7.4—7.65 (5H, m, Ph), 7.68 (1H, d, J=5.1 Hz, thiophene), 7.78 (2H, d, J=8.2 Hz, Tol), 7.84 (1H, d, J=15.6 Hz, CH=), 7.87 (1H, d, J=5.1 Hz, thiophene). IR: 3400, 3015, 1645, 1600, 1495, 1405, 1040 cm^{-1}. *Anal.* Calcd for $C_{20}H_{16}O_2S_2$: C, 68.18; H, 4.58. Found: C, 67.99; H, 4.54.

Typical Procedure for the Diels–Alder Reaction of 5 with Cyclopentadiene (Entry 5 in Table 1) Freshly sublimed $AlCl_3$ (595 mg, 4.46 mmol) was added in one portion to a cooled solution of enone **5a** (1.50 g, 4.46 mmol) in dry methylene chloride (60 ml) at −20 °C. Cyclopentadiene (9.2 ml, 0.11 mol) was then added and the resultant mixture stirred at the same temperature for 3 h. The reaction mixture was treated with saturated NH_4Cl (40 ml) and the whole was extracted with chloroform (50 ml × 2). The combined extracts were washed with saturated brine (100 ml), dried, and concentrated. The residue was purified by column chromatography on silica with hexane and then hexane–EtOAc (9:1 to 1:1) to afford the adduct **9a**—**12a** (1.79 g, 100%) in a ratio of 94:2:4: *ca.* 0. The product ratio was determined by HPLC. The major adduct **9a** was easily isolated in pure form after recrystallization of the original product mixture.

(1*S*,2*R*,3*R*,4*R*,*S*$_s$)-2-[3-(*p*-Tolylsulfinyl)-2-furoyl]-3-phenylbicyclo-[2.2.1]hept-5-ene (**9a**): mp 116—118 °C (hexane–EtOAc), $[\alpha]_D^{26}$ −541.0° (c=1.0, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 1.58 (1H, dd, J=8.7, 1.7 Hz, 7-H), 1.95 (1H, d, J=8.7 Hz, H-7), 2.37 (3H, s, Me), 3.06 (1H, br, 1-H or 4-H), 3.37 (2H, br, 4-H or 1-H and 3-H), 3.80 (1H, dd, J=5.1, 3.4 Hz, 2-H), 5.48 (1H, dd, J=5.6, 2.7 Hz, CH=), 6.41 (1H, dd, J=5.6, 3.2 Hz, CH=), 7.05 (1H, d, J=1.8 Hz, furan), 7.18—7.30 (7H, m, Ph+Tol), 7.49 (1H, d, J=1.8 Hz, furan), 7.70 (2H, d, J=8.3 Hz, Tol). IR: 3000, 1665, 1555, 1470, 1375, 1265, 1075, 1040 cm^{-1}. MS m/z: 402 (M^+), 385, 337, 320, 279, 243, 217. *Anal.* Calcd for $C_{25}H_{22}O_3S$: C, 74.60; H, 5.51. Found: C, 74.56; H, 5.52. The minor *endo* adduct **10a** in the reaction was isolated by preparative HPLC (hexane–EtOAc, 7:1) of the mother liquor separated from **9a** after crystallization of the product mixture. **10a**: mp 97—99 °C, $[\alpha]_D^{19}$ −183° (c=0.4, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 1.65 (1H, dd, J=8.6, 1.7 Hz, 7-H), 1.97 (1H, d, J=8.6 Hz, 7-H), 2.35 (3H, s, Me), 3.07 (1H, br, 1-H or 4-H), 3.38 (1H, br d, J=3.5 Hz, 3-H), 3.49 (1H, br s, 4-H or 1-H), 3.75 (1H, dd, J=5.0, 3.5 Hz, 2-H), 5.94 (1H, dd, J=5.6, 2.8 Hz, CH=), 6.51 (1H, dd, J=5.6, 2.9 Hz, CH=), 7.08 (1H, d, J=1.7 Hz, furan), 7.1—7.8 (5H, m, Ph), 7.17 (2H, d, J=8.3 Hz, Tol), 7.52 (1H, d, J=1.7 Hz, furan), 7.74 (2H, d, J=8.3 Hz, Tol). IR: 3000, 1670, 1560, 1480, 1380, 1270, 1080, 1045 cm^{-1}. MS m/z: 402 (M^+), 385, 337, 319, 279, 243, 217. *Anal.* Calcd for $C_{25}H_{22}O_3S \cdot 1/2H_2O$: C, 72.97; H, 5.63. Found: C, 72.86; H, 5.55.

For determination of the product ratio by HPLC analysis, an analytical sample of **9a**—**12a** was prepared by the following sequence. Treatment of the original product mixture **9a**—**12a** (**9a** enriched) with Zn–$TiCl_4$ afforded a roughly 9:1 mixture of sulfides, which was oxidized with *m*-CPBA to produce **9a**, *ent*-**10a**, **11a** and *ent*-**12a** in a rough ratio of 9:9:1:1. Since all these isomers were separable by HPLC, the product ratio could be determined from the peak intensities [hexane–EtOAc, 4:1; flow rate, 1 ml·min^{-1}: **11a**, 46.8 min; **9a**, 49.5 min; *ent*-**12a**, 53.4 min; *ent*-**10a**, 56.2 min]. Isolation of isomerically pure **11a** and **12a** was difficult by column chromatographic separation. **11a**: ^{1}H-NMR (270 MHz) δ: 1.52 (1H, dd, J=8.8, 1.5 Hz, 7-H), 1.73 (1H, d, J=8.8 Hz, 7-H), 2.35 (3H, s, Me), 3.02 (1H, br s, 1-H or 4-H), 3.16 (1H, br s, 4-H or 1-H), 3.35 (1H, br d, J=5.4 Hz, 2-H), 3.89 (1H, dd, J=5.4, 3.7 Hz, 3-H), 6.11 (1H, dd, J=5.6, 2.4 Hz, CH=), 6.40 (1H, dd, J=5.6, 3.2 Hz, CH=), 7.03 (1H, d, J=1.7 Hz, furan), 7.1—7.6 (7H, m, Ph+Tol), 7.43 (1H, d, J=1.7 Hz, furan), 7.73 (2H, d, J=8.3 Hz, Tol). **12a**: ^{1}H-NMR (270 MHz) δ: 1.46 (1H, dd, J=8.6, 1.6 Hz, 7-H), 1.83 (1H, d, J=8.6 Hz, 7-H), 2.34 (3H, s, Me), 3.07 (1H, br s, 1-H or 4-H), 3.17 (1H, br s, 4-H or 1-H), 3.37 (1H, br d, J=5.4 Hz, 2-H), 3.93 (1H, dd, J=5.4, 3.7 Hz, 3-H), 6.09 (1H, dd, J=5.4, 3.1 Hz, CH=), 6.43 (1H, dd, J=5.4, 3.1 Hz, CH=), 7.05 (1H, d, J=2.0 Hz, furan), 7.2—7.8 (10H, m, Ph+Tol+furan).

(1*S*,2*S*,3*R*,4*R*,*S*$_s$)-2-[3-(*p*-Tolylsulfinyl)-2-furoyl]-3-methylbicyclo-[2.2.1]hept-5-ene (**9b**): mp 121—123 °C (AcOEt), $[\alpha]_D^{23}$ −636.4°(c=1, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 1.19 (3H, d, J=7.1 Hz, Me), 1.46 (1H, dd, J=8.7, 1.7 Hz, 7-H), 1.69 (1H, d, J=8.7 Hz, 7-H), 2.1 (1H, m, 3-H), 2.36 (3H, s, Me), 2.54 (1H, br s, 1-H or 4-H), 3.15—3.25 (2H, m, 4-H or 1-H and 2-H), 5.49 (1H, dd, J=5.6, 2.7 Hz, CH=), 6.26 (1H, dd, J=5.6, 3.2 Hz, CH=), 7.05 (1H, d, J=1.8 Hz, furan), 7.24 (2H, d, J=8.2 Hz, Tol), 7.53 (1H, d, J=1.8 Hz, furan), 7.68 (2H, d, J=8.2 Hz, Tol). IR: 3000, 1660, 1540, 1460, 1360, 1060, 1020, 880 cm^{-1}. MS m/z: 340 (M^+), 323, 312, 275, 217, 167. *Anal.* Calcd for $C_{20}H_{20}O_3S$: C, 70.56; H, 5.92. Found: C, 70.32; H, 5.88.

(1*R*,2*R*,3*S*,4*S*,*S*$_s$)-2-[3-(*p*-Tolylsulfinyl)-2-furoyl]-3-methylbicyclo-[2.2.1]hept-5-ene (**10b**): ^{1}H-NMR (270 MHz) δ: 1.14 (3H, d, J=6.8 Hz, Me), 1.51 (1H, dd, J=8.8, 1.7 Hz, 7-H), 1.72 (1H, d, J=8.8 Hz, 7-H), 2.1 (1H, m, 2-H), 2.36 (3H, s, Me), 2.54 (1H, br s, 1-H or 4-H), 3.2 (1H, m, 3-H), 3.29 (1H, br s, 4-H or 1-H), 5.83 (1H, dd, J=5.6, 2.6 Hz, CH=), 6.34 (1H, dd, J=5.6, 3.2 Hz, CH=), 7.06 (1H, d, J=2.0 Hz, furan), 7.24 (2H, d, J=8.3 Hz, Tol), 7.54 (1H, d, J=2.0 Hz, furan), 7.74 (2H, d, J=8.3 Hz, Tol).

(1*R*/1*S*,2*S*/2*R*,3*R*/3*S*,4*S*/4*R*,*S*$_s$)-2-[3-(*p*-Tolylsulfinyl)-2-furoyl]-3-methylbicyclo[2.2.1]hept-5-ene (**11b**) and (**12b**): ^{1}H-NMR (270 MHz) δ: 0.89, 0.94 (total 3H, each d, J=6.6 Hz, Me), 1.43, 1.44 (total 1H, each dd, J=8.8, 1.5 Hz, 7-H), 1.61, 1.65 (total 1H, each d, J= 8.8 Hz, 7-H), 2.37 (3H, s, Me), 2.50 (2H, m, 2-H and 3-H), 2.76 (1H, br s, 1-H or 4-H), 2.87, 2.96 (total 1H, each s, 4-H or 1-H), 6.2—6.4 (2H, m, CH=), 7.06 (1H, d, J=2.0 Hz, furan), 7.26 (2H, d, J=8.3 Hz, Tol), 7.53 (1H, d, J=2.0 Hz, furan), 7.74, 7.75 (total 2H, each d, J=8.3 Hz, Tol).

The ratios of *endo*/*exo* stereoselectivity [(**9b**+**10b**) *vs.* (**11b**+**12b**)] and *exo* diastereoselectivity (**11b** *vs.* **12b**) were determined by HPLC analysis [hexane–EtOAc, 4:1; flow rate, 1 ml·min^{-1}: **11b**, 37.6 min; **12b**, 39.9 min; (**9b**+**10b**), 43.8 min]. Because of unsatisfactory separation of **9b** and **10b** by HPLC, the *endo* diastereoselectivity was estimated from the peak intensities of the olefinic signals, *i.e.* at 5.49 ppm for **9b** and 5.83 ppm for **10b**.

Typical Procedure for Diels–Alder Reaction of 6 with Cyclopentadiene (Entry 6 in Table 3) $Sm(OTf)_3$ (16.5 mg, 0.028 mmol) was added in one portion to a solution of **6** (50 mg, 0.14 mmol) in dry methylene chloride (2 ml) at room temperature. After stirring for 0.5 h, cyclopentadiene (0.3 ml, 3.64 mmol) was then added, and the mixture stirred for 22 h. Saturated NH_4Cl (5 ml) was added and the whole was extracted with chloroform (10 ml × 3). The combined extracts were washed with saturated brine (10 ml), dried, and concentrated. The residue was purified by column chromatography on silica with hexane and then hexane–EtOAc (1:2) to give a mixture of the adducts **16**—**19** (58 mg, 99%). The major adduct **16** was separated by preparative TLC (hexane–EtOAc, 3:1, 5 developments) from the mixture in 73% yield.

(1*S*,2*R*,3*R*,4*R*,*S*$_s$)-2-[3-(*p*-Tolylsulfinyl)-2-thenoyl]-3-phenylbicyclo-[2.2.1]hept-5-ene (**16**): Colorless oil, $[\alpha]_D^{21}$ −491° (c=2.5, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 1.58 (1H, dd, J=8.6, 1.5 Hz, 7-H), 1.94 (1H, d, J=8.6 Hz, 7-H), 2.36 (3H, s, Me), 3.06 (1H, br s, 1-H or 4-H), 3.28 (1H, br s, 4-H or 1-H), 3.32 (1H, d, J=3.3 Hz, 3-H), 3.60 (1H, dd, J=4.8, 3.3 Hz, 2-H), 5.31 (1H, dd, J=5.5, 2.6 Hz, CH=), 6.38 (1H, dd, J=5.5, 3.3 Hz, CH=), 7.1—7.3 (7H, m, Ph+Tol), 7.59 (1H, d, J=5.3 Hz, thiophene), 7.66 (2H, d, J=8.1 Hz, Tol), 7.80 (1H, d, J=5.3 Hz, thiophene). IR: 2980, 1670, 1420, 1080 cm^{-1}. MS m/z: 418 (M^+), 401, 353, 233, 203. HRMS (FAB) Calcd for $C_{25}H_{23}O_2S_2$ ($[M+H]^+$): 419.1139. Found: 419.1126. **17**: ^{1}H-NMR (270 MHz) δ: 1.65 (1H, dd, J=8.8, 1.5 Hz, 7-H), 1.96 (1H, d, J=8.8 Hz, 7-H), 2.34 (3H, s, Me), 3.10 (1H, br s, 1-H or 4-H), 3.35 (1H, d, J=3.5 Hz, 3-H), 3.44 (1H, br s, 4-H

or 1-H), 3.51 (1H, dd, J=4.9 Hz, 3.5 Hz, 2-H), 5.98 (1H, dd, J=5.6, 3.0 Hz, CH=), 6.52 (1H, dd, J=5.6, 3.0 Hz, CH=), 7.1—7.35 (7H, m, Ph+Tol), 7.60 (1H, d, J=5.1 Hz, thiophene), 7.75 (2H, d, J=8.1 Hz, Tol), 7.82 (1H, d, J=5.1 Hz, thiophene).

The minor *endo* product **17** was characterized by ^{1}H-NMR analysis after the following sequence: treatment of the original mixture of adducts (**16** enriched) with Zn–$TiCl_4$ in methylene chloride afforded the corresponding sulfide **20** as the major product in 58% yield. **20**: mp 113—115 °C (hexane), $[\alpha]_D^{24}$ −353° (c=1.1, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 1.65 (1H, dd, J=8.6, 1.7 Hz, 7-H), 1.98 (1H, d, J=8.6 Hz, 7-H), 2.39 (3H, s, Me), 3.10 (1H, br s, 1-H or 4-H), 3.50 (2H, m, 4-H or 1-H and 3-H), 3.69 (1H, dd, J=5.0, 3.5 Hz, 2-H), 6.02 (1H, dd, J=5.6, 2.9 Hz, CH=), 6.36 (1H, d, J=5.3 Hz, thiophene), 6.51 (1H, dd, J=5.6, 3.2 Hz, CH=), 7.22 (2H, d, J=8.0 Hz, Tol), 7.15—7.35 (5H, m, Ph), 7.48 (2H, d, J=8.0 Hz, Tol), 7.80 (1H, d, J=5.3 Hz, thiophene). IR: 3000, 1640, 1480, 1405 cm^{-1}. *Anal.* Calcd for $C_{25}H_{22}OS_2$: C, 74.61; H, 5.51. Found: C, 74.39; H, 5.57. Oxidation of the sulfide **20** with *m*-CPBA gave sulfoxide **16** and *ent*-**17** in a roughly 1:1 ratio in 72% yield as an inseparable mixture by column chromatography. The ^{1}H-NMR spectrum of synthetic *ent*-**17** was used to characterize the adduct **17**. The product ratio of the *exo* adducts **18** and **19** could not be determined by HPLC analysis [hexane–EtOAc, 3:1; flow rate, 1 ml·min^{-1}: (**18**+**19**), 33.6 min; **16**, 38.0 min; **17**, 41.5 min] because of unsatisfactory separation, but was suggested by the peak intensities of the olefinic signals in the ^{1}H-NMR spectrum [6.12 ppm (dd, J=5.6, 2.7 Hz) for **18**, 6.38 ppm (dd, J=5.6, 3.1 Hz) for **19**].

(1*R*,2*R*,3*R*,4*S*,S_s)-2-[3-(*p*-Tolylsulfinyl)-2-furoyl]-3-phenylbicyclo-[2.2.1]heptane (13a) A mixture of **9a** (1.80 g, 4.47 mmol) and 5% Pd on carbon (250 mg) in MeOH (100 ml) was stirred vigorously under a balloon-filled atmosphere of hydrogen for 2 h. The mixture was then filtered with the aid of a short pad of Celite, and the filtrate concentrated to give **13a** (1.75 g, 97%) as a crystalline solid, mp 154 °C (Et_2O), $[\alpha]_D^{24}$ −467° (c=1.0, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 0.8—0.9 (1H, m, 5-H or 6-H), 1.2—1.3 (1H, m, 6-H or 5-H), 1.4—1.6 (3H, m, 6-H or 5-H and 7-H), 1.96 (1H, d, J=9.9 Hz, 7-H), 2.37 (3H, s, Me), 2.53 (1H, d, J=4.0 Hz, 1-H), 2.81 (1H, br s, 4-H), 3.47 (1H, d, J=5.5 Hz, 3-H), 3.64 (1H, ddd, J=5.5, 4.0, 1.5 Hz, 2-H), 7.05 (1H, d, J=1.8 Hz, furan), 7.13—7.30 (7H, m, Ph+Tol), 7.49 (1H, d, J=1.8 Hz, furan), 7.74 (2H, d, J=8.1 Hz, Tol). IR: 3020, 2970, 1660, 1555, 1490, 1465, 1040 cm^{-1}. MS m/z: 404 (M^+), 387, 358, 321, 279, 263, 217. *Anal.* Calcd for $C_{25}H_{24}O_3S$: C, 74.23; H, 5.98. Found: C, 74.33; H, 5.97.

(1*R*,2*R*,3*R*,4*S*,S_s)-2-[3-(*p*-Tolylsulfinyl)-2-furoyl]-3-methylbicyclo-[2.2.1]heptane (13b) Compound **13b** was obtained in 60% yield in a similar manner to the procedure for **13a**, as a crystalline solid, mp 142—143 °C (AcOEt), $[\alpha]_D^{21}$ −467.8° (c=1.0, $CHCl_3$). ^{1}H-NMR (270 MHz) δ: 0.6—0.8 (1H, m), 0.94 (3H, d, J=7.1 Hz, Me), 1.0—1.2 (1H, m), 1.28 (2H, dd+m, J=9.8, 1.5 Hz), 1.40 (1H, m), 1.72 (1H, d, J=9.8 Hz, 7-H), 1.95 (1H, m), 2.2 (1H, m), 2.36 (3H, s, Me), 2.66 (1H, br s), 3.0 (1H, m, 2-H), 7.05 (1H, d, J=1.8 Hz, furan), 7.23 (2H, d, J=8.2 Hz, Tol), 7.51 (1H, d, J=1.8 Hz, furan), 7.72 (2H, d, J=8.2 Hz, Tol). IR: 3000, 1660, 1460, 1380, 1300, 1040, 880 cm^{-1}. MS m/z: 342 (M^+), 325, 309, 275, 235, 217. *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.15; H, 6.47. Found: C, 69.91; H, 6.45.

(1*R*,2*R*,3*R*,4*S*)-3-Phenylbicyclo[2.2.1]heptane-2-carboxylic Acid (14a) A solution of sodium metaperiodate (11.4 g, 53.4 mmol) in H_2O (75 ml) was added to a mixture of **13a** (1.20 g, 2.97 mmol) in CCl_4 (50 ml) and MeCN (50 ml). $RuCl_3\cdot 3H_2O$ (17.1 mg, 0.07 mmol) was then added to the two-phase solution and the mixture was stirred vigorously for 2 h. After dilution with Et_2O (200 ml), the organic phase (upper layer) was separated. The aqueous layer was extracted with Et_2O (150 ml × 3) and the combined extracts washed with saturated brine (300 ml), dried, and concentrated. The residue was purified by column chromatography on silica with $CHCl_3$–MeOH (10:1) to give **14a** (132 mg, 21%) as a solid, mp 97—99 °C [lit.[14] mp 105 °C for racemate, $[\alpha]_D^{25}$ −93.6° (c=1.0, $CHCl_3$]. ^{1}H-NMR (270 MHz) δ: 1.4—1.7 (6H, m, 5-, 6-H and 7-H), 2.51 (1H, d, J=3.2 Hz), 2.73 (1H, br), 2.91 (1H, dd, J=5.6, 4.4 Hz), 3.17 (1H, d, J=5.6 Hz, 2-H), 5.0—6.0 (1H, br, CO_2H), 7.1—7.3 (5H, m, Ph). IR: 3080, 2970, 2890, 1700, 1495, 1445, 1415, 1290 cm^{-1}. MS m/z: 216 (M^+), 170, 131, 125, 115, 91, 67. *Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.57; H, 7.50.

(1*R*,2*S*,3*R*,4*S*)-3-Methylbicyclo[2.2.1]heptane-2-carboxylic Acid (14b) Acid **14b** was obtained in a similar manner to the procedure for **14a**, $[\alpha]_D^{22}$ −43.6° (c=0.5, EtOH) [lit.[15] $[\alpha]_D$ +45.9° (c=5.42, 95% EtOH) for the enantiomer].

Methyl (1*R*,2*R*,3*R*,4*S*)-3-Phenylbicyclo[2.2.1]heptane-2-carboxylate (15) Acid **14a** (20 mg, 0.09 mmol) in MeOH (2 ml) was treated with an excess of ethereal diazomethane at room temperature. The solvents and unreacted diazomethane were evaporated off with caution (with glasswares in which the edge of the ground joints were not broken off) using a rotary evaporator, and the residue was purified by preparative TLC on silica with hexane–EtOAc (20:1) to give **15** (20 mg, 99%) as a colorless oil, $[\alpha]_D^{25}$ −70.5° (c=0.5, $CHCl_3$) for 98% ee determined by chiral HPLC [Chiralcel OD; hexane–2-propanol, 400:1; flow rate, 1.0 ml·min^{-1}; retention time: **15**, 12.2 min; enantiomer of **15**, 14.0 min]. Racemic sample was prepared according to the procedure reported previously.[14]

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References and Notes

1) This paper is dedicated to the late Professor Toru Koizumi (Toyama Medical & Pharmaceutical University, deceased on January 12, 1998).
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