# Asymmetric Diels–Alder Reaction of Optically Active α-(2-*exo*-Hydroxy-10-bornyl)sulfinylmaleimides and its Application to Optically Active 5-Functionalised Pyrrolines *via* Retro-Diels–Alder Reaction

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Optically pure sulfinylmaleimides **1** have been synthesized. The Diels–Alder reactions of the sulfoxides **1** with various dienes showed high diastereoselectivity. Regioselective reduction of the adducts **4c** and **6c** followed by desulfinylation afforded the γ-hydroxy lactams **17** and **27**, respectively. *N*-Acyliminium additions using compounds **17** and **27** proceeded diastereoselectively to give γ-alkyl lactams **23** and **29** by virtue of its conformationally rigid, bicyclo[2.2.1]- and 7-oxabicyclo[2.2.1]-heptene moiety, respectively. The use of compound **29** allows a simple preparation of chirally 5-functionalised $\Delta^3$-pyrrolin-2-ones of high optical purity such as compound **25** *via* retro-Diels–Alder reaction, whereas the thermal cycloreversion of adduct **23** required such forcing conditions as flash vacuum pyrolysis.

Despite a large number of highly asymmetric Diels–Alder reactions[1] that have been exploited, most of the dienophiles in the cycloadditions have been treated with reactive Diels–Alder dienes such as cyclopentadiene, but are generally unreactive towards furan under conventional conditions due to its aromaticity. Thus, development of the Diels–Alder reaction with low-reactivity dienes still remains elusive. During the course of our studies on asymmetric Diels–Alder reactions using a chiral vinyl sulfoxide as a dienophile,[1a] we focused on the utility of chiral sulfinylmaleimides. Since maleimides are quite reactive towards a variety of Diels–Alder dienes,[2] the use of chirally functionalised maleimides seemed to be attractive from the viewpoint of the enhancement of dienophilic reactivity as well as the diastereoselectivity in asymmetric Diels–Alder cycloadditions. To date, some reports of Diels–Alder cycloadditions using maleimides and chiral diene partners[3] and involving chirally *N*-substituted maleimides[4] have appeared. However, an efficient route to maleimides bearing a chiral auxiliary in the α-position is as yet unknown. We here describe the syntheses and Diels–Alder reaction of a series of chiral α-sulfinylmaleimides **1** having a (2-*exo*-hydroxy-10-bornyl)-sulfinyl group as a chiral auxiliary, in detail.[5]

## Results and Discussion

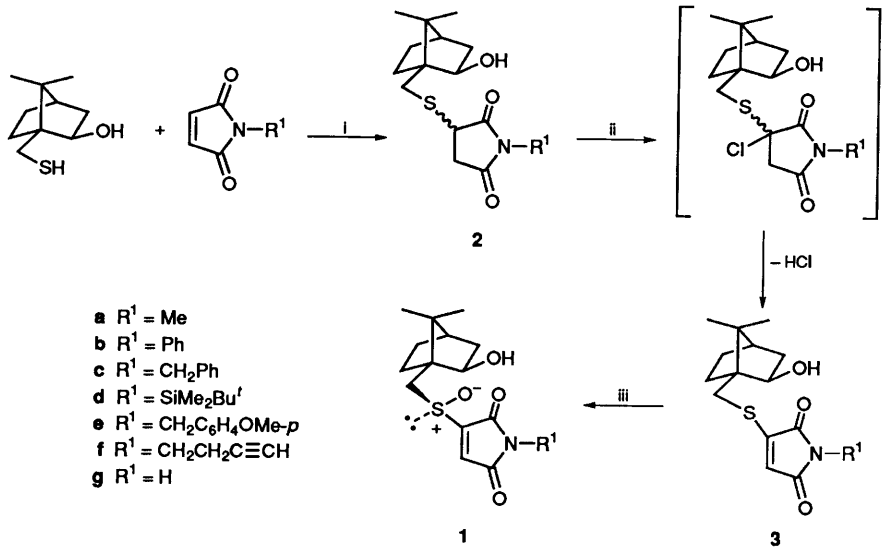
*Preparation of α-Sulfinylmaleimides.*—The first task was to prepare the chiral *N*-substituted maleimides **1** which would be readily obtained according to our procedure of preparing diastereoisomerically pure 2-*exo*-hydroxy-10-bornyl sulfoxides reported previously.[6] The addition of 10-mercaptoisoborneol to *N*-methylmaleimide in the presence of a catalytic amount of triethylamine gave the succinimide **2a** as a 1:1-mixture of diastereoisomers (Scheme 1). Heating of compound **2a** with *N*-chlorosuccinimide (NCS) at reflux in carbon tetrachloride led to the maleimide **3a** with spontaneous dehydrochlorination during the heating. Exposure of compound **3a** to *m*-chloroperbenzoic acid (MCPBA) afforded the sulfinylmaleimide **1a** as essentially a single diastereoisomer in quantitative yield. The high diastereoselectivity in the oxidation and the expected absolute stereochemistry at the sulfur centre could be explained by analogy with our earlier synthesis[6] of chiral 2-*exo*-hydroxy-10-bornyl sulfoxides. Other sulfinylmaleimides **1b–e** were also prepared in excellent yield by the same procedure, and the absolute stereochemistry of sulfoxides **1** could be assigned as $R_S$.† Sulfinylmaleimide **1f** was prepared by a Mitsunobu reaction of sulfide **3g** and but-3-yn-1-ol followed by oxidation of the resulting sulfide **3f**. All attempts to oxidise sulfide **3g** to sulfoxide **1g** were unsuccessful, resulting in polymerisation of starting material. Although the maleimides **1** obtained are sensitive to acid, base or silica gel, the crude oxidation products from sulfides **3** are essentially pure enough to be used for the cycloaddition.

*Diels–Alder Reaction of α-Sulfinylmaleimides.*—At the outset, the Diels–Alder reaction of maleimides **1** with cyclopentadiene, which is very reactive, were examined and the results are summarised in Table 1.

As one can see, in the absence of a Lewis acid ($ZnCl_2$), the cycloaddition of maleimides **1** affords two adducts **4** and **5** with moderate diastereoselectivity. Whatever substituents are incorporated onto the nitrogen atom of maleimides **1**, the Diels–Alder reaction of a dienophile **1** with cyclopentadiene in the presence of a Lewis acid proceeds with a high degree of diastereoselectivity to give an adduct **4**, along with a small amount of the corresponding stereoisomer **5**, almost exclusively. No other diastereoisomeric adducts (*i.e. exo*-imidocarbonyl adducts) were detected in the reaction products. These two *endo*-adducts **4** and **5** are generally inseparable without the aid of HPLC; however, simple recrystallisation of the original mixture affords isomerically pure stereoisomers **4** in good yield.

The adducts **4d** and **5d** were sensitive to silica gel, leading readily to the unsubstituted parent **4g** and **5g**, respectively. The product ratio of the adducts **4d** and **5d** was thus determined by the $^1H$ NMR spectrum of compounds **4g** and **5g** derived by hydrolytic cleavage of the *tert*-butyldimethylsilyl group by exposure to silica gel. The minor adducts **5a** and **5e** derived from the reaction of dienophiles **1a** and **1e** were isolated by preparative TLC (PLC) (after 30 developments) and fully characterised.

† The symbol $R_S$ in this text expresses the absolute configuration of the sulfinyl centre as *R*.

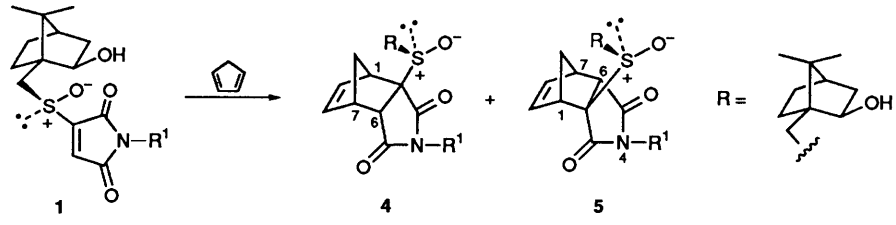



**Scheme 1** *Reagents and conditions:* i, $Et_3N$ (cat.), $CH_2Cl_2$; ii, *N*-chlorosuccinimide, $CCl_4$; iii, *m*-chloroperbenzoic acid, $CH_2Cl_2$

**Table 1** Diels–Alder reaction of maleimides **1** with cyclopentadiene

| Entry | 1 | Reaction conditions: Time (*t*/h) | Reaction conditions: Temp. (*T*/°C) | Additive (1.5 mol equiv.) | 4:5 (Product ratio) | Isolated yield (%)[c] |
|---|---|---|---|---|---|---|
| 1 | **1a** | 0.5 | 0 | | **4a**:**5a** (27:73)[a] | 99 |
| 2 | **1a** | 0.5 | 0 | $ZnCl_2$ | **4a**:**5a** (94:6)[a] | 95 |
| 3 | **1b** | 0.5 | 0 | | **4b**:**5b** (28:72)[a] | 98 |
| 4 | **1b** | 0.5 | 0 | $ZnCl_2$ | **4b**:**5b** (90:10)[a] | 97 |
| 5 | **1c** | 0.5 | 0 | | **4c**:**5c** (28:72)[a] | 97 |
| 6 | **1c** | 1 | 0 | $ZnCl_2$ | **4c**:**5c** (97:3)[a] | ~100 |
| 7 | **1d** | 0.5 | −78 | $ZnCl_2$ | **4d**:**5d** (99.5:0.5)[b] | 93 |
| 8 | **1e** | 0.5 | 0 | | **4e**:**5e** (30:70)[a] | 97 |
| 9 | **1e** | 0.5 | 0 | $ZnCl_2$ | **4e**:**5e** (98:2)[a] | 98 |
| 10 | **1f** | 0.5 | −75 | $ZnCl_2$ | **4f**:**5f** (98:2)[b] | 93 |

[a] The ratio was determined from the pertinent peaks in the $^1H$ NMR spectrum. [b] The ratio was estimated by HPLC analysis (see Experimental section). [c] Total yield of both diastereoisomers.




The *endo* stereochemistry of adducts **4** and **5** was evident from the coupling contants (*J* 3–4 Hz) between 6-H and 7-H (bridgehead) in the $^1H$ NMR spectra. The absolute stereochemistry of adducts **4** was determined on the basis of single-crystal X-ray analysis of compound **4c** (Fig. 1).* The atomic co-ordinates, bond lengths and bond angles have been deposited with the CCDC.† The absolute stereochemistry of compound **4d** was also established by protodesilylation followed by transformation of the resulting compound **4g** into the benzyl derivative **4c** under Mitsunobu conditions.

Under the chelation-controlled ($ZnCl_2$) conditions, the high diastereoselectivity in the cycloaddition can be easily explained by the mechanism reported previously,[5] as shown in Fig. 2. In the presence of a Lewis acid, the dienophile **1** would exist predominantly as the more stable conformer **A** which reacts with cyclopentadiene from the less hindered lone-pair side, to give the adduct **4**. Without a Lewis acid, however, a more stable conformer **B**, due to the dipole–dipole repulsion, would react from the sterically less hindered face, to give the adduct **5** predominantly.

To date, we have devised several chiral sulfinyl dienophiles that give high diastereoselectivity in cycloadditions with cyclo-

* Since the absolute stereochemistry of the bornyl moiety in compound **4c** is known, all other asymmetric centres are automatically established by X-ray analysis.

† *Supplementary data:* see Instructions for Authors, in the January issue.

**Table 2** Diels–Alder reaction of maleimides **1** with other dienes

| Entry | 1 | Diene | Reaction conditions[a] Time (*t*/h) | Temp. (*T*/°C) | Additive (1.5 mol equiv.) | Product (ratio) | Yield (%)[d] |
|---|---|---|---|---|---|---|---|
| 1 | **1c** | furan | 62 | −20 | | **6c**:**7c**:**8c**:**9c** (49:26:10:15)[b] | 60 |
| 2 | **1c** | furan | 0.5 | 0 | $ZnCl_2$ | **6c**:**7c** (71:29)[b] | 66 |
| 3 | **1c** | furan | 60 | 0 | $ZnCl_2$ | **6c**:**7c** (68:32)[b] | 72 |
| 4 | **1c** | furan | 1 | 10 | $ZnCl_2$ | **6c**:**7c**:**8c**:**9c** (79:9:7:5)[b] | 56 |
| 5 | **1c** | furan | 56 | 10 | $ZnCl_2$ | **6c**:**7c**:**8c**:**9c** (80:8:4:8)[b] | 68 |
| 6 | **1c** | furan | 10 | 20 | $ZnCl_2$ | **6c**:**8c** (55:45)[b] | 56 |
| 7 | **1c** | furan | 24 | 0 | | **6c**:**7c**:**8c**:**9c** (29:22:29:20)[b] | 56 |
| 8 | **1c** | furan | 5 | 25 | | **6c**:**7c**:**8c**:**9c** (22:32:24:22)[b] | 54 |
| 9 | **1e** | furan | 0.5 | 0 | $ZnCl_2$ | **6e**:**7e** (73:27)[b] | 76 |
| 10 | **1c** | cyclohexa-1,3-diene | 1 | −40 | $ZnCl_2$ | **10**:**11** (~100:0)[b] | 72 |
| 11 | **1c** | cyclohexa-1,3-diene | 10 | 25 | | **10**:**11** (22:78)[b] | 70 |
| 12 | **1c** | anthracene | 18 | −20 | $ZnCl_2$ | **12**:**13** (~100:0)[c] | 96 |
| 13 | **1c** | anthracene | 4 | 80 | | **12**:**13** (56:44)[c] | 77 |

[a] The reactions were conducted in methylene dichloride as solvent except for entry 13 (benzene as solvent). [b] HPLC analysis. [c] The ratio was determined by integration of the pertinent peaks in the $^1H$ NMR spectrum. [d] Total yield of diastereoisomers.

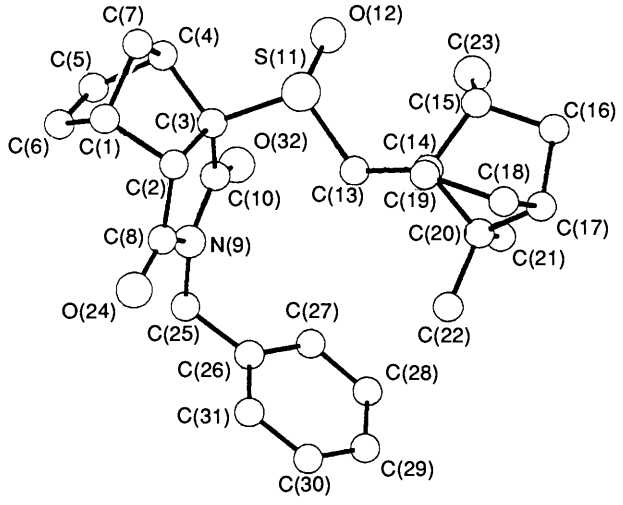



**Fig. 1** X-Ray molecular structure of compound **4c**

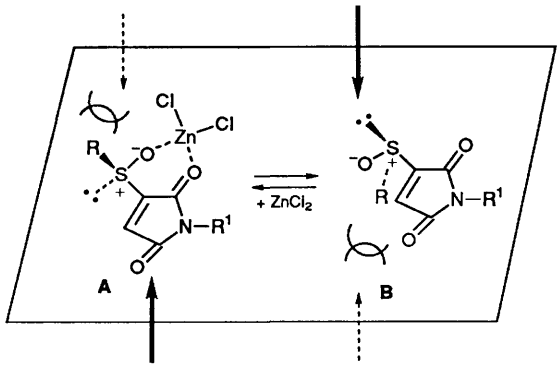
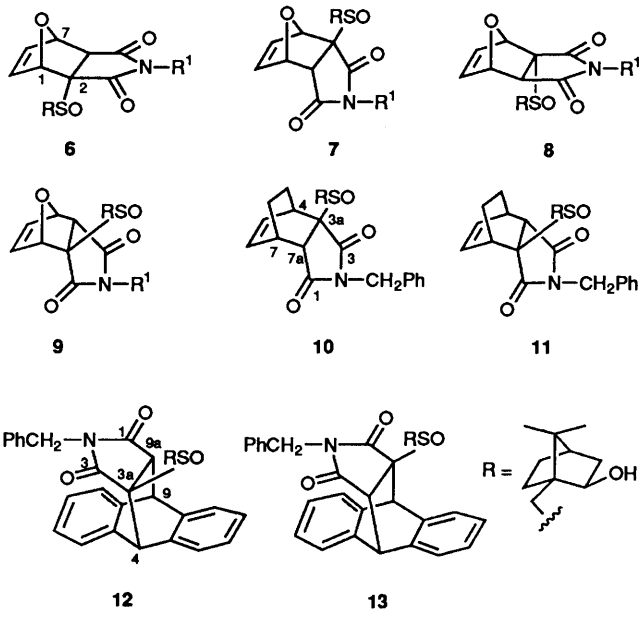



**Fig. 2**

pentadiene.[1] Among the dienophiles investigated so far, only (2-pyridylsulfinyl)acrylates[7] react with furan to afford Diels–Alder adducts. However, the reactions required long reaction times and suffered from low yields. In order to investigate the dienophilic reactivity and the diastereoselectivity of the sulfinyl maleimides **1** with several poorly reactive dienes including furan, we chose *N*-benzyl derivative **1c** since it was found that the diastereoselectivity of the reaction does not depend upon the *N*-substituent on the dienophile.

For the cycloaddition of compound **1c** with furan, notable reactivity as well as diastereoselectivity was apparent. The results are listed in Table 2. With lower reaction temperature (entry 1) the reaction afforded all four possible adducts **6c**–**9c**, while the reaction conducted at 0 °C (entries 2 and 3) gave only two adducts, **6c** and **7c**. On the other hand at higher temperature (10 °C), the *exo* adduct **6c** was formed predominantly, together with small amounts of other adducts **7c**–**9c**. At room temperature (entry 6) the reaction afforded two *exo* adducts **6c** and **8c** in roughly a 1 : 1 mixture. These results show that the initially formed mixture of *endo* adducts **7c** and **9c** undergoes thermal isomerisation, with reversion to starting materials followed by recombination. It was found that under the specified conditions (entries 4 and 5) high diastereoselectivity (**6c** *vs.* **8c**) as well as high stereoselectivity {(**6c** + **8c**) *vs.* (**7c** + **9c**)} was realized.




The adducts **6c**–**8c** were isolated and fully characterised; however, the adduct **9c** was inseparable from other products by column chromatography. The *endo* stereochemistry of adducts **7c** and **9c** was readily assigned based upon the presence of coupling between 6-H and the bridgehead 7-H ($J$ ~ 5 Hz) in

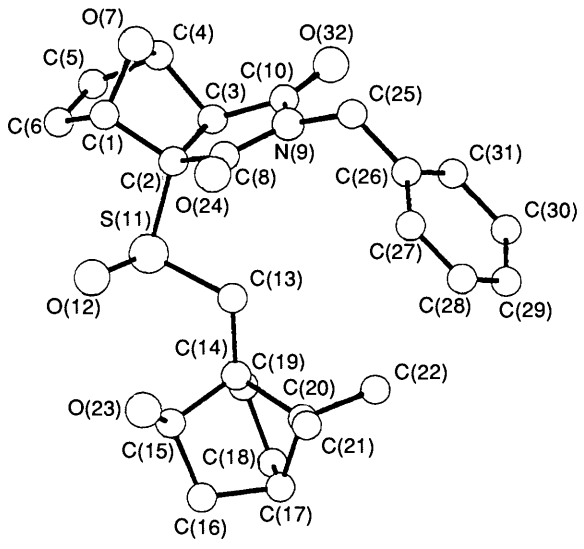



**Fig. 3** X-Ray molecular structure of compound **6c**

the $^1$H NMR spectra. The *exo* stereochemistry of adducts **6c** and **8c** was assigned on the basis of the lack of coupling between 6-H and the bridgehead 7-H in the $^1$H NMR spectra. The absolute stereochemistry of adduct **6c** was established by single-crystal X-ray analysis, shown in Fig. 3. Atomic coordinates, bond lengths and angles have been deposited with the CCDC.

Diels–Alder reaction of dienophile **1c** with cyclohexa-1,3-diene and anthracene in the presence of $ZnCl_2$ proceeded smoothly to give the adducts **10** and **12** as single products, respectively. Without a Lewis acid these reactions were slow even at 80 °C and gave a mixture of two adducts (*i.e.* **10** and **11** or **12** and **13**) in each case. The stereochemistry of adducts **10–13** was tentatively assigned on the basis of the reaction mechanism described above.

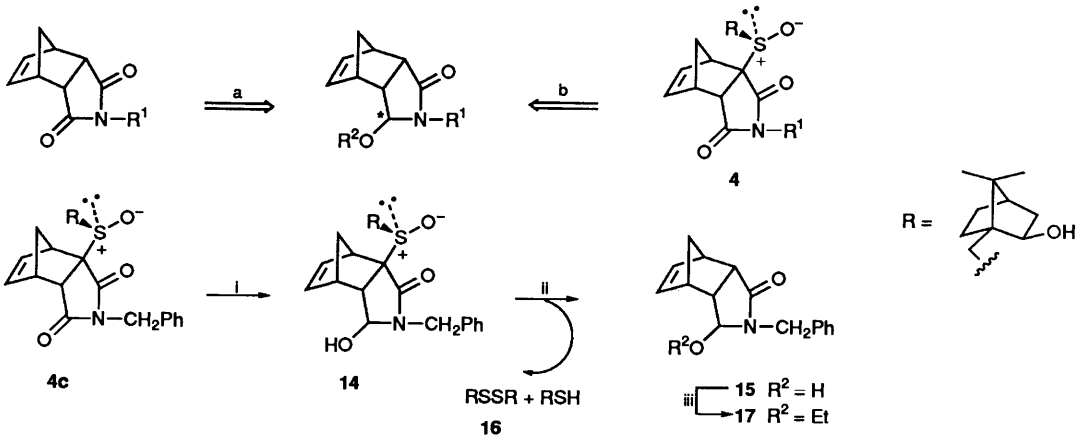
*Simple Entry to Chiral γ-Hydroxy Lactams.*—Having obtained the Diels–Alder adducts in the cycloaddition of dienophile **1**, attention was then turned to their transformation into a chiral, γ-hydroxy lactam. The utility of γ-hydroxy lactams as useful precursors for the synthesis of a number of alkaloids through *N*-acylimino addition has been well documented to date.[8] The use of a chiral γ-hydroxy lactam would thus allow a convenient, enantioselective synthesis of the alkaloids. To obtain the chiral γ-hydroxy lactam, two routes can be envisaged: (i) *via* asymmetric reduction of a *meso*-imide[9] (route a), and (ii) by diastereoselective reduction of one of the imidocarbonyl groups in a chiral imide (route b, *e.g.* **4**).[10] In spite of the pioneering work by Mukaiyama *et al.*,[9a] the former method often provides unsatisfactory results. Our approach relies on the latter route, which effects an easy access to chiral hydroxy lactams from the Diels–Alder adduct.

Reduction of adduct **4c** with $NaBH_4$ in refluxing ethanol was complete with 2 h, and led to the γ-hydroxy lactam **14** as a single product in 93% yield (Scheme 2). The method of Speckamp and co-workers[11] through acid-catalysed $NaBH_4$ reduction of imides did not work well for the imide **4c**, resulting in recovery of a substantial amount of starting material. The regiochemistry of the hydroxy group of the reduction product could not be ascertained at this stage. Desulfinylation of compound **14** with $SmI_2$[12] proceeded smoothly to give the hydroxy lactam **15** in 60% yield, with efficient recovery of the chiral auxiliary, 10-mercaptoisoborneol and the bis-sulfide **16**.[13] The ratio of 10-mercaptoisoborneol and bis-sulfide **16** depended upon the reaction conditions: without *tert*-butyl alcohol as a proton source, compound **16** was produced exclusively. The ethoxy lactam **17** was obtained by treatment of the alcohol **15** with EtOH and pyridinium toluene-*p*-sulfonate (PPTS).[14]

Alternatively, treatment of compound **6c** with $NaBH_4$ followed by acidic work-up[11] afforded the hydroxy lactam **18** as a single product in 94% yield (Scheme 3). On the other hand reduction of compound **6c** with $NaBH_4/H^+$ and basic work-up gave its epimeric lactam **19** exclusively in 92% yield. Treatment of compound **19** with NaOEt or a catalytic amount of HCl resulted in complete epimerisation into compound **18**. It was thus found that epimer **18** is the thermodynamically more stable lactam. The regiochemistry of the hydroxy group in compounds **18** and **19** was now established based upon the coupling of 5-H with 6-H in the $^1$H NMR spectra. The 5-H proton of compound **18** appears as a doublet ($J$ 6.6 Hz) by coupling with OH at $\delta$ 5.00, whereas that of epimer **19** exhibits as a doublet by coupling with 6-H ($J$ 7 Hz). Desulfinylation of sulfoxides **18** and **19** with samarium(II) iodide afforded the lactams **20** and **21**, respectively.

The sulfinyl group, which has served as a chiral auxiliary in the Diels–Alder cycloaddition, was thus employed as an efficient control element to effect the diastereoselective reduction of the imidocarbonyl group in the adducts. Next, we undertook the *N*-acyliminoaddition to the hydroxy lactams.

*N-Acyliminoaddition to γ-Hydroxy Lactams.*—For the *N*-acyliminium addition, racemic (±)-**17** and the sulfonyl derivative (±)-**22** were employed as substrates. Using organometallic compounds such as organic cuprate[15] and allylsilane,[16] we examined the alkylation of the ethoxy compound (±)-**17**, and results are summarised in Table 3. The reaction of compound (±)-**17** with allyltrimethylsilane (4 mol equiv.)

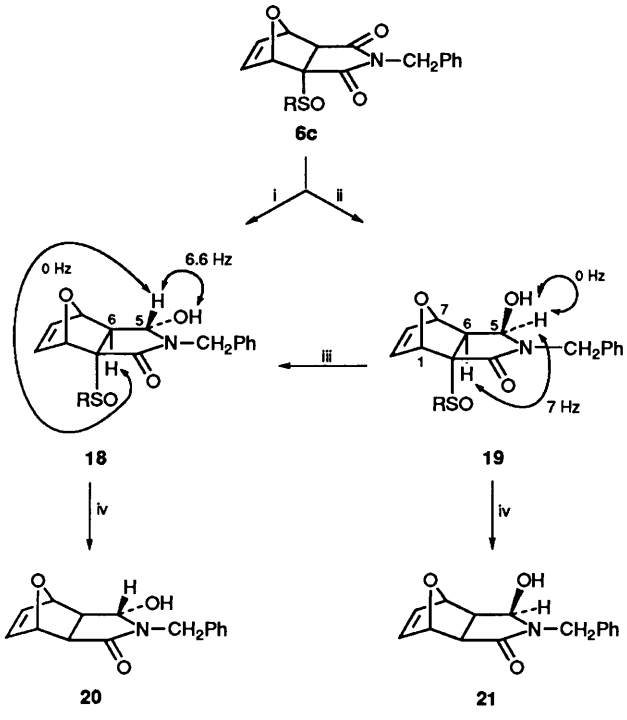



**Scheme 2** *Reagents and conditions:* i, $NaBH_4$, EtOH; ii, $SmI_2$, HMPA, Bu$^t$OH, THF; iii, PPTS, EtOH

**Table 3** *N*-Acyliminoaddition with organometallic reagents

| Entry | | Nucleophile (mol equiv.) | Lewis acid (mol equiv.) | Solvent | Temp. ($T$/°C) | Time ($t$/h) | (±)-**23**, $R^2$= | Isolated yield (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | (±)-**17** | allyltrimethylsilane, 4 | $SnCl_4$, 2.5 | $CH_2Cl_2$ | −78 ⟶ 25 | 22 | $CH_2CH{=}CH_2$ | 45[a] |
| 2 | (±)-**17** | allyltrimethylsilane, 4 | $TiCl_4$, 2.5 | $CH_2Cl_2$ | −78 | 6.5 | $CH_2CH{=}CH_2$ | 44[a] |
| 3 | (±)-**17** | allyltrimethylsilane, 4 | $TiCl_4$, 2.5 | $CH_2Cl_2$ | 0 | 1 | $CH_2CH{=}CH_2$ | 94 |
| 4 | (±)-**17** | allyltrimethylsilane, 4 | $TiCl_4$, 2.5 | $CH_2Cl_2$ | 25 | 0.5 | $CH_2CH{=}CH_2$ | 96 |
| 5 | (±)-**17** | allyltrimethylsilane, 4 | $BF_3$·$Et_2O$, 2.5 | $CH_2Cl_2$ | 0 | 24 | $CH_2CH{=}CH_2$ | 73[b] |
| 6 | (±)-**17** | allyltrimethylsilane, 4 | $BF_3$·$Et_2O$, 2.5 | $CH_2Cl_2$ | 25 | 17.5 | $CH_2CH{=}CH_2$ | 95 |
| 7 | (±)-**17** | butylmagnesium chloride, 3 | | THF | 70 | 23 | Bu | 0 |
| 8 | (±)-**17** | dibutylcopper lithium, 2 | $BF_3$·$Et_2O$, 2 | $Et_2O$ | −78 ⟶ 5 | 1 | Bu | 0 |
| 9 | (±)-**17** | vinylmagnesium bromide, 3 | | THF | 25 ⟶ 70 | 2 | $CH{=}CH_2$ | 20[c] |
| 10 | (±)-**17** | butylcopper, 2 | $BF_3$·$Et_2O$, 2 | $Et_2O$ | −78 ⟶ 25 | 2.5 | Bu | 90 |
| 11 | (±)-**17** | vinylcopper, 2 | $BF_3$·$Et_2O$, 2 | $Et_2O$ | −78 ⟶ 25 | 2.5 | $CH{=}CH_2$ | 65 |
| 12 | (±)-**17** | heptylcopper 3 | $BF_3$·$Et_2O$, 2 | $Et_2O$ | −78 ⟶ 25 | 3 | $C_7H_{15}$ | 87 |
| 13 | (±)-**22** | heptylmagnesium bromide, 4 | $ZnBr_2$, 2 | $CH_2Cl_2$ | 0 ⟶ 25 | 14 | $C_7H_{15}$ | 83 |

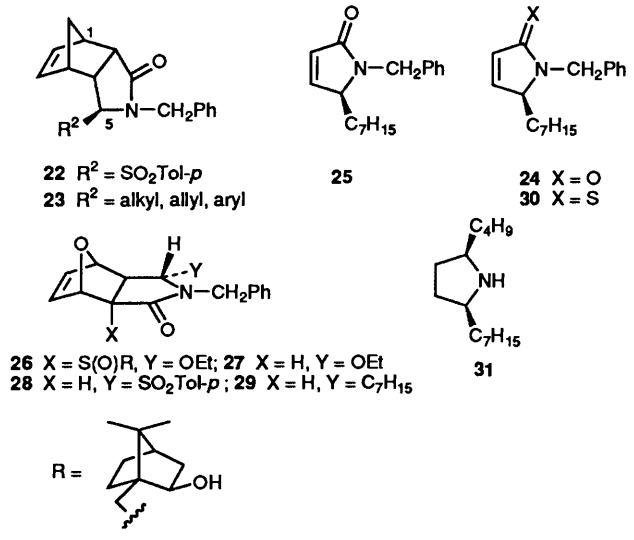
[a] Not purified. Yield was determined by integration of the pertinent peaks in the $^1H$ NMR spectrum. 48% of substrate (±)-**17** was recovered. [b] 14% of substrate (±)-**17** was recovered. [c] Substantial amounts of compounds (±)-**17** and (±)-**14** were detected in the reaction mixture.




**Scheme 3** *Reagents and conditions:* i, $NaBH_4$, EtOH–THF; then acidic work-up; ii, $NaBH_4$, EtOH–THF; then basic work-up; iii, EtONa, EtOH or conc. HCl (cat.), THF; iv, $SmI_2$, Bu$^t$OH, HMPA, THF

in the presence of $TiCl_4$ (2.5 mol equiv.) proceeded smoothly to give the allylated lactam (±)-**23** ($R^2$ = allyl) in excellent yields (entries 3 and 4). It was found that other Lewis acids such as $BF_3$·$Et_2O$ or $SnCl_4$ were less effective.[17] Similarly the cuprate/$BF_3$-mediated alkylations (entries 10–12) afforded the corresponding lactams (±)-**23**, whereas the addition of a Grignard reagent or a dialkylcuprate to compound (±)-**17** was inefficient (entries 7–9). For the reaction of compound (±)-**17** the use of a lower amount of the nucleophile and a Lewis acid decreased the yields. The reaction of a Grignard reagent with the sulfonyl lactam **22**, which was obtained from the ethoxy analogue (±)-**17** by the procedure developed by Ley and co-workers,[18] produced the alkylated lactam in 83% yield. In contrast to the reaction of the ethoxy lactam using an organocopper reagent, the route *via* a sulfonyl lactam was found to be convenient from the viewpoint of easy handling and simple operation techniques.

In all cases the reactions proceed with high diastereoselectivity to give the corresponding lactams (±)-**23** as a single diastereoisomer. The stereochemistry of the newly formed C(5) asymmetric centre could be tentatively assigned as shown because the nucleophilic attack should take place from the sterically less hindered convex face of the bicyclo[2.2.1]heptene group. The stereochemical assignment of the products **23** was unequivocally established by transformation of (+)-**23** ($R^2$ = $C_7H_{15}$) into a chiral pyrrolidin-2-one **24**[19] with known absolute configuration (*vide infra*).




In a similar manner to its racemate (±)-**23** ($R^2$ = $C_7H_{15}$), the optically active heptyl lactam (+)-**23** ($R^2$ = $C_7H_{15}$) {$[\alpha]_D^{26}$ +24.7 (*c* 2.1, $CHCL_3$)} was obtained from the sulfonyl lactam (+)-**22** {$[\alpha]_D^{24}$ +29.4 (*c* 1.97, $CHCl_3$) ~100% e.e. judged by chiral HPLC analysis}. The optical purity of (+)-**23** ($R^2$ = $C_7H_{15}$) could not be determined by chiral HPLC analysis because of unsatisfactory resolution; however, there is no doubt about the high optical purity of compound (+)-**23** ($R^2$ = $C_7H_{15}$) since it was obtained as a single diastereoisomer from optically pure sulfone (+)-**22**. Although a retro-Diels–Alder reaction of compound (+)-**23** ($R^2$ = $C_7H_{15}$) by heating in a high b.p. solvent such as toluene or *o*-dichlorobenzene did not work, flash vacuum pyrolysis[20] (FVP, 450 °C, 0.5 Pa) effecting thermal cycloreversion afforded the 5-heptylpyrrolin-2-one **25** {$[\alpha]_D^{28}$ +42.4 (*c* 2, $CHCl_3$)} in 78% yield. The enantiomeric excess (e.e.) was 74% by HPLC analysis using a chiral column. Hydrogenation of compound **25** over Pt on alumina at 3.5 atm for 5 h gave the known compound **24** {$[\alpha]_D^{26}$ −13.3 (*c* 1.2, $CH_2Cl_2$); lit., [19] $[\alpha]_D^{20}$ −21.9 (*c* 1.0, $CH_2Cl_2$)}. Our synthetic lactam **24** indicates 57–61% optical purity when compared with the evaluated optimum rotation value for ⩾94% e.e. Presum-

ably the pyrroline **25** obtained with moderate e.e., under the FVP conditions, racemised because $\Delta^3$-pyrrolin-2-ones tend to undergo thermal interconversion[21] into the corresponding $\Delta^4$-pyrrolin-2-ones at ambient or higher temperature. Other catalysts such as Pd/C and/or longer reaction period resulted in racemisation[22] of lactam **24**. The absolute stereochemistry of lactam **24** prepared above was established as *S* by comparison with the sign of the reported value[19] of the optical rotation.

To overcome the unsatisfactory enantiomeric control, we envisaged the use of a 7-oxabicyclo[2.2.1]heptene moiety that would easily effect cycloreversion under milder conditions. Attempts at ethoxylation of hydroxy lactam **20** or **21** under conditions using EtOH–$H^+$ or EtOH–PPTS met with failure. On the other hand reduction of compound **6c** followed by treatment by acid proceeded smoothly to give the ethoxy lactam **26**, which was desulfinylated with $SmI_2$ to give the lactam **27**. After sulfonylation of ethoxy lactam **27** the resulting sulfone **28** was subjected to acylimino addition with heptylmagnesium bromide to afford the heptyl derivative **29**. The cycloreversion of adduct **29** conducted in liquid phase (xylenes, reflux, 0.5 h) led to the $\Delta^3$-pyrrolin-2-one **25** {$[\alpha]_D^{24}$ +58.8 (*c* 0.8, $CHCl_3$)} of high optical purity (≥97% e.e. judged from chiral HPLC analysis). Hydrogenation of compound **25** over 5% Pt/alumina (*tert*-butyl alcohol, 3.5 atm, 2 h) and subsequent treatment of optically active lactam **24** {$[\alpha]_D^{26}$ −19.3 (*c* 0.5, $CH_2Cl_2$)} with 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (Lawesson's reagent) produced a thiolactam **30** {$[\alpha]_D^{26}$ −145.5 (*c* 0.44, EtOH), ≥93% e.e. by chiral HPLC analysis} whose spectroscopic data were identical with those {$[\alpha]_D^{20}$ −107.1 (*c* 1.3, EtOH)} reported previously.[19] Thiolactam **30** has been further transformed into *cis*-2-butyl-5-heptylpyrrolidine **31**[19] that is of some interest because of its entomological properties,[23] as well as its *trans*-isomer.[24] Furthermore, 5-substituted $\Delta^3$-pyrrolin-2-ones are widely utilised not only as Diels–Alder dienophiles[25] but also as potent intermediates[26] for alkaloids synthesis.

In conclusion, maleimide dienophiles having a (2-*exo*-hydroxy-10-bornyl)sulfinyl group as a chiral auxiliary show high diastereoselectivity in Diels–Alder reactions under chelation-controlled conditions. The Lewis acid ($ZnCl_2$) as an additive plays a role not only as a reaction promoter but also as a chelating agent of the sulfinyl oxygen with one imidocarbonyl group, resulting in a rigid Diels–Alder transition state of the dienophile. High stereocontrol in the *N*-acyliminium addition directed by a bicyclo[2.2.1]- and a 7-oxabicyclo[2.2.1]-heptene moiety has been achieved. Retro–Diels–Alder reaction of the resulting 7-oxabicyclo[2.2.1]heptene system proceeded smoothly to give a chirally 5-substituted $\Delta^3$-pyrrolin-2-one.

## Experimental

M.p.s were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. B.p.s for Kugelrohr distillation indicate bath temperature. IR spectra were recorded on a Perkin-Elmer 1605 spectrometer. NMR spectra were measured in $CDCl_3$, unless otherwise stated, with tetramethylsilane as internal standard on a JEOL GX-270 (270 MHz $^1H$) and a Varian XL-200 (50.1 MHz $^{13}C$) spectrometer. *J* Values are in Hz. Mass spectra were recorded on a JEOL JMS-300 spectrometer. Optical rotations were recorded on a JASCO DIP-140 digital polarimeter, and are given in units of $10^{-1}$ deg $cm^2$ $g^{-1}$. TLC analyses were performed using Merck pre-coated silica 60F254 plates (0.2 mm). Column chromatography was carried out on Merck silica (70–230 mesh) or Merck silica (230–400 mesh). Dry tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl prior to use. The organic extracts were dried over anhydrous magnesium sulfate which was later removed by filtration. The solvent used was concentrated by a rotatory evaporator under reduced pressure. Dry methylene dichloride was distilled from phosphorus pentaoxide and stored with 4 Å molecular sieves. MCPBA was used after purification by washing with phosphate buffer of pH 7.5 according to the literature method.[27] Zinc chloride and zinc bromide were dried at 160 °C in an oven for 2 h prior to use. High-performance liquid chromatography (HPLC) was performed on a 5 μ Develosil 60 column (4.6 mm × 250 mm). Chiral HPLC analyses were performed using a chiral column (Daicel Chemical Industries Ltd.), Chiralcel OC or Chiralpak AS (4.6 × 250 mm). Peak ratios on HPLC were determined with an integrator (Shimadzu Chromatopac C-R3A). Light petroleum refers to the fraction boiling in the range 40–60 °C.

*General Procedure for Preparation of* 2-(2-exo-*Hydroxy*-10-*bornylthio*)*succinimides* **2**.—To a solution of the parent *N*-substituted maleimide (0.16 mmol) in methylene dichloride (30 $cm^3$) at 0 °C was added a solution of 10-mercaptoisoborneol (3.0 g, 0.16 mmol) in methylene dichloride (10 $cm^3$) followed by 4 drops of triethylamine. The mixture was allowed to reach 25 °C and was stirred for a further 4–12 h. The resulting mixture was concentrated under reduced pressure and the residue was chromatographed on silica with hexane–ethyl acetate (4:1) to give the corresponding *compound* **2** as a diastereoisomeric mixture.

α-({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylthio*)-N-*methylsuccinimide* **2a**. Prepared from *N*-methylmaleimide (500 mg, 4.5 mmol) and 10-mercaptoisoborneol (880 mg, 4.73 mmol) in 89% yield. A *powder*, m.p.s 105–107 and 120–130 °C (from hexane–ethyl acetate) (Found: C, 60.9; H, 7.8; N, 4.9. $C_{15}H_{23}NO_3S$ requires C, 60.59; H, 7.80; N, 4.71%); $[\alpha]_D^{25}$ −20.5 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 3570, 2950, 1690, 1435 and 1275; $\delta_H$ 0.85 (3 H, s, Me), 1.05 and 1.09 (total 3 H, each s, diastereoisomeric Me), 1.0–1.9 (7 H, m, bornyl H), 2.55 and 2.60 (total 1 H, each dd, *J* 19 and 4.5, and 19 and 4, 4-H), 2.66 and 3.03 (total 1 H, br, OH), 2.83 and 2.96 (total 1 H, each d, *J* 11, 10′-$H^a$) 3.02 and 3.04 (total 3 H, s, NMe), 2.90 and 3.19 (total 1 H, each d, *J* 11, 10′-$H^b$), 3.17 and 3.19 (total 1 H, each dd, *J* 19 and 9, 4-H), 3.74 and 3.81 (total 1 H, each dd, *J* 9 and 4.5, 3-H) and 3.90 (1 H, m, 2′-H); *m*/*z* 297 ($M^+$), 279, 184, 145 and 108.

α({(1S,2R,4R)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylthio*)-N-*phenylsuccinimide* **2b**. Prepared from *N*-phenylmaleimide (500 mg, 2.89 mmol) and 10-mercaptoisoborneol (564 mg, 3.03 mmol) in 98% yield. A powder, as a 1:1 diastereoisomeric *mixture*, m.p. 86–89 °C (from hexane–ethyl acetate) (Found: C, 67.1; H, 7.0; N, 4.0. $C_{20}H_{25}NO_3S$ requires C, 66.83; H, 7.01; N, 3.90%); $[\alpha]_D^{25}$ −22.4 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 2950, 1710, 1500, 1380, 1180 and 850; $\delta_H$ 0.84 and 0.86 (total 3 H, each s, diastereoisomeric Me), 1.06 and 1.07 (total 3 H, each s, Me), 1.0–1.9 (7 H, m, bornyl H), 2.6–3.4 (5 H, m, 4- and 10′-$H_2$, and OH), 3.8–4.0 (2 H, m, 3- and 2′-H) and 7.2–7.6 (5 H, m, ArH); *m*/*z* 360 ($M^+$ + 1), 359 ($M^+$), 208, 206 and 175.

N-*Benzyl*-α-({(1S,2R,4R)-2-*hydroxy*-7,7-*dimethylbicyclo*-[2.2.1]*heptan*-1-*yl*}*methylthio*)*succinimide* **2c**. Prepared from *N*-benzylmaleimide[28] (11.3 g, 60 mmol) and 10-mercaptoisoborneol (11.5 g, 62 mmol) in 96% yield. An oily 1:1 diastereoisomeric *mixture* (Found: $M^+$, 373.1696. $C_{21}H_{27}NO_3S$ requires *M*, 373.1710); $\nu_{max}$(neat)/$cm^{-1}$ 2950, 1700, 1395 and 1165; $\delta_H$ 0.80 and 0.81 (total 3 H, each s, diastereoisomeric Me), 0.99 and 1.05 (total 3 H, each s, Me), 0.9–1.9 (7 H, m, bornyl H), 2.55 and 2.60 (total 1 H, each dd, *J* 19 and 4.5, 4-$H^a$), 2.74 and 2.89 (total 1 H, each d, *J* 11, 10′-$H^a$), 2.78 and 3.13 (total 1 H, each d, *J* 11, 10′-$H^b$), 2.65 and 2.95 (total 1 H, each d, *J* 3, OH), 3.14 and 3.18 (total 1 H, each dd, *J* 19 and 9, 4-$H^b$), 3.70 and 3.79 (total 1 H, each dd, *J* 9 and 4.5, 3-H), 3.87 (1 H, m, 2′-H), 4.63 and 4.64 (total 1 H, each d, *J* 14 and 13, NC*H*H), 4.70 and

4.73 (total 1 H, each dd, *J* 14 and 13, NCH*H*) and 7.2–7.4 (5 H, m, ArH); *m/z* 373 ($M^+$), 355, 222, 188 and 91.

N-(tert-*Butyldimethylsilyl*)-α-({(1S,2R,4R)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylthio*)*succinimide* **2d**. Prepared from *N*-(*tert*-butyldimethylsilyl)maleimide[29] (596 mg, 2.8 mmol) and 10-mercaptoisoborneol (500 mg, 2.7 mmol) in 99% yield. An oily 2:1 diastereoisomeric *mixture* (Found: $M^+$, 397.2072. $C_{20}H_{35}NO_3SiS$ requires *M*, 397.2105; $[\alpha]_D^{26}$ −19.8 (*c* 4.9, $CHCl_3$); $\nu_{max}$(neat)/cm$^{-1}$ 3500, 2950, 1700, 1470, 1320 and 1170; $\delta_H$ 0.35 (6 H, s, $SiMe_2$), 0.76 (2/3 × 3 H, s, diastereoisomeric Me), 0.83 (1/3 × 3 H, s, diastereoisomeric Me), 0.87 (9 H, s, $SiBu^t$), 0.95 (1/3 × 3 H, s, Me), 0.99 (2/3 × 3 H, s, Me), 0.8–1.2 (2 H, m, bornyl H), 1.4–1.8 (5 H, m, bornyl H), 2.46 (2/3 × 1 H, dd, *J* 19, 5, X of AMX pattern), 2.50 (1/3 × 1 H, dd, *J* 19 and 4, X of AMX pattern), 2.62 (1/3 × 1 H, d, *J* 11.4, 10′-H$^a$), 2.74 (1/3 × 1 H, d, *J* 11.4, 10′-H$^b$), 2.85 (2/3 × 1 H, d, *J* 11.2, 10′-H$^a$), 3.03 (2/3 × 1 H, d, *J* 11.2, 10′-H$^b$), 3.0–3.15 (1 H, m, M of AMX pattern), 3.2 (1 H, br, OH), 3.61 (2/3 × 1 H, dd, *J* 9.6 and 5, A of AMX pattern), 3.69 (1/3 × 1 H, dd, *J* 9.5 and 4, A of AMX pattern) and 3.8 (1 H, br, 2′-H); *m/z* 398 ($M^+$ + 1), 397 ($M^+$), 380, 340, 322, 246, 188 and 135.

α-({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylthio*)-N-(4-*methoxybenzyl*)*succinimide* **2e**. Prepared from *N*-(4-methoxybenzyl)maleimide[28] (34.3 g, 0.16 mol) and 10-mercaptoisoborneol (30.0 g, 0.16 mmol) in 99% yield. An oily 1:1 diastereoisomeric *mixture* (Found: $M^+$, 403.1776. $C_{22}H_{29}NO_4S$ requires *M*, 403.1816); $[\alpha]_D^{26}$ −15.5 (*c* 6.2, $CHCl_3$); $\nu_{max}$(neat)/cm$^{-1}$ 3507, 2952, 2836, 1694 and 1613; $\delta_H$ 0.80 (3 H, s, Me), 0.97 and 1.05 (total 3 H, each s, diastereoisomeric Me), 1.0–1.9 (7 H, m, bornyl H), 2.5–2.75 (3 H, m), 3.1–3.2 (2 H, m), 3.75 and 3.76 (total 3 H, each s, OMe), 3.65–3.95 (2 H, m), 4.60 and 4.64 (total 2 H, each ABq, *J* 14, $NCH_2$), 6.81 (2 H, d, *J* 8.6, ArH) and 7.32 (2 H, d, *J* 8.6, ArH); *m/z* 403 ($M^+$), 386, 251 and 218.

α({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylthio*)*succinimide* **2g**. Prepared from maleimide (300 mg, 3.09 mmol) and 10-mercaptoisoborneol (604 mg, 3.25 mmol) in 98% yield. A powdery 1:1 diastereoisomeric *mixture*, m.p. 102–105 °C (from hexane–ethyl acetate) (Found: C, 59.55; H, 7.6; N, 4.9. $C_{14}H_{21}NO_3S$ requires C, 59.35; H, 7.47; N, 4.94%); $\nu_{max}$(KBr)/cm$^{-1}$ 3500, 2950, 1775, 1705, 1350 and 1190; $\delta_H$ 0.85 (3 H, s, Me), 1.05 and 1.07 (total 3 H, each s, diastereoisomeric Me), 1.0–1.9 (7 H, m, bornyl H), 2.60 and 2.65 (total 1 H, each dd, *J* 19 and 5, and 19 and 4, 4-H$^a$), 2.79 and 3.08 (total 1 H, each d, *J* 3, OH), 2.81 and 2.92 (total 1 H, each d, *J* 11, 10′-H$^a$), 2.88 and 3.16 (total 1 H, each d, *J* 11, 10′-H$^b$), 3.21 and 3.22 (total 1 H, each dd, *J* 19 and 9, 4-H$^b$), 3.78 and 3.84 (total 1 H, each dd, *J* 9 and 5, and 9 and 4, 3-H), 3.90 (1 H, m, 2′-H) and 8.80 (1 H, br, NH); *m/z* 283 ($M^+$), 265, 109 and 108.

*General Procedure for Preparation of* α-({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylthio*)*maleimides* **3**.—A solution of the succinimide **2** (2.5 mmol) and NCS (2.7 mmol) in carbon tetrachloride (50 cm$^3$) was heated under reflux for 6–8 h in a well ventilated hood because of gaseous evolution of hydrogen chloride during the reaction. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica (20 g) with hexane–ethyl acetate (4:1) to give the corresponding maleimide **3**.

(−)-α-({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]-*heptan*-1-*yl*}*methylthio*)-N-*methylmaleimide* **3a**. Prepared from the succinimide **2a** (1.10 g, 3.7 mmol) and NCS (544 mg, 4.07 mmol) in 93% yield. Pale yellow *needles*, m.p. 177–178 °C (from hexane–ethyl acetate) (Found: C, 61.15; H, 7.3; N, 4.6. $C_{15}H_{21}NO_3S$ requires C, 61.00; H, 7.17; N, 4.74%); $[\alpha]_D^{26}$ −39.7 (*c* 1.0, $CHCl_3$); $\nu_{max}$($CHCl_3$)/cm$^{-1}$ 1700, 1550, 1450, 1390 and 975; $\delta_H$ 0.92 (3 H, s, Me), 1.11 (3 H, s, Me), 1.0–1.9 (7 H, m, bornyl H), 2.20 (1 H, d, *J* 4, OH), 2.83 (1 H, d, *J* 11, 10′-H$^a$), 3.01 (3 H, s, NMe), 3.22 (1 H, d, *J* 11, 10′-H$^b$), 3.90 (1 H, dt, *J* 7 and 4, 2′-H) and 6.16 (1 H, s, CH=); *m/z* 295 ($M^+$), 153, 143 and 108.

(−)-α-({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]-*heptan*-1-*yl*}*methylthio*)-N-*phenylmaleimide* **3b**. Prepared from the succinimide **2b** (800 mg, 2.23 mmol) and NCS (327 mg, 2.45 mmol) in 92% yield. Pale yellow *needles*, 147–148 °C (from hexane–ethyl acetate) (Found: C, 67.5; H, 6.6; N, 3.8. $C_{20}H_{23}NO_3S$ requires C, 67.21; H, 6.49; N, 3.92%); $[\alpha]_D^{26}$ −35.7 (*c* 1.0, $CHCl_3$); $\nu_{max}$($CHCl_3$)/cm$^{-1}$ 1710, 1550, 1500 and 1390; $\delta_H$ 0.94 (3 H, s, Me), 1.13 (3 H, s, Me), 0.8–1.9 (7 H, m, bornyl H), 1.98 (1 H, d, *J* 6, OH), 2.89 (1 H, d, *J* 11, 10′-H$^a$), 3.29 (1 H, d, *J* 11, 10′-H$^b$), 3.91 (1 H, m, 2′-H), 6.30 (1 H, s, CH=) and 7.3–7.5 (5 H, m, ArH); *m/z* 357 ($M^+$), 339, 205 and 85.

(−)-N-*Benzyl*-α-({(1S,2R,4R)-*hydroxy*-7,7-*dimethylbicyclo*-[2.2.1]*heptan*-1-*yl*}*methylthio*)*maleimide* **3c**. Prepared from the succinimide **2c** (4.98 g, 13.4 mmol) and NCS (1.96 g, 14.7 mmol) in carbon tetrachloride (100 cm$^3$) in 88% yield. Yellow *prisms*, 133–134 °C (from hexane–ethyl acetate) (Found: C, 68.2; H, 6.9; N, 3.8. $C_{21}H_{25}NO_3S$ requires C, 67.90; H, 6.78; N, 3.77%); $[\alpha]_D^{26}$ −31.6 (*c* 1.0, $CHCl_3$); $\nu_{max}$($CHCl_3$)/cm$^{-1}$ 1705, 1550, 1430 and 1400; $\delta_H$ 0.91 (3 H, s, Me), 1.10 (3 H, s, Me), 0.8–2.0 (8 H, m, bornyl H, OH), 2.81 (1 H, d, *J* 11, 10′-H$^a$), 3.21 (1 H, d, *J* 11, 10′-H$^b$), 3.89 (1 H, dd, *J* 8 and 4, 2′-H) 4.66 (2 H, s, $NCH_2$), 6.15 (1 H, s, CH=) and 7.2–7.5 (5 H, m, ArH); *m/z* 371 ($M^+$), 219, 191 and 91.

(−)-N-(tert-*Butyldimethylsilyl*)-α-({(1S,2R,4R)-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylthio*)*maleimide* **3d**. Prepared from the succinimide **2d** (11.4 g, 28.8 mmol) and NCS (4.23 g, 31.7 mmol) in carbon tetrachloride (200 cm$^3$) in 55% yield. Yellow *prisms*, m.p. 152–155 °C (from hexane–ethyl acetate) (Found: C, 60.7; H, 8.3; N, 3.6. $C_{20}H_{33}NO_3SiS$ requires C, 60.72; H, 8.41; N, 3.54%); $[\alpha]_D^{26}$ −31.3 (*c* 2.0, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 3452, 3072, 2955, 2882, 1757, 1691 and 1318; $\delta_H$ 0.43 (6 H, s, $SiMe_2$), 0.91 (3 H, s, Me), 0.93 (9 H, s, $SiBu^t$), 1.11 (3 H, s, Me), 1.1–1.3 (2 H, m, bornyl H), 1.6–1.8 (5 H, m, bornyl H), 2.04 (1 H, br s, OH), 2.81 (1 H, d, *J* 11, 10′-H$^a$), 3.19 (1 H, d, *J* 11, 10′-H$^b$), 3.90 (1 H, br, 2′-H) and 6.16 (1 H, s, CH=); *m/z* 396 ($M^+$ + 1), 395 ($M^+$), 378, 362, 338, 320, 187 and 186.

(−)-α-({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo* [2.2.1]-*heptan*-1-*yl*}*methylthio*)-N-(4-*methoxybenzyl*)*maleimide* **3e**. Prepared from the succinimide **2e** (30.0 g, 74.4 mmol) and NCS (10.9 g, 81.9 mmol) in carbon tetrachloride (600 cm$^3$) in 93% yield. Yellow *needles*, m.p. 111 °C (from hexane–ethyl acetate) (Found: C, 65.7; H, 6.9; N, 3.6. $C_{22}H_{27}NO_4S$ requires C, 65.82; H, 6.78; N, 3.49%); $[\alpha]_D^{25}$ −30.8 (*c* 2.8, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 2952, 1702 and 1549; $\delta_H$ 0.9 (3 H, s, Me), 1.10 (3 H, s, Me), 1.0–1.9 (7 H, m, bornyl H), 2.04 (1 H, br s, OH), 2.80 (1 H, d, *J* 11.2, 10′-H$^a$), 3.19 (1 H, d, *J* 11.2, 10′-H$^b$), 3.77 (3 H, s, OMe), 3.86 (1 H, m, 2′-H), 4.59 (2 H, s, $NCH_2$), 6.12 (1 H, s, CH=), 6.82 (2 H, d, *J* 8.7, ArH) and 7.29 (2 H, d, *J* 8.7, ArH); *m/z* 401 ($M^+$), 384, 249 and 221.

(−)-α-({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]-*heptan*-1-*yl*}*methylthio*)*maleimide* **3g**. Prepared from the succinimide **2g** (671 mg, 2.4 mmol) and NCS (332 mg, 2.5 mmol) in carbon tetrachloride (20 cm$^3$) in 95% yield. Pale yellow *prisms*, m.p. 182–184 °C (from hexane–ethyl acetate) (Found: C, 59.8; H, 6.9; N, 5.0. $C_{14}H_{19}NO_3S$ requires C, 59.77; H, 6.81; N, 4.98%); $[\alpha]_D^{25}$ −27.1 (*c* 1.0, EtOH); $\nu_{max}$(KBr)/cm$^{-1}$ 3450, 2950, 1710, 1550 and 1330; $\delta_H$ ($CDCl_3$–$CD_3OD$) 0.95 (3 H, s, Me), 1.12 (3 H, s, Me), 1.1–1.9 (7 H, m, bornyl H), 2.88 (1 H, d, *J* 11.5, 10′-H$^a$), 3.25 (1 H, d, *J* 11.5, 10′-H$^b$), 3.33 (1 H, br, OH), 3.84 (1 H, br, 2′-H) and 6.17 (1 H, s, CH=); *m/z* 282 ($M^+$ + 1), 257, 154, 135 and 109.

(−)-N-*But*-3-*ynyl*-α-({(1S,2R,4R)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylthio*)*maleimide* **3f**.—To a

solution of compound **3g** (210 mg, 0.74 mmol), triphenylphosphine (226 mg, 0.88 mmol) and but-3-yn-1-ol (0.07 ml, 0.88 mmol) in THF (30 $cm^3$) at 0 °C was added dropwise a solution of diethyl azodicarboxylate (DEAD) (0.074 $cm^3$, 0.88 mmol) in THF (5 $cm^3$). After this addition, the reaction mixture was kept at room temp. overnight. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica with hexane–ethyl acetate (4:1) to give *compound* **3f** (245 mg, 99%) as yellow prisms, m.p. 86–87 °C (from hexane–ethyl acetate) (Found: C, 64.8; H, 6.8; N, 4.1. $C_{18}H_{23}NO_3S$ requires C, 64.85; H, 6.95; N, 4.20%); $[\alpha]_D^{25}$ −33.0 (*c* 1.8, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 3550, 3290, 2960, 1760, 1700, 1550, 1400 and 980; $\delta_H$ 0.92 (3 H, s, Me), 1.11 (3 H, s, Me), 1.14–1.98 (7 H, m, bornyl H), 1.97 (1 H, t, *J* 2.7, 4″-H), 2.00 (1 H, br s, OH), 2.51 (2 H, dt, *J* 7 and 2.7, $NCH_2CH_2$), 2.84 (1 H, d, *J* 11, SC*H*H), 3.23 (1 H, d, *J* 11, SCH*H*), 3.71 (2 H, t, *J* 7, $NCH_2$), 3.90 (1 H, m, 2′-H) and 6.16 (1 H, s, CH=); *m/z* 333 ($M^+$), 317, 302, 274 and 181.

*General Procedure for Preparation of* N-*Substituted* α-({(1S,2R,4R,$R_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-yl}*methysulfinyl*)*maleimides* **1**.—To a solution of this maleimide **3** (0.85 mmol) in methylene dichloride (30 $cm^3$) at 0 °C was added dropwise a solution of MCPBA (1.2–1.4 mol equiv.) in methylene dichloride (20 $cm^3$). After this addition, the mixture was allowed to reach room temp. and was stirred for a further 2–3 h. The mixture was then cooled to −70 °C to precipitate 3-chlorobenzoic acid, which was filtered off with suction. The filtrate (~30 $cm^3$) was diluted with diethyl ether (50 $cm^3$). The organic phase was washed successively and *quickly* with cold, saturated aq. sodium hydrogen carbonate (20 $cm^3$ × 2) and saturated brine (20 $cm^3$), and was dried. The solvent was evaporated off under reduced pressure and the residue was suctioned by a vacuum pump to give the corresponding compound **1** as a semi-solid in nearly quantitative yield.

All attempts at further purification by column chromatography on silica resulted in decomposition of the product.

(−)-α-({(1S,2R,4R,$R_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*-[2.2.1]*heptan*-1-*yl*}*methysulfinyl*)-N-*methylmaleimide* **1a**. Prepared from sulfide **3a** (800 mg, 2.71 mmol) and MCPBA (563 mg, 3.26 mmol) in ~100% yield. *Prisms*, m.p. 152–155 °C (from hexane–ethyl acetate) (Found: C, 57.6; H, 6.6; N, 4.4. $C_{15}H_{21}NO_4S$ requires C, 57.86; H, 6.80; N, 4.50%); $[\alpha]_D^{23}$ −12.0 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 3400, 1700, 1440 and 1380; $\delta_H$ 0.88 (3 H, s, Me), 1.08 (3 H, s, Me), 1.0–1.9 (7 H, m, bornyl H), 3.08 (1 H, d, *J* 13, 10′-$H^a$), 3.08 (3 H, s, NMe), 3.43 (1 H, br, OH), 3.49 (1 H, d, *J* 13, 10′-$H^b$), 4.07 (1 H, br, 2′-H) and 7.18 (1 H, s, CH=); *m/z* 311 ($M^+$), 159, 135 and 93.

(+)-α-({(1S,2R,4R,$R_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*-[2.2.1]*heptan*-1-*yl*}*methysulfinyl*)-N-*phenylmaleimide* **1b**. Prepared from sulfide **3b** (1.50 g, 4.2 mmol) and MCPBA (727 mg, 4.2 mmol) in ~100% yield. Pale yellow *needles*, m.p. 129–131 °C (from pentane–diethyl ether) (Found: C, 64.15; H, 6.2; N, 3.6. $C_{20}H_{23}NO_4S$ requires C, 64.33; H, 6.21; N, 3.75%); $[\alpha]_D^{24}$ +89.2 (*c* 0.97, $CHCl_3$); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 2950, 1720, 1505, 1390 and 1080; $\delta_H$ 0.87 (3 H, s, Me), 1.10 (3 H, s, Me), 1.1–2.0 (7 H, m, bornyl H), 3.15 (1 H, d, *J* 13, 10′-$H^a$), 3.43 (1 H, br, OH), 3.59 (1 H, d, *J* 13, 10′-$H^b$), 4.11 (1 H, dd, *J* 8 and 4, 2′-H) and 7.2–7.6 (6 H, m, CH= and ArH); *m/z* 373 ($M^+$), 355, 221 and 135.

(+)-N-*Benzyl*-α-({(1S,2R,4R,$R_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methysulfinyl*)*maleimide* **1c**. Prepared from sulfide **3c** (4.05 g, 10.9 mmol) and MCPBA (2.65 g, 15.4 mmol) in ~100% yield. An amorphous *powder* (Found: C, 65.1; H, 6.5; N, 3.5. $C_{21}H_{25}NO_4S$ requires C, 65.10; H, 6.50; N, 3.62%); $[\alpha]_D^{26}$ +45.8 (*c* 1.0, $CHCl_3$); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1710, 1390, 1070 and 750; $\delta_H$ 0.87 (3 H, s, Me), 1.07 (3 H, s, Me), 0.8–2.0 (7 H, m, bornyl H), 3.06 (1 H, d, *J* 13, 10′-$H^a$), 3.42 (1 H, br, OH), 3.48 (1 H, d, *J* 13, 10′-$H^b$), 4.05 (1 H, dd, *J* 8 and 4, 2′-H), 4.64 (1 H, d, *J* 15, NC*H*H), 4.71 (1 H, d, *J* 15, NCH*H*), 7.15 (1 H, s, CH=) and 7.2–7.4 (5 H, m, ArH); *m/z* 388 ($M^+$ + 1), 370, 235, 135 and 93.

(1)-N-(tert-*Butyldimethylsilyl*)-α-({(1S,2R,4R,$R_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methysulfinyl*)-*maleimide* **1d**. Prepared from sulfide **3d** (1.83 g, 4.63 mmol) and MCPBA (882 mg, 5.1 mmol) in ~100% yield. *Needles*, m.p. 107–109 °C (from light petroleum) (Found: C, 57.1; H, 7.9; N, 3.4. $C_{20}H_{33}NO_4SiS{\cdot}1/2H_2O$ requires C, 57.11; H, 8.15; N, 3.33%); $[\alpha]_D^{25}$ +40.4 (*c* 2.1, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 3450, 2960, 1710 and 1310; $\delta_H$ 0.46 (6 H, s, $SiMe_3$), 0.88 (3 H, s, Me), 0.95 (9 H, s, $SiBu^t$), 1.10 (3 H, s, Me), 1.0–1.9 (7 H, m, bornyl H), 3.07 (1 H, d, *J* 12.7, 10′-$H^a$), 3.48 (1 H, br s, OH), 3.49 (1 H, d, *J* 12.7, 10′-$H^b$), 4.09 (1 H, m, 2′-H) and 7.14 (1 H, s, CH=).

(+)-α-({(1S,2R,4R,$R_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*-[2.2.1]*heptan*-1-*yl*}*methysulfinyl*)-N-(4-*methoxybenzyl*)*maleimide* **1e**. Prepared from sulfide **3e** (340 mg, 0.85 mmol) and MCPBA (206 mg, 1.19 mmol) in ~100% yield. A *foam* (Found: $M^+$, 417.1658. $C_{22}H_{27}NO_5S$ requires M, 417.1610); $[\alpha]_D^{24}$ +49.0 (*c* 1.1, $CHCl_3$); $\nu_{max}$(neat)/$cm^{-1}$ 3466, 2953, 1708, 1515 and 1245; $\delta_H$ 0.88 (3 H, s, Me), 1.08 (3 H, s, Me), 1.0–1.9 (7 H, m, bornyl H), 3.07 (1 H, d, *J* 13, 10′-$H^a$), 3.40 (1 H, br s, OH), 3.49 (1 H, d, *J* 13, 10′-$H^b$), 3.79 (3 H, s, OMe), 4.09 (1 H, m, 2′-H), 4.61 (1 H, A of ABq, *J* 14.4, NC*H*H), 4.67 (1 H, B of ABq, *J* 14.4, NCH*H*), 6.84–7.32 (4 H, m, ArH) and 7.14 (1 H, s, CH=); *m/z* 417 ($M^+$), 265, 135, 121 and 93.

(−)-N-*But*-3-*ynyl*-α-({(1S,2R,4R,$R_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methysulfinyl*)*maleimide* **1f**. Prepared from sulfide **3f** (5.0 g, 15 mmol) and MCPBA (2.70 g, 15.6 mmol) in 94% yield. *Prisms*, m.p. 130–131 °C (from diethyl ether) (Found: C, 61.7; H, 6.7; N, 3.9. $C_{18}H_{23}NO_4S$ requires C, 61.88; H, 6.64; N, 4.01%); $[\alpha]_D^{25}$ −59.0 (*c* 1.05, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 3400, 2950, 1720, 1700, 1400 and 1040; $\delta_H$ 0.85 (3 H, s, Me), 1.13 (3 H, s, Me), 1.25–1.89 (7 H, m, bornyl H), 1.95 (1 H, t, *J* 2.7, 4″-H), 2.57 (2 H, dt, *J* 6.7 and 2.7, $NCH_2CH_2$), 3.05 (1 H, d, *J* 14, 10′-$H^a$), 3.31 (1 H, br d, *J* 3.7, OH), 3.76 (2 H, t, *J* 6.7, $NCH_2$), 3.80 (1 H, d, *J* 14, 10′-$H^b$), 4.11 (1 H. m, 2′-H) and 7.18 (1 H, s, CH=); *m/z* 349 ($M^+$), 331, 316, 283 and 197.

*General Procedure of Diels–Alder Reaction of Maleimides* **1** *and Cyclopentadiene.*—(a) *In the presence of a Lewis acid.* To a solution of a sulfoxide **1** (0.3 mmol) in dry methylene dichloride (25 $cm^3$) at the temperature indicated in Table 1 was added zinc chloride (1.5 mol equiv.) in one portion. After the mixture had been stirred at that temperature for 0.5 h, cyclopentadiene (5–20 mol equiv.) was added *via* a syringe. The mixture was stirred at that temperature for 0.5–1 h, then was poured onto cold, 1 mol $dm^{-3}$ hydrochloric acid (15 $cm^3$), and the organic layer was separated. The aqueous phase was extracted with methylene dichloride (10 $cm^3$ × 3) and the combined organic phase was washed with saturated brine and dried. The solvent was evaporated off under reduced pressure and the residue was purified by chromatography on silica with hexane–ethyl acetate (5:1→1:1) to give the adducts **4** and **5**. The major adducts **4** obtained from the reaction were isolated in 70–80% yield by recrystallisation of the reaction mixture.

(b) *Without a Lewis acid.* To a solution of a sulfoxide **1** (~0.3 mmol) in methylene dichloride (5 $cm^3$) at 0 °C was added dropwise cyclopentadiene (20 mol equiv.) *via* a syringe. After being stirred for 0.5 h, the solvent and the excess of cyclopentadiene were evaporated off under reduced pressure. The residue was purified by chromatography on silica with hexane–ethyl acetate (6:1→1:1) to give the adducts **4** and **5**. The adducts **5a** and **5e** were separated from their diastereoisomers **4a** and **4e** by PLC [hexane–ethyl acetate (6:1), 30

developments], respectively. All attempts to isolate compounds **5b** and **5c** by chromatography were unsuccessful.

(1R,4S)-(−)-2-exo-({(1S,2R,4R,$R_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-N-*methylbicyclo*-[2.2.1]*hept*-5-*ene*-2-endo,3-endo-*dicarboximide* **4a**. A *solid*, m.p. 137–139 °C (from aq. MeOH) (Found: C, 63.9; H, 7.4; N, 3.6. $C_{20}H_{27}NO_4S$ requires C, 63.64; H, 7.21; N, 3.71%); $[\alpha]_D^{25}$ −1.3 (*c* 0.4, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 2950, 1700, 1030 and 750; $\delta_H$ 0.91 (3 H, s, Me), 1.16 (3 H, s, Me), 1.1–2.0 (8 H, m), 2.31 (1 H, d, *J* 9, 7-H$^a$), 2.89 (3 H, s, NMe), 3.13 (1 H, d, *J* 9, 7-H$^b$), 3.47 (1 H, d, *J* 13, 10′-H$^a$), 3.49 (1 H, br, CH), 3.57 (1 H, d, *J* 13, 10′-H$^b$), 3.61 (1 H, br, CH), 3.82 (1 H, br, CH), 4.01 (1 H, br, 2′-H), 6.29 (1 H, dd, *J* 5.5 and 3, CH=) and 6.36 (1 H, dd, *J* 5.5 and 3, CH=); *m*/*z* 378 ($M^+$ + 1), 360, 301, 225 and 159.

(1R,4S)-(−)-2-exo-({(1S,2R,4R,$R_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-N-*phenylbicyclo*-[2.2.1]*hept*-5-*ene*-2-endo,3-endo-*dicarboximide* **4b**. *Prisms*, m.p. 187–189 °C (from hexane–ethyl acetate) (Found: C, 68.3; H, 6.6; N, 3.1. $C_{25}H_{29}NO_4S$ requires C, 68.32; H, 6.65; N, 3.19%); $[\alpha]_D^{23}$ −23.8 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 2960, 1710, 1370 and 1190; $\delta_H$ 0.88 (3 H, s, Me), 1.16 (3 H, s, Me), 0.8–2.0 (8 H, m, bornyl H and 7-H$^a$), 2.37 (1 H, d, *J* 9, 7-H$^b$), 3.17 (1 H, d, *J* 13, 10′-H$^a$), 3.55 (1 H, d, *J* 13, 10′-H$^b$), 3.61 (1 H, d, *J* 3, OH), 3.61 (1 H, br, 1- or 4-H), 3.69 (1 H, d, *J* 4, 3-H), 3.94 (1 H, br, 4- or 1-H), 4.05 (1 H, dt, *J* 8 and 4, 2′-H), 6.45 (1 H, dd, *J* 5 and 3, CH=), 6.52 (1 H, dd, *J* 5 and 3, CH=) and 7.1–7.5 (5 H, m, ArH); *m*/*z* 440 ($M^+$ + 1), 422, 287 and 221.

(1R,4S)-(−)-N-*Benzyl*-2-exo-({(1S,2R,4R,$R_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)*bicyclo*-[2.2.1]*hept*-5-*ene*-2-endo,3-endo-*dicarboximide* **4c**. *Needles*, m.p. 172–173 °C (from hexane–ethyl acetate) (Found: C, 68.9; H, 7.0; N, 2.9. $C_{26}H_{31}NO_4S$ requires C, 68.85; H, 6.89; N, 3.09%); $[\alpha]_D^{26}$ −4.4 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 3400, 2960, 1700, 1170 and 1035; $\delta_H$ 0.77 (3 H, s, Me), 1.03 (3 H, s, Me), 1.0–1.9 (8 H, m, bornyl H and 7-H$^a$), 2.23 (1 H, d, *J* 9, 7-H$^b$), 2.86 (1 H, d, *J* 13, 10′-H$^a$), 3.33 (1 H, d, *J* 13, 10′-H$^b$), 3.39 (1 H, d, *J* 4.5, 3-H), 3.47 (1 H, br, 1- or 4-H), 3.59 (1 H, d, *J* 3.5, OH), 3.81 (1 H, br, 4- or 1-H), 3.99 (1 H, ddd, *J* 8, 4 and 3.5, 2′-H), 4.49 (1 H, d, *J* 14, NC*H*H), 4.56 (1 H, d, *J* 14, NCH*H*), 6.09 (2 H, br, CH=) and 7.2–7.4 (5 H, m, ArH); $\delta_C$ 19.8, 20.4, 27.1, 30.9, 38.4, 42.6, 45.0, 45.3, 45.5, 46.0, 48.4, 49.1, 49.9, 51.1, 71.3, 76.8, 128.1, 128.6, 128.8, 135.2, 135.8, 138.3 and 174.2; *m*/*z* 454 ($M^+$ + 1), 353, 301 and 235.

(1R,4S)-(+)-2-exo-({(1S,2R,4R,$R_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)*bicyclo*[2.2.1]*hept*-5-*ene*-2-endo,3-endo-*dicarboximide* **4g**. The adducts **4d** and **5d** were acid labile and cleavage of the $SiMe_2Bu^t$ group took place during purification by chromatography on silica. The major adduct was thus isolated as compound **4g** after protodesilylation by exposure to silica on a column for 1 day followed by elution with hexane–ethyl acetate (1:1).

*Compound* **4g**: prisms, m.p. 230–232 °C (from hexane–ethyl acetate) (Found: C, 62.7; H, 6.9; N, 3.9. $C_{19}H_{25}NO_4S$ requires C, 62.79; H, 6.93; N, 3.85%); $[\alpha]_D^{26}$ +2.4 (*c* 2.1, $CHCl_3$); $[\alpha]_D^{26}$ +11.7 (*c* 1.7, acetone); $\nu_{max}$(KBr)/$cm^{-1}$ 3500, 3210, 2950, 1770, 1710, 1340 and 1200; $\delta_H$ 0.89 (3 H, s, Me), 1.14 (3 H, s, Me), 1.1–1.3 (1 H, m, bornyl H), 1.4–1.7 (2 H, m, bornyl H), 1.7–1.95 (5 H, m, bornyl H and 7-H$^a$), 2.25 (1 H, br d, *J* 9, 7-H$^b$), 3.01 (1 H, d, *J* 13, 10′-H$^a$), 3.47 (1 H, d, *J* 13, 10′-H$^b$), 3.49 (2 H, br s, 1- or 4-H and 3-H), 3.61 (1 H, br d, *J* 3, OH), 3.82 (1 H, br s, 4- or 1-H), 4.02 (1 H, br t, *J* 4, 2′-H), 6.38 (1 H, dd, *J* 5.4 and 3.2, CH=), 6.45 (1 H, br d, *J* 5.4, CH=) and 8.36 (1 H, br s, NH); *m*/*z* 364 ($M^+$ + 1), 346, 280, 263, 211 and 135.

The diastereoisomeric excess (d.e.) was estimated as >99% by HPLC analysis [hexane–ethyl acetate–methanol (5:1:0.5), flow rate 1.5 $cm^3$ $min^{-1}$]. The absolute stereochemistry of the unstable compound **4d** was confirmed by transformation of compound **4g** into known compound **4c** under Mitsunobu conditions as follows. A solution of compound **4g** (50 mg, 0.14 mmol), triphenylphosphine (47 mg, 0.18 mmol) and benzyl alcohol (0.02 $cm^3$, 0.18 mmol) in THF (10 $cm^3$) was stirred at room temp. for 10 min, after which DEAD (0.03 $cm^3$, 0.18 mmol) as a solution in THF (5 $cm^3$) was added dropwise to the mixture. After being stirred at that temperature for 24 h, the mixture was evaporated under reduced pressure. The residue was purified by chromatography on silica with hexane–ethyl acetate (4:1) to afford compound **4c** (50 mg, 80%), identical with that obtained earlier.

(1R,4S)-(−)-2-exo-({(1S,2R,4R,$R_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-N-(4-*methoxybenzyl*)*bicyclo*[2.2.1]*hept*-5-*ene*-2-endo,3-endo-*dicarboximide* **4e**. *Prisms*, m.p. 126–127 °C (from hexane–ethyl acetate) (Found: C, 67.2; H, 6.7; N, 2.9. $C_{27}H_{33}NO_5S$ requires C, 67.05; H, 6.88; N, 2.90%); $[\alpha]_D^{23}$ −7.8 (*c* 2.0, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 3400, 2956, 1772, 1705, 1512, 1246 and 1038; $\delta_H$ 0.67 (3 H, s, Me), 0.94 (3 H, s, Me), 1.0–1.1 (1 H, m, bornyl H), 1.25–1.4 (1 H, m, bornyl H), 1.37 (1 H, d, *J* 9.3, 7-H$^a$), 1.5–1.8 (5 H, m, bornyl H), 2.13 (1 H, d, *J* 9.3, 7-H$^b$), 2.70 (1 H, d, *J* 12.9, 10′-H$^a$), 3.21 (1 H, d, *J* 12.9, 10′-H$^b$), 3.25 (1 H, d, *J* 4.4, 3-H), 3.39 (1 H, br s, 1- or 4-H), 3.52 (1 H, d, *J* 2.9, OH), 3.69 (3 H, s, OMe), 3.73 (1 H, br s, 4- or 1-H), 3.9–4.0 (1 H, m, 2′-H), 4.39 (2 H, ABq, *J* 13.9, Δν 16.6 Hz, $NCH_2$), 6.02 (2 H, s, CH=), 6.73 (2 H, d, *J* 8.6, ArH) and 7.18 (2 H, d, *J* 8.6, ArH); 483 ($M^+$), 331, 265 and 121.

(1R,4S)-(+)-2-exo-({(1S,2R,4R,$R_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-N-*But*-3-*ynylbicyclo*[2.2.1]*hept*-5-*ene*-2-endo,3-endo-*dicarboximide* **4f**. *Prisms*, m.p. 64–66 °C (from pentane–diethyl ether) (Found: C, 66.5; H, 7.3; N, 3.2. $C_{23}H_{29}NO_4S$ requires C, 66.49; H, 7.04; N, 3.37%); $[\alpha]_D^{25}$ +3.9 (*c* 2.0, $CHCl_3$); $[\alpha]_D^{25}$ +17.2 (*c* 0.8, acetone); $\nu_{max}$(KBr)/$cm^{-1}$ 3460, 3260, 2960, 1700, 1450, 1400 and 1030; $\delta_H$ 0.90 (3 H, s, Me), 1.16 (3 H, s, Me), 1.2–1.9 (8 H, m, bornyl H and 7-H$^a$), 1.95 (1 H, t, *J* 2.7, 4″-H), 2.30 (1 H, d, *J* 9.3, 7-H$^b$), 2.42 (2 H, dt, *J* 6.8 and 2.7, 2″-H), 3.10 (1 H, d, *J* 13, 10′-H$^a$), 3.46 (1 H, d, *J* 13, 10′-H$^b$), 3.52 (2 H, br s, 6- and 1- or 4-H), 3.57 (2 H, t, *J* 6.8, $NCH_2$), 3.60 (1 H, d, *J* 3.5, OH), 3.83 (1 H, br s, 4- or 1-H), 4.02 (1 H, dt, *J* 4.0, 3.5, 2′-H), 6.30 (1 H, dd, *J* 5.5, 3.0, CH=) and 6.37 (1 H, dd, *J* 5.5 and 3.0, CH=); *m*/*z* 416 ($M^+$ + 1), 398, 332, 263 and 197.

The d.e. was estimated as 96% (98:2) by HPLC analysis [hexane–ethyl acetate–methanol (10:1:0.1), flow rate 1.5 $cm^3$ $min^{-1}$; $t_R$ **4f** 19.8 min; **5f** 21.9 min].

(1S,4R)-(−)-2-exo-({(1S,2R,4R,$R_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-N-*methylbicyclo*-[2.2.1]*hept*-5-*ene*-2-endo,3-endo-*dicarboximide* **5a**. *Needles*, m.p. 186–188 °C (from aq. methanol) (Found: C, 62.6; H, 7.0; N, 3.6. $C_{20}H_{27}NO_4S{\cdot}1/3H_2O$ requires C, 62.64, H, 7.20; N, 3.61%); $[\alpha]_D^{25}$ −29.1 (*c* 0.7, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 3400, 1700, 1290 and 1000; $\delta_H$ 0.87 (3 H, s, Me), 1.13 (3 H, s, Me), 1.0–2.0 (8 H, m, bornyl H and 7-H$^a$), 2.07 (1 H, d, *J* 9, 7-H$^b$), 2.64 (1 H, d, *J* 13, 10′-H$^a$), 2.90 (3 H, s, NMe), 3.26 (1 H, br, 1- or 4-H), 3.50 (1 H, d, *J* 3, 3-H), 3.55 (1 H, br, 4- or 1-H), 3.71 (1 H, d, *J* 5, OH), 3.73 (1 H, d, *J* 13, 10′-H$^b$), 4.00 (1 H, ddd, *J* 8, 5 and 4, 2′-H), 6.26 (1 H, d, *J* 7.5, CH=) and 6.29 (1 H, d, *J* 7.5, CH=); HRMS (Found: $M^+$ + 1, 378.1703. $C_{20}H_{27}NO_4S$ requires M + 1, 378.1737); *m*/*z* 378 ($M^+$ + 1), 360, 294, 225 and 159.

The adducts **5b** and **5c** could not be isolated in pure form; $^1H$ NMR spectral data of **5b**: $\delta_H$ 0.86 (3 H, s, Me), 1.12 (3 H, s, Me), 1.1–2.0 (8 H, m, bornyl H and 7-H$^a$), 2.16 (1 H, d, *J* 9, 7-H$^b$), 2.69 (1 H, d, *J* 13, 10′-H$^a$), 3.43 (1 H, br, 1- or 4-H), 3.55 (1 H, d, *J* 3, OH), 3.62 (1 H, br, 4- or 1-H), 3.72 (1 H, d, *J* 13, 10′-H$^b$), 3.89 (1 H, d, *J* 4, 3-H), 4.04 (1 H, ddd, *J* 8, 4 and 3, 2′-H), 6.44 (2 H, br, CH=) and 7.1–7.5 (5 H, m, ArH).

$^1H$ NMR spectral data for adduct **5c**: $\delta_H$ 0.65 (3 H, s, Me), 1.00 (3 H, s, Me), 0.8–1.9 (8 H, m, bornyl H and 7-H$^a$), 2.09 (1 H,

d, *J* 9, 7-H$^b$), 2.40 (1 H, d, *J* 13, 10′-H$^a$), 3.33 (1 H, br, 1- or 4-H), 3.46 (1 H, d, *J* 3.5, 3-H), 3.50 (2 H, d + br, *J* 13, 10′-H$^b$ and 4- or 1-H), 3.73 (1 H, d, *J* 4, OH), 3.92 (1 H, m, 2′-H), 4.51 (1 H, d, *J* 14, NC*H*H), 4.57 (1 H, d, *J* 14, NCH*H*), 6.09 (2 H, br, CH=) and 7.2–7.4 (5 H, m, ArH).

(1S,4R)-(+)-2-exo-({(1S,2R,4R,R$_S$)-2-*Hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-N-(4-*methoxybenzyl*)*bicyclo*[2.2.1]*hept*-5-*ene*-2-endo,3-endo-*dicarboximide* **5e**. *Needles*, m.p. 148–150 °C (from hexane–ethyl acetate) (Found: 67.0; H, 6.6; N, 2.9. $C_{27}H_{33}NO_5S$ requires C, 67.05; H, 6.88; N, 2.90%); $[\alpha]_D^{23}$ +61.1 (*c* 2.0, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 3444, 2952, 1764, 1696 and 1034; $\delta_H$ 0.62 (3 H, s, Me), 0.98 (3 H, s, Me), 1.05–1.25 (1 H, m, bornyl-H), 1.4–1.5 (2 H, m, bornyl H), 1.6–1.85 (5 H, m, bornyl H and 7-H$^a$), 2.10 (1 H, d, *J* 9.3, 7-H$^b$), 2.32 (1 H, d, *J* 12.9, 10′-H$^a$), 3.35 (1 H, br, s, 1- or 4-H), 3.41 (1 H, d, *J* 12.9, 10′-H$^b$), 3.45 (1 H, d, *J* 3.4, OH), 3.49 (1 H, br s, 4- or 1-H), 3.71 (1 H, d, *J* 4.4, 3-H), 3.76 (3 H, s, OMe), 3.97 (1 H, ddd, *J* 8.1, 4.2 and 3.4, 2′-H), 4.44 (1 H, A of ABq, *J* 13.9, NC*H*H), 4.51 (1 H, B of ABq, *J* 13.9, NCH*H*), 6.09 (2 H, br s, CH=), 6.80 (2 H, d, *J* 8.7, ArH) and 7.26 (2 H, d, *J* 8.7, ArH); *m*/*z* 483 (M$^+$), 331, 265 and 121.

*General Procedure of Diels–Alder Reaction of Maleimides* **1c** *and* **1e** *with Furan*.—(a) *In the presence of* $ZnCl_2$. To a solution of compound **1** (0.2 mmol) in dry methylene dichloride (5 cm$^3$) at the temperature indicated in Table 4 was added $ZnCl_2$ (1.5 mol equiv.) and the mixture was stirred at that temperature for 0.5 h. To the solution was added dropwise furan (20 mol equiv.) *via* a syringe. After being stirred for 0.5–62 h, the mixture was poured onto cold, 1 mol dm$^{-3}$ HCl (10 cm$^3$). The organic phase was separated and the aqueous layer was extracted with methylene dichloride (5 cm$^3$ × 3). The combined extracts were washed with saturated brine (20 cm$^3$), dried, and concentrated. The residue was purified by chromatography on silica with hexane–ethyl acetate (2:1) to give the adducts.

(b) *Without* $ZnCl_2$. A solution of compound **1c** (80 mg, 0.21 mmol) and furan (0.3 cm$^3$, 20 mol equiv.) was stirred at 0 °C for 24 h. After the usual work-up, the crude product was purified by chromatography on silica with hexane–ethyl acetate (2:1) to give adduct **6c** (13 mg, 14%), adduct **8c** (14 mg, 15%) and an inseparable mixture of diastereoisomers **7c** and **9c** (26 mg, 27%).

(1S,2S,6S,7R)-(−)-4-*Benzyl*-2-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-10-*oxa*-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*ene*-3,5-*dione* **6c**. The reaction of compound **1c** (80 mg, 0.21 mmol) with furan (0.3 cm$^3$, 4.13 mmol) at 0 °C for 0.5 h afforded the adducts **6c** (48 mg, 51%) and **7c** (14 mg, 15%).

*Compound* **6c**: needles, m.p. 143–144 °C (from hexane–ethyl acetate) (Found: C, 66.1; H, 6.4; N, 3.2. $C_{25}H_{29}NO_5S$ requires C, 65.92; H, 6.42; N, 3.08%); $[\alpha]_D^{25}$ −26.9 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 2950, 1700, 1330, 1030 and 1020; $\delta_H$ 0.65 (3 H, s, Me), 0.96 (3 H, s, Me), 0.9–1.9 (7 H, m, bornyl H), 2.53 (1 H, d, *J* 13, 10′-H$^a$), 2.77 (1 H, s, 6-H), 3.25 (1 H, d, *J* 13, 10′-H$^b$), 3.39 (1 H, d, *J* 3.5, OH), 3.90 (1 H, dt, *J* 8 and 3.5, 2′-H), 4.66 (1 H, d, *J* 14, NC*H*H), 4.73 (1 H, d, *J* 14, NCH*H*), 5.37 (1 H, s, 1- or 7-H), 5.56 (1 H, s, 7- or 1-H), 6.69 (1 H, dd, *J* 6 and 2, CH=), 6.77 (1 H, dd, *J* 6 and 1.5, CH=) and 7.2–7.4 (5 H, m, ArH); *m*/*z* 371, 353, 235, 91 and 68.

(1R,2S,6S,7S)-(−)-4-*Benzyl*-2-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-10-*oxa*-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*ene*-3,5-*dione* **7c**. *Needles*, m.p. 125–127 °C (from hexane–ethyl acetate) (Found: C, 65.5; H, 6.4; N, 3.1%); $[\alpha]_D^{25}$ −38.0 (*c* 1.0, $CHCl_3$); $\nu_{max}$($CHCl_3$)/cm$^{-1}$ 1710, 1650, 1390, 1340 and 1070; $\delta_H$ 0.71 (3 H, s, Me), 1.00 (3 H, s, Me), 1.0–1.9 (7 H, m, bornyl H), 2.37 (1 H, d, *J* 13, 10′-H$^a$), 3.19 (1 H, d, *J* 13, 10′-H$^b$), 3.52 (1 H, d, *J* 3.4, OH), 3.61 (1 H, d, *J* 5.4, 6-H), 4.02 (1 H, ddd, *J* 8, 4 and 3.4, 2′-H), 4.54 (2 H, s, $NCH_2$), 5.41 (1 H, s, 1-H), 5.44 (1 H, d, *J* 5.4, 7-H), 6.27 (1 H, dd, *J* 5.6 and 1.4, CH=), 6.30 (1 H, dd, *J* 5.6 and 1.7, CH=) and 7.2–7.4 (5 H, m, ArH); *m*/*z* 371, 235, 135 and 91.

The reaction of compound **1c** (100 mg, 0.26 mmol) and furan (0.94 cm$^3$) conducted at 25 °C for 10 h afforded the adducts **6c** and **8c** (33 mg, 56%). The ratio **6c**:**8c** was 55:45 as judged by HPLC [hexane–ethyl acetate (2:1), flow rate 1 cm$^3$ min$^{-1}$]. The adduct **8c** was isolated by column chromatography on silica with hexane–ethyl acetate (1:1).

(1R,2R,6R,7S)-(−)-4-*Benzyl*-2-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-10-*oxa*-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*ene*-3,5-*dione* **8c**. *Needles*, m.p. 140–141 °C (from hexane–ethyl acetate) (Found: C, 65.8; H, 6.4; N, 3.3%); $[\alpha]_D^{25}$ +27.4 (*c* 0.37, $CHCl_3$); $\nu_{max}$($CHCl_3$)/cm$^{-1}$ 1710, 1390, 1350 and 1030; $\delta_H$ 0.74 (3 H, s, Me), 1.04 (3 H, s, Me), 1.0–1.9 (7 H, m, bornyl H), 2.33 (1 H, d, *J* 13, 10′-H$^a$), 3.25 (1 H, s, 6-H), 3.32 (1 H, d, *J* 3.5, OH), 3.88 (1 H, d, *J* 13, 10′-H$^b$), 3.91 (1 H, ddd, *J* 8, 4 and 3.5, 2′-H), 4.72 (2 H, s, $NCH_2$), 5.29 (1 H, br s, 1- or 7-H), 5.40 (1 H, br d, *J* 1.5, 7- or 1-H), 6.43 (1 H, dd, *J* 6 and 1.5, CH=), 6.71 (1H, dd, *J* 6 and 1.5, CH=) and 7.2–7.4 (5 H, m, ArH); *m*/*z* 235, 157, 135 and 91.

(1S,2R,6R,7R)-(−)-4-*Benzyl*-2-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-10-*oxa*-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*ene*-3,5-*dione* **9c**.—$\delta_H$ 0.80 (3 H, s, Me), 1.09 (3 H, s, Me), 1.1–1.9 (7 H, m, bornyl H), 2.62 (1 H, d, *J* 13, 10′-H$^a$), 3.43 (1 H, d, *J* 3.5, OH), 3.82 (1 H, d, *J* 13, 10′-H$^b$), 3.98 (1 H, d, *J* 5.6, 6-H), 4.00 (1 H, m, 2′-H), 4.54 (2 H, s, $NCH_2$), 5.16 (1 H, s, 1-H), 5.46 (1 H, d, *J* 5.6, 7-H), 6.25 (2 H, br s, CH=) and 7.2–7.4 (5 H, m, ArH); *m*/*z* 371, 235 and 91.

*Diels–Alder Reaction of the Maleimide* **1c** *and Cyclohexa*-1,3-*diene*.—(a) *In the presence of* $ZnCl_2$. To a solution of compound **1c** (98 mg, 0.25 mmol) in methylene dichloride (5 cm$^3$) at −40 °C was added $ZnCl_2$ (52 mg, 0.38 mmol) in one portion. After the mixture had been stirred at that temperature for 0.5 h, cyclohexa-1,3-diene (0.48 cm$^3$, 20 mol equiv.) was added dropwise. After being stirred for 1 h and worked up as usual, the crude product was analysed by HPLC, which showed only a single diastereoisomer. The crude product was purified by chromatography on silica with hexane–ethyl acetate (2:1) to give compound **10** (85 mg, 72%).

(b) *Without* $ZnCl_2$. To a solution of compound **1c** (50 mg, 0.13 mmol) in methylene dichloride (5 cm$^3$) was added cyclohexa-1,3-diene (0.25 cm$^3$, 20 mol equiv.) and the mixture was stirred for 10 h before being passed through a short pad of silica (2 g) with ethyl acetate to remove the polymerised material. Elution afforded adducts **10** and **11** (42 mg, 70%) in the ratio 22:78. The adduct **11** was separated from its diastereoisomer **10** by chromatography on silica with hexane–ethyl acetate (4:1).

(3aR,4R,7S,7aS)-(+)-2-*Benzyl*-3a-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-3a,4,-7,7a-*tetrahydro*-4,7-*ethanoisoindole*-1,3-*dione* **10**. *Needles*, m.p. 202–204 °C (from hexane–ethyl acetate) (Found: C, 69.3; H, 7.0; N, 2.8. $C_{27}H_{33}NO_4S$ requires C, 69.36; H, 7.11; N, 3.00%); $[\alpha]_D^{25}$ +28.2 (*c* 1.0, KBr); $\nu_{max}$(KBr)/cm$^{-1}$ 2590, 1700, 1350 and 1030; $\delta_H$ 0.58 (3 H, s, Me), 0.88 (3 H, s, Me), 1.1–2.0 (10 H, m), 2.26 (1 H, m), 2.29 (1 H, d, *J* 13, 10′-H$^a$), 2.62 (1 H, d, *J* 3, 7a-H), 3.11 (1 H, d, *J* 13, 10′-H$^b$), 3.26 (1 H, br, 4- or 7-H), 3.53 (1 H, d, *J* 3, OH), 3.60 (1 H, br, 7- or 4-H), 3.97 (1 H, ddd, *J* 8, 4 and 3, 2′-H), 4.58 (2 H, s, $NCH_2$), 6.20 (1 H, t, *J* 7, CH=), 6.30 (1 H, t, *J* 7, CH=) and 7.2–7.4 (5 H, m, ArH); $\delta_C$ 19.7, 20.2, 22.8, 27.0, 31.0, 32.5, 38.5, 42.6, 45.0, 46.6, 48.2, 48.5, 51.1, 66.1, 76.8, 128.3, 128.9, 133.4, 133.7, 135.3, 173.1 and 175.3; *m*/*z* 468 (M$^+$ + 1), 450, 315 and 91.

(3aS,4S,7R,7aR)-(−)-2-*Benzyl*-3a-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-3a,4,7,7a-*tetrahydro*-4,7-*ethanoisoindole*-1,3-*dione* **11**. *Prisms*, m.p. 186–187 °C (from hexane–ethyl acetate) (Found: C, 69.3;

H, 7.1; N, 2.9. $C_{27}H_{33}NO_4S$ requires C, 69.36; H, 7.11; N, 3.00%); $[\alpha]_D^{25}$ −5.5 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 1702, 1342, 1030 and 695; $\delta_H$ 0.73 (3 H, s, Me), 1.01 (3 H, s, Me), 1.1–1.9 (11 H, m), 2.43 (1 H, d, *J* 13, 10′-H$^a$), 3.22 (1 H, m, 7-H), 3.31 (2 H, br, 4- and 7a-H), 3.45 (1 H, d, *J* 3, OH), 3.57 (1 H, d, *J* 13, 10′-H$^b$), 3.96 (1 H, ddd, *J* 8, 4 and 3, 2′-H), 4.61 (2 H, s, $NCH_2$), 6.18 (2 H, m, CH=) and 7.2–7.4 (5 H, m, ArH); *m/z* 468 ($M^+$ + 1), 450, 315, 105 and 91.

*Diels–Alder Reaction of the Maleimide* **1c** *with Anthracene.*—(a) *In the presence of* $ZnCl_2$. To a solution of compound **1c** (60 mg, 0.16 mmol) in methylene dichloride (5 cm$^3$) at 0 °C was added $ZnCl_2$ (32 mg, 0.23 mmol) in one portion and the mixture was stirred for 0.5 h. To the mixture at −20 °C was added a solution of anthracene (55 mg, 0.31 mmol) in methylene dichloride (2 cm$^3$). After being stirred at that temperature for 18 h followed by the usual work-up, the crude product was analysed by $^1$H NMR spectrum, showing only a single diastereoisomer. The crude product was then purified by chromatography on silica with hexane–ethyl acetate (6:1→4:1) to afford compound **12** (84 mg, 96%).

(3a*R*,9a*S*)-(+)-2-*Benzyl*-3a-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-3a,4,9,9a-*tetrahydro*-4,9-*o*-*benzenobenz*[*f*]*isoindole*-1,3-*dione* **12**. *Prisms*, m.p. 215–216 °C (from hexane–ethyl acetate) (Found: C, 74.2; H, 6.2; N, 2.3. $C_{35}H_{35}NO_4S$ requires C, 74.31; H, 6.24; N, 2.48%); $[\alpha]_D^{25}$ +31.6 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 3400, 2940, 1700 and 1390; $\delta_H$ 0.47 (3 H, s, Me), 0.83 (3 H, s, Me), 0.9–1.9 (7 H, m, bornyl H), 1.79 (1 H, d, *J* 12.5, 10′-H$^a$), 2.84 (1 H, d, *J* 3.5, 9a-H), 2.96 (1 H, d, *J* 12.5, 10′-H$^b$), 3.41 (1 H, d, *J* 3.5, OH), 3.86 (1 H, ddd, *J* 8, 4 and 3.5, 2′-H), 4.21 (1 H, d, *J* 15, NC*H*H), 4.27 (1 H, d, *J* 15, NCH*H*), 4.84 (1 H, d, *J* 3.5, 9-H), 5.20 (1 H, s, 4-H) and 6.9–7.6 (13 H, m, ArH); *m/z* 556 ($M^+$ + 1), 230, 202, 178 and 91.

(b) *Without a Lewis acid.* To a solution of compound **1c** (70 mg, 0.18 mmol) in benzene (5 cm$^3$) was added anthracene (35 mg, 0.2 mmol) and the mixture was heated at reflux for 4 h. After removal of the solvent, the residue was purified by chromatography on silica with hexane–ethyl acetate (4:1→2:1) to give an inseparable mixture of diastereoisomers **12** and **13** (79 mg, 77%) in the ratio 56:44 as judged by $^1$H NMR spectroscopy.

(3a*S*,9a*R*)-(+)-2-*Benzyl*-3a-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-3a,4,9,9a-*tetrahydro*-4,9-*o*-*benzenobenz*[*f*]*isoindole*-1,3-*dione* **13** had $\delta_H$ 0.96 (3 H, s, Me), 1–1.85 (7 H, m, bornyl H), 1.14 (3 H, s, Me), 2.96 (1 H, d, *J* 13, 10′-H$^a$), 3.39 (1 H, d, *J* 2.9, OH), 3.67 (1 H, d, *J* 3.4, 9a-H), 3.83 (1 H, d, *J* 13, 10′-H$^b$), 3.85 (1 H, m, 2′-H), 4.31 (1 H, A of ABq, *J* 14.5, NC*H*H), 4.37 (1 H, B of ABq, *J* 14.5, NCH*H*), 4.69 (1 H, s, 4-H), 4.89 (1 H, d, *J* 3.4, 9-H) and 6.7–7.6 (13 H, m, ArH).

(1R,2R,5S,6S,7S)-(+)-4-*Benzyl*-5-*hydroxy*-2-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*en*-3-*one* **14**.—To a solution of imide **4c** (100 mg, 0.22 mmol) in EtOH (10 cm$^3$) was added in portions $NaBH_4$ (9.2 mg, 0.24 mmol) and the mixture was heated at reflux for 2 h. To the cooled mixture was added dropwise water (10 cm$^3$) and most of the solvent was evaporated off under reduced pressure. The aqueous layer was extracted with chloroform (10 cm$^3$ × 3). The combined extracts were washed with saturated brine, dried, and concentrated. The residual solid was purified by chromatography on silica with hexane–ethyl acetate (1:1) to give *compound* **14** (94 mg, 93%) as needles, m.p. 204–206 °C (from aq. methanol) (Found: C, 68.4; H, 7.4; N, 3.0. $C_{26}H_{33}NO_4S$ requires C, 68.55; H, 7.30; N, 3.08%); $[\alpha]_D^{23}$ +9.9 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 3400, 1660, 1070 and 1030; $\delta_H$ 0.86 (3 H, s, Me), 1.12 (3 H, s, Me), 1.1–2.2 (7 H, m, bornyl H), 1.61 (1 H, d, *J* 9, 10-H$^a$), 1.93 (1 H, d, *J* 9, 10-H$^b$), 2.79 (1 H, d, *J* 3.9, 6-H), 2.99 (1 H, d, *J* 13, 10′-H$^a$), 3.16 (1 H, br s, 1- or 7-H), 3.28 (1 H, d, *J* 13, 10′-H$^b$), 3.48 (1 H, d, *J* 8.8, OH), 3.56 (1 H, br s, 7-or 1-H), 3.77 (1 H, d, *J* 3, OH), 4.00 (1 H, m, 2′-H), 4.06 (1 H, d, *J* 14.5, NC*H*H), 4.42 (1 H, d, *J* 8.8, 5-H), 4.78 (1 H, d, *J* 14.5, NCH*H*), 5.83 (1 H, d, *J* 5.5 and 3, CH=), 6.23 (1 H, dd, *J* 5.5 and 3, CH=) and 7.2–7.4 (5 H, m, ArH); *m/z* 456 ($M^+$ + 1), 438, 303, 237 and 91.

(1R,2S,5S,6R,7S)-(+)-4-*Benzyl*-5-*hydroxy*-4-*azatricyclo*-[5.2.1.0$^{2,6}$]*dec*-8-*en*-3-*one* **15**.—To a deoxygenated solution of sulfoxide **14** (80 mg, 0.18 mmol) and dry *tert*-butyl alcohol (0.17 cm$^3$, 1.76 mmol) in dry THF (10 cm$^3$) was added a solution of $SmI_2$ (14.1 cm$^3$, 1.41 mmol, 0.1 mol dm$^{-3}$ in THF) followed by hexamethylphosphoric triamide (HMPA) (0.8 cm$^3$, 4.4 mmol). The intense purple suspension was stirred for 1.5 h and quenched with cold, 1 mol dm$^{-3}$ HCl (10 cm$^3$). The mixture was extracted with chloroform (10 cm$^3$ × 3) and the combined extracts were washed successively with dil. aq. sodium thiosulfate (10 cm$^3$) and saturated brine (10 cm$^3$). The organic phase was dried, and concentrated under reduced pressure. The residue was purified by chromatography on silica with hexane–ethyl acetate (2:1→0:1) to give a mixture of 10-mercaptoisoborneol and the bis-sulfide **16**[12] (26 mg) in the ratio 48:33, and *compound* **15** (27 mg, 60%) as needles, m.p. 143–145 °C (from hexane–ethyl acetate) (Found: C, 75.2; H, 6.9; N, 5.4. $C_{16}H_{17}NO_2$ requires C, 75.27; H, 6.71; N, 5.49%); $[\alpha]_D^{23}$ +8.9 (*c* 0.95, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 1640, 1450, 1330, 1060 and 700; $\delta_H$ 1.36 (1 H, d, *J* 8.5, 10-H$^a$), 1.54 (1 H, d, *J* 8.5, 10-H$^b$), 2.64 (1 H, dd, *J* 8 and 4, 6-H), 3.07 (1 H, br, 1- or 7-H), 3.20 (1 H, d, *J* 8.5, OH), 3.2–3.3 (1 H, m, 2-H), 3.26 (1 H, br, 7- or 1-H), 3.97 (1 H, d, *J* 14.5, NC*H*H), 4.34 (1 H, d, *J* 8.5, 5-H), 4.80 (1 H, d, *J* 14.5, NCH*H*), 5.65 (1 H, dd, *J* 5.5 and 3, CH=), 6.07 (1 H, dd, *J* 5.5 and 3, CH=) and 7.2–7.4 (5 H, m, ArH); *m/z* 255 ($M^+$), 189, 106 and 91.

(1R,2S,5S,6R,7S)-(+)-4-*Benzyl*-5-*ethoxy*-4-*azatricyclo*-[5.2.1.0$^{2,6}$]*dec*-8-*en*-3-*one* **17**.—A mixture of the alcohol **15** (1.350 g, 5.3 mmol) and PPTS (10 mg) in dry EtOH (70 cm$^3$) was stirred at room temperature for 12 h. To the mixture was added anhydrous sodium carbonate (100 mg) and the mixture was filtered. The filtrate was concentrated under reduced pressure, and recrystallisation of the residue from diethyl ether afforded *compound* **17** (1.313 g, 88%) as a solid, m.p. 68–70 °C (Found: C, 76.25; H, 7.4; N, 5.2. $C_{18}H_{21}NO_2$ requires C, 76.29; H, 7.47; N, 5.16%); $[\alpha]_D^{24}$ +26.1 (*c* 2.0, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 2978, 1678, 1429, 1244 and 1082; $\delta_H$ 1.20 (3 H, t, *J* 7.1, Me), 1.38 (1 H, d, *J* 8.4, 10-H$^a$), 1.54 (1 H, dt, *J* 8.4 and 1.6, 10-H$^b$), 2.65 (1 H, ddd, *J* 8.5, 4.2 and 1, 6-H), 3.0 (1 H, br, 1- or 7-H), 3.22 (1 H, dd, *J* 8.5 and 4.6, 2-H), 3.3 (1 H, br, 7- or 1-H), 3.4 (2 H, m, $OCH_2$), 3.81 (1 H, dd, *J* 14.4 and 1, NC*H*H), 4.07 (1 H, s, 5-H), 4.88 (1 H, d, *J* 14.4, NCH*H*), 5.66 (1 H, dd, *J* 5.6 and 2.8, CH=), 6.11 (1 H, dd, *J* 5.6 and 2.9, CH=) and 7.15–7.35 (5 H, m, ArH).

Racemate (±)-**17** (m.p. 78 °C) was obtained from the Diels–Alder adduct[30] of *N*-benzylmaleimide with cyclopentadiene.

(1S,2S,5S,6S,7R)-(+)-4-*Benzyl*-5-*hydroxy*-2-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-10-*oxa*-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*en*-3-one **18**.—To a solution of imide **6c** (94 mg, 0.21 mmol) in EtOH (8 cm$^3$)–THF (3 cm$^3$) was added $NaBH_4$ (8.6 mg, 0.23 mmol) and the mixture was stirred for an additional 6.5 h. The reaction mixture was poured into ice–water (~10 g) and most of the solvent was evaporated off under reduced pressure. The aqueous phase was adjusted to pH ~4 by addition of dil. HCl using a pH test paper, and was extracted with chloroform (10 cm$^3$ × 3). The

combined extracts were washed with saturated brine, dried, and concentrated to give *compound* **18** (89 mg, 94%) as a solid, m.p. 150 °C (from chloroform–hexane) (Found: C, 65.5; H, 6.8; N, 3.0. $C_{25}H_{31}NO_5S$ requires C, 65.62; H, 6.83; N, 3.06%); $[\alpha]_D^{26}$ +23.2 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 3390, 2950, 1660, 1455, 1080 and 1010; $\delta_H$ 0.83 (3 H, s, Me), 1.12 (3 H, s, Me), 1.1–1.9 (7 H, m, bornyl H), 2.19 (1 H, s, 6-H), 3.10 (1 H, d, *J* 12.9, 10′-H$^a$), 3.32 (1 H, d, *J* 12.9, 10′-H$^b$), 3.37 (1 H, d, *J* 6.6, OH), 3.55 (1 H, d, *J* 3.4, OH), 3.95 (1 H, m, 2′-H), 4.40 (1 H, d, *J* 15.4, NC*H*H), 4.81 (1 H, d, *J* 15.4, NCH*H*), 5.00 (1 H, d, *J* 6.6, 5-H), 5.03 (1 H, br s, 1- or 7-H), 5.45 (1 H, br s, 7- or 1-H), 6.58 (1 H, dd, *J* 5.9 and 1.7, CH=), 6.68 (1 H, dd, *J* 5.9 and 1.5, CH=) and 7.3–7.4 (5 H, m, ArH).

(1S,2S,5R,6S,7R)-(+)-4-*Benzyl*-5-*hydroxy*-2-({(1S,2R,4R,R$_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-10-*oxa*-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*en*-3-*one* **19**.—In a similar manner to compound **18**, the adduct **6c** (250 mg, 0.55 mmol) was treated with $NaBH_4$ (125 mg, 3.3 mmol) in methanol (25 cm$^3$). After the mixture had been stirred for 6.5 h, cold water (20 cm$^3$) was added and the resultant mixture was stirred for 0.5 h. The precipitate was collected, and recrystallised from hexane–chloroform to give *compound* **19** (232 mg, 92%) as prisms, m.p. 142–145 °C (Found: C, 65.3; H, 6.9; N, 2.87. $C_{25}H_{31}NO_5S$ requires C, 65.62; H, 6.83; N, 3.06%); $[\alpha]_D^{26}$ +108.1 (*c* 1.0, pyridine); $\nu_{max}$(KBr)/cm$^{-1}$ 3385, 3270, 2950, 1655 and 1055; $\delta_H$ ([$^2H_5$]pyridine) 0.74 (3 H, s, Me), 1.02 (1 H, br t, *J* 7.3, bornyl H), 1.29 (3 H, s, Me), 1.4–1.8 (5 H, m, bornyl H), 1.9–2.1 (1 H, m, bornyl H), 2.80 (1 H, d, *J* 7, 6-H), 3.18 (1 H, d, *J* 13, 10′-H$^a$), 3.87 (1 H, d, *J* 13, 10′-H$^b$), 4.24 (1 H, dd, *J* 8 and 4, 2′-H), 4.47 (1 H, d, *J* 15, NC*H*H), 5.0 (2 H, br, OH), 5.22 (1 H, d, *J* 15, NCH*H*), 5.73 (1 H, d, *J* 7, 5-H), 5.9 (2 H, m, 1- and 7-H), 6.65 (1 H, dd, *J* 5.5 and 2, 8-H), 6.95 (1 H, dd, *J* 5.5 and 1.5, 9-H) and 7.3–7.6 (5 H, m, ArH).

*Isomerisation of the Alcohol* **19** *into compound* **18**.—(*a*) To a mixture of compound **19** (3 mg) in EtOH (10 cm$^3$) was added sodium (800 mg, 0.04 mol) and the mixture was stirred at room temperature for 2 days. To the mixture was added ice–water (10 cm$^3$) and the aqueous phase was extracted with chloroform (10 cm$^3$ × 3). The combined extracts were washed with saturated brine, dried, and concentrated to give compound **18** (1.3 mg, 43%).

(*b*) To a solution of compound **19** (5 mg, 0.01 mmol) in THF (15 cm$^3$) was added conc. HCl (1 drop) at room temperature. The mixture was stirred for 4 days and similar work-up to that in the method (*a*) afforded compound **18** (3 mg, 60%).

(1S,2R,5S,6S,7R)-(+)-4-*Benzyl*-5-*hydroxy*-10-*oxa*-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*en*-3-*one* **20**.—In a similar manner to the reduction of compound **14** (⟶ **15**), a solution of sulfoxide **18** (60 mg, 0.13 mmol) and *tert*-butyl alcohol (0.12 cm$^3$, 1.3 mmol) in THF (30 cm$^3$) was treated with a solution of $SmI_2$ (7.9 cm$^3$, 0.79 mmol, 0.1 mol dm$^{-3}$ in THF) and HMPA (0.3 cm$^3$) afforded *compound* **20** (33 mg, 98%) as needles, m.p. 153–155 °C (from hexane–ethyl acetate) (Found: C, 70.25; H, 5.85; N, 5.3. $C_{15}H_{15}NO_3$ requires C, 70.02; H, 5.88; N, 5.44%); $[\alpha]_D^{24}$ +79.8 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 3180, 1655, 1470, 1450 and 1080; $\delta_H$ 2.25 (1 H, dd, *J* 7 and 1, 2- or 6-H), 2.79 (1 H, d, *J* 7, 6- or 2-H), 3.13 (1 H, d, *J* 8, OH), 4.20 (1 H, d, *J* 15, NC*H*H), 4.86 (1 H, d, *J* 15, NCH*H*), 4.86 (1 H, d, *J* 8, 5-H), 4.92 (1 H, br d, *J* 2, 1- or 7-H), 5.21 (1 H, br d, *J* 2, 7- or 1-H), 6.38 (1 H, dd, *J* 6 and 2, CH=N), 6.45 (1 H, dd, *J* 6 and 2, CH=) and 7.2–7.4 (5 H, m, ArH).

(1S,2R,5R,6S,7R)-(+)-4-*Benzyl*-5-*hydroxy*-10-*oxa*-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*en*-3-*one* **21**.—In a similar manner to the preparation of compound **20**, a solution of compound **19** (45 mg, 0.1 mmol) in THF (40 cm$^3$) was treated with $SmI_2$ (7.9 cm$^3$, 0.79 mmol) and HMPA (0.2 cm$^3$) to give *compound* **21** (20 mg, 79%) as a solid, m.p. 135–137 °C (from hexane–ethyl acetate) (Found: 70.0; H, 5.85; N, 5.5%); $[\alpha]_D^{25}$ +169.8 (*c* 1.0, $CHCl_3$); $\nu_{max}$(KBr)/cm$^{-1}$ 3140, 1635, 1455 and 1120; $\delta_H$ 2.58 (1 H, dd, *J* 7.4 and 7, 6-H), 2.67 (1 H, d, *J* 7.4, 2-H), 2.68 (1 H, d, *J* 12.9, OH), 4.15 (1 H, d, *J* 14.7, NC*H*H), 4.86 (1 H, d, *J* 14.7, NCH*H*), 5.03 (1 H, dd, *J* 12.9 and 7, 5-H), 5.15 (1 H, br d, *J* 1.5, 1- or 7-H), 5.25 (1 H, br d, *J* 1.5, 7- or 1-H), 6.38 (1 H, dd, *J* 5.8 and 1.7, CH=), 6.55 (1 H, dd, *J* 5.8 and 1.7, CH=) and 7.3–7.4 (5 H, m, ArH).

(1R*,2S*,5S*,6R*,7S*)-4-*Benzyl*-5-(p-*tolylsulfonyl*)-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*en*-3-*one* **22**.—To a solution of toluene-*p*-sulfinic acid (1.02 g, 6.55 mmol) in methylene dichloride (20 cm$^3$) was added powdered $CaCl_2$ (727 mg, 6.55 mmol). After the mixture had been stirred for 5 min, a solution of racemate (±)-**17** (370 mg, 1.31 mmol) in methylene dichloride (5 cm$^3$) was added and the mixture was stirred for 0.5 h before being washed successively with water (10 cm$^3$), saturated aq. sodium hydrogen carbonate (10 cm$^3$) and saturated brine (10 cm$^3$), dried and concentrated. The residue was purified by chromatography on silica with hexane–ethyl acetate (3:1) to give *compound* (±)-**22** (368 mg, 71%) as a solid, m.p. 151–152 °C (from hexane–ethyl acetate) (Found: C, 70.2; H, 5.8; N, 3.6. $C_{23}H_{23}NO_3S$ requires C, 70.21; H, 5.89; N, 3.56%); $\nu_{max}$(neat)/cm$^{-1}$ 3060, 2980, 1740, 1700, 1400, 1300, 1290 and 1130; $\delta_H$ 1.19 (1 H, d, *J* 8.8, 10-H$^a$), 1.42 (1 H, d, *J* 8.8, 10-H$^b$), 2.33 (1 H, dd, *J* 8 and 4, 2-H), 2.47 (3 H, s, Me), 2.84 (1 H, ddd, *J* 8, 4 and 1.5, 6-H), 2.98 (1 H, br s, 1- or 7-H), 3.12 (1 H, br s, 7- or 1-H), 3.99 (1 H, br d, *J* 1.5, 5-H), 4.32 (1 H, d, *J* 14, NC*H*H), 5.12 (1 H, d, *J* 14, NCH*H*), 5.23 (1 H, dd, *J* 5 and 3, CH=), 5.91 (1 H, dd, *J* 5 and 3, CH=), 7.32 (5 H, m, ArH), 7.40 (2 H, d, *J* 8, ArH) and 7.74 (2 H, d, *J* 8, ArH); *m*/*z* 394 (M$^+$ + 1), 352, 344, 336, 254, 238 and 174.

Optically active sulfone (+)-**22** was obtained similarly from the ether (+)-**17**, as prisms, m.p. 161–163 °C (from hexane–ethyl acetate); $[\alpha]_D^{26}$ +29.4 (*c* 1.97, $CHCl_3$); ~100% e.e. determined by chiral HPLC analysis [Chiralcel OC; hexane–EtOH (5:1), flow rate 0.5 cm$^3$ min$^{-1}$, $t_R$ (+)-**22**, 55 min; (−)-**22**, 64 min].

*General Procedure for Preparation of* (1R*,2S*,5S*,6R*,7S*)-4-*Benzyl*-4-*azatricyclo*[5.2.1.0$^{2,6}$]*dec*-8-*en*-3-*ones* **23**.—The reaction was conducted on a 0.35–0.5 mmol scale.

(a) *Using an organocopper reagent.* To a suspension of an organocuprate (2–3 mol equiv., prepared from 1.56 mol dm$^{-3}$ organolithium or ~0.5 mol dm$^{-3}$ Grignard reagent and CuBr·$Me_2S$ complex) in diethyl ether (10 cm$^3$) was added a Lewis acid under argon at the temperature indicated in Table 3. After the mixture had been stirred at that temperature for 15 min, a solution of the ether (±)-**17** (0.35–0.5 mmol) in diethyl ether (5 cm$^3$) was added *via a* syringe. The reaction mixture was allowed to reach the temperature in Table 3 and was quenched with saturated aq. $NH_4Cl$ (20 cm$^3$). The aqueous layer was extracted with methylene dichloride (20 cm$^3$ × 3) and the combined extracts were washed with saturated brine, dried, and concentrated. The residue was purified by chromatography on silica with hexane–ethyl acetate (2:1 for $R^2$ = vinyl; 3:1 for $R^2$ = butyl; 1:1 for $R^2$ = allyl; 8:1 for $R^2$ = heptyl) to afford compound (±)-**23** or a product mixture.

(b) *Using allyltrimethylsilane.* To a solution of the ether (±)-**17** (0.35–0.5 mmol) in dry methylene dichloride (20 cm$^3$) at the temperature indicated in Table 7 was added allyltrimethylsilane (4 mol equiv., 1.4–2 mmol) followed by a Lewis acid (2.5 mol equiv., 0.9–1.25 mmol; 1 mol dm$^{-3}$ $SnCl_4$ in $CH_2Cl_2$ or 1 mol dm$^{-3}$ $TiCl_4$ in $CH_2Cl_2$ or $BF_3$·$Et_2O$ complex). After being stirred for the appropriate time, the mixture was quenched with cold water (20 cm$^3$) followed by 2 mol dm$^{-3}$ hydrochloric acid

(10 $cm^3$). The aqueous layer was extracted with methylene dichloride (10 $cm^3$ × 4) and the extracts were washed with saturated brine (10 $cm^3$), dried, and concentrated. The product (±)-**23** ($R^2$ = allyl) was isolated after column chromatography on silica.

(c) *From a sulfonyl lactam.* To a stirred suspension of zinc bromide (263 mg, 1.17 mmol) in dry THF (10 $cm^3$) was added a 0.35 mol $dm^{-3}$ solution of heptylmagnesium bromide in THF (6.7 $cm^3$, 2.34 mmol) *via* a syringe. After the mixture had been stirred for 0.5 h, a solution of compound **22** (230 mg, 0.59 mmol) in dry THF (10 $cm^3$) was added at 0 °C. The mixture was allowed to reach room temperature and was stirred for 14 h. The reaction mixture was cooled to 0 °C and quenched with 1 mol $dm^{-3}$ hydrochloric acid (10 $cm^3$). The aqueous layer was extracted with diethyl ether (20 $cm^3$ × 4) and the extracts were washed with saturated brine (30 $cm^3$), dried, and concentrated. The residue was purified by flash chromatography on silica to give compound **23** ($R^2$ = heptyl) (164 mg, 83%).

*Compound* (±)-**23** ($R^2$ = vinyl) was an oil (Found: $M^+$ 265.1485. $C_{18}H_{19}NO$ requires M, 265.1465); $\nu_{max}$(neat)/$cm^{-1}$ 2971, 1681, 1422 and 1245; $\delta_H$ 1.32 (1 H, d, *J* 8.4, 10-H[a]), 1.52 (1 H, dt, *J* 8.4 and 1.7, 10-H[b]), 2.48 (1 H, ddd, *J* 9.3, 4 and 2.9, 6-H), 2.99 (1 H, br s, 1- or 7-H), 3.15–3.25 (2 H, m, 5- and 6-H), 3.30 (1 H, br s, 7- or 1-H), 3.57 (1 H, dd, *J* 14.4 and 1, NC*H*H), 4.98 (1 H, d, *J* 14.4, NCH*H*), 5.06 (1 H, d, *J* 17, CH=), 5.19 (1 H, br d, *J* 10, CH=), 5.63 (1 H, ddd, *J* 17, 10 and 8.8, CH=), 5.69 (1 H, dd, *J* 5.6 and 2.7, CH=), 6.19 (1 H, dd, *J* 5.6 and 2.9, CH=) and 7.05–7.35 (5 H, m, ArH); *m/z* 265 ($M^+$), 199, 118 and 91.

*Compound* (±)-**23** ($R^2$ = Bu) was an oil (Found: $M^+$, 295.1892. $C_{20}H_{25}NO$ requires M, 295.1934); $\nu_{max}$(neat)/$cm^{-1}$ 2930 and 1654; $\delta_H$ 0.89 (3 H, br t, *J* 7, Me), 1.05–1.67 (6 H, br, 3 × $CH_2$), 1.34 (1 H, d, *J* 8.4, 10-H[a]), 1.52 (1 H, dt, *J* 8.4 and 1.7, 10-H[b]), 2.42 (1 H, ddd, *J* 9.2, 3.9 and 2.9, 6-H), 2.72 (1 H, ddd, *J* 6.9, 2.9 and 2.5, 5-H), 2.90 (1 H, br s, 7-H), 3.13 (1 H, dd, *J* 9.2 and 4.4, 2-H), 3.29 (1 H, br s, 1-H), 3.65 (1 H, dd, *J* 14.7 and 1, NC*H*H), 4.98 (1 H, d, *J* 14.7, NCH*H*), 5.70 (1 H, dd, *J* 5.6 and 2.9, CH=), 6.19 (1 H, dd, *J* 5.6 and 3.0, CH=) and 7.15–7.35 (5 H, m, ArH); *m/z* 295 ($M^+$), 229, 186, 172 and 91.

*Compound* (±)-**23** ($R^2$ = allyl) was obtained as plates, m.p. 81–82 °C (from hexane–ethyl acetate) (Found: C, 81.7; H, 7.3; N, 4.75. $C_{19}H_{21}NO$ requires C, 81.68; H, 7.58; N, 5.01%); $\nu_{max}$(KBr)/$cm^{-1}$ 2986, 2939, 1664, 1426, 1246 and 707; $\delta_H$ 1.34 (1 H, d, *J* 8.5, 10-H[a]), 1.52 (1 H, dd, *J* 8.5 and 1.4, 10-H[b]), 2.18 (1 H, m, 1′-H[a]), 2.33 (1 H, m, 1′-H[b]), 2.48 (1 H, ddd, *J* 8.8, 3.3 and 2.9, 6-H), 2.84 (1 H, m, 5 H), 2.9 (1 H, br, 7-H), 3.12 (1 H, dd, *J* 8.8 and 4.4, 2-H), 3.3 (1 H, br s, 1-H), 3.69 (1 H, d, *J* 14.9, NC*H*H), 5.00 (1 H, d, *J* 14.9, NCH*H*), 5.1–5.2 (2 H, m, $CH_2$=) 5.6–5.7 (1 H, m, CH=), 5.72 (1 H, dd, *J* 5.6 and 2.9, 8-H), 6.20 (1 H, dd, *J* 5.6 and 2.1, 9-H) and 7.2–7.35 (5 H, m, ArH); *m/z* 279 ($M^+$), 238, 172 and 91.

*Compound* (±)-**23** ($R^2$ = heptyl) was an oil (Found: $M^+$, 337.2385. $C_{23}H_{31}NO$ requires *M*, 337.2404); $\nu_{max}$(neat)/$cm^{-1}$ 2927, 2856, 1681 and 1428; $\delta_H$ 0.89 (3 H, br t, *J* 6.7, Me), 1.25 (12 H, br, 6 × $CH_2$), 1.34 (1 H, d, *J* 8.4, 10-H[a]), 1.52 (1 H, dt, *J* 8.4 and 1.7, 10-H[b]), 2.42 (1 H, ddd, *J* 9.3, 4 and 3, 6-H), 2.73 (1 H, dt, *J* 8 and 3, 5-H), 2.91 (1 H, br s, 1- or 7-H), 3.13 (1 H, dd, *J* 9.3 and 4.6, 2-H), 3.29 (1 H, br s, 7- or 1-H), 3.66 (1 H, dd, *J* 14.7 and 1, NC*H*H), 4.97 (1 H, d, *J* 14.7, NCH*H*), 5.70 (1 H, dd, *J* 5.6 and 2.9, CH=), 6.19 (1 H, dd, *J* 5.6 and 2.9, CH=) and 7.15–7.35 (5 H, m, ArH); *m/z* 337 ($M^+$), 294, 271, 238, 186 and 172.

In a similar manner to racemate (±)-**23**, compound (+)-**23** ($R^2$ = heptyl) was obtained from sulfone (+)-**22** as an oil; $[\alpha]_D^{24}$ +24.7 (*c* 2.1, $CHCl_3$).

(5S)-(+)-1-*Benzyl*-5-*heptyl*-1,5-*dihydropyrrol*-2-*one* **25** *by Flash Vacuum Pyrolysis.*—The lactam (+)-**23** ($R^2$ = heptyl) (184 mg, 0.55 mmol) was subjected to pyrolysis (sublimation at 150 ⟶ 220 °C; quartz tube: length, 48 cm; diameter, 16 mm; oven temp. 450 °C at 0.5 Pa, for 4 h) to give *compound* **25** (116 mg, 78%) as an oil (Found: $M^+$, 271.1914. $C_{18}H_{25}NO$ requires M, 271.1934); $[\alpha]_D^{28}$ +42.4 (*c* 2.0, $CHCl_3$); $\nu_{max}$(neat)/$cm^{-1}$ 2926, 2855, 1684 and 1406; $\delta_H$ 0.87 (3 H, br t, *J* 6.5, Me), 1.1–1.4 (10 H, br, 5 × $CH_2$), 1.4–1.6 (1 H, m), 1.7–1.85 (1 H, m), 3.95–4.0 (1 H, m, 5-H), 4.07 (1 H, d, *J* 15, NC*H*H), 5.12 (1 H, d, *J* 15, NCH*H*), 6.21 (1 H, dd, *J* 5.9 and 1.5, 3-H), 7.02 (1 H, dd, *J* 5.9 and 1.5, 4-H) and 7.2–7.4 (5 H, m, ArH); *m/z* 271 ($M^+$), 186, 173 and 91.

E.e. 74% by chiral HPLC [Chiralpak AS; hexane–propan-2-ol (19:1), flow rate 1 $cm^3$ $min^{-1}$; $t_R$ (−)-**25**, 39.2 min; (+)-**25**, 44.4 min]. Racemate (±)-**25** was prepared from racemate (±)-**22** ($R^2$ = heptyl) by FVP.

(5S)-(−)-1-*Benzyl*-5-*heptylpyrrolidine*-2-*one* **24**.—A solution of compound (+)-**25** (25 mg) {$[\alpha]_D^{28}$ +42.4 (*c* 2.0, $CHCl_3$)} and containing 5% Pt on alumina (200 mg) in *tert*-butyl alcohol (5 $cm^3$) was hydrogenated at 3.5 atm for 5 h. The mixture was filtered and the filtrate was concentrated to give the saturated lactam (+)-**24**[19] (24 mg, 95%) as an oil, $[\alpha]_D^{26}$ −13.3 (*c* 1.2, $CH_2Cl_2$) {lit.,[19] $[\alpha]_D^{20}$ −21.9 (*c* 1.2, $CH_2Cl_2$) for ⩾94% e.e.}.

(1S,2S,5S,6S,7R)-(+)-4-*Benzyl*-5-*ethoxy*-2-({(1S,2R,4R,$R_S$)-2-*hydroxy*-7,7-*dimethylbicyclo*[2.2.1]*heptan*-1-*yl*}*methylsulfinyl*)-10-*oxa*-4-*azatricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **26**.—A mixture of imide **6c** (1.43 g, 3.14 mmol) and $NaBH_4$ (360 mg, 9.24 mmol) in THF (30 $cm^3$)–EtOH (100 $cm^3$) was heated at 50 °C for 3 h. After the mixture had cooled to 0 °C, water (0.2 $cm^3$), followed by conc. HCl (0.2 $cm^3$), was added to the mixture. The mixture was heated at 50 °C for 2 days. Most of the solvent was evaporated off and the residue was partitioned between water (10 $cm^3$) and chloroform (30 $cm^3$). The aqueous layer was extracted with chloroform (20 $cm^3$ × 4). The combined organic phases were washed with saturated brine (20 $cm^3$), dried, and concentrated to give *compound* **26** (1.40 g, 92%) as prisms, m.p. 145–147 °C (from hexane–ethyl acetate) (Found: C, 66.9; H, 7.1; N, 3.2. $C_{27}H_{35}NO_5S$ requires C, 66.78; H, 7.27; N, 2.88%); $[\alpha]_D^{26}$ +27.1 (*c* 0.47, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 2956, 1697, 1422 and 1074; $\delta_H$ 0.83 (3 H, s, Me), 1.12 (3 H, s, Me), 1.1–1.2 (1 H, m, bornyl H), 1.15 (3 H, t, *J* 7.0, Me), 1.4–1.6 (2 H, m, bornyl H), 1.7–1.9 (4 H, m, bornyl H), 2.14 (1 H, s, 6-H), 3.22 (1 H, d, *J* 13, 10′-H[a]), 3.35 (1 H, d, *J* 13, 10′-H[b]), 3.45 (2 H, dq, *J* 6.9 and 4.9, $OCH_2$), 3.63 (1 H, br, OH), 3.96–3.98 (1 H, m, 2′-H), 4.22 (1 H, d, *J* 15, NC*H*H), 4.62 (1 H, s, 5-H), 4.94 (1 H, d, *J* 15, NCH*H*), 4.97 (1 H, br s, 7-H), 5.49 (1 H, br s, 1-H), 6.58 (1 H, dd, *J* 5.8 and 1.6, CH=), 6.73 (1 H, dd, *J* 5.8 and 1.2, CH=) and 7.24–7.36 (5 H, m, ArH).

(1S,2R,5S,6S,7R)-(+)-4-*Benzyl*-5-*ethoxy*-10-*oxa*-4-*azatricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **27**.—To a deoxygenated solution of the sulfoxide **26** (1.50 g, 3.1 mmol), *tert*-butyl alcohol (3 $cm^3$, 31 mmol) and HMPA (5.6 $cm^3$, 31 mmol) in THF (100 $cm^3$) was added a solution of $SmI_2$ (154 $cm^3$, 15.4 mmol, 0.1 mol $dm^{-3}$ in THF) over a period of 5 min. After an additional 0.5 h, the mixture was quenched with water (10 $cm^3$). Most of the THF was evaporated off and 1 mol $dm^{-3}$ HCl (20 $cm^3$) was added to the mixture. The aqueous layer was extracted with chloroform (20 $cm^2$ × 5). The combined extracts were washed successively with aq. 0.5% sodium thiosulfate (10 $cm^3$) and saturated brine (10 $cm^3$), dried, and concentrated. The residue was purified by chromatography on silica with hexane–ethyl acetate (2:1) to give *compound* **27** (810 mg, 92%) as an oil (Found: $M^+$, 285.1351. $C_{17}H_{19}NO_3$ requires M, 285.1363); $[\alpha]_D^{26}$ +74.1 (*c* 2.3, $CHCl_3$); $\nu_{max}$(neat)/$cm^{-1}$ 2976, 2927, 1694, 1445 and 1080; $\delta_H$ 1.16 (3 H, t, *J* 7, Me), 2.25 (1 H, d, *J* 7.1, 2- or 6-H), 2.77 (1 H, d, *J* 7.1, 6- or 2-H), 3.39 (2 H, dq, *J* 12.9 and 7.0, $OCH_2$), 4.05 (1 H, d, *J* 15.3, NC*H*H), 4.60 (1 H, s, 5-H), 4.85 (1 H, s, 1- or 7-H), 4.94 (1 H, d, *J* 15.3, NCH*H*), 5.21 (1 H, s, 7- or 1-H), 6.37 (1 H,

d, *J* 5.7, CH=), 6.43 (1 H, d, *J* 5.7, CH=) and 7.22–7.30 (5 H, m, ArH); *m/z* 285 ($M^+$), 217, 186, 91 and 77.

(1S,2R,5S,6S,7R)-(+)-4-*Benzyl*-5-(p-*tolylsulfonyl*)-10-*oxa*-4-*azatricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **28**.—In a manner similar to compound (±)-**22**, the ethoxy lactam **27** (810 mg, 2.8 mmol) was treated with toluene-*p*-sulfinic acid (2.7 g, 17.1 mmol) and powdered $CaCl_2$ (1.9 g, 17.1 mmol) in methylene dichloride (80 $cm^3$) at room temperature for 17 h to give *compound* **28** (870 mg, 78%) as plates, m.p. 134–135 °C (from hexane–ethyl acetate) (Found: C, 66.8; H, 5.4; N, 3.8. $C_{22}H_{21}NO_4S$ requires C, 66.82; H, 5.35; N, 3.54%); $[\alpha]_D^{24}$ +75.3 (*c* 2.5, $CHCl_3$); $\nu_{max}$(KBr)/$cm^{-1}$ 3029, 2988, 1702 and 1595; $\delta_H$ 2.02 (1 H, d, *J* 7, 2- or 6-H), 2.47 (3 H, s, Me), 2.49 (1 H, d, *J* 7, 6- or 2-H), 4.32 (1 H, d, *J* 15, NC*H*H), 4.38 (1 H, s, 5-H), 4.82 (1 H, s, 1-H), 5.17 (1 H, s, 7-H), 5.27 (1 H, d, *J* 15, NCH*H*), 6.36 (1 H, dd, *J* 5.8 and 1.6, CH=), 6.40 (1 H, dd, *J* 5.8 and 1.5, CH=), 7.2–7.35 (5 H, m, ArH), 7.39 (2 H, d, *J* 8, ArH) and 7.69 (2 H, d, *J* 8, ArH); *M/z* 240, 172, 148 and 91.

~ 100% E.e. was confirmed by chiral HPLC [Chiralcel OC; hexane–ethyl acetate (5:1), flow rate 1 $cm^3$ $min^{-1}$; $t_R$ (+)-**28**, 56 min; (−)-**28**, 78.4 min]. Racemate (±)-**28** (m.p. 145–147 °C) was prepared from racemic (±)-**27**.

(1S,2R,5S,6R,7R)-(+)-4-*Benzyl*-5-*heptyl*-10-*oxa*-4-*azatricyclo*[5.2.1.$0^{2,6}$]*dec*-8-*en*-3-*one* **29**.—In a similar manner to its analogue (±)-**23**, *compound* (+)-**29** (441 mg, 100%) was obtained by treatment of sulfone (+)-**28** (510 mg, 1.29 mmol) in methylene dichloride (20 $cm^3$) with solutions of heptylmagnesium bromide (13.8 $cm^3$, 0.56 mol $dm^{-3}$ in diethyl ether, 7.74 mmol) and $ZnBr_2$ (871 mg, 3.87 mmol) in diethyl ether (50 $cm^3$). Compound **29** was an oil (Found: $M^+$, 339.2169. $C_{22}H_{29}NO_2$ requires M, 339.2197); $[\alpha]_D^{27}$ +66.4 (*c* 2.0, $CHCl_3$); $\nu_{max}$(neat)/$cm^{-1}$ 2927, 2856, 1682 and 1445; $\delta_H$ 0.88 (3 H, t, *J* 6.7, Me), 1.23 (10 H, br, 5 × $CH_2$), 1.3–1.7 (2 H, m), 2.06 (1 H, dd, *J* 7.6 and 2.7, 6-H), 2.72 (1 H, d, *J* 7.6, 2-H), 3.29 (1 H, m, 5-H), 3.91 (1 H, d, *J* 15.4, NC*H*H), 4.74 (1 H, br s, 7-H), 5.03 (1 H, d, *J* 15.4, NCH*H*), 5.30 (1 H, br s, 1-H), 6.36 (1 H, dd, *J* 5.9 and 1.5, 8-H), 6.44 (1 H, dd, *J* 5.9 and 1.5, 9-H) and 7.1–7.4 (5 H, m, ArH).

~ 100% E.e. by chiral HPLC [Chiralcel OC; hexane–propan-2-ol (19:1), flow rate 1 $cm^3$ $min^{-1}$; $t_R$ (+)-**29**, 25.0 min; (−)-**29**, 30.6 min]. The racemate (±)-**29** was prepared in 86% yield from racemate (±)-**28**.

(5S)-(+)-1-*Benzyl*-5-*heptyl*-1,5-*dihydropyrrol*-2-*one* **25** *by Heating of Compound* **29** *in Xylenes*.—A solution of tricycle **29** (86 mg, 0.26 mmol) in xylenes (3 $cm^3$) was heated at reflux for 35 min. The reaction mixture was charged directly to a silica column. Elution with hexane–ethyl acetate (1:0→3:1) gave compound **25** (49 mg, 71%); $[\alpha]_D^{26}$ +58.8 (*c* 0.8, $CHCl_3$), e.e. ≥97%.

This compound was further transformed into the saturated lactam (−)-**24** {$[\alpha]_D^{26}$ −19.3 (*c* 0.5, $CH_2Cl_2$)} by hydrogenation, as described above.

(−)-1-*Benzyl*-5-*heptylpyrrolidine*-2-*thione* **30**.—A solution of (−)-**24** {$[\alpha]_D^{26}$ −19.3 (*c* 0.5, $CH_2Cl_2$), 14 mg × $10^{-5}$ mol} and Lawesson's reagent (12.4 mg, 3.1 × $10^{-5}$ mol) in dry benzene (5 $cm^3$) was heated at reflux for 1.5 h under a hood. The solvent was evaporated and the residue (31 mg) was purified by chromatography on silica with hexane–ethyl acetate (10:1) to give compound **30**[18] (14 mg, 94%) as an oil; $[\alpha]_D^{26}$ −145.5 (*c* 0.44, EtOH) {lit.,[19] $[\alpha]_D^{20}$ −107.1 (*c* 1.3, EtOH)}. The e.e. of product (−)-**30** was estimated ≥93% by chiral HPLC [Chiralpak AS; hexane–propan-2-ol (40:1), flow rate 0.5 $cm^3$ $min^{-1}$; $t_R$ (−)-**30**, 29.6 min; (+)-**30**, 23.9 min].

*X-Ray Crystallography*.—*Compound* **4c**: $C_{26}H_{31}NO_4S$, M = 453.6, monoclinic, space group $P2_1$, *a* = 14.917(2), *b* = 7.129(1), *c* = 11.137(2) Å, *β* = 98.20(1)°, *Z* = 2, *V* = 1172.2(3) $Å^3$, $D_c$ = 1.285 g $cm^{-3}$, $\mu$(Cu-K$\alpha$) = 14.6 $cm^{-1}$, crystal size = 0.3 × 0.07 × 0.02[3], number of reflections ($2\theta \leqslant 110°$) = 1569, *R* = 0.042 for 1404 reflections with $F_o > 3\sigma(F_o)$.

Compound **6c**: $C_{25}H_{29}NO_5S$, M = 455.6, monoclinic, space group $P2_1$, *a* = 9.742(1), *b* = 16.703(3), *c* = 7.041(2) Å, *β* = 92.39(2)°, *Z* = 2, *V* = 1144.7(4) $Å^3$, $D_c$ = 1.322 g $cm^{-3}$, $\mu$(Cu-K$\alpha$) = 15.3 $cm^{-1}$, crystal size = 0.5 × 0.05 × 0.05 $mm^3$, number of reflections ($2\theta \leqslant 110°$) = 1499, *R* = 0.051 for 975 reflections with $F_o > 3\sigma(F_o)$.

Intensity data were collected on a Rigaku AFC-5R diffractometer in $\omega$–$2\theta$ scan mode using Cu-K$\alpha$ radiation ($\lambda$ = 1.541 78 Å). The structures were solved by use of the program of MULTAN[31] and were refined by the block-diagonal least-squares method for the positional parameters of all the atoms, using anisotropic thermal parameters of the non-hydrogen atoms. The temperature factor of each hydrogen atom was assumed to be isotropic and equal to $B_{eq}$ of the bonded atom.

Full lists of fractional atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited as supplementary material with the Cambridge Crystallographic Data Centre.*

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