# Benzyl Methyl (*S*)-2-(*p*-Tolylsulfinyl)maleate, an Efficient Dienophile in Asymmetric Diels–Alder Reactions

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The enantiomerically pure dienophile **3** [1-benzyl 4-methyl (*S*)-(*p*-tolylsulfinyl)maleate] was readily prepared in a three-step sequence from benzyl acetate and (−)-(*S*)-menthyl *p*-toluenesulfinate (46% overall yield). This vinyl sulfoxide reacted in high yields and with very high regioselectivities and stereoselectivities with a wide variety of 1,3-dienes (10 examples) at low temperature in the presence of $Eu(fod)_3$ or $TiCl_4$. Whereas cycloadditions catalyzed by $TiCl_4$ (usually carried out at −78 °C) occurred with complete regioselectivity, *endo* selectivity, and π-facial selectivity, the cycloaddition catalyzed by $Eu(fod)_3$ (usually performed at 0 °C) also occurred with very high regioselectivity and π-facial selectivity, but with low *endo* selectivity. Interestingly, all the adducts (excepting the adducts from cyclopentadiene) are unstable at room temperature, undergoing spontaneous sulfinyl elimination to give 1,3-cyclohexadienes **7** and/or 1,4-cyclohexadienes **11**, in excellent yields. Regardless of the catalyst, compounds **7** showed a very high optical purity (ee ≥ 96%). Finally, some models based on the conformational equilibrium of vinyl sulfoxide **3** have been proposed to explain the observed stereoselectivities.

## Introduction

During the past decade, the asymmetric Diels–Alder reaction has become one of the most powerful tools in asymmetric synthesis[1] due to its capacity of creating up to four chiral centers in one step and in a highly stereoselective manner. Although high stereochemical control has been achieved by the use of chiral dienophiles, chiral dienes, or chiral Lewis acids, the vast majority of work on asymmetric Diels–Alder reactions deals with the use of chiral dienophiles because they usually show higher and more predictable facial stereoselectivities. In this context, the ability of the sulfinyl group to control the π-facial selectivity in the asymmetric Diels–Alder reaction has provided the impetus for the use of enantiomerically pure α,β-unsaturated sulfoxides as dienophiles. In order to take advantage of this ability, it is essential that the vinyl sulfoxide possesses another electron-withdrawing functional group at the double bond,[2] which will have the property of both increasing its dienophilic reactivity and restricting the conformational mobility around the C–S bond. In this sense, the pioneering studies with enantiomerically pure α-sulfinylacrylates from the Koizumi,[3] De Lucchi,[4] and Maignan[5] groups are very significant. Asymmetric Diels–Alder reactions with α-sulfinyl enones[6] and β-nitro-α,β-unsaturated sulfoxides[7] have also been reported. Usually, despite the second electron-withdrawing group at the double bond, the reactivity of these vinyl sulfoxides is rather moderate, and this is probably the reason which justifies that the majority of the published studies deal only with the use of cyclopentadiene as diene. In order to overcome this important limitation, and to obtain dienophiles which are able to react with other dienes, mainly with acyclic dienes of low reactivity, the 2-sulfinylmaleates emerge as one of the most obvious substrates because they have an additional electron-withdrawing group at the double bond.[8] Additionally, these dienophiles could act as interesting chiral equivalents of acetylenedicarboxylate esters in Diels–Alder reactions. In this sense, the reactions of dienophiles **1** (R = isobornyl)[9] and **2** (**2A**: R = $^t$Bu, R′ = H; **2B**: R = $^t$Bu, R′ = Me; **2C**: R = H, R′ = Me)[10] with cyclopentadiene have been reported, the best results being obtained from **2B**[10b] (Figure 1). Nevertheless, after studying the reaction of **2B** with acyclic dienes, some problems related to the stability of the $CO_2{}^t$Bu group in the presence of Lewis acids used as catalysts led us to change the protective group. In a recent preliminary paper we described that the enantiomerically pure α,β-unsaturated sulfoxide **3**, possessing a benzyl ester instead of a *tert*-butyl one, reacted in the presence of $TiCl_4$ with several acyclic dienes in a very highly regio-, *endo*-, and π-facial selective manner.[11] In addition to the

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(1) (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876. (b) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Ibid.* **1985**, *24*, 1. (c) Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods*; Sheffold, R., Ed.; Springer-Verlag: Berlin, Heidelberg, 1986; Vol. 4, p 262. (d) Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **1987**, *70*, 436. (e) Kagan, H. B.; Riant, O. *Chem. Rev.* **1992**, *92*, 1007.

(2) Kagan has recently reported that vinyl sulfoxides can be efficiently activated to achieve highly stereoselective Diels–Alder reactions by transformation into their alkoxysulfonium salts (Ronan, B.; Kagan H. B. *Tetrahedron: Asymmetry* **1991**, *2*, 75).

(3) (a) Takahashi, T.; Kotsubo, H.; Koizumi, T. *Tetrahedron: Asymmetry* **1991**, *2*, 1035. (b) Takahashi, T.; Kotsubo, H.; Iyobe, A.; Namiki, T.; Koizumi, T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3065. (c) Arai, Y.; Takadoi, M.; Koizumi, T. *Chem. Pharm. Bull.* **1988**, *36*, 4162. (d) Koizumi, T.; Arai, Y.; Takayama, H. *Tetrahedron Lett.* **1987**, *28*, 3689. (e) Takayama, H.; Hayashi, K.; Koizumi, T. *Tetrahedron Lett.*, **1986**, *27*, 5509. (f) Arai, Y.; Kuwayama, S-I.; Takeuchi, Y.; Koizumi, T. *Tetrahedron Lett.* **1985**, *26*, 6205. (g) Koizumi, T.; Hakamada, I.; Yoshii, E. *Tetrahedron Lett.* **1984**, *25*, 87.

(4) (a) De Lucchi, O. *Tetrahedron Lett.* **1987**, *28*, 107. (b) De Lucchi, O.; Lucchini, V.; Marchioro, C.; Valle, G.; Modena, G. *J. Org. Chem.* **1986**, *51*, 1457.

(5) Maignan, C.; Guessous, A.; Rouessac, F. *Tetrahedron Lett.* **1984**, *25*, 1727.

(6) (a) Alonso, I.; Carretero, J. C.; García Ruano, J. L. *Tetrahedron Lett.* **1989**, *30*, 3853. (b) Maignan, C.; Guessous, A.; Rouessac, F. *Tetrahedron Lett.* **1986**, *27*, 2603.

(7) Fuji, K.; Tanaka, K.; Abe, H; Itoh, A.; Node, M.; Taga, T.; Miwa, Y.; Shiro, M. *Tetrahedron: Asymmetry* **1991**, *2*, 179.

(8) The use of α-sulfinyl maleimides (Arai, Y.; Matsui, M.; Koizumi, T.; Shiro, M. *J. Org. Chem.* **1991**, *56*, 1983) and of 2-sulfinylquinones (Carreño, M. C.; García Ruano, J. L.; Urbano, A. *Tetrahedron Lett.* **1989**, *30*, 4003) as dienophiles in asymmetric Diels–Alder reaction has also been reported.

(9) Arai, Y.; Hayashi, K.; Koizumi, T.; Shiro, M.; Kuriyama, K. *Tetrahedron Lett.* **1988**, *29*, 6143.

(10) (a) Alonso, I.; Carretero, J. C.; García Ruano, J. L. *Tetrahedron Lett.* **1991**, *32*, 947. (b) Alonso, I.; Cid, M. B.; Carretero, J. C.; García Ruano, J. L.; Hoyos, M. A. *Tetrahedron: Asymmetry* **1991**, *2*, 1193.

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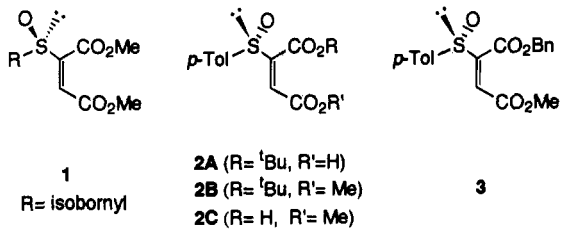


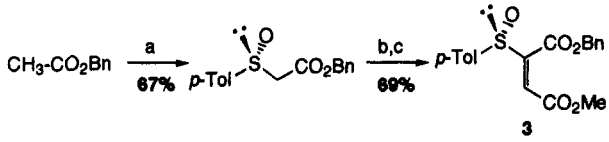

1
R= isobornyl

2A (R= tBu, R'=H)
2B (R= tBu, R'= Me)
2C (R= H, R'= Me)

3

**Figure 1.**

**Scheme 1**[a]




3

[a]Key: (a) $BrMgN^iPr_2$/(*S*)-*p*-Tol-$SO_2$ menthyl/ether (1 h, 0 °C); (b) $CHOCO_2H{\cdot}H_2O/Et_3N$/pyrrolidine/DMF (5 h, 0 °C); (c) $NaHCO_3$/MeI/DMF (2 h, rt).

detailed description of this piece of work, in this paper we report the effect of different Lewis acids and propose stereochemical models to rationalize the observed stereoselectivities. Moreover, we also report the results obtained with cyclic dienes in order to extend the scope of dienophile **3** and to check our mechanistic proposals.

## Results and Discussion

**Synthesis of the Dienophile.** The synthesis of 1-benzyl 4-methyl (*S*)-2-*p*-tolylsulfinyl maleate (**3**) was carried out as shown in Scheme 1, following a synthetic sequence identical to that used for the synthesis of **2B**.[10b] The Andersen reaction of the magnesium enolate of benzyl acetate with (−)-(*S*)-menthyl *p*-toluenesulfinate[12] in ether at 0 °C gave (*R*)-benzyl *p*-tolylsulfinylacetate in 67% yield, whose Knoevenagel condensation with glyoxylic acid in DMF at 0 °C, in the presence of pyrrolidine (0.35 equiv), followed by methylation with MeI afforded stereoselectively the maleate **3** in 69% yield after chromatography. The overall yield in the preparation of **3** from benzyl acetate was 46% and its enantiomeric purity, determined by $^1H$ NMR by using Yb(hfc)$_3$, was higher than 96%.[13]

**Reactions with Cyclic Dienes.** We have studied the reactions of dienophile **3** with an excess of cyclopentadiene (diene **a**) and cyclohexadiene (diene **b**). In the first case we have carried out the reaction in the presence of a wide variety of Lewis acids.[14] The best results, achieved with $ZnBr_2$, Eu(fod)$_3$, and $TiCl_4$ as catalysts and $CH_2Cl_2$ as solvent, are collected in Table 1 (for comparative purposes the results obtained in the reactions with dienophile **2B**[10b] are also included). All the cycloadditions afforded mixtures of three adducts (*endo*-**4a** + *endo*-**4'a** + *exo*-**4a**) which were purified by chromatography.[15] It should be pointed out that all these reactions yielded only one *exo* adduct (*exo*-**4a**) regardless of the catalyst used, whereas the two possible *endo* adducts were obtained, their ratio being very dependent on the catalyst.

From a thorough comparison of the results shown in Table 1, it can be deduced that **3** is a better dienophile than **2B**, although both dienophiles (**3** and **2B**) show similar behavior. The reactivity of **3** is slightly higher than that of **2B** (lower reaction times are required to get similar or better yields). Additionally, both the $\pi$-facial selectivity for the *endo* approach and the *endo* selectivity (see footnotes *c* and *d* in Table 1) are also higher with dienophile **3**. Finally, **3** is much more stable than **2B** in the presence of highly electrophilic Lewis acids such as $TiCl_4$. Thus, in the conditions reported in entry 3, a partial hydrolysis of the $CO_2{}^tBu$ group was observed (17% of *endo* + *exo* adducts with the free COOH group was isolated in the reaction from **2B**). This higher stability of **3** allowed us to increase the amount of $ZnBr_2$ (1.8 equiv, entry 5) which improved the results obtained in the standard conditions (1.2 equiv, entry 4).

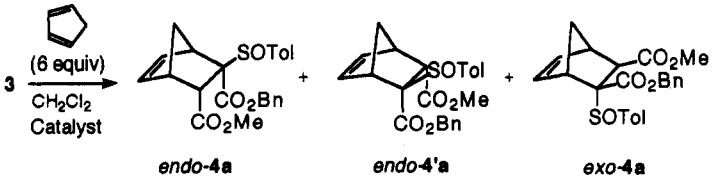
As the most significant finding of this new study, $TiCl_4$ seems to be a much more efficient catalyst than any other previously used for these reactions. In its presence (entry 3), the reactions are faster, allowing the use of lower temperatures (−78 °C), and the $\pi$-facial selectivity is similar to that observed with Eu(fod)$_3$ (adduct *endo*-**4a** is the major one, entries 2 and 3) but opposite to the $\pi$-facial selectivity observed with $ZnBr_2$ (which favors *endo*-**4'a**, entries 4 and 5). Additionally, the *endo* selectivity is as high as that observed from $ZnBr_2$ (entries 3–5), which contrasts with the low *endo* selectivity obtained in reactions catalyzed by Eu(fod)$_3$ (entry 2).

The $^1H$ NMR spectra of adducts **4a** are almost identical to those derived from **2B** and cyclopentadiene, the stereochemical assignment of which was unambiguously established by chemical correlations and X-ray analysis.[10b] Moreover, the pyrolytic elimination of the sulfinyl group from *endo*-**4a** (DBU, toluene, 70 °C) afforded the previously reported norbornadiene (−)-**5a**,[16] whereas its enantiomer (+)-**5a** was obtained from the adducts *endo*-**4'a** or *exo*-**4a**. These facts enabled us to make their configurational assignments as indicated in Scheme 2. It should be remarked that this two-step sequence (**3** + **a** → **4a** → **5a**) to get the enantioselective synthesis of compound **5a** (which is a key intermediate in the synthesis of the carbocyclic nucleosides neplanocin A and arysteromycin[17]) is shorter than that previously reported starting from dienophile **1** (Figure 1), which requires two additional steps in order to avoid symmetrization.[9]

The reactivity of cyclohexadiene was much lower than that observed with cyclopentadiene (Table 2). Thus, the Diels–Alder reactions only took place in the presence of Eu(fod)$_3$ or $TiCl_4$, the reaction catalyzed by $ZnBr_2$ (entry 2) and the noncatalyzed reaction (entry 1) being unsuccessful. In the presence of Eu(fod)$_3$ (entry 3), 7 days at room temperature were necessary to obtain **5b** (44% yield) resulting from the spontaneous pyrolytic elimination of the sulfinyl group from the adducts **4b**. This adduct could not be detected by NMR, even after the reaction was stopped before completion, which demonstrates that its thermal stability must be lower than that of the corresponding cyclopentadiene adducts **4a**. In agreement with

(11) Alonso, I.; Carretero, J. C.; García Ruano J. L. *J. Org. Chem.* **1993**, *58*, 3231.
(12) Solladié, G. *Synthesis* **1981**, 185.
(13) The racemic dienophile (±)-**3**, necessary for the $^1H$ NMR studies in the presence of chiral shift reagents, was prepared in 44% overall yield following the same synthetic sequence shown in Scheme 1 by using (±)-methyl *p*-toluenesulfinate instead of (−)-(*S*)-menthyl *p*-toluenesulfinate.
(14) $ZnBr_2$, $ZnI_2$, $LiClO_4$, $EtAlCl_2$, $BF_3OEt_2$, $MgBr_2OEt_2$, $SiO_2$, and $TiCl_4$ were used as catalysts.
(15) During the chromatographic purification, compound *exo*-**4a** was easily separated from the mixture of adducts. However, the separation of *endo*-**4a** + *endo*-**4'a** was not possible in our hands.
(16) Lit $[\alpha]_D$ for (−)-**5** = −10.6, see: Arai, Y.; Hayashi, K.; Matsui, M.; Koizumi, T.; Shiro, M.; Kuriyama, K. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1709. From a 86/14 mixture of *endo*-**4a**/*endo*-**4'a** was obtained norbornadiene (−)-**5** with ee = 66% ($[\alpha]_D$ = -7.0). On the other hand, from *exo*-**4a** was obtained (+)-**5** with ee ≥ 96% ($[\alpha]_D$ = -10.3)
(17) Borthwick, A. D.; Biggadike, K. *Tetrahedron* **1992**, *48*, 571.

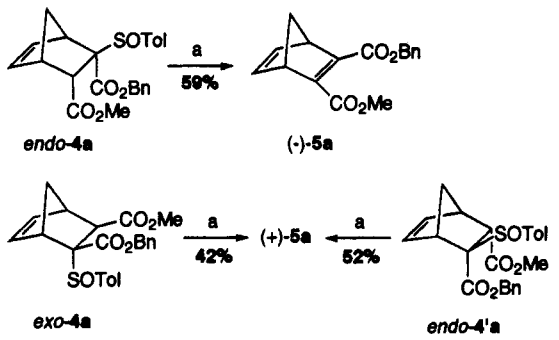
**Table 1. Diels–Alder Reactions of Dienophiles 3 and 2B (Values in Parentheses)[10b] with Cyclopentadiene**




| | | | | | product ratios[a] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| entry | catalyst | equiv | $T$ (°C) | $t$ (h) | *endo*-4a | *endo*-4'a | *c* | *exo*-4a | *d* | yield[b] (%) |
| 1 | | | rt | 10 (41) | 73 | 8 | 9.1 (6.6) | 19 | 4.3 (3.2) | 93 (93) |
| 2 | $Eu(fod)_3$ | 1.2 | −20 | 2 (12) | 66 | 3 | 22.0 (15.0) | 31 | 2.2 (1.7) | 100 (81) |
| 3 | $TiCl_4$ | 1.2 | −78 | 2 (6)[e] | 83 (65)[e] | 13 (13)[e] | 6.4 (5.0)[e] | 4 (22)[e] | 24 (3.5)[e] | 84 (70)[e] |
| 4 | $ZnBr_2$ | 1.2 | −20 | 6 (7) | 7 | 88 | 0.08 (0.07) | 5 | 19 (19) | 95 (95) |
| 5 | $ZnBr_2$ | 1.8 | −20 | 5 | 6 | 91 | 0.07 | 3 | 32.3 | 96 |

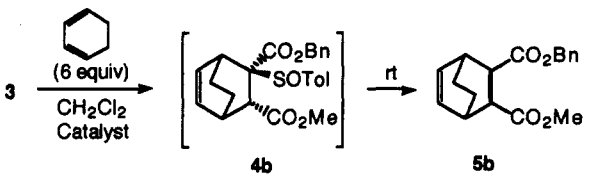
[a] Determined by $^1H$ NMR. [b] In pure adducts after chromatographic purification. [c] *endo*-4a/*endo*-4'a ratio ($\pi$-facial selectivity). [d] *Endo*/*exo* ratio (*endo* selectivity). [e] Data not included in ref 10b.

**Scheme 2[a]**




[a] Key: (a) DBU, toluene, 70 °C.

**Table 2. Diels–Alder Reactions of Compounds 3 with Cyclohexadiene**




| | cycloaddition condns | | | | |
|---|---|---|---|---|---|
| entry | catalyst (1.2 equiv) | $T$ (°C) | $t$ (days) | yield[a] (%) | ee (%) |
| 1 | | rt | 7 | | |
| 2 | $ZnBr_2$ | rt | 7 | <10 | |
| 3 | $Eu(fod)_3$ | rt | 7 | 44 | <5 |
| 4 | $TiCl_4$ | −20 | 1 | 90[b] | >90 |

[a] Pure **5b** after chromatography. [b] After the cycloaddition, the crude mixture was allowed to stand at rt for 24 h.

the higher efficiency of $TiCl_4$ as a catalyst, when the reaction was carried out in the presence of 1.2 equiv of $TiCl_4$ at −20 °C (entry 4), after 24 h and a careful work up at 0 °C, only one adduct **4b** could be characterized from the $^1H$ NMR spectrum of the reaction mixture.[18] Compound **5b** was isolated in 90% yield after 24 h at room temperature.

The optical purity of **5b** depends on the catalyst. Thus, the enantiomeric excess of the sample obtained in the presence of $Eu(fod)_3$ is lower than 5% [evaluated by the use of the chiral shift reagents $Pr(hfc)_3$ and $Yb(hfc)_3$], whereas its value became higher than 90% for the sample obtained in the reaction catalyzed by $TiCl_4$.[19] Taking into account the high *endo*- and $\pi$-facial selectivities observed in the reaction of dienophile **3** with cyclopentadiene in the presence of $TiCl_4$ (entry 3, Table 1) and that the pyrolytic eliminations from **4b** must be similar to those depicted in Scheme 2 for **4a**, the high optical purity of **5b** obtained in the presence of $TiCl_4$ suggests that the cycloaddition with cyclohexadiene occurred with almost complete $\pi$-facial and *endo* selectivities, resulting in the formation of only one adduct *endo*-**4b**, which agrees with the presence of only one adduct in the NMR spectra of the crude mixture.[18] On the contrary, in the reactions conducted under $Eu(fod)_3$ catalysis, the low ee of **5b** suggests a strong decrease of the *endo* selectivity or of the $\pi$-facial selectivity.

**Reactions with Acyclic Dienes. (a) Butadiene and 2-Substituted Dienes.** The results obtained in reactions of **3** with butadiene and some 2-substituted dienes are collected in Table 3. As in the case of cyclohexadiene, the cycloadditions required the use of $Eu(fod)_3$ or $TiCl_4$ as catalysts[20] and the corresponding adducts (**6**) were not stable, undergoing spontaneous sulfinyl elimination[21] at room temperature to give exclusively 1,3-cyclohexadienes **7**. From the $^1H$ NMR spectra of the crude mixtures isolated just after dienophile **3** had completely disappeared, the signals corresponding to the adducts **6c–6f** could be recognized. These spectra reveal that only one adduct was formed in each case. Adducts **6** totally evolve into cyclohexadienes **7** on standing 48 h in $CH_2Cl_2$ solution at room temperature. Thus, compounds **7c-7f** were obtained in excellent overall yield from **3** after silica gel chromatography (usually 80–90%).

The very high optical purity of compounds **7c** and **7d** (ee ≥ 96%) evidences that butadiene and 2,3-dimethylbutadiene react with total $\pi$-facial selectivity regardless of the catalyst used.[22] The same conclusion can be deduced from the reaction of **3** with isoprene, which also yields

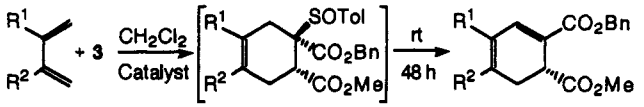
(18) The NMR spectrum of the crude Diels–Alder reaction after 24 h shows the signals corresponding to only one adduct, **4b**, and those of the diene **5b** which initially appears in very low proportion but slowly increases at rt.

(19) We could not obtain a more precise value for the ee of this sample of **5b** due to the small separation of the signals of both enantiomers in the presence of the chiral shift reagent. Nevertheless, the fact that only one adduct was observed in the $^1H$ NMR spectrum of the crude mixture after cycloaddition suggests that its optical purity should be higher than 96%.[18]

(20) Despite the interesting effect of $ZnBr_2$ on the $\pi$-facial and *endo* selectivities in the reactions with cyclopentadiene, its influence on the reactivity of **3** is very low. Thus, with acyclic dienes (as well as with cyclohexadiene) cyclohexadienes **7** have been isolated in yields ≤20% after 7 days at rt. Longer reaction times did not improve the yields due to diene polymerization.

(21) Spontaneous elimination of sulfenic acid to give 1,3-cyclohexadienes has also been observed in the Diels–Alder reaction of acyclic dienes with racemic $\alpha$-phenylsulfinyl $\alpha,\beta$-unsaturated ketones (Alexandre, C.; Belkadi, O.; Maignan, C. *J. Chem. Res. (Synop.)* **1992**, 48).

**Table 3. Diels–Alder Reactions of 3 with Butadiene and 2-Substituted Dienes**




c ($R^1$= $R^2$= H) 6 7
d ($R^1$= $R^2$= Me)
e ($R^1$= H, $R^2$= Me)
f ($R^1$= H, $R^2$= OMe)

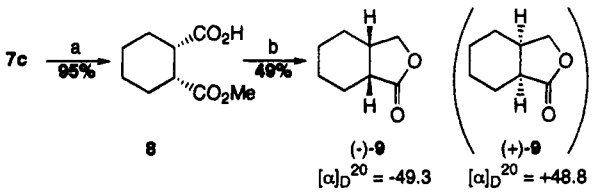
| | | cycloaddition condns | | | | | |
|---|---|---|---|---|---|---|---|
| entry | diene[a] | catalyst (1.2 equiv) | T (°C) | t (h) | product | yield[b] (%) | ee[c] (%) |
| 1 | c | $Eu(fod)_3$ | 0 | 48 | 7 c | 91 | ≥96 |
| 2 | c | $TiCl_4$ | −78 | 90 | 7 c | 83 | ≥96 |
| 3 | d | $Eu(fod)_3$ | 0 | 72 | 7 d | 83 | ≥96 |
| 4 | d | $TiCl_4$ | −78 | 28 | 7 d | 66 | ≥96 |
| 5 | e | $Eu(fod)_3$ | 0 | 72 | 7 e | 86 | ≥96 |
| 6 | e | $TiCl_4$ | −78 | 28 | 7 e | 91 | ≥96 |
| 7 | f | $Eu(fod)_3$ | 0 | 96 | 7f[d] | 87 | 83 |
| 8 | f | $TiCl_4$ | −78 | 28 | 7 f | | e |

[a] 6.0–10.0 equiv of diene was used. [b] After silica gel chromatography. [c] Determined by $^1H$ NMR by using 0.1–0.3 equiv of $Pr(hfc)_3$[23]. [d] Sulfinyl elimination required 96 h at rt. [e] The diene polymerizes under these conditions.

only one enantiomerically pure cyclohexadiene (**7e**). This result also indicates that the regioselectivity of the cycloaddition is complete, being totally controlled by the sulfinyl group. Finally, the reactions of **3** with 2-methoxy-1,3-butadiene are less satisfactory. As $TiCl_4$ is not a suitable catalyst, because of decomposition of the diene even at −78 °C, only $Eu(fod)_3$ could be used. Under the standard conditions (1.2 equiv of catalyst), the ee of the resulting cyclohexadiene **7f** was lower (ee = 83%, entry 7)[23] than that observed with the other dienes. The incomplete association of the catalyst with the sulfinyl group, due to its coordination with the OMe group, which decreases its effective concentration,[24] and the partial isomerization of the dienophile, as a result of the long reaction time required to get high yields of **7f**,[25] have been invoked to explain the decrease of the optical purity.

The structure and stereochemistry of the adducts **6** have been inferred from those of their respective elimination products **7**, whose absolute configuration was unequivocally determined in the case of compound **7c**, obtained from 1,3-butadiene. **7c** was chemically correlated with the known enantiomerically pure lactone **9**[26] (Scheme 3). The exhaustive hydrogenation of **7c** ($H_2$, $PtO_2$, AcOEt) gave stereoselectively the *cis* carboxylic acid **8** (95% yield). This compound reacted smoothly with $BH_3SMe_2$ at 0 °C in THF, leading to the formation of lactone (−)-**9** whose optical rotation was identical ($[\alpha]^{20}_D$ = −49.3 (*c* = 0.48, $CHCl_3$)) but with opposite sign to that reported in the literature[26] for lactone (+)-**9** ($[\alpha]^{20}_D$ = +48.8 (*c* = 0.5, $CHCl_3$)). Therefore, **7c** has the (*R*)-configuration.

**Scheme 3[a]**




[a] Key: (a) $PtO_2/H_2$, AcOEt (24 h, rt); (b) $BH_3$·$SMe_2$, THF (48 h, 0 °C).

Although the absolute configurations of **7d**, **7e**, and **7f** have not been unequivocally established, from a mechanistic point of view, the same $\pi$-facial selectivity can be expected for the cycloadditions of dienophile **3** with all the studied dienes, which suggests that all cyclohexadienes **7c–7f** are configurationally homogeneous [all of them with (*R*)-configuration].

**(b) 1-Substituted Dienes.** These dienes allowed us to study the *endo* selectivity of **3** in its cycloadditions with acyclic dienes. The most significant results are shown in Table 4.

As in the case of 2-substituted dienes, the resulting adducts **10** were not stable at room temperature, undergoing a spontaneous elimination of the chiral auxiliary (sulfinyl group). However, when the crude mixtures isolated after the cycloadditions were immediately analyzed by $^1H$ NMR, only one adduct **10** (together with a small amount of cyclohexadienes **7** and **11**) was detected in the reactions catalyzed by $TiCl_4$, whereas two adducts **10** were observed in those conducted under $Eu(fod)_3$. With respect to the sulfinyl elimination, compounds **10** usually evolved in a less regioselective way than that observed in adducts **6** derived from 2-substituted dienes, giving a mixture of the two possible elimination products, 1,3-cyclohexadienes **7** and 1,4-cyclohexadienes **11**,[27] readily separated by silica gel chromatography. Whereas conjugated cyclohexadiene **7g** is predominant starting from *trans,trans*-2,4-hexadiene (entries 1 and 2), the nonconjugated diene **11h** is the major regioisomer in the reactions of **3** with piperylene (entries 3 and 4). In the absence of catalysts the reaction of **3** with 1-methoxybutadiene (40

(22) Elimination of the sulfinyl group from each of the adducts **6** resulting from the approach of the dienes from each face of dienophile **3** would yield a different enantiomer **7**. Therefore, the $\pi$-facial selectivity is parallel to the ee of the isolated cyclohexadiene.

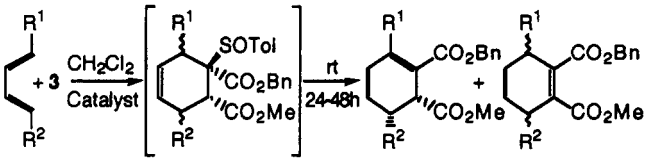
(23) In order to evaluate the optical purity, racemic samples of (±)-**7** and (±)-**11**, prepared from (±)-**3**,[18] were previously studied in the presence of chiral shift reagents.

(24) When 2 equiv of $Eu(fod)_3$ was used, the ee of **7f** increased up to 87%.

(25) A slow isomerization of dienophile **3** into a mixture of both *E*/*Z* geometric isomers has been observed at room temperature in the presence of $Eu(fod)_3$. Thus, a $CH_2Cl_2$ solution of **3** containing 1.2 equiv of $Eu(fod)_3$ evolved into a 56:44 mixture of (*E*)-**3**/(*Z*)-**3** in 96 h. At 0 °C, the isomerization is much slower (a 97:3 mixture of *E*/*Z* isomers was observed after standing at 0 °C for 14 days). This isomerization precludes the use of higher temperatures in the reactions of **3**. For instance, the ee of a sample of **7d** obtained at room temperature in the presence of $Eu(fod)_3$ was only 86%.

(26) (a) Toone, E. J.; Jones, J. B. *Tetrahedron: Asymmetry* **1991**, *2*, 207. (b) Jakovac, I. J.; Goodbrand, H. B.; Lok, K. P.; Jones, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 4659.

**Table 4. Diels–Alder Reactions of 3 with 1-Substituted Dienes**




**g** ($R^1$= $R^2$= Me) **10** **7** **11**
**h** ($R^1$= Me; $R^2$= H)
**i** ($R^1$= OMe; $R^2$= H)

| | | cycloaddition condns | | | product 7 | product 11 |
|---|---|---|---|---|---|---|
| entry | diene[a] | catalyst (1.2 equiv) | T (°C) | t (h) | yield (%)[b]; ee[c] (%) | yield[b] (%); ee[c] (%) |
| 1 | **g** | $Eu(fod)_3$ | 0 | 24 | 54; ≥96 | 31; *d* |
| 2 | **g** | $TiCl_4$ | −78 | 22 | 64; ≥96 | 27; *d* |
| 3 | **h** | $Eu(fod)_3$ | 0 | 144 | 25; ≥96 | 59; 38 |
| 4 | **h** | $TiCl_4$ | −78 | 24 | 31; ≥96 | 41; ≥96 |
| 5 | **i** | | 40 | 72 | *e* | *e* |
| 6 | **i** | $Eu(fod)_3$ | 0 | 3 | *f* | 67; ≥96 |
| 7 | **i** | $TiCl_4$ | −78 | 24 | *g* | *g* |

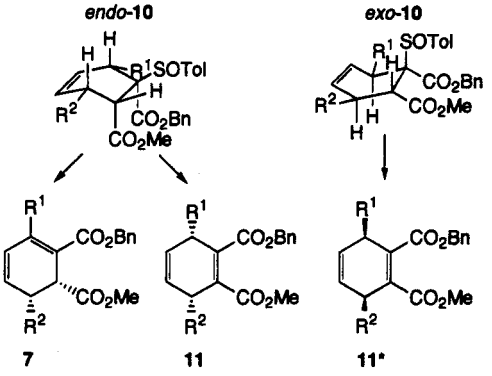
[a] 6.0 equiv of diene was used. [b] After chromatographic purification. [c] Determined by $^1H$ NMR by using 0.1–0.3 equiv of $Pr(hfc)_3$. [d] The ee could not be determined (see text). [e] Benzyl methyl phthalate was isolated in 80% yield. [f] The adduct **10i** (23%) was also isolated. [g] The diene polymerizes in these conditions.

°C, 3 days) afforded the aromatic diester benzyl methyl phthalate in 80% yield (entry 5), as a result of the further eliminations of the sulfinyl and methoxy groups in the adduct **10i**. The use of $TiCl_4$ as a catalyst was unsuccessful due to diene polymerization (entry 7). The best results were obtained under $Eu(fod)_3$ catalysis at 0 °C. Compounds *endo*-**10i**, *exo*-**10i**, and **11i** were identified by $^1H$ NMR analysis of the reaction mixture isolated after 3 h at 0 °C, which upon standing 2 h at 30 °C ($CH_2Cl_2$ solution) was transformed into a mixture of *exo*-**10i** (23%) and **11i** (67%)[28] (entry 6). It is interesting to note that the thermal stability of the adduct *exo*-**10i** is even larger than that of the cyclohexadiene **11i**.[29] Concerning the regioselectivity of the cycloaddition, as in the case of isoprene or 2-methoxybutadiene, the results obtained from piperylene and 1-methoxy butadiene indicate that these reactions are completely regioselective, affording the expected "ortho" adducts.

An interesting finding concerns the optical purity of cyclohexadienes **7** and **11**. The ee of 1,3-cyclohexadienes **7** are higher than 96% regardless of the catalyst used, whereas those of 1,4-cyclohexadienes **11** seem to be dependent on the catalyst. Thus, **11h** is optically pure when it is obtained in the presence of $TiCl_4$, but its ee is only 38% (entry 3) with $Eu(fod)_3$. A similar situation has been observed in the reactions with cyclohexadiene (Table 2).

These results can be readily explained by assuming that the sulfinyl group completely controls the π-facial selectivity in the approaches of acyclic dienes. Therefore, only one face of the dienophile is accesible to the diene, which results in the formation of only one *endo* and only one *exo* adduct (see Scheme 4). The *syn* character of the elimination of the sulfinyl moiety determines that the adducts *endo*-**10** can evolve into a mixture of the 1,3- and the 1,4-cyclohexadienes (**7** and **11**), whose ratio could be regulated by their relative stability, whereas the adducts *exo*-**10**

**Scheme 4**




would evolve only into 1,4-cyclohexadienes **11***, which are the enantiomers of **11**. This evolution justifies the high optical purity of all 1,3-cyclohexadienes **7** (they can only derive from adducts *endo*-**10**), and it associates the optical purity of the 1,4-cyclohexadienes **11** to the *endo* selectivity of the cycloadditions (each enantiomer **11** comes from an *endo* or an *exo* adduct), which is controlled by the catalyst. Thus, the high optical purity of the cyclohexadienes obtained with $TiCl_4$ suggests a complete *endo* selectivity in these reactions, whereas the moderate ee of the cyclohexadienes **11** obtained in the presence of $Eu(fod)_3$ indicates that mixtures of *endo* and *exo* adducts must be formed. This behavior is similar to that observed in reactions with cyclopentadiene (Table 1) and cyclohexadiene (Table 2).

The fact that **11i** exhibits an ee higher than 96% despite being obtained under $Eu(fod)_3$ catalysis (entry 6, Table 4) indicates that it must derive from only one of the adducts (*endo*-**10i** or *exo*-**10i**). The other adduct is stable under the reaction conditions, and it has been purified by chromatography (23% yield). Although it was not possible to establish the stereochemistry of this adduct by NMR

(27) It is remarkable that cyclohexadienes **7** and **11** described in this paper can be stored unaltered for months in the refrigerator (at −20°C). **11i** is the compound that more easily evolves into its aromatization product, and therefore its isolation and purification must be quickly carried out at low temperature.

(28) Compound *endo*-**10i** completely evolved into **11i**, whereas *exo*-**10i** was recovered in these conditions. The yields were calculated after silica gel chromatography at low temperature (~0 °C).

(29) **11i** was quantitatively transformed into the aromatic diester benzyl, methyl phthalate on standing for 24 h at room temperature (it must be stored under −40 °C to avoid the spontaneous elimination of MeOH). By contrast, *exo*-**10i** is only slighly altered in these conditions but it also evolves into the aromatic diester by increasing the reaction times or the temperatures. The isolation or characterization of the cyclohexadiene intermediate involved in this transformation was not possible in our hands.

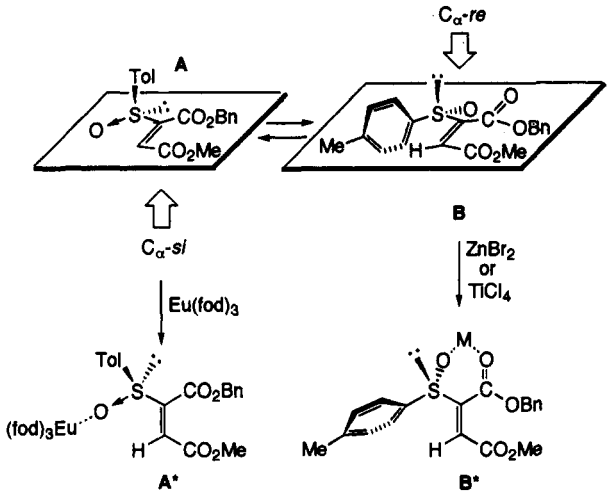



**Figure 2.** Reactive conformations of dienophile 3 depending on the catalyst.

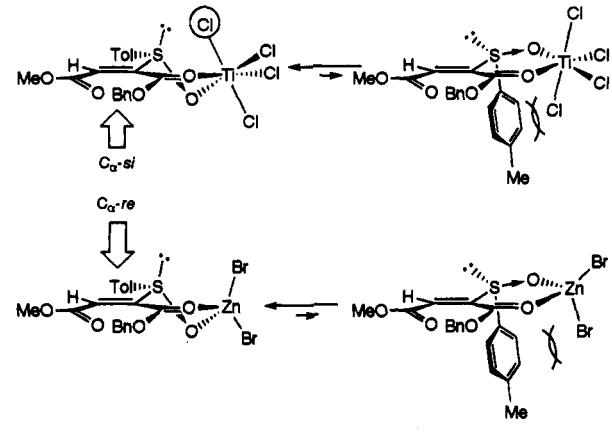



**Figure 3.** Spatial arrangement of substituents in chelated conformations.

analysis, there are several indirect proofs which allowed us to make this assignment. Thus, the fact that **11i** was obtained in 67% yield demonstrates that it derives from the major adduct which presumably must be *endo*-**10i**, because all these Diels–Alder reactions have been shown to be *endo* selective. On the other hand, both the sign of the specific rotations for **11i** and **11h** and the relative positions of their signals in the spectra of racemic samples recorded in the presence of $Pr(hfc)_3$ are identical.[23] Taking into account that **11i** and **11h** only differ in the substituent at C-3 (Me or OMe), these facts suggest the same configuration for both compounds.

**Stereochemistry of the Cycloadditions.** The stereochemical results obtained in these reactions can be summarized as follows: (a) Acyclic dienes and cyclohexadiene react with complete $\pi$-facial selectivity regardless of the catalyst used. The *endo* selectivity is also complete with $TiCl_4$ but moderate with $Eu(fod)_3$. (b) Cyclopentadiene reacts with high but not complete $\pi$-facial selectivity with all the catalysts. This facial selectivity with $ZnBr_2$ is opposite to that found with $Eu(fod)_3$ and $TiCl_4$. The *endo* selectivity is very high (but not complete) with $TiCl_4$ and $ZnBr_2$ but much lower with $Eu(fod)_3$.

The $\pi$-facial selectivity can be understood by assuming a steric control governed by the spatial arrangement of the substituents around the C–S bond. The presumably most stable conformations of dienophile **3** in the absence of catalysts are depicted in Figure 2.[30] Regardless of their relative stability, the conformation with the sulfinyl oxygen in the *s-cis* arrangement (**A** in Figure 1) must be the most reactive one because the steric interactions between cyclopentadiene and the aromatic ring in conformation **B** strongly destabilize both *endo* and *exo* approaches. Therefore, the predicted favored approach of the diene must take place from the less hindered face of the dienophile in conformation **A** ($C_\alpha$-*si* face). The stereochemistry of the adduct *endo*-**4a**, obtained as the major product in these reactions, is in agreement with this prediction.

The increase of the $\pi$-facial selectivity observed in reactions with cyclopentadiene in the presence of $Eu(fod)_3$ can be explained by assuming that this catalyst (of low chelating ability) will be mainly associated to the sulfinyl oxygen (the most basic center of the dienophile). The bulky size of $Eu(fod)_3$ determines the relative stabilization of the **A** rotamer (**A***) because of the larger steric restrictions imposed to this association in the other possible conformations. Therefore, the formation of the *endo*-**4a** adduct is also favored in reactions catalyzed by $Eu(fod)_3$.

With $TiCl_4$ or $ZnBr_2$ as catalysts the reactions must take place on chelated species **B***, resulting from the simultaneous bonding of sulfinyl and carbonyl oxygens with the metals. In Figure 3 the spatial arrangements of the substituents in both complexes are depicted. As we can deduce from the steric interactions between the *p*-tolyl group and the halogens, the conformational equilibria must be shifted to the left,[31] mainly in the case of the titanium complexes. The $C_\alpha$-*re* face, supporting the lone electron pair at sulfur, must be the most accessible in the *endo* approach on the $ZnBr_2$ chelates (the $C_\alpha$-*si* face is sterically and electronically more hindered by the sulfinyl oxygen). The octahedral spatial arrangement of the substituent around the titanium atom determines that one of the chlorine atoms is directed toward the $C_\alpha$-*re* face, making the approach of the diene to the $C_\alpha$-*si* face easier and thus promoting an inversion of the $\pi$-facial selectivity.

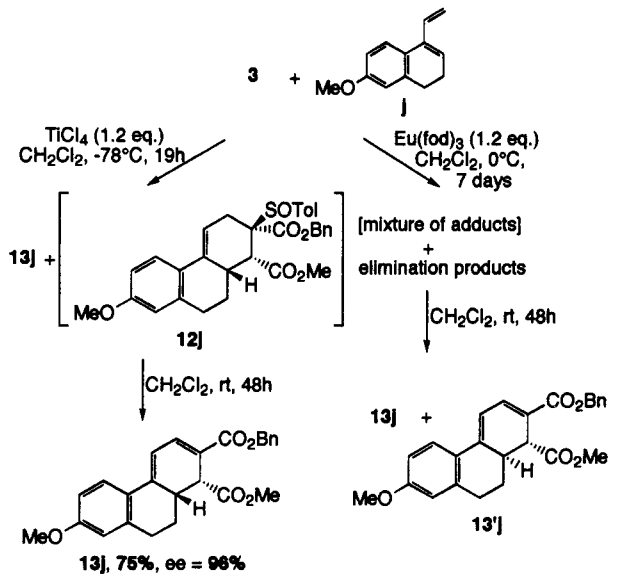
The different values for the *endo* selectivity of these reactions, depending on the catalyst [higher with $TiCl_4$ and $ZnBr_2$ than with $Eu(fod)_3$] and the diene (acyclic dienes > cyclic dienes), can be rationalized by taking into account the following: (i) the electronic effect of the Lewis acid on the *endo*-director character of the substituent at the double bond and (ii) the steric interactions of the diene with the sulfur substituent in *s-cis* arrangement with respect to the double bond.

It is well known that the association of Lewis acids to heterosubstituted functional groups of the dienophile usually increases the *endo* selectivity of the cycloadditions. In the case of compound **3**, the use of $Eu(fod)_3$, which

(30) Although the rotamer **A** has been postulated as the most stable one from theoretical studies,[3d] the contribution of the **B** conformations with the aryl group in the *s-cis* arrangement must also be important because they must be stabilized by a donor–aceptor interaction $n^2$–$d^0$ between the carbonyl oxygen lone electron pair and the empty *d* orbitals at sulfur (see: Carretero, J. C.; García Ruano, J. L.; Martínez, M.C.; Rodríguez, J. H. *Tetrahedron* **1985**, *41*, 2419). The preference for conformations with stereochemistry similar to **B** has been postulated to explain the results obtained in the Diels–Alder reactions of 2-(*p*-tolylsulfinyl)quinone with cyclopentadiene (see: Carreño, M. C.; García Ruano, J. L; Urbano, A. *J. Org. Chem.* **1992**, *57*, 6870 and references cited therein).

(31) It must be pointed out that in Figure 3 the *p*-tolyl group is placed perpendicularly to the plane of the dienophilic double bond, and therefore, it hardly should affect the $\pi$-facial selectivity control. This is important because the strong steric effect of this group had been so far invoked to explain the $\pi$-facial selectivity of all reactions involving chelated species derived from $\beta$-keto sulfoxides.

**Scheme 5**




became associated only to the sulfinyl oxygen (**A*** rotamer, Figure 2), must increase the *endo* director ability of the SOTol group, favoring the formation of the *exo*-**4** and *exo*-**10** adducts (which are *endo* with respect to the sulfinyl group). The use of $ZnBr_2$ and $TiCl_4$ as catalysts determines the formation of chelated species **B*** (Figure 2), where the metal coordinates both the $CO_2Bn$ and SOTol groups and thus increases the *endo* director character of both substituents.

The steric effects reinforce the trend imposed by the electronic ones in the case of acyclic dienes. These dienes evolve with complete *endo* selectivity in the reactions catalyzed by $TiCl_4$, but with moderated *endo* selectivity in those performed with Eu(fod)$_3$. In the first case, the *exo* approach of the diene to the **B** conformation (chelated by titanium atom, must be destabilized by the interactions with the tolyl ring, whereas in the second case, such an approach to the conformation **A** [associated to Eu(fod)$_3$] does not show strong steric interactions with the associated sulfinyl oxygen. This steric trend is partially counterbalanced in the case of cyclic dienes where the relative stability of the *endo* approaches is modified in a similar sense due to the interactions of the methylene bridge with the *s-cis* substituent in each conformation. This could explain that the *endo* selectivity of the reactions catalyzed by $TiCl_4$ was lower with cyclopentadiene than with acyclic dienes.

**Reactions with Dane's Diene.** In order to extend the use of dienophile **3** we have studied its reaction with 3,4-dihydro-6-methoxy-1-vinylnaphthalene (Dane's diene).[32] This 1,2-substituted diene (diene **j**) would allow us to obtain compounds readily transformable into steroidal structures.[33] When $TiCl_4$ (1.2 equiv) was used as a catalyst, the reaction was complete after 19 h at −78 °C. From the $^1$H NMR spectrum of the crude mixture only one adduct (**12j**) was detected, showing that the cycloaddition again occurred with very high regioselectivity, *endo* selectivity, and π-facial selectivity in the presence of this catalyst. After 2 days at room temperature, adduct **12j** (Scheme 5) was completely transformed into **13j** which was isolated in 75% yield after chromatographic purification. The high optical purity of **13j** [ee = 96%, determined by $^1$H NMR with Pr(hfc)$_3$] agrees with the detection of only one adduct in the crude reaction mixture. On the other hand, the *cis* stereochemistry of this compound at $C_1$–$C_{10a}$ (deduced from its $^1$H NMR data, *vide infra*) confirms the *endo* character of the cycloaddition.

By contrast, the reaction of **3** with Dane's diene required 7 days at 0 °C in the presence of 1.2 equiv of Eu(fod)$_3$, yielding a complex mixture of products. After sulfinyl elimination ($CH_2Cl_2$, rt, 2 days) and chromatographic purification, the two major identified products (overall yield ~40%) were cyclohexadiene **13j** (*endo*-structure) and its epimer **13'j** (*exo*-structure). The relative configurations of these two products were established from their $^1$H NMR spectra (the most significant data are depicted in Figure 4). Thus, the large difference observed in the value of $^3J_{1,10a}$ (8.6 Hz for **13j** and 17.4 Hz for **13'j**) suggests an *antiperiplanar* arrangement of $H_1/H_{10a}$ in **13'j** and a *gauche* arrangement in **13j**. Taking into account the relationship between the allylic long-range coupling constant and the dihedral angle of the involved protons ($J \approx 0$ Hz when $0° < \phi < 90°$, but $J \approx 3$ Hz when $\phi = 90°$), the values of $^4J_{1,3}$ and $^4J_{1,10a}$ reinforce the above assignment. As can be seen in Figure 4, where compound **13'j** shows large values for both constants, only one of them ($^4J_{1,10a}$) reaches a high value in the case of **13j**.

Therefore, as was observed with the previously studied 1-substituted dienes, where the reaction of **3** with Dane's diene, catalyzed by $TiCl_4$, was completely regioselective and *endo*- and π-facial selective, the same reaction catalyzed by Eu(fod)$_3$ took place with lower *endo* selectivity (**13'j** comes from an *exo* adduct).

## Conclusions

In summary, the readily available enantiomerically pure vinyl sulfoxide **3** reacted in high yields and at low temperatures with a wide variety of 1,3-dienes in the presence of Eu(fod)$_3$ or $TiCl_4$. These cycloadditions occurred with complete regioselectivity and π-facial selectivity. Additionally, when $TiCl_4$ was used as a catalyst the reactions also took place with complete *endo* selectivity. The adducts, except those derived from cyclopentadiene, underwent spontaneous sulfinyl elimination at room temperature giving 1,3-cyclohexadienes **7** and/or 1,4-cyclohexadienes **11** of very high optical purity (ee ≥ 96%) in excellent yields. Enantiomerically pure cyclohexadienes **7** and **11** could be of interest as chiral building blocks in asymmetric synthesis.

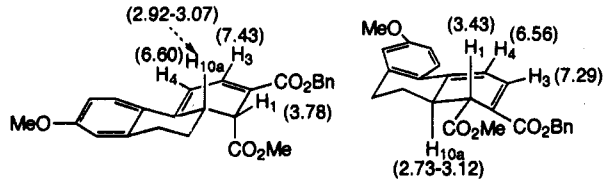
## Experimental Section

Melting points are uncorrected. $^1$H NMR (200 MHz) spectra and $^{13}$C NMR (50 MHz) spectra were recorded in $CDCl_3$. Both chemical shifts (ppm downfield from internal tetramethylsilane) and coupling constants (Hz) were obtained by first order analysis of spin patterns. Mass spectra (MS) were recorded with electron impact (EI, 70 eV) or at chemical ionization (CI, $NH_3$). Mass data are reported in mass units ($m/z$), and the values in brackets report the relative intensity from the base peak (as 100%). High-resolution mass spectra were determined at an ionizing voltage of 70 eV.

Analytical thin-layer chromatography was performed on DC-Alufolien 0.2 mm silica gel 60-F plates (MERCK). Visualization was accomplished with UV light, iodine, and ethanolic phosphomolybdic acid solution followed by heating. Flash chroma-

(32) (a) Symmes, C.; Quin, L. D. *J. Org. Chem.* **1979**, *44*, 1048. (b) Hajos, Z. G.; Parrish, D. R.; Goldberg, M. W. *J. Org. Chem.* **1965**, *30*, 1213. (c) Robins, P. A.; Walker, J. *J. Chem. Soc.* **1956**, 3249.

(33) For a recent use of Dane's diene in (−)-estrone synthesis, see: Takano, S.; Moriya, M.; Ogasawara, K. *Tetrahedron Lett.* **1992**, *33*, 1909.




| 13j | 13'j |
|---|---|
| $J_{1,10a}$ = 8.6 Hz (*cis*) | $J_{1,10a}$ = 17.4 Hz (*trans*) |
| $J_{1,3} \approx 0$ Hz ($0 < \phi < 90$) | $J_{1,3}$ = 2.5 Hz ($\phi \approx 90$) |
| $J_{3,4}$ = 6.3 Hz | $J_{3,4}$ = 6.3 Hz |
| $J_{4,10a}$ = 3.0 Hz ($\phi$ = 90) | $J_{4,10a}$ = 2.7 Hz ($\phi \approx 90$) |

**Figure 4.** Significant coupling constants in compounds **13j** and **13'j** (chemical shifts values are in parentheses).

tography was performed by use of silica gel (MN-Kieselgel 60, 230–400 mesh).

All solvents were dried before use. THF and $Et_2O$ were distilled from sodium–benzophenone under argon. $CH_2Cl_2$ and $CHCl_3$ were distilled from $P_2O_5$. DMF was distilled from molecular sieves (4 Å). Diisopropylamine was distilled from sodium hydroxide. Cyclopentadiene was freshly distilled. $Eu(fod)_3$, $TiCl_4$, $PtO_2$, $BH_3SMe_2$, *trans*, *trans*-2,4-hexadiene, *trans*-1,3-pentadiene, isoprene, 2,3-dimethylbutadiene, pyrrolidine, and iodomethane were purchased from Aldrich and used without further purification. Butadiene was generated from sulfolene and stored at −40 °C. 1-Methoxybutadiene,[34] 2-methoxybutadiene,[35] and Dane's[32] diene were prepared according to reported procedures.

Cyclohexadienes **7** and **11** did not give satisfactory elemental analyses probably due to their rapid aromatization under the combustion conditions.

**(+)-(*R*)-Benzyl *p*-Tolylsulfinylacetate.** Diisopropylamine (12.39 g, 120 mmol, 6 equiv) in $Et_2O$ (83 mL) was added to a solution of ethylmagnesium bromide [prepared from magnesium (2.97 g, 120 mmol, 6 equiv) and ethyl bromide (13.34 g, 120 mmol, 6 equiv) in $Et_2O$ (120 mL)] under argon. After being heated at reflux for 1 h, the mixture was cooled to 0 °C. A solution of benzyl acetate (7.66 g, 50 mmol, 2.5 equiv) and (−)-(*S*)-menthyl *p*-toluenesulfinate (6 g, 20 mmol, 1.0 equiv) in $Et_2O$ (68 mL) was slowly added under vigorous stirring. Then, the mixture was allowed to stand at rt for 1 h, a solution of saturated $NH_4Cl$ (120 mL) was added, and the mixture was extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers were washed with water (50 mL), dried ($MgSO_4$), filtered through Celite, and concentrated. The residue was purified by flash chromatography (hexane–ethyl acetate (4:1). Yield: 3.93 g (67%). $[\alpha]^{20}_D$ = +96.7 (*c* = 1.64, $CHCl_3$). IR ($CHCl_3$): 3000, 1725, 1495, 1455, 1265, 1175, 1110, 1085, and 1045 $cm^{-1}$. $^1H$ NMR δ: 2.40 (s, 3H), 3.68 and 3.90 (AB system, 2H, *J* = 13.4 Hz), 5.11 (s, 2H), 7.26–7.35 (m, 7H) and 7.52 (half of an AA'BB' system, 2H). $^{13}C$ NMR δ: 21.1, 61.0, 67.1, 123.8, 128.1, 129.6, 134.4, 139.2, 141.9, and 164.2. MS (EI): 289 (1.5), 288 (7.8, $M^+$), 141 (6.5), 140 (27.7), 139 (100.0), 91 (34.3), and 65 (6.4). Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59. Found: C, 66.54; H, 5.31.

**(*S*)-1-Benzyl 4-Methyl 2-*p*-Tolylsulfinylmaleate (3).** To a solution of (+)-(*R*)-benzyl *p*-tolylsulfinylacetate (3.0 g, 10.4 mmol, 1.0 equiv) in DMF (52 mL) cooled to 0 °C were added, sequentially, glyoxylic acid monohydrate (2.87 g, 31.2 mmol, 3 equiv), $Et_3N$ (3.15 g, 31.2 mmol, 3 equiv), and pyrrolidine (0.26 g, 3.64 mmol, 0.35 equiv). The mixture was stirred at 0 °C for 8 h, and then 1% HCl was added to pH = 1. The solution was extracted with $Et_2O$ (3 × 50 mL). The combined ether phases were washed with water (25 mL), dried ($MgSO_4$), and concentrated. The residue was dissolved in dry DMF (52 mL), and $NaHCO_3$ (2.62 g, 31.2 mmol, 3 equiv), iodomethane (14.76 g, 104 mmol, 10 equiv), and 4-Å molecular sieves (1 g) were added. The reaction was kept, under argon, at rt for 4 h. The mixture was treated with 20% $NH_4Cl$ (40 mL) and extracted with $Et_2O$ (3 × 50 mL). The combined organic layers were washed with water (25 mL), dried ($MgSO_4$), and concentrated. The residue was purified by chromatography ($CH_2Cl_2$ and $CH_2Cl_2$–$Et_2O$ (50:1)). Yield: 2.47 g (67%). MP: 66–69 °C. $[\alpha]^{20}_D$ = +158.6 (*c* = 1, $CHCl_3$), ee ≥ 96% [by using $Yb(hfc)_3$ as chiral shift reagent]. IR ($CHCl_3$): 3010, 2960, 1730, 1640, 1600, 1460, 1440, 1340, 1270, 1175, 1095, and 1070 $cm^{-1}$. $^1H$ NMR δ: 2.37 (s, 3H), 3.67 (s, 3H), 5.05 (s, 2H), 6.99 (s, 1H), 7.16–7.46 (m, 9H). $^{13}C$ NMR δ: 21.2, 52.2, 67.6, 125.7, 125.9, 128.2, 128.3, 128.4, 129.8,. 133.8, 136.9, 142.9, 150.4, 161.1, and 164.0. MS (EI): 358 (1.1, $M^+$), 252 (7.8), 235 (15.5), 203 (8.2), 139 (33.9), 123 (18.1), 113 (35.9), 91 (100.0), 69 (34.4), and 57 (32.1). Anal. Calcd for $C_{19}H_{18}O_5S$: C, 63.67; H, 5.06. Found: C, 63.98; H, 5.35.

**General Procedure for the Diels–Alder Reactions of 3 Cat yzed by Eu(fod)$_3$.** A solution of dienophile **3** (200 mg, 0.56 mol, 1.0 equiv) in 1.4 mL of dichloromethane was added, und an argon atmosphere, to a solution of $Eu(fod)_3$ (695.5 mg, 0.67 mol, 1.2 equiv) in 1.4 mL of $CH_2Cl_2$ (the temperature is indi ted in Tables 1–4). The mixture was stirred for 10 min, and hen 6 equiv (3.36 mmol) of the corresponding diene was add l. Stirring was continued until the dienophile disappeared according to TLC (the reaction times are indicated in Tables 1–4). Then, 5% HCl (10 mL) was added (except for the reaction with 2-methoxybutadiene). The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 15 mL). The combined organic layers were washed with water (5 mL), dried ($MgSO_4$), and carefully concentrated (without heating). The residue was inmediately analyzed by $^1H$ NMR.

In the case of using cyclopentadiene, this mixture of adducts was purified by flash chromatography (hexane–ethyl acetate (4:1)) to give the mixture of *endo* adducts **4a** + **4'a** ($R_f$ = 0.13) in 67% and the *exo* adduct **4a** ($R_f$ = 0.05) in 33% yield (100% overall yield for the cycloaddition). With all of the other dienes the crude adducts were redissolved in $CH_2Cl_2$ (5 mL) and allowed to stand at rt until complete sulfinyl elimination (24–48 h, except for the reaction with 1-methoxybutadiene that required only 2 h at 30 °C). The solvent was concentrated, and the mixture of 1,3 and/or 1,4-cyclohexadienes (compounds **7** and **11**) was purified by flash chromatography (the eluent used and the yields are indicated below for every case).

**General Procedure for the Diels–Alder Reactions of 3 Catalyzed by TiCl$_4$.** The Lewis acid (0.67 mmol, 1.2 equiv from a solution 1.0 M in $CH_2Cl_2$) was added dropwise, under argon atmosphere, to a solution of dienophile **3** (200 mg, 0.56 mmol, 1.0 equiv) in 2.8 mL of $CH_2Cl_2$ at −78 °C. The mixture was stirred for 10 min, and then 6 equiv (3.36 mmol) of the corresponding diene was added. Stirring was continued untill dienophile disappeared by TLC (the reaction times are indicated in Tables 1–4). Then, 10% $NaHCO_3$ (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 15 mL).The combined organic layers were washed with water (5 mL), dried ($MgSO_4$), and carefully concentrated (without heating). The mixture of adducts was immediately analyzed by $^1H$ NMR.

The adducts obtained from cyclopentadiene were purified by flash chromatography (hexane–ethyl acetate (4:1)) to give a mixture of *endo* adducts **4a** + **4'a** in 77% and *exo* adduct **4a** in 7% yield (84% overall yield). With the other dienes the adducts reacted by sulfinyl elimination at rt [see general procedure for the reactions catalyzed by $Eu(fod)_3$].

**Diels–Alder Reaction of 3 with Cyclopentadiene Catalyzed by ZnBr$_2$.** A solution of dienophile **3** (41.6 mg, 0.12 mmol, 1.0 equiv) in 0.4 mL of $CH_2Cl_2$ was added, under argon atmosphere, to a suspension of $ZnBr_2$ (31.4 mg, 0.14 mmol, 1.2 equiv) in 0.2 mL of $CH_2Cl_2$ at −20 °C. The mixture was stirred for 10 min, and 60 μL (0.72 mmol, 6 equiv) of cyclopentadiene was added. Stirring was continued for 6 h. Then, 10% $NaHCO_3$ (5 mL) was added. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 10 mL). The combined organic layers were washed with water (2 mL), dried ($MgSO_4$), and concentrated in vacuo. The mixture of adducts was analyzed by $^1H$-NMR and purified by flash chromatography (hexane–ethyl acetate 4:1). A 41.5-mg (84%) portion of *endo* adducts **4a** + **4'a** and 4.3 mg (9%) of *exo* adduct **4a** were obtained (93% overall yield).

**(*R*$_1$,*R*$_2$,*S*$_3$,*S*$_4$,*S*$_5$)-2-Benzyl 3-Methyl 2-*p*-(Tolylsulfinyl)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (*endo*-4a).** Data corresponding to a mixture 95:5 of adducts **4a**/**4'a**. $[\alpha]^{20}_D$ = −12.4

(34) (a) Montagna, A. E.; Hirsh, D. H. U. S. Patent 2,905,722, 1959; *Chem. Abstr.* **1960**, *54*, 2168e. (b) (b) Fariña, F.; Martin, M. V. *An. Quim.* **1971**, *67*, 315.

(35) Dolby, L. J.; Marshall, K. S. *Org. Prep. Proc.* **1969**, *1*, 229.

(c = 1.57, $CHCl_3$). IR ($CHCl_3$): 3010, 2960, 1735, 1500, 1460, 1440, 1380, 1335, 1270, 1085, and 1050 $cm^{-1}$. $^1H$ NMR δ: 1.38 (dt, 1H, J = 1.2 and 9.1 Hz), 2.11 (bd, 1H, J = 9.1 Hz), 2.39 (s, 3H), 3.12 (bs, 1H), 3.19 (s, 3H), 3.56 (m, 1H), 3.68 (d, 1H, J = 3.0 Hz), 4.76 and 4.93 (AB system, 2H, J = 12.2 Hz), 5.96 (dd, 1H, J = 3.0 and 5.5 Hz), 6.70 (dd, 1H, J = 3.0 and 5.5 Hz), 7.18–7.53 (m, 9H). $^{13}C$ NMR δ: 21.3, 44.3, 44.4, 45.5, 50.9, 53.7, 66.9, 81.0, 123.7, 125.8, 128.4, 128.8, 129.6, 132.8, 134.2, 137.4, 142.2, 142.3, 166.4, and 172.2. MS (CI): 443 (17.8), 442 (65.3, $M^+$+18), 426 (2.6), 425 (8.2), 424 (0.2, $M^+$), 304 (37.1), 303 (20.0), 302 (100.0), and 285 (35.9). HRMS: exact mass calcd for $C_{24}H_{24}O_5S$ ($M^+$) 424.1344, found 424.1290.

**($S_1$,$S_2$,$R_3$,$R_4$,$S_5$)-2-Benzyl 3-Methyl 2-(p-Tolylsulfinyl)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (*endo*-4'a).** Data corresponding to a mixture 7:93 of adducts **4a**/**4'a**. $[\alpha]^{20}_D$ = +33.2 (c = 1.23, $CHCl_3$). IR ($CHCl_3$): 3040, 3000, 2980, 1730, 1715, 1600, 1495, 1460, 1440, 1360, 1335, 1260, 1160, 1085, and 1055 $cm^{-1}$. $^1H$ NMR δ: 1.45 (dt, 1H, J = 1.7 and 9.3 Hz), 2.11 (bd, 1H, J = 9.3 Hz), 2.40 (s, 3H), 3.19 (m, 1H), 3.39 (s, 3H), 3.49 (dd, 1H, J = 1.5 and 3.1 Hz), 3.55 (d, 1H, J = 3.1 Hz), 4.79 and 4.91 (AB system, 2H, J = 12.3 Hz), 6.10 (dd, 1H, J = 3.0 and 5.4 Hz), 6.56 (dd, 1H, J = 3.0 and 5.4 Hz), 7.22–7.54 (m, 9H). $^{13}C$ NMR δ: 21.5, 45.2, 47.0, 48.9, 50.7, 51.5, 67.2, 81.3, 123.9, 125.7, 128.4, 129.3, 129.8, 134.6, 136.8, 140.6, 142.4, 166.6, and 171.9. MS (CI): 444 (10.2), 443 (27.5), 442 (100.0, $M^+$ + 18), 426 (13.1), 425 (26.5), 304 (31.4), 303 (11.9), 302 (52.8), and 285 (19.9). HRMS: exact mass calcd for $C_{24}H_{24}O_5S$ ($M^+$) 424.1344, found 424.1360.

**($S_1$,$R_2$,$S_3$,$R_4$,$S_5$)-2-Benzyl 3-Methyl 2-(p-Tolylsulfinyl)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (*exo*-4a).** $[\alpha]^{20}_D$ = +11.4 (c = 1.05, $CHCl_3$). IR ($CHCl_3$): 3000, 2950, 1725, 1595, 1490, 1450, 1430, 1350, 1260, 1080, and 1060 $cm^{-1}$. $^1H$ NMR δ: 1.73 (ddd, 1H, J = 1.0, 2.1, and 9.4 Hz), 2.22 (bd, 1H, J = 9.4 Hz), 2.38 (s, 3H), 3.12 (m, 1H), 3.25 (d, 1H, J = 2.1Hz), 3.37 (m, 1H), 3.42 (s, 3H), 4.63 and 4.77 (AB system, 2H, J = 12.7 Hz), 6.44 (m, 2H), 7.22–7.50 (m, 9H). $^{13}C$ NMR δ: 21.5, 47.5, 47.7, 48.3, 48.5, 52.0, 67.2, 82.2, 124.9, 127.9, 128.1, 128.4, 129.5, 134.7, 135.8, 137.6, 139.0, 142.3, 166.6, and 173.7. MS (CI): 444 (9.6), 443 (27.3), 442 (100.0, $M^+$ + 18), 426 (6.8), 425 (22.6), 304 (27.3), 303 (7.4), 302 (31.2), and 285 (12.2). HRMS: exact mass calcd for $C_{24}H_{24}O_5S$ ($M^+$) 424.1344, found 424.1294.

**($R_1$,$R_2$,$S_3$,$S_4$,$S_5$)-2-Benzyl 3-Methyl 2-(p-Tolylsulfinyl)-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate (*endo*-4b).** $^1H$ NMR δ: 1.5–2 (m, 4H), 2.39 (s, 3H), 2.94–2.98 (m, 1H), 3.29 (s, 3H), 3.44–3.48 (m, 1H), 3.59 (d, 1H, J = 1.7 Hz), 4.56 and 4.86 (AB system, 2H, J = 12.5 Hz), 6.18 (t, 1H, J = 7.1 Hz), 6.57 (t, 1H, J = 7.1 Hz), 7.19–7.38 (m, 7H), 7.53 (half of an AA'BB' system, 2H).

**(+)-(1*R*,4*S*)-2-Benzyl 3-Methyl Bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (+)-(5b).** Eluent: hexane–ethyl acetate (20:1). By using $Eu(fod)_3$, yield 44%; ee = 0%. By using $TiCl_4$, yield 82%; ee >90%. $[\alpha]^{20}_D$ = +1.0 (c = 1.0, $CHCl_3$). IR ($CHCl_3$): 2960, 2880, 1725, 1715, 1645, 1605, 1460, 1430, 1375, 1360, 1270, 1220, 1080, 1070, 965, 760, and 710 $cm^{-1}$. $^1H$ NMR δ: 1.37–1.51 (m, 4H), 3.50 (s, 3H), 3.97–4.04 (m, 1H), 4.04–4.13 (m, 1H), 5.19 (s, 2H), 6.35–6.39 (m, 2H), and 7.26–7.39 (m, 5H). $^{13}C$ NMR δ: 24.5, 26.5, 38.6, 39.2, 51.9, 66.9, 133.4, 133.9, 135.5, 143.0, 165.6, and 167.7. MS (EI): 267 (0.6), 238 (1.0), 192 (67.8), 164 (33.8), 163 (45.5), 149 (19.7), 136 (13.7), 135 (10.3), 105 (14.2), 104 (12.1), 92 (19.8), 91 (100.0), 77 (15.8), and 65 (12.3). HRMS: exact mass calcd for $C_{18}H_{18}O_4$ ($M^+$) 298.1205, found 298.1193.

**($R_1$,$S_2$,$S_3$)-1-Benzyl 2-Methyl 1-(p-Tolylsulfinyl)-4-cyclohexene-1,2-dicarboxylate (6c).** $^1H$ NMR δ: 2.13–2.26 (m, 1H), 2.37 (s, 3H), 2.72–2.83 (m, 1H), 2.86–3.09 (m, 2H), 3.55 (s, 3H), 3.96 (dd, 1H, J = 1.1 and 5.2 Hz), 4.68 and 4.93 (AB system, 2H, J = 12.5 Hz), 5.66–5.74 (m, 1H), 5.80–5.88 (m, 1H), 7.11–7.37 (m, 7H, Ar), 7.47 (half of an AA'BB' system, 2H).

**(*R*)-2-Benzyl 1-Methyl 2,4-Cyclohexadiene-1,2-dicarboxylate (7c).** Eluent: hexane–ethyl acetate (12:1). By using $Eu(fod)_3$, yield 91%; ee ≥ 96%. By using $TiCl_4$, yield 83%; ee ≥ 96%. $[\alpha]^{20}_D$ = +53.6 (c = 0.65, $CHCl_3$). IR ($CHCl_3$): 3000, 2950, 1725, 1710, 1640, 1570, 1453, 1360, 1270, 1210, 1095, 1055, and 1025 $cm^{-1}$. $^1H$ NMR (δ: 2.53 (dd, 1H, J = 9.9 and 18.5 Hz), 2.93 (ddd, 1H, J = 3.4, 4.7 and 18.4 Hz), 3.62 (s, 3H), 3.71 (dd, 1H, J = 3.3 and 9.9 Hz), 5.19 and 5.29 (AB system, 2H, J = 12.5 Hz), 6.10–6.14 (m, 2H), 7.18–7.21 (m, 1H), 7.34–7.40 (m, 5H). $^{13}C$ NMR δ: 26.1, 36.4, 51.9, 66.0, 123.4, 124.8, 127.6, 127.8, 128.2, 132.0, 134.1, 135.9, 166.1, and 173.2. MS (EI): 272 (0.7, $M^+$), 270 (0.7), 213 (4.3), 181 (1.9), 165 (2.2), 164 (10.0), 163 (11.0), 155 (2.2), 149 (10.3), 137 (5.1), 136 (5.5), 135 (2.3), 106 (3.5), 105 (26.7), 92 (18.0), 91 (100.0), and 77 (14.2). HRMS: exact mass calcd for $C_{16}H_{16}O_4$ ($M^+$) 272.1049, found 272.1060.

**($R_1$,$S_2$,$S_3$)-1-Benzyl 2-Methyl 4,5-Dimethyl-1-(p-tolylsulfinyl)-4-cyclohexene-1,2-dicarboxylate (6d).** $^1H$ NMR δ: 1.68 (s, 3H), 1.71 (s, 3H), 2.0 (d, 1H, J = 19.1 Hz), 2.38 (s, 3H), 2.61 (d, 1H, J = 17.8 Hz), 2.80–3.05 (m, 2H), 3.53 (s, 3H), 3.89 (bd, 1H, J = 6.0 Hz, $H_2$), 4.71 and 4.93 (AB system, 2H, J = 12.6 Hz), 7.14–7.32 (m, 7H), 7.43 (half of an AA'BB' system, 2H, Ar).

**(*R*)-2-Benzyl 1-Methyl 4,5-Dimethyl-2,4-cyclohexadiene-1,2-dicarboxylate (7d).** Eluent: hexane–$CH_2Cl_2$ (1:1). By using $Eu(fod)_3$, yield 83%; ee ≥ 96%. By using $TiCl_4$, yield 66%; ee ≥ 96%. $[\alpha]^{20}_D$ = +32.5 (c = 2.23, $CHCl_3$). IR ($CHCl_3$): 3030, 2990, 2950, 1725, 1710, 1585, 1455, 1435, 1385, 1305, 1275, 1230, 1215, and 1135 $cm^{-1}$.$^1H$ NMR δ: 1.78 (m, 3H), 1.82 (bs, 3H), 2.43–2.77 (ABX system, 2H, $J_{AB}$ = 17.7 Hz, $\delta_A$ = 2.51, $\delta_B$ = 2.71), 3.61 (s, 3H), 3.62–3.68 (ABX system, 1H, $J_{AX}$ = 3.1 Hz, $J_{BX}$ = 9.2 Hz, $\delta_X$ = 3.65), 5.17 and 5.29 (AB system, 2H, J = 12.4 Hz), 7.06 (bs, 1H), and 7.34–7.40 (m, 5H). $^{13}C$ NMR δ: 17.1, 19.6, 33.3, 37.7, 52.1, 66.2, 122.1, 124.3, 128.0, 128.5, 135.8, 136.4, 140.4, 166.6, and 173.9. MS (EI): 300 (1.5, $M^+$), 241 (2.0), 209 (2.0), 192 (3.6), 191 (4.2), 177 (5.7), 134 (6.0), 133 (65.5), 105 (13.2), 92 (11.6), 91 (100.0), 77 (5.2), 65 (6.7), and 59 (5.1). HRMS: exact mass calcd for $C_{18}H_{20}O_4$ ($M^+$) 300.1362, found 300.1377.

**($R_1$,$S_2$,$S_3$)-1-Benzyl 2-Methyl 4-Methyl-1-(p-tolylsulfinyl)-4-cyclohexene-1,2-dicarboxylate (6e).** $^1H$ NMR δ: 1.76 (s, 3H), 2.16 (bd, 1H, J = 20.6 Hz), 2.36 (s, 3H), 2.61 (bd, 1H, J = 20.0 Hz), 2.82–3.0 (m, 2H), 3.53 (s, 3H), 3.94 (d, 1H, J = 6.9 Hz), 4.66 and 4.91 (AB system, 2H, J = 12.5 Hz), 5.37–5.39 (m, 1H), 7.11–7.37 (m, 7H), 7.45 (half of an AA'BB' system, 2H).

**(*R*)-2-Benzyl 1-Methyl 5-Methyl-2,4-cyclohexadiene-1,2-dicarboxylate (7e).** Eluent: hexane–$CH_2Cl_2$ (1:1). By using $Eu(fod)_3$, yield 86%; ee ≥ 96%. By using $TiCl_4$, yield 91%; ee ≥ 96%. $[\alpha]^{20}_D$ = +80.6 (c = 0.33, $CHCl_3$). IR ($CHCl_3$): 3010, 2960, 1725, 1705, 1590, 1435, 1380, 1270, 1175, 1080, 1045, and 980 $cm^{-1}$. $^1H$ NMR δ: 1.90 (bs, 3H), 2.49 (ddt, 1H, J = 1.8, 9.6 and 17.9 Hz), 2.75 (dd, 1H, J = 3.4 and 17.9 Hz), 3.62 (s, 3H), 3.73 (dd, 1H, J = 3.5 and 9.5 Hz), 5.18 and 5.29 (AB system, 2H, J = 12.5 Hz), 5.84 (dc, 1H, J = 2.0 and 5.8 Hz), 7.16 (d, 1H, J = 5.8 Hz), and 7.30–7.40 (m, 5H). $^{13}C$ NMR δ: 23.5, 31.8, 37.6, 52.2, 66.2, 118.9, 122.2, 128.0, 128.3, 128.5, 135.7, 135.9, 144.0, 166.6, and 173.7. MS (EI): 286 (4.9, $M^+$), 227 (8.8), 211 (12.0), 178 (7.6), 177 (10.3), 163 (7.9), 150 (6.1), 119 (34.6), 105 (5.0), 92 (17.8), 91 (100.0), 77 (5.5) and 65 (11.9). HRMS: exact mass calcd for $C_{17}H_{18}O_4$ ($M^+$) 286.1205, found 286.1203.

**($R_1$, $S_2$, $S_3$)-1-Benzyl 2-Methyl 4-Methoxy-1-(p-tolylsulfinyl)-4-cyclohexene-1,2-dicarboxylate (6f).** $^1H$ NMR δ: 2.29 (s, 3H), 2.40–3.20 (m, 4H), 3.49 (s, 3H), 3.52 (s, 3H), 3.82 (dd, 1H, J = 3.4 and 8.5 Hz), 4.56–4.58 (m, 1H), 4.77 and 5.02 (AB system, 2H, J = 12.6 Hz), 7.10–7.41 (m, 9H).

**(*R*)-2-Benzyl 1-Methyl 5-methoxy-2,4-cyclohexadiene-1,2-dicarboxylate (7f).** The mixture of adducts **6** was allowed to stand at rt (without adding 5% HCl) for 96 h. Eluent: hexane–ethyl acetate 13:1. Yield: 90%; ee = 83%. $[\alpha]^{20}_D$ = −7.1 (c = 0.74, $CHCl_3$). IR ($CHCl_3$): 2960, 2880, 1725, 1690, 1640, 1560, 1455, 1440, 1380, 1230, 1170, 1090, 1040, and 995 $cm^{-1}$. $^1H$ NMR δ: 2.72 (ddd, 1H, J = 1.7, 8.8 and 17.3 Hz), 2.85 (dd, 1H, J = 3.5 and 17.3 Hz), 3.65 (s, 3H), 3.67 (s, 3H), 3.86 (dd, 1H, J = 3.7 and 8.8 Hz), 5.13 (dd, 1H, J = 1.1 and 6.7 Hz), 5.18 and 5.31 (AB system, 2H, J = 12.5 Hz), and 7.31–7.40 (m, 6H, $H_3$+Ar). $^{13}C$ NMR δ: 30.1, 38.4, 52.3, 55.5, 66.0, 92.5, 116.8, 127.9, 128.4, 136.5, 137.7, 164.3, 166.3, and 173.4. MS (EI): 302 (4.3, $M^+$), 243 (4.5), 135 (20.3), 108 (4.2), 92 (10.3), 91 (100.0), 77 (5.9), and 65 (11.4). HRMS: exact mass calcd for $C_{17}H_{18}O_5$ ($M^+$) 302.1154, found 302.1154.

**(1*R*,6*R*)-2-Benzyl 1-Methyl 3,6-Dimethyl-2,4-cyclohexadiene-1,2-dicarboxylate (7g).** Eluent: hexane–$CH_2Cl_2$ (2:1 and 1:1). By using $Eu(fod)_3$, yield 54%; ee ≥ 96%. By using $TiCl_4$, yield 64%; ee ≥ 96%. $[\alpha]^{20}_D$ = +15.6 (c = 0.73, $CHCl_3$). IR ($CHCl_3$): 3000, 2940, 1720, 1580, 1450, 1435, 1375, 1350, 1205, 1090, 1055, and 995 $cm^{-1}$. $^1H$ NMR δ: 1.15 (d, 3H, J = 7.4 Hz), 2.22 (d, 3H, J = 0.9 Hz), 2.73–2.92 (m, 1H), 3.54 (s, 3H), 3.62 (dd, 1H, J = 1.5 and 8.7 Hz), 5.14 and 5.23 (AB system, 2H, J = 12.5 Hz), 5.82 (dd, 1H, J = 2.9 and 9.5 Hz), 5.92 (dd, 1H, J = 2.4 and 9.5 Hz), and 7.31–7.39 (m, 5H). $^{13}C$ NMR δ: 16.5, 20.6, 31.9, 45.6, 51.3, 66.1, 120.1, 128.1, 128.6, 129.9, 132.5, 136.6, 145.0, 167.3,

and 172.3. MS (EI): 300 (3.5, $M^+$), 192 (3.7), 191 (3.7), 165 (3.7), 164 (3.4), 133 (22.3), 105 (8.5), 91 (100.0), 84 (7.4), and 65 (5.7). HRMS: exact mass calcd for $C_{18}H_{20}O_4$ ($M^+$) 300.1362, found 300.1366.

**(3*R*,6*S*)-1-Benzyl 2-Methyl 3,6-Dimethyl-1,4-cyclohexadiene-1,2-dicarboxylate (11g).** Eluent: hexane–$CH_2Cl_2$ (2:1 and 1:1). By using $Eu(fod)_3$, yield 31%. By using $TiCl_4$, yield 27%; ee undetermined. $[\alpha]^{20}_D$ = −4.8 (*c* = 1.2, $CHCl_3$). IR ($CHCl_3$): 2950, 2920, 2860, 2850, 1710, 1450, 1370, 1260, 1090, 1040, and 910 $cm^{-1}$. $^1H$ NMR δ: 1.21 (d, 3H, *J* = 6.9 Hz), 1.22 (d, 3H, *J* = 6.6 Hz), 3.04–3.23 (m, 2H), 3.58 (s, 3H), 5.21 (s, 2H), 5.66 (d, 2H, *J* = 3.0 Hz) and 7.34–7.41 (m, 5H, Ar). $^{13}C$ NMR δ: 22.0, 22.2, 32.7, 33.0, 51.9, 67.0, 127.7, 128.2, 128.4, 128.5, 132.5, 135.5, 137.1, 138.6, 167.6, and 168.5. MS (EI): 300 (0.38, $M^+$), 194 (26.6), 192 (8.4), 191 (11.5), 177 (13.6), 165 (7.1), 139 (6.0), 133 (13.0), 119 (6.8), 105 (11.5), 92 (11.7), 91 (100.0), 77 (7.8), 65 (11.1), and 59 (6.7). HRMS: exact mass calcd for $C_{18}H_{20}O_4$ ($M^+$) 300.1362, found 300.1286.

**(*R*)-2-Benzyl 1-Methyl 3-Methyl-2,4-cyclohexadiene-1,2-dicarboxylate (7h).** Eluent: hexane–$CH_2Cl_2$ (2:1 and 1:1). By using $Eu(fod)_3$, yield 25%; ee ≥ 96%. By using $TiCl_4$, yield 31%; ee ≥ 96%. $[\alpha]^{20}_D$ = +31.2 (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): 3010, 2950, 2920, 1725, 1700, 1580, 1435, 1290, 1210, 1070, and 910 $cm^{-1}$. $^1H$ NMR δ: 2.25 (bs, 3H), 2.43 (ddt, 1H, *J* = 2.6, 9.1 and 18.0 Hz), 2.80 (ddd, 1H, *J* = 3.4, 5.5 and 18.0 Hz), 3.57 (s, 3H), 3.76 (dd, 1H, *J* = 3.2 and 9.2 Hz), 5.17 and 5.27 (AB system, 2H, *J* = 12.5 Hz), 5.94 (dd, 1H, *J* = 2.5 and 9.6 Hz), 6.05 (ddd, 1H, *J* = 2.7, 5.5 and 9.6 Hz) and 7.28–7.41 (m, 5H). $^{13}C$ NMR δ: 20.8, 26.1, 38.7, 52.0, 66.0, 119.2, 128.0, 128.4, 130.6, 130.7, 136.2, 145.0, 167.2, and 174.1. MS (EI): 286 (6.9, $M^+$), 227 (8.1), 178 (32.2), 177 (16.8), 150 (6.2), 119 (25.5), 92 (14.5), 91 (100.0), 65 (7.1). HRMS: exact mass calcd for $C_{17}H_{18}O_4$ ($M^+$) 286.1205, found 286.1200.

**(*S*)-2-Benzyl 1-Methyl 3-Methyl-1,4-cyclohexadiene-1,2-dicarboxylate (11h).** Eluent: hexane–$CH_2Cl_2$ (2:1 and 1:1). By using $Eu(fod)_3$, yield 59%; ee = 38%. By using $TiCl_4$, yield 41%; ee ≥ 96%. $[\alpha]^{20}_D$ = +38.7 (*c* = 0.4, $CHCl_3$). IR ($CHCl_3$): 2980, 2920, 2870, 1715, 1635, 1450, 1435, 1380, 1260, 1160, 1100, 1045, and 700 $cm^{-1}$. $^1H$-NMR δ: 1.13 (d, 3H, *J* = 7.0 Hz), 2.78–3.12 (m, 2H), 3.24 (dc, 1H, *J* = 2.3 and 7.0 Hz), 3.59 (s, 3H), 5.20 and 5.26 (AB system, 2H, *J* = 12.2 Hz), 5.58–5.72 (m, 2H), and 7.28–7.42 (m, 5H). $^{13}C$ NMR δ: 20.4, 27.1, 32.4, 52.0, 67.0, 121.2, 128.3, 128.5, 128.6, 128.9, 129.8, 135.4, 139.6, 167.7, and 168.4. MS (EI): 286 (0.19, $M^+$), 271 (1.2), 181 (12.1), 180 (100.0), 179 (10.1), 178 (25.4), 177 (45.3), 163 (25.1), 151 (11.4), 119 (14.8), 105 (7.9), 92 (13.6), 91 (84.1), and 65 (4.1). HRMS: exact mass calcd for $C_{17}H_{18}O_4$ ($M^+$) 286.1205, found 286.1184.

**(*S*$_1$,*S*$_2$,*R*$_3$,*S*$_3$)-2-Benzyl 1-Methyl 3-Methoxy-2-(*p*-tolylsulfinyl)-4-cyclohexene-1,2-dicarboxylate (10i).** Eluent: hexane–$CH_2Cl_2$ (1:1 and 1:2). Yield: 23%. $[\alpha]^{20}_D$ = -65.6 (*c* = 1.02, $CHCl_3$). IR ($CHCl_3$): 2960, 2920, 2900, 1710, 1430, 1320, 1300, 1200, 1080, 1060, and 1035 $cm^{-1}$. $^1H$ NMR δ: 2.40 (s, 3H), 2.52–2.65 (m, 1H), 2.92-3.08 (m, 1H), 3.40 (s, 3H), 3.51 (s, 3H), 3.92 (dd, 1H, *J* = 1.9 and 6.7 Hz), 4.52 and 4.60 (AB system, 2H, *J* = 12.2 Hz), 4.62–4.64 (m, 1H), 5.81–5.97 (m, 2H), 7.10–7.34 (m, 7H, Ar), and 7.63 (half of an AA'BB' system, 2H). MS (EI): 369 (0.4), 270 (0.82), 167 (5.3), 164 (43.2), 163 (28.4), 149 (12.5), 140 (13.6), 135 (6.8), 105 (16.7), 104 (5.7), 92 (27.8), 91 (100.0) 77 (16.8), and 65 (15.2). HRMS: exact mass calcd for $C_{24}H_{26}O_6S$ ($M^+$) 442.1450, found 442.1523.

**(*S*)-2-Benzyl 1-Methyl 3-Methoxy-1,4-cyclohexadiene-1,2-dicarboxylate (11i).** Eluent: hexane–$CH_2Cl_2$ (1:1). Yield: 67%. $[\alpha]^{20}_D$ = +67.7 (*c* = 1.7, $CHCl_3$). IR ($CHCl_3$): 3010, 2950, 1720, 1575, 1440, 1265, 1150, 1070, and 1010 $cm^{-1}$. $^1H$ NMR δ: 2.76–3.27 (m, 2H), 3.22 (s, 3H), 3.59 (s, 3H), 4.91–4.99 (m, 1H), 5.23 and 5.31 (AB system, 2H, *J* = 12.3 Hz), 5.83–6.11 (m, 2H) and 7.31–7.43 (m, 5H). MS (EI): 270 (4.8), 165 (10.4), 164 (83.7), 163 (87.6), 149 (34.7), 136 (15.9), 135 (18.3), 132 (13.9), 105 (25.3), 104 (22.7), 92 (34.5), 91 (100.0), 77 (25.1), 76 (14.4), and 65 (19.7). HRMS: exact mass calcd for $C_{16}H_{14}O_4$ ($M^+$) 270.0892, found 270.0833.

**(1*R*,10a*S*)-2-Benzyl 1-Methyl 7-Methoxy-1,9,10,10a-tetrahydrophenanthrene-1,2-dicarboxylate (13j).** Eluent: $CH_2Cl_2$–hexane: (3:1). Yield: 75%. $[\alpha]^{20}_D$ = −25.1 (*c* = 0.6, $CHCl_3$, ee = 96%). IR ($CHCl_3$): 2990, 2930, 2830, 1720, 1685, 1600, 1540, 1490, 1450, 1370, 1215, 1165, 1100, and 1065 $cm^{-1}$. $^1H$ NMR δ: 1.68 (dc, 1H, *J* = 4.6 and 12.8 Hz), 2.12–2.24 (m, 1H), 2.65–2.92 (m, 2H), 2.92–3.07 (m,1H), 3.56 (s, 3H), 3.78 (d, 1H, *J* = 8.6 Hz), 3.81 (s, 3H), 5.18 and 5.31 (AB system, 2H, *J* = 12.5 Hz), 6.60 (dd, 1H, *J* = 3.0 and 6.3 Hz), 6.64 (d, 1H, *J* = 3.3 Hz), 6.77 (dd, 1H, *J* = 3.3 and 8.8 Hz), 7.33–7.40 (m, 5H), 7.43 (d, 1H, *J* = 6.3 Hz), and 7.69 (d, 1H, *J* = 8.8 Hz). MS (EI): 404 (26.1, $M^+$), 344 (7.2), 237 (8.3), 210 (9.3), 209 (9.6), 165 (8.2), 163 (6.1), 162 (8.6), 151 (7.1), 113 (7.0), 92 (10.0), 91 (100.0), and 65 (6.3). HRMS: exact mass calcd for $C_{25}H_{24}O_5$ ($M^+$) 404.1624, found 404.1611.

**(1*R*,10a*R*)-2-Benzyl 1-Methyl 7-Methoxy-1,9,10,10a-tetrahydrophenanthrene-1,2-dicarboxylate (13'j).** Eluent: $CH_2Cl_2$–hexane (3:1). Obtained as a 1:1 mixture of isomers **13j** + **13'j** in the reaction of **3** with Dane's diene catalyzed by $Eu(fod)_3$ (40% yield). $^1H$ NMR δ: 1.54–1.60 (m, 1H), 1.94–2.02 (m, 1H), 2.73–3.12 (m, 3H), 3.43 (dd, 1H, *J* = 2.5 and 17.4 Hz), 3.67 (s, 3H), 3.82 (s, 3H), 5.14 and 5.25 (AB system, 2H, *J* = 12.4 Hz), 6.56 (dd, 1H, *J* = 2.7 and 6.3 Hz), 6.63 (d, 1H, *J* = 2.6 Hz), 6.77 (dd, 1H, *J* = 2.6 and 8.8 Hz), 7.29 (dd, 1H, *J* = 2.5 and 6.3 Hz), 7.22–7.40 (m, 5H) and 7.67 (d, 1H, *J* = 8.9 Hz).

**General Procedure for Sulfinyl Elimination in Adducts Derived from Cyclopentadiene.** To a solution of 50 mg (0.12 mmol, 1.0 equiv) of adduct **4** in dry toluene (0.5 mL) was added 108.5 mg (0.71 mmol, 1.2 equiv) of DBU. The solution was stirred at 70 °C for 4–20 h, and 20% $NH_4Cl$ (15 mL) was added. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 15 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (hexane–ethyl acetate (20:1)).

**(+)-(1*S*,4*R*)-2-Benzyl 3-Methyl Bicyclo[2.2.1]hepta-2.5-diene-2,3-dicarboxylate [(+)-5a].** From a mixture of adducts **4a** (*endo*-**4a**/*endo*-**4'a**/*exo*-**4a** = 6/91/3). Yield: 52%. $[\alpha]^{20}_D$ = +10.1 (*c* = 0.83, $CHCl_3$) [lit.[16] for enantiomer (−)-**5**, $[\alpha]^{20}_D$ = −10.6 (*c* = 2.19, $CHCl_3$). From the *exo*-**4a** adduct. Yield: 42%. $[\alpha]^{20}_D$ = +10.3 (*c* = 0.89, $CHCl_3$).

**(−)-(1*R*,4*S*)-2-Benzyl 3-Methyl Bicyclo[2.2.1]hepta-2.5-diene-2,3-dicarboxylate [(−)-5a].** From a mixture of *endo*-**4a**/*endo*-**4'a** = 86/14. Yield: 59%. $[\alpha]^{20}_D$ = −7 (*c* = 1.71, $CHCl_3$).

**(1*S*,2*R*)-2-(Methoxycarbonyl)cyclohexane-1-carboxylic Acid (8).** To a suspension of $PtO_2$ (6 mg, 0.026 mmol, 0.1 equiv) in ethyl acetate (0.5 mL) was added a solution of compound **4a** (70.3 mg, 0.26 mmol, 1.0 equiv) in ethyl acetate (1.5 mL). The mixture was stirred under a hydrogen atmosphere (1 atm) for 24 h at rt. The reaction mixture was filtered over Celite and concentrated, giving the desired product (45.5 mg, 95% yield) which was used without further purification. $[\alpha]^{20}_D$ = -1.7 (*c* = 1.08, $CHCl_3$). IR ($CHCl_3$): 3520, 2940, 2860, 1730, 1710, 1450, 1440, 1375, 1310, 1250, 1210, 1130, 1040, 995, 925, and 725 $cm^{-1}$. $^1H$ NMR δ: 1.31–1.65 (m, 4H), 1.65–1.82 (m, 2H), 1.85–2.15 (m, 2H), 2.77–2.92 (m, 2H), 3.68 (s, 3H), and 10.13 (bs, 1H). $^{13}C$ NMR δ: 23.6, 23.7, 26.0, 26.2, 42.3, 42.6, 51.6, 174.2, 180.0. MS (EI): 186 (0.2, $M^+$), 168 (8.8), 155 (14.2), 154 (10.1), 142 (1.8), 141 (3.9), 140 (37.8), 126 (26.0), 109 (16.0), 108 (41.7), 99 (5.2), 97 (6.1), 82 (20.1), 81 (100.0), 80 (40.6), 79 (29.5), 77 (11.3), 67 (32.8), 59 (14.7), 55 (26.0), 54 (20.1), and 53 (21.5).

**(1*S*,6*R*)-8-Oxabicyclo[4.3.0]nonan-7-one (9).** To a solution of the carboxylic acid **8** (45.5 mg, 0.24 mmol, 1.0 equiv) in THF (0.6 mL) at 0 °C was added $BH_3SMe_2$ (150 μL of a 2 M solution in THF, 0.3 mmol, 1.2 equiv). The mixture was stirred at 0 °C for 24 h. Then, $BH_3SMe_2$ (150 μL) was added, and stirring was continued for an other 24 h at 0 °C. HCl (5%, 2 mL) was added, and the mixture was stirred for 15 min. The reaction mixture was extracted with ethyl acetate (3 × 10 mL), dried ($MgSO_4$) and concentrated. The crude product was purified by flash chromatography (hexane–ethyl acetate (6:1)) to afford 16.8 mg (49%) of compound **9**. $[\alpha]^{20}_D$ = −49.3 (*c* = 0.48, $CHCl_3$) [lit.[26] for (1*R*, 6*S*)-isomer $[\alpha]^{20}_D$ = +48.8 (*c* = 0.5, $CHCl_3$)].

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**Supplementary Material Available:** $^1H$ NMR spectra of *endo*-**4a**, *endo*-**4'a**, *exo*-**4a**, **5b**, **7c-7h**, **11g-11i**, *exo*-**10i**, and **13j** (15 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.