Diastereoselective Diels–Alder Cycloadditions with Chiral 1-(Alkylsulfinyl)-2-nitroalkenes

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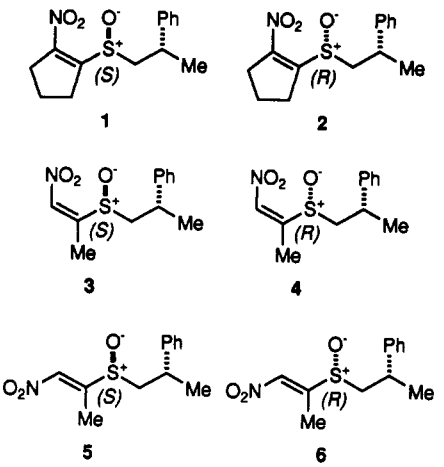
Several chiral 2-nitro-1-sulfinylalkenes were prepared and examined for their utility as dienophiles for asymmetric [4 + 2] cycloaddition. Trisubstituted dienophiles **3–6** undergo diastereoselective cycloaddition with cyclopentadiene in the presence of Lewis acids. Even the tetrasubstituted chiral sulfinyl dienophiles **1** and **2** could be coerced into undergoing [4 + 2] cycloaddition to afford the cycloadducts in high yield without concomitant elimination if the reaction was conducted under high pressure. Generally, the *Z*-sulfinyl dienophiles **1–4** showed higher diastereo- and *endo*/*exo*-selectivity than the *E*-dienophiles **5** and **6**.

Introduction

The asymmetric Diels–Alder reaction is one of the most efficient of ways of constructing optically active cyclohexenes bearing up to four stereogenic centers in a single operation.[1] Recently, much attention has been paid to the versatility of chiral sulfinylalkenes as novel dienophiles in the asymmetric Diels–Alder reaction.[2] Since simple sulfinylalkenes are inert toward ordinary dienes, oxidative conversion to the sulfoxide[3] or sulfoximine[4] has been found to activate the dienophilicity of the parent sulfinylalkene. An additional electron-withdrawing group has also been introduced into the sulfinylalkene to activate the dienophilicity.[5] Typically, ester functionality has been introduced at the α-[6] or β-position[7] or both[8] positions of the sulfinylalkene. Diels–Alder cycloadditions of sulfinylalkenes conjugated with ester groups were extensively investigated by Koizumi and co-workers, and a correlation between steric factors and stereoselectivity was found.[9] We recently reported the preparation of novel chiral dienophiles, 1-(alkylsulfinyl)-2-nitroalkenes **1** and **2**, and demonstrated that their asymmetric Diels–Alder reactions proceeded smoothly.[10] Both of the dienophiles **1** and **2** were reactive with highly oxygenated electron-rich dienes such as Danishefsky's diene. However, they showed poor reactivity toward nonactivated dienes under conventional thermal conditions.



Addition of a Lewis acid lowers the LUMO energy level of the dienophile and facilitates [4 + 2] cycloaddition.[11] Asymmetric Diels–Alder reactions employing optically active Lewis acids[12] invoke a great deal of interest among asymmetric synthesis. Because of the large negative activation volume ($\Delta V^{\ddagger}$) of the reaction, the intermolecular Diels–Alder reaction can also be accelerated by high pressure.[13] In this paper, we describe the Lewis acid-

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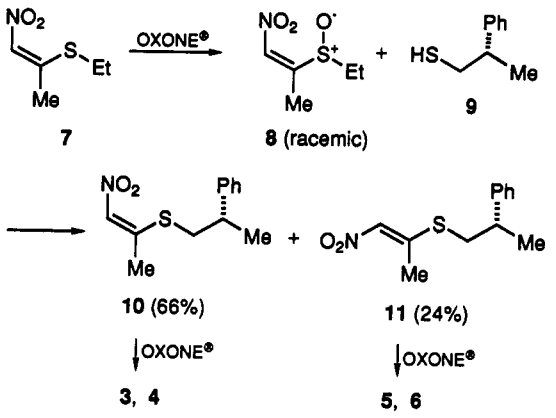
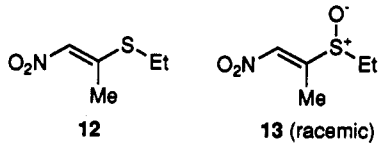
Scheme 1



promoted and high pressure-prompted Diels–Alder cycloadditions with optically active 1-(alkylsulfinyl)-2-nitroalkenes as chiral dienophiles.[14]

Results and Discussion

Preparation of Chiral Dienophiles. Chiral sulfinyl dienophiles 3–6 were prepared in a manner similar to that previously reported for cyclic counterparts 1 and 2[10] as shown in Scheme 1. Oxidation of sulfide 7[15] with Oxone gave a racemic sulfinyl compound 8 in good yield without any isomerization to the corresponding *E*-form 13, which could be obtained from *E*-sulfide 12 by the same oxidation in 91% yield. The sulfur–sulfur exchange reaction was



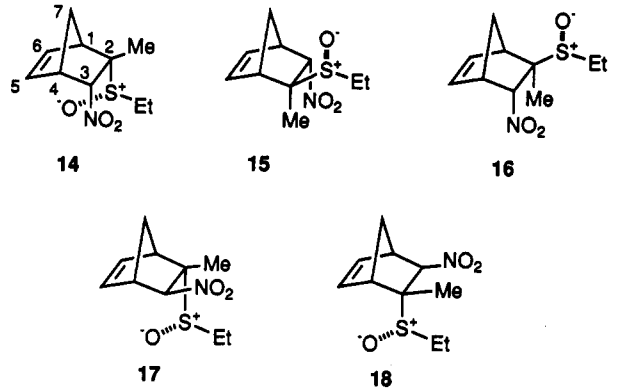
successfully applied to the transformation of the chiral sulfide. Thus, the racemic sulfoxide 8 was treated with (*S*)-2-phenylpropanethiol (9)[16] to give a mixture of chiral sulfides 10 (66%) and 11 (24%). Oxidation of 10 with Oxone provided a 98% yield of a separable mixture of two diastereomers 3 and 4 in a 3:1 ratio. The chiral vinyl sulfide 11 was similarly oxidized to a 2:1 mixture of 5 and 6 in good yield. The major sulfoxides 3 and 5 were subjected to single X-ray diffraction analyses[17] to determine their absolute structures. Thus, the single X-ray analyses showed that both have an *S*-configuration at the sulfur atom, which implied the *R*-configuration for the sulfur atom of the minor sulfoxides 4 and 6.

Table 1. Diels–Alder Cycloaddition of Racemic Sulfinyl Compounds 8 and 13 with Cyclopentadiene[a]

entry	dienophile	Lewis acid	solvent	time (h)	product	yield[b] (%)
1	8	none	CH_2Cl_2	15	14	25
2	8	ZnI_2	CH_2Cl_2	2	14	47
3	8	$ZnBr_2$	CH_2Cl_2	2	14	77
4	8	$ZnCl_2$	CH_2Cl_2	2	14	82
5	8	$EtAlCl_2$	CH_2Cl_2	2	14	39
6	8	$SnCl_4$[c]	CH_2Cl_2	2		0[e]
7	8	$TiCl_4$[c]	CH_2Cl_2	2		0[e]
8	13	none	CH_2Cl_2	15	15, 16, 17, 18	1.4, 0.5, 0.4, trace
9	13	none	neat	15	15, 16, 17, 18	28, 14, 10, 3
10	13	ZnI_2	neat	15	15, 16, 17, 18	62, 8, 18, 10
11	13	ZnI_2[d]	neat	15	15, 16, 17, 18	18, 2, 4, 2
12	13	$ZnBr_2$	neat	15	15, 16, 17, 18	51, 8, 20, 8
13	13	$ZnCl_2$	neat	15	15, 16, 17, 18	38, 8, 14, 8
14	13	$LiClO_4$	neat	15	15, 16, 17, 18	46, 7, 15, 9
15	13	$TiCl_4$[d]	neat	15		0[e]
16	13	$BF_3{\cdot}Et_2O$[d]	neat	15		0[e]

[a] Cycloadditions were carried out at room temperature. [b] Yields are determined by ^1H NMR integration using benzaldehyde as an internal standard. [c] At −78 °C. [d] At −22 °C. [e] Polymerization.

Diels–Alder Reactions under Atmospheric Pressure. Preliminary experiments on the Diels–Alder reaction using the racemic sulfinyl dienophiles 8 and 13 were carried out in order to evaluate the efficiency of the Lewis acid catalyst. It was found that zinc halides effectively accelerated cycloadditions of the sulfinyl compounds with cyclopentadiene (Table 1). Zinc chloride was found to be among the best catalysts for the cycloaddition with (*Z*)-sulfinylnitroalkene 8, in which cycloadduct 14 was the sole product irrespective of catalysts employed. The cycloaddition with *E*-dienophile 13 proceeded smoothly with zinc iodide or zinc chloride to afford a mixture of four diastereomers 15–18.



On the basis of the above results, the Diels–Alder reaction of chiral dienophiles 3–6 with cyclopentadiene was investigated in the presence of zinc halides (Table 2). For cycloaddition reactions of (*Z*)-sulfinyl dienophiles 3 and 4, zinc chloride was chosen as a Lewis acid catalyst, while for (*E*)-sulfinyl dienophiles 5 and 6, zinc iodide was used. A similar diastereoselectivity to the racemic series 8 and 13 was observed in the optically active series. The sole adduct 19 or 20 was produced from the (*Z*)-sulfinyl dienophiles 3 or 4 (entries 2–5), while a mixture of three to four diastereomers was obtained from the *E*-dienophiles 5 or 6 (entries 6–9). Thus, highly controlled diastereoselectivity as well as *endo* selectivity was observed for the cycloaddition with *Z*-dienophiles. The reactions with the *E*-dienophiles proceeded with moderate *endo*/*exo* and

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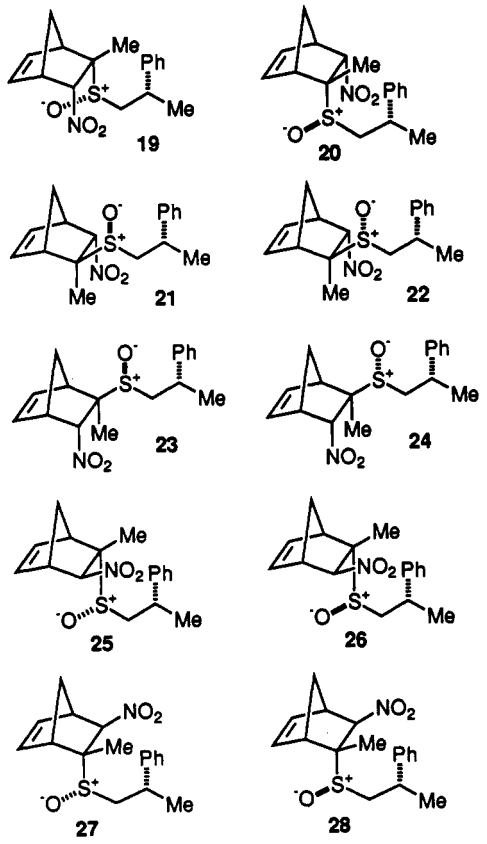
Table 2. Diastereoselective Diels–Alder Cycloaddition of Chiral Sulfinyl Compounds 3–6 with Cyclopentadiene[a]

entry	dienophile	Lewis acid	solvent	time (h)	product	yield[b] (%)
1	3	none	CH_2Cl_2	2	19	5
2	3	$ZnCl_2$	CH_2Cl_2	2	19	55
3	3	$ZnCl_2$	CH_2Cl_2	15	19	89
4	4	$ZnCl_2$	CH_2Cl_2	2	20	77
5	4	$ZnCl_2$	CH_2Cl_2	6	20	84[c]
6	5	$ZnCl_2$	CH_2Cl_2	15	21, 23, 25, 27	32, 4, 9, 2
7	5	ZnI_2	CH_2Cl_2	15	21, 23, 25, 27	30, –, 9, 2
8	5	ZnI_2	neat	15	21, 23, 25, 27	71, –, 22, 5
9	6	ZnI_2	neat	15	22, 24, 26, 28	4, 71, 2, 18

[a] All reactions were run at room temperature. [b] Yields were determined by ^1H NMR integration using benzaldehyde as internal standard. [c] Isolated yield.

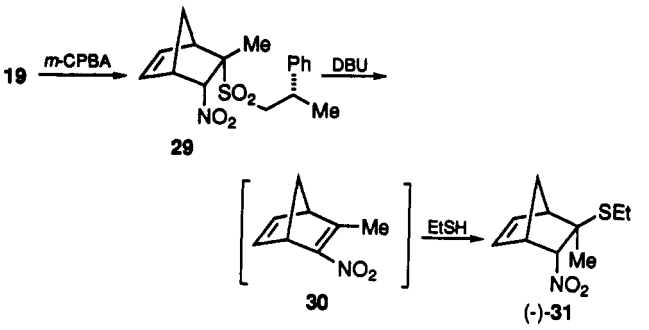
diastereofacial selectivities. The structure of cycloadduct **19** was unambiguously determined by a single X-ray crystallographic analysis.[17]

Stereochemical Assignment of the Products. Cycloadduct **19** was oxidized with *m*-CPBA giving a chiral sulfone **29**. Treatment of **29** with DBU in the presence of



ethanethiol provided the chiral sulfide (–)-**31** arising from *exo*-addition of the thiol to the intermediate nitroolefin **30** (Scheme 2). The *endo*-methyl at C2 and the *exo*-H3 in (–)-**31** were confirmed by the nuclear Overhauser effects shown in Figure 1. Chiral sulfones **32** and **33**, derived from **20** and **21**, respectively, underwent a similar elimination–addition reaction to that for **29** to afford the same product, (+)-**31**, establishing the absolute structures of **20** and **21**. This implies that the determining factor of the absolute stereochemistry in the Diels–Alder products is not the stereogenic center at the side chain but the sulfur atom in the dienophile.[10] The coupling constant and chemical shift of the proton geminal to the nitro group in ^1H NMR spectra are of diagnostic importance. The data

Scheme 2



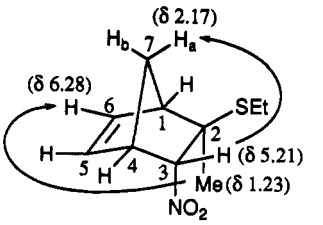


Figure 1. NOE experiments on **31**.

Table 3. Chemical Shifts (δ ppm) and Coupling Constants (Hz) of the Proton Geminal to the Nitro Group of Cycloadducts 14–28

cycloadduct[a]	chemical shift	coupling constant
endo		
14	5.01	3.4
19	4.94	3.4
20	4.98	3.4
endo-major		
15	4.77	3.3
21	4.27	3.3
24	4.66	3.3
exo-major		
17	3.99	1.8
25	3.58	1.7
28	3.91	1.6
endo-minor		
16	5.47	3.3
22	5.30	
23	5.50	
exo-minor		
18	4.84	2.2
26	4.85	
27	4.78	

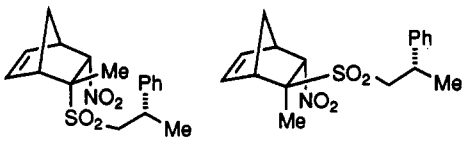
are compiled in Table 3. The larger coupling constants (~3.4 Hz) are indicative of *exo*-stereochemistry of adducts. Furthermore, there is a closeness in chemical shifts for each group of three compounds, **14**, **19**, **29**; *endo*-major adducts (**15**, **21**, **24**); *exo*-major adducts (**17**, **25**, **28**); *endo*-minor adducts (**16**, **22**, **23**); and *exo*-minor adducts (**18**, **26**, **27**). Since chemical shift of the protons must be almost equally affected in a similar class of compounds by an anisotropy due to the neighboring sulfinyl group and the double bond in the six-membered ring, these groupings may provide helpful information for the structural assignment. The relative stereochemistry of (±)-**14** was easily deduced from the ^1H NMR data on H3. Formation of **14** from *Z*-olefin **8** as the sole product is quite reasonable because the reaction should proceed through a similar transition state to that for the chiral sulfoxide **3** giving **19**. The *endo*-nitro group epimerized easily with a base to afford the *exo*-major adduct **17**. This finding confirmed the structure of another *exo*-isomer **18**. The close similarity of relative stereochemistries of **25** and **28** with that of **17** was indicated by the chemical shifts and coupling constants as shown in Table 3. Since the chirality at the sulfur

Table 4. High-Pressure Diels–Alder Cycloadditions of 1, 2, 3, and 5[a]

entry	dienophile	diene	product	yield[b] (%)
1	1	1,3-pentadiene	34	80
2[c]	1	1,3-pentadiene		0
3	1	2,3-dimethyl-1,3-pentadiene	36	77
4[d]	1	cyclopentadiene	34	39
			38[e]	61
5[c]	1	cyclopentadiene	39	14
			38	32
6	2	1,3-pentadiene	35	88
7	2	2,3-dimethyl-1,3-pentadiene	37	68
8	2	cyclopentadiene	41	41
			40	59
9[c]	2	cyclopentadiene	41	19
			40	32
10	3	1,3-pentadiene	42	81
11	3	2,3-dimethyl-1,3-pentadiene	43	71
12	3	isoprene	45, 46 (5:1)[f]	64
13	5	2,3-dimethyl-1,3-pentadiene	47, 48 (2:1)[f]	61
14	5	1,3-pentadiene	49, 50, 51, 52 (3:1:2:1)[f]	72

[a] The reaction conditions were not optimized. [b] Isolated yield. [c] Cycloaddition was carried out under 1 atm for 11 days at room temperature. [d] THF was used as solvent. [e] 92% de by ^{1}H NMR analysis. [f] The ratio was determined by ^{1}H NMR.

atom determines the absolute stereochemistry of the bicyclo[2.2.1] ring system, the absolute configuration of **25**, derived from (*S*)-sulfoxide **5**, must be opposite to that of **28**. Although there is no definite chemical or spectral evidence for the structures of compounds of the *endo*-minor group, mechanistic considerations provide a basis for their structures. A diene should approach from the less hindered face of the dienophile regardless of the *endo*- or *exo*-attack. Thus, the *endo*-major products (**15**, **21**, and **24**) were obtained by attack of the diene to the dienophile from the same diastereomeric face as that for *exo*-major products. The structures **16**, **22**, and **23** were estimated in a similar way. Since the asymmetric induction is determined only by the absolute stereochemistry at sulfur, the cycloadducts **22**, **24**, **26**, and **28** from the (*R*)-sulfoxide **6** must have the opposite configuration to **23**, **21**, **27**, and **25**, respectively, at the [2.2.1]bicyclo ring system.



32 33

Diels–Alder Reactions under High-Pressure Conditions. Tetrasubstituted olefins are generally inert to the cycloaddition even with Lewis acid catalyst. Actually, the tetrasubstituted olefins such as **1** or **2** were found to be inactive toward a variety of dienes. However, a high-pressure technique has been employed to the Diels–Alder reaction to surmount the lack of reactivity caused by steric or electronic factors. This technique was successfully applied to the cycloaddition involving olefin **1** or **2**, and the results are summarized in Table 4.[14] The cycloaddition proceeded quite smoothly with satisfactory yield under the conditions of 8 kbar at room temperature without any aromatization or elimination of the sulfinyl group. Complete diastereoselectivity was again observed with the (*Z*)-sulfinyl compounds **1**–**3** but poor selectivity with the *E*-olefin **5**. The regioselectivity was considerably influenced by the structure of the diene employed. Thus, the reaction of *Z*-olefin **3** with 1,3-pentadiene proceeded regioselectively (entry 10), while the reaction with isoprene led to poor selectivity (entry 12). The absolute structures of cycloadducts **34**, **38**, and **43** were established by X-ray diffraction analyses[17] and led to the deduction of the structures of the related cycloadducts **35** and **39**. Structures of cycloadducts **36**, **37**, **40**–**42**, **45**, and **46** from the *Z*-olefins can be deduced from the mechanistic considerations discussed earlier. The structures of **47**–**52** were tentatively assigned as the corresponding formulas shown in the text based on the related cycloadditions shown in Table 2 (entries 6–8).

Origin of Difference in Selectivity between *Z*- and *E*-Dienophiles. The (*Z*)-sulfinyl compounds exhibited high diastereoselectivity under the Lewis acid-promoted conditions as well as under high pressure. Addition of zinc halide had little effect on the stereochemistry and diastereomeric ratio of the products, although it markedly enhanced the reaction rate (see entries 1, 2, and 8–12 in Table 1 and entries 1 and 2 in Table 2). These findings clearly reject the chelation of (*Z*)-sulfoxides with zinc halide shown in Figure 2a because this model should show diastereofacial selectivity opposite to that actually observed. Another chelation involving two oxygen atoms of the nitro group (Figure 2b) can rationalize the marked rate acceleration by a Lewis acid but the small change in diastereoselectivity.

The high diastereoselectivity with (*Z*)-sulfoxides could be well explained on the basis of the conformation of the dienophiles.[18] The *s-trans* conformation for C=CS=O of **3** in the crystalline state should be maintained in the solution due to the strong dipole–dipole repulsive interaction between the sulfinyl and the nitro groups. Figure 3 illustrates the possible *endo*-approach of 2,3-dimethylbutadiene to nitroolefin **3**, which demonstrates that an attack from the top face of **3** is an energetically favorable process that gives **43** predominantly. The bottom-face attack of the diene giving **44** is shielded by the bulky alkyl group. On the other hand, as can be seen from the crystal structure of the (*E*)-sulfinyl compound, **5** showed the *s-cis* geometry of the C=CS=O moiety. The approach of 2,3-dimethylbutadiene *endo* to the nitro group is shown in Figure 4 using the crystalline conformation for **5**. This diagram predicts that **48** is the major product because the top-face attack of the diene is blocked by the side chain on the sulfur atom. However, the experimental results do not agree with this, possibly due to the easy rotation of the C–S bond of (*E*)-sulfinyl compound **5** in solution. Thus, the poor diastereoselectivity observed in the cycloaddition with the (*E*)-sulfinyl dienophiles **5** and **6** may be attributed to the lack of conformational rigidity around the C=CS=O single bond in solution.

Conclusions

The chiral 1-(alkylsulfinyl)-2-nitroalkenes have been developed as useful dienophiles for asymmetric Diels–Alder reactions. By adjusting the reaction conditions by Lewis acid catalyst or a high-pressure technique, the

(18) Torrens, F.; Ruiz-López, M.; Cativiela, C.; Garcia, J. I.; Mayoral, J. A. *Tetrahedron* **1992**, *48*, 5209.

Chart 1

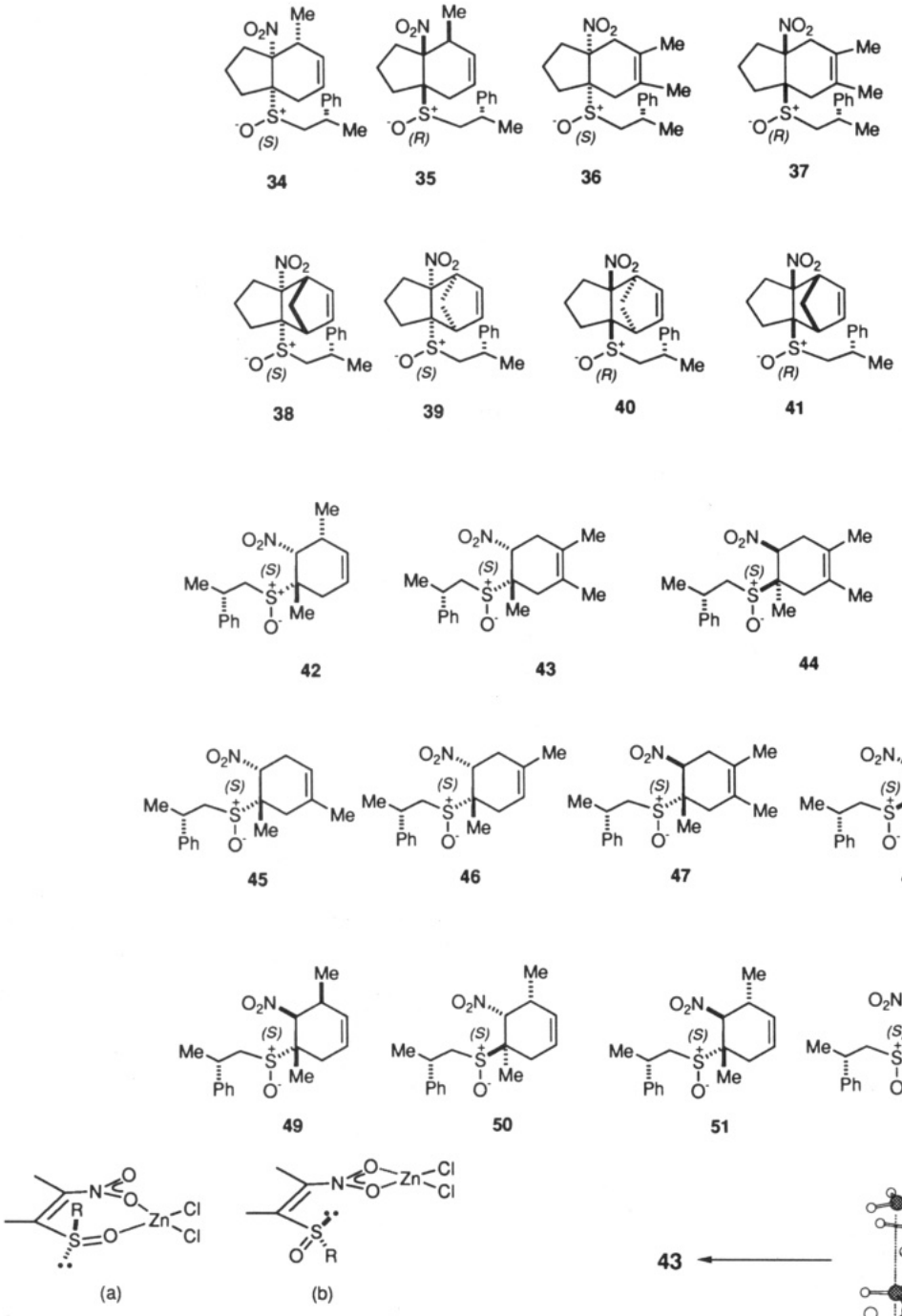


Figure 2. Two possible chelation models for (*Z*)-sulfoxides.

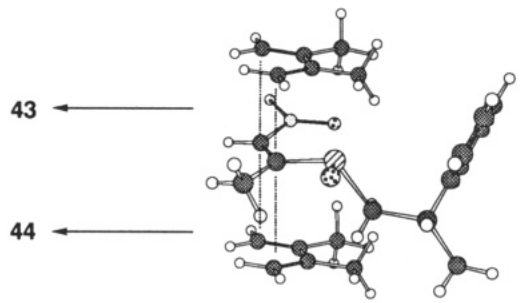


Figure 3. Possible *endo*-approach of 2,3-dimethylbutadiene to the nitroolefin **3**, generated through Chem3D. The conformation in the crystalline state is adopted.

cycloaddition proceeds smoothly resulting in the cycloadduct in good chemical yield as well as with satisfactory diastereoselectivity. The successful construction of functionalized optically active cyclohexene derivatives by diastereoselective [4 + 2] cycloadditions utilizing the chiral sulfinyl dienophiles is promising and can be applied to the asymmetric synthesis of biologically active compounds.

Experimental Section

General Aspects. Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were taken at 200 or 400 MHz in $CDCl_3$ with chemical shifts being reported as δ ppm from tetramethylsilane as an internal standard, and couplings are expressed in hertz. THF was distilled from sodium benzophenone and dichloromethane was from calcium hydride. Unless otherwise noted, all reactions were run under an argon or nitrogen atmosphere. All extractive organic solutions were dried over anhydrous magnesium sulfate. Column chromatography was carried out with Wako-gel C-200, and silica gel 60 F254 plates (Merck) were used for preparative TLC.

(*Z*)-2-(Ethylsulfinyl)-1-nitro-1-propene (8). To a solution of (*Z*)-2-(ethylthio)-1-nitro-1-propene (**7**) (7.4 g, 50 mmol) in a mixture of THF (60 mL), methanol (30 mL), and water (60 mL) was added portionwise Oxone (20.1 g, 33 mmol). The mixture was vigorously stirred for 1 h at 0 °C. After extractive workup

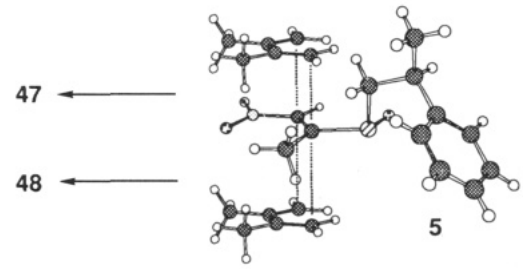


Figure 4. Possible approach of 2,3-dimethylbutadiene to the nitroolefin **5** *endo* to the nitro group leading to **47** and **48** generated through Chem3D. The conformation in the crystalline state is adopted.

with CH_2Cl_2, the extract was washed with brine, dried, and evaporated to leave crystalline **8** (8.0 g, 98%) which was recrystallized from EtOH to yield yellow needles, mp 48–49 °C: IR ($CHCl_3$) 3000, 1525, 1345, 1065 cm^{-1}; ^1H NMR (200 MHz) δ 1.48 (t, 3H, J = 7.3), 2.25 (d, 3H, J = 1.7), 2.98 (dq, 1H, J = 13.6, 7.3), 3.11 (dq, 1H, J = 13.6, 7.3), 7.30 (brs, 1H); HRMS m/z 163.0290 ($C_5H_9NO_3S$ requires 163.0303). Anal. Calcd for $C_5H_9NO_3S$: C, 36.80; H, 5.56; N, 8.58. Found: C, 36.54; H, 5.53; N, 8.57.

(*Z*)-(2*S*)-1-Nitro-2-[(2-phenylpropyl)thio]-1-propene (10) and (*E*)-(2*S*)-1-Nitro-2-[(2-phenylpropyl)thio]-1-propene (11). Triethylamine (114 μL, 809 μmol) was added dropwise to a solution of **8** (113 mg, 809 μmol) and (*S*)-2-phenylpropanethiol (**9**)[16] (124 mg, 814 μmol) in dry CH_2Cl_2 (4 mL) at −78 °C. The resulting mixture was further stirred at the same temperature for 1 min. The reaction mixture was poured into dilute HCl at 0 °C and extracted with dichloromethane. The extracts were washed with brine and dried. The solvent was removed under reduced pressure to give a residue which was subject to preparative TLC with hexane–AcOEt (2:1) to yield **10** (126 mg, 66%) and **11** (47 mg, 24%) as a yellow oil.

10: $[\alpha]^{22}_D$ −128.8 (*c* 0.89, $CHCl_3$); IR ($CHCl_3$) 1570, 1480, 1330, 1295 cm^{-1}; ^1H NMR (200 MHz) δ 1.42 (d, 3H, J = 6.2), 2.16 (s, 3H), 2.90–3.25 (m, 3H), 7.17–7.40 (m, 6H). Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37; N, 5.90. Found: C, 60.69; H, 6.34; N, 5.87.

11: $[\alpha]^{20}_D$ +37.6 (*c* 1.22, $CHCl_3$); IR ($CHCl_3$) 1580, 1500, 1330 cm^{-1}; ^1H NMR (200 MHz) δ 1.43 (d, 3H, J = 6.5), 2.45 (s, 3H), 2.94–3.15 (m, 3H), 6.83 (s, 1H), 7.13–7.45 (m, 5H). Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37; N, 5.90. Found: C, 60.76; H, 6.56; N, 5.62.

(*E*)-2-(Ethylsulfinyl)-1-nitro-1-propene (13). To a solution of (*E*)-2-(ethylthio)-1-nitro-1-propene (**12**) (1.9 g, 13 mmol) in a mixture of THF (16 mL), MeOH (8 mL), and water (16 mL), was added Oxone (5.0 g, 8.2 mmol). The mixture was vigorously stirred for 1 h at rt. After extractive workup with CH_2Cl_2, the extract was washed, dried, and evaporated to leave a crystalline residue of **13** (1.9 g, 91%), which was recrystallized from CH_2Cl_2–ether to give pale yellow prisms: mp 42.5–44 °C; IR ($CHCl_3$) 3000, 1525, 1345, 1065 cm^{-1}; ^1H NMR (200 MHz) δ 1.33 (t, 3H, J = 7.5), 2.30 (d, 3H, J = 1.6), 2.75 (dq, 1H, J = 13.8, 7.5), 3.08 (dq, 1H, J = 13.8, 7.5), 7.39 (q, 1H, J = 1.6); MS m/z 163 (M^+). Anal. Calcd for $C_5H_9NO_3S$: C, 36.80; H, 5.56; N, 8.58. Found: C, 36.54; H, 5.62; N, 8.49.

(*Z*)-(S*S*,2*S*)-1-Nitro-2-[(2-phenylpropyl)sulfinyl]-1-propene (3) and (*Z*)-(S*R*,2*S*)-1-Nitro-2-[(2-phenylpropyl)sulfinyl]-1-propene (4). To a solution of **10** (1.4 g, 6.1 mmol) in a mixture of THF (20 mL), MeOH (10 mL), and water (20 mL) was added Oxone (2.4 g, 3.9 mmol). The mixture was vigorously stirred at 0 °C for 3 h. The reaction mixture was extracted with CH_2Cl_2, and the extract was washed with brine and dried to give a mixture of **3** and **4** (1.5 g, 98%) in a 3:1 ratio judging from integration of the ^1H NMR spectrum. The mixture was subjected to silica gel flash chromatography with hexane–AcOEt (1:1). The product from the more polar fractions was recrystallized from ether to give **3** and the less polar fractions from ether to give **4**.

3: $[\alpha]^{20}_D$ −10.4 (*c* 0.72, $CHCl_3$); mp 98–100 °C (needles); IR ($CHCl_3$) 1525, 1350, 1065 cm^{-1}; ^1H NMR (400 MHz) δ 1.47 (d, 3H, J = 6.8), 2.25 (d, 3H, J = 1.9), 3.08 (dd, 1H, J = 12.0, 5.4), 3.26 (t, 1H, J = 12.0), 3.47–3.53 (m, 1H), 7.20 (q, 1H, J = 1.9), 7.26–7.40 (m, 5H). Anal. Calcd for $C_{12}H_{15}NO_3S$: C, 56.90; H, 5.97; N, 5.53. Found: C, 56.91; H, 5.97; N, 5.54. Crystal data: space group $P2_1$ with a = 9.474(1) Å, b = 10.362(2) Å, c = 6.906(2) Å, and D_c = 1.303 g cm^{-1} for Z = 2.

4: $[\alpha]^{20}_D$ +286.6 (*c* 0.78, $CHCl_3$); mp 71–75 °C (needles); IR ($CHCl_3$) 1520, 1345, 1065, cm^{-1}; ^1H NMR (200 MHz) δ 1.62 (d, 3H, J = 6.9), 2.20 (d, 3H, J = 1.1), 3.13 (d, 2H, J = 5.6), 3.47 (m, 1H), 7.18–7.45 (m, 6H). Anal. Calcd for $C_{12}H_{15}NO_3S$: C, 56.90; H, 5.97; N, 5.53. Found: C, 56.67; H, 5.86; N, 5.55.

(*E*)-(S*S*,2*S*)-1-Nitro-2-[(2-phenylpropyl)sulfinyl]-1-propene (5) and (*E*)-(S*R*,2*S*)-1-Nitro-2-[(2-phenylpropyl)sulfinyl]-1-propene (6). To a solution of **11** (524 mg, 2.2 mmol) in a mixture of THF (10 mL), MeOH (5 mL), and water (10 mL) was added Oxone (883 mg, 1.4 mmol) at 0 °C. The mixture was allowed to warm to rt and vigorously stirred for 6 h. After extractive workup with CH_2Cl_2, the extracts were washed with brine, dried, and concentrated under reduced pressure to afford a mixture of **5** and **6** (439 mg, 78%) in a 2:1 ratio, which was determined by integration of the ^1H NMR spectrum. The residue was subjected to silica gel column chromatography with hexane–ethyl acetate (4:1) to give **5** from the more polar fractions and **6** from the less polar fractions. Recrystallization of **5** and **6** from ether afforded pale yellow crystals, respectively.

5: $[\alpha]^{20}_D$ −59.6 (*c* 0.57, $CHCl_3$); mp 102–104 °C (prisms); IR ($CHCl_3$) 1525, 1340, 1060 cm^{-1}; ^1H NMR (200 MHz) δ 1.47 (d, 3H, J = 7.0), 2.22 (d, 3H, J = 1.6), 2.95 (dd, 1H, J = 12.7, 4.9), 3.10 (dd, 1H, J = 12.7, 10.5), 3.50 (m, 1H), 7.22–7.46 (m, 6H). Anal. Calcd for $C_{12}H_{15}NO_3S$: C, 56.90; H, 5.97; N, 5.53. Found: C, 56.60; H, 6.02; N, 5.30. Crystal data: space group C_2 with a = 10.149 (4) Å, b = 6.925 (2) Å, c = 18.940 (10) Å, and D_c = 1.266 g cm^{-1} for Z = 4.

6: $[\alpha]^{20}_D$ −68.3 (*c* 1.04, $CHCl_3$); mp 64–65 °C (needles); IR ($CHCl_3$) 1520, 1345, 1065 cm^{-1}; ^1H NMR (200 MHz) δ 1.52 (d, 3H, J = 7.0), 2.17 (d, 3H, J = 1.6), 3.01 (dd, 1H, J = 13.1, 6.3), 3.09 (dd, 1H, J = 13.1, 7.9), 3.50 (m, 1H), 7.17–7.40 (m, 6H). Anal. Calcd for $C_{12}H_{15}NO_3S$: C, 56.90; H, 5.97; N, 5.53. Found: C, 56.70; H, 5.98; N, 5.36.

General Procedure for Diels–Alder Cycloaddition of Sulfinyl Compounds with Cyclopentadiene (Tables 1 and 2). Lewis acid (1 mol equiv) was added to a solution of sulfinyl compound (20 mg) and cyclopentadiene (6 mol equiv) in CH_2Cl_2 (1 mL) or freshly distilled cyclopentadiene (1 mL), and the reaction mixture was stirred at rt. After the mixture was poured into water (20 mL) and extracted with CH_2Cl_2, the organic layer was washed with brine, dried, and evaporated to leave an oily residue. The residue was subjected to silica gel short column chromatography with AcOEt to remove cyclopentadiene dimer. Yields were determined by integration of the ^1H NMR by use of benzaldehyde as an internal standard and are reported in Tables 1 and 2. In the case of the formation of a mixture of cycloadducts, repeated preparative TLC was carried out with a solvent system of AcOEt–hexane, 2-PrOH–hexane, or CH_2Cl_2–hexane to separate each isomer. However, all attempts to isolate **22**, **23**, **26**, and **27** in a pure form were unfruitful.

14: prisms; mp 66–68 °C (ether); IR ($CHCl_3$) 3000, 1550, 1380, 1040, 1015 cm^{-1}; ^1H NMR (200 MHz) δ 1.37 (t, 3H, J = 7.6), 1.73 (s, 3H), 1.68–1.85 (m, 2H), 2.45 (dq, 1H, J = 12.6, 7.6), 2.66 (dq, 1H, J = 12.6, 7.6), 3.08 (brs, 1H), 3.54 (brs, 1H), 5.01 (d, 1H, J = 3.4), 6.41 (dd, 1H, J = 5.7, 2.8), 6.77 (dd, 1H, J = 5.7, 2.9); MS m/z 229 (M^+). Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.11. Found: C, 52.17; H, 6.66; N, 6.03.

15: amorphous; IR ($CHCl_3$) 3000, 1550, 1380, 1020 cm^{-1}; ^1H NMR (400 MHz) δ 1.13 (s, 3H), 1.50 (t, 3H, J = 7.7), 1.67 (d, 1H, J = 9.9), 2.04 (d, 1H, J = 9.9), 2.67 (dq, 1H, J = 13.2, 7.7), 3.04 (dq, 1H, J = 13.2, 7.7), 3.36 (brs, 1H), 3.44 (brs, 1H), 4.77 (d, 1H, J = 3.3), 6.37 (dd, 1H, J = 5.5, 3.3), 6.58 (dd, 1H, J = 5.5, 2.9). Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.11. Found: C, 52.42; H, 6.72; N, 6.13.

16: amorphous; IR ($CHCl_3$) 3000, 1550, 1380, 1020 cm^{-1}; ^1H NMR (400 MHz) δ 1.01 (s, 3H), 1.43 (t, 3H, J = 7.3), 1.49 (d, 1H, J = 9.5), 2.40 (d, 1H, J = 9.5), 2.81 (dq, 1H, J = 12.8, 7.3), 2.97 (dq, 1H, J = 12.8, 7.3), 3.10 (brs, 1H), 3.38 (brs, 1H), 5.47 (d, 1H, J = 3.3), 6.41 (dd, 1H, J = 5.5, 3.3), 6.65 (dd, 1H, J = 5.5, 2.6). Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.11. Found: C, 52.41; H, 6.72, N; 6.17.

17: amorphous; IR ($CHCl_3$) 3000, 1550, 1360, 1050, 1020 cm^{-1}; ^1H NMR (400 MHz) δ 1.42 (s, 3H), 1.42 (t, 3H, J = 7.5), 1.94 (ddd, 1H, J = 9.9, 2.9, 1.5), 2.28 (d, 1H, J = 9.9). 2.56 (dq, 1H, J = 13.2, 7.5), 2.85 (dq, 1H, J = 13.2, 7.5), 3.08 (brs, 1H), 3.43 (d, 1H, J = 1.5), 3.99 (d, 1H, J = 1.8), 6.23 (dd, 1H, J = 5.5, 3.3), 6.63 (dd, 1H, J = 5.5, 2.9). Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.11. Found: C, 52.48; H, 6.68; N, 6.26.

18: amorphous; IR ($CHCl_3$) 3000, 1550, 1370, 1060, 1020 cm^{-1}; ^1H NMR (400 MHz) δ 1.34 (s, 3H), 1.38 (t, 3H, J = 7.7), 1.87 (ddd, 1H, J = 9.9, 3.7, 1.8), 2.36 (d, 1H, J = 9.9), 2.65 (dq, 1H, J = 12.8, 7.7), 2.81 (dq, 1H, J = 12.8, 7.7), 2.83 (brs, 1H), 3.43 (d, 1H, J = 1.5), 4.84 (d, 1H, J = 2.2), 6.19 (dd, 1H, J = 5.5, 3.3), 6.32 (dd, 1H, J = 5.5, 2.9). Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.11. Found: C, 52.31; H, 6.74; N, 6.00.

19: prisms; $[\alpha]^{20}_D$ –68.2 (c 0.40, $CHCl_3$); mp 117–120 °C (hexane–CH_2Cl_2); IR ($CHCl_3$) 3000, 1550, 1455, 1380, 1020 cm^{-1}; ^1H NMR (200 MHz) δ 1.45 (d, 3H, J = 7.0), 1.73 (s, 3H), 1.50–1.85 (m, 2H), 2.62 (dd, 1H, J = 12.6, 7.5), 2.96 (dd, 1H, J = 12.6, 8.1), 3.05 (brs, 1H), 3.30 (m, 1H), 3.48 (brs, 1H), 4.94 (d, 1H, J = 3.4), 6.32 (dd, 1H, J = 5.6, 2.9), 6.70 (dd, 1H, J = 5.6, 2.9), 7.15–7.40 (m, 5H). Anal. Calcd for $C_{17}H_{21}NO_3S$: C, 63.92; H, 6.63; N, 4.39. Found: C, 63.80; H, 6.65; N, 4.54. Crystal data: space group $P2_12_12_1$ with a = 12.048(1) Å, b = 11.772(1) Å, c = 11.486(1) Å, and D_c = 1.298 g cm^{-1} for Z = 4.

20: needles; $[\alpha]^{20}_D$ +131.6 (c 0.68, $CHCl_3$); mp 92–95 °C (ether); IR (KBr) 1540, 1455, 1050, 1025 cm^{-1}; ^1H NMR (200 MHz) δ 1.38 (d, 3H, J = 6.9), 1.69 (s, 3H), 1.72 (d, 1H, J = 10.0), 1.81 (d, 1H, J = 10.0), 2.74 (m, 2H), 3.08 (brs, 1H), 3.33 (m, 1H), 3.54 (brs, 1H), 4.98 (d, 1H, J = 3.4), 6.43 (dd, 1H, J = 5.5, 3.2), 6.79 (dd, 1H, J = 5.5, 2.6), 7.17–7.39 (m, 5H); HRMS m/z 319.1276 ($C_{17}H_{21}NO_3S$ requires 319.1242). Anal. Calcd for $C_{17}H_{21}NO_3S$: C, 63.92; H, 6.63; N, 4.39. Found: C, 63.83; H, 6.75; N, 4.33.

21: oil; $[\alpha]^{20}_D$ +51.7 (c 1.69, $CHCl_3$); IR ($CHCl_3$) 3000, 1550, 1450, 1370, 1035, 1025 cm^{-1}; ^1H NMR (200 MHz) δ 1.15 (s, 3H), 1.49 (d, 3H, J = 6.6), 1.54 (d, 1H, J = 10.3), 1.77 (d, 1H, J = 10.3), 2.81 (dd, 1H, J = 11.2, 9.1), 3.28 (brs, 2H), 3.46 (m, 2H), 4.27 (d, 1H, J = 3.3), 6.33 (dd, 1H, J = 5.5, 3.3), 6.55 (dd, 1H, J = 5.5, 2.9), 7.20–7.44 (m, 5H); HRMS m/z 319.1245 ($C_{17}H_{21}NO_3S$ requires 319.1242).

24: oil; $[\alpha]^{25}_D$ –9.0 (c 1.75, $CHCl_3$); IR ($CHCl_3$) 3000, 1550, 1055, 1025 cm^{-1}; ^1H NMR (200 MHz) δ 1.11 (s, 3H), 1.53 (d, 3H, J = 6.8), 1.65 (d, 1H, J = 9.9), 2.04 (d, 1H, J = 9.9), 2.86 (dd, 1H, J = 12.8, 3.1), 3.25 (dd, 1H, J = 12.8, 10.9), 3.34 (brs, 1H), 3.38–3.55 (m, 2H), 4.66 (d, 1H, J = 3.3), 6.35 (dd, 1H, J = 5.6, 3.5), 6.57 (dd, 1H, J = 5.6, 2.8), 7.19–7.40 (m, 5H); HRMS m/z 319.1263 ($C_{17}H_{21}NO_3S$ requires 319.1242).

25: needles; $[\alpha]^{20}_D$ +98.3 (c 0.58, $CHCl_3$): mp 151–153 °C (ether); IR ($CHCl_3$) 3000, 1555, 1360, 1035, 1025 cm^{-1}; ^1H NMR (200 MHz) δ 1.44 (s, 3H), 1.45 (d, 3H, J = 6.2), 1.88 (d, 1H, J = 10.0), 2.24 (d, 1H, J = 10.0), 2.71 (dd, 1H, J = 12.4, 3.5), 3.01 (brs, 1H), 3.25 (t, 1H, J = 12.4), 3.33 (s, 1H), 3.35 (m, 1H), 3.58 (d, 1H, J = 1.7), 6.02 (dd, 1H, J = 5.6, 3.2), 6.47 (dd, 1H, J = 5.6, 2.7), 7.17–7.40 (m, 5H); HRMS m/z 319.1247 ($C_{17}H_{21}NO_3S$ requires 319.1242). Anal. Calcd for $C_{17}H_{21}NO_3S$: C, 63.92; H, 6.63; N, 4.39. Found: C, 63.71; H, 6.68; N, 4.25.

28: oil; $[\alpha]^{25}_D$ –40.1 (c 0.66, $CHCl_3$); IR ($CHCl_3$) 3000, 1555, 1055, 1025 cm^{-1}; ^1H NMR (200 MHz) δ 1.40 (s, 3H), 1.46 (d, 3H, J = 6.9), 2.92 (d, 1H, J = 10.0), 2.28 (d, 1H, J = 10.0), 2.77 (dd, 1H, J = 12.9, 3.3), 3.05 (dd, 1H, J = 12.9, 11.2), 3.08 (brs, 1H), 3.35 (m, 1H), 3.42 (brs, 1H), 3.91 (d, 1H, J = 1.6), 6.24 (dd, 1H, J = 5.6, 3.2), 6.65 (dd, 1H, J = 5.6, 2.9), 7.20–7.40 (m, 5H); HRMS m/z 319.1226 ($C_{17}H_{21}NO_3S$ requires 319.1242).

Chiral Sulfone 29. To a solution of **19** (105 mg, 329 μmol) in CH_2Cl_2 (8 mL) was added 80% m-CPBA (71 mg, 329 μmol) at 0 °C. After being stirred for 19 h at 0 °C, the mixture was washed with saturated aqueous sodium carbonate and then dried. The solvent was removed in vacuo, and the residue was subjected to silica gel column chromatography with hexane–AcOEt (7:3) to give **29** (100 mg, 90%) as an oil; $[\alpha]^{20}_D$ –28.5 (c 0.80, $CHCl_3$); IR ($CHCl_3$) 1555, 1300, 1045, 1015 cm^{-1}; ^1H NMR (200 MHz) δ 1.49 (d, 3H, J = 6.8), 1.65 (m, 2H), 1.91 (s, 3H), 3.17 (brs, 1H), 3.18 (A of ABX, 1H, J = 12.5, 10.4), 3.36–3.55 (m, 2H), 3.73 (B of ABX, 1H, J = 12.5, 3.1), 4.86 (d, 1H, J = 3.3), 6.49 (dd, 1H, J = 5.5, 2.9), 6.56 (dd, 1H, J = 5.5, 2.9), 7.19–7.40 (m, 5H); HRMS m/z 335.1185 ($C_{17}H_{21}NO_4S$ requires 335.1191). Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.88; H, 6.31; N, 4.18. Found: C, 60.94; H, 6.56; N, 4.07.

Chiral Sulfone 32. To a solution of **20** (97 mg, 304 μmol) in CH_2Cl_2 (8 mL) was added 80% m-CPBA (66 mg, 304 μmol) at 0 °C. After being stirred for 20 h at the same temperature, the mixture was washed with saturated aqueous sodium carbonate and then dried. The solvent was removed in vacuo, and the residue was subjected to silica gel column chromatography with hexane–AcOEt (7:3) to give **32** (77 mg, 75%) as an oil: $[\alpha]^{20}_D$ –27.6 (c 0.70, $CHCl_3$); IR ($CHCl_3$) 1560, 1305, 1115 cm^{-1}; ^1H NMR (200 MHz) δ 1.43 (d, 3H, J = 6.0), 1.63 (m, 2H), 1.89 (s, 3H), 3.11 (brs, 1H), 3.37–3.65 (m, 4H), 4.91 (d, 1H, J = 3.3), 6.46 (dd, 1H, J = 5.6, 2.7), 6.51 (dd, 1H, J = 5.6, 2.8), 7.17–7.40 (m, 5H); HRMS m/z 335.1202 ($C_{17}H_{21}NO_4S$ requires 335.1191). Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.88; H, 6.31; N, 4.18. Found: C, 60.79; H, 6.47; N, 4.07.

Chiral Sulfone 33. To a solution of **21** (93 mg, 292 μmol) in CH_2Cl_2 (8 mL) was added 80% m-CPBA (63 mg, 292 μmol) at 0 °C. The mixture was stirred for 20 h at 0 °C, washed with saturated aqueous sodium carbonate, and then dried. Concentration of the solution under reduced pressure gave a residue which was subjected to silica gel column chromatography with hexane–AcOEt (9:1) to give **33** (69 mg, 70%) as an oil: $[\alpha]^{20}_D$ +65.5 (c 0.69, $CHCl_3$); IR ($CHCl_3$) 1550, 1290, 1140 cm^{-1}; ^1H NMR (200 MHz) δ 1.27 (s, 3H), 1.55 (d, 3H, J = 7.0), 1.58 (d, 1H, J = 9.9), 2.41 (d, 1H, J = 9.9), 3.36 (m, 1H), 3.42 (brs, 1H), 3.57 (brs, 1H), 3.54–3.80 (m, 2H), 5.47 (d, 1H, J = 3.3), 6.38 (dd, 1H, J = 5.5, 3.4), 6.63 (dd, 1H, J = 5.5, 2.9), 7.20–7.42 (m, 5H). Anal. Calcd for $C_{17}H_{21}NO_4S$: C, 60.88; H, 6.31; N, 4.18. Found: C, 61.14; H, 6.58; N, 3.92.

Chiral Sulfide (–)-31. To a solution of **29** (73 mg, 218 μmol) in CH_2Cl_2 (7 mL) was added ethanethiol (19 μL, 262 μmol) and DBU (39 μL, 262 μmol) at 0 °C. The mixture was stirred for 10 min at the same temperature and then poured into 1 N HCl. After extractive workup, the extract was washed with brine, dried, and evaporated. The resulting residue was purified by preparative TLC with hexane–AcOEt (4:1) to give (–)-**31** (21 mg, 47%) as an oil: $[\alpha]^{20}_D$ –161.2 (c 1.03, $CHCl_3$); IR ($CHCl_3$) 2980, 1540, 1370 cm^{-1}; ^1H NMR (200 MHz) δ 1.23 (s, 3H), 1.30 (t, 3H, J = 7.4), 1.66 (d, 1H, J = 9.2), 2.17 (d, 1H, J = 9.2), 2.78–2.95 (m, 3H), 3.37 (brs, 1H), 5.21 (d, 1H, J = 3.4), 6.28 (dd, 1H, J = 5.3, 3.3), 6.44 (dd, 1H, J = 5.3, 2.7). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.09; N, 6.57. Found: C, 56.47; H, 7.31; N, 6.30.

Chiral Sulfide (+)-31 from 32. In a way similar to the above procedure, the sulfide (+)-**31** (16 mg, 57%) was obtained as an oil from **32** (44 mg, 130 μmol). Spectroscopic data of (+)-**31** were completely identical with those of (–)-**31** synthesized above except for the specific rotation value of $[\alpha]^{20}_D$ +168.3 (c 0.79, $CHCl_3$).

Chiral Sulfide (+)-31 from 33. In a way similar to the above procedure, the sulfide (+)-**31** (15 mg, 53%) was obtained as an oil from **33** (44 mg, 130 μmol): $[\alpha]^{20}_D$ +157.4 (c 0.74, $CHCl_3$).

General Procedure for High-Pressure Diels–Alder Cycloaddition (See Table 4 for Conditions and Results). A solution of chiral sulfinyl compound (150 μmol), diene (5 mmol), and hydroquinone (1.0 mg, 10 μmol) in CH_2Cl_2 (1.0 mL) was allowed to stand under 8 kbar at rt for 5 days in a Teflon capsule of the high-pressure reaction apparatus. Removal of volatile materials under reduced pressure gave a residue, which was subjected to column chromatography on silica gel with AcOEt–hexane (1:1) to give the cycloadducts. For separation of a mixture of cycloadducts, repeated preparative TLC was performed with ether or CH_2Cl_2 as an eluent.

34: prisms; $[\alpha]^{22}_D$ –211.3 (c 0.43, $CHCl_3$); mp 118.5–119 °C (AcOEt); IR ($CHCl_3$) 2980, 1545, 1370, 1325, 1040 cm^{-1}; ^1H NMR (200 MHz) δ 0.98 (d, 3H, J = 7.2), 1.45 (d, 3H, J = 7.1), 1.40–2.20 (m, 6H), 2.50 (m, 1H), 2.80 (A of ABX, 1H, J = 12.4, 5.1), 2.91 (m, 1H), 2.93 (B of ABX, 1H, J = 12.4, 10.2), 3.14 (m, 1H), 3.39 (m, 1H), 5.47 (d, 1H, J = 10.0), 5.82 (m, 1H), 7.20–7.40 (m, 5H). Anal. Calcd for $C_{19}H_{25}NO_3S$: C, 65.68; H, 7.25; N, 4.03. Found: C, 65.35; H, 7.35; N, 4.17. Crystal data: space group $P2_1$ with a = 11.259(4) Å, b = 10.328(2) Å, c = 8.552(4) Å, and D_c = 1.229 g cm^{-1} for Z = 2.

35: oil; $[\alpha]^{25}_D$ +154.4 (c 0.52, $CHCl_3$); IR ($CHCl_3$) 2980, 1545, 1455, 1055 cm^{-1}; ^1H NMR (200 MHz) δ 1.04 (d, 3H, J = 7.2), 1.49 (d, 3H, J = 6.9), 1.62–2.32 (m, 6H), 2.57 (m, 1H), 2.72 (A of ABX, 1H, J = 11.2), 2.87 (B of ABX, 1H, J = 11.2, 3.4), 3.00–3.20

(m, 2H), 3.39 (m, 1H), 5.49 (m, 1H), 5.80 (m, 1H), 7.20–7.40 (m, 5H); HRMS m/z 329.1445 [$C_{19}H_{23}NO_2S$ (M – H_2O)$^+$ requires 329.1449].

36: prisms; $[\alpha]^{20}_D$ –49.7 (c 1.27, $CHCl_3$); mp 111–112 °C (ether–CH_2Cl_2); IR ($CHCl_3$) 3000, 1540, 1455, 1350, 1020 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.44 (d, 3H, J = 7.0), 1.64 (s, 3H), 1.69 (s, 3H), 1.75–2.15 (m, 7H), 2.33–2.66 (m, 2H), 2.82 (dd, 1H, J = 12.0, 10.0), 2.70–3.04 (m, 2H), 3.45 (m, 1H), 7.15–7.39 (m, 5H). Anal. Calcd for $C_{20}H_{27}NO_3S$: C, 66.45; H, 7.53; N, 3.87. Found: C, 66.31; H, 7.71; N, 3.89.

37: prisms; $[\alpha]^{20}_D$ +41.9 (c 0.65, $CHCl_3$); mp 145 °C (ether–CH_2Cl_2); IR ($CHCl_3$) 3000, 1540, 1455, 1355, 1060, 1020 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.47 (d, 3H, J = 6.8), 1.69 (s, 6H), 1.79–2.20 (m, 6H), 2.45 (d, 1H, J = 16.8), 2.59 (A of ABX, 1H, J = 12.0), 2.62 (m, 1H), 2.90 (B of ABX, 1H, J = 12.0, 2.9), 2.94–3.20 (m, 2H), 3.36 (m, 1H), 7.18–7.40 (m, 5H). Anal. Calcd for $C_{20}H_{27}NO_3S$: C, 66.45; H, 7.53; N, 3.87. Found: C, 66.13; H, 7.69; N, 3.81.

38: needles; $[\alpha]^{20}_D$ –47.5 (c 0.96, $CHCl_3$); mp 176–177 °C (hexane–CH_2Cl_2); IR ($CHCl_3$) 2980, 1535, 1455, 1360, 1050 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.48 (d, 3H, J = 6.6), 1.40–1.95 (m, 3H), 2.12 (m, 3H), 2.45 (m, 1H), 2.55–2.83 (m, 2H), 3.16 (brs, 1H), 3.42 (brs, 1H), 3.35–3.50 (m, 2H), 6.30 (dd, 1H, J = 5.7, 2.9), 6.61 (dd, 1H, J = 5.7, 2.9), 7.18–7.40 (m, 5H); ^{13}C NMR (50 MHz) δ 22.33; 28.62, 32.59, 36.26, 41.29, 43.90, 51.19, 52.08, 58.15, 82.21, 109.45, 127.20, 127.54, 129.06, 137.46, 138.61, 144.67. Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05. Found: C, 65.81; H, 6.77; N, 3.95. Crystal data: space group $P2_1$ with a = 10.632(3) Å b = 10.762(7) Å, c = 8.371(3) Å, and D_c = 1.297 g cm^{-1} for Z = 2.

39: oil; $[\alpha]^{20}_D$ –47.60 (c 0.79, $CHCl_3$); IR ($CHCl_3$) 3000, 1540, 1450, 1345, 1035 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.48 (d, 3H, J = 6.7), 1.40–2.10 (m, 6H), 2.37 (m, 1H), 2.60 (d, 1H, J = 9.6), 2.88 (A of ABX, 1H, J = 12.5, 6.2), 3.04 (B of ABX, 1H, J = 12.5, 9.2), 3.39 (brs, 1H), 3.41 (m, 1H), 3.58 (brs, 1H), 6.40 (dd, 1H, J = 5.5, 3.3), 6.47 (dd, 1H, J = 5.5, 2.9), 7.20–7.40 (m, 5H). Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05. Found: C, 66.15; H, 6.89; N, 3.99.

40: needles; $[\alpha]^{20}_D$ +110.2 (c 0.66, $CHCl_3$); mp 95–96 °C (needles from ether); IR ($CHCl_3$) 3000, 1540, 1460, 1360, 1015 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.46 (d, 3H, J = 6.9), 1.60–1.92 (m, 3H), 2.04–2.20 (m, 3H), 2.49 (m, 1H), 2.66 (m, 1H), 2.77 (A of ABX, 1H, J = 11.6, 2.9), 3.19 (brs, 1H), 3.26 (B of ABX, 1H, J = 11.6), 3.36 (brs, 1H), 3.42 (m, 1H), 6.39 (dd, 1H, J = 5.6, 2.7), 6.70 (dd, 1H, J = 5.6, 2.9), 7.20–7.40 (m, 5H). Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05. Found: C, 66.17; H, 6.79; N, 3.97.

41: oil; $[\alpha]^{22}_D$ +72.1 (c 0.97, $CHCl_3$); IR ($CHCl_3$) 3000, 1540, 1455, 1350, 1060, 1025 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.48 (m, 1H), 1.51 (d, 3H, J = 6.9), 1.76–2.15 (m, 5H), 2.48 (m, 1H), 2.64 (m, 1H), 2.82 (A of ABX, 1H, J = 12.2), 2.94 (B of ABX, 1H, J = 12.2, 3.7), 3.37 (brs, 1H), 3.44 (m, 1H), 3.61 (brs, 1H), 6.45 (m, 2H), 7.20–7.40 (m, 5H); HRMS m/z 345.1439 ($C_{19}H_{23}NO_3S$ requires 345.1399). Anal. Calcd for $C_{19}H_{23}NO_3S$: C, 66.06; H, 6.71; N, 4.05. Found: C, 65.88; H, 6.75; N, 3.97.

42: needles; $[\alpha]^{20}_D$ –197.4 (c 0.57, $CHCl_3$); mp 128–129 °C (ether); IR ($CHCl_3$) 2980, 1555, 1455, 1375, 1030 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.09 (d, 3H, J = 7.0), 1.34 (s, 3H), 1.47 (d, 3H, J = 7.1), 2.23 (dd, 1H, J = 16.4, 3.8), 2.58–2.80 (m, 2H), 2.77 (A of ABX, 1H, J = 12.1, 5.5), 2.98 (B of ABX, 1H, J = 12.1, 10.0), 3.40 (m, 1H), 4.58 (d, 1H, J = 5.2), 5.47 (d, 1H, J = 10.2), 5.84 (m, 1H), 7.20–7.42 (m, 5H); HRMS m/z 321.1415 ($C_{17}H_{23}NO_3S$ requires 321.1399). Anal. Calcd for $C_{17}H_{23}NO_3S$: C, 63.52; H, 7.21; N, 4.36. Found: C, 63.31; H, 7.32; N, 4.27.

43: prisms; $[\alpha]^{20}_D$ –84.2 (c 1.10, $CHCl_3$); mp 122–122.5 °C (ether); IR ($CHCl_3$) 3000, 1555, 1455, 1375, 1020 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.34 (s, 3H), 1.46 (d, 3H, J = 7.0), 1.65 (s, 3H), 2.09 (d, 1H, J = 17.0), 2.34–2.65 (m, 3H), 2.70 (A of ABX, 1H, J = 12.1, 5.5), 3.02 (B of ABX, 1H, J = 12.1, 9.9), 3.41 (m, 1H), 4.70 (t, 1H, J = 5.6), 7.20–7.40 (m, 5H); HRMS m/z 335.1555 ($C_{18}H_{25}NO_3S$ requires 335.1555). Anal. Calcd for $C_{18}H_{25}NO_3S$: C, 64.45; H, 7.51; N, 4.18. Found: C, 64.32; H, 7.65; N, 4.14. Crystal data: space group $P2_1$ with a = 9.061(2) Å, b = 13.633(3) Å, c = 7.432(2) Å, and D_c = 1.214 g cm^{-1} for Z = 2.

45 and 46: inseparable mixture (5:1); IR ($CHCl_3$) 3000, 1560, 1450, 1055 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.35 (s, 3 × 5/6H), 1.39 (s, 3 × 1/6H), 1.47 (d, 3H, J = 7.0), 1.72 (s, 3 × 5/6H), 1.80 (s, 3 × 1/6H), 2.12 (d, 1H, J = 8.4), 2.52 (d, 1H, J = 8.4), 2.73 (A of ABX, 1H, J = 12.0, 5.1), 2.80 (m, 1H), 3.05 (B of ABX, 1H, J = 12.0, 11.6), 3.14–3.50 (m, 2H), 4.68 (t 1 × 5/6H, J = 5.2), 4.74 (t, 1 × 1/6H, J = 5.2), 5.36 (brs, 1 × 5/6H), 5.44 (brs, 1 × 1/6H), 7.15–7.40 (m, 5H); HRMS m/z 321.1392 ($C_{17}H_{23}NO_3S$ requires 321.1399).

47: oil; $[\alpha]^{25}_D$ –42.9 (c 0.46, $CHCl_3$); IR ($CHCl_3$) 3000, 1555, 1455, 1365 cm^{-1}; ^{1}H NMR (200 MHz), δ 1.34 (s, 3H), 1.46 (d, 3H, J = 6.9), 1.57 (s, 3H), 1.60 (s, 3H), 2.09, 2.22 (AB, 2H, J = 18.0), 2.62 (m, 2H), 2.77 (A of ABX, 1H, J = 12.3, 5.2), 2.94 (B of ABX, 1H, J = 12.3, 10.0), 3.36 (m, 1H), 4.93 (t, 1H, J = 6.5), 7.18–7.40 (m, 5H); HRMS m/z 318.1530 [$C_{18}H_{24}NO_2S$ (M – OH)$^+$ requires 318.1528].

48: oil; $[\alpha]^{25}_D$ –16.9 (c 0.37, $CHCl_3$); IR ($CHCl_3$) 3020, 1555, 1455, 1365 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.21 (s, 3H), 1.46 (d, 3H, J = 7.1), 1.63 (s, 3H), 1.66 (s, 3H), 1.90 (d, 1H, J = 16.7), 2.34 (dd, 1H, J = 17.1, 5.5), 2.62–2.85 (m, 4H), 3.40 (m, 1H), 4.92 (dd, 1H, J = 9.6, 6.1), 7.18–7.40 (m, 5H); HRMS m/z 318.1535 [$C_{18}H_{24}NO_2S$ (M – OH)$^+$ requires 318.1528].

49: oil; $[\alpha]^{25}_D$ –74.8 (c 0.25, $CHCl_3$); IR ($CHCl_3$) 3000, 1555, 1370, 1025 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.07 (d, 3H, J = 7.3), 1.31 (s, 3H), 1.47 (d, 3H, J = 7.0), 1.74–2.10 (m, 2H), 2.57 (m, 1H), 2.78 (A of ABX, 1H, J = 12.7, 5.8), 2.88 (B of ABX, 1H, J = 12.7, 9.4), 3.38 (m, 1H), 4.98 (d, 1H, J = 5.9), 5.33–5.56 (m, 2H), 7.18–7.40 (m, 5H); HRMS m/z 302.1197 [$C_{17}H_{20}NO_2S$ (M – H_3O)$^+$ requires 302.1215].

50: oil; $[\alpha]^{25}_D$ +169.6 (c 0.11, $CHCl_3$); IR ($CHCl_3$) 3020, 1555, 1365, 1025 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.90 (d, 3H, J = 7.3), 1.30 (s, 3H), 1.48 (d, 3H, J = 7.0), 1.80 (m, 1H), 2.27 (m, 1H), 2.60 (m, 1H), 2.77 (m, 2H), 3.41 (m, 1H), 4.46 (d, 1H, J = 5.9), 5.33 (m, 1H), 5.68 (m, 1H), 7.18–7.40 (m, 5H); HRMS m/z 321.1426 ($C_{17}H_{23}NO_3S$ requires 321.1399).

51: oil; $[\alpha]^{25}_D$ –110.3 (c 0.33, $CHCl_3$); IR ($CHCl_3$) 3000, 1555, 1455, 1370, 1030 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.08 (d, 3H, J = 6.8), 1.24 (s, 3H), 1.45 (d, 3H, J = 7.1), 2.07 (m, 1H), 2.64–2.80 (m, 2H), 2.80–3.02 (m, 2H), 3.37 (m, 1H), 4.67 (d, 1H, J = 10.3), 5.48 (m, 1H), 5.68 (m, 1H), 7.18–7.40 (m, 5H); HRMS m/z 321.1426 ($C_{17}H_{23}NO_3S$ requires 321.1399).

52: oil; $[\alpha]^{25}_D$ +18.8 (c 0.19, $CHCl_3$); IR ($CHCl_3$) 3000, 1555, 1455, 1385, 1030 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.07 (d, 3H, J = 6.8), 1.45 (s, 3H), 1.46 (d, 3H, J = 7.0), 2.15 (m, 1H), 2.38 (m, 1H), 2.78 (dd, 1H, J = 12.2, 5.2), 2.92–3.12 (m, 2H), 3.39 (m, 1H), 4.49 (d, 1H, J = 10.2), 5.52 (m, 1H), 5.64 (m, 1H), 7.20–7.40 (m, 5H); HRMS m/z 321.1418 ($C_{17}H_{23}NO_3S$ requires 321.1399.

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Supplementary Material Available: The perspective views of **3**, **5**, **19**, **34**, **38**, and **43** (3 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.